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Philippe Négrel

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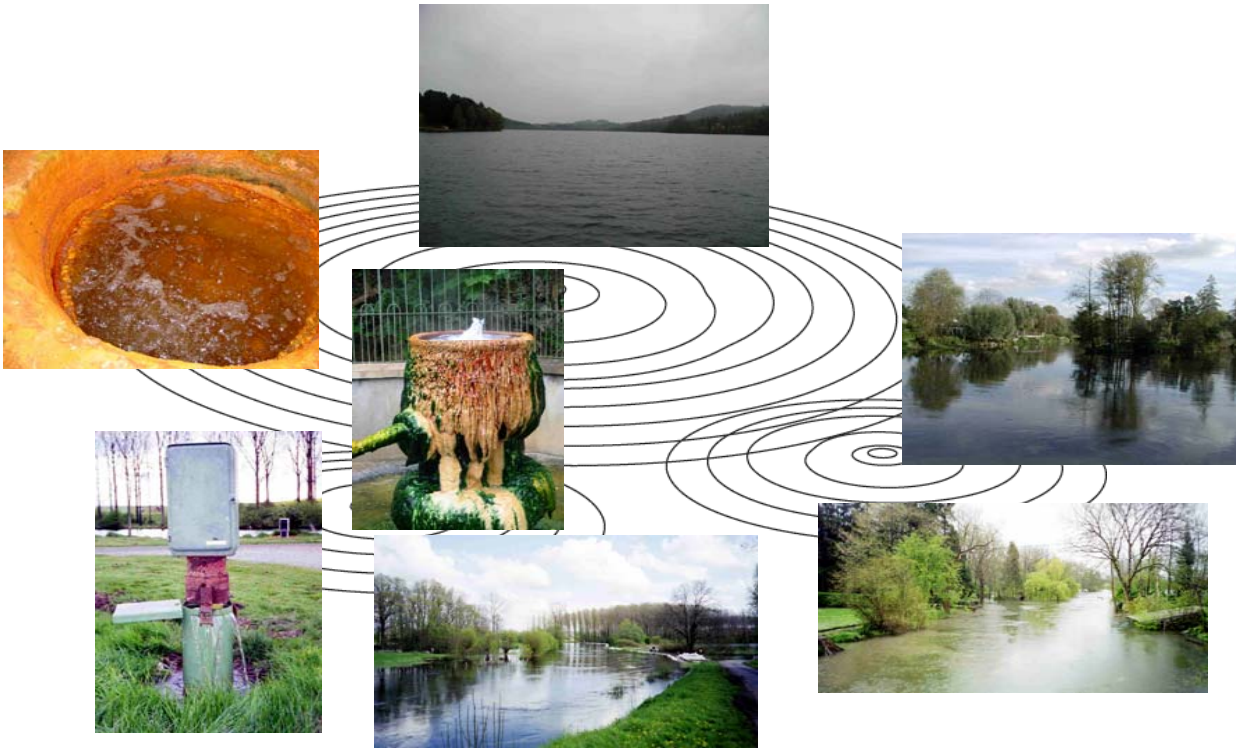
Le cycle de l’eau de l’aérien au souterrain : voyage des isotopes



Le cycle de l'eau de l'aérien au souterrain : voyage des isotopes

Mémoire des études réalisées dans le cadre des projets de recherche du BRGM

Philippe Négrel

Habilitation à diriger des recherches présentée à l'Université Paul Sabatier, Toulouse

Soutenue le mercredi 2 février 2005 devant le jury composé de :

- Jean Louis DANDURAND, PR Université de Toulouse, président
- Gérard BLANC, PR Université de Bordeaux, rapporteur
- Christian FRANCE-LANORD, DR CRPG-CNRS Nancy, rapporteur
- François CHABAUX, PR Université de Strasbourg, rapporteur
- Bernard DUPRE, DR CNRS Université de Toulouse, directeur
- Christian FOUILLAC, Directeur de la Recherche BRGM, examinateur

Géosciences pour une Terre durable
brgm

Préambule

Ce mémoire a pour objectif de présenter une partie de mes activités de recherche menée au BRGM depuis 1993 dans le domaine de l'application des méthodes isotopiques à la meilleure connaissance du cycle de l'eau. Ce mémoire n'est pas exhaustif et ne comprend qu'une sélection des travaux menés. Le bilan établi dans ce mémoire est complété par la présentation de tous mes travaux de recherche, de valorisation et de transfert des connaissances sous la forme d'un curriculum vitae. Une sélection des travaux et principales publications choisies est également jointe à ce mémoire.

Mots clés : Cycle de l'eau, isotopes, précipitations, rivières, eau souterraine, érosion, flux, bassin versant.

Synthèse

Ce mémoire est axé sur l'utilisation de traceurs isotopiques radiogéniques (Strontium, Néodyme, Plomb) et stables (Bore…) dans les études environnementales et tout particulièrement le long du cycle de l'eau.

Les circulations et les interactions des eaux, qu'elles soient de surface ou souterraines, avec les roches encaissantes sont de plus en plus renseignées par l'utilisation de la géochimie et tout particulièrement par l'application des traçages isotopiques. Illustrée par plusieurs exemples dans différentes régions en France et Europe, la compilation d'études présentée ici repose principalement sur les systématiques isotopiques du strontium, du néodyme, et du plomb (couplée avec les déterminations élémentaires Sr, Terres Rares, éléments traces). Elle permet de définir pour chacun des sites ou systèmes étudiés, l'origine naturelle ou non des éléments chimiques, leurs comportements, leur transport dans des compartiments différents (e.g. forme dissoute et/ou particulaire pour les fleuves), des schémas de circulation des eaux et fluides profonds et les interactions entre les eaux et les différents types de roches encaissantes.

Pratiquement, cette compilation est organisée en trois parties distinctes et recouvrant les trois grandes étapes du cycle de l'eau. Elle ne présente qu'une partie de mes travaux de recherche et ne comprend qu'une sélection des publications.

La première partie est consacrée aux précipitations. Elle se veut à la fois dédiée à appréhender une meilleure compréhension, via les traçages isotopiques, des mécanismes d'acquisition de la chimie des pluies et également a permettre de contraindre le signal d'entrée vers les bassins versants.

La deuxième partie est focalisée sur la partie surficielle du cycle de l'eau via les fleuves et les rivières. Au travers des items développés le long de cette partie, sont illustrés les transports dissous et solides par le fleuve Loire en terme de bilans érosifs et d'origine des éléments, les mêmes types de transports au travers des petits bassins versants de lithologie monotone, la variation de l'érosion au cours des dix derniers millénaires grâce à des enregistrements sédimentaires fluviatiles et enfin, les liens avec les eaux souterraines sont approchés par l'étude du bassin versant du Maroni en Guyane.

La troisième partie est dédiée aux eaux souterraines via les études des eaux minérales et des eaux profondes en milieux de socle fracturé. Le système des eaux profondes de la Vienne met en exergue le problème de l'origine des fluides, le processus initiateur de la salinité des eaux est étudiée dans l'hydrosystème de Palmottu en Finlande avec comme contraintes supplémentaires un climat plus froid et un impact plus important des variations climatiques passées sur la chimie des eaux profondes ; enfin, le système hydrominéral du Massif Central permet de mettre en exergue l'importance des traçages isotopiques dans la connaissance des circulations et des interactions eau-roches.

Une sélection non exhautive de publications illustre ce mémoire.

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1. Introduction

L'EAU, ELEMENT FAÇONNANT DE LA TERRE

L'eau recouvre les trois quarts de la surface de notre planète. On la trouve partout, et sous de multiples formes : pluie, cours d'eau, mers, océans, lacs, nappes souterraines, vapeur, nuages, glaces... sans oublier toute l'eau contenue dans le sol et la végétation. Tous ces éléments participent à ce que l'on appelle "le cycle de l'eau". En effet, depuis qu'elle est apparue sur Terre, il y a quelques 4 milliards d'années, la quantité d'eau présente sur la planète, évaluée à plus de 1 milliard de km^3 au total, n'a pas changé. C'est toujours le même volume d'eau qui ne cesse de se transformer, passant par les différents stades de vapeur, d'eau liquide et glace, pour perpétuer le cycle permanent de l'eau. De formule chimique simple, (H_2O), il s'agit d'un corps complexe résultant de la combinaison de 3 isotopes de l'oxygène (^{16}O, ^{17}O, ^{18}O) et de 3 de l'hydrogène (^{1}H, Deutérium, Tritium) qui peut donc exister sous 18 formes différentes. De part sa structure atomique complexe, capable de créer des champs électriques assurant les liens et ponts entre les molécules, d'étonnantes particularités physiques de l'eau en résultent (forte tension superficielle, constante électrique élevée…). La structure moléculaire de l'eau, qui permet aux atomes H^+ de s'associer avec des anions et aux atomes O^- de se lier à des cations, lui donne de forte capacité de dissolution.

Le cycle de l'eau ou encore cycle hydrologique est la série de transformations qui se produit dans la circulation de l'eau. Les précipitations se transforment en ruissellement, en humidité du sol et en eau souterraine. L'eau souterraine circule à nouveau vers la surface, et de la surface, toute l'eau issue des rivières, nappes, sol, végétation retourne à l'atmosphère par évaporation et transpiration. Deux structures du milieu naturel organisent ensembles l'écoulement des eaux. Une, visible, est le réseau hydrographique d'arborescence plus ou moins dense et hiérarchisé. Selon les cas et les formes de conduits, ce réseau peut disperser ou centraliser les eaux avec une capacité de transport très variable. L'autre structure est cachée et est constituée par l'agencement des terrains aquifères dans le sous-sol. Cette dernière structure est principalement constituée de milieux conducteurs et de réservoirs.

On ne compte plus, par exemple en France, les torrents, ruisseaux et rivières qui dévalent des montagnes ainsi que les grands cours d'eau qui serpentent en plaine. Toute rivière, de sa source à son embouchure, est un ensemble fonctionnel. Les caractéristiques géomorphologiques d'une rivière évoluent progressivement depuis sa source jusqu'à son embouchure, principalement à cause de l'évolution de la pente. En amont, la pente de la rivière est forte. La rivière est étroite, le courant important et la rivière érode fortement les berges. Plus en aval, la pente diminue, la rivière s'élargit, les méandres sont nombreux et les processus de sédimentation commencent. Vers l'embouchure, la pente est de plus en plus faible. La rivière s'élargit encore, le courant diminue et les matériaux les plus fins sédimentent. A un niveau plus local, l'hétérogénéité de la rivière s'exprime par des alternances de radiers ou seuils (faible hauteur d'eau, vitesse de courant importante, érosion dominante) et de mouilles (hauteur d'eau importante, vitesse de courant faible, sédimentation dominante).

Une rivière n'est pas un élément isolé. Elle est étroitement associée avec les annexes fluviales au sein d'une plaine alluviale, le tout formant un hydrosystème. Les annexes sont des bras morts, des bras secondaires, des plans d'eau plus ou moins temporaires, des zones humides, la ripisylve... En période de crues, ces annexes sont submergées et servent alors de bassins écrêteurs. Chacune de ces annexes a, en outre, une fonction particulière et participe au maintien de l'équilibre de l'ensemble. Les marais et les zones humides laissent l'eau s'infiltrer et recharger les nappes phréatiques. Les forêts alluviales produisent de la matière organique pour la rivière. Elles filtrent les eaux de surface qui arrivent à la rivière. Les bras morts, les bras secondaires sont des réservoirs biologiques et des zones de frayères. Lorsqu'on y ajoute les nombreux lacs, les récentes retenues de barrages et les vastes étangs de plaine, on comprend bien que la plupart des zones continentales disposent d'un vaste et dense réseau d'eau de surface.

Au-delà de cette riche hydrographie drainant les continents, l'homme a toujours été fasciné par les eaux souterraines, les pertes et résurgences froides des milieux karstiques, les résurgences souvent chaudes, voire salées, pétillantes, ou même pétrifiantes des eaux qui émegent sur beaucoup de pentes de la plupart des massifs montagneux et les avant-pays montagneux. Ces eaux

souterraines, ressource essentielle, sont intimement liées à la géologie. D'une manière générale, l'eau occupe et circule au sein des vides de la roche, de taille microscopique, situés entre les grains constitutifs de celle-ci. Dans ces vides, l'eau est en contact étroit avec la roche ce qui permet de nombreuses réactions physiques et chimiques. Les grandes couches de roches perméables (souvent sédimentaires) comportent généralement une zone saturée en eau, siège d'un écoulement significatif d'une nappe souterraine, le tout formant un aquifère. Les aquifères peuvent être petits, ne couvrant que quelques hectares de superficie, ou très grands, sous-jacents à des milliers de kilomètres carrés de surface. Ils peuvent avoir des épaisseurs de quelques mètres seulement jusqu'à des centaines de mètres. Cette eau souterraine peut finalement réapparaître au-dessus du sol et ainsi se déverser dans les cours d'eau, les lacs et les océans, ou bien son émergence peut se présenter sous forme de sources.

Dans les domaines de socle (granites et basaltes en constituent des exemples), l'eau souterraine circule à travers des zones fissurées en suivant un parcours complexe dans les profondeurs, entre les couches géologiques, pour remonter vers la surface à la faveur de zones de roches fracturées ou de failles qui jouent un double rôle de drains-barrières.

Plus en profondeur, l'existence de fluides, présentant des salinités variables, est un phénomène plus que largement répandu dans de nombreuses régions du globe, et souvent dans des formations géologiques de socle (voir synthèse dans Kloppmann et al., 2002). Ces fluides, prélevés ou non à grande profondeur, font l'objet de multiples études à l'aide d'outils géochimiques de plus en plus variés au cours des dernières décennies : traceurs conservatifs Cl-Br, isotopes stables de l'eau, isotopes du soufre, du strontium… L'accès à ces fluides se fait soit par l'intermédiaire de forages profonds, soit grâce aux émergences d'eaux minérales. Ces forages dans les socles continentaux sont *pro parte* issus du besoin de connaissance sur la croûte continentale en regard des circulations de fluides et complétés par la nécessité d'envisager un stockage en formation géologique profonde des déchets radioactifs. Les divers programmes de forages ont permis d'étudier des portions de croûte continentale jusqu'à 12 km de profondeur en Russie (voir synthèse dans Aquilina, 1997). Sans exception dans ces forages, des fluides ont été trouvés, collectés et analysés. Leur salinité fluctue entre quelques grammes et plusieurs centaines de grammes et leur composition chimique est variable, incluant les termes Na(Ca)Cl et Na(Ca)SO_4. L'origine de la salinité de ces fluides est l'objet de controverses depuis longtemps entre les partisans d'une origine marine et/ou une migration de saumures de bassins sédimentaires et ceux prônant l'influence des interactions eau-roches (hydrolyse des minéraux, lessivage d'inclusions fluides…). L'origine, l'évolution et la migration de telles solutions salées sont de première importance dans la compréhension et la gestion de ce "proche" sous-sol en terme de stockage.

Les eaux minérales peuvent émerger à la surface de la terre avec une gamme de températures très variable, depuis des températures relativement basses (10-15°C) jusqu'à atteindre des températures élevées : plus de 70°C (Chaudes-Aigues dans le sud du Massif Central, Ax les thermes dans les Pyrénées et à Pechelbronn en Alsace). L'explication de l'origine des eaux minérales et de leurs processus de venue en surface sont à rechercher dans le circuit hydraulique entre la ou les zones d'alimentation, la zone de minéralisation et la zone d'émergence. L'eau de pluie s'infiltre dans des terrains perméables ou via des fractures, elle circule gravitairement soit jusqu'à une couche imperméable (cas des aquifères sédimentaires) ou à l'intérieur du circuit hydraulique descendant (cas des aquifères fracturés). Les grands réseaux de fractures avec des directions liées aux grandes phases structurantes, par exemple les orogenèses pyrénéenne et alpine ont morcelé les massifs cristallins et ont favorisé les circulations ascendantes d'eau minérale. L'émergence en surface d'eaux qui, d'après leurs températures ont dû parfois atteindre plusieurs kilomètres de profondeur, peut s'expliquer par le phénomène d'artésianisme où la pression exercée sur l'eau la force à remonter vers la surface. L'émergence de ces eaux peut également s'expliquer par le phénomène de thermosiphon : l'eau en profondeur est soumise à de fortes températures et l'eau chaude, plus légère peut remonter vers la surface en repoussant des masses d'eau froide. Ce phénomène est dans certaines régions accompagné de dégagements gazeux issus de zones profondes. Le mélange eau-gaz forme une émulsion plus légère que l'eau sans gaz ce qui provoque une remontée de l'eau. Image en surface des eaux souterraines, les sources minérales sont, à l'image des basaltes qui permettent de reconstruire l'évolution et les processus de fonctionnement des zones profondes de la terre, un des moyens d'étudier les interactions profondes entre eau et roches.

LE VOYAGE DES ISOTOPES ET LE CYCLE DE L'EAU : APPROCHE SYNTHETIQUE

L'eau est une substance réactive omniprésente, intervenant dans tous les processus géodynamiques internes et externes. Il est bien rare que l'explication d'un phénomène géologique ne fasse pas intervenir l'eau, à quelque échelle que ce soit. La surface de la Terre peut être considérée comme un interface physique entre la lithosphère d'une part, constituée de roches solides et de formations superficielles qui englobe tous les éléments du relief des continents, et l'atmosphère d'autre part, constituée de gaz et de particules en mouvement. Cette dernière contient de la vapeur d'eau, qui peut se condenser sous forme de précipitations et qui entre ainsi dans le cycle de l'eau en alimentant les sols, la végétation et les cours d'eau. C'est à cet interface que se situe le *Cycle de l'Eau* correspondant à la circulation générale de l'eau, en circuit fermé et avec changements d'état, entre les réservoirs de l'hydrosphère (e.g. ensemble des étendues d'eau qui recouvrent la surface de la Terre : océans, mers, bordières, mers intérieures, fleuves, rivières et lacs) et la surface et le sous-sol des terres émergées – qui met en jeu les phénomènes d'évaporation, de convection, de condensation et de précipitation, d'écoulement et d'infiltration, ainsi que les variations et renouvellements des stocks dans ces réservoirs (http://webworld.unesco.org/water/ihp/db/glossary/glu/FRDIC/DICCYCLE.HTM).

Comprendre les mécanismes d'interaction fluide (au sens large)-roche dans la croûte supérieure est important en sciences de la Terre. En effet, les fluides sont présents à tous les niveaux de la croûte et jouent un rôle fondamental dans pratiquement tous les processus physico-chimiques qui affectent la croûte terrestre en étant un catalyseur ou un constituant indispensable au déroulement des réactions chimiques. Ils influencent de part leur composition la nature des roches ou des sédiments dans lesquelles ils sont présents et/ou circulent. Ils sont le vecteur privilégié de la mobilité des éléments chimiques, mobilité qui permet les réactions chimiques et se traduit par des transferts de matières à différentes échelles.

Les concepts d'origine, de sources, de processus et de bilans font souvent appel à des outils et des raisonnements communs parmi lesquels l'utilisation des traceurs géochimiques tient une part prépondérante. Les traceurs utilisés permettent l'identification des sources de matière, des conditions et des processus de leur formation ou transformation, la quantification des flux, l'estimation des processus de transfert des éléments entre différents réservoirs ainsi que l'identification des sources des éléments d'origine naturelle ou anthropique. Ces traceurs sont souvent sélectionnés pour leurs caractères spécifiques et le but ultime de leur utilisation est d'intégrer l'ensemble des données dans un modèle hydrochimique destiné à déterminer les flux d'eau, les flux de matière (taux d'érosion, bilans de transfert…) dans les différents compartiments du bassin.

Les circulations et les interactions des eaux, qu'elles soient de surface ou souterraines, avec les roches encaissantes sont de plus en plus renseignées par l'utilisation de la géochimie et tout particulièrement par l'application des traçages isotopiques. Illustrée par plusieurs exemples dans différentes régions en France et Europe, la compilation d'études présentée ici repose principalement sur les systématiques isotopiques du strontium, du néodyme, et du plomb (couplées avec les déterminations élémentaires Sr, Terres Rares, éléments traces). Elles permettent de définir pour chacun des sites ou systèmes étudiés, l'origine naturelle ou non des éléments chimiques, leurs comportements, leur transport dans des compartiments différents (e.g. forme dissoute et/ou particulaire pour les fleuves), des schémas de circulation des eaux et fluides profonds et les interactions entre les eaux et les différents types de roches encaissantes.

Ainsi, cette compilation est organisée en trois parties distinctes et recouvre les trois grandes étapes du cycle de l'eau.

La *première partie* est consacrée aux précipitations. Elle se veut à la fois dédiée à améliorer la compréhension des mécanismes d'acquisition de la chimie des pluies via les traçages isotopiques et également à contraindre le signal d'entrée vers les bassins versants.

La *deuxième partie* présente les études de la partie surficielle du cycle de l'eau via les fleuves et les rivières. Au travers des items développés le long de cette partie, sont illustrés :

- les transports dissous et solides par le fleuve Loire en termes de bilans érosifs et d'origine des éléments ;
- les mêmes types de transports au travers des petits bassins versants de lithologie monotone situés dans le Massif Central ;

- la variation de l'érosion sur le bassin versant de la Loire au cours des dix derniers millénaires grâce à des enregistrements sédimentaires fluviatiles (peu communs en continu sur de telles périodes de temps) ;
- enfin, les liens entre eaux de surface et eaux souterraines sont approchés par l'étude du bassin versant du Maroni en Guyane.

La *troisième partie* est dédiée aux eaux souterraines via les études des eaux minérales et des eaux profondes en milieux de socle fracturé. Au travers de 3 items développés le long de cette partie, sont illustrés :

- le système des eaux profondes de la Vienne, étudié dans le cadre des études préliminaires à l'implantation d'un site de stockage de déchets radioactifs en formation géologique profonde ;
- l'hydrosystème de Palmottu en Finlande avec comme contraintes supplémentaires un climat plus froid et un impact plus important des variations climatiques passées sur la chimie des eaux profondes ;
- enfin, le système hydrominéral du Massif Central permet de mettre en exergue l'importance des traçages isotopiques dans la connaissance des circulations et des interactions eau-roches.

LES METHODOLOGIES ET OUTILS GEOCHIMIQUES.

Les éléments dont la masse est supérieure à 40 présentent des variations d'abondance de certains isotopes à la suite à la désintégration radioactive naturelle. Ces isotopes dits radiogéniques sont issus de la désintégration d'isotopes radioactifs. L'utilisation de ces désintégrations au travers des variabilités isotopiques permet de développer le concept de traceur isotopique.

☞ Les isotopes du strontium

Le strontium est membre de la famille des Alcalino-Terreux, groupe IIA du tableau périodique des éléments chimiques. Le couple Rb-Sr se caractérise par un comportement géochimique très contrasté entre le rubidium (élément alcalin proche du potassium) et le strontium (élément alcalino-terreux proche du calcium). Rb et Sr sont présents en tant qu'éléments traces (teneur < 0.5%) dans les différents types de roches. Ainsi, le rubidium est présent en quantités évoluant entre le µg g^{-1} (roches ultrabasiques) et la centaine de µg g^{-1} (roches de la famille des granites); le strontium est toujours présent avec des quantités supérieures à la centaine de µg g^{-1}. Le rubidium se localise préférentiellement dans les minéraux potassiques (biotites, muscovites, feldspaths potassiques) tandis que le strontium se situe préférentiellement dans les minéraux calciques tels que les plagioclases et les carbonates.

De part le comportement opposé de ces deux éléments, des fractionnements très importants (matérialisés par de grandes variations du rapport Rb/Sr) se produisent au cours des processus géologiques tels que : fusion partielle, cristallisation fractionnée, réaction entre fluides et minéraux... Ainsi, dans le processus de cristallisation fractionnée d'un magma, le strontium tend à être concentré dans les plagioclases, alors que le rubidium reste dans la phase liquide. Par conséquent, le rapport Rb/Sr du magma résiduel augmente graduellement au cours de la cristallisation progressive. Dans les processus d'altération, le strontium a un comportement plus soluble que le rubidium vis à vis de la solution lixiviante. Par conséquent, le rapport Rb/Sr augmente dans les minéraux résiduels lors de lessivages progressifs alors que celui du fluide est toujours bas.

Le strontium a quatre isotopes de masse 88, 87, 86 et 84. Les isotopes 88, 86 et 84 sont stables et ont des abondances liées à la nucléosynthèse (ensemble des processus aboutissant à la formation d'éléments chimiques). L'isotope 87 est radiogénique, c'est à dire qu'il est issu de la désintégration radioactive β^- du ^{87}Rb selon :

$$^{87}Rb \Rightarrow {}^{87}Sr + \beta^-$$

La relation entre ces deux éléments découle de la loi fondamentale de la radioactivité exprimée selon :

$$(^{87}Sr)_m = (^{87}Sr)_i + (^{87}Rb)_m\,(e^{\lambda t-1}) \text{ où } (^{87}Sr)_m \text{ et } (^{87}Rb)_m$$

correspondant au nombre d'atomes de ces isotopes par unité de poids dans le système à l'instant présent. $(^{87}Sr)_m$ est la valeur initiale inconnue correspondante au nombre d'atomes de cet isotope au moment de la formation du système; λ représente la constante de désintégration du ^{87}Rb soit 1,42 10^{-11} ans^{-1} ce qui correspond à une période (ou 1/2 vie) de 48,8 10^9 ans; t correspond au temps écoulé. En utilisant comme référence l'isotope 86 non radiogénique stable et pour lequel $(^{86}Sr)_m = (^{86}Sr)_i$ on obtient : $(^{87}Sr/^{86}Sr)_m = (^{87}Sr/^{86}Sr)_i + (^{87}Rb/^{86}Sr)_m (e^{\lambda t-1})$. Le rapport isotopique $^{87}Sr/^{86}Sr$ d'un fluide est directement relié à celui du minéral ou à des associations minéralogiques avec lesquelles le fluide a interagi. Les effets des fractionnements isotopiques liés à la différence de masse ne sont pas détectables pour des éléments dont la masse est proche de 80. De plus, les effets de variations du rapport $^{87}Sr/^{86}Sr$ liés à la décroissance radioactive du nucléide père (^{87}Rb) en nuclide fils (^{87}Sr) ne sont pas significatifs, compte tenu de la courte échelle de temps de ces processus par rapport à la période de décroissance.

Dans le cas d'une roche silicatée (granites...) les différents minéraux présentent des rapports chimiques Rb/Sr différents et donc des rapports isotopiques $^{87}Sr/^{86}Sr$ différents en liaison avec leur formation. Lors des phénomènes d'interaction eau-roches, le rapport $^{87}Sr/^{86}Sr$ de la fraction de strontium libéré sera différent de la roche totale et typique du ou des minéraux altérés et ceci en liaison avec la "résistance" des minéraux vis-à-vis de l'agressivité du fluide. Globalement, le strontium solubilisé dans la roche et transporté vers l'extérieur du système formé par la roche est beaucoup moins radiogénique (c'est-à-dire de rapport $^{87}Sr/^{86}Sr$ plus bas) que le strontium dans la roche non altérée. Le strontium des argiles résiduelles, issues de l'altération de la roche, est beaucoup plus radiogénique.

Compte tenu de la précision des déterminations isotopiques, de faibles variations des rapports peuvent être interprétées (Andersson et al., 1996, Bullen et al., 1997). Les variations isotopiques observées dans les fluides peuvent être issues du mélange de Sr de compositions isotopiques différentes provenant de différentes sources. Ainsi, dans le cas simple où deux sources de rapport isotopique ou chimique sont présentes, la composition du mélange peut être déterminée (Albarède et Michard, 1987, Stueber et al., 1993, Palmer et Edmond, 1992, Anderson et al., 1992).

Dès le départ du cycle de l'eau, les isotopes du strontium peuvent être appliqués. Ainsi, dans les *précipitations atmosphériques* (pluies et neiges), des valeurs très variables ont été reportées par différents auteurs (Graustein et Armstrong, 1983, Gosz et Moore, 1989, Aberg et al., 1989, Anderson et al. 1990, Dupré et al., 1994, Herut et al., 1993, Simonetti et al., 2000) dans des zones géographiques variées (USA, Suède, Scandinavie, Afrique, Canada…). Ces variations dans les pluies sont toujours liées aux sources des aérosols dans l'atmosphère.

Les variations du rapport isotopique du strontium dans un *hydrosystème* donnent des informations sur l'origine et les proportions de mélange des différents composants fluides ainsi que sur la nature et l'intensité des processus d'interaction roche-eau liés notamment à l'altération et à l'érosion. Un pré-requis à l'utilisation des isotopes du strontium est l'existence d'une variabilité suffisante dans les roches exposées à l'altération (Zuddas et al., 1995, Capo et al., 1998). De telles variabilités existent à la fois dans des bassins versants composés de roches variées non silicatées (Faure et al., 1967, Eastin et Faure, 1970, Curtiss et Stueber, 1973, Steele et Pushkar, 1973; Stueber et al., 1972, 1975, Fisher et Stueber, 1976, Albarède et Michard, 1987, Palmer et Edmond, 1992, Miller et al., 1993, Verdoux et al., 1995, BenOthmann et al., 1997, Luck et BenOthmann, 1998, Petelet et al., 1998, Katz et al., 1998), dans des bassins versants composés de roches granitiques ou silicatées (Aberg et Wickman, 1987, Aberg et al., 1989, Löfvendhal et al., 1990, Blum et al., 1994, 1997, Bain et Bacon, 1994, Bullen et al., 1996, 1997, Andersson et al., 1996, Bailey et al., 1996, Lent et al., 1997, Louvat et Allègre, 1997, Bain et al., 1998, Riotte et Chabaux, 1999), mixtes (silicates, carbonates, évaporites, Zhang et al., 1995, Stewart et al., 1998, Harris et al., 1998, Roy et al., 1999, English et al., 2000, Villiers et al., 2000, Wiegand et al., 2001) mais aussi dans des hydrosystèmes anthropisés (Martin et McCulloch, 1999, Roy et al., 1999, Probst et al., 2000, Böhlke et Horan, 2000, Semhi et al., 2000, Douglas et al., 2002).

Les isotopes du strontium ont été largement employés sur les *grands bassins* comme ceux de l'Amazone, du Congo, du Ganges, de l'Indus, des fleuves de l'Himalaya, du Guiana Shield, de Russie, du Canada…, en terme d'étude des processus d'érosion (Sarin et al., 1989, Négrel et al., 1993, Pande et al., 1994, Allègre et al., 1996, Gaillardet et al., 1997, Edmond et al., 1995, Wadleigh et al, 1985, Krishnaswami et al., 1992, Palmer et Edmond, 1992, Cameron et al., 1995, Yang et al., 1996, Rachold et al., 1997, Cameron et Hattori, 1997, Huh et al., 1998, Galy et al., 1999, Karim et Veizer, 2000, Chabaux et al., 2001, Dessert et al., 2001, Millot et al., 2002), de bilans à l'océan (Goldstein et Jacobsen, 1987, Palmer et Edmond, 1989, Israelson et Buchardt, 1999, Taylor et Lasaga, 1999, Stein

et al., 2000, Dessert et al., 2001, Jacobson et al., 2002, Quade et al., 2003) et de fonctionnement hydrologique (Négrel et Dupré, 1995a, b, Singh et al., 1998, Viers et al., 2000, Eikenberg et al., 2001, Sharp et al., 2002, Pawellek et al., 2002).

Ces mêmes systématiques isotopiques sont maintenant de plus en plus utilisés dans les études des interactions entre *eaux de surface et eaux souterraines* (Katz et Bullen, 1996, Hogan et al., 2000, Eikenberg et al., 2001, Ojiambo et al., 2003), et dans les *eaux souterraines s.s.* afin de caractériser les aquifères et les circulations (Stueber et al., 1972, 1975, Aberg et al., 1989, Johnson et DePaolo, 1994, , Plagnes et al., 1997, Naftz et al., 1997, Lent et al., 1997, Barker et al., 1998. Hunt et al., 1998, Jorgensen et al., 1999, Land et al., 2000, Siegel et al., 2000, Swarzenski et al., 2001, Sharp et al., 2002, Dogramaci et Herczeg, 2002, Dowling et al., 2003, Harrington et al ., 2003 ; Gosselin et al., 2004). Les circulations plus profondes sont, elles, étudiées via les eaux minérales (ou thermo-minérales) et les systèmes géothermaux (Michard et al., 1976, Stetller, 1977, Stetller et Allègre, 1978, Albarède et al., 1981, Pauwels et al., 1997, Möller et al., 1998, Gerstenberger et al., 1999, Grimes et al., 2000, Butterfield et al., 2001; Barbieri et Morotti, 2003). Toutefois, l'essentiel des études à l'aide des isotopes du strontium a porté sur les saumures en relation avec les réservoirs pétroliers (Chauduri, 1978, Sunwall et Pushkar, 1979, Stueber et al., 1984, 1987, 1993, Starinsky et al., 1983, Chauduri et al., 1987, Smalley et al., 1988a, 1994, Banner et al., 1989, Brannon et al., 1991, Moldovani et al., 1993, Cai et al., 2001) et sur les eaux salées telles que les saumures (primaires, secondaires) et les eaux salées résultant des interactions eaux-roches (Franklyn et al., 1991, McNutt et al., 1984, 1987a, b, 1990, Edmunds et al., 1984, 1987, Kay et Darbyshire, 1986, Clauer et al., 1989, Fritz et al. 1987, 1992, Stuckless et al., 1991, Bottomley et Veizer, 1992, Lyons et al., 1995, Seimbille et al., 1998, Smalley et al., 1988b, Peterman et Wallin, 1999, Kloppmann et al., 2001, Pierret et al., 2001).

Enfin, en terme de *paléohydrologie*, les déterminations des isotopes du strontium des solides soit dans les fractures des batholites granitiques (calcites, dolomites…) ou aux émergences d'eaux plus où moins minéralisées (travertins), soit de certains carbonates en milieux marin permettent d'avoir accès à un enregistrement des signatures des eaux à partir desquelles ces solides ont précipité (Clauer et al., 1989, McNutt et al., 1990, Stuckless et al., 1991, Marshall et al., 1992, Gao et al., 1992, Huh et Edmond, 1998, Wallin et Peterman, 1999, Barrat et al., 2000, Barbieri, 2002). Les paléosalinités des eaux saumatres ont pu être approchées au travers des rapports isotopiques du strontium de coquilles fossiles calcaires bien préservées (Holmden et al., 1997). Les enregistrements isotopiques dans les paléosols himalayens démontrent le rôle des processus d'érosion de cette zone dans le contrôle des rapports isotopiques du strontium de l'océan (Chesley et al., 2000).

☞ Les isotopes du néodyme

Les Terres Rares (REE) comprennent 14 éléments depuis le Lanthane (Z = 57) jusqu'au Lutétium (Z = 71) et font partie du groupe IIIB de la série des lanthanides de la tableau périodique des éléments chimiques. Les propriétés physiques et chimiques des Terres Rares sont proches, en liaison avec la configuration similaire de leurs couches électroniques. Sous des conditions de température et de pression normales, les Terres Rares existent sous une forme trivalente (3+). Deux d'entre elles (Europium Eu et Cérium Ce) peuvent se trouver sous des états d'oxydation différents (4+) pour Ce et 2+ pour Eu) selon les états d'oxydoréduction des environnements où elles se trouvent.

Classiquement, les Terres Rares sont subdivisées en deux sous-groupes, les Terres Rares légères (LREE) incluant La- Eu et lourdes (HREE) incluant Sm-Lu. De plus en plus fréquemment, elles sont subdivisées en trois sous-groupes, les Terres Rares moyennes (MREE) incluant Sm-Tm s'intercalant entre les LREE (La-Nd) et HREE (Dy-Lu). Les Terres Rares sont un constituant important des roches ignées alors qu'elles représentent un constituant mineur de l'eau de mer (DeBaar et al., 1985, Bertram et Elderfield, 1993). Dans les océans, les concentrations en Terres Rares avoisinent quelques ng l^{-1} et présentent un temps de résidence très court (1800 ans pour le néodyme), notamment par rapport au Sr (environ 2 Ma). Les Terres Rares sont incorporées dans les diverses phases solides précipitées en milieu océanique, elles s'incorporent alors avec la même signature que celle de l'eau de mer. Elles sont relativement peu mobilisées par les processus d'altération des roches à la surface des continents (Nesbitt, 1979, Anderton et al., 1980, Humphris, 1984). Principalement associées aux feldspaths et aux micas comme éléments traces et comme constituants majeurs des minéraux accessoires (Henderson, 1984), leur mobilisation lors des processus d'interaction eau-roche dépend de différents facteurs (Johannesson et al., 1995a, b, c). Parmi ceux-ci, on note l'abondance des Terres Rares dans les roches, leur distribution dans les phases minérales primaires et la stabilité

de ces minéraux en regard des processus d'altération (Nesbitt 1979, Humphris 1984, Dupré et al., 1996). Il est généralement admis que les Terres Rares légères sont moins mobiles que les Terres Rares lourdes et que ces dernières sont enrichies dans les solides résiduels des processus d'altération (Nesbitt 1979, Humphris 1984, Braun et al., 1990, 1998, Dupré et al., 1996). En dépit de leurs similitudes physico-chimiques, les Terres Rares peuvent être fractionnées partiellement par différents processus géochimiques. Les profils de Terres Rares évoluent en fonction de ces processus. Par exemple, la fixation de Terres Rares sur des oxy-hydroxydes de fer ou de manganèse génère des profils enrichis en Terres Rares moyennes (Johannesson et al., 1996).

L'étude des Terres Rares dans les eaux naturelles a débutée par l'examen de leur présence dans les eaux marines et côtières ainsi que dans les estuaires (Fleet 1984, Elderfield et al. 1990, Bertram et Elderfield 1993, Sholkovitz, 1995) et dans les émergences d'eaux issues de circulations profondes en milieux marin et continental (Michard et Albarède, 1986, Michard et al., 1987). Les mesures étaient alors réalisées par les méthodes nucléaires ou de spectrométrie de masse (Keasler et Loveland, 1982, Hoyle et al. 1984, Michard et Albarède, 1986, Michard et al., 1987, Sanjuan et al., 1988). Le fort développement de cette thématique des Terres Rares dans les années 1985-1995 est liée au progrès analytique de la spectrométrie de masse à source plasma induite (ICP-MS, Smedley, 1991, Fee et al., 1992, Stetzenbach et al., 1994, Johannesson et al., 1994, 1995a, 1996). Dès lors, l'application des Terres Rares est devenue monnaie courante dans les eaux continentales comme *les fleuves, les rivières et les estuaires* (Keasler et Loveland 1982, Hoyle et al., 1984, Gaillardet et al., 1995, 1997, Tricca et al., 1999, Douglas et al., 1999, Sholkovitz et Szymczak, 2000, Deberdt et al., 2002), *les lacs et eaux souterraines* (Fee et al., 1992, Johannesson et Lyons, 1995a, Johannesson et al., 1996, Ingri et al., 2000, Biddau et al., 2002, Möller et al., 2003). Pour ces dernières, l'application des Terres Rares permet de délimiter les mélanges et circulations (Smedley, 1991, Johannesson et al., 1995b, 1997, 2000, Sondag et al., 1997, Johannesson et Hendry, 2000, Stille et al., 2003) Les eaux acides ont été très largement étudiées de part les particularités de la spéciation des Terres Rares dans ces environnements hors du commun (Johannesson et al., 1994, 1995a, b, 1996, Johannesson et Zhou, 1999, Åström, 2001). C'est encore plus d'actualité avec les études de drainages acides liées à la diminution des activités minières, soit avec la forte exploitation de certaines ressources minérales (Worral et Pearson, 2001a, b, Hannigan et Sholkovitz, 2001). Les systèmes hydrothermaux et les eaux minérales de zones granitiques ont été également étudiées du point de vue des Terres Rares (Michard et Albarède, 1986, Michard et al., 1987, Sanjuan et al., 1988, Alaux-Négrel, 1991, Alaux-Négrel et al., 1993, Hass et al., 1995, Lewis et al., 1998, Bank et al., 1999).

Les différents paramètres mis en œuvre pour caractériser les spectres des Terres Rares concernent les rapports de fractionnement comme Lu/La et Er/Nd normalisés représentés par $(Lu/La)_N$ et $(Er/Nd)_N$. et qui sont définis comme les rapports $(Lu_{échantillon}/La_{échantillon})/(Lu_{UCC}/La_{UCC})$ et $(Er_{échantillon}/Nd_{échantillon})/(Er_{UCC}/Nd_{UCC})$. La référence UCC correspond à la composition de la croûte continentale supérieure et répond à la définition et à la composition donnée par Taylor et McLennan (1985). Les anomalies en cérium et europium, représentées par Ce/Ce* et Eu/Eu*, sont calculées d'après la formule donnée par De Baar et al. (1985) et définies comme $Ce/Ce^* = 2Ce_N /[La_N + Pr_N]$ et $Eu/Eu^* = 2Eu_N /[Sm_N + Gd_N]$. Ce_N, La_N, Pr_N, Eu_N, Sm_N et Gd_N correspondent aux concentrations normalisées à la croûte continentale supérieure UCC.

Une des Terres Rares, le néodyme, possède 7 isotopes stables (142, 143, 144, 145, 146, 148, 150). Selon le même principe que pour le couple Rb-Sr, un des isotopes du samarium (^{147}Sm) est radioactif et décroît par émission alpha en un isotope stable du néodyme (^{143}Nd). De même que précédemment, on obtient : $(^{143}Nd/^{144}Nd)_m = (^{143}Nd/^{144}Nd)_i + (^{147}Sm/^{144}Nd)_m (e^{\lambda t-1})$ ce qui correspond à une isochrone. Cependant la période (106 10^9 ans) et les faibles variations du rapport Sm/Nd se traduisent par de faibles variations isotopiques du rapport $^{143}Nd/^{144}Nd$, variations de l'ordre de 1,15% en 4,55 milliards d'années pour la terre entière par rapport au réservoir chondritique CHUR. La mesure du rapport isotopique $^{143}Nd/^{144}Nd$ est souvent utilisé en géochimie, aussi bien dans le domaine marin au travers du traçage des masses d'eaux (e.g. Piepgras et al., 1979, Piepgras et Wasserburg 1980, Bertram et Elderfield, 1993, Jeandel, 1993) que dans le domaine continental (datation des roches ignées, Faure, 1986). Tout comme le Sr, l'utilisation des isotopes du Nd dans les traçages d'autres processus (interaction eau-roches par exemple) se développe de plus en plus. Les très faibles variations isotopiques du rapport $^{143}Nd/^{144}Nd$ ont amené la mise en place d'une notation dite "paramètre epsilon" {$\varepsilon Nd(0)$} qui représente la déviation exprimée en part par 10^4 (unités ε) du rapport $^{143}Nd/^{144}Nd$ d'un réservoir chondritique avec une valeur actuelle CHUR de 0.512636 (DePaolo et Wasserburg, 1976).

Tout comme les compositions isotopiques du strontium (Palmer et Edmond 1989), celles du néodyme sont bien connues dans les différents bassins océaniques (Piepgras et al., 1979, Piepgras et Wasserburg 1980, Bertram et Elderfield, 1993, Jeandel, 1993). Sur le domaine continental, l'application des isotopes du néodyme est encore balbutiante, Goldstein et Jacobsen (1987, 1988) ont déterminé les rapports isotopiques du Nd sur la fraction dissoute de grandes rivières d'Amérique du Nord, d'Australie, du Japon, des Philippines et du Vénézuela. Ces données ont été principalement utilisées pour caractériser le comportement du néodyme durant les processus d'altération et pour mieux comprendre le bilan de cet élément aux océans. Par la suite, Andersson et al. (1992) ont mesuré les isotopes du Nd dans les rivières drainant le bassin de la mer Baltique afin de caractériser les processus de mélange dans cette gigantesque zone estuarienne et Allègre et al. (1996) ont étudié les matières en suspensions des grands bassins Congo et Amazone afin de caractériser l'érosion continentale à l'échelle de très larges portions de continents. Les autres études impliquent les isotopes du Nd sur des bassins de taille plus réduite et visent à mieux comprendre le comportement de Terres Rares par le biais des déterminations isotopiques. C'est le cas pour les études sur les rivières boréales (Andersson et al., 2000), sur les Vosges et le Rhin (Tricca et al., 1999, Aubert et al., 2001). L'application des isotopes du néodyme sur les eaux minérales a permis de mieux contraindre leur origine et les circulations profondes (Gerstenberger et al., 1999, Möller et al., 1998).

Les rapports isotopiques du néodyme dans l'eau sont modifiés en fonction des différentes sources de Nd dans le système. Les différents minéraux des roches silicatées répondent différemment aux processus d'érosion et d'altération et donc il est possible que les compositions isotopiques du Nd dans l'eau ne reflètent pas complètement celle des roches totales (Andersson et al., 2000). Dans les études des isotopes du Nd dans des fleuves ou rivières, de faibles différences entre le rapport isotopique εNd(0) des fractions dissoutes et particulaires dans un même cours d'eau ont été mises en évidence (Goldstein et Jacobsen, 1987, 1988, Tricca et al., 1999, Aubert et al., 2001). Dans les rivières drainant les roches silicatées (ignées et métamorphiques), la dissolution préférentielle de minéraux tels que les plagioclases, pyroxènes, amphiboles, et grenats peut être plus importante que pour les autres minéraux porteurs de Terres Rares et être responsable de l'écart observé sur les compositions isotopiques du Nd. En dépit de cette possible divergence, quoique relativement faible, la composition isotopique du Nd est un très bon indicateur des roches mères soumises à l'érosion et à l'altération. Ainsi, Henry et al. (1997) ont appliqué cette systématique isotopique afin de contraindre les processus d'érosion dans les Alpes au travers du traçage des sédiments molassiques péri-Alpin. Sur de grands systèmes fluviaux, les traçages à l'aide des isotopes du néodyme ont permis d'étudier les portions de continents soumis aux processus d'érosion (Allègre et al., 1996, Cameron et Hattori, 1997) et plus récemment, Clift et al. (2002) ont appliqué cette systématique sur les sédiments transportés par le système fluvial de l'Indus afin d'étudier les sources des matières transportées et l'hétérogénéité crustale à l'échelle de l'Himalaya.

☞ Les isotopes du plomb

Le plomb possède 4 isotopes majeurs : 204, 206, 207 et 208. Seul l'isotope 204 est non radiogénique, c'est à dire que son abondance est restée constante au cours du temps depuis la formation de la terre (Faure, 1986). Les trois autres sont radiogéniques, c'est à dire qu'ils sont issus de la décroissance radioactive d'un élément père. L'isotope 206 découle de la désintégration de l'uranium 238, le 207 découle de l'uranium 235 tandis que le 208 découle de la chaîne de désintégration du thorium 232. L'utilisation des isotopes du plomb met en œuvre les rapports des isotopes 206, 207 et 208 normés à l'isotope stable 204. Les compositions isotopiques du plomb dépendent des concentrations originelles en Pb, U et Th et de l'âge de la formation émettrice; la gamme de variation dans les compositions isotopiques des différentes sources géologiques est donc importante.

Le plomb dispersé dans l'atmosphère par différents processus (incinération, combustion...) garde la composition isotopique de la source (e.g. minerai…) dont il dérive. Ceci permet d'utiliser les isotopes du plomb pour discriminer les différentes sources de plomb dans l'atmosphère via les aérosols et les pluies, principalement d'origines anthropogéniques (Settle et Patterson, 1982, Sturges et Barrie, 1987, Maring et al., 1987, Hamelin et al., 1989, Hopper et al., 1991, Grousset et al., 1994, Bucher, 1994, Brännvall et al., 1999, Roy et Allègre, 1995, Erel et al., 1997, Monna et al., 1997, Deboudt et al., 1999, Dunlap et al ., 1999, Farmer et al., 2000, Mukai et al., 1994, 2001, Bollhöfer et Rosman 2000, 2001a, b, Takeda et al., 2000, Renberg et al., 2000, Bing-Quan et al., 2001, Aberg et al., 1999, 2001, Luck et BenOthman, 2002, Flament et al., 2002, Kurkjian et al., 2002). Les enregistrements temporels tels que neige et longues séquences carottées de glace ont été également

utilisés (Rosman et al. 1993, 1994a, b, 1998a, 1999, 2000, Boyle et al., 1994, Simonetti et al., 2000, Vallelonga et al., 2002).

Les isotopes du plomb ont surtout été appliqués sur les sols pour déterminer l'origine du plomb (anthropique ou naturelle, Puchelt et al., 1993, Bacon et al., 1996, Brännvall et al., 1997, Harlavan et al., 1998, Hansmann et Köppel, 2000, Teutsch et al., 2001, Emmanuel et Erel, 2002, Wong et al., 2002, Sutherland et al., 2003) et sur les sols et sédiments afin de caractériser les impacts des activités minières (Monna et al., 2000, MacKenzie et Pulford, 2002).

Sur les bassins versants, les isotopes du plomb ont surtout été appliqués sur les sédiments lacustres ou estuariens *en terme de source naturelles et d'impact anthropique* (Shirahata et al., 1980, Elbaz-Poulichet et al., 1984, 1986, Monna et al., 1995, 1999, Ritson et al. , 1994, Moor et al., 1996, Bindler et al., 2001, Dong et al., 2002, 2003, Chillrud et al., 2003, Renberg et al., 2002) *en terme d'évolution pré-historique et historique des apports de plomb* (Graney et al., 1995, Rosman et al., 1997, Shotyk et al., 1998, 2001, Brännvall et al., 1999, Munksgaard et Parry, 2001, Weiss et al., 1997, 1999a, 2002, Outridge et al., 2002, Eades et al., 2002, Martínez Cortizas et al., 2002, Alfonso et al., 2003) *en terme d'érosion continentale* (Asmeron et Jacobsen, 1993, Allègre et al., 1996, Clift et al., 2001) *et d'apport de sédiments dans les zones côtières* (Hamilton et Clifton, 1979, Ferrand et al., 1999, Monna et al., 2000, Douglas et al., 1999, Clift et al., 2002, Hinrichs et al., 2002, Elberling et al., 2002).

Les porteurs biologiques (moules, mousses, lichen, bois, tissus humains…) sont également utilisés comme enregistreurs des pollutions atmosphériques ou des origines du plomb dont les isotopes permettent d'en différentier l'origine (Keinonen, 1992, Marcantonio et al., 1998, Rosman et al. 1998b, Yoshinaga et al., 1998, Kunert et al., 1999, Weiss et al., 1999b, Tommasini et al., 2000, Labonne et al., 2001, Doucet et Carignan, 2001, Bellis et al., 2002, Watmough et Hutchinson, 2002, Simonetti et al., 2003).

Leur application dans le domaine de l'eau est de plus en plus développée, à nouveau grâce aux progrès des appareillages d'analyses ICP-MS (Cocherie et al., 1998) et ICP-MS à secteur magnétique. La systématique isotopique du plomb est alors utilisée en tant que traceur de sources du Pb et des circulations des eaux (Flegal et al., 1989, Erel et al., 1990, Mariner et al., 1997, Petelet et al., 1997, 1999, Luck et BenOthman, 1998, Aries et al., 2001, Munksgaard et Parry, 2001, Widerlund et al;, 2002) y compris dans les environnements miniers (Gulson et al., 1989). L'application des isotopes du plomb sur les eaux minérales a permis de mieux contraindre leur origine et les circulations profondes (Gerstenberger et al., 1999). L'autre application sur des liquides concerne l'étude des signatures dans les vins (Augagneur et al., 1997, Rosman et al., 1998c)

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2. Le cycle des précipitations

Les aérosols sont la source principale des éléments chimiques transportés par les pluies. L'atmosphère, par le biais des dépôts secs (aérosols) ou humides (pluies), est reconnue comme une source majeure des éléments dissous dans les rivières (Gibbs, 1970, Likens et al., 1977, Bourrié, 1978, Meybeck, 1983, 1986, Négrel, 1992, 1999, Seimbille et al., 1989, Négrel et al., 1993, Wedraogo-Dumazet. 1983, Stallard et Edmond, 1983, Sarin et al., 1989).

Les composants dissous dans l'eau de pluie peuvent être divisés en trois groupes ainsi que Berner et Berner (1987) les ont résumés :

- ceux dérivés des aérosols marins (Galloway et al., 1982, Galloway et Gaudry, 1984),
- ceux dérivés des aérosols terrigènes (poussières des sols, émissions biologiques, Ichikuni, 1978, Duce et al., 1980, Prospero et al., 1981),
- et ceux dérivés des activités anthropiques (industrie, agriculture…, Pearson et Fisher, 1971, Wagner et Steele, 1987, Loye-Pilot et Morelli, 1988).

Les aérosols terrigènes peuvent provenir de sources locales par érosion des sols environnant la zone de collection des pluies, de sources plus lointaines du même continent, voire de sources situées dans d'autres continents (Prospero et al., 1981, Galloway et al, 1982, Dupré et al., 1994). De même, les aérosols dérivés des activités anthropiques peuvent provenir de zones proches ou à l'opposé plus lointaines de la zone de collection des pluies (Lantzy et Mckenzie, 1979, Thornton et Eisenreich, 1982).

Cette partie est dédiée à l'étude des précipitations tant du point de vue de la chimie des pluies qu'en terme de signal d'entrée dans les bassins versants. Les isotopes mis en jeu dans le cadre de ces études concernent les systématiques du strontium et du plomb, traceurs des sources des aérosols dans les pluies (Graustein et Armstrong, 1983, Gosz et Moore, 1989, Herut et al., 1993, Hamelin et al., 1989, Erel et al., 1990, Grousset et al., 1994) et des isotopes stables de la molécule d'eau.

(I) LA DECONVOLUTION DES CONTRIBUTIONS NATURELLES ET ANTHROPIQUES SUR LES PLUIES (NEGREL ET ROY, 1998[1], COCHERIE ET AL., 1998[2], ROY ET NEGREL, 2001[3]).

Les rapports isotopiques du strontium, du plomb et les concentrations en éléments majeurs et traces ont été mesurés dans des eaux de pluies collectées sur une période de 15 mois dans le Massif Central (Négrel et Roy, 1998, Roy et Négrel, 2001). Chaque échantillon représente une série mensuelle d'évènements pluvieux prélevée automatiquement. Un des objectifs de cette étude est de coupler les isotopes du strontium (Négrel et Roy, 1998) avec les éléments majeurs et traces pour déterminer les différentes sources (sels marins et sources crustales) des éléments chimiques dans les pluies. Le second objectif est de coupler les isotopes du plomb avec les éléments traces dans le but de caractériser leur comportement et leur région source (Cocherie et al., 1998, Roy et Négrel, 2001).

Les proportions des différents apports (i.e. marin, continental distant ou local) sont déterminées dans cette étude. Les isotopes du strontium ont été utilisés pour caractériser les sources non marines (e.g. continentales et anthropiques) après soustraction de la part d'origine marine. Les rapports $^{87}Sr/^{86}Sr$ pour celles-ci varient de manière importante entre 0.7092 et 0.71625, indiquant l'existence de plusieurs sources, tant locales que lointaines, naturelles ou anthropiques (Figure 1). L'étude des rapports $^{87}Sr/^{86}Sr$ montre la prédominance de signatures carbonatées dans bon nombre d'échantillons, indiquant l'origine des aérosols et constituant le premier composant. Ces apports de type carbonates peuvent trouver leur origine dans les sédiments tertiaires (calcaires miocènes et oligocènes) proches du site d'étude ou dans les dépôts marins du Bassin de Paris (Jurassique à Oligocène), du Bassin d'Aquitaine et de la vallée du Rhône. Les différentes signatures de ces zones

[1] Négrel Ph., Roy, S. 1998. Chemistry of rainwater in the Massif Central (France) : a strontium isotope and major element study. Applied Geochemistry 13, 941-952.

[2] Cocherie, A., Négrel, Ph., Roy, S., Guerrot, C. 1998. Direct determination of Pb/Pb isotopic ratios in rainwater using ICP-MS. Journal of Analytical Spectrometry 13, 1069-1073.

[3] Roy, S., Négrel, Ph. 2001. A Pb isotope and trace element study of rainwater from the Massif Central (France). The Science of the Total Environment 277, 225-239.

sources sont approchées par l'étude de la fraction dissoute de rivières ne drainant qu'un faciès unique (e.g. Jurassique Inférieur, Jurassique Supérieur…, Négrel et al., 1989). Toutefois, l'abondance de ces types de roches au nord, sud-est et sud-ouest de la zone d'étude ne permet pas de déterminer l'origine exacte des masses d'air ayant véhiculé les aérosols en utilisant les isotopes du strontium seuls. La deuxième source est à relier à l'émission de poussières dans l'atmosphère en provenance de terrains de type silicatés dans le Massif Central et de zones plus lointaines (Margeride, Morvan, Lozère). Les rapports $^{87}Sr/^{86}Sr$ de ce type de composant sont approchés par l'étude des fractions dissoutes des rivières drainant ce type de roches (Négrel et al., 1988; 1989; Seimbille et al., 1991; Négrel et Deschamps, 1996; Négrel, 1999). La dernière source est liée aux apports anthropiques comme les engrais. Les rapports $^{87}Sr/^{86}Sr$ de ce composant sont compris entre 0.7079 et 0.7087 (Négrel et Deschamps, 1996, Négrel, 1999). La répartition des signatures des pluies corrigées des apports marins avec les composants précédemment décrits, se fait donc entre trois extrêmes, un correspond aux sources silicatées, un autre à la source locale de carbonates et un dernier englobant les sources lointaines de carbonates et les engrais, comme illustré sur la figure 1.

Pour ce qui est des éléments traces, les variations de leurs concentrations dans les pluies sont principalement liées aux variations des sources des aérosols telles que les changements dans les proportions relatives des phases minérales porteuses des éléments traces et l'influence des sources anthropiques comme les industries, l'agriculture (incluant les engrais), etc. (Lantzy et Mackenzie, 1979, Thornton et Eisenreich, 1982, Pacyna, 1986). Aucun des éléments traces analysés ne montre de relation avec la quantité de pluies tombée et aucune relation inter-élémentaire ne peut être mise en évidence. Les fortes concentrations observées impliquent des taux de dépôts très élevés, en pondérant par la quantité de pluie tombée, clairement plus forts que ceux trouvés dans les zones dites non polluées (Jickells et al., 1984, Barrie et Schemenauer, 1989, Alloway, 1990). Ainsi, le plomb est l'élément trace le plus amené par les pluies avec une valeur moyenne de 996 $\mu g/m^2/an$. L'antimoine est l'élément le moins amené (1.12 $\mu g/m^2/an$).

Les compositions isotopiques en plomb dans les pluies varient fortement comme mis en évidence par l'étude du rapport $^{206}Pb/^{204}Pb$ (17.94-19.22). Les données, reportées dans les diagrammes classiques de corrélation isotopique ($^{206}Pb/^{204}Pb$ *vs.* $^{207}Pb/^{204}Pb$ et $^{206}Pb/^{204}Pb$ *vs.* $^{208}Pb/^{204}Pb$) définissent des alignements (Figure 2). Les données des pluies du Massif Central présentent des compositions isotopiques qui sont plus élevées que les pluies du bassin parisien (Roy, 1996). Un modèle de mélange prenant en compte 5 composants doit être envisagé pour expliquer les variations et les cinq signatures en plomb sont

- une signature du type *essence* (Roy, 1996, Monna et al., 1995) ;
- une signature du type du *fond naturel* comme montré dans les sédiments pré-industriels (Elbaz-Poulichet et al., 1984, Ferrand et al., 1999, Monna et al., 1997, Moor et al., 1996) ;
- une signature du type des *apports industriels* avec de multiples origines très difficiles à contraindre (Petit, 1977, Elbaz-Poulichet et al., 1986, Monna et al. 1997) ;
- une signature du type *amendement agricole* (engrais, amendements minéraux, Roy et Négrel, 2001) ;
- et une signature due aux *stériles miniers* (Marcoux, 1986).

Toutefois, aucune contribution relative de ces 5 composants ne peut être déterminée car toutes les sources s'alignent dans les diagrammes classiques Pb-Pb.

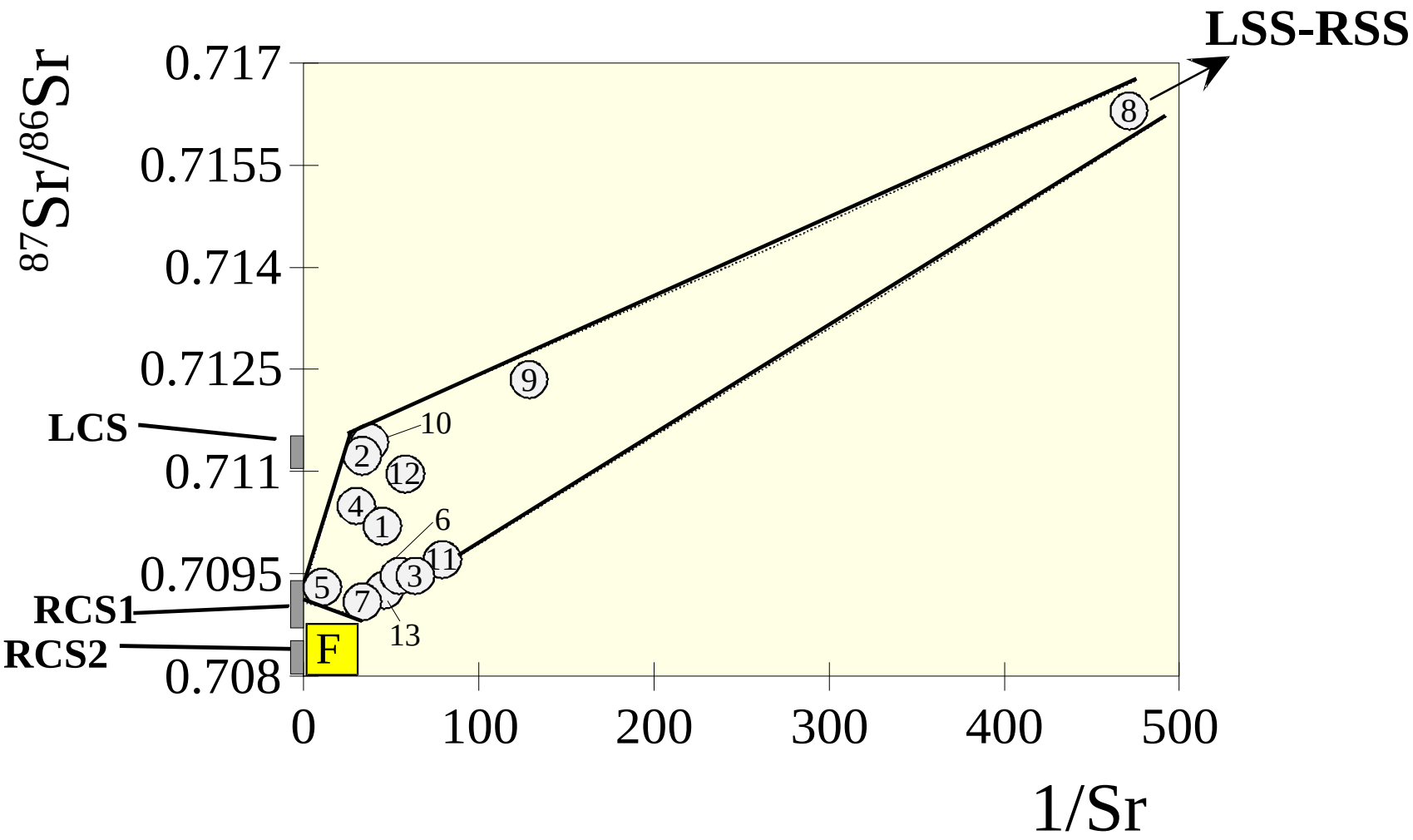

Figure 1. Relation entre les rapports $^{87}Sr/^{86}Sr$ et l'inverse de la concentration en Sr (exprimée en µmole/l) de chaque échantillon de pluies mensuelles après soustraction de l'apport lié aux aérosols marins, figure extraite de Négrel et Roy (1998, Applied Geochemistry 13, 941-952). LSS et RSS correspondent respectivement aux sources silicatées locales et de zones plus lointaines ; LCS correspond à la source carbonatée locale et RCS aux sources carbonatées lointaines ; F correspond aux apports liés aux engrais.

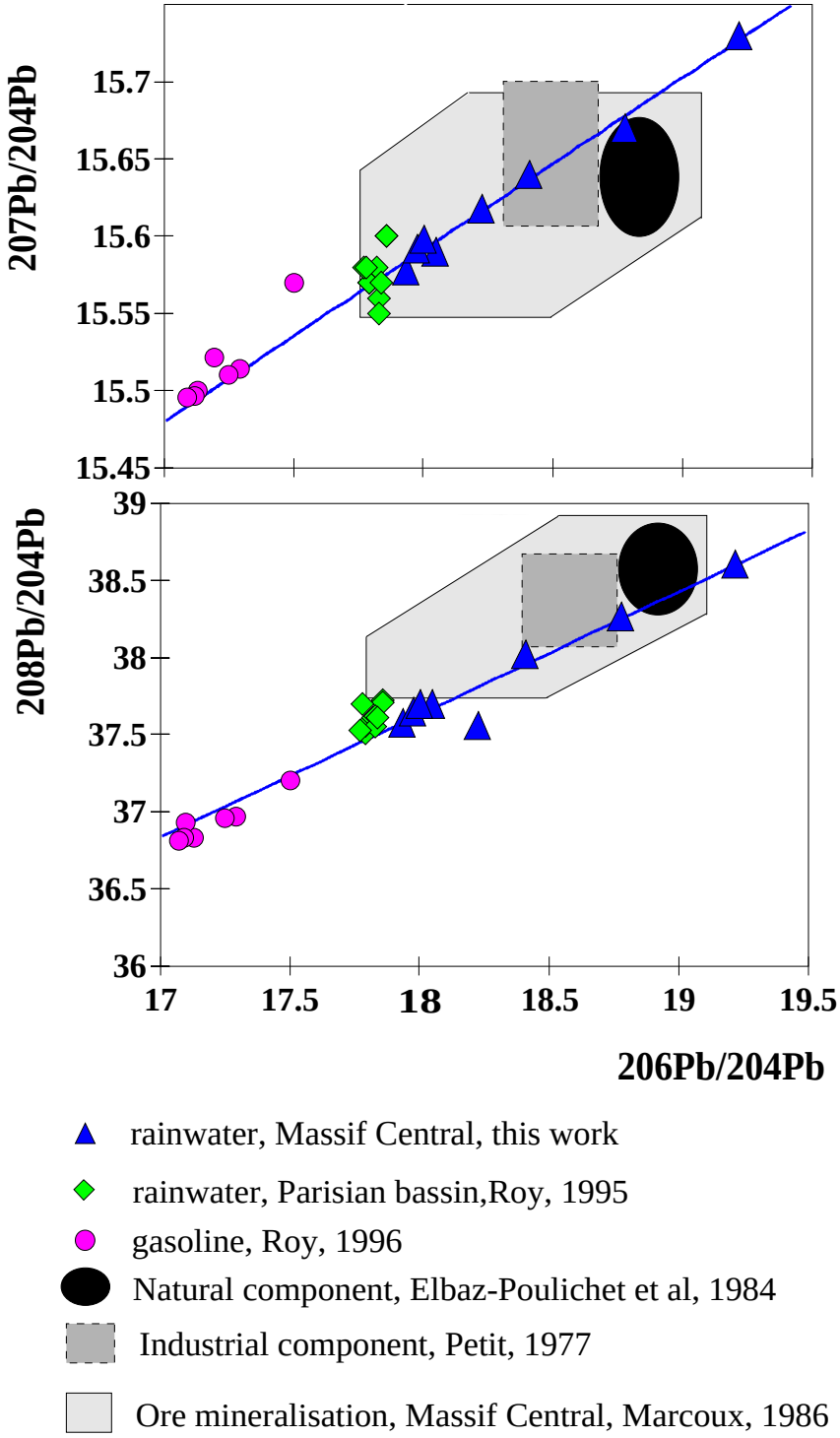

Figure 2. Corrélations entre les rapports $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ et $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$ dans les pluies du Massif Central, figure extraite de Roy et Négrel (2001, The Science of the Total Environment 277, 225-239).

(II) LES PLUIES, UN PREMIER REFERENTIEL INDISPENSABLE : EXEMPLE DE LA GUYANE (NEGREL ET AL., 1997[4]).

Les précipitations journalières à Cayenne (Guyane) ont été collectées sur une année et ont été analysées pour les ions majeurs et les isotopes stables de l'eau O et H. L'anion dominant est systématiquement le chlorure suivi par les sulfates ; nitrates et bicarbonates sont présents en quantités plus faibles. Pour les cations, l'ordre de prédominance n'est pas constant au cours du temps. La relation classique entre δ^2H et $\delta^{18}O$ sur les pluies mensuelles et les évènements ponctuels en Guyane est une parfaite relation linéaire dont l'équation est : $\delta^2H = 10.43 + 7.72\ \delta^{18}O$; r = 0.99. Cette relation, complétée des 6 échantillons de pluies de Négrel et Lachassagne (2001) donne une équation améliorée qui est : $\delta^2H = 9.22 \pm 2.10 + 7.34 \pm 0.56\ \delta^{18}O$ (n = 19, r = 0.99).

Il est possible de comparer les données de Cayenne avec celles plus à l'intérieur des terres en Guyane (Grimaldi, 1988; Farah, 1994) avec celles décrites dans la littérature pour des zones géographiquement proches telle que l'Amazonie (Stallard et Edmond, 1981; Forti et Moreira-Nordemann, 1991) et avec des valeurs de pluies côtières (Berner et Berner, 1987; Négrel et al., 1993). Les valeurs mesurées en Guyane sont en règle générale du même ordre de grandeur. Un fait remarquable concerne les fortes valeurs en Ca et les rapports élevés Ca/Cl de certaines pluies guyanaises qui sont expliqués par un apport de Ca d'origine continentale (Galloway et Gaudry, 1984; Losno et al., 1991). Ce calcium peut être lié soit à des apports de poussières continentales entre les pluies et issues de source(s) locale(s), soit à une circulation de particules carbonatées plus générale à l'échelle de l'atmosphère comme l'ont déjà montré certains travaux (Ichikuni, 1978; Duce et al., 1980; Suzuki et Tsunogai, 1988). La forte concentration en K des pluies guyanaises peut s'expliquer par un effet végétatif (Crozat, 1979).

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3. Le cycle des eaux de surface

Les principaux cycles, celui de l'eau et celui de la matière, gouvernent les échanges entre les principaux réservoirs terrestres, l'atmosphère, les océans et les roches. Les fleuves occupent une fonction centrale dans ce système. Système de transfert, le fleuve est le vecteur des agents et des produits des réactions qui ont lieu à l'interface entre atmosphère et croûte terrestre (Gibbs, 1970). Ces réactions ne sont autres que les phénomènes d'érosion, qu'elles soient chimiques ou mécaniques. La charge naturelle d'un fleuve apparaît donc comme le produit de l'interaction soit chimique soit mécanique, entre les précipitations et les roches. Dans le premier cas, ce produit est sous forme dissoute. Dans le second, il est sous forme particulaire. Dans un système fluvial et son bassin versant, le cheminement de l'eau est un continuum depuis les précipitations atmosphériques jusqu'à l'océan, à travers le ruissellement, l'évapotranspiration, l'infiltration, l'écoulement dans les rivières, la zone non saturée (ZNS) et les systèmes aquifères. De fait, l'approche du fonctionnement hydrique des systèmes fluviaux doit être globale. Fait récent et objet des préoccupations écologiques actuelles, l'homme, par ses différentes activités, intervient dans le cycle général des éléments. Que ce soit sous la forme de productions d'aérosols (gaz d'échappement, par exemple), de pollutions directes des sols (amendement, engrais...) ou de rejets directs dans les hydrosystèmes (eaux industrielles, centrales d'épuration...), l'activité humaine influe sur tous les réservoirs.

L'identification et la quantification des flux d'éléments dissous et particulaires transportés par une rivière passe par l'étude des différentes sources potentielles d'apport qu'elles soient naturelles ou anthropiques. L'objectif ultime étant d'identifier et de quantifier les flux (e.g. matières en suspension, sels dissous, éléments traces métalliques…) naturels et anthropiques et les différentes sources potentielles d'apport à différentes échelles sur le bassin versant du fleuve afin d'accroître la connaissance des systèmes fluviaux pour améliorer les méthodes et les outils d'aide à leur gestion. Ainsi une rivière intègre à la fois les apports anthropiques, atmosphériques, et les produits de l'érosion des roches (Berner et Berner, 1987). Cependant, la compréhension et la quantification des phénomènes d'érosion nécessitent d'établir des distinctions à l'intérieur du réservoir roche. En effet, les nombreuses études réalisées sur de grands fleuves mondiaux (Sarin et al., 1989, Mortatti et al., 1992, Négrel et al., 1993, Pande et al., 1994, Allègre et al., 1996, Gaillardet et al., 1997, Edmond et al., 1995, Wadleigh et al, 1985, Krishnaswami et al., 1992, Huh et al., 1998, Galy et al., 1999, Chabaux et al., 2001, Dessert et al., 2001, Millot et al., 2002) se sont toutes trouvés confrontées à la difficulté d'évaluer les phénomènes d'érosion propres à chaque entité lithologique constituant le bassin étudié. Le caractère global des différentes relations générales qui ont pu être mises en évidence par des études sur les grands fleuves met avant tout en évidence l'intégration et la "dilution" des hétérogénéités des terrains drainés par les cours d'eau. Il devient alors délicat d'estimer, d'abord l'importance de l'érosion, et ensuite l'apport respectif de chaque formation lithologique à la charge transportée par le fleuve.

Une des rares approches possibles de ces phénomènes semblent être l'étude de petits bassins versants présentant une unité lithologique clairement définie et protégée le plus possible des pollutions (Meybeck, 1986). Ainsi les principaux types lithologiques, roches magmatiques, volcaniques, métamorphiques, carbonatées et évaporitiques, doivent être étudiés au travers de petits cours d'eau (Tardy, 1971, Edwards, 1973a, b, Miller et Drever, 1977, Bourrié, 1978, Beaucaire et Michard, 1982, Drever et Hurcomb, 1986, Albarède et Michard, 1987, Giovanolli et al., 1988, Mast et Drever, 1990, Drever et Zobrist, 1992, Négrel et Deschamps, 1996, Négrel, 1999). L'intégration à l'échelle du fleuve de ces résultats, pondérés par l'influence effective de ces entités géologiques, devrait permettre de mieux cerner les phénomènes d'érosion et par la même, de mieux quantifier les différents flux, naturels et anthropiques (Probst et Bazerbachi, 1986, Petelet et al., 1998).

La Loire a été l'objet d'un suivi régulier. Tous les mois, eau, matières en suspension (MES), sédiments ont été prélevés puis quasiment quotidiennement, les eaux et MES de la Loire ont été échantillonnées à Orléans et analysés chimiquement et isotopiquement. Ce suivi a permis de déterminer les différents flux, naturels et anthropiques transportés par ce fleuve. Ces mêmes thèmes d'études ont été appliqués sur trois petits bassins versants avec des types lithologiques différents :

- Le bassin de l'Allanche qui s'étend sur les plateaux basaltiques du Cézallier (Cantal, Puy-de-Dôme) ;

- La Desges (Haute-Loire) et ses petits affluents qui draine différentes formations du massif de la Margeride (granite, micaschiste, gneiss) ;
- La Bertrande (Cantal), affluent de la Truyère, qui traverse les roches volcaniques du strato-volcan cantalien, puis différents terrains métamorphiques.

La variation de l'érosion au cours des dix derniers millénaires sera approchée sur le bassin de la Loire grâce à des enregistrements sédimentaires fluviatiles (peu communs en continu sur de telles périodes de temps) et au travers des traçages isotopiques.

L'écoulement dans les rivières, les liens avec la zone non saturée (ZNS) et les systèmes aquifères associés ont été tout particulièrement étudiés dans le cas de la Guyane avec l'étude du fleuve Maroni bordant tout l'ouest de la Guyane.

(I) LA DECONVOLUTION DE LA CONTRIBUTION DES APPORTS NATURELS (PLUIES, EROSION) ET ANTHROPIQUES (ENGRAIS, CONTAMINANTS INDUSTRIELS) DANS LA FRACTION DISSOUTE DE LA LOIRE (GROSBOIS ET AL., 2000, 2001[5, 6])

Le fleuve Loire, avec un des plus grands bassins en France, a été suivi au niveau d'Orléans et de Tours durant plusieurs cycles hydrologiques. Les paramètres physico-chimiques, les éléments majeurs et traces et les rapports isotopiques du strontium ont été déterminés sur la fraction dissoute sur des intervalles de temps variant entre deux jours et une semaine en fonction du débit du fleuve. Le lieu d'échantillonnage représente 34% du bassin total de la Loire et englobe 76% de roches silicatées et 24% de roches carbonatées. Hormis la caractérisation chimique et isotopique de la fraction dissoute de la Loire, un des objectifs de cette étude est de décrire le modèle de mélange dont résulte la fraction dissoute et de bâtir un modèle permettant de calculer les contributions de chacun des composants de cette fraction que l'on peut supposer complexe.

La quantité de sels dissous est majoritaire dans le cas de la Loire, avec des rapports des sels dissous totaux (TDS) et des matières en suspensions (MES) variant globalement entre 2 et 17. L'altération chimique des roches et des sols est le mécanisme dominant dans le contrôle de la fraction dissoute de la Loire. Toutefois, les plus forts rapports TDS/MES sont certainement liés aux apports anthropiques. Inséré dans le contexte français, la Loire se situe dans la même gamme de sels dissous que la Garonne (Probst et Bazerbachi, 1986), la Seine (Roy, 1996, Roy et al., 1998) et le Rhin (Meybeck et Ragu, 1996, Tricca et al., 1999). La charge solide transportée par la Loire est de l'ordre de 10^6 t.an^{-1} (Figueres et al., 1985, Négrel, 1997a), soit 3% de la masse totale des MES transportées par les fleuves drainant l'Europe de l'Ouest (moyenne pondérée des fleuves Seine, Oder, Vistule, Rhin et Garonne, Milliman et Meade, 1983).

Les rapports isotopiques du strontium de la fraction dissoute varient de manière concomitante avec le débit liquide du fleuve mettant en avant l'existence de deux types de rapports isotopiques, un bas lors des basses eaux et plus forts lors des hautes eaux (Figure 3). Ce type de relation avec le débit liquide a été déjà mis en évidence par Négrel et Dupré (1995) sur le bassin de l'Oubangui en Centrafrique. Replacée dans la connaissance des rapports $^{87}Sr/^{86}Sr$ des fractions dissoutes des fleuves français, la Loire se situe proche des compositions isotopiques observées sur la Garonne (Albarède et Michard, 1987, Sehmi et al., 2000). A contrario, la Seine (Roy, 1996, Roy et al., 1998) et l'Hérault (Albarède et Michard, 1987, Petelet et al., 1998) montrent des rapports $^{87}Sr/^{86}Sr$ plus bas en liaison avec un drainage de roches carbonatées plus important. Le Rhône (Albarède et Michard, 1987, Tricca et al., 1999) présente des rapports isotopiques bas et une plus forte concentration en Sr.

A partir des relations entre éléments chimiques et débits d'un côté et entre rapport isotopique et débit de l'autre, la fraction dissoute de la Loire apparaît résulter d'un mélange entre des apports de pluies, des apports de l'altération des roches silicatées et carbonatées formant les soubassements du bassin versant et des apports anthropiques d'origine agricole et des rejets urbains. Les flux dissous totaux durant un cycle hydrologique sont estimés à 1300. 10^3 t an^{-1} à Orléans et 1620. 10^3 t an^{-1} à Tours. Chacun des composants de la fraction dissoute est présent avec des contributions variables selon les périodes et avec des caractéristiques chimiques et isotopiques propres. La contribution de

[5] Grosbois, C, Négrel, Ph., Fouillac, C., Grimaud, D. 2000. Dissolved Load of the Loire river: Chemical and isotopic characterization. Chemical Geology 170, 179-201.

[6] Grosbois, C, Négrel, Ph., Fouillac, C., Grimaud, D. 2001. An overview of dissolved and suspended matter fluxes in the Loire river basin: natural and anthropogenic inputs. Aquatic Geochemistry 7, 81-105.

chacun des composants à la fraction dissoute a pu être calculée avec une approche de bilan de type "mass balance" pour les éléments bilantiels majeurs. Les flux exportés dus à l'altération des roches et aux apports anthropiques sont calculés et montrent que les apports naturels issus de l'érosion des roches du bassin représentent 60% de la composition chimique de la fraction dissoute tandis que les apports anthropiques représentent 40%. Le rapport entre les apports naturels issus de l'érosion des roches et les apports anthropiques varient de 1.48 à 1.58 au cours des cycles hydrologiques. Après soustraction des apports atmosphériques et anthropiques, les taux d'altération spécifiques des silicates du bassin sont de l'ordre de 11 t an^{-1} km^{-2} et ceux des carbonates sont respectivement de 47 t an^{-1} km^{-2} à Orléans et de 23 t an^{-1} km^{-2} à Tours donnant des rapports d'exportation carbonate/silicate variant entre 2 et 4, plus faibles que celui donné pour la Seine (~ 8, Roy et al., 1998).

La valeur de 1300. 10^3 t an^{-1} pour la fraction dissoute transportée est d'un facteur 3.5 plus forte que le transport sous forme particulaire (voir § suivant). Ce facteur est typiquement du même ordre de grandeur que ceux déterminés sur d'autres bassins tels que la Seine (Roy, 1996; Roy et al., 1998) et la Garonne (Probst et Bazerbachi, 1986), clairement plus bas que pour le Rhin (17.8, Meybeck et Ragu, 1996) et plus fort que pour le Rhône (0.6, Meybeck et Ragu, 1996).

(II) LA CARACTERISATION DES FLUX D'ELEMENTS CHIMIQUES NATURELS ET ANTHROPIQUES TRANSPORTES PAR LES MATIERES EN SUSPENSIONS (GROSBOIS ET AL., 2001[6], NEGREL ET GROSBOIS, 1999[7])

Durant les différents cycles hydrologiques étudiés, les déterminations des quantités de matières en suspension ont varié entre 3 mg l^{-1} et 100 mg l^{-1}. Aucun lien évident avec le débit du fleuve n'a été mis en évidence (Meade, 1985, Olivry et al., 1988) et cette absence de relation peut s'expliquer par la présence de nombreux barrages sur le bassin de la Loire. Du point de vue de la minéralogie, les matières en suspension de la Loire sont constituées principalement de quartz et de feldspaths potassiques pendant les périodes de hautes eaux avec une augmentation très marquée de la présence de calcites pendant les périodes de basses eaux. Ces variations minéralogiques et chimiques sont liées aux différentes sources des sédiments transportés en suspension par le fleuve sous des conditions hydrologiques très variables au cours du temps. Ces multiples sources de sédiments peuvent être distinguées par l'utilisation des rapports isotopiques du strontium. Les rapports $^{87}Sr/^{86}Sr$ varient de manière concordante avec le débit du fleuve, à savoir que le rapport isotopique augmente durant les hautes eaux et vice versa (Figure 4). Ce rapport isotopique augmente donc aussi avec l'abondance des feldspaths potassiques et la diminution de l'abondance des calcites. Cette similarité suggère l'existence d'au moins deux réservoirs de matière particulaire transportée par le fleuve. L'une est liée à la fraction détritique provenant de l'érosion de silicates, l'autre de l'érosion de carbonates.

La ressemblance des rapports isotopiques mesurés dans la fraction dissoute et dans la fraction particulaire lors des périodes de basses eaux laisse à penser à la présence forte de calcite authigène dans le flux de matières en suspension. A l'opposé, la divergence des deux rapports lors des périodes de hautes eaux correspond à la période de transports détritiques provenant de l'érosion de silicates. Le flux de matière solide transporté par le fleuve et mesuré lors des cycles hydrologiques étudiés permet de calculer un taux spécifique d'érosion mécanique (cf. Meade et al., 1990). Celui ci est de 9.5 t an^{-1} km^{-2} à Orléans et de 7 t an^{-1} km^{-2} à Tours. Ces deux valeurs sont très proches et sont du même ordre de grandeur que celles données pour différents bassins mondiaux (Berner et Berner, 1987, Olivry et al., 1988, Meade, 1985, Meade et al., 1990). La quantité de matière solide authigène représente 16% du flux annuel de matières solides à Orléans et 25% à Tours. Après soustraction de cette matière solide authigène, le taux spécifique d'érosion mécanique est estimé à 8 t an^{-1} km^{-2}, ce qui est plus faible que celui donné par Manickam et al. (1985), Figueres et al. (1985) et Négrel (1997a) dans la partie fluviale de l'estuaire de la Loire. La différence entre ces valeurs d'érosion spécifique associée à la différence de débit entre la zone d'étude et l'entrée de l'estuaire permet de calculer la concentration moyenne en matières en suspensions qui provient de l'érosion de la partie du bassin entre ces deux points d'étude. Les valeurs trouvées (40 à 146 mg l^{-1}) correspondent à celles mesurées par l'Agence de l'eau Loire-Bretagne et sont à relier avec les processus d'érosion des terrains carbonatés par la Loire, ou par ses affluents. En regard de la valeur de 8 t an^{-1} km^{-2}, celles déterminés sur d'autres bassins fluviaux en France, la Seine (9 t an^{-1} km^{-2}, Meybeck et Ragu, 1996, 6 t

[7] Négrel, Ph., Grosbois, C. 1999. Changes in chemical and $^{87}Sr/^{86}Sr$ signatures distribution patterns of suspended matter and bed sediments in the upper Loire River basin (France). Chemical Geology 156, 231-249.

an^{-1} km^{-2} à Paris, Roy et al., 1998), le Rhin (15 t an^{-1} km^{-2}, Meybeck et Ragu, 1996) et la Garonne (20 t an^{-1} km^{-2}, Probst et Bazerbachi, 1986) sont soit du même ordre de grandeur, soit plus fortes.

(III) L'ETUDE DE LA FRACTION LABILE DES MATIERES SOLIDES SUR LA LOIRE: EXISTENCE D'UN RESERVOIR D'OXY-HYDROXYDES DE FE ET MN ; CONTROLE DES ELEMENTS TRACES ; NOTION DE GENERATION DANS LES PARTIES AMONT DU BASSIN ET DE TRANSPORT (NEGREL ET AL., 2000[8], NEGREL ET ROY, 2002[9]).

Les matières en suspension de la Loire sont constituées principalement de quartz et feldspaths potassiques pendant les périodes de hautes eaux avec une augmentation très marquée de la présence de calcites pendant les périodes de basses eaux. Cette partie concerne l'étude de la fraction labile des matières en suspension, fraction extraite par de l'acide chlorhydrique (0.2N, attaque à froid). Cette fraction extraite par le lessivage acide (nommée AEM) représente 8% lors des périodes de hautes eaux et 47% pendant les périodes de basses eaux. La dispersion des teneurs de la fraction AEM permet de différencier un domaine de précipitation de $CaCO_3$ et un domaine où les processus d'érosion sont prédominants (Négrel et Grosbois, 1999), en accord avec les travaux de Roy et al., (1998) sur la Seine.

Les concentrations des éléments traces et des Terres Rares varient de manière importante et généralement diminuent avec l'augmentation de la teneur de la fraction AEM. Du point de vue des profils de Terres Rares, avec une normalisation à la croûte continentale (Taylor et McLennan, 1985), un enrichissement en Terres Rares moyennes (par rapport aux Terres Rares lourdes et légères) est observé pour l'ensemble des échantillons. Ce type d'enrichissement, souvent démontré dans les eaux continentales telles que celles des rivières (Sholkovitz, 1995, Gaillardet et al., 1997, eaux acides – Johannesson et al., 1996) et dans les lessivages acides de roches et de minéraux (roches métasédimentaires, grès, apatites, etc.) par de nombreux auteurs (Gosselin et al., 1992, Granjean-Lecuyer et al., 1993, Schaltegger et al., 1994, Zhou et al., 1995), est à rapprocher à la présence d'oxy-hydroxydes de fer et de manganèse liés aux particules transportées par le fleuve (Sposito, 1989, Robinson, 1993, Tricca, 1997, Shine et al., 1995). Les variations des teneurs en strontium confirment l'effet de dilution du composant terrigène (oxy-hydroxydes de fer et de manganèse) présent lors des hautes eaux par la précipitation de la calcite lors des basses eaux. On se trouve donc en présence de deux composants majeurs dans le contrôle des concentrations des éléments chimiques (i.e. les oxy-hydroxydes de fer et de manganèse et les carbonates authigènes).

Les rapports isotopiques $^{87}Sr/^{86}Sr$ de la fraction AEM montrent deux tendances différentes quand ils sont comparés avec les teneurs en AEM (Figure 5), plaidant en faveur de l'existence de deux composants : les oxy-hydroxydes avec les plus bas rapports $^{87}Sr/^{86}Sr$ ($\approx$ 0.7105) et les carbonates authigènes avec les plus élevés ($\approx$ 0.7115). Ces derniers sont en parfaits accord avec les rapports $^{87}Sr/^{86}Sr$ de la fraction dissoute de la Loire à la même époque de l'année (Négrel et al., 2000, Grosbois et al., 2000). Les isotopes stables du carbone et de l'oxygène dans la fraction AEM de la Loire (Négrel et al., 2000), lors des périodes de basses eaux, confirment la formation de calcites authigènes en équilibre isotopique avec l'eau de la Loire (Fontes et al., 1973, Dever et al., 1983). Lors des périodes hydrologiques où les processus d'érosion dominent dans le transport solide, les rapports $^{87}Sr/^{86}Sr$ des oxy-hydroxydes de fer et de manganèse divergent de ceux de la fraction dissoute de la Loire. Ceci implique que les oxy-hydroxydes se sont formés dans une eau avec un rapport $^{87}Sr/^{86}Sr$ plus bas et suggère (i) que la localisation des zones de formation de ces oxy-hydroxydes se situe plus en amont dans le bassin (Négrel et al., 1997a; Négrel et Roy, 2002) et (ii) qu'il n'y a pas de ré équilibration isotopique des oxy-hydroxydes lors du transport aval par les matières en suspension.

[8] Négrel, Ph., Grosbois, C., Kloppmann, W. 2000. The labile fraction of suspended matter in the Loire river (France): multi-element chemistry and isotopic (Rb-Sr and C-O) systematics. Chemical Geology 166, 271-285.

[9] Négrel, Ph., Roy S. 2002. Investigating the sources of the labile fraction in sediments from silicate-drained rocks using trace elements, and strontium and lead isotopes. The Science of the Total Environment 298, 163-182.

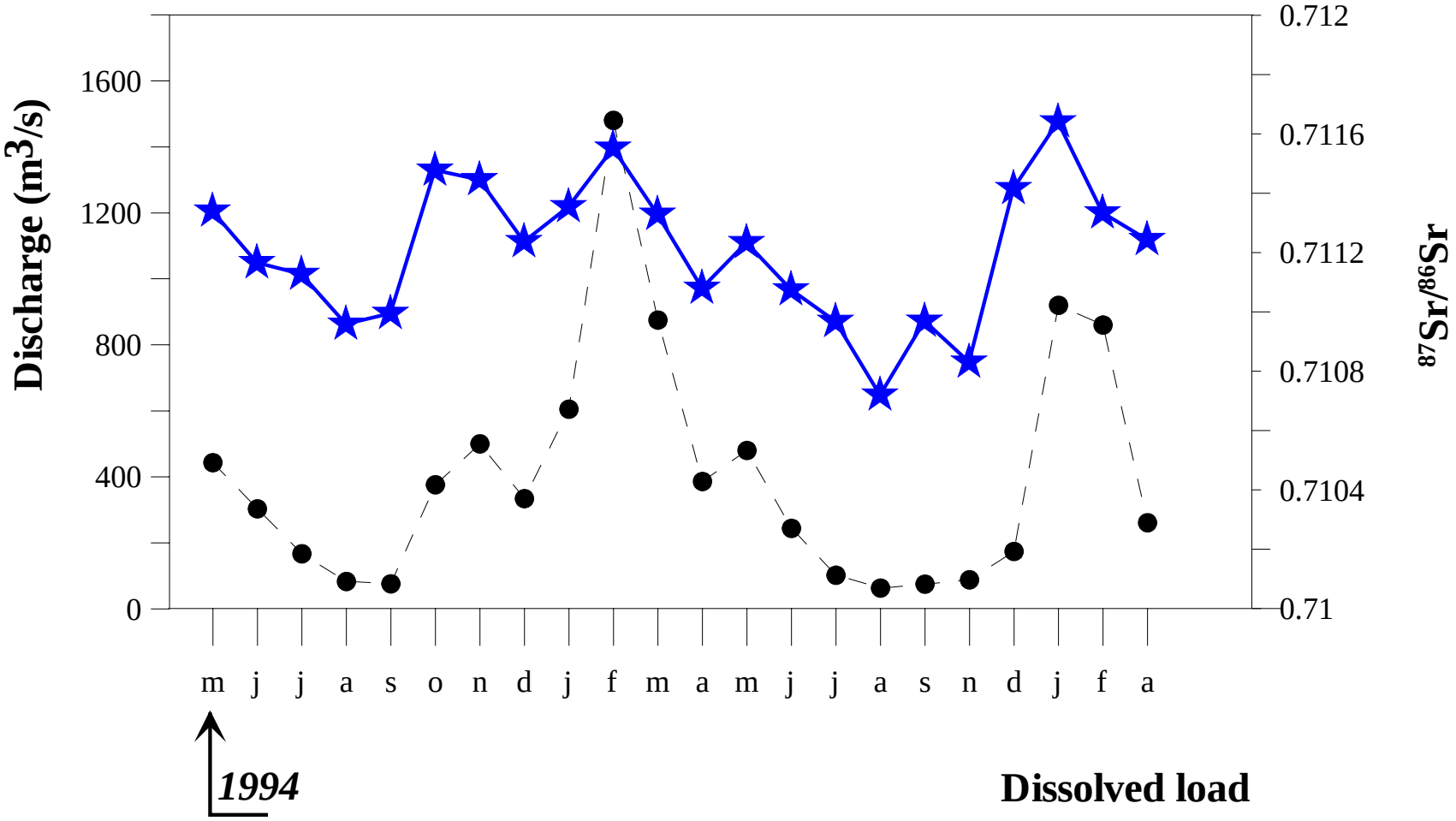

Figure 3. Fluctuations des rapports $^{87}Sr/^{86}Sr$ dans la fraction dissoute (★) en fonction du débit de la Loire (●) selon les mois depuis le début de la période de prélèvements en Mai 1994, figure extraite de Grosbois et al. (2000, Chemical Geology 170, 179-201) .

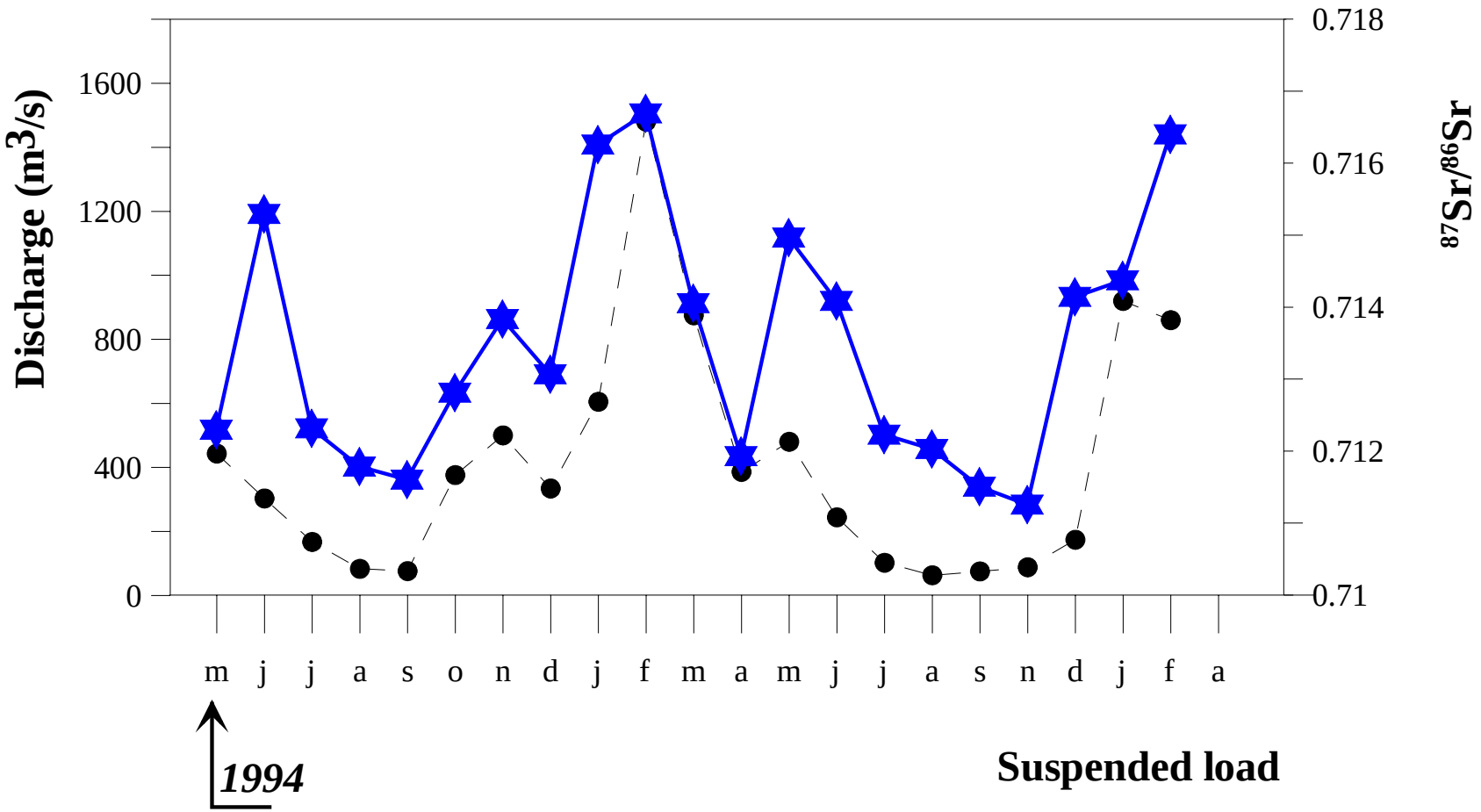

Figure 4. Fluctuations des rapports $^{87}Sr/^{86}Sr$ dans les matières en suspensions (★) en fonction du débit de la Loire (▭) selon les mois depuis le début de la période de prélèvements en Mai 1994, figure extraite de Négrel et Grosbois (1999, Chemical Geology 156, 231-249).

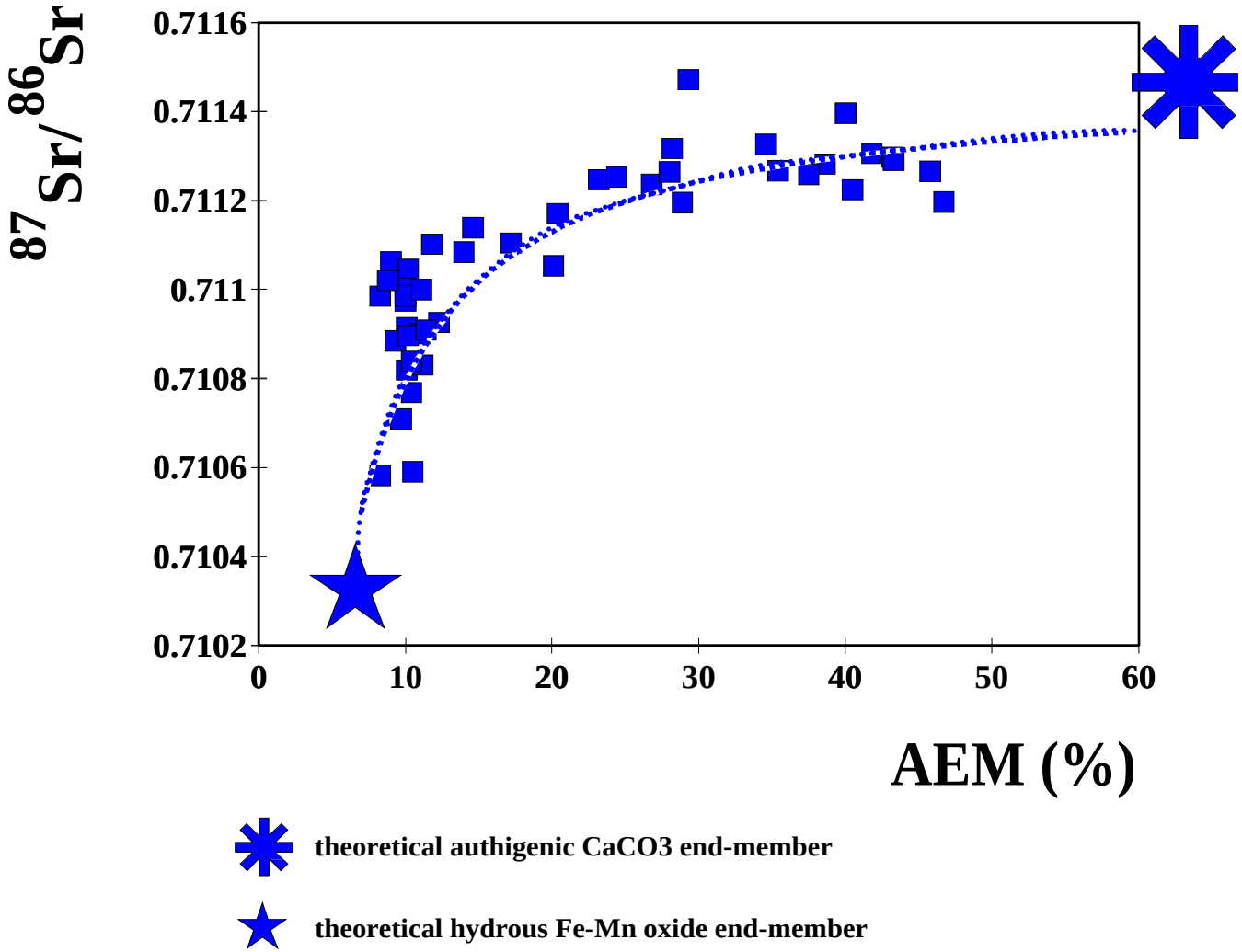

Figure 5. Variations des rapports $^{87}Sr/^{86}Sr$ de la fraction labile des matières en suspensions de la Loire en fonction de la quantité de matière extraite (AEM en %), figure extraite de Négrel et al. (2000, Chemical Geology 166, 271-285).

(IV) LA DECONVOLUTION DES CONTRIBUTIONS NATURELLES ET ANTHROPIQUES SUR LES PETITS BASSINS VERSANTS DANS LE MASSIF CENTRAL (NEGREL ET DESCHAMPS, 1996[10], NEGREL, 1997[11], 1999[12]).

Cette partie concerne l'étude de trois bassins versants situés dans le Massif Central représentatifs des trois types de lithologies constituant la partie amont du bassin de la Loire, à savoir les granites, les gneiss et les basaltes. Les objectifs majeurs de cette étude sont de caractériser la signature chimique et isotopique de tous les composants qui influent sur les compositions chimiques dissoutes et solides: pluies, altération des roches, apports anthropiques, ainsi que les fluctuations des compositions chimiques et isotopiques sur le(s) bassin(s) versant(s) lors de périodes hydrologiques différentes.

La rivière *Allanche*, drainant un petit bassin versant de 150 km^2 constitué par des coulées basaltiques, a été étudié du point de vue chimique et isotopique sur les fractions dissoutes et particulaires ainsi que sur des sédiments de berges (Négrel et Deschamps, 1996). La qualité de l'eau d'un cours d'eau peut être influencée par des apports naturels (pluies, altération de roches) et par des apports anthropiques (engrais, sel de route...). Ces apports anthropiques peuvent être illustrés au travers de l'augmentation des rapports $^{87}Sr/^{86}Sr$ conjointement avec les teneurs en Cl par rapport au drainage des basaltes par les pluies (Figure 6), qui donne des rapports $^{87}Sr/^{86}Sr$ compris entre 0.7036 et 0.7037 pour de faibles concentrations en Cl (environ 1.3 mg l^{-1}). Ces apports anthropiques sont majoritairement liés aux épandages d'engrais, riches en chlorures et en strontium avec des rapports $^{87}Sr/^{86}Sr$ variant entre 0.7083 et 0.709.

Les pluies sont un vecteur important d'apport de substances dissoutes dans un hydrosystème. Pour contraindre cet apport par les pluies, une étude systématique des précipitations a été menée (Négrel et Roy, 1998, Roy et Négrel, 2001, *c.f. Le cycle des précipitations*). La correction des apports de pluie (Meybeck, 1983, Négrel et al., 1993) a été réalisée sur la fraction dissoute en utilisant le chlore comme référence et appliquée sur les éléments chimiques et les rapports $^{87}Sr/^{86}Sr$. Après correction des apports de pluie, le bilan des apports anthropiques et naturels est estimé au travers de la systématique isotopique du strontium associée à des rapports d'éléments majeurs et traces et grâce à un modèle de mélange à deux composants. Le bilan donne, par exemple pour le calcium et le sodium 10% issus des précipitations, 40 à 80% des épandages d'engrais et 15 à 50% de l'altération des roches. Les flux liés à l'altération chimique peuvent être calculés et sont de l'ordre de 0.3 g s^{-1} km^{-2} en basses eaux et 0.6 g s^{-1} km^{-2} en hautes eaux, donnant un taux de dénudation de 5.3 mm 1000 ans^{-1}.

La rivière *Desges* draine un bassin versant de 89 km^2 constitué de granites et gneiss dans les montagnes de Margeride. Les fractions dissoutes et particulaires ainsi que des sédiments et des sols ont été étudiés du point de vue chimique et isotopique (Négrel, 1999). Comme pour la rivière Allanche, la correction des apports de pluies a été réalisée sur la fraction dissoute en utilisant le chlore comme référence. Le bilan de cette correction montre des apports de pluies de l'ordre de 50% pour Ca, 30% pour Na et Sr, 15% pour Mg. La composition chimique des eaux, en dehors de toute perturbation anthropique, et contrôlée par les processus d'interaction avec les roches du bassin se positionne dans le champ de stabilité de la kaolinite par application de l'approche thermodynamique (Giovanolli et al., 1988, Drever et Zobrist, 1992).

[10] Négrel, Ph., Deschamps, P. 1996. Natural and anthropogenic budgets of a small watershed in the Massif Central (France): Chemical and strontium isotopic characterization in water and sediments. Aquatic Geochemistry 2, 1-27.

[11] Négrel, Ph. 1997. Traçage des apports anthropiques sur un petit bassin versant : utilisation des rapports isotopiques du strontium. C.R. Académie des Sciences 324, série II, 907-914.

[12] Négrel, Ph. 1999. Geochemical study in a granitic area, the Margeride, France: chemical element behavior and $^{87}Sr/^{86}Sr$ constraints. Aquatic Geochemistry 5, 125-165.

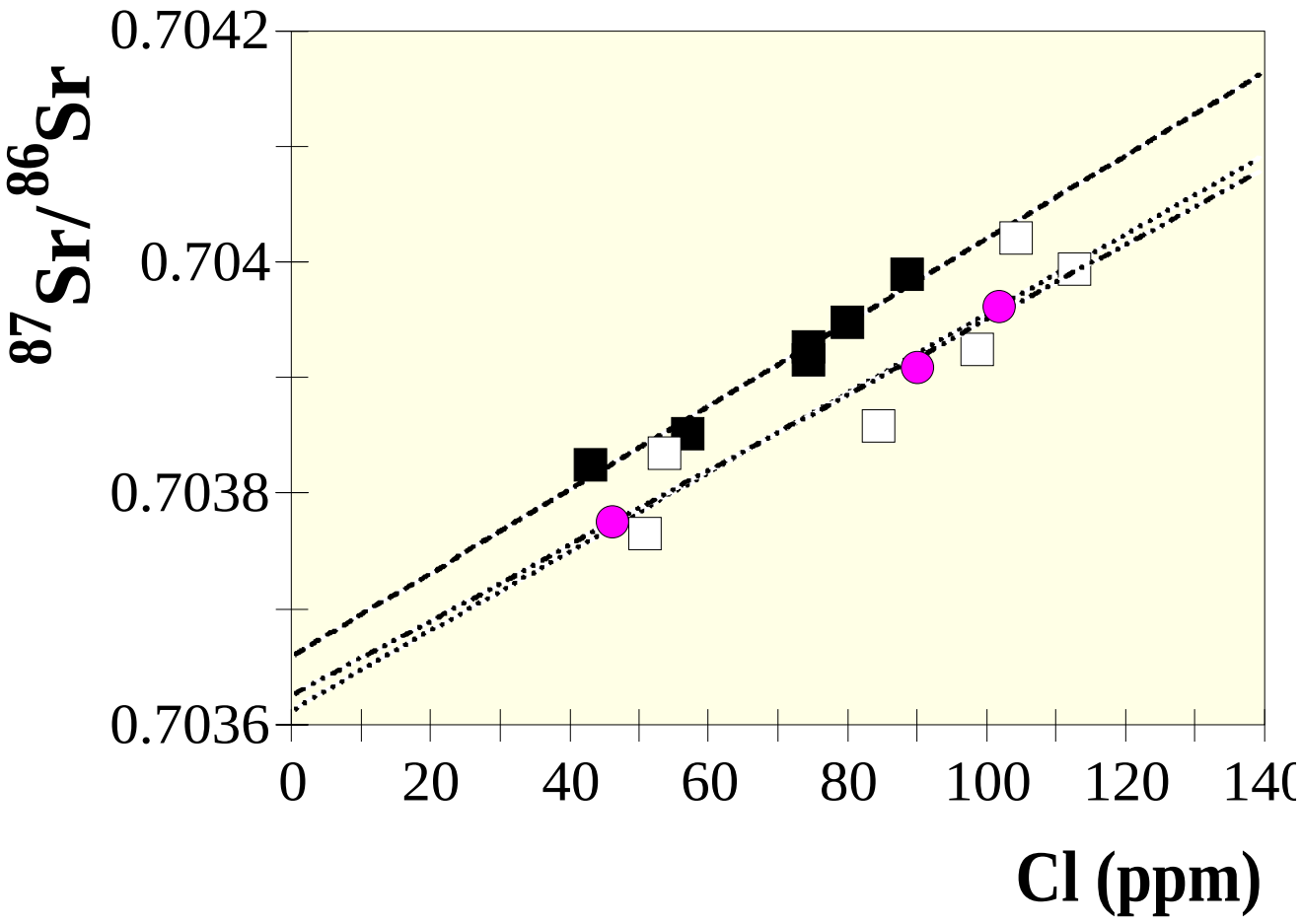

Figure 6. Relation entre les rapports $^{87}Sr/^{86}Sr$ et les teneurs en Cl (en ppm) lors de trois campagnes de prélèvements sur le cours majeur de la rivière Allanche (mai 1994 en carrés noirs, septembre 1994 en carrés blancs et avril 1995 en ronds noirs), figure extraite de Négrel et Deschamps (1996, Aquatic Geochemistry 2, 1-27).

La gamme de variation de l'indice d'altération (RE = 2 (3K + 3Na + 2Ca - Si)/(K + Na + Ca, Tardy, 1971, Mortatti et al., 1992, Stallard, 1980) indique que la formation de kaolinite est un processus dominant comme montré par Tardy (1971) et Bourrié (1978).

Les rapports $^{87}Sr/^{86}Sr$ des eaux non perturbées par les apports anthropiques (e.g. Cl = 0 après correction des apports de pluies) sont en règle générale inférieurs à ceux observés dans les roches totales (0.7211-0.7704, Couturié et al., 1979). Ces rapports sont majoritairement contrôlés par des mélanges entre eaux de surface et des eaux souterraines issues de la zone superficielle des altérites. L'utilisation du diagramme classique entre les rapports $^{87}Sr/^{86}Sr$ en fonction de l'inverse de la concentration en Sr met en évidence deux droites de mélanges suggérant trois composants. Une source de Sr est prédominante en basses eaux avec un rapport $^{87}Sr/^{86}Sr$ bas (0.715) et une autre est prédominante en hautes eaux avec des rapports $^{87}Sr/^{86}Sr$ plus élevés, de l'ordre de 0.717 sur les granites et 0.720 sur les gneiss.

Du point de vue du fonctionnement des profils d'altération, lors des périodes de bas débits de la rivière, l'eau provient de la base des profils avec une alimentation maximale par de l'eau souterraine d'origine peu profonde. Lors des périodes de forts débits de la rivière, l'eau a pour origine les parties hautes des profils d'altération. A la base des profils, les rapports isotopiques ressemblent plus à ceux de la roche totale tandis qu'au sommet de ces mêmes profils l'altération des minéraux résiduels induit des rapports plus élevés. Un calcul de mélange binaire donne des proportions d'eau souterraine variant de 0.3 à 27%. Dans les parties du bassin soumises à la pression anthropique (engrais, amendements, sels de route), une relation générale existe entre les rapports $^{87}Sr/^{86}Sr$ et la concentration en chlorure ainsi qu'entre les rapports $^{87}Sr/^{86}Sr$ et l'inverse de la concentration en Sr. Ces relations sont expliquées par des mélanges à trois composants roches (gneiss, micaschistes et granites) et un apport anthropique de plus bas rapport isotopique.

La rivière *Bertrande* a été étudiée le long du cours d'eau depuis les têtes de bassins des différents affluents jusqu'à l'exutoire (Négrel, 1997b). Le bassin comprend une partie amont formée de roches volcaniques et une partie aval formée de roches métamorphiques. Les teneurs en Ca, Na, Mg, K, B et Sr dans la fraction dissoute sont liées aux apports par les trois composants (pluies, roches, polluants) et augmentent linéairement le long des cours d'eau. Les concentrations en Cl et NO_3 augmentent régulièrement et ne sont liées qu'avec la source atmosphérique et les apports anthropiques. La proportion d'engrais en tête de bassin varie de 10 à 25% et est de 43% sur le cours principal de la Bertrande. Les rapports $^{87}Sr/^{86}Sr$ n'augmentent pas lors du passage brutal entre les formations volcaniques et le domaine métamorphique, comme on aurait pu s'y attendre, mais augmentent conjointement à l'augmentation des teneurs en Cl traceur des pollutions.

(V) LA PRISE EN COMPTE DE LA VARIATION DANS LE TEMPS A L'ECHELLE DES 10 DERNIERS MILLIERS D'ANNEES PERMET DE RECONSTRUIRE L'EVOLUTION DU FLEUVE (GARCIN ET AL., 1999[13], NEGREL ET AL., 2002[14])

Cette partie est dédiée à l'étude de la distribution de certains éléments traces (V, Sr) ainsi qu'aux rapports isotopiques du Sr dans la fraction labile de sédiments fluviatiles collectés par carottages dans la vallée alluviale de la Loire. Les fonds de vallées sont des aires de stockage des particules issues de l'érosion à l'échelle des bassins versants (Meade, 1988) et constituent de ce fait des sites d'enregistrement privilégiés des événements passés ayant affecté le bassin versant. Les accumulations alluvionnaires en Loire moyenne atteignent 7 m d'épaisseur au sein d'un dispositif morphologiquement structuré, à nombreuses incisions, bras morts ou chenaux liés à la migration d'un méandre. Les carottes étudiées dans ce site couvrent une période temporelle comprise entre 0 et plus de 10 000 ans BP (Garcin et al., 1999).

Les proportions de matière extraite (AEM, *voir §iii*) par l'attaque à l'acide faible HCl 0.2N dans les sédiments varient entre 6 et 52%. Elles sont associées à de grandes variations des concentrations des éléments traces Mn, V, Rb et Sr. Les oxy-hydroxydes de fer et de manganèse agissent comme le principal pourvoyeur des éléments traces dans la fraction labile des sédiments (Robinson, 1993)

[13] Garcin, M., Giot, D., Farjanel, G., Gourry, J.-C., kloppmann, W., Négrel, Ph. 1999 Géométrie et âge du remplissage Holocène de la Loire Moyenne, exemple du Val d'Avaray (France, Loire et Cher). C. R. Académie des Sciences 329, 405-412.

[14] Négrel, Ph., Kloppmann, W., Garcin, M., Giot, D. 2002. Strontium isotopic record of signatures of Holocene fluvial sediments in the Loire valley, France. Hydrology and Earth System Sciences 6, 849-858.

tandis que les carbonates agissent comme un pourvoyeur d'ampleur moindre. V, Rb et Pb proviennent de l'altération et de l'érosion des silicates (Schiller et Mao, 2000) et sont fixés par les oxy-hydroxydes de fer et de manganèse (Wehrli et Stumm, 1989). Ils peuvent par conséquent être utilisés comme un index de l'érosion de ces terrains dans l'enregistrement sédimentaire. La distribution du Sr ne peut être directement utilisée pour tracer directement l'altération et l'érosion des silicates car cet élément est contrôlé *pro-parte* par les carbonates et les oxy-hydroxydes. Cependant, l'utilisation des isotopes du Sr permet de contraindre les contributions des deux pourvoyeurs d'éléments traces que sont les oxy-hydroxydes et les carbonates.

Les variations des rapports $^{87}Sr/^{86}Sr$ de la fraction AEM permettent de définir deux champs distincts comme illustré sur la figure 7.

Dans le premier champ, la proportion extraite est toujours faible (AEM de l'ordre de 10%) et les rapports $^{87}Sr/^{86}Sr$ montrent une large dispersion depuis 0.7086 jusqu'à 0.710. Ce champ correspond aux oxy-hydroxydes dont l'origine se situe dans le Massif Central. Leurs signatures isotopiques dérivent de l'altération des différentes roches, principalement les granites-gneiss et les basaltes (Négrel et Deschamps, 1996, Négrel et al., 1997a, Négrel, 1999, Négrel et Roy, 2002) de la partie amont du bassin. D'autre part, ils montrent une plus grande variabilité des rapports $^{87}Sr/^{86}Sr$ que celle mesurée sur les matières en suspensions actuelles (Négrel et al., 2000).

Le second champ correspond à des proportions extraites plus importantes (AEM de 20 à 50%). Le rapport $^{87}Sr/^{86}Sr$ ne fluctue quasiment pas (0.709-0.7095). Ce champ, qui correspond au pôle carbonate, a des rapports $^{87}Sr/^{86}Sr$ très significativement différent des rapports $^{87}Sr/^{86}Sr$ des carbonates authigènes actuels (Négrel et al., 2000, Grosbois et al., 2000). Cette grande différence des rapports $^{87}Sr/^{86}Sr$ peut refléter des apports de carbonates à la fois authigènes et détritiques où la composante authigène est importante en quantité et requière un équilibre avec des eaux de bas rapports isotopiques, différents de ceux de la Loire actuelle. On peut envisager des apports d'eau souterraine dans la zone de dépôt des sédiments avec des rapports $^{87}Sr/^{86}Sr$ bas, ce qui est en accord avec les signatures isotopiques obtenues sur des tests de gastéropodes analysés le long de la carotte.

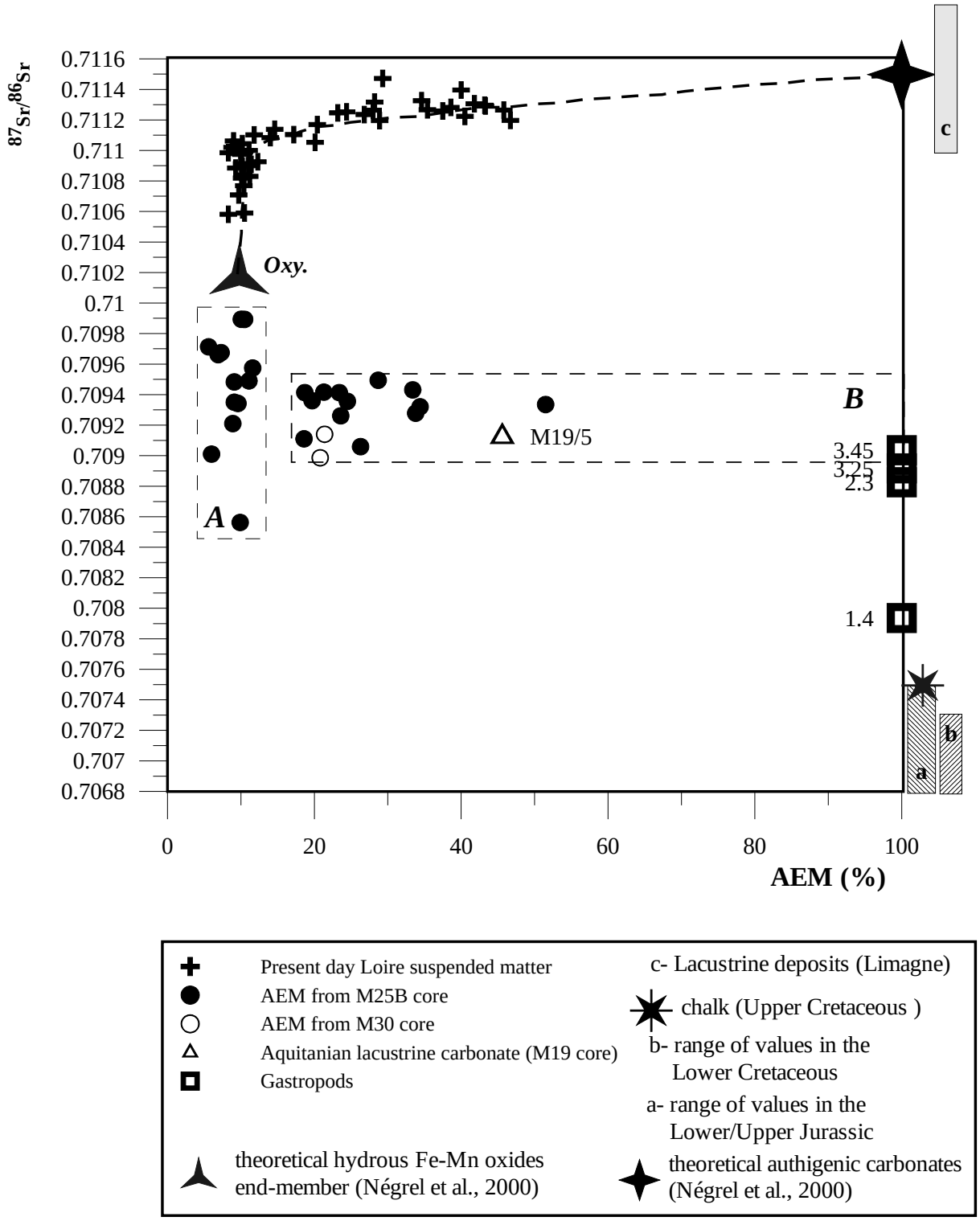

Figure 7. Représentation des rapports $^{87}Sr/^{86}Sr$ la fraction labile de sédiments fluviatiles (AEM) couvrant une période temporelle Holocène entre 0 et plus de 10 000 ans BP, figure extraite de Négrel et al. (2002, Hydrology and Earth System Sciences 6, 849-858).

(VI) LE BASSIN VERSANT : UN REFERENTIEL POUR LES EAUX SOUTERRAINES, EXEMPLE DE LA GUYANE (NEGREL ET LACHASSAGNE, 2000[15]).

Le fleuve Maroni, qui draine une zone de 60000 km^2, se jette dans l'océan Atlantique entre la Guyane et le Surinam. Menée durant la période de basses eaux, cette étude est basée sur l'application des éléments majeurs et traces, des isotopes stables de l'eau et des isotopes du strontium afin :

- de caractériser les apports atmosphériques sur le bassin versant pour confirmer les travaux précédents menés près de la côte à Cayenne en 1995 (Négrel et al., 1997b) ;
- de caractériser à la fois les compositions chimiques et isotopiques du Maroni et de ses affluents pour produire un référentiel de la qualité des eaux superficielles ;
- de caractériser, au travers des petits tributaires, la composition chimique et isotopique des interactions eau-roche ;
- et de produire une première série d'informations chimiques et isotopiques sur les eaux souterraines.

Toutes les compositions chimiques des eaux de surface du bassin versant du Maroni sont en accord avec le champ "*precipitation dominance*" (Gibbs, 1970) et les données acquises sur les rivières du Guyana Shield, de l'Orénoque et de l'Amazone (Stallard, 1980, Stallard et Edmond, 1987, Mortatti et al., 1992, Edmond et al., 1995, Gaillardet et al., 1997). Les eaux souterraines collectées dans des puits peu profonds ressemblent largement aux eaux de surface, tandis que les eaux souterraines plus profondes, collectées par forages, reflètent une augmentation de l'interaction eau-roche de part l'évolution de leur chimie. Les isotopes stables de l'eau montrent que les points des eaux superficielles et souterraines du bassin du Maroni sont très proches de la droite des pluies locales (Négrel et al., 1997b), bien que certains échantillons s'éloignent de cette droite, mettant en évidence des processus d'évaporation.

Les corrections des apports de pluies (Meybeck, 1983, Négrel et al., 1993), en utilisant le chlorure comme élément de référence, ont été calculées pour tous les éléments chimiques et le rapport $^{87}Sr/^{86}Sr$. Dans un diagramme classique de mélange ($^{87}Sr/^{86}Sr$ vs. 1/Sr, corrigés des apports de pluies), deux alignements décrivent un modèle de mélange simple entre trois composants. Le premier composant est commun aux deux lignes de mélange et correspond au drainage de roches volcaniques et dérivées (Paramaca Inférieur : schistes, quartzites, métavolcanites). Le deuxième composant correspond au drainage des schistes, des micashistes, et des grès (Paramaca Supérieur). Le troisième composant correspond au drainage des séries du plutonisme "Guyanais" (orthogneiss/graniodiorites/migmatites).

Les points relatifs au Maroni sont relativement peu dispersés et se situent sur la droite de mélange entre les deux composants extrêmes (Paramaca Inférieur et Supérieur). Le triangle de mélange ainsi défini correspond aux plus grandes lithologies identifiables sur le bassin du Maroni avec les schistes comme composant le plus radiogénique, les métavolcanites comme composant le moins radiogénique et les séries granitiques comme troisième composant. Les eaux souterraines se positionnent dans ce système de mélange.

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4. Le cycle souterrain

Après une restitution *pro-parte* de la pluie vers l'atmosphère, les conditions naturelles du sol et du sous-sol divisent l'écoulement des eaux en lui offrant deux voies différentes. Le ruissellement et l'écoulement superficiel dans les cours d'eau, traité dans la partie précédente, constituent la voie rapide. A contrario, l'infiltration et l'écoulement souterrain dans les aquifères constituent la voie lente.

La plupart des milieux rocheux contiennent de l'eau, soit dans les pores existant entre les minéraux des roches, soit dans les fissures, plus ou moins nombreuses et ouvertes. Ainsi, un volume de 1 m^3 de sable et de graviers saturé d'eau en contient de 200 à 300 litres. Compte tenu de la disparité entre eau libre et eau retenue par capillarité, le même volume de sable et de graviers ne contient que de 150 à 250 litres d'eau mobile. Un même volume de craie contient de 10 à 50 litres d'eau mobile tandis que 1 m^3 de granite fissuré en contient de 1 à 20 litres. Ainsi les roches les plus perméables sont de bons conducteurs d'eau et ont donc une forte perméabilité. Celle ci est définie comme le débit d'eau qui peut passer à travers une section de roche définie pour un gradient hydraulique donné. On observe des perméabilités de $1\ 10^{-2}$ à $1\ 10^{-4}$ m s^{-1} (soit 1000 à 10 m j^{-1} pour un gradient de 100%) pour la craie, tandis que des valeurs de $1\ 10^{-5}$ à $1\ 10^{-10}$ m. s^{-1} (1 m à 0.01 mm j^{-1}) pour les granites.

Les associations de roches, couches superposées ou juxtaposées, organisent la répartition et la circulation des eaux souterraines en leur faisant obstacle ou en créant des voies de cheminement. Des volumes de roches assez perméables et suffisamment étendus pour qu'une part importante de l'écoulement régional y transite et y séjourne constituent des aquifères. Ces derniers fuient en permanence et l'eau s'en échappe par des voies nombreuses ou rares, visibles ou cachées, localisées ou diffuses et toujours situées aux points les plus bas de la surface de l'aquifère. En fonction de la topographie, les exutoires des aquifères sont les sources (émergences) de déversement ou de débordement).

Une eau minérale est une eau souterraine susceptible d'agir efficacement sur la santé de part sa nature (éléments chimiques, gaz,…). Elle se distingue nettement des autres eaux destinées à la consommation humaine par sa salinité. Elle témoigne dans le cadre des fluctuations naturelles connues d'une stabilité de ses caractéristiques essentielles. Sa composition chimique et sa température à l'émergence ne sont pas affectées par le débit de l'eau prélevée. Une eau minérale peut être froide ou chaude. Dans ce dernier cas, elle répond au terme d'eau thermale et correspond à une eau d'origine souterraine naturellement chaude à son émergence. Sa température est supérieure à un seuil (par exemple la valeur moyenne des nappes de la région) ce qui la rend utilisable à diverses fins, notamment sanitaires ou thérapeutiques. Les eaux chaudes ont été recherchées par l'homme pour se soigner dès le tout premier âge de l'humanité. Les premiers témoignages de l'utilisation des eaux chaudes à usage médical, ont été datés entre 5000 et 3 000 ans avant J.C.

Cette partie est dédiée aux eaux souterraines via les études des eaux minérales et des eaux profondes en milieu de socle fracturé. Elle s'intéresse tout particulièrement au mode d'acquisition des signatures isotopiques strontium, néodyme et bore en regard de l'origine des eaux salées et des circulations de ces eaux dans des zones de socle fracturé. Les études des eaux profondes dans la Vienne et dans l'hydrosystème de Palmottu (Finlande) ont été réalisées dans le cadre de la problématique du stockage des déchets radioactifs.

(I) LES EAUX PROFONDES DE LA VIENNE : HISTOIRE DES EAUX SOUTERRAINES ET ISOTOPES (NEGREL ET AL., 2001[16, 17], CASANOVA ET AL., 2001[18], KLOPPMANN ET AL., 2002[19], NEGREL ET AL. , 2002[20])

Les eaux profondes dans les batholites granitiques de part le monde présentent des salinités élevées (Beaucaire et al., 1999, Fritz et Frape, 1987). L'existence de fluides salés dans des formations géologiques à grande profondeur est un phénomène mondial fortement étudié au cours des dernières décennies à l'aide d'un panel d'outils géochimiques variés : traceurs réputés conservatifs (Cl-Br, $\delta^{18}O$ et $\delta^{2}H$, Fritz et Frape, 1987, Bottomley et al., 1994) et les isotopes du strontium (McNutt et al., 1984, 1987, 1990). En particulier, l'origine de la salinité est l'objet de controverses (Fritz et Frape, 1987, Bottomley et al., 1994) entre les partisans d'une origine autochtone (i.e. d'interaction avec les roches) et ceux d'une origine allochtone (i.e. intrusion marine, saumure d'évaporite résiduelle, migration de fluides secondaires issus de la dissolution d'évaporites).

Le système aquifère de la Vienne (Matray et al., 1998, Michelot, 1999) montre des eaux avec des salinités inférieures à 0.5 mg l^{-1} dans les aquifères sédimentaires superficiels (Dogger et Infra-Toarcien et plus élevées (0.5-10 g l^{-1}) dans l'encaissant granitique. La plupart des teneurs élémentaires augmentent avec la profondeur (Michelot, 1999, Casanova et al., 2001). Une boîte à outils géochimique et isotopique contenant U, B, Sr, H et O a été utilisée sur les eaux profondes des granites de la Vienne dans le but de contraindre leur origine (Négrel et al., 1997b, 1999, 2001a,b, Kloppmann et al., 1999, 2000, 2002, Casanova et Aranyossy, 1998, Casanova et al., 2001). La combinaison d'outils isotopiques aide à restreindre les hypothèses sur la nature des interactions entre eau et roche ainsi qu'à caractériser les différents composants impliqués dans les processus de mélange des eaux.

Les isotopes du bore. Les concentrations en bore varient depuis 2 µg g^{-1} jusqu'à plus de 6 µg g^{-1}, dépassant ainsi celles de l'océan (4 µg g^{-1}). Les rapports isotopiques $\delta^{11}B$ s'échelonnent entre +24.9‰ et +36.1‰. Les aquifères sédimentaires, outre des teneurs en bore plus faibles, présentent des $\delta^{11}B$ aux alentours de +13‰ pour l'Infra-Toarcien et de -2.4‰ pour le Dogger. Les compositions isotopiques $\delta^{11}B$ des eaux profondes convergent vers la valeur marine et sont très différentes de celles des eaux minérales du Massif Central (Casanova et al., 2001). Ceci suggère l'influence d'un composant très minéralisé avec une signature isotopique proche de celle de l'océan dans les eaux profondes de la Vienne. Les signatures isotopiques de ces eaux s'inscrivent dans un éventail d'interaction eaux-roches cristallines, tout en présentant une forte convergence de signature avec des paléo-fluides sédimentaires très anciens (océans Dogger-Toarcien). Cette convergence de signature est encore plus marquée dans une représentation entre les rapports $\delta^{11}B$ et les teneurs en Cl (Casanova et al., 2001). Les eaux profondes de la Vienne se répartissent sur une ligne de mélange entre des eaux minéralisées (type Massif Central) et l'eau de mer. Un tel modèle de mélange met en évidence une proportion de 20% d'eau de mer dans les eaux profondes de la Vienne (Casanova et al., 2001).

Les isotopes du strontium. Le rapport $^{87}Sr/^{86}Sr$ est un traceur des interactions avec la roche mais la mesure directe de ces rapports dans les eaux profondes obtenues lors des campagnes de forages peut être entachée d'une contamination par les fluides de forages (Kloppmann et al., 2001, Négrel et al., 2001a). Une correction de cette contamination a été appliquée sur les 26 échantillons d'eaux profondes. A l'issue de cette correction, les données sur les eaux profondes de la Vienne mettent en évidence de grandes variations dans les concentrations en Sr de 11 à 80 µmol l^{-1} (Figure 8). Les rapports $^{87}Sr/^{86}Sr$ varient de 0.70781 à 0.70909 mais peu au sein d'un même forage. La variation toute limitée des rapports $^{87}Sr/^{86}Sr$ contraste avec la gamme plus étendue mise en évidence

[16] Négrel, Ph., Casanova, J., Aranyossy, J.F. 2001. Strontium isotope systematics used to decipher the origin of groundwaters sampled from granitoids: the Vienne case (France). Chemical Geology 177, 287-308.

[17] Négrel, Ph., Casanova, J., Kloppmann, W., Aranyossy, J.F. 2001. Investigating water-rock interaction in the Vienne crystalline basement (France). In Proceedings of the tenth International Symposium on Water Rock Interaction, WRI 10, Italy, Cidu, R. (ed), Balkema, Lisse, 1557-1560.

[18] Casanova, J., Négrel, Ph., Kloppmann, W., Aranyossy, J.F. 2001. Origin of deep saline groundwaters in the Vienne granitoids (France). Constrains inferred from Boron and Strontium isotopes. Geofluids 1, 91-102.

[19] Kloppmann, W., Girard, J.P., Négrel, Ph. 2002. Exotic stable isotope compositions of saline waters and brines from the crystalline basement. Chemical Geology 184, 49-70.

[20] Négrel, Ph., Casanova, J., Kloppmann, W., Aranyossy, J.F. 2002. A combined isotopic tool for water-rock interaction studies: $^{87}Sr/^{86}Sr$, $\delta^{11}B$, $\delta^{18}O$, $\delta^{2}H$ and U-series in deep groundwater from the vienne granite (France). In Water-Rock Interaction, special issue EUGX, Kluwer, Stober & Bucher (eds.), 39-59.

sur les eaux de surface. Les données sur les eaux profondes et superficielles du granite de la Vienne, les eaux des aquifères de l'Infra-Toarcien et du Dogger (Négrel et al., 2001a), représentées en fonction de la profondeur mettent en évidence différentes signatures isotopiques qui suggèrent une absence de connexion entre les différents systèmes (Figure 8).

Pour connaître la signature isotopique en Sr théorique d'une eau interagissant avec un granite, il est nécessaire d'utiliser un modèle de dissolution (Bullen et al., 1997). Un tel modèle a été développé (Négrel et al., 2001a) en faisant l'hypothèse que la plus grande partie du Sr libéré par l'altération provient des trois minéraux principaux suivants : plagioclases, feldspaths potassiques et biotites (Zuddas et al., 1995). Dans ce modèle, les nouvelles phases minérales formées sont considérées en équilibre isotopique avec leurs solutions mères. En effet, la formation de nouvelles phases minérales induira une diminution de la teneur en Sr de la solution mère mais sans modification du rapport isotopique. Pour ce modèle, il est nécessaire de connaître pour la roche mère de type granite ou gneiss : la teneur en Sr et la composition isotopique en Sr des trois phases minérales principales (plagioclases, feldspaths potassiques et biotite) ; la proportion de chacun de ces trois minéraux au sein du granite ; l'altérabilité de chacun de ces trois minéraux. Dans ces conditions, le rapport isotopique d'une eau en équilibre avec un granite de composition connue s'écrit :

$$iSr_{th} = \frac{(iSr_{Pl} \times Sr_{Pl} \times \%_{Pl} \times Alt_{Pl}) + (iSr_B \times Sr_B \times \%_B \times Alt_B) + (iSr_{FK} \times Sr_{FK} \times \%_{FK} \times Alt_{FK})}{(Sr_{Pl} \times \%_{Pl} \times Alt_{Pl}) + (Sr_B \times \%_B \times Alt_B) + (Sr_{FK} \times \%_{FK} \times Alt_{FK})}$$

avec : iSr : rapport $^{87}Sr/^{86}Sr$; Sr : teneur en Sr ; % : pourcentage du minéral dans la roche ; Alt : altérabilité relative du minéral ; th : théorique ; Pl : plagioclase ; B : biotite ; FK : feldspath potassique.
Soit :

$$iSr_{th} = \frac{\sum (iSr_{mx} \times Sr_{mx} \times \%_{mx} \times Alt_{mx})}{\sum (Sr_{mx} \times \%_{mx} \times Alt_{mx})}$$

si $mSr_{mx} = Sr_{mx} + \%_{mx} + Alt_{mx}$ correspond à la masse de Sr issue du minéral mx et iSr_{mx} représente le rapport $^{87}Sr/^{86}Sr$ du minéral mx alors :

$$\boxed{iSr_{th} = \frac{\sum (iSr_{mx} \times mSr_{mx})}{\sum (mSr_{mx})}}$$

Le calcul des rapports iSr_{th} donnent des valeurs basses pour les tonalites (0.70463) et plus fortes pour les monzogranites (0.70704). Ces résultats indiquent que les eaux profondes de la Vienne ne peuvent être directement reliées à l'altération des tonalites et des monzogranites comme considéré dans le modèle au vue des gammes de valeurs trouvées dans ces eaux ($^{87}Sr/^{86}Sr$ 0.70781 ± 0.00012 à 0.70909 ± 0.00019. Une source additionnelle de Sr, avec un rapport $^{87}Sr/^{86}Sr$ plus élevé que celui calculé par le modèle, doit être invoquée, comme celle avec des paléo-fluides sédimentaires très anciens (océans Dogger-Toarcien).

Les données des *isotopes stables*, corrigées de la contamination montrent que les eaux profondes sont décalées à gauche de la droite mondiale (Kloppmann et al., 2000, 2001, 2002). Ceci suggère, comme montré dans d'autres sites granitiques (Kloppmann et al., 2002), que des interactions entre eau et roche sous de faible gradient de température et pour des faibles porosités modifient les $\delta^{18}O$ et $\delta^{2}H$ de l'eau.

Les isotopes de l'uranium. Le rapport $^{234}U/^{238}U$ est généralement supérieur à 1 (gamme de 1.9 à 3.4, traduisant des conditions réductrices (Négrel et al., 2001b). Les eaux profondes, avec de faibles concentrations en U qui diminuent avec la profondeur alors que celles en Th augmentent (Casanova et Aranyossy, 1998), ont des rapports $^{234}U/^{238}U$ qui augmentent en liaison avec les processus de recul. Les eaux moins profondes du site, avec de plus fortes concentrations en U, ont des rapports $^{234}U/^{238}U$ qui indiquent une mise en solution plus importante de l'uranium 234.

Les signatures isotopiques de la boite à outils (U, B, Sr, H et O) indiquent que les eaux du socle de la Vienne s'inscrivent dans un éventail de solutions d'interaction eaux-roches cristallines, tout en présentant une forte convergence de signature avec des paléo-fluides sédimentaires très anciens (océans Dogger-Toarciens).

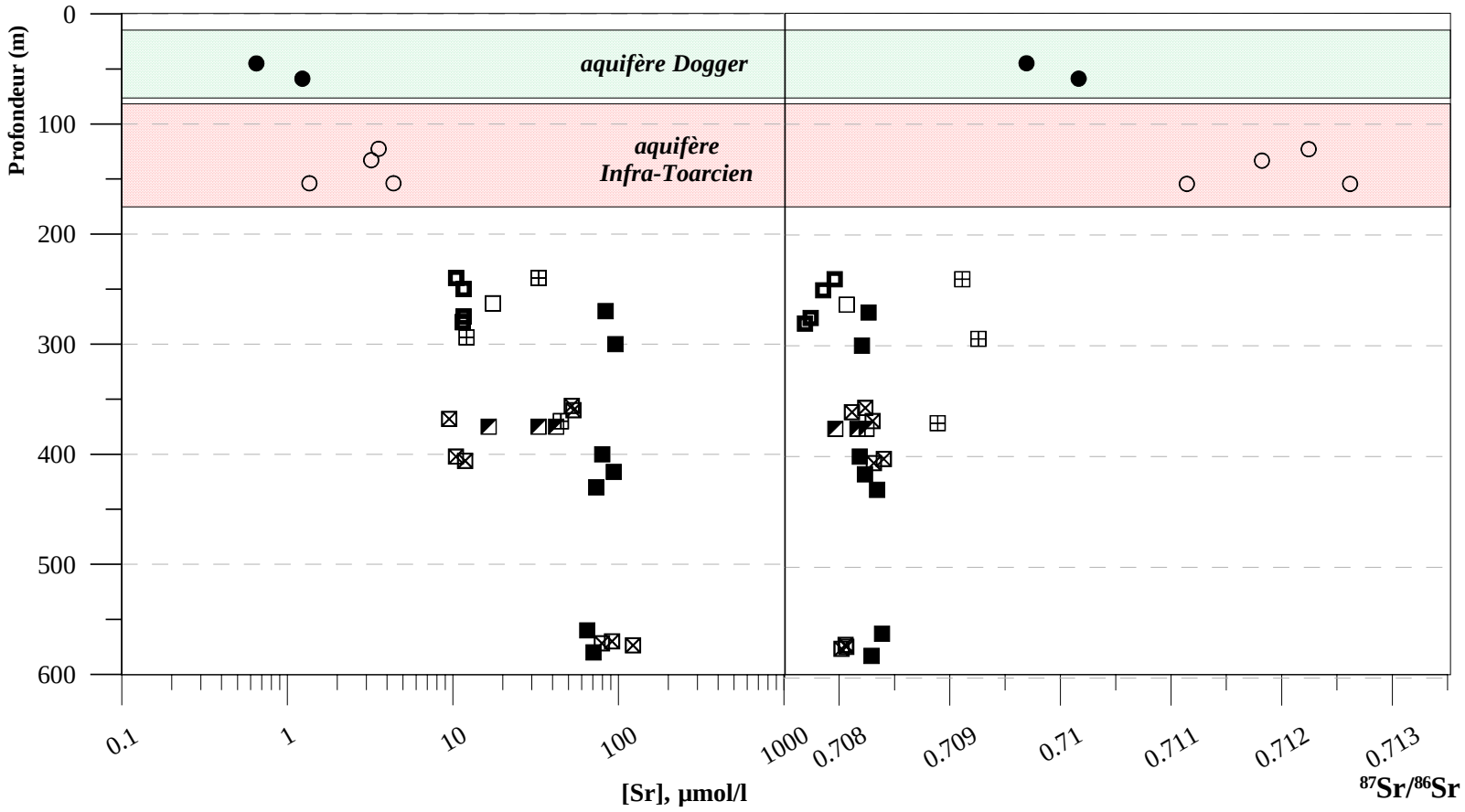

Figure 8. Représentation en fonction de la profondeur dans les aquifères du Dogger et de l'Infra-Toarcien et dans le batholite de granite de la Vienne des concentrations en strontium et des rapports $^{87}Sr/^{86}Sr$, figure extraite de Négrel et al. (2001, Chemical Geology 177, 287-308).

(II) LES EAUX SOUTERRAINES DE PALMOTTU (FINLANDE) : UN SYSTEME DE SOCLE FRACTURE SOUS CLIMAT FROID (NEGREL ET AL, 2001[21], CASANOVA ET AL., 1999[22], NEGREL ET AL., 2003[23])

Le site granitique de Palmottu est localisé au sud de la Finlande et est utilisé comme analogue naturel dans les études de transport de radionuclides à partir d'un gisement d'uranium. Pendant le dernier million d'années, la zone de Palmottu a été soumise à plusieurs glaciations dont la dernière, Yoldia, s'est terminée il y a 10 000 ans. La zone de Palmottu a émergé de la Mer Baltique immédiatement après le retrait du glacier et des quantités importantes d'eau de glacier ont pénétré dans le site de Palmottu.Dans ce contexte, les isotopes du bore, du strontium et du néodyme ont été utilisés pour établir l'origine de la salinité, le degré d'interaction eau-roche et pour clarifier les processus de mélanges des différentes eaux souterraines. Ces dernières montrent de grandes variations dans leur composition chimique évoluant depuis des eaux de type Ca-HCO_3, Ca-Na-HCO_3 et Na-Ca-HCO_3 vers des eaux de type Na-Cl, Na-SO_4-Cl (Pitkänen et al., 2002).

Dans l'hydrosystème de Palmottu, une large gamme de variations des compositions isotopiques du strontium est mis en évidence dans les eaux profondes (i.e. 0.720-0.750, Casanova et al., 1999a, Négrel et al., 2002, soumis) sans lien avec les types d'eaux observés (Na-Cl, Na-SO_4, etc). Le modèle d'altération visant à déterminer le rapport $^{87}Sr/^{86}Sr$ (iSr_{th}) de l'eau ayant interagi avec le granite, et développé pour le site de la Vienne (Négrel et al., 2001a), a été appliqué sur les granites du site de Palmottu. Le calcul des rapports iSr_{th} indique que la moitié des rapports $^{87}Sr/^{86}Sr$ mesurés dans les eaux souterraines peuvent être expliqués par l'altération des granites encaissants. Pour expliquer l'autre moitié des valeurs observées, un composant de plus bas rapport $^{87}Sr/^{86}Sr$ doit être évoqué dans les processus de mélange des eaux.

Les différentes relations entre les rapports $^{87}Sr/^{86}Sr$ et les rapports élémentaires (Ca/Na, Mg/Na, Sr/Na, Cl/Na) qui mettent en jeu les types d'eau (Ca-HCO_3…) montrent pour les eaux de type Ca-HCO_3, et à un moindre degré Ca-Na-HCO_3 un contrôle par la dissolution de calcite. Pour les eaux de type Na-Cl, Na-SO_4-Cl… une origine via des fluides hydrothermaux est suspectée. Pour les eaux de type Na-Ca-HCO_3, un mélange entre des eaux issues de l'interaction avec les granites (fort $^{87}Sr/^{86}Sr$) et des saumures (type Na-Cl à bas rapport $^{87}Sr/^{86}Sr$) est envisagé.

Les isotopes du néodyme des principaux types d'eaux de l'hydrosystème de Palmottu (Négrel et al., 2001c) suggèrent des interactions eau-roches auxquelles se surajoutent des processus de mélanges. Les isotopes du néodyme confirment *pro-parte* les résultats dérivés de la systématique Sr et affinent les processus d'interaction eau-roches permettant une meilleure caractérisation des interactions avec les roches mères. Un seul échantillon montre clairement un rapport $\varepsilon Nd(0)$ identique à ceux des granites tandis que tous les autres échantillons montrent des $\varepsilon Nd(0)$ plus radiogéniques. L'ensemble des valeurs est clairement différent de celles mesurées dans la mer Baltique (Andersson et al., 1992). Les variations des rapports isotopiques du Nd dans une sélection des eaux souterraines du site amène de nouvelles informations sur l'histoire de l'hydrosystème de Palmottu. Les processus de mélanges sont montrés en comparant les rapports $\varepsilon Nd(0)$ et Rb/Nd qui mettent en évidence deux droites de mélanges (Figure 9). Toutefois, la source des rapports radiogéniques reste non contrainte pour le moment et des investigations complémentaires (roches, minéraux…) sont nécessaires.

L'évolution locale des eaux souterraines de l'hydrosystème de Palmottu montre que les eaux souterraines les plus anciennes et profondes, du type Na-Cl, sont à relier aux eaux de fontes glaciaires mélangées avec des saumures déjà existantes (Casanova et al., 1999a). Suite à cette recharge profonde, les interactions entre eau et roches granitiques génèrent une suite d'eaux souterraines de nature aussi variée que les différents types d'encaissants (Pitkänen et al., 2002, Négrel et al., 2001c). La profondeur limite entre la recharge profonde et les eaux souterraines générées par les interactions eaux-roches se situe aux alentours de 200 m durant la dernière période glaciaire. Les eaux souterraines peu profondes et récentes situées entre la surface et 200 m de profondeur s'alignent sur plusieurs droites de mélanges avec les saumures glaciaires (Pitkänen et al., 2001).

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[21] Négrel, Ph., Casanova, J., Blomqvist, R. 2001. Nd isotope variation in groundwater and mixing phenomena from Palmottu (Finland). Water Research 35, (6), 1617-1623.

[22] Casanova J., Négrel Ph., Frape S., Kaija J., Blomqvist R. 1999. Multi isotopes geochemistry of the Palmottu hydrosystem (Finland). In Geochemistry of the Earth's Surface (Armannsson Ed.), Balkema, Rotterdam. 483-486.

[23] Négrel, Ph., Casanova, J., Blomqvist, R., Kaija, J., Frape, S. 2003. Strontium isotopic characterisation of the Palmottu hydrosystem (Finland): Water-rock interaction and geochemistry of groundwaters. Geofluids 3, 161-175.

(III) LES EAUX MINERALES DU MASSIF CENTRAL : LE REFERENTIEL DES EAUX MINERALES ET LES LIENS ENTRE EAUX DE SURFACE ET EAUX MINERALES (NEGREL ET AL., 1997[24, 25], 2000[26]).

Le Massif Central est le siège de nombreuses émergences d'eaux minérales froides ou chaudes (Limagne, Cantal, Cézallier), toutes appartenant au groupe carbo-gazeux fréquemment rencontré dans le Massif Central (Michard et al., 1981, 1987). Les zones d'émergences se situent tout particulièrement dans les vallées et ces eaux résultent de mélanges entre des eaux superficielles diluées (faibles concentrations en chlorure, signature isotopique en deutérium et en oxygène-18 proche de celles des eaux météoriques) et des eaux profondes beaucoup plus minéralisées. Elles se chargent en CO_2 profond dans le granite encaissant à une température proche de 200°C (géothermomètres Na-K, Na-K-Ca et Na-Li). Les eaux sont associées à de fortes pressions de CO_2 et acquièrent ainsi leur faciès bicarbonaté sodique (Michard et al., 1981, 1987a). Les eaux remontent lentement à travers les fissures des granites en raison de leurs colmatages en surface, comme le suggère le faible débit des sources et leur dispersion. Près de la surface, la composition de ces eaux est modifiée par mélange avec des eaux superficielles, par acquisition secondaire de sulfates provenant probablement de l'altération de dépôts sulfurés ou bien encore, par dégazage. Les eaux très chargées en CO_2 perdent du gaz près de la surface et engendrent des dépôts de carbonates de calcium qui forment des travertins susceptibles d'obstruer les émergences. L'oxydation par l'air est la cause de la précipitation d'oxy-hydroxydes de fer. La plupart des éléments traces vont se distribuer entre solution et ces phases précipitées (Beaucaire et al., 1986, Casanova et al., 1999b).

La vallée de l'Allier entre Clermont-Ferrand et Issoire (zone de la ***Limagne d'Allier***) est le siège de nombreuses émergences d'eaux minérales (Fouillac et al., 1975, Stettler, 1977). Cette première partie de l'étude des eaux minérales concerne les données chimiques relatives aux éléments majeurs et traces, ainsi qu'aux données des isotopes de l'eau (O, D) et des isotopes du strontium ($^{87}Sr/^{86}Sr$) acquises sur les eaux minérales de la Limagne d'Allier tant d'un point de vue spatial que temporel.

La fluctuation temporelle des caractéristiques chimiques et isotopiques des eaux minéralisées a été étudiée sur un forage non exploité (site de Sainte Marguerite, Négrel et al., 1997c) dans le granite de St Yvoine. Le suivi périodique de l'eau minéralisée montre des variations parfois importantes des teneurs des éléments chimiques analysés, à l'exception du chlorure qui n'a varié que de 4% sur la période de suivi de 18 mois. Les rapports $^{87}Sr/^{86}Sr$ sont peu variables entre décembre 1993 et octobre 1994, puis une significative augmentation de ce rapport de $8.\ 10^{-5}$ apparaît à partir de novembre 1994 jusqu'en mai 1995, avant de revenir à l'état initial. Cette augmentation du rapport isotopique observée dans l'eau minéralisée ne peut être expliquée par un apport d'eau superficielle (du type nappe alluvialle de l'Allier) qui impliquerait une diminution du rapport $^{87}Sr/^{86}Sr$. On peut également rejeter l'hypothèse de mélange eau profonde-eau superficielle de la nappe sédimentaire de Limagne ainsi que l'hypothèse d'une interaction différente dans le réservoir profond entre eau et granite, qui mènerait à une ouverture de minéraux plus radiogéniques et qui entraînerait de concert une augmentation isotopique et une augmentation du rapport Rb/Sr, ce qui n'est pas observée. Les modifications isotopiques de l'eau peuvent être reliées à des phénomènes de mélanges mettant en

[24] Négrel, Ph., Fouillac, C., Brach, M. 1997. A strontium isotopic study of mineral and surface waters from the Cezallier (Massif Central, France): implications for the mixing processes in areas of disseminate emergences of mineral waters. Chemical Geology 135, 89-101.

[25] Négrel, Ph., Fouillac, C., Brach, M. 1997. Variations spatio-temporelles de la composition chimique et des rapports $^{87}Sr/^{86}Sr$ des eaux minérales de la Limagne d'Allier. C.R. Académie des Sciences 324, 119-124.

[26] Négrel, Ph., Guerrot, C., Cocherie, A., Azaroual, M., Brach, M., Fouillac, C. 2000. Rare Earth Elements, neodymium and strontium isotopic systematics in mineral waters: evidence from the Massif Central, France. Applied Geochemistry 15, 1345-1367.

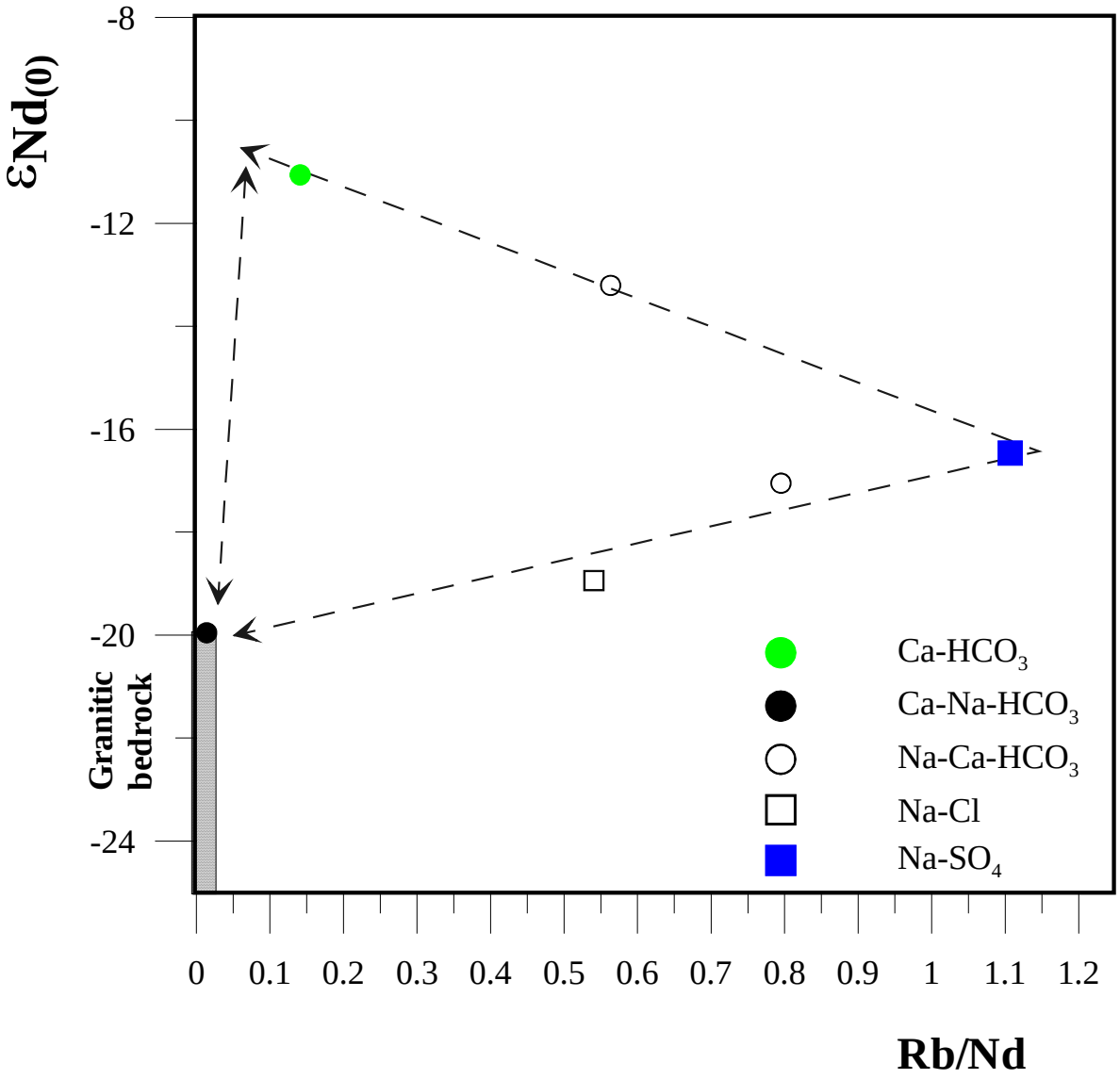

Figure 9. Diagramme des rapports εNd(0) en fonction des rapports Rb/Nd dans les eaux souterraines de l'hydrosystème de Palmottu ; les eaux sont classées par types, figure extraite de Négrel et al. (2001, Water Research 35 (6), 1617-1623).

cause deux réservoirs d'eau minéralisée, de rapports $^{87}Sr/^{86}Sr$ différents mais de caractéristiques identiques du point de vue des teneurs en chlorure.

Dans cette zone de Limagne, les émergences d'eaux minérales sont communes et bon nombre peuvent être vues dans le lit de l'***Allier***. Les eaux de surface de cette rivière ont été échantillonnées durant une période de 13 mois et une étude sur des sections transverses a été réalisée lors des basses eaux d'août dans le but d'estimer les débits d'eau minérale dans le lit de la rivière (Négrel et al., 1997d). Les rapports $^{87}Sr/^{86}Sr$ du suivi mensuel sont très bien corrélés avec l'inverse de la concentration en Sr et définissent un mélange binaire entre le pôle des eaux minérales (Négrel et al., 1997c) et un pôle Allier *s.s.* Les processus de mélanges ont été étudiés en utilisant les rapports $^{87}Sr/^{86}Sr$ et un élément conservatif (Cl). A l'exception d'un échantillon, les apports d'eau minérale ne sont jamais supérieurs à 2%. Un calcul de bilan global des apports d'eaux minérales dans le lit de l'Allier a été réalisé en utilisant la somme des cations et des anions. A la station de jaugeage de l'Allier, en aval de la zone d'émergence des eaux minéralisées, le débit d'eaux minérales était de l'ordre de 0.02 m^3/s dans le lit de l'Allier sur la période d'étude (soit 0.1% du débit de la rivière).

Quatre groupes géographiques englobent **l*es sources minérales du socle métamorphique hercynien du Cézallier*** de part leurs compositions chimiques (Berthier et al., 1982 Fouillac, 1983, 1985, Beaucaire et al., 1987, Michard et al., 1987a). A l'échelle du Cézallier, la dispersion des points dans une représentation entre les rapports $^{87}Sr/^{86}Sr$ et 1/Sr s'explique par l'existence de trois composants (Négrel et al., 2000). Le composant le plus dilué correspond à l'interaction superficielle. Les deux autres composants plus minéralisés présentent à la fois des rapports isotopiques et des concentrations différentes. Un des deux composants est caractérisé par un rapport $^{87}Sr/^{86}Sr$ bas et des teneurs en Sr élevées. L'autre, le plus minéralisé, présente une signature $^{87}Sr/^{86}Sr$ plus radiogénique et des teneurs en Sr plus faibles. Il n'y a pas de lien direct entre les eaux qui émergent des granites de Limagne et de Margeride et celles du Cézallier.

Les concentrations individuelles des Terres Rares dans les eaux minérales varient de plusieurs ordres de grandeur tout en étant non dépendantes des paramètres principaux de l'eau (salinité, T, pH, carbone organique total). Ces teneurs sont du même ordre de grandeur que celles données par Michard et al. (1987b) et Sanjuan et al. (1988) pour d'autres zones du Massif Central. Les variations des teneurs des Terres Rares dissoutes peuvent être illustrées par celles du néodyme qui varient entre 5 et 378 ng l^{-1} dans le Cézallier où tous les groupes d'eaux montrent des variations identiques. Les teneurs en Nd sont dans une gamme identique en Limagne d'Allier tandis que dans la Margeride, elles n'atteignent que 170 ng l^{-1}. Par comparaison, Alaux-Négrel (1991) donne une gamme allant de 100 à 160 ng l^{-1} dans les eaux minérales des Pyrénées tandis que Sanjuan et al. (1988) et Michard et al. (1987b) observent des teneurs en Nd de l'ordre de 7-15 ng l^{-1} pour d'autres zones du Massif Central.

De toutes les eaux minérales du Massif Central (Cézallier, Limagne d'Allier et Margeride), il n'y a aucune évidence de relation entre pH et les Terres Rares. Ceci peut être dû à la très faible variation des valeurs du pH dans les eaux minérales (valeur moyenne 6.48 ± 0.26). Ces résultats sont en accord avec ceux montrés par Michard et al. (1987b) et Sanjuan et al. (1988) sur les systèmes d'eaux minérales riches en CO_2. Ces auteurs ont mis en évidence l'absence de lien entre les teneurs en Terres Rares et le dégazage de CO_2 à l'émergence des sources d'eaux minérales qui ne sont donc pas dépendantes du pH. Ce type de relation entre pH et teneurs en Terres Rares est pourtant généralement mis en avant dans d'autres études mais sur des eaux non minérales (Goldstein et Jacobsen 1987, Elderfield et al. 1990, Keasler et Loveland 1982, Fee et al. 1992, Johannesson et al. 1994, Dupré et al. 1996).

Les Terres Rares dissoutes dans les eaux minérales sont normalisées aux concentrations de la croûte continentale supérieure (Taylor et McLennan, 1985) et montrent des profils enrichis en Terres Rares lourdes $\{(La/Yb)_N < 0.4, (Pr/Yb)_N < 0.6\}$ et des anomalies positives en Eu. Des profils similaires sont observés dans le bassin de Vichy et à Vals les bains (Michard et al. 1987b, Sanjuan et al. 1988) ainsi que dans les Pyrénées (Alaux-Négrel, 1991). Les évolutions temporelles des profils de Terres Rares d'une même eau minérale ne montrent pas de fluctuations significatives. Deux des terres Rares (Eu et Ce) peuvent développer des anomalies dues à des modifications de leur degré d'oxydation. Le plus stable est la forme III, mais sous des conditions oxydantes ou réductrices, Ce^{4+} et Eu^{2+} représentent l'autre forme pour Ce et Eu. La réduction de Eu, et par la même l'anomalie positive est mise en évidence dans les roches magmatiques (Henderson, 1984) et les systèmes

hydrothermaux (Michard et Albarède, 1986). Si la forme Ce^{3+} solubilisée est oxydée en Ce^{4+}, le Ce précipite à partir de la solution pour donner la cérianite (CeO_2) très insoluble. En conséquence, la solution montre une anomalie négative en Ce. Cependant, l'existence de la cérianite dans la nature a été très rarement reportée (Braun et al., 1990) et l'appauvrissement en Ce peut alors être contrôlé par les oxydes de fer et de manganèse qui incorporent préférentiellement la forme Ce^{4+}. La plupart des anomalies en Eu des eaux minérales sont positives indiquant sa prédominance dans sa forme solubilisée sans contrôle par des oxydes par exemple, ou bien par l'altération préférentielle des feldspaths (Cullers et Graf 1984, Sverjensky, 1984). Avec l'exception de deux anomalies positives, la plupart des anomalies en Ce des eaux minérales sont négatives, ce qui est en accord avec l'oxydation des eaux à l'émergence (Beaucaire et al. 1986) et le contrôle préférentiel par les oxydes de fer. Les calculs de spéciations des Terres Rares dissoutes (Haas et al., 1995, Johannesson et al., 1994, 1995 1996) démontrent la domination des complexes CO_3^{2-} (> 80%) par rapport à la forme libre, et aux autres complexes F^-, SO_4^{2-} et HCO_3^-. L'étude détaillée de la spéciation des Terres Rares montre que l'enrichissement en Terres Rares lourdes dans les eaux minérales riches en CO_2 et de pH neutre est essentiellement du à la prédominance des complexes CO_3^{2-} (Négrel et al., 2000).

Comparativement aux isotopes du strontium, les isotopes du Nd n'ont pas été employés intensivement dans les études hydrogéologiques. Parmi les données disponibles, on note celles obtenues sur des rivières (Goldstein et Jacobsen 1987, Martin et McCulloch, 1999) et sur des fluides hydrothermaux (Michard et al. 1987b) mais peu sont disponibles sur les eaux minérales bien que la composition isotopique du Nd apparaisse être un excellent traceur des roches mères altérées (Martin et McCulloch, 1999).

Les rapports isotopiques du néodyme dans les eaux minérales se répartissent entre εNd(0) +4 et -12 et peuvent être comparés avec ceux des roches mères (granites et gneiss) comme illustré sur la figure 10. Il apparaît que 75% d'entre eux sont en accord avec les valeurs des roches mères, quelques eaux de la Margeride ont des εNd(0) légèrement inférieurs aux valeurs des roches mères. La seule exception concerne quatre eaux minérales du Cézallier dont la composition isotopique est plus positive (εNd(0) de +2.7 à +6.8) et se situent largement en dehors de la gamme des roches mères. Une des hypothèses pour expliquer ces valeurs est d'envisager des circulations souterraines qui drainent des soubassements basaltiques. Les basaltes dans le Cézallier ont des εNd(0) variant entre +2.7 et +6.8 (Chauvel, 1982) et ont donc des compositions isotopiques pouvant tout à fait induire la gamme des signatures observées dans les eaux minérales.

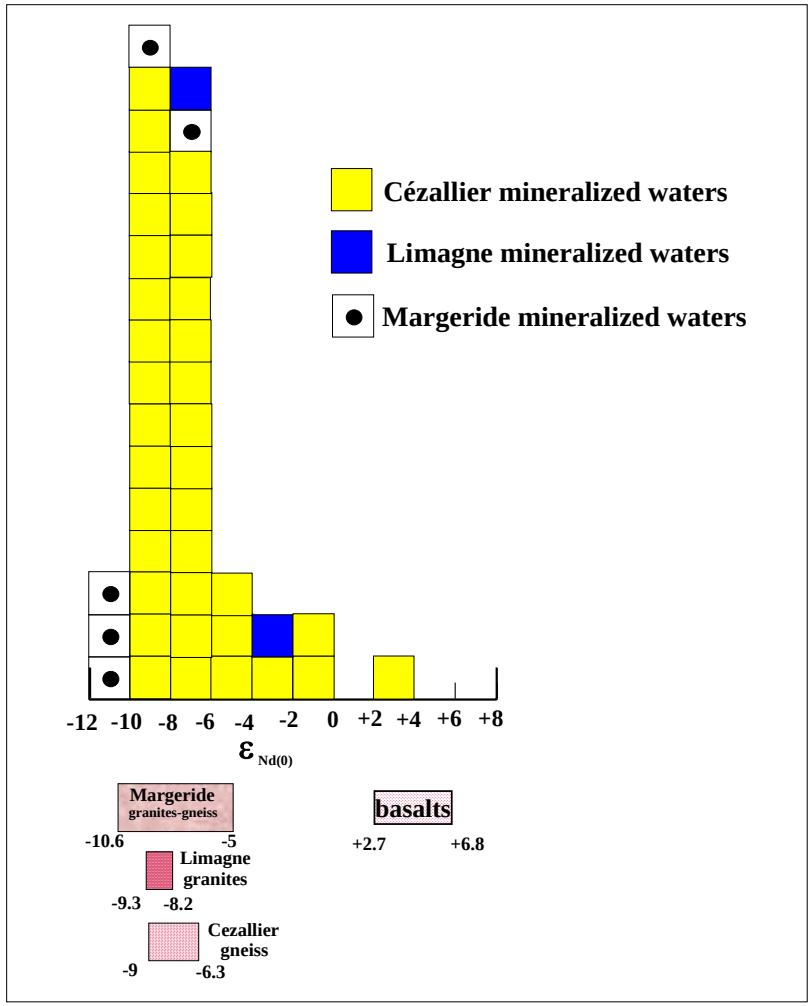

Figure 10. Histogramme des rapports εNd(0) dans les eaux minérales du Massif Central, figure extraite de Négrel et al. (2000, Applied Geochemistry 15, 1345-1367).

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5. Conclusion générale et perspectives

CONCLUSION

Dans le cycle des précipitations, *l'eau de pluie* est communément considérée pure. En fait, elle constitue une solution souvent riche en sels minéraux dissous (sels minéraux présents dans les nuages ou "capturés" pendant le trajet de l'eau de pluie dans l'atmosphère avant son contact avec le sol). La chimie de la pluie est d'un intérêt important pour un grand nombre d'éléments chimiques à la surface de la terre et notamment dans la partie terrestre du cycle de l'eau. Ainsi la détermination des effets d'altération des roches, des processus biologiques ou de l'origine des éléments dans les eaux de surface et les aquifères ne peut se faire qu'après prise en compte de l'apport par les pluies. Cette approche est largement développée sur un certain nombre de bassins versants de grande taille ou à l'opposé sur de tous petits bassins versants. Les traçages isotopiques permettent de mieux contraindre les origines des éléments chimiques dans les pluies et de caractériser le signal d'entrée sur les bassins versants. La répartition des signatures isotopiques $^{87}Sr/^{86}Sr$ des pluies sur le site du Massif Central corrigées des apports marins se fait entre trois extrêmes : un correspond aux sources silicatées, un autre à la source locale de carbonates et le dernier englobe les sources lointaines de carbonates et les engrais. Un total de 5 composants doit être envisagé pour expliquer les variations des signatures isotopique en Pb des pluies. Ces cinq composants sont les essences, le fond naturel comme montré dans les sédiments pré-industriels, les apports industriels avec de multiples origines très difficiles à contraindre, les engrais et les amendements minéraux agricoles et les stériles miniers.

De par leur capacité intégratrice, les *fleuves* lissent la multiplicité des lithologies de la portion de continent qu'ils drainent. Les compositions chimiques et isotopiques sont donc une vision moyenne d'importantes surfaces soumises aux processus d'altération et d'érosion. Ces compositions peuvent être déconvoluées grâce à l'apport des études sur de petits bassins versants présentant des lithologies monotones. Cependant, lorsque la signature naturelle des lithologies est superposée avec une ou plusieurs signatures anthropiques, la déconvolution est rendue d'autant plus difficile. Cette déconvolution multiple entre trois composants "lithologiques" et deux composants anthropiques a pu être réalisée sur le bassin de la Loire en deux points différents et sur trois cycles hydrologiques. Pour cela, on s'est appuyé sur la connaissance des précipitations ainsi que sur celle acquise sur les petits bassins versants. La Guyane présente la particularité d'être dans une zone peu anthropisée, en regard des éléments chimiques considérés, et d'être en climat tropical. Le bassin versant du Maroni sert de référentiel afin de faire un transfert de la connaissance de la géochimie des eaux de surface vers les eaux souterraines dans une zone géographique où elles sont très méconnues. La principale conclusion découlant de l'utilisation des isotopes du strontium est le gain important dans la visualisation du fonctionnement du bassin du Maroni. Par rapport à l'utilisation des éléments chimiques seuls, la caractérisation des différentes lithologies drainées est possible.

Les différentes systématiques isotopiques mises en œuvre dans le cadre de ces études permettent de pénétrer dans le fonctionnement du monde de *l'eau souterraine*. Pour le strontium, un modèle d'interaction eau-roches a été développé en faisant l'hypothèse que la plus grande partie du Sr libéré par l'altération provient des plagioclases, des feldspaths potassiques et des biotites. Ce modèle permet de calculer la composition théorique d'une eau ayant interagit avec une roche de type silicate. Si les isotopes du strontium sont le socle de ces études, certainement de part l'abondance de cet élément dans les eaux souterraines, les isotopes du néodyme apportent beaucoup d'informations complémentaires sur les interactions eau-roches. Ce fut tout particulièrement le cas dans le Massif Central, où seul les isotopes du neodyme ont permis de mettre en evidence le rôle des roches volcaniques dans les circulations des eaux minérales.

ETUDES RECENTES ET PERSPECTIVES

Pour les ***eaux de surface***, l'étude des processus et des relations tant entre eaux de surface qu'avec des eaux souterraines de faible profondeur, mis en place dans le cadre du Programme National de Recherche sur les Zones Humides (PNRZH), a permis de mettre en évidence le fonctionnement des zones adjacentes au fleuve Loire avec des connections entre eaux de surface et eaux souterraines (e.g. le(s) nappe(s) alluvialle(s)) jusqu'à présent non envisagées[27]. Cette thématique se poursuit au travers de l'étude des relations nappe-rivière dans la plaine alluviale du fleuve Allier. Une approche identique a été menée sur un bassin de plus grande ampleur (le bassin de l'Hérault) en prenant en compte les relations entre fleuve et eaux souterraines des réseaux karstiques et des nappes alluvialles[28]. Enfin, les zones humides sont étudiées en contexte de forte pression anthropique avec une gestion des ressources en eaux souterraines délicate. C'est la cas en Bretagne où l'application conjointe des isotopes du soufre et du strontium permet de contraindre les liens entre les aquifères en zone fissuré (e.g. profond) par rapport à ceux en zone d'altérite, plus superficiels[29]. L'approche des signatures isotopiques des interactions eau-roches en contexte anthropisé requiert de corriger de ces pressions extérieures au système eau-roches et par la suite la variabilité des signatures sur des eaux drainant des roches peut être approchée[30]. Cette approche des signatures isotopiques est également mis en œuvre sur les matières solides véhiculées par les rivières et permet de caractériser les sources naturelles et anthropiques[31,32].

Un autre concept d'étude des eaux de surface concerne la prise en compte de la variation dans le temps à l'échelle des 10 derniers milliers d'années et permet de reconstruire l'évolution du fleuve. Cette partie est dédiée à l'étude de la distribution de certains éléments traces (V, Sr, Pb) ainsi qu'aux rapports isotopiques du Sr et du Pb dans la fraction labile de sédiments fluviatiles collectés par carottages dans la vallée alluviale de la Loire. Les fonds de vallées sont des aires de stockage des particules issues de l'érosion à l'échelle des bassins versants et constituent, de ce fait, des sites d'enregistrement privilégiés des événements passés ayant affecté le bassin versant. En Loire moyenne, un bras mort subsiste à l'emplacement de l'ancien lit ne recevant plus que les dépôts de crue et des sédiments argilo-tourbeux palustres. L'enregistrement couvre une période temporelle de 0 à plus de 10 000 ans BP.

Les oxy-hydroxydes de fer et de manganèse agissent comme le principal pourvoyeur des éléments traces dans la fraction labile des sédiments tandis que les carbonates agissent comme un pourvoyeur d'ampleur moindre. V, Rb et Pb proviennent de l'altération et de l'érosion des silicates. Ils sont fixés par les oxy-hydroxydes de fer et de manganèse et peuvent par conséquent être utilisés comme un index de l'érosion de ces terrains dans l'enregistrement sédimentaire holocène. Le plomb dans l'enregistrement sédimentaire provient majoritairement de l'altération et de l'érosion des silicates. La systématique isotopique du plomb indique l'existence d'au moins trois pôles purs participants au cycle du plomb dans l'enregistrement sédimentaire. Les deux potentiels pôles crustaux sont les basaltes et les granites-gneiss et ils constituent les deux pôles concentrés en Pb. Le troisième pôle, peu concentré en Pb, est relié aux apports carbonatés dont les signatures sont compatibles avec celles des apports par l'érosion des dépôts carbonatés présents sur le bassin[33]. Cette étude nous permet d'approcher l'évolution du bassin versant Loire sur le période Holocène.

Le dernier axe d'étude, en fort développement à l'heure actuelle, concerne l'étude des crues. Les inondations fluviales sont liées à l'augmentation du débit d'un fleuve, elles ne sont que le

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phénomène résultant de la crue qui est une véritable respiration du fleuve. Les inondations résultantes des crues de nappes sont dues à un débordement indirect. En effet, à la suite de fortes précipitations prolongées, les nappes peuvent être saturées en eau. Le niveau du sol n'étant pas le même partout, le surplus d'eau ressort aux points les plus bas inondant les alentours. Les crues de la Somme en 2001 ont été étudiées du point de vue chimique (éléments majeurs et traces) et isotopique (isotopes de l'oxygène, de l'hydrogène, du tritium et du strontium). La composition chimique et isotopique des rivières et des eaux de nappe est influencée par la lithologie des bassins drainés et les influences anthropiques même mineures peuvent être décryptées.

L'utilisation conjointe de la chimie des eaux et des traçages isotopiques a permis de mettre en évidence la nature des flux d'eau, e.g. ruissellement et apports de nappes, lors de la période maximale d'inondation en Avril 2001[34, 35]. Lors de cette période extrème et par comparaison avec des périodes de plus bas niveau, la géochimie isotopique confirme et apporte des éléments nouveaux à l'analyse hydrodynamique des phénomènes d'inondations résultant des crues de nappes[36].

Pour les ***eaux souterraines***, la géochimie isotopique est également mise en œuvre pour préciser la structure et les modalités de fonctionnement des hydrosystèmes, qui comprennent des eaux souterraines (aquifères profonds, aquifères superficiels, etc.) et des eaux de surface. Ces ressources sont intimement liées ; le débit d'étiage des cours d'eau provient intégralement des eaux souterraines. Les outils géochimiques appliqués à la caractérisation des eaux et à leur environnement hydrogéologique - analyses chimiques et isotopiques notamment - contribueront fortement aux actions suivantes :

- étude et quantification des mélanges entre les eaux de différentes origines ;
- prospection et caractérisation du ou des gisements d'eau souterraine ;
- préciser les conditions de gisement d'eau souterraine en étudiant les interactions eau-roches et les circulations dans les différents milieux ;
- détermination de l'origine de l'eau souterraine et des solutés ;
- évaluation des temps de résidence dans les systèmes aquifères.

D'un point de vue environnemental, une retombée immédiate sera l'amélioration de la traçabilité de l'origine des eaux souterraines, particulièrement en cas de mélanges d'eaux d'origine différente, et une meilleure prise en compte de la variabilité de leur caractéristique géochimique. Les caractéristiques de l'eau souterraine présente dans les zones de socle sont essentiellement dues à la conjonction de 2 phénomènes mis en œuvre successivement. Le premier phénomène concerne le signal d'entrée constitué par les précipitations humides (pluies) alors que le deuxième concerne l'interaction entre cette eau de pluie et le ou les encaissants rocheux (alluvions, altérites, socle fracturé). Comprendre ce qui détermine cette composition chimique, à la fois par des modèles d'interaction eau-roche et en utilisant les traceurs isotopiques permettant de retracer les circulations, améliore la connaissance des réservoirs d'eau. Parmi les études réalisées ou en cours de finalisation, le couplage entre géochimie, traçage isotopique et approche hydrogéologique a permis de comprendre le fonctionnement des hydrosystèmes en zone de socle fracturé tels que l'hydrosystème guyanais[37] tout en mettant en œuvre des systématiques isotopiques développées depuis peu[38]. Dans cette même zone géographique de la Guyane, le couplage Terres Rares et isotopes du strontium et du néodyme a été mis en application sur les eaux souterraines de la Guyane afin de caractériser les interactions eau-roches. On peut espérer beaucoup de l'approche des isotopes du néodyme dans la reconstitution précise des roches en interaction avec les eaux de part le fonctionnement de cette

[34] Négrel, Ph, Petelet-Giraud, E., Doerfliger, N., Pointet, Th., Pennequin, D. 2003. Apport des traçages isotopiques à la compréhension des inondations : le cas de la Somme. La Houille Blanche, 6, 104-111.

[35] Pointet, Th., Amraoui, N., Golaz, C., Mardhel, V., Négrel, Ph., Pennequin, D, Pinault, J.L. 2003. La contribution des eaux souterraines aux crues exceptionnelles de la Somme en 2001. Observations, hypothèses, modélisation. La Houille Blanche, 6, 112-122.

[36] Négrel, Ph., Petelet-Giraud, E. 2003. Strontium isotope as tracers of groundwater-induced floods: the Somme case (France). Journal of Hydrology. Soumis.

[37] Lachassagne, P., Négrel, Ph., Gandolfi, J.M. Structure and functioning of hardrock aquifers in French Guiana. Hydrogeological concepts and groundwater geochemistry. Journal of Hydrology. En préparation.

[38] Négrel, Ph., Petelet-Giraud, E., Casanova, J., Kloppmann, W. 2002. Boron isotope signatures in the coastal groundwaters of French Guiana. Water Resources Research. 10.1029/2002WR001299.

systématique dans un hydrosystème comme celui de la Guyane[39] ou des systèmes plus complexes comme celui de Lupin dans le nord du Canada[40].

Les eaux de précipitations correspondent au signal d'entrée dans les systèmes hydrogéologiques, et le suivi isotopique (O et H) des pluies permet alors d'estimer un référentiel pour la fonction d'entrée des aquifères. Cependant, les données sur les pluies ne sont pas suffisament renseignées pour exprimer correctement le signal d'entrée dans les aquifères. Des eaux de surface (lacs) peuvent être prises en compte pour estimer la teneur isotopique moyenne dans les précipitations et reconstruire des cartes d'isovaleurs du signal d'entrée à l'échelle du quart sud-ouest de la France[41].

La salinisation des eaux souterraines et la gestion des ressources en eaux (recherge forcée, exploitation) au travers de la géochimie des eaux ont été étudié dans la plaine de la batinah (Sultanat d'Oman)[42].

Autre face des eaux souterraines, l'existence de fluides salés dans des formations géologiques à grande profondeur est un phénomène mondialement répandu et qui a donné lieu à de nombreuses études dans les dernières décennies à l'aide d'un panel d'outils géochimiques variés. L'objectif fort de ces études concerne tout particulièrement l'origine de la salinité, origine qui est très souvent l'objet de controverses entre une origine autochtone (i.e. interaction avec les roches) et une origine allochtone (i.e. intrusion marine, saumure d'évaporite résiduelle, migration de fluides secondaires issus de la dissolution d'évaporites). Là aussi, la géochimie isotopique est tout à fait à même d'amener des contraintes quant aux origines et aux processus mis en œuvre dans la génération de fluides salés[43, 44, 45]. Parmi les projets qui ont permis de mettre en avant les méthodes isotopiques et parfois de permettre de progresser dans la connaissance d'un outil ou dans des couplages entre les outils isotopiques, le Projet PAGEPA (Paléohydrologie et scénarios d'évolution pour le stockage de déchets nucléaires), a concerné les eaux souterraines d'un site géologique (Aspö/Laxemar) en Suède tandis que le Projet PALMOTTU (Transport des radionucléides dans un analogue naturel) a concerné les eaux souterraines de différents sites géologiques en Finlande. Ces études ont permis de contraindre le fonctionnement de la systématique bore en contexte climatique froid et dans une vision paléohydrologique décrivant l'histoire des eaux souterraines salées résultant des dernières glaciations[46]. L'histoire de ces eaux salées du site de Palmottu est visitée par les isotopes du strontium[47]. La reconstitution des connections de l'ensemble des eaux salées du bouclier Fennoscandien, en relation avec l'histoire de la mer Baltique, est étudiée par cette même systématique isotopique[48]. A plus grande échelle, l'histoire des fluides salés à grandes profondeurs dans les socles est comparée, entre les boucliers canadiens et fennoscandiens toujours au travers des isotopes du strontium[49].

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[39] Négrel, Ph., Petelet-Giraud, E. Geochemistry and isotopic composition (O, D, Sr, Nd) in the groundwaters of French Guiana as indicators of their origin and interrelation. Applied Geochemistry. En préparation.

[40] Négrel, Ph., Casanova, J., Blomqvist, R. 2004. Origin and mixing of groundwaters from Lupin (Canada): Nd isotopes evidence. In Proceedings of the tenth International Symposium on Water Rock Interaction, WRI 11, Saratoga Springs, New York June 27-July 2, 2004. Sous presse

[41] Petelet-Giraud, E., Casanova, J., Chery, L., Négrel, Ph., Buchaert, S. 2003. Caractérisation isotopique ($\delta^{18}O$ et $\delta^{2}H$) du signal météorique actuel à l'échelle du quart Sud-Ouest de la France. La Houille Blanche. Soumis.

[42] Casanova, J., Kloppmann, W., Négrel, Ph, Machard de Gramont, H, Al-Mushaikhi, K. Isotopic geochemistry of the Wadi Ahin catchment (Sultanate of Oman). Journal of Hydrology. En préparation.

[43] Kloppmann, W., Négrel, Ph., Casanova, J., Klinge, H., Schelkes, K., Guerrot, C. 2001 Halite dissolution derived brines in the vicinity of a Permian salt dome (N German Basin). Evidence from boron, strontium, oxygen and hydrogen isotopes. Geochimica et Cosmochimica Acta 65, 4087-4101.

[44] Kloppmann, W., Girard, J.P., Négrel, Ph. 2002. Exotic stable isotope compositions of saline waters and brines from the crystalline basement. Chemical Geology 184, 49-70.

[45] Levet, S., Toutain, J.P., Munoz, M., Berger, G., Négrel, Ph., Jendrewjevski, N., Agrinier, P., Sortino, F. 2002. Geochemistry of the Bagneres de Bigorre thermal waters from the North Pyrenean zone (France). Geofluids 2, 25-40.

[46] Casanova, J., Négrel, Ph., Blomqvist, R. Boron isotope fractionation in groundwaters as an indicator of permafrost past conditions in the fractured crystalline bedrock of the Fennoscandian Shield. Water Research. Soumis.

[47] Négrel, Ph., Casanova, J., Blomqvist, R., Kaija, J., Frape, S. 2003. Strontium isotopic characterisation of the Palmottu hydrosystem (Finland): Water-rock interaction and geochemistry of groundwaters. Geofluids, 3, 161-175.

[48] Négrel, Ph., Casanova, J., Blomqvist, R. $^{87}Sr/^{86}Sr$ isotopes in brines from the Fennoscandian Shield: a synthesis. Journal of Canadian Earth Sciences. Soumis.

[49] Négrel, Ph., Casanova, J. 2003. Comparing the Sr isotopic signatures in brines between the Canadian and Fennoscandian Shields. Applied geochemistry. Sous presse.

Des eaux salées se trouvent à très grande profondeur, en particulier dans le grabben d'Alsace et une étude est en cours sur les fluides très profonds (> 5000m) par couplage des isotopes du strontium, du bore, du néodyme, de l'oxygène, de l'hydrogène et du soufre, en complément de la géochimie élémentaire et des Terres Rares. De nouvelles hypothèses sur la génération et les migrations de ces fluides devrait découler de ce couplage[50].

L'application des outils isotopiques amène à reconstruire l'évolution passée des circulations des eaux et des interactions avec les roches à partir de phases solides issues de ces processus. La ***paléohydrologie*** permet donc le passage vers l'histoire de l'eau. Les remplissages de fractures dans les granites du socle de la Vienne ont été étudiés pour reconstruires les circulations passées[51] et témoigner des fluides anciens. Les circulations de fluides d'origine météorique dans les dépôts sédimentaires provoquent des modifications des soubassements rocheux (dissolution, précipitation, recristallisations, karstification…), modifications enregistrées par les différentes systématiques isotopiques comme cela a été montré sur un profil d'altération des dépôts marins de l'Oxfordien dans la région de Bourges[52].

Traces des apports passés par les fleuves, les enregistrement sédimentaires en plate-forme péri-récifale montrent l'évolution des apports marins et détritiques par les différences des signatures des isotopes du néodyme[53] le long d'une séquence carottée couvrant un intervalle de 30 millions d'années entre le Bathonien et le Thitonien. Les interactions possibles avec des apports d'eau continentale au sein de ce même enregistrement sont tracées par la systématique isotopique du Sr tandis que les isotopes stables (O et C) reflétent pour l'essentiel la composition isotopique du milieu de sédimentation de plate-forme[54]. L'analyse de l'état de déséquilibre des familles U-Th appliquée sur des échantillons totaux et sur des profils spécifiques le long de l'enregistrement sédimentaire permet de mettre en évidence les processus de mobilité de l'uranium de nature et d'intensité différentes à l'échelle de l'enregistrement sédimentaire[55] et pour des conditions du milieu différentes.

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[50] Kloppmann, W., Négrel, Ph., Casanova, J., Stober I., Bucher K., Azaroual, M. Sanjuan B. Superdeep fluids in the continental crystalline basement: New insights from B, Nd, Sr, O, H, S isotopes and REE systematic of the 5000 m fluid of Soultz sous Forêt (France). Geochimica et Cosmochimica Acta. En préparation.

[51] Négrel, Ph., Casanova, J., Bourguignon, A. 2002. Paleo water-rock interaction determined through isotopic tracing (Sr, O, C, U) in fracture-fill minerals: evidence from the Vienne granitoids (France). Geochimica et Cosmochimica Acta. Soumis.

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[53] Négrel, Ph., Casanova, J., Brulhet, J. Rare earth elements and neodymium isotopic covariations in callovo-oxfordian carbonate platform. Journal of Sedimentary Research. Soumis.

[54] Casanova, J., Négrel, Ph., Brulhet, J. 2003. Late Jurassic isotope geochemistry ($\delta^{13}C$, $\delta^{18}O$, $^{87}Sr/^{86}Sr$) and carbonate production in the eastern Paris Basin (France). Palaeogeography, Palaeoclimatology, Palaeoecology. En préparation.

[55] Casanova, J., Négrel, Ph., Brulhet, J. 2003. Behaviour of nuclides and U-series disequilibrium in clayey sediments: application to the late jurassic record from the eastern paris basin. Journal of Geochemical Exploration. Sous presse.

6. Sélection de publications

Les articles joints à ce mémoire concernent les trois axes majeur du cycle de l'eau développé dans ce mémoire. Ils sont extraits de la bibliographie plus générale incluse dans le curriculum vitae.

Un article illustre le cycle des précipitations :

- Roy, S., **Négrel, Ph.** 2001. A Pb isotope and trace element study of rainwater from the Massif Central (France). *The Science of the Total Environment* 277, 225-239.

Dans le cycle des eaux de surface, deux articles concernent les flux dissous et solides transportés par le fleuve Loire :

- Grosbois, C, **Négrel, Ph.**, Fouillac, C., Grimaud, D. 2000. Dissolved Load of the Loire river: Chemical and isotopic characterization. *Chemical Geology* 170, 179-201.

- **Négrel, Ph.**, Grosbois, C. 1999. Changes in chemical and $^{87}Sr/^{86}Sr$ signatures distribution patterns of suspended matter and bed sediments in the upper Loire River basin (France). *Chemical Geology* 156, 231-249.

Pour le cycle souterrain, un article illustre les eaux souterraines profondes de la Vienne :

- **Négrel, Ph.**, Casanova, J., Aranyossy, J.F. 2001. Strontium isotope systematics used to decipher the origin of groundwaters sampled from granitoids: the Vienne case (France). *Chemical Geology* 177, 287-308.

Et un article illustre l'application des isotopes dans les eaux thermominérales du Massif Central :

- **Négrel, Ph.**, Guerrot, C., Cocherie, A., Azaroual, M., Brach, M., Fouillac, C. 2000. Rare Earth Elements, neodymium and strontium isotopic systematics in mineral waters: evidence from the Massif Central, France. *Applied Geochemistry* 15, 1345-1367.

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The Science of the Total Environment 277 (2001) 225–239

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A Pb isotope and trace element study of rainwater from the Massif Central (France)

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Abstract

Lead isotope ratios and Zn, Pb, Cu, Cd, Sb and Rb contents were measured in samples of rainwater collected over a period of 15 months from the Massif Central (France). Each sample, collected automatically at monthly intervals, represents a series of rainfall events. Rainwater chemistry was interpreted in terms of the chemical contributions from wet deposition and from different source regions for dust in the centre of France. Trace element concentrations in rainwater samples showed a wide range, particularly for Pb (1.30–465 μg/l), with variations decreasing for Cd (0.07–1.70 μg/l), Zn (1.00–54.00 μg/l), Cu (0.20–25.00 μg/l), Sb (~ 0–0.33 μg/l) and Ni (~ 0–15.00 μg/l). Trace element contents do not correlate with rainfall amount and no inter-element correlations are evident in the data. Lead is the most common trace metal found in the rainwater (mean value = 996 $\mu g/m^2/y$) while Sb is the least common element measured (mean value = 1.12 $\mu g/m^2/y$). The composition of rainwater collected from the Massif Central shows a range in Pb isotope ratios from 17.935 to 19.22 ($^{206}Pb/^{204}Pb$), 15.578 to 15.73 ($^{207}Pb/^{204}Pb$) and 37.559 to 38.606 ($^{208}Pb/^{204}Pb$). A five-component mixing model involving contributions from the natural background, gasoline inputs from industrial and agricultural activity and a source resulting from mining waste may be used to explain both the Pb isotope signature and the fluctuations in trace metal contents of Massif Central rainwater. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lead isotope ratios; Heavy metals; Rainwater; Massif Central; France

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1. Introduction

The chemical composition of the atmosphere is largely dominated by anthropogenic influence in the Northern Hemisphere. The main source of heavy metal emission into the atmosphere are man-made, including industrial activity, coal burning and automobile exhaust (Thornton and Eisenreich, 1982; Pacyna, 1986; Alloway, 1990a). Anthropogenic particles such as heavy metals in aerosols, will readily dissolve in the low pH conditions that characterise polluted rainwater (Migon et al., 1993). Hence, heavy metals in the atmosphere occur as aerosols that are mainly dissolved in rainwater (Barrie and Schemenauer, 1989; Heaton et al., 1990). The heavy metal budget of catchments is small but the influence of rainwater may be relatively important. The quantification of the atmospheric input to the dissolved load carried by river water requires that the heavy metal content of rainwater be monitored (Lantzy and MacKenzie, 1979; Dillon et al., 1988). In a previous paper (Négrel and Roy, 1998) strontium isotope ratios, along with major and trace elements were used to decipher the different natural sources (sea salts and terrestrial sources) of elements in rainwater and to trace their deposition on the continent. Each sample collected during the studied period represents a series of complete rain events collected from the beginning to the end of the rainfall using an automatic collector developed by BRGM. Rainwater samples showed a wide range in element concentrations with the $^{87}Sr/^{86}Sr$ ratios varying considerably from 0.7092 to 0.71625, indicating the existence of multiple sources for the crustal component in the analysed rainwater.

Trace metals are usually measured and interpreted in terms of inputs due to pollution (Heaton et al., 1990) and air mass transfer (Hoffman et al., 1977). Lead isotopes are used to trace the sources of these metals (Settle and Patterson, 1982; Hamelin et al., 1989; Hopper et al., 1991; Erel et al., 1997; Tommasini et al., 2000; Rosman et al., 2000). In this paper, we present data on trace metals (Zn, Pb, Sb, Cu, Cd, Ni), the trace element (Rb) and Pb isotope ratios of rainwater samples (referred to hereafter as PSM, which stands for the name of the sampling site) collected in the Massif Central (France). The aim of this study is to look at artificial sources of trace metals in rainwater collected from the centre of France and to estimate a seasonal budget for wet deposition of heavy metals from the atmosphere.

2. Collection procedure, sampling site and analytical method

To collect rainwater for measurements of trace metals and lead isotopes, an automatic precipitation sampler was designed and constructed at Bureau de Recherches Géologiques et Minières (BRGM). This is a polypropylene funnel (45 cm in diameter) with a removable PVC lid, which covers the funnel when no rain is falling. The details of which are described in Négrel and Roy (1998). It implies that wet-only samples were collected and analysed. Because of the low level (typically $\mu g/l$) of trace metals commonly encountered in rainwater samples (Lindberg, 1982; Migon et al., 1993), elaborate precautions were taken during sample collection to avoid possible contamination. The sample collector and the polypropylene storage bottles were cleaned in the laboratory by storage in ultra pure water (pH 2, Milli-Q water system plus redistilled concentrated HNO_3) and conditioned with ultra pure water for a minimum of several weeks prior to use. Samples were collected every month from March 1994 to June 1995 except when precipitation levels were high and samples were collected every 15 days.

The sampling site is in an open area selected to minimise local pollution, i.e. distant from dirt roads and other sources of pollution, in the French Massif Central (Fig. 1). There are no trees or rock outcrops in the vicinity of the collector. The Mediterranean Sea is located 300 km to the south while the Atlantic Ocean is situated 380 km to the west. The nearest towns, Clermont–Ferrand and Issoire, are located 15 km to the Northwest, and 14 km to the south, respectively.

Weather patterns were obtained from the local office of the National Météorological Service, located 4 km from the sampling point, and their record obtained over twenty years (Centre

Départemental du Puy de Dôme). It indicates that mean air masses originate from four sectors (Fig. 1). Jaffrezo (1987) and Colin (1988) studied weather patterns in the area and showed that the predominant source of precipitation originated from the west sector (52% of rain events) while less than 5% of rain events originated from the east sector. The NE–NW and SE–SW sectors are responsible for 16 and 27% of the rain events, respectively. We assume that a similar sector pattern operated during our sampling period but due to the sampling procedure (sampling periods of up to one month), it is not possible to calculate back trajectories for air masses responsible for individual rain events.

The rainfall amounts are reported in Table 1 according to the sampling period. Higher amounts are generally observed in summer and fall and no general trend between rainfall and season can be shown. The annual precipitation collected at the site was 990 mm of water. It totally agrees with water levels collected and recorded by the National Météorological Service over twenty years which range between 900 and 1050 mm/year.

For trace metal determinations, all samples were filtered using a pre-cleaned Nalgene apparatus and a pre-washed 0.2-μm Millipore PVDF filter. A 250-ml aliquot of each filtered rainwater sample was placed in an acid-washed Nalgene polypropylene bottle. Polypropylene storage bottles were cleaned with ultra pure water (pH 2) and conditioned with ultra pure water for a mini-

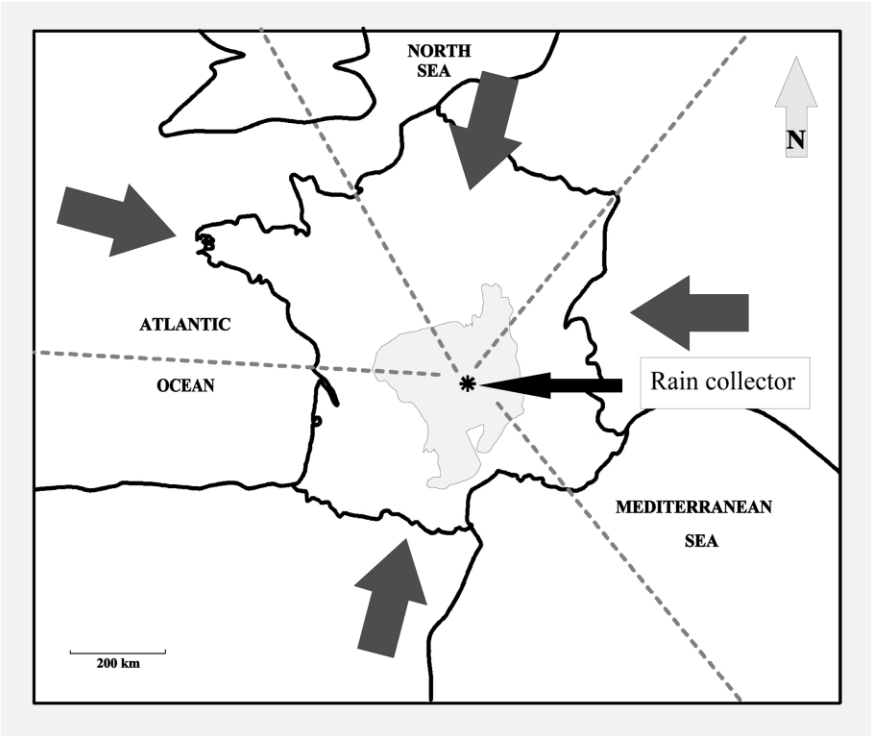

Fig. 1. Map of the location of the rainwater collector in the Massif Central (France). The shaded area corresponds to the Massif Central. The dotted lines represent the air mass source regions and arrows indicate the main directions of the air mass movements. Air masses from the west are mainly of marine in origin (Atlantic Ocean) but also contain a terrestrial component as the air crosses over both the Aquitanian Basin and the silicate part of the western Massif Central. Air masses from the NE–NW are both oceanic (North Atlantic and North Sea) and continental (Great Britain) in origin with air crossing over some polluted areas. Easterly air masses are totally continental in origin with air passing over polluted areas (Germany and other countries to the east). Lastly, air masses sourced from the SE–SW are of marine origin and may also contain natural aerosols from Africa and pollution from Spain.

Table 1
Field data and analytical results for rainwater samples collected during the survey of precipitation in the Massif Central over 1994 and 1995. *Q* represents the amount of collected water expressed in litres. *RFA* represents the rainfall amount in mm for each collection period. Field measurements included; temperature *T* (in °C), pH, electrical conductivity C (in μS/cm standardised to 20°C). Trace element concentrations are expressed as μg/l of dissolved load in rainwater samples

Sample reference (PSM)	Sampling period	*Q* (l)	*RFA*	*T* (°C)	*C* (μS/cm)	pH	Rb (μg/l)	Zn (μg/l)	Ni (μg/l)	Pb (μg/l)	Cd (μg/l)	Cu (μg/l)	Sb (μg/l)
1	31-3-94/22-4-94	12	120	26	40.9	4.29	0.42	54.00	2.00	465.00	1.00	5.30	0.33
2	22-4-94/3-5-94	4	40	14.9	9.26	5.1	0.33	4.50	0.50	2.74	0.07	0.68	0.07
3	3-5-94/25-5-94	11	110	12.2	9.15	5.55	0.20	4.00	0.20	2.46	0.08	0.46	0.05
4	25-5-94/17-6-94	3.7	37	12.3	14.6	6.2	0.80	13.20	1.30	1.30	0.23	1.30	0.11
5	17-6-94/28-7-94	9.5	95	24.3	51.6	6.05	1.20	2.70	< 0.2	15.50	0.80	1.50	0.14
6	28-7-94/18-8-94	11	110	19.6	17.5	4.53	0.20	22.00	< 0.2	64.00	1.70	2.10	< 0.03
7	19-9-94/5-10-94	12	120	8.6	7.06	6.04	0.20	3.10	< 0.2	1.95	0.14	0.20	0.1
8	5-10-94/27-10-94	11	110	9.7	5.36	4.95	0.53	4.10	< 0.2	12.10	0.13	2.10	0.1
9	27-10-94/17-11-94	11	110	11	4.95	5.22	0.20	3.40	< 0.2	4.54	0.07	0.60	0.05
10	17-11-94/16-12-94	0.5	5	0.8	25.4	4.54	0.50	1.00	0.90	61.30	0.25	25.00	0.3
11	16-12-94/17-1-95	2.8	28	5.5	24.6	4.56	0.30	31.00	< 0.2	50.00	0.90	5.20	0.24
12	17-1-95/30-1-95	2	20	16.5	5.05	5.05	0.40	40.00	15.00	5.03	0.11	6.60	0.06
13	30-1-95/6-3-95	6.5	65	7.1	7.85	5.76	0.17	8.10	< 0.2	8.70	0.14	1.60	0.1
14	6-3-95/6-4-95	2	20	19.5	27.4	6.31	0.19	9.30	2.70	20.00	0.39	2.50	0.07
15	6-4-95/12-5-95	5.8	58	13.5	28.4	4.33	0.19	11.00	< 0.2	49.00	0.54	2.70	0.16
16	12-5-95/15-6-95	11.5	115	12.7	17.8	5.3	0.35	18.00	< 0.2	40.00	0.52	7.00	0.21

mum of several weeks. Samples were acidified to pH 2 using distilled nitric acid (HNO_3) and analysed for trace elements contents (Zn, Pb, Cu, Ni, Sb and Cd, and Rb) using conventional ICP-MS techniques on a VG Plasma Quad 2 Plus ICP-MS located in the common BRGM-INSU-LPS Laboratory at Saclay. Blank measurements never exceeded 10% for Zn, 3% for Pb, Ni, and Cu, 1% for Cd and Sb from the whole procedure, a level considered to be negligible. Lead isotopes were also determined by routine ICP-MS measurements using the procedure of Cocherie et al. (1998). The procedure allows the precise and accurate Pb/Pb determination of rainwater samples with an external precision (2σ) of 0.50, 0.50, 0.70 and 0.30% for $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$ and $^{207}Pb/^{206}Pb$, respectively. The accuracy and precision of ICP-MS isotope data is illustrated in a plot by Cocherie et al. (1998), showing the good agreement between isotope results obtained from ICP-MS with those obtained via TIMS.

3. Results and discussion

3.1. Trace metal contents

Rainwater samples contained trace metals below the detection limit for Ni (9 samples) and Sb (1 sample). Results for all samples are summarised in Table 1. It is obvious that very large variations occur in the concentration of several elements during the sampling periods but none of the element contents correlate with rainfall amount. According to the observed range in element concentrations reported in Table 1, the largest fluctuations in measurements occurred for Pb (factor up to 500) with variations decreasing for Cd (factor close to 60), Zn and Cu (factor close to 30) and Sb (factor of 14). For Ni, which is not systematically detected, the fluctuation is close to a factor of 12. Fluctuations in trace element contents can mostly be related to variations in the chemistry of aerosol sources, such as the relative proportions of trace metal-bearing phases present.

Fig. 2 illustrates the fluctuations in element concentrations as a function of the season. Trace metal contents exhibit identical patterns through time. In contrast to the studies of Lindberg (1982) and Heaton et al. (1990), no significant seasonal effects can be observed from the data. For example, trace element contents do not reach a maximum during warm weather periods. The cyclical succession of decreases and increases in trace element contents reflects the influence of both temporal (rainy or dry season...) and spatial (origin of air masses...) factors on rainwater composition.

A comparison of trace metal contents in rainwaters, as listed in Table 1, allows five different patterns of rainwater composition to be defined. According to this classification, it is clear that the most abundant of the measured metals in the collected rainwater over the sampling period is Pb followed in decreasing order by Zn, Cu and Ni. Cd and Sb contents differ by approximately an order of magnitude. Rb contents measured in rainwaters show the same trends as those of Cd. The arithmetic mean values for measured trace elements over the studied period are 50.2 μg/l for Pb, 14.3 for Zn, 4.05 for Cu, 0.44 for Cd, 0.14 for Sb and 3.2 for Ni. Element concentrations adjusted for the total precipitation volume gave mean values for the same elements of 64.3, 13.8, 2.5, 0.48, 0.12 and 1.96 μg/l. These results can be compared with the ranges in trace element contents for rainwater samples reported by other workers (Table 2). From this review of previous trace element studies in rainwater samples from different localities it seems clear that, the Pb contents obtained during this work agree with the ranges given by several workers with the exception of the studies of Migon et al. (1993), Heaton et al. (1990) and Heaton et al. (1992) where Pb contents differ by an order of magnitude. On the other hand, Zn, Sb and Cd contents are in agreement with earlier works.

3.2. Wet depositional fluxes of anthropogenic trace metals

Wet deposition of metals from the atmosphere can be estimated for the Massif Central by multiplying the concentration of the element in a sample of rainwater by the volume of precipitation

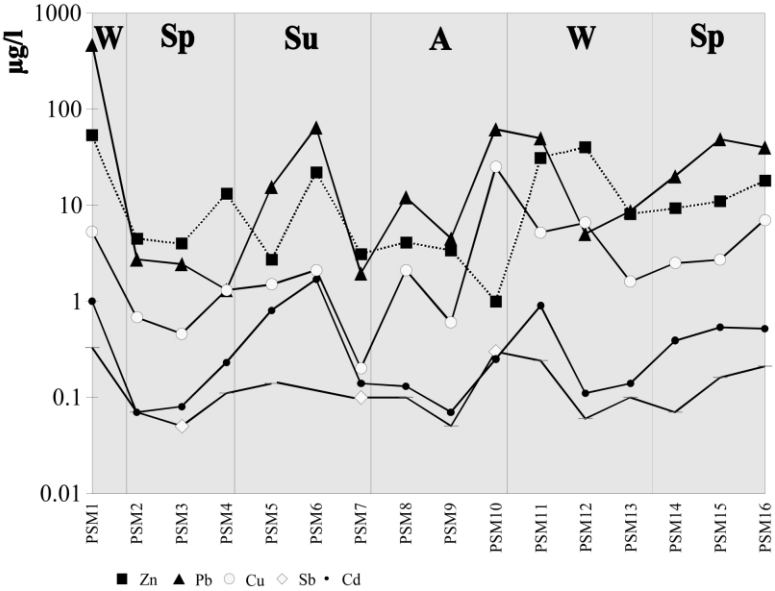

Fig. 2. Fluctuations in element concentrations of rainwater samples as a function of season [summer (Su) and fall (A), winter (W) and spring (Sp)]. The cyclical pattern of increases and decreases in trace element contents reflects both temporal (rainy or dry season...) and spatial (origin of air masses...) factors influencing rainwater composition.

that occurred during the sampling period. Temporal variability of trace metals is illustrated in Fig. 3.

Lead is a widespread contaminant of soils and has a long residence time that can be regarded as essentially infinite in soils (Davies, 1990). The

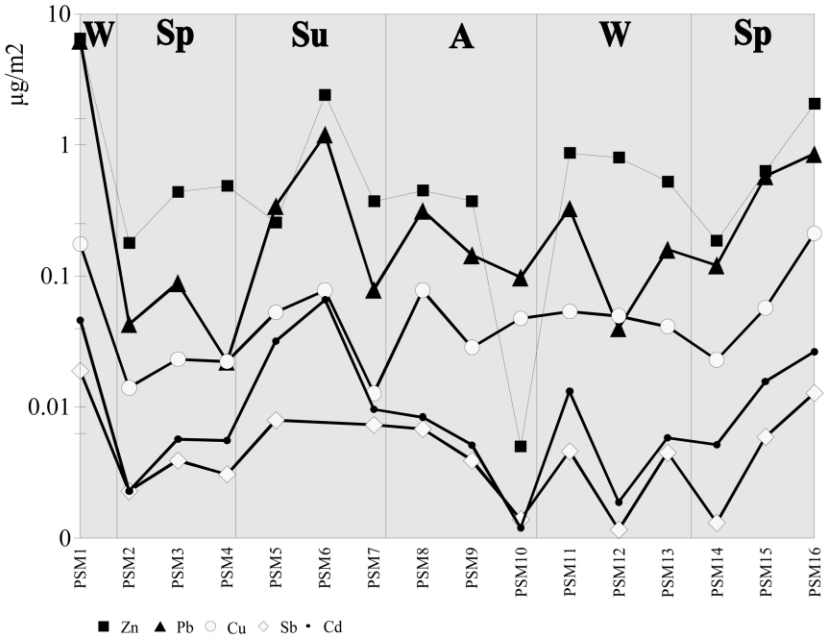

Fig. 3. Wet deposition of metals ($\mu g/m^2$) by rainwaters from the Massif Central as a function of the season (see Fig. 2).

main source of Pb in the atmosphere is from automobile exhaust. Lead is the most abundant trace metal in these rains with mean amount value of 996 $\mu g/m^2$ leading to an annual flux of Pb from rainwaters in the Massif Central reaching 15.4 mg/m^2 per year. These values fall in the range summarised by Davies (1990) for total Pb deposition in Europe and the U.S. One hypothesis to explain the high amount of Pb deposited is the possible influence of sewage sludge and other organic residues that are largely used as soil additives and that can provide heavy Pb-enriched dusts to the atmosphere and hence to rainwaters (Davies, 1990).

The burning of coal and other fossil fuels, smelting of non ferrous metals and disposal of sewage sludges are the major sources of zinc contributing to pollution in the atmosphere (Kiekens, 1990). The mean amount of Zn accumulated by wet deposition in the Massif Central is close to 62.4 $\mu g/m^2$ and Zn is the second most abundant trace metal accumulated by wet deposition. This leads to a flux of Zn from rainwaters of around 7.4 mg/m^2 per year.

Atmospheric deposition of copper from precipitation on land varies considerably according to the distance from industries emitting Cu-containing fumes and with the type and quantity of windblown dust (Baker, 1990). Furthermore, Cu may be linked to agricultural materials like fertilisers. The mean amount of Cu accumulated by wet deposition is 11.5 $\mu g/m^2$ leading to a flux of around 1.4 $mg/m^2/$ per year for Cu. This mean amount value is lower than that of Baker (1990) who reports a range of 100–500 mg/m^2 for wet and dry deposition amounts combined. As for Pb, sewage sludges are capable of substantially increasing the level of Cu in soils that may then contribute to Cu in rainwater via transport of dust particles.

The major sources of atmospheric emission of cadmium are the production of non ferrous metals, fossil fuel combustion, refuse incineration, iron and steel production, and the manufacture and application of agricultural materials like phosphate fertilisers and farmyard manure and finally the disposal of sewage sludges (Lindberg, 1982; Alloway, 1990b). Our data for the amount of Cd accumulated by wet deposition shows a mean value of 4.1 $\mu g/m^2$ giving a Cd flux of around 0.4 mg/m^2 per year, lower than the deposition range summarised by Alloway (1990b) for Cd in Europe (3–30 mg/m^2).

Antimony can form part of agricultural soils through both wet and dry deposition from incineration and fossil fuel combustion (Jones et al., 1990; Heaton et al., 1992) and from addition of soil additives (e.g., chemical fertilisers, sewage sludges, fly ash). Wet deposition of Sb from the rains in the Massif Central shows a mean value of 1.12 $\mu g/m^2$ leading to a flux close to 0.07 mg/m^2 per year.

Nickel in the atmosphere originates mainly from the burning of fuel and residual oils (diesel exhausts) but the potential contribution of Ni from sewage sludges cannot be discounted (McGrath and Smith, 1990). The seven samples where Ni was detected show a mean value of 5.3 $\mu g/m^2$ and a flux of 0.4 mg/m^2 per year.

3.3. Origin of trace metals in rainwater from the Massif Central: constraints from lead isotopes

3.3.1. Sources of trace metals in rainwater

Dissolved trace metals in rainwater can be divided into three groups: (a) those derived from sea salt aerosols; (b) those derived from terrestrial aerosols (soil dust, biological emissions) and (c) those derived from anthropogenic sources (industry, agriculture, burning fossil fuels, fertilisers). The determination of sea salt or terrestrial inputs alone cannot indicate the anthropogenic contribution to rainwater trace metal contents. The sea salt contribution can be calculated using Na and trace element/Na ratios in seawater as a reference, as previously shown by Négrel and Roy (1998). Sea salt calculations assume that there is no element fractionation between species during transport from the source to the collector. The sea salt contribution is always negligible for the selected trace metals analysed ($< 0.1\%$) and Rb ($< 0.5\%$)

The classical use of enrichment factors compared to a standard continental crust composition

allows us to classify the elements (Rahn, 1976). Studies of rainwater from Canada (Poissant et al., 1994) and from the Paris basin (Roy, 1996) have shown that Rb exhibits an enrichment factor close to unity implying that this element is derived exclusively from a terrestrial source. In the present study, Rb ranges from 0.25 μg/l to 1.5 pbb (Fig. 4). The higher Rb values are observed at the end of spring and in the summer of 1994 and can be related to an increase in wind erosion of soils (Heaton et al., 1990). However, low values are nevertheless observed during both summer and winter and therefore, the fluctuations in Rb contents appear to be essentially dependent on wind conditions and thus, on the dust concentration in air. Calculation of an enrichment factor according to Rahn (1976) using Rb values for reference shows that trace metals mentioned in this study are derived from anthropogenic sources. In rainwater from France, Pb and Zn originate from anthropogenic emission along the coastal Mediterranean (Migon et al., 1993; Losno et al., 1988). A recent study conducted on rainwaters from the Paris Basin (Roy, 1996) has demonstrated an anthropogenic contribution for Cu, Zn, Pb, Cd and Ni. Trace metals of anthropogenic origin are commonly associated with particles less than 1 μm, which have long atmospheric residence times and small deposition velocities. These particles are most often derived from high temperature combustion sources such as coal-fired power plants, smelters and automobiles (Thornton and Eisenreich, 1982). Trace metals derived from anthropogenic activity can originate from both local and remote sources of similar nature (Jickells et al., 1984).

In the Massif Central, agricultural activity along with the residue from mining operations can be important local sources of trace metals in the atmosphere. Two fertiliser components were analysed (Table 3) and determination of their trace metal contents shows a large range (in μg/g). The two carbonaceous additives in fertilisers show a wide range in trace metal contents (Table 3), excepted for Cd, which was not found in these samples. Mining waste has a wide range in trace metal contents with levels higher than 30 μg/g for Ni, 100 μg/g for Cu, 200 μg/g for Zn, 500 μg/g for Sb and 1000 μg/g for Pb (Négrel, unpublished data). Note that automotive exhaust

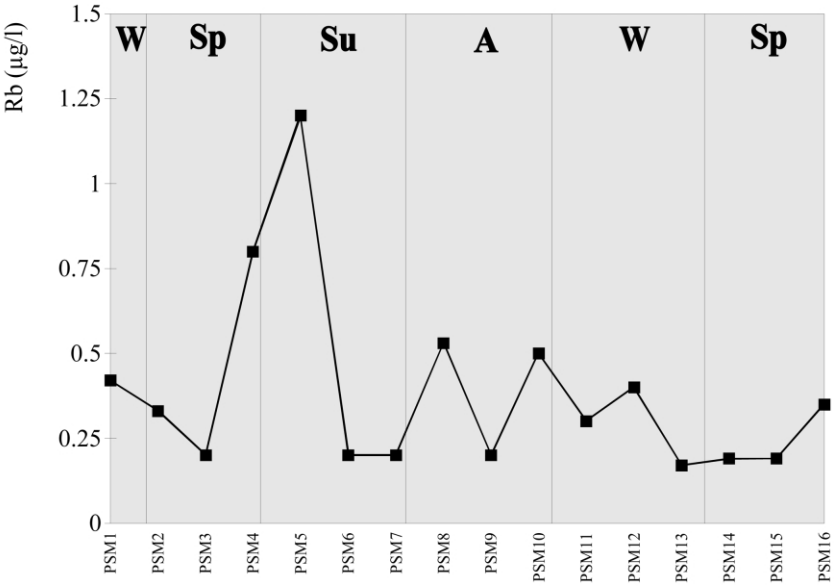

Fig. 4. Fluctuation in Rb content of rainwater samples shown as a function of the season (see Fig. 2).

Table 2
Ranges and/or mean values in trace element contents for rainwater samples reported by other workers over the world, comparison with the data from this study

Study area	Zn (μg/l)	Pb (μg/l)	Cd (μg/l)	Sb (μg/l)	Reference
Ontario, Canada	–	23	0.63	–	Sanderson and Marchand, 1988
Mediterranean basin	–	5–8.6	–	–	Migon et al., 1993
S.E. of U.S.A.	1.2–13	2.3–8.4	0.28–0.55	–	Lindberg, 1982 Lindberg, 1989
Rhodes Island and urban area, USA.	–	4.5	0.05	0.31–1.14	Heaton et al., 1990 Heaton et al., 1992
N.W. of United Kingdom		14–60	5.0–18	–	Jaworowski et al., 1981
Paris, France	23.4–235.2	10–30	0.17 – 0.65	–	Roy, 1996
Massif Central, France	14.3	50.2	0.44	0.14	this work

and industrial activity may have an impact on trace metal contents (Roy, 1996) but these sources do not dominate in this area.

3.3.2. Constraints from lead isotopes on the sources of trace metals

Lead has four stable isotopes: ^{208}Pb, ^{207}Pb, ^{206}Pb and ^{204}Pb. The 208, 207 and 206 isotopes are radiogenic produced by the radioactive decay of ^{232}Th, ^{235}U and ^{238}U, respectively. The ^{204}Pb isotope, which is used as the normalising one, is non-radiogenic. Depending on the U/Th/Pb values in natural materials and time, a wide range of lead isotope ratios have been produced. This allow the use of lead isotopes as tracer of different sources of lead in various environmental studies (Elbaz-Poulichet et al., 1984, 1986; Erel et al., 1997; Ferrand et al., 1999; Grousset et al., 1994; Hamelin et al., 1989; Hopper et al., 1991; Monna et al., 1995, 1997; Moor et al., 1996; Roy, 1996; Tommasini et al., 2000). Lead isotope ratios moved along the lead growth curve from the original ratios towards present day values (Faure, 1986).

The Pb isotope composition of rainwater collected from the Massif Central, summarised in Table 4, ranged from 17.80 (PSM9) to 19.26 (PSM1) for ^{206}Pb/^{204}Pb, from 15.51 (PSM7) to 15.78 (PSM1) for ^{207}Pb/^{204}Pb and from 37.46 (PSM7, 9) to 38.63 (PSM1) for ^{208}Pb/^{204}Pb. Moreover, a HBr leach of the solid matter collected during filtration of rainwater samples displays similar Pb isotope ratios to the rainwater. For example, in sample PSM1 the HBr leachate gives a ^{206}Pb/^{204}Pb ratio of 19.07 ± 0.1 while rainwater has a ratio of 19.26 ± 0.1 reflecting the similarity between Pb isotope signatures in the dissolved load and in the mobile fraction leached from the solid matter. Similar agreement is found in sample PSM15: ^{206}Pb/^{204}Pb of 17.83 ± 0.09 and 17.78 ± 0.05. Roy (1996) has previously observed this similarity between Pb isotope signatures of dissolved load and bulk load from rains collected in downtown Paris. Other samples show more slightly divergent values as exemplified by sample PSM6: ^{206}Pb/^{204}Pb ratio of 17.96 ± 0.09 and 17.59 ± 0.06, respectively; PSM14: ^{206}Pb/^{204}Pb ratio of 17.74 ± 0.09 and 18.06 ± 0.06.

Results are plotted in classical isotope correlation diagrams (Fig. 5) with Pb isotope data from rainwater samples defining linear relationships with high correlation coefficients in plots of ^{206}Pb/^{204}Pb vs. ^{207}Pb/^{204}Pb ($r = 0.86$) and ^{206}Pb/^{204}Pb vs. ^{208}Pb/^{204}Pb ($r = 0.93$). Taken as a whole, our results have higher lead isotope ratios than comparable samples of Parisian rainwater (Roy, 1996). When compared to other data sets, our rainwater data fall between four different domains. The Pb isotope signature of rainwater is more radiogenic than gasoline (Roy, 1996; Monna et al., 1995, 1997; Rosman et al., 2000),

Table 3
Trace element concentrations expressed in μg/g and Pb isotope ratios ($^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$) in fertilisers and carbonaceous additives

Sample	Reference	Rb (μg/g)	Cd (μg/g)	Sb (μg/g)	Ni (μg/g)	Cu (μg/g)	Zn (μg/g)	Pb (μg/g)	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	
Fertiliser	D10	18	17	1	11	17	585	42	24.45	16.33	39.32	ICP-MS
Fertiliser	ME	0.10	0.03	< 0.01	0.90	0.10	0.70	0.11	65.57	56.24	133.40	ICP-MS
Ca amendment	MA	48	d.l	20	237	269	133	184	200.73	25.945	1597.4	TIMS
Ca amendment	ME	1.37	0.08	8.6	13	2.8	33	0.94	19.21	15.17	33.3	ICP-MS

less radiogenic than unpolluted river sediments (Elbaz-Poulichet et al., 1984; Ferrand et al., 1999), less radiogenic than industrial sources (Petit, 1977) and similar to the Pb isotope signature of ore deposits in the Massif Central (Marcoux, 1986). Note that the regression calculation was only applied to data from this work and that one sample (PSM1) clearly plots outside these four fields. As emphasised by Monna et al. (1997), the linear relationship in Pb–Pb diagrams for aerosols collected from France and the United Kingdom cannot be related to simple binary mixing between two Pb sources. Similarly, a three-component model involving mixing of Pb from gasoline, natural background and industrial sources cannot be used to explain the data in this study with at least one more radiogenic component required.

To constrain this radiogenic mixing end-member, the $^{206}Pb/^{207}Pb$-isotope ratio is of most use as tracer because it is commonly reported in the literature and so rainwater results can be compared with a large database of information. The rainwater samples from the Massif Central have $^{206}Pb/^{207}Pb$ ratios ranging from 1.15 to 1.222. The $^{206}Pb/^{207}Pb$ composition of the different sources that could contribute to Pb in rainwater from the Massif Central are illustrated in Fig. 6 and include the following:

- Lead from gasoline: a large component of Pb in the atmosphere originates from automotive exhausts due to the use of Pb as an anti-knock agent in gasoline. The Pb isotope composition of additives depends on the source of the Pb ore used. In France, Roy (1996) and Monna et al. (1995) reported $^{206}Pb/^{207}Pb$ ratios in the range 1.09–1.124.
- Natural lead signature: this signature can be obtained by studying the pre-industrial sediments deposited in major French rivers (Elbaz-Poulichet et al., 1984; Ferrand et al., 1999) and lakes (Monna et al., 1997, with a summary of the European Pb signature given in Moor et al., 1996). The $^{206}Pb/^{207}Pb$ ratio for pre-industrial sources is in the range 1.195–1.206. However, for the case of a single carbonaceous source contributing to rainwater Pb signatures via dust emission from carbonate rocks, Petelet (1994) and Monna et al. (1995) give $^{206}Pb/^{207}Pb$ ratios ranging from 1.198 to 1.234.
- Industrial signature: the multiplicity of industrial sources makes it difficult to constrain this end-member. Petit (1977) and Elbaz-Poulichet et al. (1986) report $^{206}Pb/^{207}Pb$ ratios in the

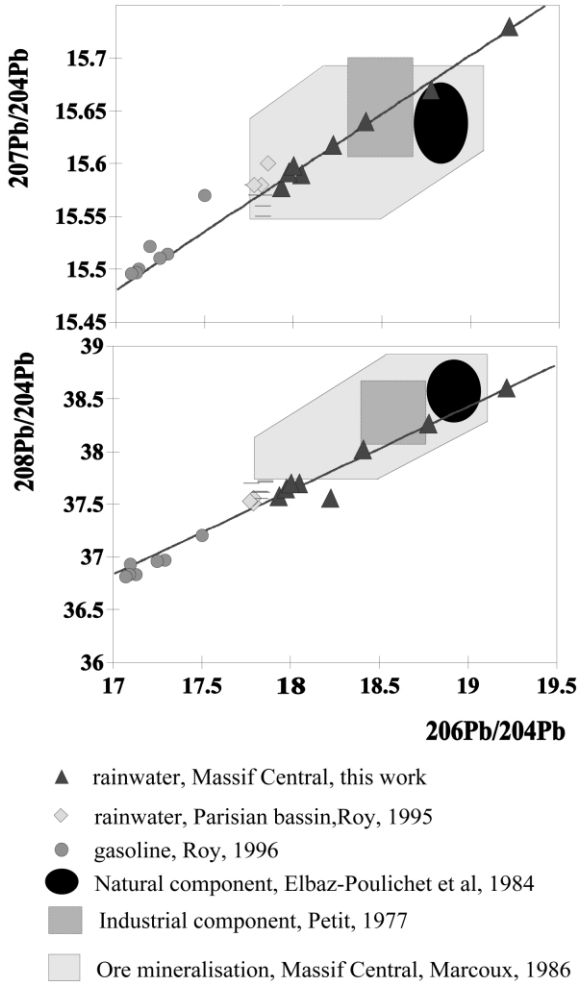

Fig. 5. Plots of $^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$. Triangles represent rainwater samples from the Massif Central (this work), diamonds represent rainwater samples from the Paris Basin (Roy, 1996), circles represent gasoline (Roy, 1996), shaded squares represent industrial sources (Petit, 1977) and shaded circles represent the natural component (Elbaz-Poulichet et al., 1984).

range 1.13–1.18 for industrial sources while Monna et al. (1997) give a range of $^{206}Pb/^{207}Pb$ ratios from 1.143 to 1.155 by using fly ashes to represent the industrial Pb signature.

- Agricultural signature: very few Pb isotope ratios exist in the literature for fertilisers and carbonaceous additives. Table 2 shows four fertilisers and carbonaceous additives that have a wide range of Pb contents and Pb isotope signatures. The $^{206}Pb/^{207}Pb$ ratios for these samples show a range from 1.16 to 1.50. Note the Pb content of sample MA (carbonaceous additive) close to 200 μg/g with a $^{206}Pb/^{207}Pb$ ratio of more than 7, a result that has been verified by repeat measurements but can not be readily explained.
- Mining activities signature: the Pb isotope ratio of ore deposits from the Massif Central have been investigated by Marcoux (1986) who found the $^{206}Pb/^{207}Pb$ ratio ranged from 1.135 to 1.215.

From these different sources, only the agricultural source (fertilisers and carbonaceous additives) can explain the highest $^{206}Pb/^{207}Pb$ ratio and high Pb content (645 μg/l) of rainwater sample PSM1. The high $^{206}Pb/^{207}Pb$ ratio is consistent with the work of Grousset et al. (1994), who showed that the $^{206}Pb/^{207}Pb$ ratio of European aerosols has continuously increased since 1980 and mimic that of the pre-industrial sediments deposited in major French rivers (Elbaz-Poulichet et al., 1984; Ferrand et al., 1999).

The linear relationship in Pb–Pb diagrams obviously refers to a mixing of lead from various sources. Among the different sources previously defined, at least three of them are needed: gasoline; the agricultural source and the industrial source. Nevertheless, the natural background and the influence of mining activities, with identical isotopic composition and hugely different lead content, must be considered as representative source of lead in the mixing. A 5-component mixing model is supposed to explain the fluctuations in trace element contents of the rainwater samples. However, with five different sources as variables it is difficult to separate the relative contribution of each because their lead isotope composition displays a straight line (see above). In order to differentiate the respective contributions from the five identified source regions, the simultaneous use of isotopic tracers and trace element contents on both the bulk load of rainwater and riverwater requires further study.

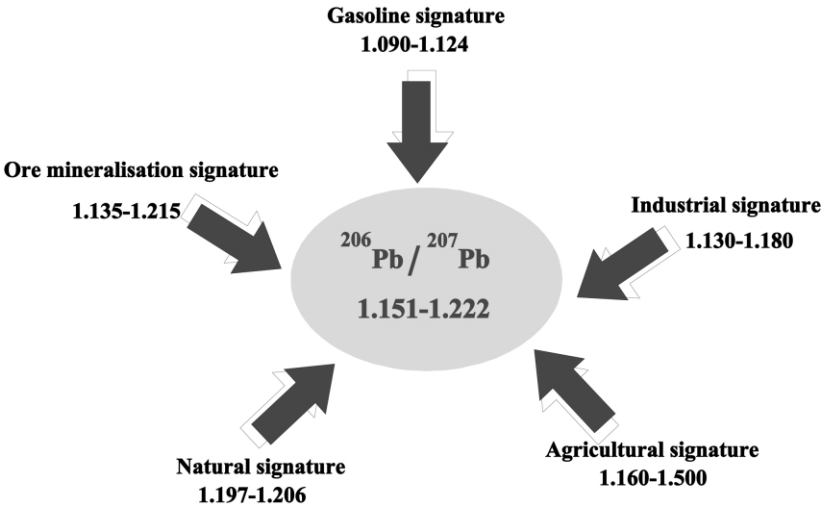

Fig. 6. Summary of the $^{207}Pb/^{206}Pb$ ratios from different sources that could contribute to the Pb signature of rainwaters from the Massif Central.

Table 4
Pb isotope ratios in rainwater samples collected during the survey in the Massif Central ($^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$). nd refers to a non-determined value

Sample reference (PSM)	$^{206}Pb/^{204}Pb$	+/−	$^{207}Pb/^{204}Pb$	+/−	$^{208}Pb/^{204}Pb$	+/−
1	19.26	0.10	15.78	0.08	38.63	0.27
2	nd	nd	nd	nd	nd	nd
3	18.34	0.09	15.61	0.08	38.04	0.27
4	nd	nd	nd	nd	nd	nd
5	18.04	0.09	15.61	0.08	37.66	0.26
6	17.96	0.09	15.63	0.08	37.68	0.26
7	17.86	0.09	15.51	0.08	37.46	0.26
8	nd	nd	nd	nd	nd	nd
9	17.80	0.09	15.57	0.08	37.46	0.26
10	17.98	0.09	15.56	0.08	38.06	0.27
11	18.22	0.09	15.64	0.08	37.93	0.27
12	17.98	0.09	15.57	0.08	37.73	0.26
13	17.93	0.09	15.60	0.08	37.64	0.26
14	17.74	0.09	15.60	0.08	37.42	0.26
15	17.83	0.09	15.62	0.08	37.48	0.26
16	17.88	0.09	15.59	0.08	37.62	0.26

4. Conclusions

The purpose of this study was to investigate the input of trace metals by rainwaters in the centre of France and to trace the source regions of metal-bearing aerosols in this area. The most striking outcome of this study is the recognition of very high trace element concentrations in rainwater samples from the Massif Central. The variations in trace metal concentrations can be mostly related to variations in aerosol sources such as industrial activity, agriculture, burning of vegetation and fossil fuels, and the use of fertilisers. None of the trace element contents are correlated with rainfall amount and no inter-element relationships were found. The high trace element contents in rainwater induce a high wet deposition rate, clearly higher than that found in unpolluted areas. Lead (mean value 996 $\mu g/m^2$ per year) is the most abundant trace metal in this rainwater, while Sb (mean annual value is 1.12 $\mu g/m^2$ per year) is the least abundant.

The Pb isotope composition of rainwater collected from the Massif Central ranges greatly as exemplified by the $^{206}Pb/^{204}Pb$ (17.935–19.22). A mixing model involving 5 components can be used to explain variations in the classical isotope correlation diagram ($^{206}Pb/^{204}Pb$ vs. $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ vs. $^{208}Pb/^{204}Pb$). The five different Pb isotope signatures consist of: (i) a gasoline component; (ii) a natural background component measured from pre-industrial sediments; (iii) industrial inputs, with so many multiple sources that it is difficult to adequately constrain this end-member; (iv) an agricultural signature from additives; and (v) a source resulting from mining waste. It is not possible to calculate the respective contribution of each end-member because they all plot on a straight line in Pb isotope space.

Ongoing studies focus on the sources and behaviour of heavy metals in a non-anthropogenic aquatic environment, i.e. small watersheds. This study based on heavy metal concentrations and lead isotopes in the labile fraction from sediments and soils aims to investigate if lead in the labile fraction can originate from atmospheric deposition and the characterisation of rainwaters, presented in this work is a necessary pre-require.

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Dissolved load of the Loire River: chemical and isotopic characterization

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Abstract

The Loire River, with one of the largest watersheds in France, has been monitored just outside the city of Orleans since 1994. Physico-chemical parameters and major and trace elements were measured between 2-day and 1-week intervals according to the river flow. The sampling site represents 34% of the total Loire watershed with 76% silicate rocks and 24% carbonate rocks.

Elements are transported mainly in the dissolved phase with the ratio of total dissolved salts (TDS) to suspended matter (SM) ranging between 1.6 and 17.4. Chemical weathering of rocks and soils are thus the dominant mechanisms in the Loire waters composition. The highest TDS/SM ratios are due to dissolved anthropogenic inputs. The database shows no link between NO_3^- content and river flow. The Na^+, K^+, Mg^{2+}, SO_4^{2-}, and Cl^- concentrations are seen to decrease with increasing discharge, in agreement with a mixing process involving at least two components: the first component (during low flow) is concentrated and may be related with input from the groundwater and sewage station water, the second component (during high flow) is more dilute and is in agreement with bedrock weathering and rainwater inputs. A geochemical behaviour pattern is also observed for HCO_3^- and Ca^{2+} species, their concentrations increase with increasing discharge up to 300 m^3/s, after which, they decrease with increasing discharge. The Sr isotopic composition of the dissolved load is controlled by at least five components — a series of natural components represented by (a) waters draining the silicate and carbonate bedrock, (b) groundwater, and (c) rainwaters, and two kinds of anthropogenic components.

The aim of this study is to describe the mixing model in order to estimate the contribution of each component. Finally, specific export rates in the upper Loire watershed were evaluated close to 12 t $year^{-1}$ km^{-2} for the silicate rate and 47 t $year^{-1}$ km^{-2} for the carbonate rate. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Loire River; Major and trace elements; Sr isotopic ratio; Mixing model; Anthropogenic end-members; Export rate

1. Introduction

Weathering processes dominate the dissolved and suspended loads of most of the world's major rivers. Specifically, chemical weathering of rocks and soils is one of the essential processes in the geochemical cycling of elements in rivers (Garrels and McEnzie, 1971; compilation in Berner and Berner, 1987; Drever, 1988). The weathering process is affected by the climatic impacts, such as moisture and temperature (Berner and Berner, 1987; Drever, 1988; Hem et

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al., 1990). The natural balance of chemical species is disturbed by anthropogenic additions deriving from the domestic and industrial activities (e.g., fertilizers, sewage waters, road water runoff, etc. (Meybeck, 1979; Etchantu and Probst, 1988).

A river catchment is usually a good area for studying the supply of surface waters through the dissolved load of the river (Edwards, 1973a,b; Likens et al., 1977; Miller and Drever, 1977). The surface waters of the upper Loire drainage basin offer unusual opportunities for the selected geochemical studies because: (a) the Loire drains areas with two main types of bedrock — the silicate basement of the Massif Central and the sedimentary area of the southern Paris Basin (Fig. 1); (b) the watershed is an inland basin in which atmospheric input can be characterized by local rains; and (c) parts of the watershed are industrialized and parts are agricultural, where anthropogenic activities may contribute in varying degrees to the dissolved load.

Systematic sampling of the river water should enable the identification of different geochemical signatures since the chemical composition of the water appears to be controlled by (a) rainwater inputs, (b) water–rock interactions, and (c) human activities. One aim of the present study was to characterize the chemistry of the dissolved load of the upper Loire with regard to the temporal fluctua-

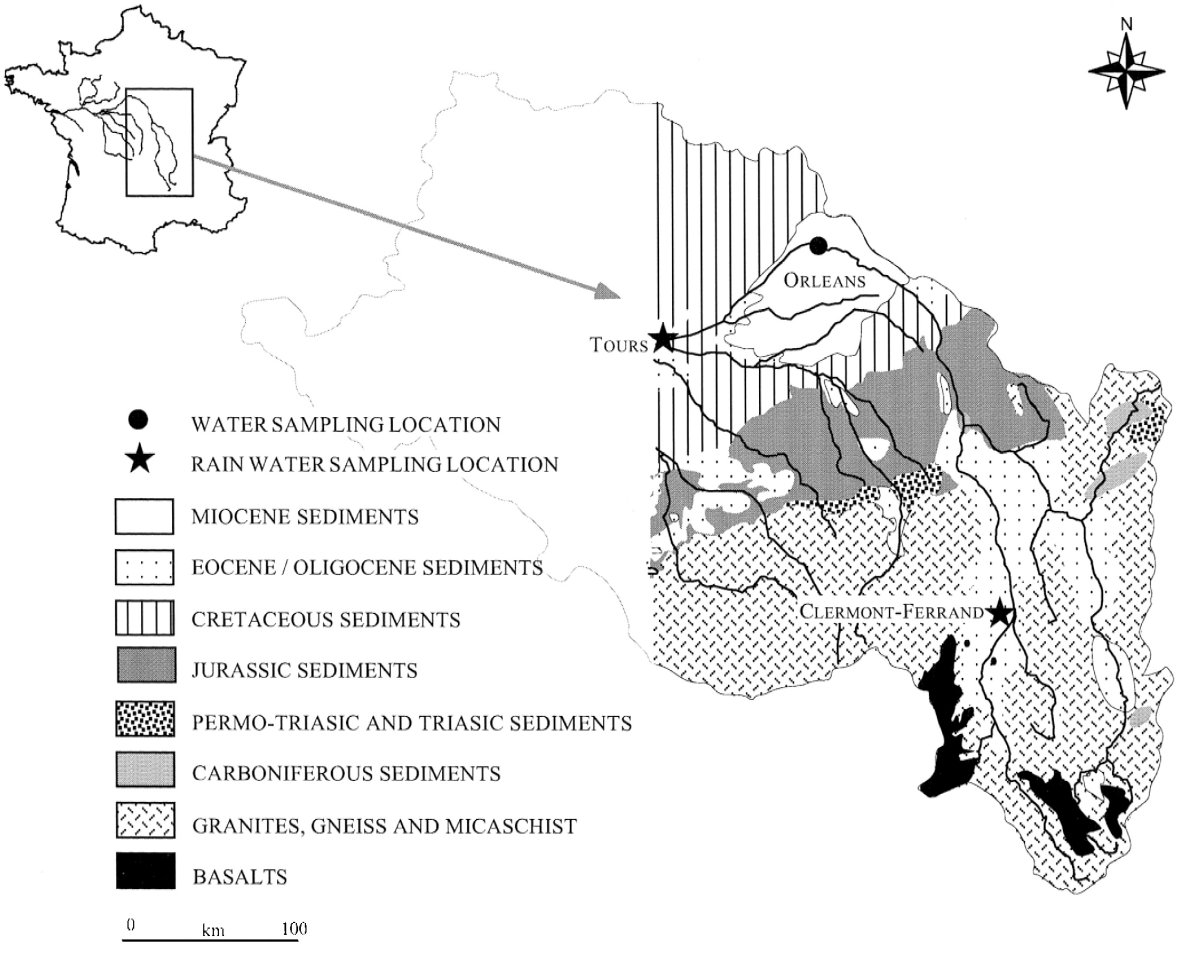

Fig. 1. Simplified geological map of the upper Loire watershed and location of the sampling points for the dissolved load and for rainwater.

tions of the major and trace elements and strontium isotopic ratios. From this, a second aim was to identify and quantify each geochemical signature in order to calculate chemical weathering rates and anthropogenic fluxes.

Major and trace (Rb, Sr) elements associated with the strontium isotopic compositions were investigated, as in many studies on major river basins, in terms of weathering processes and fluxes to the ocean (Sarin et al., 1989; Négrel et al., 1993; Pande et al., 1994; Zhang, 1995; Gaillardet et al., 1995). For the strontium systematic, the $^{87}Sr/^{86}Sr$ ratio varies according to the Rb/Sr ratio and the age of the material (Faure, 1986). Since any natural processes do not fractionate Sr isotopes, the measured $^{87}Sr/^{86}Sr$ ratio differences are due to the mixing of Sr derived from various sources and to different isotopic compositions. Thus, $^{87}Sr/^{86}Sr$ ratio variations within an hydrosystem can provide information about the sources of Sr and the different involved mixing processes (Albarède and Michard, 1987; Anderson et al., 1992; Palmer and Edmond 1992; Stueber et al., 1993).

2. Geography, geology and meteorology of the Loire watershed

The Loire River, from its source in the Massif Central to the Atlantic Ocean, is 1010 km long (Fig. 1) and the total basin area is 117 800 km^2. In the upstream basin, which represents 46% of the total basin surface, the Loire River flows roughly from south to north, draining old plutonic and volcanic rocks (Bureau de Recherche Géologiques et Minières, 1980). Numerous small tributaries are present in this mountainous region (maximum elevation 1500 m).

Then the stream flows westward and its valley stretches toward the Atlantic Ocean. The intermediate part of the basin is underlain by the sedimentary series of the Paris Basin (mainly carbonate deposits, from 200 to 6 Ma). Three major tributaries flow into the Loire River from the left bank (Cher, Indre, and Vienne) and one from the right bank (Maine).

On a Western European scale, the Loire is one of the major fluvial inputs to the Atlantic Ocean with a water discharge of 26 km^3/year and a mean annual discharge of 850 m^3/s in the estuary (Figueres et al., 1985). In the middle of the basin, the Loire discharge fluctuated widely, between 53 m^3/s (August 1995) and 1480 m^3/s (January 1995). The hydrological cycle of the river encompasses three different periods with an annual recurrence. These periods are seasonally marked with: (a) a low flow during two or three warm months in summer, (b) a high flow in winter, generally from December to February with short higher floods, and (c) a smaller high flow, which occurs during the spring and is related to the Massif Central snow melt.

In addition to the physical characterization of the watershed, meteorological parameters are also important for evaluating the rainfall effects. The Loire basin is characterized by its diversity of air-mass trajectories divided into four major origins. One is westerly and originates from the Atlantic Ocean. This west sector is predominant with 52% of the rain events (Jaffrezo, 1987; Colin, 1988). The second sector is northeasterly to northwesterly, still with a marine origin (North Atlantic and North Sea), it passes over Great Britain and the industrialized countries from France to Eastern Europe. The third is easterly with a continental origin; its geochemical signature is different because it passes over polluted countries and a large forested area. The last is southeasterly to southwesterly, originating in the Mediterranean Sea, and carries natural Saharan aerosols and pollution from Spain.

3. Sampling and analytical methodology

3.1. Sampling and analysis of the dissolved load

The water sampling was carried out at two sites about 10 km apart at the inflexion of the Loire River and with no important tributaries between them (Fig. 1). The two sites integrate 34% of the total Loire watershed and correspond to a drainage area of 42 103 km^2. They represent the drainage of the whole silicate basement of the Massif Central and of about 24% of the sedimentary formations, just before the drainage of the extensive agricultural Beauce area.

The sampling strategy was divided into two periods. From May 1994 to February 1996, the Loire

Table 1
Major and trace element concentrations (μmol/l) and $^{87}Sr/^{86}Sr$ ratios of the dissolved load collected during the daily survey (jlo samples, A) and the monthly survey (L samples, B) nd = non-determined values
d.l. = detection limit.

(A)

Sample name	Date	W (m^3/s)	pH[a]	T (°C)	Conductivity (μS/cm)	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	Ca^{2+}	Na^+	K^+	Mg^{2+}	Rb	Sr	$^{87}Sr/^{86}Sr$
jlo1	05/16/1995	310	8.28	14.8	235	1860	392.1	190.2	142.9	970.5	491.3	79.2	209.6	0.05	1.44	nd
jlo2	05/17/1995	339	8.21	14.9	227	1590	383.4	177.1	143.9	857.8	473.5	85.4	194.6	0.05	1.30	nd
jlo3	05/18/1995	351	7.79	14.3	221	1560	355.8	165.9	147.3	860.0	416.5	79.2	174.2	0.05	1.15	nd
jlo4	05/19/1995	389	8.05	13.4	229	1700	331.8	169.0	163.5	734.3	407.8	81.8	163.3	0.15	3.99	nd
jlo5	05/20/1995	433	7.51	14.2	222	1770	305.1	159.1	161.1	724.0	360.0	72.1	148.8	0.12	3.13	0.711253
jlo6	05/21/1995	475	7.47	15.7	214	1620	301.1	157.1	154.5	875.8	338.7	75.9	161.3	0.20	5.27	nd
jlo7	05/22/1995	460	7.68	17.0	203	1760	262.5	135.7	115.8	811.0	331.3	63.8	152.5	0.05	1.17	nd
jlo8	05/23/1995	372	7.40	19.4	202	1630	279.2	140.0	121.6	807.8	340.9	66.4	152.9	0.05	1.15	nd
jlo9	05/24/1995	341	7.56	17.8	211	1620	305.1	152.7	130.0	838.5	360.9	70.8	164.2	0.05	1.20	0.711336
jlo10	05/25/1995	317	7.50	18.2	214	1730	286.2	142.2	114.8	875.3	382.6	72.8	174.2	0.05	1.24	nd
jlo11	05/26/1995	308	7.55	19.1	217	1680	312.4	157.8	123.7	933.8	423.9	74.4	187.5	0.05	1.31	nd
jlo12	05/28/1995	272	7.55	21.5	222	1840	344.5	165.9	108.9	761.3	370.4	61.5	161.7	0.05	1.36	0.711262
jlo13	05/31/1995	220	7.50	18.6	244	1860	376.3	177.4	114.8	834.8	420.4	64.6	177.9	nd	nd	nd
jlo14	06/03/1995	254	7.46	17.7	234	1880	352.7	173.9	116.8	1245.8	587.0	103.3	285.8	0.06	1.43	nd
jlo15	06/05/1995	352	7.73	18.1	209	1400	354.6	160.3	95.2	992.0	590.0	87.9	245.4	0.05	1.18	nd
jlo16	05/12/1995	197	7.43	17.7	228	1730	372.7	178.1	81.6	1144.5	629.1	98.5	290.4	0.05	1.40	0.711372
jlo17	06/17/1995	170	7.32	19.1	233	1710	415.8	191.4	89.5	1114.5	699.6	103.6	302.9	0.06	1.50	nd
jlo18	06/23/1995	128	7.29	18.0	225	1530	440.6	202.4	66.3	928.5	736.5	121.0	310.0	0.13	2.85	0.711388
jlo19	06/25/1995	171	7.41	21.5	215	1490	429.9	202.1	43.1	954.3	755.7	117.7	306.7	0.11	2.48	nd
jlo20	06/29/1995	122	7.28	23.3	211	1390	436.9	194.1	51.5	835.5	728.3	135.9	316.3	0.07	1.35	0.711379
jlo21	07/01/1995	99	7.10	24.1	222	1360	468.2	207.3	40.2	545.0	584.3	76.9	303.3	0.10	1.69	nd
jlo22	07/03/1995	101	7.31	24.7	240	1580	466.8	213.2	28.2	625.8	520.0	85.6	212.5	0.13	2.49	0.711334
jlo23	07/06/1995	115	7.11	25.9	226	1400	437.5	190.5	5.2	678.8	719.1	117.4	305.8	0.11	2.05	nd
jlo24	07/12/1995	91	7.26	26.3	213	1540	393.0	173.3	16.5	780.8	630.9	126.9	273.3	0.08	1.38	nd
jlo25	07/20/1995	91	7.01	27.6	227	1390	447.9	192.7	8.7	687.0	704.3	129.7	290.8	0.08	1.39	0.711322
jlo26	07/25/1995	71	6.93	26.0	237	1130	434.1	192.3	0.0	492.8	694.8	131.5	310.4	0.08	1.35	0.711338
jlo27	07/28/1995	61	7.40	22.2	247	1650	474.9	206.5	46.0	831.5	766.1	137.7	314.6	0.08	1.59	nd
jlo28	08/03/1995	56	7.03	28.5	230	1250	503.7	199.8	2.1	629.0	827.8	133.8	306.7	0.08	1.31	0.711246
jlo29	08/11/1995	71	7.22	23.4	224	1450	472.4	197.3	0.0	678.3	828.7	141.5	340.8	0.08	1.44	0.711241
jlo30	08/15/1995	65	7.09	23.9	214	1160	448.5	174.1	0.0	548.0	801.3	156.2	295.0	0.07	1.25	nd
jlo31	08/18/1995	53	7.02	23.4	212	1120	466.8	185.1	83.7	525.5	811.3	139.7	294.6	0.08	1.22	0.711271
jlo32	08/24/1995	55	7.00	24.3	225	1240	474.4	189.2	35.2	581.3	827.8	226.4	317.1	0.08	1.32	nd

jlo33	08/27/1995	55	7.07	21.3	238	1480	478.6	188.9	0.0	723.0	864.3	136.4	338.3	nd	nd	0.711261
jlo34	08/30/1995	55	7.02	18.4	231	1300	486.5	191.4	0.0	651.3	896.1	179.5	368.8	0.07	1.35	nd
jlo35	09/05/1995	59	7.18	15.9	241	1570	480.3	196.5	0.0	942.5	1071.7	173.1	381.3	0.07	1.50	0.711465
jlo36	09/14/1995	108	7.10	15.8	264	1550	499.4	216.0	9.7	966.0	1137.8	152.6	362.9	0.07	1.46	0.711393
jlo37	09/19/1995	121	7.22	17.2	270	1650	474.9	219.2	11.1	1079.3	1124.8	164.1	330.0	0.06	1.31	0.711724
jlo38	09/25/1995	307	8.00	13.8	248	1430	403.4	195.6	6.0	972.3	928.7	157.7	312.5	0.06	1.20	0.711786
jlo39	10/02/1995	177	7.52	15.3	253	1620	405.6	186.7	0.0	1033.3	883.9	129.7	335.0	0.10	2.14	0.711653
jlo40	10/09/1995	237	7.20	17.2	273	1770	424.8	191.3	78.1	1231.5	922.6	153.6	321.7	0.06	1.35	0.711504
jlo41	10/16/1995	168	7.02	19.0	258	1670	407.9	189.3	0.0	1093.8	883.0	179.0	335.0	0.06	1.28	0.711591
jlo42	10/23/1995	137	7.81	12.2	275	1700	439.4	202.0	13.4	1147.0	929.1	166.4	329.6	0.06	1.32	0.711594
jlo43	11/15/1995	145	6.95	19.9	270	2000	445.6	187.8	14.5	1249.5	892.6	157.2	329.2	0.06	1.50	0.711377
jlo44	11/27/1995	152	7.32	6.3	253	1740	402.8	175.6	23.4	1095.0	800.4	152.6	299.2	0.06	1.30	0.711402
jlo45	12/03/1995	251	6.76	6.6	203	1380	362.0	152.4	7.7	847.8	724.3	118.5	257.9	0.06	1.04	0.711543
jlo46	12/12/1995	174	6.70	3.9	227	1620	401.1	163.0	4.8	1021.8	767.0	128.2	288.8	0.06	1.21	0.711455
jlo47	12/17/1995	165	6.65	3.2	222	1530	398.0	158.4	4.4	984.5	763.0	132.1	277.1	0.05	1.13	0.711401
jlo48	01/03/1996	760	6.48	5.6	196	1230	349.3	155.9	162.4	688.8	346.5	82.8	153.8	0.05	0.98	0.711551
jlo49	01/05/1996	935	6.50	5.7	186	1150	331.8	147.3	169.7	629.8	347.4	120.5	223.8	0.05	0.93	0.711606
jlo50	01/07/1996	920	6.51	6.4	184	1200	341.7	147.8	226.9	647.5	354.8	89.2	122.5	0.06	1.23	0.71168
jlo51	01/09/1996	965	6.48	7.1	194	1300	395.8	163.6	257.9	671.8	297.4	103.3	135.0	0.05	1.01	0.711579
jlo52	01/11/1996	935	6.50	7.1	194	1270	360.3	160.7	238.2	691.3	317.4	120.0	124.2	0.07	1.54	0.711556
jlo53	01/14/1996	1040	6.50	7.8	188	1290	339.2	146.9	177.2	758.0	326.1	37.2	138.8	0.04	0.92	0.711579
jlo54	01/16/1996	1050	6.47	6.1	179	1100	320.9	141.1	167.4	624.5	343.5	63.1	119.2	0.04	0.87	0.711696
jlo55	01/18/1996	830	6.51	5.8	182	1190	322.7	145.5	160.9	582.3	281.7	115.6	116.3	0.07	1.57	0.711778
jlo56	01/21/1996	620	6.57	4.5	186	1190	323.1	148.8	65.9	653.5	301.7	88.5	150.8	0.04	0.96	0.7117
jlo57	01/22/1996	560	6.63	5.5	191	1260	328.3	149.9	39.1	685.0	346.1	70.8	177.1	0.04	0.98	0.711641
jlo58	01/26/1996	525	6.99	4.1	198	1120	331.1	152.6	22.4	682.3	357.8	95.1	171.7	0.04	0.99	0.711592
jlo59	01/29/1996	605	7.84	4.7	165	1270	280.5	131.1	0.0	558.3	305.7	82.8	150.0	0.03	0.85	0.711591
jlo60	02/01/1996	500	7.53	3.8	183	1200	305.5	149.8	0.0	633.8	337.8	67.2	166.7	0.00	0.11	0.711558
jlo61	02/06/1996	460	7.02	3.3	204	1500	320.3	156.3	194.8	719.0	338.3	63.8	174.6	0.04	1.03	0.71139
jlo62	02/12/1996	450	6.88	4.7	208	1500	401.1	160.3	202.3	746.0	391.7	69.2	174.6	0.04	1.07	0.711399
jlo63	02/15/1996	860	6.74	3.8	212	1490	307.9	147.3	60.0	819.0	329.6	72.6	161.3	0.04	1.08	0.711325
jlo64	02/19/1996	700	6.68	3.8	189	1270	287.9	127.8	138.7	682.5	317.0	61.5	141.3	0.04	0.87	0.711597
jlo65	02/22/1996	735	6.52	1.8	202	1410	309.6	135.7	57.9	748.8	329.6	66.4	144.6	nd	nd	nd
jlo66	02/27/1996	510	6.61	7.0	200	1440	392.4	148.2	117.6	594.0	417.4	72.8	127.5	0.14	3.83	0.711558
jlo67	03/08/1996	515	6.72	4.5	204	1320	385.1	142.1	147.3	487.3	432.2	69.7	160.0	0.03	0.89	0.711796
jlo68	03/18/1996	341	6.62	7.6	235	1530	441.7	174.9	174.7	837.5	486.5	75.1	205.4	0.04	1.30	0.711652
jlo69	04/02/1996	381	nd	6.6	184	nd	324.2	140.2	131.1	605.5	386.1	65.4	170.0	0.04	0.97	nd
jlo70	04/07/1996	344	nd	10.6	205	nd	387.0	159.7	148.5	696.8	439.1	67.7	198.3	0.04	1.16	nd

(*continued on next page*)

Table 1 (*continued*)

(B)

Sample name	Date	W (m^3/s)	pH	T (°C)	Conductivity ($\mu S/cm$)	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	Ca^{2+}	Na^+	K^+	Mg^{2+}	Rb	Sr	$^{87}Sr/^{86}Sr$
L1	5/05/94	443	8.20	15.1	189	1394	299.0	157.3	135.5	668.7	335.8	61.6	129.9	0.04	1.26	0.71134
L2	7/06/94	303	8.02	17.8	263	2046	375.2	180.2	154.8	920.7	396.7	71.1	164.5	0.04	1.76	0.711166
L3	4/07/94	167	9.05	23.7	220	1299	358.3	169.8	64.5	553.9	439.3	81.8	153.9	0.08	1.65	0.711127
L4	9/08/94	83	9.03	23.8	234	1662	423.1	188.5	46.8	611.3	465.4	81.8	164.6	0.07	2.12	0.710959
L5	9/09/94	76	8.59	14.9	293	2101	713.7	236.5	d.l	783.4	565.5	87.0	192.1	0.07	1.95	0.710995
L6	3/10/94	376	8.00	15.6	230	1444	434.4	180.2	d.l	648.7	448.0	81.8	239.1	0.05	1.67	0.711478
L7	7/11/94	500	7.37	12.8	223	1686	363.9	156.3	d.l	856.5	381.0	94.6	226.1	0.05	1.75	0.711446
L8	9/12/94	334	8.15	9.5	345	1851	351.8	163.5	43.5	1047.4	461.1	83.6	214.3	0.07	2.59	0.711237
L9	5/01/95	605	8.61	4.3	317	1619	263.2	122.8	175.6	864.5	328.8	77.2	150.6	0.06	1.87	0.711355
L10	30/01/95	1480	7.78	15.2	179	1373	249.4	119.3	69.8	692.9	280.6	74.2	123.7	0.05	1.44	0.711552
L11	10/03/95	875	8.10	8.1	202	1277	261.5	111.3	124.2	790.7	322.7	67.0	147.6	0.03	1.19	0.711329
L12	5/04/95	386	8.07	13.8	236	1696	321.9	136.5	228.7	970.8	394.5	61.4	176.4	0.04	1.42	0.71108
L13	5/05/95	480	9.14	20.3	215	1654	325.8	160.9	91.1	862.0	390.6	73.9	165.7	0.05	1.42	0.711234
L14	9/06/95	244	9.13	19.2	248	1850	283.8	153.1	107.3	1176.1	548.1	92.6	269.3	0.05	1.50	0.711075
L15	10/07/95	102	9.36	28	290	1350	318.2	132.3	87.3	822.9	631.6	108.2	169.4	0.07	1.48	0.710968
L16	9/08/95	63	9.28	21.8	292	2020	405.6	185.3	68.7	648.7	826.4	136.8	213.0	0.08	1.95	0.71072
L17	12/09/95	75	8.28	16.2	309	1770	415.5	204.3	89.0	1153.2	846.0	125.6	288.3	0.49	1.88	0.710969
L18	14/11/95	88	n.d	n.d	n.d	1530	325.8	160.9	91.1	1631.0	863.0	129.4	197.3	0.06	1.68	0.710831
L19	12/12/95	174	6.70	3.9	227	1620	401.7	163.0	4.8	962.1	725.5	121.0	215.8	0.40	1.50	0.711416
L20	7/01/96	920	6.51	6.4	184	1200	342.2	147.8	226.9	697.6	431.1	96.2	136.1	0.26	0.96	0.711641
L21	15/02/96	860	6.74	3.8	212	1490	308.3	147.3	60.0	817.4	329.7	72.4	197.4	0.39	1.50	0.711334
L22	12/04/96	261	n.d	n.d	n.d	1752	413.2	163.4	181.7	706.3	448.5	71.1	169.0	n.d	n.d	0.711244

[a] measured in the laboratory.

River was sampled once a month at the Beaugency station (monthly survey). The second period of sample collection (daily survey) was between May 1995 and March 1996 inside Orleans and in the same water mass as at the Beaugency station. The sampling interval ranged between 2 days and 1 week according to the fluctuations of the river discharge.

All of the water samples were collected in polyethylene bottles and filtered through precleaned 0.22 μm Teflon (PVDF) Millipore filters using a precleaned Nalgene filter apparatus. The electrical conductivity, standardized to 20°C, and the water temperature of each sample were measured on site. The pH was measured on site for the monthly survey samples and in the laboratory as soon as possible after the collection for the daily survey samples.

Chemical analyses of the water samples were performed by atomic absorption spectrometry (Ca^{2+}, Na^{+}, K^{+}, Mg^{2+}), ion chromatography (Cl^{-}, SO_4^{2-}, NO_3^{-}), inductively coupled plasma mass spectrometry (Sr and Rb trace elements), HCl titration, and Gran's method for alkalinity. Chemical separation and mass spectrometric procedures for strontium followed the standard method used at BRGM (Négrel and Deschamps, 1996). An average internal precision of $\pm 10 \times 10^{-6}$ (2σ) was obtained during this study. The reproducibility of the $^{87}Sr/^{86}Sr$ ratio measurements was tested through duplicate analyses of the NBS 987 standard, and the mean value appears to be close to $0.710227 \pm 17 \times 10^{-6}$ (2σ, $n = 70$).

The discharge of the Loire River was measured continuously by the Environmental Agency (DIREN-Agence de l 'Eau) at a gauging station located in the vicinity of the sampling point. A mean daily value was obtained throughout the hydrological cycle (Table 1).

3.2. Rainwater sampling

Two rainwater samplers were installed in the Loire watershed. One sampling site was near Clermont-Ferrand in the Massif Central, 200 km upstream from Orleans, this was fitted with an automatic sampler (Négrel and Roy, 1998) that functioned from March 1994 to March 1995. The second sampling site was at Tours, 110 km downstream from Orleans, and was operated during each rain event from September 1996 to January 1998. These two collectors enabled a mean geochemical signature of rainwater to be determined for the Loire watershed above Orleans.

4. Results and discussion

4.1. Chemical element distribution and Sr isotopic variation in rain events

4.1.1. The upper part of the watershed: the Massif Central

Thirteen samples of rainwater (970 mm) were collected between March 1994 and March 1995, with one sample representing all the rainwater that fell during a period of 1 month. During the sampling period, the electrical conductivity ranged from 5 (October–November 1994) to 52 μS/cm. (June–July 1994) with an annual mean of 17.2 ± 14.8 μS/cm. The pH of the rainwater was always acid and ranged between 4.3 (March–April 1994) and 6.0 (June–July and September–October 1994) with an annual mean of 5.2 ± 0.6.

The eight major elements, the trace element Sr, and the $^{87}Sr/^{86}Sr$ isotopic ratio were analysed, with the results presented and discussed in Négrel and Roy (1998). To summarise, the order of cation abundance was $Ca^{2+} > Na^{+} > K^{+} > Mg^{2+}$, with the Ca^{2+} and Na^{+} species giving a mean weighted concentrations of 17.7 and 14 μmol/l, respectively. The cation concentrations showed large variations during the sampling period: the Na^{+} concentration varied 100-fold (from 0.4 μmol/l in October–November 1994 to 43 μmol/l in February–March 1995), the Ca^{2+} concentration varied 80-fold, and the K^{+} concentration varied 20-fold.

The order of anion abundance is $NO_3^{-} > SO_4^{2-} > Cl^{-}$, but their mean weighted contents were very similar (26, 23, and 19 μmol/l, respectively). Their variations were less than those of the cations, between 5- and 10-fold. The charge imbalance showed an anionic excess close to 36% in the Massif Central, which is usual for dilute waters (Edmond et al., 1995). The main explanation for this charge imbalance is the absence of NH_4^{+} analysis. Actually, NH_4^{+} ions were present in all the rainwater samples as a

minor element, supplied from the ammonia atmospheric cycle, essentially due to fertilizer release and biological decay (Sloan et al., 1994; Berner and Berner, 1996).

The trace element Sr varied greatly, but was around 1000 times lower than in the Loire waters. Its concentration in the rainwater ranged from 0.008 (October–November 1994) to 0.121 μmol/l (June–July 1994). The $^{87}Sr/^{86}Sr$ isotope ratio ranged from 0.709198 (September 1994) to 0.71314 (October 1994) with a mean annual average of 0.7097, this ratio increased and decreased several times during the sampling period.

4.1.2. The lower part of the Loire watershed: the city of Tours

An identical survey was carried out in the sedimentary part of the watershed (Fig. 1). Seven samples of rainwater (190 mm) were collected each month in the city of Tours from September 1996 to September 1997. As with the automatic sampler, one sample represented all the rainwater that fell during one month. The pH of the rainwater was again acid, varying between 3.3 (September 1997) and 5.8 (March 1997) with an annual mean of 4.4 ± 1.0. The electrical conductivity was very low and ranged between 17 (May 1997) and 31 μS/cm (September 1997) with an annual mean of 20.5 ± 0.9.

The cation abundance was $Na^+ > Mg^{2+} > Ca^{2+}$ and K^+. The mean weighted Na^+ concentration was 203 μmol/l, with the mean weighted Mg^{2+} concentration being 30 times lower at 6.7 μmol/l and the mean weighted Ca^{2+} concentration being 2.7 μmol/l. The K^+ concentration was often below the detection limit of the analysis (between 5 and 10 μmol/l).

The anion abundance was $Cl^- > SO_4^{2-} > NO_3^- > \Sigma P$, except for January 1997 when NO_3^- was the most abundant species. The mean weighted Cl^- concentration was 104 μmol/l, with the mean weighted SO_4^{2-} concentration being six times lower at 16 μmol/l and the mean weighted NO_3^- concentration being at the same order of magnitude as SO_4^{2-} at 15 μmol/l. The inversion of the Cl^- and NO_3^- species abundances was due to different air-mass origins. During January 1997, the dominant wind directions and air-mass trajectories were clearly easterly; they passed over all of the Eastern European forested areas to give dominant NO_3^-. Moreover, during November 1996, the Cl^- concentration varied twofold because of the dominant westerly wind directions with an oceanic origin for the air mass.

The Rb and Sr concentrations were fairly uniform, except for the January 1997 rainwater. Sr concentrations varied from 0.012 (December 1996) to 0.04 μmol/l (January 1997) and the Rb concen-

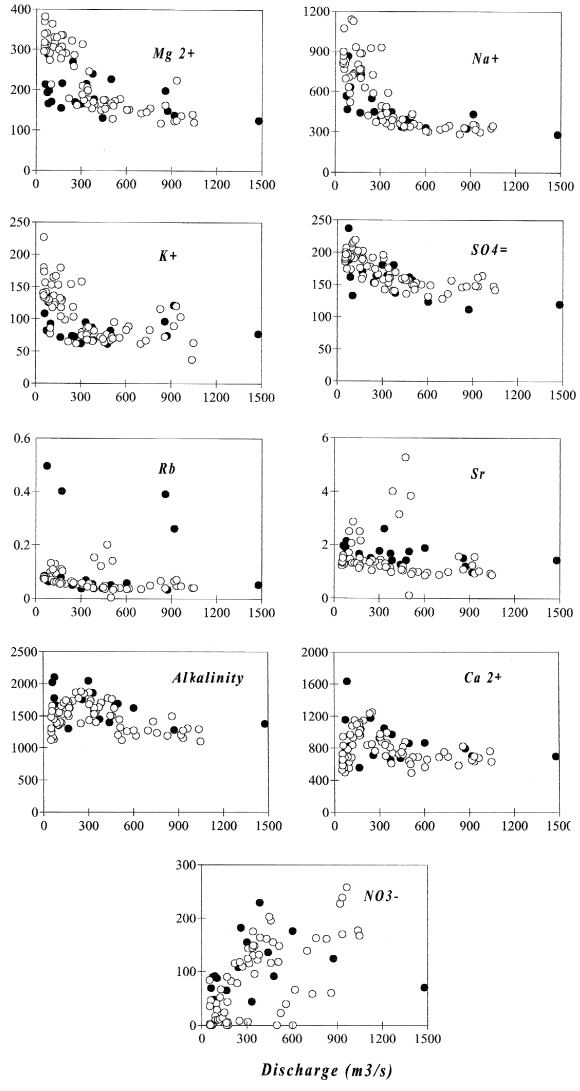

Fig. 2. Evolution of element concentrations with discharge for the daily survey (jlo samples, open circles) and the monthly survey (L samples, filled circles). Analytical errors are in symbols.

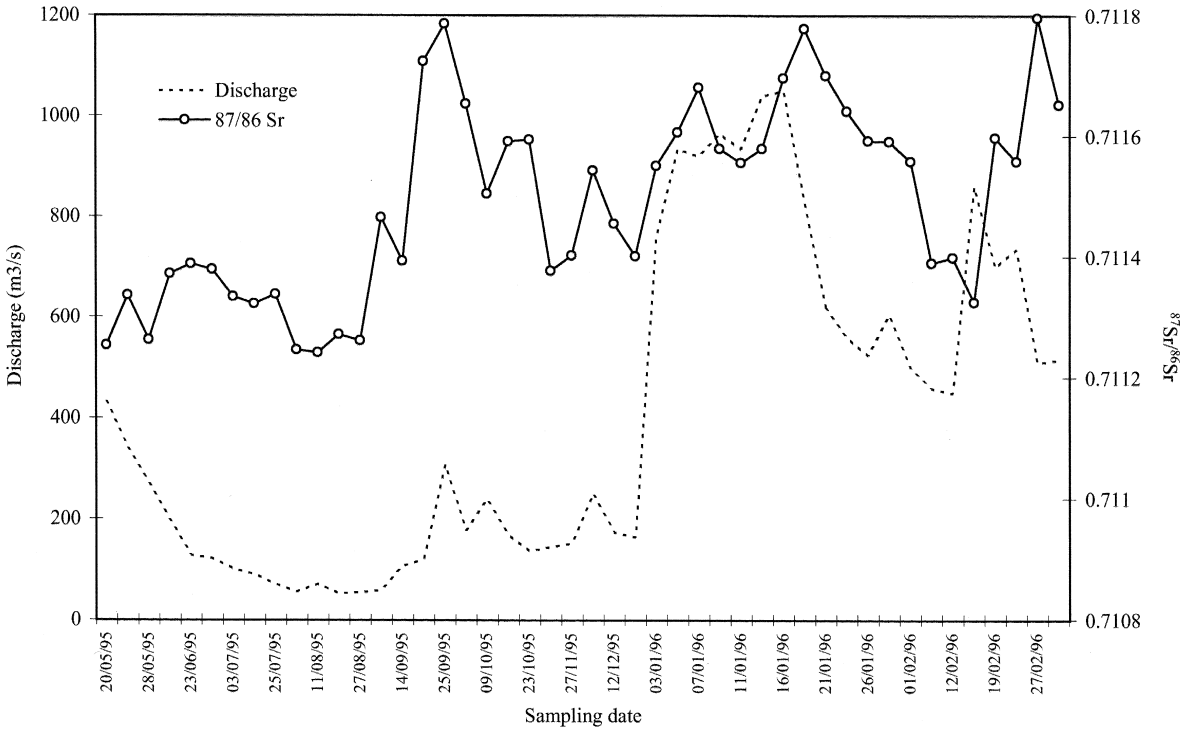

Fig. 3. Fluctuations of $^{87}Sr/^{86}Sr$ and discharge in the dissolved load for the daily survey samples.

trations from 0.0009 (June 1997) to 0.0014 μmol/l (March 1997). The $^{87}Sr/^{86}Sr$ isotope ratio ranged between 0.70901 (May 1996) and 0.70106 (March 1997) with a weighted mean of 0.70943, this ratio was very stable during the sampling period.

4.1.3. Comparison of the two surveys

Compared to the rainwater in the Massif Central, the rainwater at Tours was four times more concentrated in chloride species (104 against 26 μmol/l) and 15 times more concentrated in sodium species (204 against 14 μmol/l). The marine influence was more marked in the rainwater at Tours than in the Massif Central. Conversely, calcium concentrations were six times more concentrated in the Massif Central (17.7 as against 2.7 μmol/l) because of the more marked influence of carbonate wind dust. Sulphates and nitrates were 1.5 times more concentrated. The concentration of magnesium species was of the same order of magnitude at the two sampling

Table 2
Major and trace element concentrations (μmol/l) and $^{87}Sr/^{86}Sr$ ratios of the dissolved load collected during July 1988 on monolithologies in the Seine watershed

Locality	Bedrock age	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-	Ca^{2+}	Na^+	K^+	Mg^{2+}	Sr	$^{87}Sr/^{86}Sr$
Villeneuve	Upper Cretaceous	4000	225	52	2.0	1800	148	16	60	1.2	0.70837
Eglény	Lower Cretaceous	2200	300	132	1.3	900	160	113	100	1.3	0.709548
Migé	Upper Lias	3830	350	168	5.7	1900	115	113	110	1.1	0.708454
Lucy le bois	Lias	2940	435	333	1.7	1500	400	135	158	2.2	0.710022
Vault de lugny		2090	220	106	0.7	650	175	137	183	1.5	0.713715

points, as were the Sr and Rb concentrations. The isotopic ratio of the rainwater was lower at Tours than in the Massif Central (0.70943 and 0.70972, respectively), but the isotopic composition was more constant.

4.2. Major geochemical parameters of the Loire

The total cationic charge ($TZ^+ = Na^+ + K^+ + 2Mg^{2+} + 2Ca^{2+}$) ranged between 1794 (January 1996) and 4207 μeq/l (November 1995) with an annual average of 2753 μeq/l. The anionic charge ($TZ^- = HCO_3^- + NO_3^- + Cl^- + 2SO_4^{2-}$) ranged from 1779 (January 1996) to 2836 μeq/l (November 1995) with an annual average of 2250 μeq/l.

The database showed a charge imbalance mainly in favour of a positive charge excess or inversely, to a negative charge deficit. A greater imbalance appeared during the low flow period. This deficit of negative charges could be related to the absence of the analysis of organic matter (Sigg et al., 1992; Berner and Berner, 1996), which is mainly produced during spring and summer by biological activities.

The total dissolved salts (TDS) ranged from 136 mg/l at the high stage to 241 mg/l at the end of the low flow with a mean annual value of 181 mg/l. Identical orders of annual average TDS values are observed in other rivers in France, e.g., 174 mg/l for the upstream of the Garonne River (Probst and Bazerbachi, 1986), 461 mg/l for the Seine (Roy, 1996), and 600 mg/l for the Rhine (Meybeck and Ragu, 1996).

The annual flux of dissolved salts, calculated from the daily survey samples, is 13 10^5 t/year at Orleans. This flux is four times greater than the annual transport of suspended matter (SM) of almost 3.5×10^5 t/year (Négrel and Grosbois, 1999). The

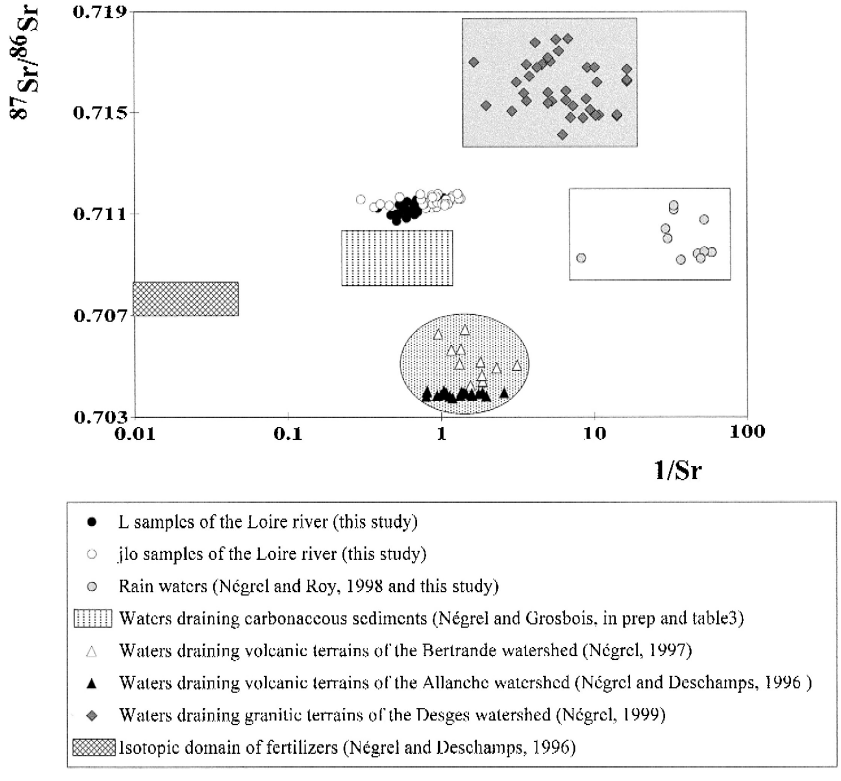

Fig. 4. Relationship between the $^{87}Sr/^{86}Sr$ ratio of the dissolved load in the jlo and L samples and the 1/Sr ratio. Isotopic and chemical domains of the dissolved load in water draining monolithologic watersheds and different French rivers are drawn (see text).

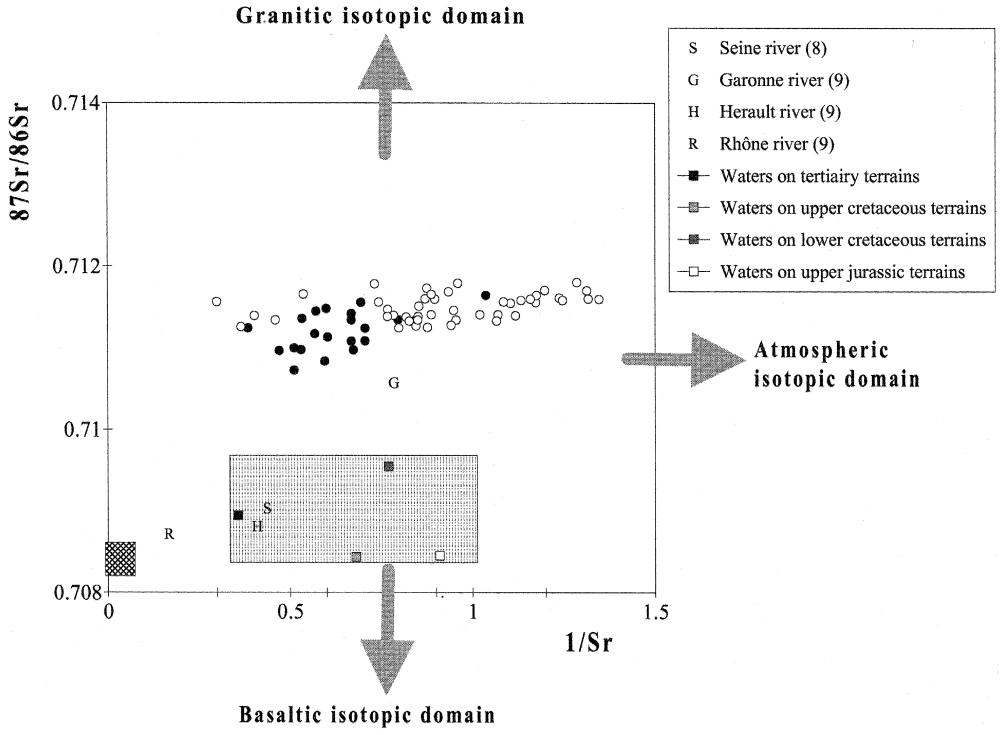

Fig. 4 (*continued*).

major characteristic of the Loire is that the annual flux of dissolved salts always dominates that of SM, independent of the discharge. However, the dissolved load of the Loire is of the same order of magnitude as those of the Garonne and Seine Rivers (11.9 10^5 t/year, Probst and Bazerbachi, 1986; and 6.5 10^5 t/year, Roy, 1996). The Rhine dissolved flow (60.5 10^6 t/year, Meybeck and Ragu, 1996) is 46 times higher than that of the Loire and is the greatest of any river in West Europe.

4.3. Chemical element distribution in the Loire dissolved load

Table 1a and b shows the chemical and isotopic composition of the dissolved load for the daily and monthly survey samples, respectively. The order of cation abundance was $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$ and that for anion abundance was $HCO_3^- > Cl^- > NO_3^- > SO_4^{2-} > CO_3^{2-}$. The Loire waters plot in the calcium bicarbonate field. Calcium and bicarbonate species, respectively represent between 13% and 33% and between 43% and 58% of the TDS. The concentrations of the bicarbonate ions are strongly related to those of calcium ions, which reflects the carbonate nature of part of the drainage basin.

The seasonal fluctuations of dissolved concentrations compared with those of discharge (Fig. 2) reveal three geochemical behaviour patterns.

The first geochemical behaviour pattern was observed for nitrate, which tends to increase with increasing discharge. The increased river flow during the autumn and winter seasons indicates a larger runoff, and therefore, greater leaching of the watershed soils. The highest inputs of nitrates in the river water originate from leaching because NO_3^- comes mainly from fertilizer applications (Meybeck, 1982; Probst, 1985). Moreover, any NO_3^- consumption by plants or algae could induce a decrease of NO_3^- concentrations.

The second geochemical behaviour pattern applies to most species (Na^+, Mg^{2+}, K^+, SO_4^{2-}, Cl^-) with

concentrations being highest during low flow and decreasing with increasing discharge until a stable stage above 400 m^3/s. The dissolved element contents reveal two signatures, one dominating during high flow with low concentrations, and the other one, dominating during the low flow with higher concentrations. The high flow signature is in agreement with rock weathering and rainwater inputs (Gibbs, 1970). The summer low flow signature can be related to groundwaters and anthropogenic inputs such as urban sewage and farming waters. Rb and Sr fall into the second geochemical behaviour pattern with several values higher than the trend.

The third geochemical behaviour pattern was more complex because the calcium and bicarbonate concentrations increased only up to an intermediate flow of 300 m^3/s. More than two signatures was needed to explain this geochemical behaviour since it is clearly not a binary relation.

It is noticeable that one chemical signature at a hydrological period can encompass several end-members and therefore, the isotopic characteristics were used to differentiate between them.

4.4. Strontium isotopic variations in the Loire dissolved load

Systematic sampling of the dissolved load shows a wide range in the $^{87}Sr/^{86}Sr$ ratio with variations clearly greater than the analytical errors — i.e., the strontium isotopic data showed variations around 10^{-3} between the lower value (0.71072) observed in August 1995 and the higher value (0.71196) observed in March 1996, whereas the analytical uncertainties were close to 2.10^{-6}. The fluctuations of the $^{87}Sr/^{86}Sr$ ratio of the dissolved load correlates well with the discharge of the river as illustrated in Fig. 3. The ratio is lowest at low flow and increases with increasing discharge. Each high stage peak exhibits a high $^{87}Sr/^{86}Sr$ both in the daily survey samples (0.71179) and in the monthly survey samples (0.71164). When the discharge decreased, the isotopic ratio also decreased. This kind of relationship, previously demonstrated by Négrel and Dupré (1995) on the Oubangui basin in Central Africa, can be related to a mixing model with two signatures. The first, present during high flow, was the highest of the hydrological cycle and agreed with the geochemical signature of the weathered silicate bedrock of the Massif Central, the second, present during the low flow, was the lowest of the hydrological cycle and agreed with the geochemical signature of weathered carbonate bedrock, carbonate groundwaters, and fertilizers inputs. The decrease in element concentrations cannot be explained simply by a process of rainwater dilution because of the increasing $^{87}Sr/^{86}Sr$ ratio during peak discharge. The weighted isotopic composition of rainwater in the upper Loire basin was around 0.70962 (0.70969 in the Massif Central, 0.70943 in the sedimentary part) and was, in every case, lower than the Loire river data.

In order to correlate the geochemical and isotopic signatures, the classical $^{87}Sr/^{86}Sr$ vs. $1/Sr$ contents diagram (Faure, 1986) was used. Natural inputs and anthropogenic additions influence the river water chemistry. Natural inputs were represented by the rainwater of the Massif Central (Négrel and Roy, 1998) and of the Tours (this work) and by the waters weathering carbonate, granitic, and basaltic terrains that were included in small monolithologic watersheds in the headwater of the Loire watershed (Table 2; Négrel, unpublish data, 1997, 1999; Négrel and Deschamps, 1996). The watersheds are polluted mainly by agricultural activities (fertilizers, Négrel and Deschamps, 1996) and by sewage waters from towns and industries. The isotopic signature of each natural and anthropogenic component was determined and plotted in the diagram. The isotopic signature of the dissolved load of the Loire is scattered between all the different isotopic fields (Fig. 4). In detail, the isotopic field of the dissolved load of the Loire plots near the isotopic composition of the Garonne River (Albarède and Michard, 1987). The Seine (Roy, 1996) and Herault (Albarède and Michard, 1987) Rivers plot in the isotopic field of waters draining carbonate terrain. The Rhône River (Albarède and Michard, 1987) plots near the isotopic field of fertilizers. The sewage waters are clearly included in the same isotopic field as the Loire water because they originate mainly from the pumping of the Loire groundwaters. The influence of weathered silicate and carbonate terrains, rainwater, and fertilizers is well marked. The different geochemical signatures, which could contribute to the $^{87}Sr/^{86}Sr$ ratio of the dissolved load of the Loire, were composed

with several end-members that made it possible to explain the geochemical behaviour of different dissolved species. In conclusion, the use of the $^{87}Sr/^{86}Sr$ vs. 1/Sr systematic revealed the existence of at least five end-members.

The next step will be focused on the different contributions of the different end-member inputs to the total dissolved load since any calculation of the export rate of chemical species of natural or anthropogenic origin requires the quantification of each end-member. An approach using a mass balance calculation can provide answers to this problem.

5. Identification and quantification of natural and anthropogenic inputs

A general mass balance equation for the budget can be written as follows (Meybeck, 1983; Drever and Hurcomb, 1986; Drever and Zobrist, 1992):

rock weathering + atmospheric input

+ human activities input

= dissolved load + solid load

The mass balance approach requires the determination of an output–input budget (Velbel, 1985; Mast and Drever, 1990) with the determination of element origins. It is commonly accepted that chloride ions come mostly from airborne sea salt (Erickson, 1955; Junge, 1963; Meybeck, 1983) and also, from human activities (Meybeck, 1986). Other chemical species may have several origins, such as sodium species with a marine origin and a silicate weathering origin. The abundance of major and trace elements can be influenced by human activities, thus, the large increase in the concentration of nitrate, sulfate, chloride, and potassium in river water can be related to a marked increase in fertilizer applications (Etchantu and Probst, 1988; Ramos, 1996). Moreover, the mobility of chemical species can be affected by the use of nitrogen fertilizers (Meybeck, 1979; Etchantu and Probst, 1988; Négrel, 1997, 1999; Négrel and Deschamps, 1996) or regulated by biochemical processes (Johnson et al., 1969).

The mass balance approach tries to evaluate the contribution of atmospheric inputs, fertilizer applications or other anthropogenic impacts, and rock weathering processes.

5.1. Atmospheric inputs correction: methodology and results

Some solutes in rainfall can constitute an important fraction of dissolved species appearing in surface waters (Meybeck, 1983). The aim of the atmospheric input correction is to quantify and subtract the portion of the elements carried by rainwater in the chemical composition of the river water. The quantification of atmospheric input due to rainwater requires knowledge of the chemical composition of the rainfall on the total watershed (Likens et al., 1977; Meybeck, 1983).

The estimation of the mean rainwater input on the whole watershed required the data of the two sampling databases and the meteorological data. The chemical composition of each monthly rainwater sample from the two sampling sites was weighted by the percent of rainfall in the same month.

Rainwater inputs in the dissolved load carried by the Loire had two distinct origins: (a) rainwater falling on the Massif Central, for which the chemical and isotopic characteristics are discussed elsewhere (Négrel and Roy, 1998) and briefly described in Section 4.1; and (b) rainwater falling between the Massif Central and the sampling point, for which the chemical and isotopic characteristics may be approached through the rainwater study near Tours in the sedimentary area (see Section 4.1). The rainwater inputs at the sampling site are approximately 25% rainwater of the sedimentary area (i.e., 9500 km^2 drained area between Orleans and Tours) and 75% rainwater of the Massif Central type (i.e., 32500 km^2 drained area between Orleans and the Massif Central).

In precipitation at Orleans station, sodium was the most concentrated species (61 μmol/l), chloride concentration was approximately 41 μmol/l, sulfate and nitrate, around 20 μmol/l, and calcium, 13 μmol/l. Other species (K^+, Mg^{2+}) were estimated to be approximately 5 μmol/l. For the trace elements, Sr was close to 0.03 μmol/l and Rb is 10 times lower at 0.04 μmol/l. The Sr isotopic ratio of rainwater inputs at Orleans was close to 0.70962.

Classically (Meybeck, 1983), for any element 'Z' in the river (Z)r, the correction of atmospheric contribution to a river (r) is estimated by reference to the Cl concentration called $(Cl)_{ref}$ multiplied by the Z/Cl ratios of rainwater (rw):

$$(Z)_{rw} = (Cl)^{*}_{ref}(Z/Cl)_{rw}. \quad (1)$$

$$(Z)_{r,rw\,corrected} = (Z)_{initial\,r} - (Z)_{rw}. \quad (2)$$

Chloride ions in the atmosphere originate from sea salt and human activities. The release of Cl due to rock weathering has not been demonstrated clearly except in the weathering of salt rock (Meybeck, 1979). Furthermore, as chloride ions behave conservatively through the hydrological cycle (Meybeck, 1979), they have been used as a reference of atmospheric inputs in many unpolluted hydrosystems (Meybeck, 1983; Sarin et al., 1989; Négrel et al., 1993; Gaillardet et al., 1997). However, chloride ions can also result from a wide range of human activities (Meybeck, 1986; Sherwood, 1989). For the mass balance equations, the highest concentrations of Cl ions issued from rainwater, termed $(Cl)_{ref}$, had to be determined. The $(Cl)_{ref}$ was calculated with each mean weighted chloride content for the sampling station at Tours and for the sampling station in the Massif Central, multiplied by the concentration factor F of each region. This factor F represents the concentration effect of evapotranspiration and is related to the total quantity of rainwater P (in mm) and the evapotranspiration process E (in mm) by the equation:

$$F = P/(P - E). \quad (3)$$

According to Eq. (3), the F value was equal to 1.2 in the Massif Central and to 2.2 in the sedimentary area for the two sampling periods. The general equation to calculate the $(Cl)_{ref}$ was as follows:

$$(Cl)_{ref} = (Cl)^{*}_{SA}\,0.25\,{}^{*}F_{SA} + (Cl)^{*}_{MC}\,0.75\,{}^{*}F_{MC}, \quad (4)$$

where $(Cl)_{SA}$ and $(Cl)_{MC}$ correspond to the weighted concentrations of chloride in the sedimentary area and the Massif Central, F_{SA} and F_{MC} correspond to the concentration factors in the sedimentary area and the Massif Central, and 0.25 and 0.75 correspond to the respective proportions of sedimentary area and Massif Central area.

The $(Cl)_{ref}$ was estimated at 74 μmol/l and represents the highest chloride concentration in the rainwater input to the river. When the chloride content measured in the dissolved load of the river (Table 1a and b) was lower than the $(Cl)_{ref}$, the whole chloride content of the river was assigned to atmospheric origin. When the chloride content measured in the dissolved load of the river was higher than the $(Cl)_{ref}$, the atmospheric correction was applied with $(Cl)_{ref}$ as the rainwater input. The residual chloride $(Cl)_{res}$ in the river was attributed only to human activities.

$$(Cl)_{res} = (Cl)_{measured} - (Cl)_{ref}. \quad (5)$$

The estimate of the mean rain input at Orleans was calculated. Because the order of species abundance in the mean rainwater composition was $Na^{+} > Cl^{-} > NO_3^{-} > SO_4^{2-} > Ca^{2+} > K^{+} > Mg^{2+}$, the atmospheric input corrections were important only for sodium and chloride. The main atmospheric correction was for sodium with a mean input of 23 ± 9%, i.e., ranging from 10% (September 1995) to 40% (January 1996), the atmospheric input of sodium varied widely throughout the year. The atmospheric correction for sulfate was of the same order of magnitude close to 20 ± 3% and ranging from 15% (September 1996) to 26% (February 1996). Corrections for chloride and potassium were two times lower than those for sodium (11 ± 2% and 10 ± 3%, respectively). Corrections for magnesium and calcium were similar, close to 3 ± 1%. The samples taken in summer generally presented lower rainwater input than the samples taken in winter because of the fewer rain events.

Note that the atmospheric input of NO_3^{-} in the river water (39 ± 20% and ranging from 16% (January 1996) to 97.7% (June 1995)) could not be calculated with mass balance considerations for 19 samples of Loire water taken in the period between July 1995 and December 1995. Their NO_3^{-} contents were too low relative to the rainwater content and this resulted in a 100% higher atmospheric input in the river. The low NO_3^{-} content in the river water was due to the biological pump of aquatic plants and algae, depending on the water temperature. From

July to December 1995, the water temperature ranged between 23°C and 6°C. After this period, the water temperature was too low for biological functions and the amount of nitrates increased because of no consumption.

For the trace elements, Rb exhibited the highest input by rainwater at $12.2 \pm 4.3\%$ (ranging from 3.5% (May 1995) to 22.1% (March 1996)), and Sr, a lower input at $3.8 \pm 1.1\%$ (ranging from 1% (May 1995) to 6% (January 1996)).

5.2. Budgets of human activities: methodology and results

When the rainwater influence was subtracted from the river water composition, the general mass balance equation showed that the dissolved load carried by the Loire was composed by the mixing of two individualized signatures: rock weathering and human activities. The influence of anthropogenic inputs needed to be quantified in order to evaluate the chemical weathering on the Loire watershed.

Human activities generate both diffuse contamination sources, including atmospheric transport, fertilizer applications, and local contamination sources that include urban and industrial wastewaters. It is well known that phosphorus and nitrogen forms, and potassium and chloride ions are mostly derived from agricultural fertilizers, animal waste, and municipal and industrial sewage (Meybeck, 1986; Dojlido and Best, 1996; Ramos, 1996), these species can be used as an indicator of both population and agricultural impacts. Sulfates are the product of the bacterial oxidation of some industrial products and of the mineralization of organic matter (Mackenzie and Garrels, 1966; Probst, 1986).

In order to identify anthropogenic and rock weathering end-members in the dissolved load of the Loire, atmospheric corrected samples were plotted in X vs. residual Cl^- diagrams, where X represents Na^+, Ca^{2+}, Mg^{2+}, K^+ and HCO_3^- (Fig. 5a,b,c,d,e). Residual Cl^- in these atmospheric corrected samples has only an anthropogenic origin because there are no evaporitic rocks in the Loire watershed. Other anionic species (NO_3^-, SO_4^{2-}) could not be plotted because of, the uncorrected atmospheric data and the lack of data for the different end-members, respectively. Waters of the Desges (Négrel, 1999), Allanche (Négrel and Deschamps, 1996), and Bertrande watersheds (Négrel, 1997) were plotted on the same diagrams to represent silicate weathering end-members. Several samples of water representing the weathering of carbonate monolithologies of the Seine watershed (Négrel, unpublish data) were used to represent carbonate weathering end-members. Those of the Loir River, a tributary of the Loire just downstream of Orleans, represent the Tertiary basement of the Loire watershed (Négrel and Grosbois, in prep.). Local samples of sewage station and industrial inputs represent waters with an anthropogenic activity origin. All these samples, except the samples of sewage station and industrial inputs, were corrected of rainwater inputs but still showed an anthropogenic influence (agricultural or urban). They cannot be considered as pure end-members, but as a mixing of monolithologic rock weathering and anthropogenic components. Moreover, for this first approach, the geochemical compositions of natural and anthropogenic end-members are considered constant. Seasonal variations in composition could not be evaluated and results will be calculated over the full hydrological cycle 1995–1996.

Thus, in the diagrams of Fig. 5(a,b,c,d,e), all the Loire River samples are scattered within the silicate, carbonate, Tertiary, and anthropogenic component fields. Two different anthropogenic end-members were distinguished to explain the dispersion of points for the Loire: one, called ANT1 (mainly related to sewage station), is characterized by a high residual chloride of over 1000 μmol/l and by low amounts of X chemical species, the other, called ANT2 (related to agricultural activities), is characterized by a residual chloride close to 500 μmol/l and higher amounts of X chemical species than ANT1.

The silicate end-member has the lowest anthropogenic chloride signature (<100 μmol/l). The calcareous end-member has an intermediate anthropogenic chloride content ranging from 200 to 400 μmol/l. The variation of residual chloride of the Loire samples ranged between 250 and 450 μmol/l.

The inputs of the X chemical species carried by each pure end-member was evaluated by maximizing the highest value of the different end-members in order to encompass the Loire samples. To quantify the silicate signature for each chemical species, the linear regression was used with a residual chloride

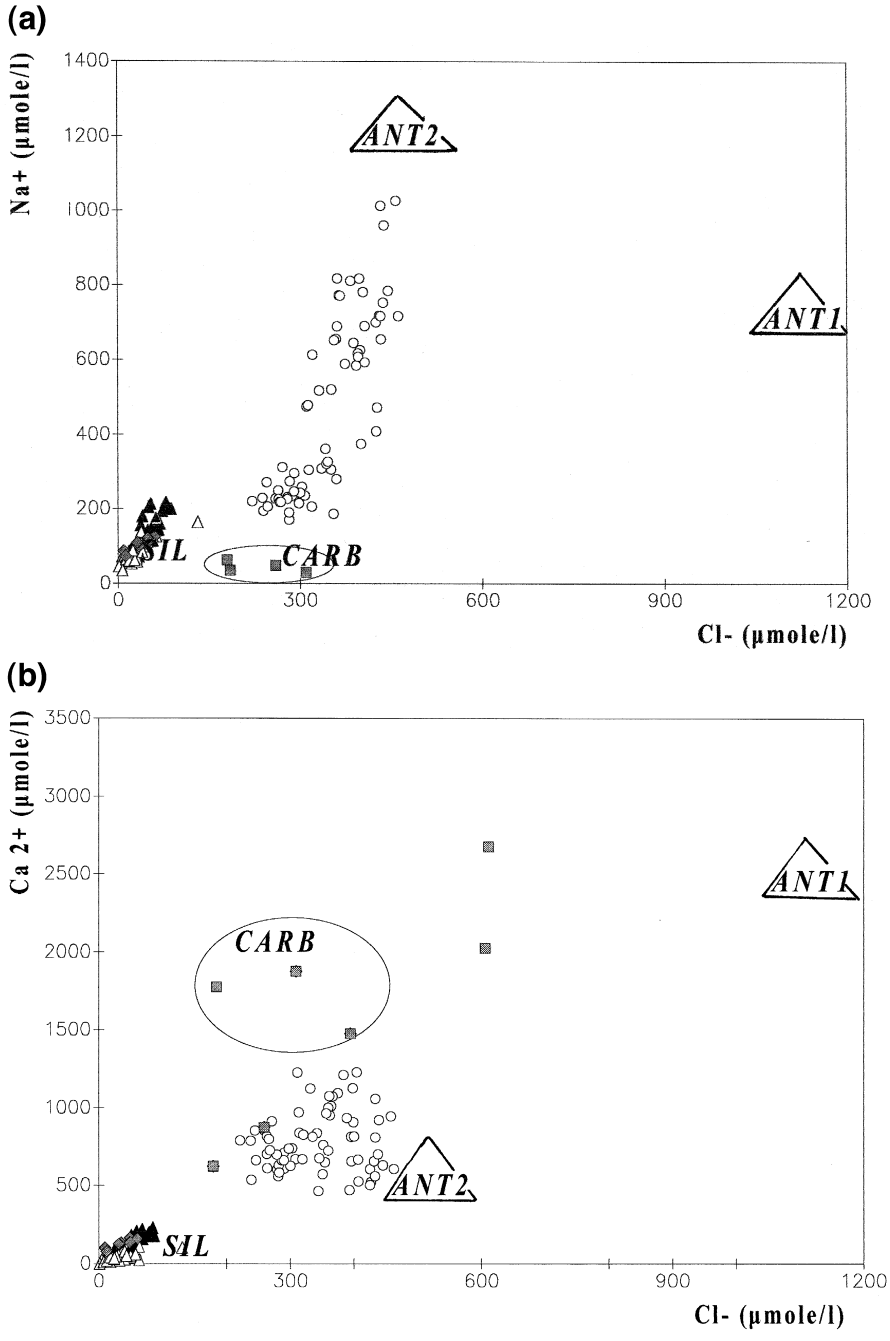

Fig. 5. Relationships between Cl^- and X chemical species in the dissolved load of the daily survey samples and water draining monolithological terrains. $X = Na^+$ (a), Ca^{2+} (b), K^+ (c), Mg^{2+} (d) and HCO_3^- (e). Symbols and references are identical to those in Fig. 4. The dissolved load was corrected for atmospheric inputs (see text for the calculation procedure). SIL represent the silicated end-member, CAR the carbonate end-member, and ANT1 and ANT2 the two types of anthropogenic end-members.

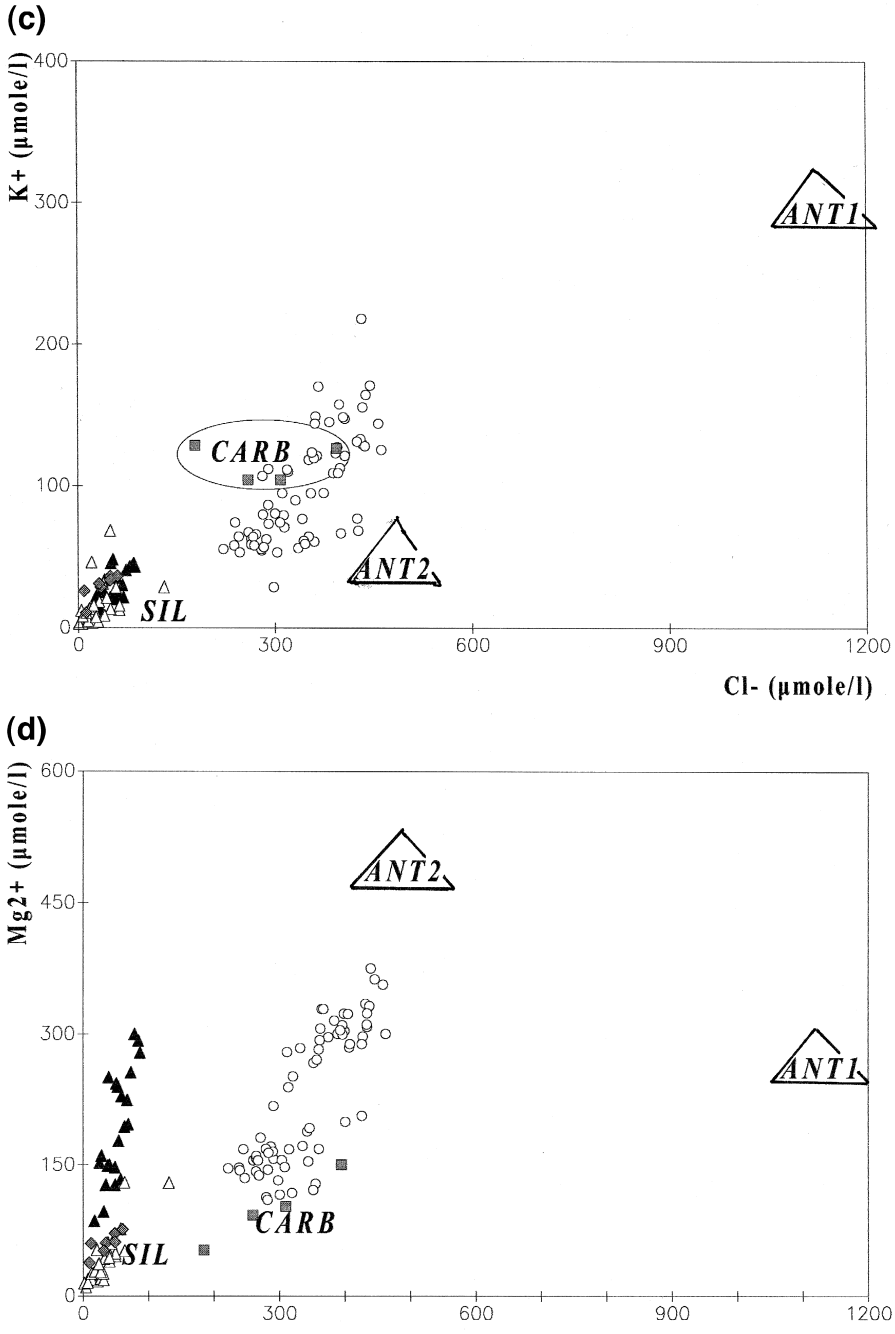

Fig. 5 (*continued*).

reduced to zero. This estimation showed that for the Na^+ signature of the different reservoirs, the anthropogenic ANT1 reservoir carried 750 μmol/l, two times lower than ANT2 (1200 μmol/l), 20 times

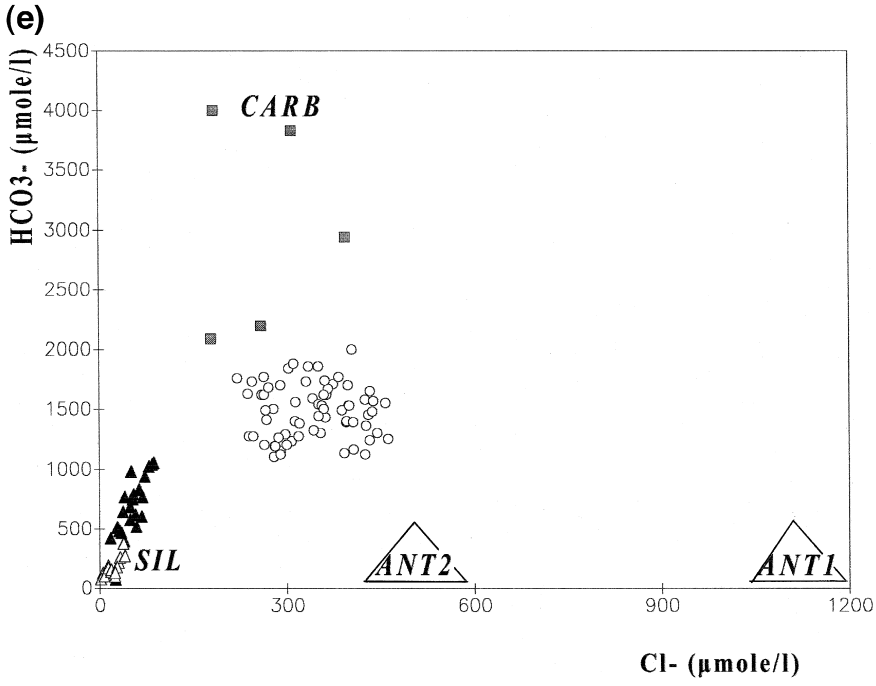

Fig. 5 (*continued*).

higher than the silicate end-member (60 μmol/l) and 60 times higher than the carbonate end-member (20 μmol/l).

For the Ca^{2+} signature, the most important reservoirs were the anthropogenic end-member ANT1 (2500 μmol/l) and the carbonate end-member (2000 μmol/l), which represents both groundwaters inputs and carbonate bedrocks weathering. This is also true for the K^+ signature (respectively, 300 and 125 μmol/l). The second anthropogenic end-member, ANT2, carried 500 μmol/l of Ca^{2+} and 75 μmol/l of K^+. The silicate end-member carried 70 μmol/l of Ca^{2+} and 35 μmol/l of K^+.

Finally, for the Mg^{2+} signature, the ANT1 end-member was lower (250 μmol/l) than the ANT2 end-member (500 μmol/l), the carbonate and silicate end-members carried 100 and 50 μmol/l, respectively.

The inputs of the different end-members to the dissolved load could be calculated using this estimation of the chemical signature of the pure end-members. For each chemical species, the contributions for the silicate (SIL), carbonate (CAR), and anthropogenic (ANT1, ANT2) end-members were calculated for each sample of Loire water using the following Eq. (6):

$$[X]_{riv} = a[X]_{SIL} + b[X]_{CAR} + c[X]_{ANT1} + d[X]_{ANT2}, \quad (6)$$

with the condition: $a + b + c + d = 1$,where X represents each cationic species, [X] represents the amounts (in μmol/l) of X in the SIL, CAR, ANT1 and ANT2 end-members, and *a*, *b*, *c*, *d* represent the proportions (%) of each end-member contribution.

The proportions of weathered terrains and anthropogenic contributions resulting from the mass balance calculations show that dissolved Na^+ inputs are dominated by both silicate weathering (20.8 ± 1.1%) and carbonate weathering (20.9 ± 1.2%). These two inputs from rock weathering increased with increasing discharge. The anthropogenic inputs of end-members ANT1 and ANT2 were quite similar with a proportion close to 17 ± 2%, they were more impor-

tant during low flow than during high flow, being higher than the rock weathering end-members.

Dissolved Ca^{2+} inputs were controlled both by silicate weathering (34.6 ± 3.9%) and anthropogenic inputs ANT2 (34.3 ± 4.9%). This influence of silicate and ANT2 inputs on Ca^{2+} proportions was present over the entire hydrological cycle except during the summer flow. The influence of carbonate weathering was also important (23 ± 4%). The ANT1 proportions had the lowest (9.5 ± 6.9%) over the hydrological cycle for Ca^{2+} inputs but this end-member ANT1 was mainly present during low flow, equal to carbonate inputs during this period.

Dissolved K^+ inputs were clearly controlled by silicate weathering (34.5 ± 5.2%) and its proportion increased with increasing discharge. A large proportion of the dissolved K^+ could be related with the anthropogenic end-member ANT2 (30.3 ± 1.2%), but this proportion decreased with increasing discharge. The carbonate end-member inputs carried about 23% of total amount of dissolved K^+. As for the silicate end-member, its proportions increased with increasing discharge. The anthropogenic end-member ANT1 was preponderant only during the summer period between mid-August and November 1995, outside this period, it was negligible for dissolved K^+ inputs.

The dissolved Mg^{2+} was mainly controlled by silicate and carbonate weatherings (27.5 ± 1.2% and 26.7 ± 8.9%, respectively) during the autumn and winter seasons. During the spring and summer seasons, it was controlled by the ANT2 and ANT1 end-members (20.1 ± 1.5% and 22.6 ± 0.6%, respectively).

Finally, the dissolved HCO_3^- input was controlled by carbonate weathering (48.2 ± 7.5%) throughout the hydrological cycle. The silicate end-member was still present and constant (25.6 ± 0.2%). The ANT2 end-member was of the same order of magnitude (22.3 ± 4%), but decreased during two periods (May 1995 and October–November 1995) while the ANT1 end-member increased to almost 15%. Outside of these two periods, the ANT1 end-member gave the lowest contribution to the dissolved HCO_3^- input (3.9 ± 4.8%).

Thus, the contributions to the dissolved load of the different end-members varied greatly. Each end-member was significant at different periods of the hydrological cycle and had a characteristic geochemical behaviour.

5.3. Natural and anthropogenic export in the upper Loire watershed

The results of the preceding calculation using the mixing Eq. (6) made it possible to determine natural and anthropogenic exports from the upper Loire watershed. The export rates ω (in t/day) due to rock weathering or anthropogenic additions can be calculated for each end-member (SIL, CAR, ANT1, and ANT2) and for each hydrological period as follows:

$$\omega = \Sigma\left(\alpha[Ca^{2+}] + \alpha[Mg^{2+}] + \alpha[K^+] + \alpha[Na^+] + \alpha[HCO_3^-] + \alpha[Si]\right)^* W \quad (7)$$

where [X] represents the concentration expressed in g/l, W represents the discharge (m^3/s) measured at the sampling points during the considered hydrological period, and α represents the proportion of an end-member for the sample i.

The rock weathering and anthropogenic rates were calculated and the results of ω showed different behaviours according to the hydrological period (Table 3). During high flow, the export rate for each end-member is always greater because of the high daily water discharge. This is the main hydrological period for dissolved export and about 71% of dissolved elements with a silicate origin are exported, 69% with an ANT1 origin, 66% with a carbonate origin, and 58% with an ANT2 origin. On the average, 68% of the total annual dissolved flow is transported during the high flood while this period represented only 40% of the hydrologic year.

The total annual dissolved flow is close to 1300 $\times 10^3$ t/year. In detail, the carbonate weathering rate is 430×10^3 t/year, about 33% of the total annual dissolved flow (Table 3). The daily rate for carbonate weathering is always the highest, except during the high stage 95/96 when ANT1 exportation rate is of the same order because of leaching of the cultivated soils and nutrients mobilization.

The export rate for silicate weathering is 360 $\times 10^3$ t/year, about 28% of the total annual dissolved

Table 3
Dissolved export for each end-member during each hydrological period

	Mean daily discharge (m^3/s)	Total water volume (t/period)	Duration of the period (d)	ANT1 (t/d)	ANT2 (t/d)	SILICATE (t/d)	CARBONATE (t/d)	% of total annual flow
End of high flow 95	301	7.2×10^5	23	1233	157	1285	1908	8
Low flow 95	126	2.1×10^6	217	567	213	483	676	32
High flow 95/96	567	5.5×10^6	124	1997	481	1810	1926	60
Total annual flow (t/year)	–	–	–	401×10^3	110×10^3	360×10^3	430×10^3	
% of the total annual flow	–	–	–	31	8	28	33	

flow. The ratio of carbonate /silicate weathering rates ranges between 1.2 during the high flood and 1.4 during the low stage. As usual, carbonate rock weathering is more productive for the dissolved load than silicate weathering (Meybeck, 1994), which in comparison, exports more dissolved elements during the high stage than carbonate weathering in the same period.

For exported dissolved elements from anthropogenic origins, ANT1 export (close to 401×10^3 t/year) is four times higher than the ANT2 export (close to 110×10^3 t/year) over the hydrological cycle. It represents 31% of the total annual export and it is on the same order with silicate weathering export over the full year. At the Orleans station, about 40% of the total dissolved load have an anthropogenic origin (mainly agricultural) over the hydrological cycle. The ratio of rock weathering/anthropogenic rates is evaluated throughout the sampling period. It ranges from 1.48 during low flow to 1.58 during high flow. Thus, the ratio was around 1.5 implying that the rock weathering processes were the main source of the dissolved load.

The sampling point can be considered as a sub-basin. Therefore, the specific dissolved exportation rates ϖ for silicate and carbonate weatherings (expressed in t $year^{-1}$ km^{-2}) can be calculated from the respective drained areas as follows:

$$\varpi = (\omega)/S, \tag{8}$$

where ω (t/year) is the export rates and S is the drainage area of the sub-basins (km^2).

The export rate for silicate rocks is close to 360×10^3 t/year with a respective specific export rate close to 12 t $year^{-1}$ km^{-2}. The export rate for carbonate rocks is higher than for silicate rocks (430×10^3 t/year) with a specific export rate close to 47 t $year^{-1}$ km^{-2}. This exportation rate is of the same order as the export rate for carbonate terrain in the Seine watershed (42 t $year^{-1}$ km^{-2}; Roy, 1996). The ratio of carbonate/silicate rock export rates is close to 3.9 for the upper Loire watershed. By comparison, this ratio is two times greater in the Seine watershed (Roy, 1996) at close to 7.9.

The total exportation at the sampling point is 1300×10^3 t/year for the dissolved transport. It has been determined to be close to 370×10^3 t/year for the SM transport on the same hydrological cycle (Négrel and Grosbois, 1999) and close to 1200×10^3 t/year for bed sediments at Belleville station, 120 km upstream from the Orleans station (study between 1979 and 1994, Hydratec, 1985; Anonymous, 1993). The dissolved export is a factor of 3.5 higher than the SM export for the upper Loire. This ratio is of the same order of magnitude as for the Seine (Roy, 1996) or the Garonne (Probst and Bazerbachi, 1986), and clearly, lower than for the Rhine (close to 17.8; Meybeck and Ragu, 1996). For the Rhône, which is one of the rivers where particulate transport is preponderant, the ratio is close to 0.6 (Meybeck and Ragu, 1996).

The dissolved export is of the same order as solid export when SM and bed sediments are considered. But bed sediments transport values are often unreliable because of their strong variability both in time and space, and remobilization and storage in the mean stream of the river (Meade 1986, Meade et al., 1990).

6. Conclusions

The seasonal fluctuations of dissolved concentrations compared with those of the discharge reveal different geochemical behaviour patterns. The high flow signature is in agreement with rock weathering and rainwater inputs and the low flow signature can be related to groundwaters and anthropogenic inputs, such as urban sewage and farming waters. The correlation between discharge and the $^{87}Sr/^{86}Sr$ ratio reveals two geochemical signatures. The chemical composition of the Loire water appears to be controlled by rainwater inputs, by silicate and carbonate weathering inputs and by the two kinds of anthropogenic input. Each end-member appears at different periods during the hydrological cycle and has a characteristic geochemical behaviour. The contributions of the different end-members to the dissolved load were calculated with the mass balance approach and vary greatly for each chemical species. The export rates due to rock weathering and anthropogenic additions were also calculated. The ratio of weathering rates/anthropogenic rates ranged between 1.48 and 1.58. Anthropogenic inputs represent 40% of the dissolved load over the full hydrological cycle.

Transport at the Orleans sampling point reached 1300×10^3 t/year for the dissolved transport, a factor of 3.5 higher than the particulate transport (Négrel and Grosbois, 1999). The specific exportation rate for each lithology was generally of the same order of magnitude as for the other watersheds in France. The ratio of carbonate rock/silicate rock export rates is close to 3.9 on the upper Loire watershed.

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Changes in chemical and $^{87}Sr/^{86}Sr$ signature distribution patterns of suspended matter and bed sediments in the upper Loire river basin (France)

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Abstract

The mineralogy of the suspended particulate matter (SPM) transported by the upper Loire river consists mainly of quartz and K-feldspar during periods of high river flow, with an increase in calcite concentration during periods of low flow. Concurrently, large fluctuations are observed in the levels of CaO and Fe_2O_3, the main oxides present in the SPM along with SiO_2. The analysed trace elements also fluctuate significantly. The bed sediments (BS) have a similar oxide content to the SPM, but lower Zn and Pb levels and higher Zr levels. Fluctuations in the chemical-element concentrations with river discharge are related to fluctuation in the mineral assemblages present in the SPM. Thus K, Ti and Rb levels increase with increasing in K-feldspar abundance during high flow, and Ca and Sr levels decrease with increasing discharge due to a decrease in calcite abundance. These mineralogical and chemical variations relate to different sources of sediments under different flow conditions—sources that can be distinguished by Sr isotopic study. The Sr isotopic composition fluctuates according to the rate of river discharge; i.e., the $^{87}Sr/^{86}Sr$ ratio increases with increasing discharge and reaches a maximum with peak flow, and vice versa. The $^{87}Sr/^{86}Sr$ ratio also increases with the combined increase in K-feldspar abundance and decrease in calcite abundance. These similarities suggest the existence of at least two particulate-matter reservoirs, one with detrital silicates and the other with carbonates. Finally, the relationship between the $^{87}Sr/^{86}Sr$ ratios in the suspended and dissolved loads suggests the coexistence of authigenic calcite in the carbonate reservoir. The SPM flow is related to a specific mechanical erosion rate over the whole Loire watershed ranging from 9 to 23 t km^{-2} yr^{-1}. During the survey at Orleans, the SPM flow of the Loire river was $37 \cdot 10^4$ t yr^{-1}, providing an estimate of the specific erosion rate of around 9.8 t km^{-2} yr^{-1}. From the shift in the SPM flux between the sampling point and the mouth of the Loire river and the divergence in the mean annual discharge, a calculation was made of the input of solid matter by the tributaries and by supplementary erosion processes along the river. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Loire river; Suspended matter; Bed load; $^{87}Sr/^{86}Sr$; Authigenic calcite

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1. Introduction

Residual products from chemical and mechanical weathering are carried by rivers and streams to the ocean (Garrels and Mackenzie, 1971; Berner and Berner, 1987; Drever, 1988) as suspended load, typically smaller than a few microns in diameter, and as bed load representing the coarser fraction that moves along the river bottom by a process of saltation. The weathering, transportation and deposition processes are all controlled by environmental factors. Transportation in rivers is usually the inn the form of solid matter (Berner and Berner, 1987), which is also an important transporting vector in the movement of trace metals within the hydrological cycle through adsorption and precipitation processes. The flux of suspended matter reaching the oceans is close 13–18 $\cdot 10^9$ t yr^{-1} (Miliman and Meade, 1983), whereas that of bed sediments is thought to be only about 10% of this value (Meade et al., 1990).

The chemical composition of bed sediments in small catchments has been reported for various lithologies (Albarède and Semhi, 1995; Négrel and Deschamps, 1996). However, a chemical analysis of the sediments alone, without reference to the petrography and sources of solid matter within a catchment area, can lead to an overestimation of natural and/or anthropogenic contributions (Prohic and Juracic, 1989). Consequently, an estimate of the natural level of the sediments' chemical composition is required.

Trace-metal contamination has been intensively studied in small watersheds containing contaminated industrial wasteland (Bird, 1987; Brook and Moore, 1988; Voutsinou-Taliadousi and Varnavas, 1995). Moreover, Sinclair et al. (1989) have shown that the solid load can be more significant in the transport of pollutants than the dissolved load; many pollutants are virtually insoluble and tend to adsorb onto sediment load or organic matter (Hem et al., 1990). Few studies, however, have focused on both the suspended matter and bed sediments within the same river system, and previous investigations of the two show differences in the chemical composition of their solid phases (Stallard, 1988; Gaillardet et al., 1995; Dupré et al., 1996).

The aim of the present work was to study the temporal distribution of chemical species in the suspended matter (SPM) and bed sediments (BS) of the Loire watershed, using the geochemical behaviour of soluble and insoluble elements, as well as of inert or 'reactive' elements, to determine the role of these materials in relation to their capacity to transport pollutant elements. Other objectives were to identify particle sources and weathering mechanisms, to investigate and quantify the natural and anthropogenic elemental concentrations, and to calculate the solid load transport.

2. Location and description of the Loire watershed

The Loire river in central France is 1010 km long and drains an area of 117,800 km^2 characterized by varying topographies (Fig. 1). In the upstream basin, the Loire and Allier rivers flow in a roughly south to north direction, join near Nevers and continue as the Loire up to the city of Orleans, 650 km from the source (Fig. 1). Here the Loire river turns to follow a general east to west direction to the Atlantic ocean. The bedrock composition in the upstream section of the watershed encompasses older plutonic rocks (granite, gneiss and mica schist; 500 to 300 Ma) and a large volcanic area which represent 46% of the total basin surface (BRGM, 1996). In the intermediate part of the watershed, the sedimentary series of the Paris Basin (200 to 6 Ma) drained by the Loire river consist primarily of carbonate deposits.

The Loire river carries one of the principal European riverine inputs to the Atlantic ocean ($26 \cdot 10^9$ m^3 yr^{-1}) with a mean annual discharge of 850 m^3 s^{-1} (Figueres et al., 1985). The solid load output ranges from 10^6 t yr^{-1} (Figueres et al., 1985) to $4.3 \cdot 10^6$ t yr^{-1} (Négrel, 1997), and the suspended load represents 3% of the total suspended sediment load for rivers draining western Europe based on the weighted average of the Seine, Oder, Vistula, Rhine and Garonne (Miliman and Meade, 1983). Near the city of Orleans, large variations in water discharge can be observed between the summer low stage (around 50 m^3 s^{-1}) and that of winter high stage (>1000 m^3 s^{-1}). The Rhône river (Jansen et al., 1979; Meybeck and Ragu, 1996) with a similar drainage area has twice the discharge of water and a

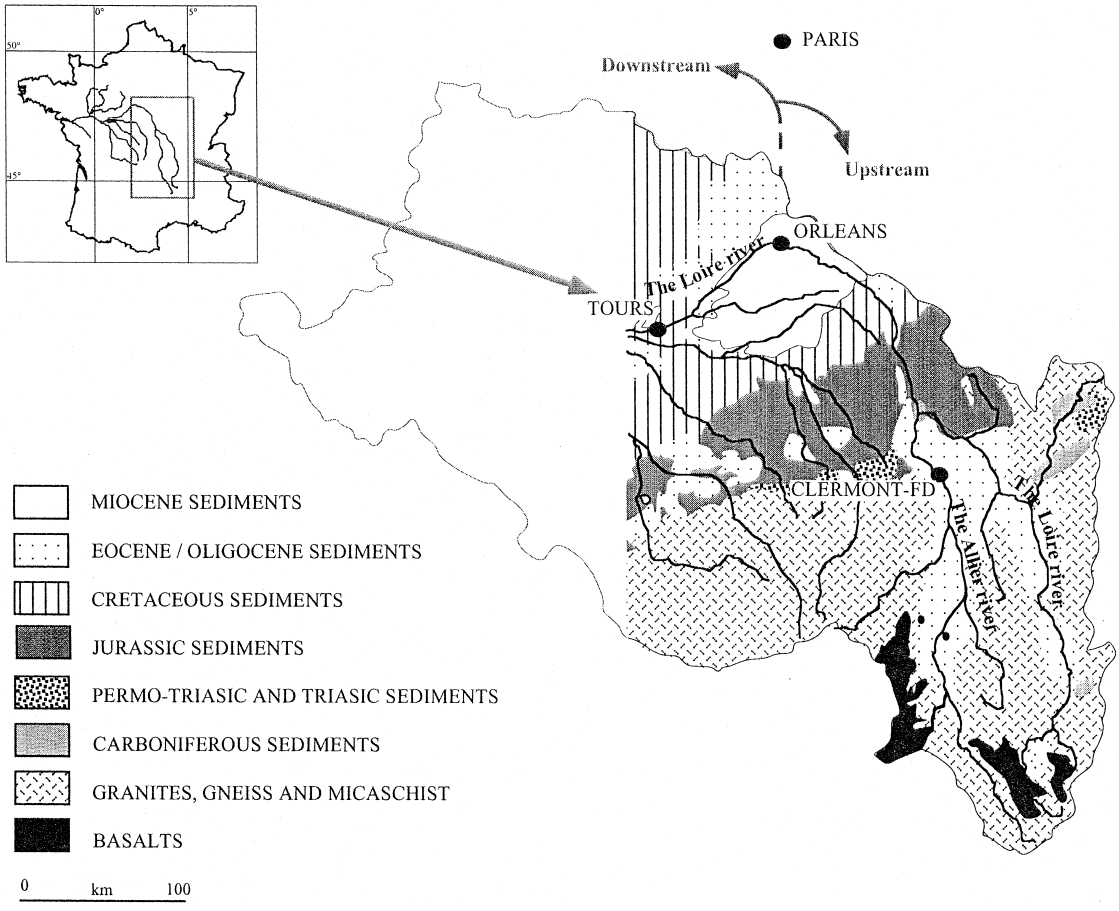

Fig. 1. Simplified geological map of the Loire river basin. The location of the sampling points is in town of Orleans.

much higher suspended sediment discharge ($31 \cdot 10^6$ t yr^{-1}).

3. Sampling and analysis

3.1. SPM and BS sampling

Sampling of the SPM in the Loire river waters was carried out at two locations separated by a distance of about 10 km without any major intermediate tributaries (Fig. 1). The load thus represents the contribution of 34% of the total Loire catchment and corresponds to a drainage area of $40 \cdot 10^3$ km^2, including the entire silicates basement of the Massif Central and about 24% of the sedimentary formations. The sampling strategy was divided into two periods. During the first period, from May 1994 to November 1995, the river was sampled at 'monthly' intervals, after which the sampling frequency was increased to a 'daily' interval (in reality between 2 days and 1 week, depending on the river discharge) from May 1995 to March 1996. Each sample was collected from the centre of the main river channel.

Total SPM masses (in mg l^{-1}) were determined by weight differences between dried filters before and after the filtration of 1 l of water through acetate cellulose membranes (0.22 μm). Two procedures were used for the collection of particulate matter: (1) for the 'monthly' survey, 60 l of Loire water were filtered using an ultrafiltration technique (Pellicon® Cassette System; 0.22 μm PVDF membrane by

Table 1
Major-element (wt.% of dried sediment at 70°C) and trace-element (ppm) concentrations and mineralogical composition of the SPM collected during the 'daily' survey (jlo samples) and 'monthly' survey (L samples); the $^{87}Sr/^{86}Sr$ ratios were determined on the L samples

Sample name	Date	SPM concentration (mg/l)	Discharge (m^3/s)	SiO_2 (wt.%)	K_2O (wt.%)	CaO (wt.%)	TiO_2 (wt.%)	Fe_2O_3 (wt.%)
jlo 1	20/05/95	35.0	433	56.43	2.38	2.86	0.99	7.55
jlo 2	24/05/95	22.6	341	57.51	2.63	2.58	0.95	7.55
jlo 3	28/05/95	20.7	272	59.33	2.40	6.15	0.77	5.65
jlo 4	30/05/95	26.4	197	64.81	2.26	8.89	0.74	5.55
jlo 5	12/06/95	17.8	128	51.00	1.84	> 17	0.64	3.91
jlo 6	23/06/95	22.3	122	55.34	2.09	> 17	0.60	3.05
jlo 7	29/06/95	17.1	101	49.34	2.05	11.19	0.53	4.18
jlo 8	03/07/95	17.5	91	36.59	2.23	> 17	0.68	3.62
jlo 9	20/07/95	45.5	71	34.42	1.88	> 17	0.57	2.69
jlo 10	25/07/95	45.8	56	29.69	1.86	> 17	0.62	3.17
jlo 11	03/08/95	60.9	71	16.00	1.67	> 17	0.77	3.18
jlo 12	11/08/95	25.0	53	18.18	1.60	> 17	0.68	2.75
jlo 13	18/08/95	32.8	55	34.38	1.78	> 17	0.75	3.49
jlo 14	27/08/95	25.3	59	56.53	1.59	> 17	0.56	2.49
jlo 15	05/09/95	56.0	108	31.73	1.51	> 17	0.69	2.92
jlo 16	14/09/95	41.0	121	33.93	1.73	> 17	0.74	3.99
jlo 17	25/09/95	51.5	307	47.18	2.27	16.05	0.90	5.77
jlo 18	02/10/95	27.8	177	49.24	2.31	14.41	0.90	6.07
jlo 19	09/10/95	36.8	239	53.93	2.26	13.37	0.91	5.84
jlo 20	16/10/95	20.8	168	54.94	2.45	11.88	0.93	6.59
jlo 21	23/10/95	20.3	137	47.27	2.21	12.17	0.81	5.96
jlo 22	09/11/95	10.5	96	54.04	1.71	7.33	0.61	2.82
jlo 23	27/11/95	4.8	152	50.57	2.11	8.25	0.73	5.96
jlo 24	03/12/95	40.1	251	56.72	2.29	4.77	1.00	6.99
jlo 25	12/12/95	5.3	174	55.08	2.50	4.20	0.91	7.02
jlo 26	17/12/95	3.3	165	52.55	2.29	4.06	0.86	3.14
jlo 27	03/01/96	57.4	760	51.82	2.43	3.27	1.10	7.11
jlo 28	05/01/96	82.2	935	55.82	2.71	3.22	1.09	7.68
jlo 29	07/01/96	55.4	920	55.60	2.77	3.05	1.17	7.79
jlo 30	09/01/96	65.1	965	55.61	2.62	3.32	1.06	7.57
jlo 31	11/01/96	48.0	935	55.96	2.68	2.90	1.11	7.73
jlo 32	14/01/96	52.9	1040	56.23	2.68	3.08	1.10	7.50
jlo 33	16/01/96	60.4	1050	59.89	2.99	2.84	1.20	7.98
jlo 34	18/01/96	34.4	830	58.28	3.01	3.37	1.25	8.37
jlo 35	21/01/96	25.1	620	54.64	3.02	3.13	1.18	8.46
jlo 36	22/01/96	22.3	560	54.77	2.63	3.44	1.14	8.05
jlo 37	26/01/96	25.1	525	53.99	2.56	2.59	1.15	8.34
jlo 38	29/01/96	26.3	605	53.99	2.74	2.60	1.22	8.00
jlo 39	01/02/96	24.4	500	52.97	2.69	3.28	1.17	7.84
jlo 40	06/02/96	24.0	460	54.56	2.58	2.48	1.11	8.00
jlo 41	12/02/96	31.6	450	52.33	2.47	2.70	1.10	7.37
jlo 42	15/02/96	100.1	860	56.74	2.35	2.96	1.12	6.82
jlo 43	19/02/96	34.0	700	56.11	2.46	2.06	1.11	8.64
jlo 44	22/02/96	58.8	735	56.57	2.39	1.88	1.08	8.49
jlo 45	27/02/96	13.2	510	53.96	2.29	2.57	1.08	8.67
jlo 46	08/03/96	25.9	515	54.22	2.37	2.16	1.08	9.17
jlo 47	18/03/96	11.6	341	53.39	2.47	3.13	0.99	7.32
L1	05/94	16.3	433	58.03	2.43	2.01	0.99	7.70
L2	06/94	18.1	341	58.74	2.42	2.08	1.00	7.64

Table 1 (continued)

Sample name	Date	SPM concentration (mg/l)	Discharge (m^3/s)	SiO_2 (wt.%)	K_2O (wt.%)	CaO (wt.%)	TiO_2 (wt.%)	Fe_2O_3 (wt.%)
L3	07/94	21.3	272	61.58	1.20	> 17	0.73	4.27
L4	08/94	22.5	197	54.94	1.28	15.41	0.57	3.69
L5	09/94	44.7	128	56.89	1.33	> 17	0.56	2.57
L6	10/94	34.3	122	50.07	2.49	8.90	1.03	6.68
L7	11/94	84.2	101	56.27	2.60	2.83	1.14	8.02
L8	12/94	21.3	91	48.25	2.51	7.99	1.05	7.75
L9	01/95	40.1	71	53.42	2.84	3.31	1.09	8.11
L10	02/95	80.5	56	55.43	2.66	2.00	1.12	7.89
L11	03/95	24.9	71	52.62	2.54	3.40	1.03	7.53
L12	04/95	18.7	53	54.66	2.79	7.20	0.92	7.01
L13	05/95	22.2	55	56.80	2.57	3.99	0.94	6.85
L14	06/95	28.0	59	62.04	2.24	3.17	0.79	6.40
L15	07/95	39.8	108	34.17	2.04	> 17	0.69	3.75
L16	08/95	24.7	121	25.00	2.08	> 17	0.62	2.80
L17	09/95	30.2	307	32.73	1.35	> 17	0.58	2.37
L18	11/95	5.1	177	55.09	1.83	10.65	0.66	4.78

Sample name	Date	Zn (ppm)	Pb (ppm)	Rb (ppm)	Sr (ppm)	Zr (ppm)	$^{87}Sr/^{86}Sr$
jlo 1	20/05/95	323	91	187	174	210	n.d.
jlo 2	24/05/95	361	107	179	159	164	n.d.
jlo 3	28/05/95	366	94	131	236	146	n.d.
jlo 4	20/05/95	323	73	110	180	112	n.d.
jlo 5	12/06/95	229	55	70	269	89	n.d.
jlo 6	23/06/95	232	37	71	316	73	n.d.
jlo 7	29/06/95	1141	74	68	169	60	n.d.
jlo 8	03/07/95	341	55	78	344	65	n.d.
jlo 9	20/07/95	261	68	60	382	58	n.d.
jlo 10	25/07/95	300	42	73	375	98	n.d.
jlo 11	03/08/95	229	34	67	477	118	n.d.
jlo 12	11/08/95	218	28	59	421	100	n.d.
jlo 13	18/08/95	281	51	70	397	126	n.d.
jlo 14	27/08/95	308	41	51	312	65	n.d.
jlo 15	05/09/95	196	36	62	461	100	n.d.
jlo 16	14/09/95	263	52	83	397	124	n.d.
jlo 17	25/09/95	279	75	135	329	180	n.d.
jlo 18	02/10/95	340	68	134	306	158	n.d.
jlo 19	09/10/95	365	73	129	281	145	n.d.
jlo 20	16/10/95	387	99	133	252	137	n.d.
jlo 21	23/10/95	400	122	94	186	91	n.d.
jlo 22	09/11/95	222	109	37	57	28	n.d.
jlo 23	27/11/95	369	108	103	201	78	n.d.
jlo 24	03/12/95	409	135	177	222	193	n.d.
jlo 25	12/12/95	439	141	86	99	59	n.d.
jlo 26	17/12/95	252	135	29	37	22	n.d.
jlo 27	03/01/96	334	103	198	198	197	n.d.
jlo 28	05/01/96	326	125	223	218	221	n.d.
jlo 29	07/01/96	311	121	227	241	228	n.d.
jlo 30	09/01/96	284	102	216	209	218	n.d.
jlo 31	11/01/96	475	115	222	199	207	n.d.
jlo 32	14/01/96	450	114	218	204	217	n.d.

Table 1 (continued)

Sample name	Date	Zn (ppm)	Pb (ppm)	Rb (ppm)	Sr (ppm)	Zr (ppm)	$^{87}Sr/^{86}Sr$
jlo 33	16/01/96	390	100	225	222	211	n.d.
jlo 34	18/01/96	338	109	225	248	197	n.d.
jlo 35	21/01/96	357	117	202	227	167	n.d.
jlo 36	22/01/96	354	101	203	228	171	n.d.
jlo 37	26/01/96	339	101	217	216	182	n.d.
jlo 38	29/01/96	260	88	211	273	188	n.d.
jlo 39	01/02/96	275	99	188	242	172	n.d.
jlo 40	06/02/96	299	102	210	206	173	n.d.
jlo 41	12/02/96	304	115	207	195	189	n.d.
jlo 42	15/02/96	222	90	191	188	227	n.d.
jlo 43	19/02/96	348	114	257	199	220	n.d.
jlo 44	22/02/96	306	104	250	184	221	n.d.
jlo 45	27/02/96	318	175	220	198	193	n.d.
jlo 46	08/03/96	403	128	218	214	177	n.d.
jlo 47	18/03/96	323	128	102	104	75	n.d.
L1	05/94	343	90	154	153	131	0.712298
L2	06/94	370	95	155	151	127	0.715295
L3	07/94	203	44	89	307	121	0.712316
L4	08/94	321	47	74	259	76	0.711784
L5	09/94	294	54	53	326	55	0.711603
L6	10/94	424	135	164	327	187	0.712813
L7	11/94	275	61	203	220	210	0.713835
L8	12/94	752	200	153	224	194	0.713066
L9	01/95	334	95	231	194	174	0.716257
L10	02/95	248	82	237	180	194	0.716691
L11	03/95	287	79	208	202	173	0.714055
L12	04/95	257	86	144	226	135	0.711929
L13	05/95	512	169	187	222	197	0.714964
L14	06/95	1669	97	134	131	110	0.714086
L15	07/95	421	181	87	338	111	0.712228
L16	08/95	186	29	69	416	86	0.712029
L17	09/95	271	38	46	377	74	0.711505
L18	11/95	499	159	56	109	42	0.711256

Sample name	Date	Quartz (%)	K-feldspar (%)	Plagioclases (%)	Illite (%)	Kaolinite (%)	Calcite (%)
jlo 1	20/05/95	35	19	19	5	10	12
jlo 2	24/05/95	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
jlo 3	28/05/95	27	17	15	12	13	16
jlo 4	20/05/95	18	9	11	7	8	47
jlo 5	12/06/95	6	3	4	4	3	80
jlo 6	23/06/95	8	16	6	3	3	64
jlo 7	29/06/95	13	14	7	6	5	55
jlo 8	03/07/95	8	6	4	3	4	75
jlo 9	20/07/95	4	6	2	4	4	80
jlo 10	25/07/95	6	4	21	2	3	64
jlo 11	03/08/95	8	6	3	2	3	78
jlo 12	11/08/95	8	4	3	3	3	79
jlo 13	18/08/95	13	12	12	11	–	52
jlo 14	27/08/95	–	18	15	–	–	67
jlo 15	05/09/95	6	8	4	6	–	76

Table 1 (continued)

Sample name	Date	Quartz (%)	K-feldspar (%)	Plagioclases (%)	Illite (%)	Kaolinite (%)	Calcite (%)
jlo 16	14/09/95	5	11	9	4	4	67
jlo 17	25/09/95	13	11	13	9	7	47
jlo 18	02/10/95	10	15	14	8	8	45
jlo 19	09/10/95	13	13	12	8	8	46
jlo 20	16/10/95	13	13	13	13	11	37
jlo 21	23/10/95	12	14	15	10	7	42
jlo 22	09/11/95	13	23	30	9	8	17
jlo 23	27/11/95	20	20	15	5	8	32
jlo 24	03/12/95	13	20	33	11	9	14
jlo 25	12/12/95	19	20	15	18	18	10
jlo 26	17/12/95	17	17	18	19	15	15
jlo 27	03/01/96	15	26	27	13	13	6
jlo 28	05/01/96	21	33	19	13	14	–
jlo 29	07/01/96	15	22	26	17	20	–
jlo 30	09/01/96	22	22	17	16	16	7
jlo 31	11/01/96	28	25	14	14	13	6
jlo 32	14/01/96	24	24	18	15	11	8
jlo 33	16/01/96	25	24	25	9	11	6
jlo 34	18/01/96	22	24	21	13	13	7
jlo 35	21/01/96	20	21	20	16	17	6
jlo 36	22/01/96	28	19	19	13	14	7
jlo 37	26/01/96	20	24	22	12	14	8
jlo 38	29/01/96	14	20	23	20	16	7
jlo 39	01/02/96	17	17	31	17	12	6
jlo 40	06/02/96	24	18	18	12	19	9
jlo 41	12/02/96	25	20	16	18	13	8
jlo 42	15/02/96	28	22	21	11	12	6
jlo 43	19/02/96	24	21	21	13	14	7
jlo 44	22/02/96	33	19	18	8	15	7
jlo 45	27/02/96	27	23	21	12	10	7
jlo 46	08/03/96	19	30	23	13	15	–
jlo 47	18/03/96	18	27	25	10	13	7
L1	05/94	30	–	20	10	10	30
L2	06/94	40	20	–	20	15	5
L3	07/94	10	10	–	10	10	60
L4	08/94	10	15	–	10	5	60
L5	09/94	5	5	10	–	–	80
L6	10/94	20	15	5	5	5	50
L7	11/94	10	27	–	26	10	27
L8	12/94	25	20	–	5	10	40
L9	01/95	30	30	10	10	10	10
L10	02/95	32	32	11	10	10	5
L11	03/95	20	30	–	20	20	10
L12	04/95	20	30	–	20	10	20
L13	05/95	25	40	–	25	10	–
L14	06/95	25	25	–	25	25	–
L15	07/95	5	–	5	5	5	80
L16	08/95	10	–	10	5	5	70
L17	09/95	5	5	10	–	–	80
L18	11/95	5	20	5	–	–	70

n.d. = non-determined value. For the mineralogical composition of the SPM, semi-quantitative percents were obtained for each mineral by calculating the ratio of the height of its most intense peak against the sum of all the most intense mineral peaks.

Millipore). The SPM samples obtained in this way are referred to in the results section as L x, where x represents the different samples; (2) for the 'daily' survey, 60 to 90 l of Loire water were collected in precleaned polypropylene containers and left to settle over several days. The efficiency of this separation, tested through replicate filtrations of 1 l samples of water after settling, showed that between 0.5 and 3 mg l^{-1} of the SPM were lost by this procedure, with between 800 and 3500 mg l^{-1} being collected. The SPM samples obtained in this way are referred to in the results as jlo x, where x represents the different samples.

With both procedures, the SPM samples were oven-dried at 70°C, powdered and dry-sieved through a 165 μm nylon mesh to extract fresh coarse organic matter (wood, etc.) prior to analysis.

Recent BS samples were collected with plastic spatulas at the river bank and stored in polypropylene containers to avoid contamination. The samples were oven-dried at 70°C, homogenized, quartered and dry-sieved through a 165 μm nylon mesh, without the use of a dispersion agent so as to avoid contamination and modification of the samples. A similar analysis of BS from the Allier River was performed on 17 samples taken over a 15-month study period (May 1994 to August 1995) near Clermont-Ferrand (Négrel et al., 1997).

3.2. Major- and trace-element determination and isotopic measurements

The analytical procedures and analysis methods are described in detail by Négrel and Deschamps (1996) and Négrel (1997). All sediment samples were analysed for major and trace elements by X-ray fluorescence energy dispersive spectrometry (XRF) using a Syrano 2/501. Two certified reference materials (GBW 07311; GBW 07306) were run to verify the calibration. Analytical accuracy was monitored by the repeated analysis of an in-house standard of similar mass and physical conditions as the experimental samples—precision was between 2 and 10%.

The $^{87}Sr/^{86}Sr$ ratios were measured on the SPM samples collected during the monthly survey. Following standard acid-dissolution procedures of the SPM samples, Sr isotopic ratios were determined using a Finnigan MAT 262 mass spectrometer after chemical separation using a cation exchange column (Dowex AG50X8; 2 N HCl as the eluant). The total blank for Sr was less than 1 ng for the entire chemical procedure. The $^{87}Sr/^{86}Sr$ ratios obtained were normalized to an $^{88}Sr/^{86}Sr$ of 0.1194. The reproducibility of the $^{87}Sr/^{86}Sr$ ratio measurements were tested by duplicate analysis of the NBS 987 standard, with a mean value close to $0.710227 \pm 17 \cdot 10^{-6}$ (2σ; $n = 70$).

3.3. Mineral phases and clay determination

Each bulk SPM sample was homogenized by hand-crushing with an agate mortar, following which 5 mg of crushed powder were mixed with 3 ml of distilled water and placed on glass slides. Thereafter, the suspensions were dried in air for 3 h. The mineralogical composition of the SPM sample was determined by X-ray diffraction using a Rigaku analyser, Cu-K_α ray with a Ni-K_β filter. Qualitative mineralogical analyses were carried out by identifying diffraction spectra (Brown, 1961). Semi-quantitative percents were obtained for each mineral by calculating the ratio of the height of its most intense peak against the sum of all the most intense mineral peaks (Hotzapssel, 1985).

4. Results and discussion

4.1. Variations in SPM concentrations

The relationship between SPM and discharge for large or moderate drainage basins usually follows clockwise loops (hysteresis curves) (Wood, 1977; Meade, 1985; Probst and Bazerbachi, 1986; Olivry et al., 1988; Sinclair et al., 1989; Zhang, 1990). However, the SPM concentrations of the Loire river collected over the two study periods varied widely from 3.3–5 mg l^{-1} to 80–100 mg l^{-1} (Table 1 and Fig. 2) and show neither a linear relationship (correlation coefficient = 0.40) nor a cyclical relationship with river flow; only a weak correlation of increasing SPM concentration with increasing river discharge could be identified.

This lack of relationship between SPM and discharge can be explained by the large human occupation in the Loire watershed and the exploitation of

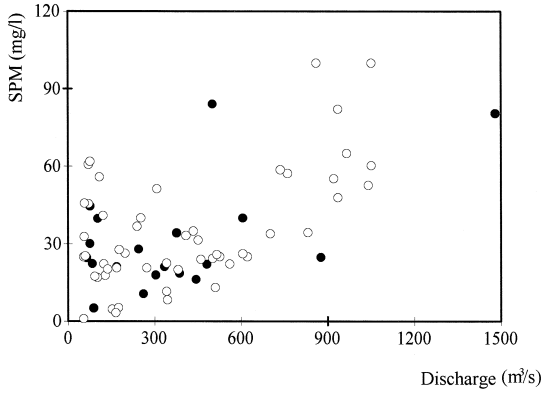

Fig. 2. Evolution of SPM concentration with discharge for the daily (open circles) and monthly (filled circles) samples; analytical errors are represented by the size of the circles.

the river. Multiple developments (dredging for gravel extraction, etc.) have led to significant changes to the channel morphology and are responsible for a constant degradation of the river banks, resulting in both storage and transport of fine particles irrespective of the discharge level of the river. Furthermore, one of the most pervasive influences on the SPM load is due to the large number of dams and reservoirs that have been built on the rivers of the Loire watershed (e.g., six major dams along the Loire and Allier rivers; 30 hydroelectric reservoirs over the entire catchment area). These man-made structures interrupt the down-river flow of sediments, with much of the solid load being trapped in the reservoirs (Meade et al., 1990). The existence of dams along the Loire river implies that, whereas the suspended particles originate from the natural erosion of the watershed, the suspended load could be controlled by non-natural processes.

4.2. Mineralogical composition

A semi-quantitative XRD analysis of the SPM shows that quartz (5–40%), K-feldspar and plagioclase (0–40%) and calcite (0–80%) represent the main mineral phases (Table 1). The quartz and K-feldspar contents increase with increasing discharge and are the dominant minerals present during high flow; during low flow, their contents fall to 5–10% (Fig. 3). By contrast, the calcite concentration varies significantly from 0% during high river flow to 80% during periods of low flow (Fig. 3). Both illite and kaolinite are dominant clay minerals (0–25%), but only the illite content seems to fluctuate with river discharge. Similar mineralogical associations were found by Manickam et al. (1985) in the SPM of the Loire river just upstream of the estuary.

In the Allier and Loire rivers, the main gravel and sand components of the BS are of granitic–gneissic and basaltic origin from the Massif Central; carbonates from the Limagne d'Allier can also be a source of material. Quartz, feldspar, calcite, biotite and clays are the main phases, and augite, hornblende, olivine, and zircon are the main heavy accessory minerals (Brossé, 1979; Macaire, 1985; Kroonenberg et al., 1988; Roger, 1988).

4.3. Chemical composition: main feature and variations with the Loire river flow

The chemical data for the Loire river SPM and BS are summarized in Table 1 (SPM) and Table 2 (BS). Major-element compositions are expressed in terms of weight percentage (wt.%) and trace-element abundances in parts per million (ppm).

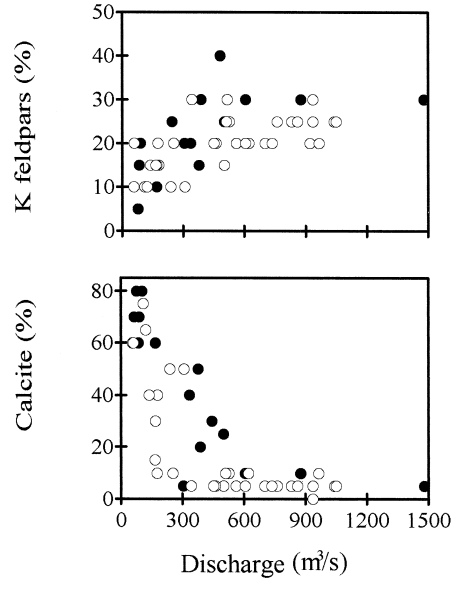

Fig. 3. Evolution of calcite and K-feldspar abundances with river discharge. (Symbols identical to those in Fig. 2.)

Table 2
Major-element (wt.% of dried sediment at 70°C) and trace-element (ppm) concentrations of bed sediments collected from the Loire and Allier rivers

Sample name	Date	SiO_2 (%)	K_2O (%)	CaO (%)	TiO_2 (%)	Fe_2O_3 (%)
Loire bed sediments						
BSL1	03/94	61.79	2.63	4.34	1.07	5.94
BSL2	04/94	57.62	1.86	10.61	0.92	5.64
BSL3	05/94	64.68	2.76	3.79	0.90	4.98
BSL4	08/94	60.01	1.67	16.47	0.72	3.68
BSL5	09/94	59.17	2.05	11.52	0.98	4.89
BSL6	10/94	51.91	2.10	13.59	0.94	4.96
BSL7	11/94	53.41	2.40	10.22	0.99	5.70
BSL8	12/94	61.68	2.49	4.01	0.78	3.01
BSL9	01/95	63.38	2.80	4.54	1.00	4.94
BSL10	03/95	64.76	2.57	3.94	0.88	4.08
BSL11	03/95	63.94	2.69	3.70	0.74	3.66
BSL12	03/95	64.35	2.63	3.82	0.81	3.87
BSL13	05/95	58.57	2.61	4.21	0.93	5.23
BSL14	06/95	58.82	2.50	4.43	0.98	6.94
BSL15	06/95	59.43	2.58	4.79	1.02	6.94
BSL16	07/95	49.25	2.24	15.06	0.92	4.47
BSL17	08/95	60.68	2.59	7.95	0.63	3.11
Allier bed sediments						
BSA1	03/94	55.60	2.73	1.95	1.06	5.64
BSA2	04/94	56.93	2.97	1.71	0.94	5.32
BSA3	05/94	57.03	2.33	2.78	1.05	5.37
BSA4	06/94	56.26	2.38	2.84	1.03	5.61
BSA5	08/94	52.50	1.94	2.91	1.26	7.12
BSA6	09/94	48.86	2.10	2.74	1.28	8.24
BSA7	10/94	61.43	2.39	2.43	0.80	4.29
BSA8	10/94	61.10	2.49	2.35	0.77	4.22
BSA9	11/94	54.32	2.82	2.72	1.25	7.38
BSA10	11/94	54.30	2.70	3.18	1.35	7.16
BSA11	12/94	56.53	2.46	2.46	1.01	4.96
BSA12	01/95	51.17	2.70	2.05	1.16	6.79
BSA13	05/95	59.08	2.55	2.35	1.15	6.20
BSA14	05/95	60.97	2.68	1.86	0.97	5.48
BSA15	05/95	57.86	2.77	2.05	1.20	7.01
BSA16	08/95	59.53	2.37	1.98	1.09	6.52
BSA17	08/95	60.16	3.05	0.94	0.91	5.69

Sample name	Date	Zn (ppm)	Pb (ppm)	Rb (ppm)	Sr (ppm)	Zr (ppm)	Sn (ppm)	Ba (ppm)
Loire bed sediments								
BSL1	03/94	196	76	188	243	312	16	805
BSL2	04/94	191	52	147	261	269	17	556
BSL3	05/94	140	61	181	245	338	15	817
BSL4	08/94	118	43	136	326	278	21	739
BSL5	09/94	102	53	143	289	418	22	765
BSL6	10/94	188	61	155	333	284	22	682
BSL7	11/94	220	48	162	310	280	22	448
BSL8	12/94	86	60	152	256	334	9	823
BSL9	01/95	133	67	180	260	313	9	804

Table 2 (continued)

Sample name	Date	Zn (ppm)	Pb (ppm)	Rb (ppm)	Sr (ppm)	Zr (ppm)	Sn (ppm)	Ba (ppm)
Loire bed sediments								
BSL10	03/95	80	74	157	243	414	15	786
BSL11	03/95	116	62	168	257	292	12	849
BSL12	03/95	98	68	163	250	353	14	818
BSL13	05/95	186	81	185	226	363	16	739
BSL14	06/95	307	104	192	198	263	27	621
BSL15	06/95	327	107	190	203	250	25	611
BSL16	07/95	143	76	142	285	536	48	673
BSL17	08/95	96	77	154	268	345	54	745
Allier bed sediments								
BSA1	03/94	112	55	191	251	233	19	804
BSA2	04/94	114	68	185	245	226	20	771
BSA3	05/94	106	48	145	286	445	10	831
BSA4	06/94	102	45	161	308	461	13	788
BSA5	08/94	181	37	150	324	477	20	628
BSA6	09/94	262	57	175	330	314	20	600
BSA7	10/94	70	41	153	305	220	6	844
BSA8	10/94	72	46	145	298	145	7	825
BSA9	11/94	126	56	185	291	362	13	835
BSA10	11/94	146	51	176	315	413	12	850
BSA11	12/94	82	48	157	303	252	11	826
BSA12	01/95	138	69	196	251	393	17	793
BSA13	05/95	123	81	156	271	437	13	832
BSA14	05/95	106	73	151	275	337	17	915
BSA15	05/95	152	76	195	293	547	17	705
BSA16	08/95	125	66	127	269	> 900	38	741
BSA17	08/95	115	100	181	194	647	70	1042

The order of abundance in the SPM was similar during the two hydrological cycles ($SiO_2 > CaO > Fe_2O_3 > K_2O > TiO_2$). The larger fluctuations are observed for Fe_2O_3 (34%) and CaO (a factor of 10); all the trace-element concentrations fluctuate significantly. The mean values agree with those published by Manickam et al. (1985). Binary correlations, illustrated by the correlation coefficients *R* (Table 3a; bold *R* are statistically significant), show good relationships between chemical elements usually associated with silicates (Ti, K, Zr, Rb). Iron, partitioned between minerals and clays (Price and Calvert, 1973), shows good *R* coefficients with these elements. CaO and Sr associated within silicate and calcareous phases show good correlation with each other and a strongly negative correlation with Ti, K, Zr and Rb. The trace elements, apart from a few exceptions, do not correlate with each other. Similar relationships have been measured in other main French rivers (Meuse, Rhine, Rhône, Garonne; Martin and Meybeck, 1978; Probst and Bazerbachi, 1986; Nolting et al., 1989).

The BS (Table 2) show similar orders of major-oxide abundance and variations as the SPM, although Fe_2O_3 and CaO are less concentrated. Similarly, Zn and Pb are less concentrated than in the SPM whereas Zr concentration is higher and Sr, Rb are similar.

The CaO content in the Allier BS is 30% lower than in the Loire BS, although the levels of other major oxides and trace elements are similar for both rivers. The chemical composition of the Allier terraces (Kroonenberg et al., 1988) is in agreement with our measurements, apart from the lower Fe_2O_3, Zn, Pb, Rb and Zr values. The changes in inter-element correlations in the BS (Table 3b and c) can be

Table 3
Pearson correlation coefficients obtained between the nine elements measured for the Loire SPM over the two periods studied (a), and obtained for the 13 elements measured in the BS of the Loire river (b) and Allier river (c)

(a) Loire SPM $n = 67$	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	Zn	Pb	Rb	Sr	Zr
K_2O	0.41	1.00								
CaO	**−0.65**	**−0.79**	1.00							
TiO_2	−0.30	**−0.81**	**−0.77**	1.00						
Fe_2O_3	**0.63**	**0.82**	**−0.90**	**0.83**	1.00					
Zn	0.21	0.07	−0.16	−0.12	0.11	1.00				
Pb	0.41	0.51	**−0.59**	−0.41	0.59	0.29	1.00			
Rb	0.52	0.77	**−0.81**	**0.85**	**0.91**	−0.01	0.42	1.00		
Sr	**−0.76**	−0.49	**0.77**	−0.33	**−0.62**	−0.33	**−0.62**	−0.39	1.00	
Zr	0.36	**0.64**	**−0.63**	**0.81**	**0.76**	−0.09	0.32	**0.92**	−0.15	1.00

(b) Loire BS $n = 17$	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	Zn	Pb	Rb	Sr	Zr	Sn	Ba	La	Ce
K_2O	0.51	1												
CaO	**−0.73**	**−0.87**	1											
TiO_2	−0.27	0.10	−0.09	1										
Fe_2O_3	−0.27	0.04	−0.10	**0.84**	1									
Zn	**−0.36**	0.03	−0.07	0.61	0.91	1								
Pb	0.04	**0.49**	−0.47	0.29	0.50	0.60	1							
Rb	0.32	**0.73**	−0.74	0.49	0.62	0.60	0.68	1						
Sr	−0.47	−0.63	**0.80**	−0.23	−0.41	−0.40	**−0.79**	**−0.75**	1					
Zr	−0.20	0.03	0.19	−0.06	−0.37	−0.51	−0.03	−0.39	0.11	1				
Sn	−0.52	−0.17	0.46	−0.24	−0.06	0.09	0.28	−0.27	0.15	0.37	1			
Ba	0.68	0.39	−0.41	−0.37	−0.58	−0.66	−0.06	0.05	−0.14	0.28	−0.31	1		
La	0.10	0.09	0.04	−0.43	−0.60	−0.63	0.09	−0.41	−0.02	**0.84**	0.41	0.51	1	
Ce	0.05	−0.01	0.16	−0.48	−0.60	−0.63	0.05	**−0.48**	0.07	**0.82**	0.52	0.45	**0.98**	1

(c) Allier BS $n = 17$	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	Zn	Pb	Rb	Sr	Zr	Sn	Ba	La	Ce
SiO_2	1													
K_2O	0.31	1												
CaO	**−0.45**	−0.64	1											
TiO_2	**−0.75**	−0.20	0.49	1										
Fe_2O_3	**−0.75**	−0.15	0.29	**0.92**	1									
Zn	**−0.76**	−0.36	0.25	**0.75**	**0.88**	1								
Pb	**0.25**	0.66	**−0.79**	−0.03	0.14	0.07	1							
Rb	−0.45	0.60	−0.24	0.32	0.37	0.28	0.35	1						
Sr	**−0.34**	**−0.74**	0.89	0.36	0.24	0.31	**−0.77**	−0.31	1					
Zr	0.08	0.03	−0.21	0.30	0.39	0.20	0.42	−0.22	−0.25	1				
Sn	0.14	0.35	−0.71	0.08	0.14	0.14	0.69	0.11	**−0.70**	0.63	1			
Ba	0.61	0.65	−0.49	−0.50	−0.52	−0.66	0.45	0.02	−0.63	0	0.36	1		
La	0.33	0.05	−0.45	−0.04	0.09	−0.01	0.47	−0.37	−0.43	**0.90**	**0.75**	0.20	1	
Ce	0.34	0.05	−0.46	−0.05	0.09	−0.02	0.47	−0.37	−0.43	**0.90**	**0.76**	0.20	1	1

R coefficients in bold are statistically representative (SPM: $R > 0.5$, $n = 67$; BS: $R > 0.7$, $n = 17$).

explained by the fact that the Loire drains mainly carbonates between the Allier and the sampling points near Orleans.

Although the above results appear to show no linear trend between the SPM concentration and water discharge (Fig. 2), relationships do exist be-

tween the chemical species in the SPM. Plotted against the hydrological regime of the river, the chemical elements can be classified into three groups.

In the first group, K_2O, TiO_2, Fe_2O_3, Si, Zr and Rb concentration levels increase with increasing discharge, showing a logarithmic trend (Fig. 4). In the second group, CaO levels decrease sharply with increasing discharge up to around 300 m^3 s^{-1}, although with a significant scattering of the data (especially for Sr); thereafter, the fluctuations remain low

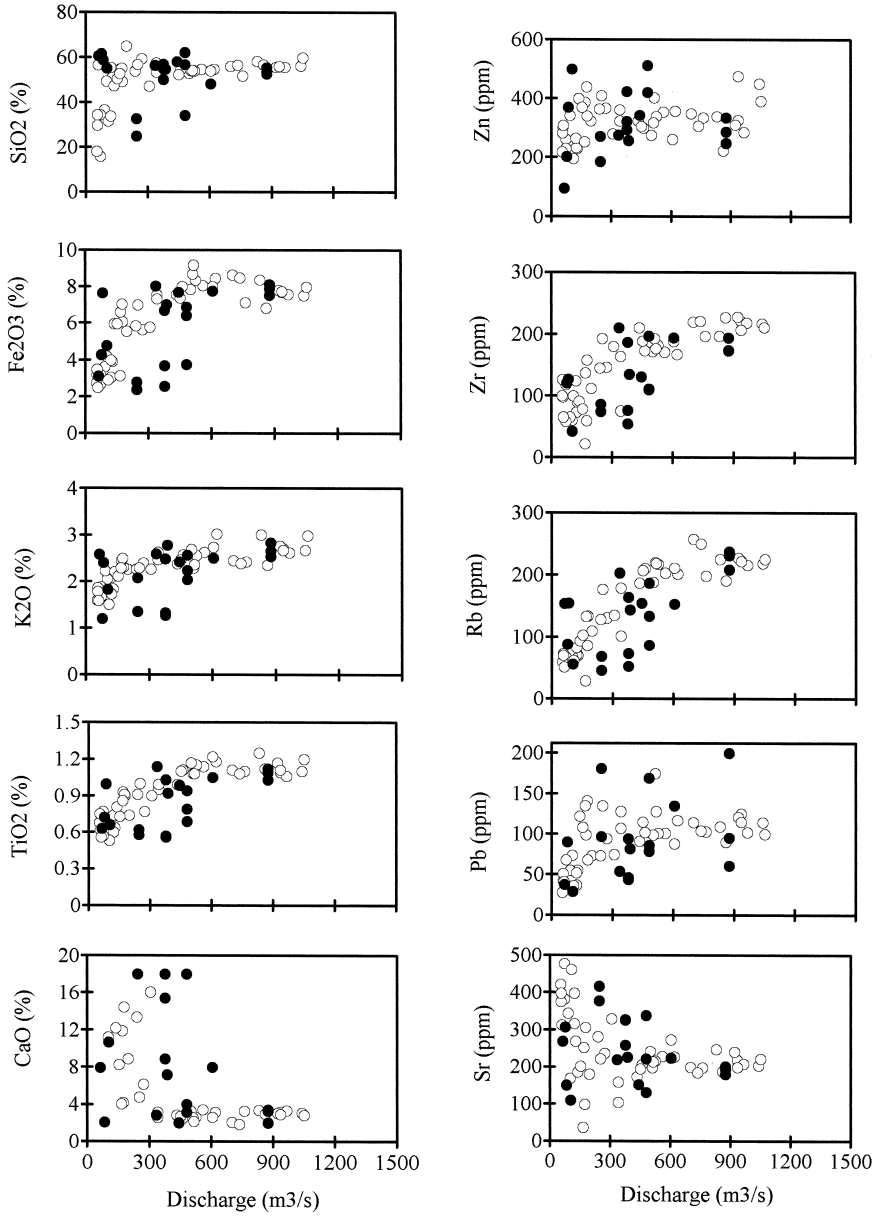

Fig. 4. Evolution of major- and trace-element concentrations with discharge. (Symbols identical to those in Fig. 2.)

up to the maximum discharge. In the last group, Pb and Zn fluctuations cannot be easily related to the discharge.

Because the SPM consists of a wide range of mineralogical phases, the concentrations of chemical species can be related to fluctuations in the mineralogical assemblages. The logarithmic tendencies can be explained either by the presence of at least two mineral-bearing phases, one with high and the other with low elemental concentrations, or by fluctuations in the abundance of the mineral phase that contains most of the element. K-feldspar and illite are the main carriers of both K and Rb, and can also contain significant amounts of Ti, Fe and Zr (Clauer et al., 1993). These minerals are more abundant in the SPM during high flood (Fig. 3). Thus, elevated levels of K, Rb and Ti during high flow and their decrease with attenuating discharge can be related to the abundance of illite and K-feldspar. The levels of silica, Fe and Zr can also be explained in this way.

The decrease in Ca and Sr with increasing discharge can be related to the change in the abundance of the Ca–Sr-bearing phase, for which the two main carriers are calcite and plagioclase. Plagioclase alone does not fluctuate noticeably with the level of river discharge (see Section 4.2), unlike the calcite abundance which reaches a maximum during low flow (Fig. 3). Thus, it appears that the fluctuation of Ca–Sr concentrations in the SPM must be related to the abundance of calcite (correlation coefficient between percent calcite and [Sr] is 0.71).

As Pb and Zn in the SPM cannot be related to fluctuations of a specific mineral, their variations in concentration at similar rates as those in river discharge may be due to an adsorption of dissolved Pb and Zn onto particles.

The large increase in calcite abundance at the sampling stations, and the associated fluctuations in chemical-element concentrations, can be related to different chemical and mineral sources that can be determined under different flow conditions through an isotopic tracing of the SPM.

4.4. Isotope systematics: presence of authigenic calcite in the SPM of the Loire river

The Sr isotopic composition ($^{87}Sr/^{86}Sr$) of the SPM shows large fluctuations of more than $5 \cdot 10^{-3}$, which is higher than the analytical errors for the procedure ($2 \cdot 10^{-5}$). The $^{87}Sr/^{86}Sr$ ratio varies from 0.71126–0.71193 to 0.71626–0.71669; it correlates neither with the SPM concentration nor with pH of the water, but nevertheless follows the river discharge fluctuations (Fig. 5). The $^{87}Sr/^{86}Sr$ ratio increases and decreases rapidly with increasing and decreasing river discharge and reaches a maximum at peak flow and a minimum at low flow. The link between $^{87}Sr/^{86}Sr$ and discharge implies the existence of at least two main reservoirs of particles that control the isotopic signature of the SPM. Such a link has already been shown by Négrel and Dupré (1995) in SPM carried by the Oubangui river in Central Africa, and might also exist for other rivers; however, as few studies have attempted to examine the temporal variation in SPM isotopic signatures, this phenomenon is not yet well known.

Considering the mineralogical phases present in the SPM of the Loire river, the lower $^{87}Sr/^{86}Sr$ ratio may correspond to plagioclase and calcite, while the higher $^{87}Sr/^{86}Sr$ ratio may be related to K-feldspar and clay minerals. Because K-feldspar and calcite are the most variable mineral phases present in relation to the river discharge, it is not unlikely that the fluctuations in the $^{87}Sr/^{86}Sr$ ratio of the SPM are related mostly to changes in the abundance of these two phases. Thus an increase of the $^{87}Sr/^{86}Sr$ ratio with increasing K-feldspar abundance and, conversely, a decrease in the $^{87}Sr/^{86}Sr$ ratio with increasing calcite abundance (see Fig. 6). Furthermore, the relationship between $^{87}Sr/^{86}Sr$ and Rb/Sr ratios (not shown) yields a regression line fitted by the relation $^{87}Sr/^{86}Sr = 0.71083 + 0.0036\ Rb/Sr$, with a correlation coefficient of $R = 0.84$. Compared to

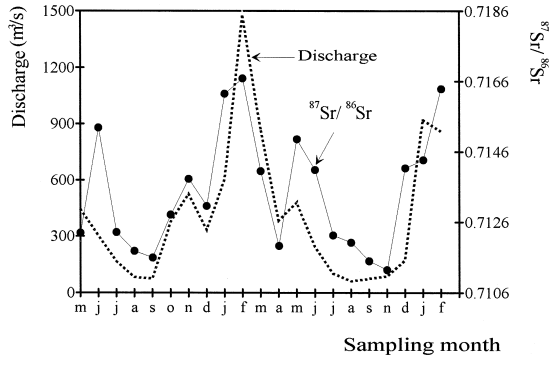

Fig. 5. Fluctuations in $^{87}Sr/^{86}Sr$ and discharge of the Loire river as a function of month of the year.

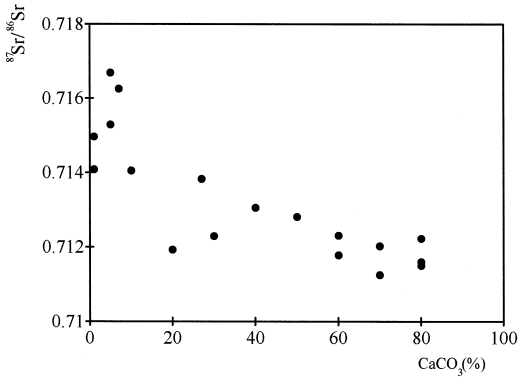

Fig. 6. Relationship between $^{87}Sr/^{86}Sr$ ratio and calcite abundance in the suspended particulate matter of the Loire river.

Sr, Rb is weakly incorporated into calcite, such that the Rb/Sr ratio of calcite is low, and is abundant in K-feldspar where high Rb/Sr ratios are observed (Faure, 1986). Because the $^{87}Sr/^{86}Sr$ ratio fluctuates accordingly to the inverse fluctuation of calcite and K-feldspar with river discharge, the relationship between the $^{87}Sr/^{86}Sr$ and Rb/Sr ratios clearly indicates binary mixing between the calcite and K-feldspar end-members.

The $^{87}Sr/^{86}Sr$ ratio of 0.71083 could be close to the ratio of the calcite reservoir, which may originate from the mechanical erosion of Jurassic to Oligocene deposits in the 'Limagne' (Allier and Loire rivers, before their confluence) and/or from the Jurassic to Cretaceous deposits located between the 'Limagne' and the sampling points. As calcite contains strontium whose $^{87}Sr/^{86}Sr$ ratio is identical to that of the sea water from which the calcite precipitated (Faure, 1986), the sea-water $^{87}Sr/^{86}Sr$ ratio is an indirect indicator of the isotopic signature of the detrital calcite in the SPM. Several investigators have reported systematic variations in the $^{87}Sr/^{86}Sr$ ratios of calcium carbonates and barites from the Jurassic to the Neogene (Clauer, 1981; Elderfield, 1986; Hess et al., 1986; Paytan et al., 1993; Jones et al., 1994) ranging from 0.7069 to 0.7088, but always lower than 0.71083. This implies that the Sr isotopic signature for calcite in the SPM (see Fig. 6) is not only from a detrital source because it includes a component with a $^{87}Sr/^{86}Sr$ ratio greater than 0.71083. Our hypothesis is that the relatively high calcite isotopic signature in the Loire SPM reflects a coexistence of the detrital calcite reservoir with authigenic calcite having a $^{87}Sr/^{86}Sr$ ratio close to that of the dissolved load. This is supported (a) by the possible occurrence of calcite precipitation in the lower Loire at the end of the fluviatile zone, as suggested by Manickam et al. (1985), and (b) by the calculation of the calcite saturation index for waters of the Loire river (Grosbois et al., in preparation).

Fig. 7 illustrates the relationship between the $^{87}Sr/^{86}Sr$ ratio in the SPM of the upper Loire river (this study) and that of the dissolved load (DL) (Grosbois et al., in preparation). The two ratios are well correlated ($R = 0.66$). The lower ratios in the SPM are close to the lower ratios in the DL, with points for both plots lying close to the 1:1 line. Thereafter, the $^{87}Sr/^{86}Sr$ ratios in the SPM increase significantly, whereas the $^{87}Sr/^{86}Sr$ ratios in DL fluctuate only slightly. Similarities between the $^{87}Sr/^{86}Sr$ ratios near the 1:1 line confirm the existence of authigenic calcite in the SPM and imply the considerable abundance of this phase primarily during low river flow. The increase in $^{87}Sr/^{86}Sr$ ratios in the SPM is linked to the corresponding increase in K-feldspar abundance.

4.5. Estimation of solid matter flow

Solid matter flow by suspension reflects the amount of SPM within a hydrological cycle. For this study, the flux Φ, calculated according to Eq. (1)

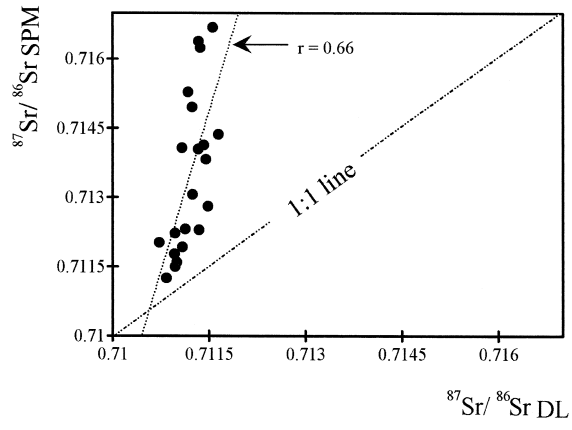

Fig. 7. Relationship between $^{87}Sr/^{86}Sr$ ratios of the suspended particulate matter and of the dissolved load.

following Meybeck (1992), can be converted into an erosion rate when it is extrapolated back to the area of the watershed.

$$\Phi = Q(\Sigma Q_i[\mathrm{SM}])/(\Sigma Q_i) \quad (1)$$

where Q is the mean discharge over the whole hydrological cycle (m^3/s), Q_i is the daily discharge (m^3/s), [SM] is the daily SM concentration (mg l^{-1}).

The lower measured flow of solid matter at the Loire river mouth, given by Figueres et al. (1985) and Manickam et al. (1985), ranges from 1.0 to $1.5 \cdot 10^6$ t yr^{-1} and the higher measured flow ranges from $2.7 \cdot 10^6$ t yr^{-1} (given by the Agence de l'eau Loire-Bretagne (personal communication) to $4.6 \cdot 10^6$ t yr^{-1} (given by Négrel, 1997). However, in the study of Négrel (1997), 53% of the flux was related to fluviatile sediments, while the remaining 47% was related to particulate matter produced in situ in the estuary; this reduces the solid matter flux calculation to $2.3 \cdot 10^6$ t yr^{-1}. Therefore, the specific mechanical erosion rate over the whole Loire watershed ranges from 9 to 23 t km^{-2} yr^{-1}. This rate is very low in comparison to other rates observed for large watershed around the world (summarized by Berner and Berner, 1987). With respect to other watersheds in France, this rate is similar to that observed for the Garonne (Probst and Bazerbachi, 1986) and lower than those observed for the Rhône (Jansen et al., 1979).

During the 'daily' survey at Orleans from May 1995 to March 1996, the suspended solid matter flow was $37 \cdot 10^4$ t yr^{-1}, resulting in a specific erosion rate of around 9.5 t km^{-2} yr^{-1}. At this sampling location, the watershed is composed mainly of silicate terrains (76%). When compared with other major rivers draining silicate areas, such as the Yeni and Lena (Berner and Berner, 1987) and the Congo (Olivry et al., 1988), the specific erosion rate of the Loire river is at the same order of magnitude.

The shift in SPM flux between the sampling point ($37 \cdot 10^4$ t yr^{-1}) and the mouth of the Loire (range from 1 to $2.7 \cdot 10^6$ t yr^{-1}) corresponds to $6.3 \cdot 10^5$ to $2.3 \cdot 10^6$ t yr^{-1}, while the variation in the mean annual discharge is around 500 m^3 s^{-1} ($1.6 \cdot 10^{10}$ m^3 yr^{-1}). This variation in discharge corresponds to the input of water from tributaries of the Loire river. The increase in SPM fluxes corresponds to the input of solid matter by the tributaries of the Loire, as well as to supplementary erosion processes along the river (banks and streambed).

The average SPM concentration transported by the tributaries of the Loire can be calculated using differences in the various reported SPM fluxes (Figueres et al., 1985; Manickam et al., 1985; Négrel, 1997; Agence de l'eau Loire-Bretagne, personal communication) and the river discharge. The lower value obtained from this calculation is 40 mg l^{-1} and the upper value is 146 mg l^{-1}. Observations provided by Manickam et al. (1985) over a complete hydrological cycle give rise to a range of SPM concentrations from 20 to 120 mg l^{-1}, with a mean of 46 ± 24 mg l^{-1}. Results provided by the Agence de l'eau Loire-Bretagne, personal communication) suggest an average value of 100 mg l^{-1}, whereas an estimate of the input of tributaries corresponds to 50 mg l^{-1} (Agence de l'eau Loire-Bretagne, personal communication). All of these data are in general agreement, with the increase in the SPM flux between the location of our study and the mouth of the river corresponding to mechanical erosion processes within the watershed.

The large increase in SPM fluxes can be related to an increase in the specific erosion rate between the sampling point and the mouth of the river. This increase, by a factor 3 to 7, is due mainly to the drainage of carbonate terrains, which are more sensitive to erosion than silicate terrains. However, these mechanical erosion rates could be overestimated by the existence of authigenic calcite stemming from the chemical dissolution of carbonates.

5. Conclusion

This study reports on the temporal distribution of major- and trace-element concentrations and Sr isotopic ratios in suspended particulate matter transported by the upper Loire river. The sampling site integrates 34% of the total Loire watershed and represents the drainage of the entire igneous and metamorphic basement and 24% of sedimentary formations. Two different experimental surveys were carried out, with measurements of the suspended matter concentration ranging from 3 mg l^{-1} to 100 mg l^{-1}, but showing only a weak link with the rate of river discharge. One hypothesis to explain the

weak of relationship between SPM concentration and discharge rate could be the existence of numerous dams located in the upper basin.

The mineralogy of the suspended matter consists mainly of quartz and K-feldspar during high river flow, with a rise in calcite levels during periods of low river flow. SiO_2, CaO and Fe_2O_3 are the main oxides in the SPM, with larger fluctuations seen in the CaO and Fe_2O_3 concentrations. The concentrations of trace elements, which are present in noticeable quantities, fluctuate extensively. Bed-sediment contents are similar to those in the suspended matter for SiO_2, K_2O and TiO_2, lower for CaO, Fe_2O_3, Zn and Pb, and higher for Zr.

In the suspended matter, fluctuations in elemental concentrations with discharge levels can be related to the fluctuation of the contained mineral assemblages. The concentrations of K, Ti and Rb increase along with the increase in K-feldspar abundance at high flow, whereas the concentrations of Ca and Sr decrease with increasing discharge due to a decrease in calcite abundance.

The Sr isotopic composition fluctuates with the discharge of the river. The $^{87}Sr/^{86}Sr$ ratio increases when discharge increases and reaches a maximum corresponding to high flow and vice versa. This relationship implies the existence of at least two reservoirs of particulate matter; one with a high $^{87}Sr/^{86}Sr$ ratio and the other with a lower ratio. This fluctuation also reflects variations in mineral assemblages. The $^{87}Sr/^{86}Sr$ ratio also increases when both K-feldspar abundance increases and calcite level decreases. This was confirmed by the relationship between the $^{87}Sr/^{86}Sr$ and Rb/Sr ratios. However, the $^{87}Sr/^{86}Sr$ ratio of the calcite pool, given by the relationship between $^{87}Sr/^{86}Sr$ and Rb/Sr, is higher than the signature that can be provided by the detrital calcite reservoir. Moreover, the relationship between the $^{87}Sr/^{86}Sr$ ratios in the suspended and dissolved load enables one to postulate the coexistence of authigenic calcite with a $^{87}Sr/^{86}Sr$ ratio similar to that of the dissolved load.

The solid matter flow by suspension enabled a specific mechanical erosion rate to be calculated for the entire Loire watershed, which ranged from 9 to 23 t km^{-2} yr^{-1}. During the survey at Orleans, the solid suspended matter flow of the Loire river by suspension was $37 \cdot 10^4$ t yr^{-1}, giving a specific erosion rate of around 9.5 t km^{-2} yr^{-1}. The shift in SPM flux between the sampling point at Orleans and the mouth of the Loire river, together the divergence in the mean annual discharge rate, allowed the input of solid matter by the tributaries of the Loire river and supplementary erosion processes along the river (banks and streambed) to be calculated. The lower value obtained by this calculation was 40 mg l^{-1}, and the upper limit corresponded to 146 mg l^{-1}. The large increase in SPM fluxes can be related to an increase in the specific erosion rate between the sampling point and the mouth of the river. This increase, by a factor 3 to 7, is due mainly to the drainage of carbonate terrains, which are more sensitive to weathering than silicated terrains.

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Strontium isotope systematics used to decipher the origin of groundwaters sampled from granitoids: the Vienne Case (France)

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Abstract

Sr isotope data from surface, shallow and deep groundwaters from the granitoids of the Vienne District (France) are presented in this paper. In surface waters, the Sr contents in the rocks and groundwaters agree with previous data for groundwaters sampled from granitic and sedimentary rocks in France where a large range in $^{87}Sr/^{86}Sr$ ratios is observed. After correction for the Sr input from rain, the surface water samples plot within a mixing field that can be explained by three end-members, one anthropogenic (low $^{87}Sr/^{86}Sr$ and high Cl/Sr ratio) and two end-members characterised by low Cl/Sr ratios and a large range in $^{87}Sr/^{86}Sr$ ratios (from around 0.707–0.720).

For deep groundwaters, the $^{87}Sr/^{86}Sr$ ratios and Sr contents are also determined by applying a correction to account for the influence of cleaning waters during drilling operations. The results are scattered amongst five different groups and the lack of a direct linear relationship between any of the samples implies that, as found for the shallow groundwaters, the results are due to mixing between more than two end-members.

A model to determine the $^{87}Sr/^{86}Sr$ ratio (Irf) of groundwater after interaction with an actively weathering granite is developed. The results yield a low Irf value for waters associated with weathering of the tonalite (0.70463) and a higher one for waters associated with weathering of the monzogranite (0.70704). Given the much higher Irf values derived from the deep groundwater samples, these results indicate that the deep groundwaters analysed within the Vienne hydrosystem cannot be directly related to weathering of either tonalite or monzogranite. It is speculated that this high $^{87}Sr/^{86}Sr$ source originated from marine incursions during the Jurassic and have been diluted by mixing with former groundwaters produced by water–rock interaction (WRI) with the granites. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Deep groundwaters; Granite; Strontium isotopes; Weathering; Vienne; France

1. Introduction

A good understanding of both the regional and local groundwater flow and chemistry conditions of candidate areas is an important consideration in determining geological sites suitable for the safe disposal of nuclear waste. The geological characterisation of different sites (i.e. crystalline, sedimentary and salty bedrocks) has been the subject of numerous studies by different government agencies (e.g., Agence Nationale de Gestion des Déchets Radioactifs, ANDRA). As part of a preliminary program (1995–1998) investigating granitoid dominated

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bedrock in the Vienne district, western France (Fig. 1), a series of deep boreholes as deep as 900 m have been drilled by ANDRA (Fig. 2). The granitoid batholith targeted for investigation is composed mainly of dioritic and tonalitic to granodioritic plutons and is located below a 150 m thick cover of Jurassic sedimentary rocks (Capdeville et al., 1983; Mourier et al., 1989).

A salinity gradient is found in groundwaters within these granitoids (Matray et al., 1998), varying from approximatelly 1 g/l at the top of the basement (under the sedimentary cover) up to 10 g/l in the deeper part (from 400 to 600 m depth). The origin of salinity in deep groundwaters from granitoids in the Vienne district has previously been investigated by the coupled use of boron and strontium systematics (Casanova et al., 2001) together with Cl, Br, B and Sr concentrations. The aim of this paper is to contribute to site evaluation by investigating the geochemical characteristics of groundwater using Sr isotopes as tracers of groundwater movement. We report on the isotopic composition of strontium in waters collected in the Vienne district from deep boreholes in the Charroux-Civray region and from

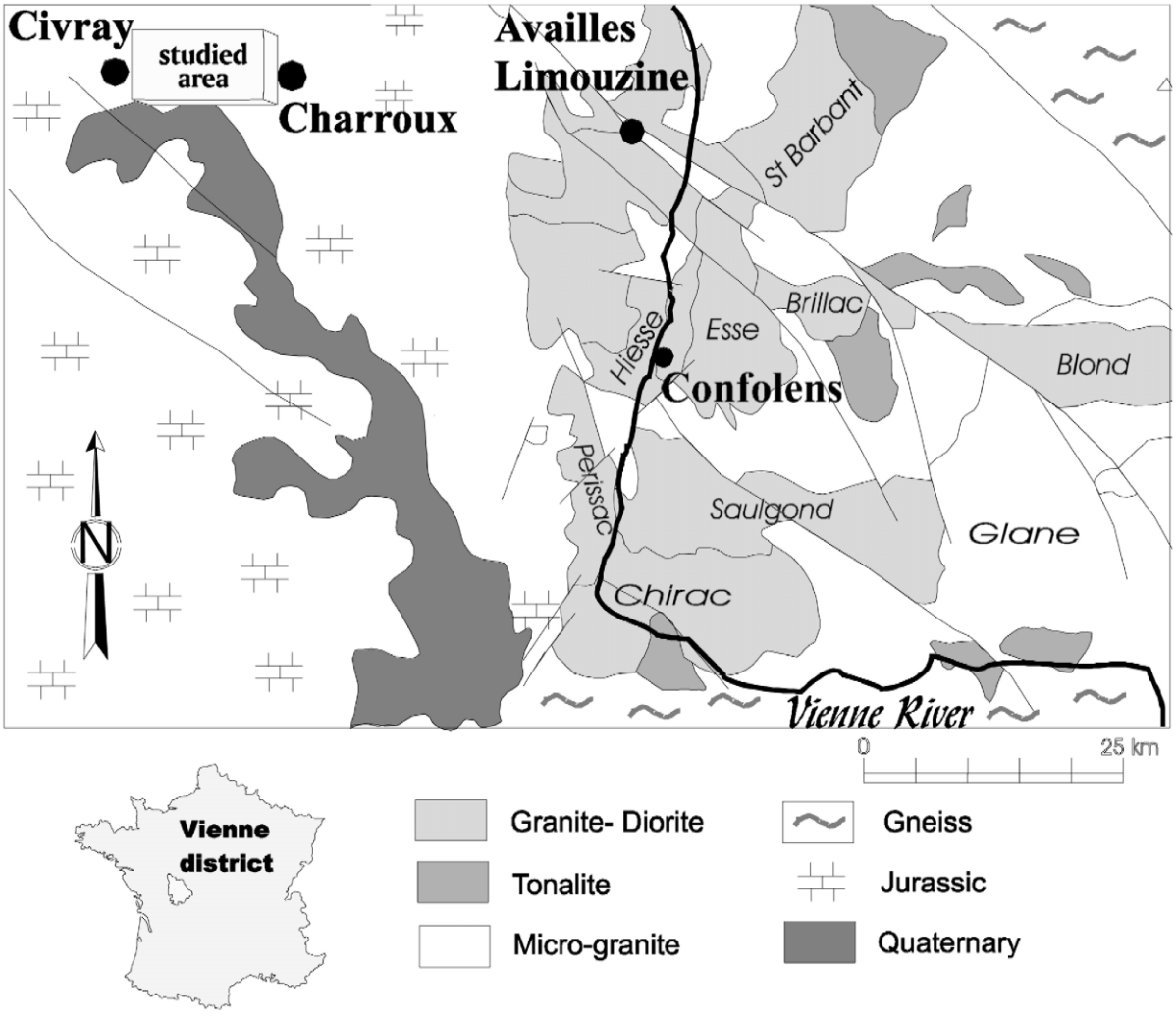


Fig. 1. Location map of the Vienne granitoids in the west of the French Massif Central and illustration of the regional geology.

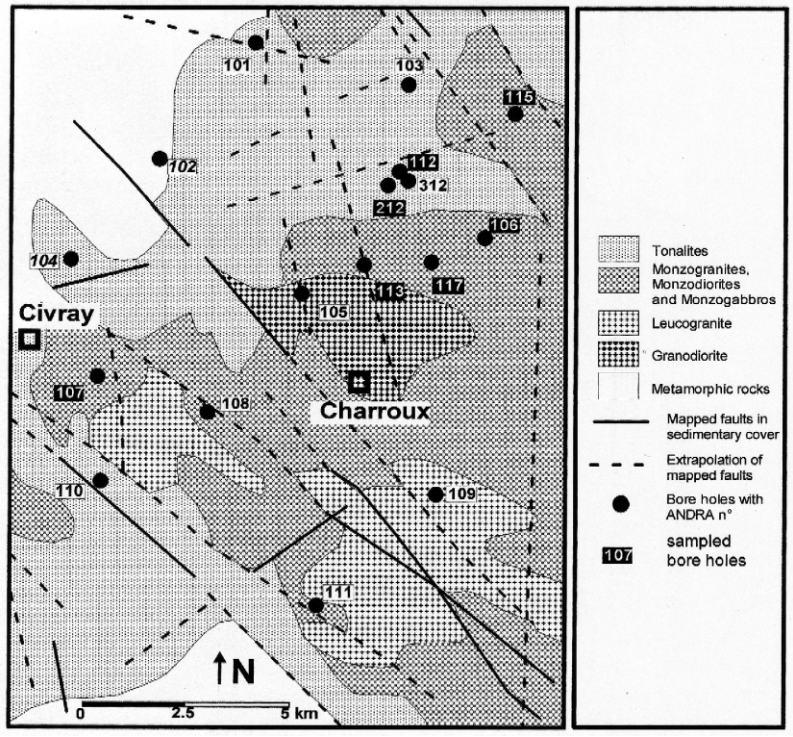


Fig. 2. Site locations illustrated on geological map showing the four main bedrock facies and the associated boreholes.

springs and rivers in the Vienne district (Fig. 2). This work was carried out during the course of geochemical investigations of the Vienne granite managed by ANDRA (Négrel et al., 1997b; Matray et al., 1997; Beaucaire and Tresonne, 1997; Casanova and Aranyossy, 1998; Michelot, 1999; Kloppmann et al., 2001; Casanova et al., 2001).

The $^{87}Sr/^{86}Sr$ ratio variations within a hydrologic system can provide information about the number and type of Sr sources sampled by groundwater movement and the different mixing processes that may operate between the sources (Albarede and Michard, 1987; Stueber et al., 1993; Palmer and Edmond, 1992; Andersson et al., 1994). This is an important consideration for understanding groundwater exchange between a potential nuclear waste repository and the surrounding environment. Generally, a large range of Sr isotope signatures (expressed as the $^{87}Sr/^{86}Sr$ ratio) exists in natural groundwaters but due to the high levels of precision achievable on isotope measurements by mass spectrometry (close to 20×10^{-6}), it is possible to interpret small variations in the isotope signatures (Andersson et al., 1996; Bullen et al., 1997; Négrel et al., 1997a). Chemical weathering causes rocks with different chemical characteristics and ages to release strontium into water (Faure, 1986; Négrel et al., 1993; Gaillardet et al., 1997). The $^{87}Sr/^{86}Sr$ ratio varies according to the Rb/Sr ratios and the age of the weathered material (Faure, 1986). Since natural processes do not fractionate Sr isotopes, the variability in the $^{87}Sr/^{86}Sr$ ratios found in groundwaters is due to the mixing of Sr derived from various sources with different Sr isotopic compositions.

Sr isotope systematics have been extensively used to study formation waters and brines in reservoirs (Stueber et al., 1984, 1993; Smalley et al., 1988; Banner et al., 1989; Brannon et al., 1991; Peterman and Wallin, 1999; Négrel et al., 2000) and to investigate water–rock interactions (Franklyn et al., 1991; McNutt et al., 1987, 1990). McNutt et al. (1990) suggested that Sr in groundwaters within the Canadian Shield is mainly derived from plagioclase dissolution. Edmunds et al. (1984, 1987) and Kay and

Darbyshire (1986) also suggested such an origin for Sr in brines in the Carnmenellis granite (SW England), although fluorite and carbonates may also be a significant source of Sr. In the Stripa granite (Central Sweden), Fritz et al. (1987) and Clauer et al. (1989) have identified chlorite (a product of biotite alteration) as the main source of Sr in saline waters. The aim of this work is to determine the Sr isotopic signature in deep groundwaters from a granite matrix in terms of water–rock interaction (WRI) and mixing processes in groundwaters to better understand the recent hydrogeological and hydrogeochemical conditions of the site, and to aid in the design of a conceptual groundwater flow model.

2. Site location

The Vienne granitoids are located west of the French Massif Central (Fig. 1). On both sides of the Vienne river, the weathered metamorphic and granitic bedrocks define an old peneplain (Capdeville et al., 1983; Mourier et al., 1989). The crystalline bedrock is comprised of Devonian metamorphic units (gneiss, migmatites and amphibolites) intruded by Carboniferous granitoids. The granitic plutons are composed of massive rocks cut by dykes, all emplaced as the result of several separate magmatic injections. The quartzitic diorites are the oldest rocks (360 Ma) followed by calc-alkaline granites and leucogranites (300 Ma). A range of batholiths, including calc-alkaline granite (Chirac, Esse, Hiesse), diorite (Saulgond, Abzac, St. Barband) and granodiorite (Availles) were investigated in this study along with gneiss.

Further to the west (Fig. 1), the studied site is composed of several intrusions with variable mineralogies and geochemistries partially covered by sedimentary deposits. The four main bedrock types and the location of boreholes, from which water samples were derived, are shown in Fig. 2. The calc-alkaline series, located north/northwest of the area is composed of (i) tonalites and leucogranites and includes the boreholes CHA101–103, CHA112, CHA212 and (ii) diorites and includes the boreholes CIV104 and CHA110. The peraluminous series, located southeast of the area, is formed of leucogranites and includes the borehole CHA109. The sub-alkaline series, located northeast/southwest of the area, is formed of (i) monzodiorites, monzogranites and includes the boreholes CHA106, CHA108, CHA111, CHA113, CHA117 and CIV107 and (ii) monzogabbrodiorites (CHA115).

The Jurassic sedimentary cover (Hantzpergue et al., 1997) is made up of 150 m of bioclastic limestones (Dogger), argillaceous limestones and marls (Upper Lias), limestones, dolomite, sands and sandstones (Lower Lias: Infra-Toarcian). The Dogger formations contain an unconfined aquifer while the infra-Toarcian formations contain a captive aquifer.

3. Material and methods

Deep and shallow groundwater samples from the granitoid basement (CHA106, 107, 113, 115, 117, 212) and from the two overlying sedimentary aquifers (Dogger/Infra-Toarcian, CHA115 and 312) were collected from 17 boreholes during hydrogeological surveys (packered pumping test and individual sampling, (Matray et al., 1998). Surface collection of mineral springs, dilute springs, rivers and lakes was carried out during 1995–1998 in the Limousin region. Water samples were collected from a range of lithologies including, undifferentiated gneiss and calc-alkaline granite (Chirac, Esse, Hiesse), diorite (Saulgond, Abzac, St. Barband) and granodiorite (Availles) batholiths (Fig. 1 and Table 1).

All water samples used for cation and isotope measurements were filtered on site through 0.2-μm cellulose acetate filters and stored in precleaned polypropylene bottles, acidified to pH 2 with ultrapure HNO_3. One bottle for each sample was not acidified and was used for anion determination.

Electrical conductivity and water temperature were measured using a WTW LF96 microprocessor conductivity meter standardised to 20°C. The pH was measured on site using an Ingold combined pH electrode and an Orion 250 pH-meter previously calibrated using two standard buffers. Chemical analysis of water samples was carried out by capillary ion electrophoresis for major cation and anions and inductively coupled plasma mass spectrometry (ICP-MS) for Rb and Sr. Precision was greater than $\pm 5\%$ for the determination of major elements and Sr measurements.

The Sr isotope ratio measurements were performed on surface waters (springs, lakes), shallow

Table 1
Cl, NO_3, and Sr contents (μmol/l), $^{87}Sr/^{86}Sr$ ratios, electrical conductivity (EC) (μS/cm) and pH in samples of surface waters from the Vienne District

Sample	Spring name	Bedrock	Acronym	Cl (μmol/l)	NO_3 (μmol/l)	Sr (μmol/l)	$^{87}Sr/^{86}Sr$	EC	pH
V95-2	Source Sagaud	Dogger	j1	602	1020	0.58	0.70923	625*	6.78*
V95-5	Source de Rochemenault	Dogger	j1	411	561	0.34	0.71055	638*	7.05*
V95-7	Source de Fontbonne	granite Chirac	γ3M	327	472	1.22	0.70777	147*	5.52*
V95-9	Source Fonte minérale d'Abzac	granite Hiesse	γ3M	41600	0	77.60	0.71275	5400*	7.24*
V95-10	Source Fonte minérale d'Abzac	granite Hiesse	γ3M	60400	0	154.00	0.71272	8300*	7.23*
V95-11	Source carrière Fonte minérale	granite Hiesse	γ3M	117	0	0.87	0.70924		
V95-12	Source Grande Vergne	diorite St. Barband	η1-2	394	511	1.39	0.70885	555*	7.03*
V95-13	Source Les Genets	granite Availles	*p*γ3-4	465	311	1.48	0.70706	203*	6.11*
V95-15	Source La Maurie	Diorite pressac-Abzac	η2M	352	56	1.97	0.70737	285*	6.15*
V95-18	Source l'infirmerie	Dogger	j1	578	856	0.59	0.70993	675*	6.93*
V96-4	Source La Grollerie	Dogger	j1	511	990	0.56	0.71002		
V96-9	Source Fonte minérale d'Abzac	granite Hiesse	γ3M	31700	77	54.00	0.71276		
V96-21		Dogger	j1	450	595	0.52	0.71043		
V97-7	Source de Fontbonne	granite Chirac	γ3M	321	427	1.23	0.70784	114	5.45
V97-9	Source Fonte minérale d'Abzac	granite Hiesse	γ3M	27831	63	49.08	0.71272	3280	7.3
V97-11	Source carrière Fonte minérale	granite Hiesse	γ3M	163	48	0.63	0.70926	196	7.12
V97-12	Source Grande Vergne	diorite St. Barband	η1-2	411	311	1.50	0.70894	396	6.63
V97-13	Source Les Genets	granite Availles	*p*γ3-4	586	494	1.39	0.70706	190	6.46
V97-15	Source La Maurie	Diorite pressac-Abzac	η2M	645	1000	2.49	0.70735	216	6.4
V97-100	Source la Barde	granite Hiesse	*p*γ3M	600	932	1.04	0.71112	117	5.84
V97-101	Source La Partoucie	granite Hiesse	*p*γ3M	586	968	1.99	0.71067	202	6.08
V97-102	Source Mas Marteau	granite Hiesse	*p*γ3M	245	52	0.81	0.70913	89	6.37
V97-103	Source Ansac/Vienne	gneiss	τ1−2	586	595	2.47	0.71042	315	6.43
V98-14	Source Chardat	IT	l7-8	2135	413	1.40	0.71160	770	7.22
V98-101	Source La Partoucie	granite Hiesse	*p*γ3M	375	311	1.29	0.71065	131	5.81
V98-103	Source Ansac/Vienne	gneiss	τ1−2	592	648	2.45	0.71043	330	6.41
V98-104	Ruisseau Crochatière	Dogger	j1	445	247	0.56	0.71048	500	7.41
V98-105	Source Chadenat	granite Chirac	γ3M	175	< 16	0.38	0.70788	60	6.18
V98-106	Source Poursac	gneiss	τ2	403	519	1.31	0.70872	227	6.52
V98-107	Source Brigueil	granite Glane	*p*γ3M	254	21	0.69	0.71611	135	5.02
V98-108	Etang Negade	granite Glane	γ3AL	192	< 16	0.19	0.71730	50	7.26
V98-109	Source Pierre Fixe	μgranite (biot) bordure Esse	α γ3M	282	202	1.19	0.70958	152	6.25
V98-110	Source Abzac Village	granite Hiesse	γ3M	656	29	1.54	0.71054	417	7.44
V98-111	Source Serail	granite Hiesse	*p*γ3-4	223	95	0.29	0.71009	79	5.91
V98-112	Source Le Marnier	granite Hiesse	μγ	287	81	1.36	0.71104	197	7.32

* pH and EC from C. Beaucaire, personal communication.

and deep groundwaters. Depending on the Sr content, aliquots of 1–30 cc were evaporated before chemical separation. The standard procedure was adopted for chemical separation and mass spectrometry for strontium (Négrel and Deschamps, 1996). Sr was separated using a cation exchange column (DOWEX AG50X8) with HCl 2 N as eluant. The total blank for Sr was less than 0.5 ng for the entire procedure. After chemical separation, 1/5 of the sample was loaded onto a single tungsten filament and analysed using a Finnigan MAT 262 multiple collector mass spectrometer. The $^{87}Sr/^{86}Sr$ ratios were normalised to a $^{86}Sr/^{88}Sr$ ratio of 0.1194. The overall precision of the $^{87}Sr/^{86}Sr$ ratio determination is approximately $\pm 10 \times 10^{-6}$ (2σ errors). The reproducibility of $^{87}Sr/^{86}Sr$ ratio measurements was tested by duplicate analyses of the NBS 987 standard and the mean value obtained during the course of this study was $0.710233 \pm 19 \times 10^{-6}$ (2σ, $n = 214$).

Three primary minerals were analysed from a monzogranite (apatite, microcline and biotite, CHA106) and three others were analysed from a tonalite (apatite, plagioclase and biotite, CHA112). Following standard acid-dissolution procedures of the primary minerals and chemical separation described for waters, Sr isotopic compositions were measured by mass spectrometry and contents of Rb and Sr by ICP-MS.

4. Results and discussion

4.1. Surface waters

4.1.1. Water chemistry

The results of the strontium isotope measurements, major (Cl and NO_3) and trace element (Sr) contents for surface waters are presented in Table 1, along with the electrical conductivity (EC) and pH for each sample. The electrical conductivity (EC) is a useful indicator of the total dissolved inorganic components. Variation in dissolved solids are indicated by the range in the EC:50–400 μS/cm in the granitic area, around 500 μS/cm in the Dogger aquifer and 700 μS/cm in the Infra-Toarcian aquifer (Table 1). The pH values vary between 5.0 (V98-107) and 7.4 (V98-110) for the water in the granitic area and from 6.8 to 7.2 in the waters from the sedimentary aquifers (Table 1).

As shown by Meybeck (1986) during his work on unpolluted streams, EC and pH are covariant. The most mineralised waters (i.e. higher EC) generally display a high pH value. The increased order of EC and pH corresponds to rivers draining plutonic and metamorphic rocks, volcanic rocks, non-carbonate detrital rocks, limestones and dolomites and evaporitic rocks. EC and pH measured in waters from the Vienne district are plotted in Fig. 3, also with fields previously obtained in catchments draining granitic rocks (Meybeck, 1986, DW, BW, Négrel, 1997, 1999) and volcanic rocks (Meybeck, 1986, BW, ALW Négrel and Deschamps, 1996), carbonate rocks (Meybeck, 1986, LW, Négrel et al., in preparation), non-carbonate detrital rocks (Meybeck, 1986) and rainwater (RW, Négrel and Roy, 1998; Grosbois et al., 2000). The different fields form three groups of EC and pH. Two of them have pH around 8 and EC close to 50–100 μS/cm (granitic and volcanic water drainage) and >400 μS/cm (carbonate water drainage). The third have low pH and low EC (rainwater and non-carbonate water drainage).

Water samples from the Vienne district (Louvat et al., 1997, this study) are distributed between these three groups forming two main trends. Most surface waters plot along a line between the fields defined by rainwaters and non-carbonate detrital rocks and the carbonate rock field. Samples of water collected from the sedimentary aquifers plot in the vicinity of water drainage fields for LW and carbonate rocks. The water samples collected on the crystalline basement plot near the fields for water drainage from rainwater and non-carbonate detrital rock and also near the fields for granitic and volcanic water drainage.

The Cl and NO_3 contents of waters collected in the Vienne District (Louvat et al., 1997, this study) are well correlated ($r = 0.73$) reflecting a common source for these two elements, mainly from the use of mineral fertilisers in agriculture. Moreover, Cl and Sr also display a positive trend although the correlation coefficient ($r = 0.51$) indicate a larger scatter. Sr is less influenced by fertilisers than Cl or NO_3 (Négrel and Deschamps, 1996; Négrel, 1999). The increase of Cl in water is clearly linked with an increase in Sr and/or NO_3 contents. However, Cl

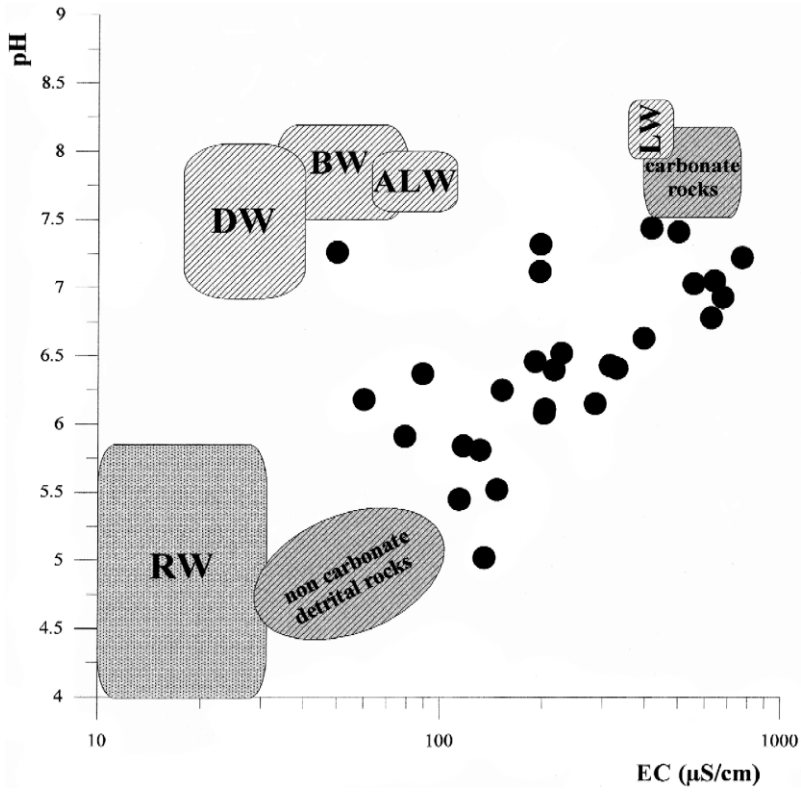


Fig. 3. Plot of the electrical conductivity (EC, µS/cm, normalised to 20°C) and pH measured in waters from the Vienne district, also with fields previously obtained in catchments draining granitic rocks (Meybeck, 1986, DW, Négrel, 1997, 1999) and volcanic rocks (Meybeck, 1986, BW, ALW, Négrel and Deschamps, 1996), carbonate rocks (Meybeck, 1986, LW, Négrel et al., in preparation), non-carbonate detrital rocks (Meybeck, 1986) and rainwater (RW, Négrel and Roy, 1998, Grosbois et al., 2000).

can be present in large amounts even when NO_3 contents are close to 0. This can be linked with the reactive behaviour of NO_3 that can be removed from the system in the water cycle (Berner-Kay and Berner, 1987).

Sr contents are low in water samples collected from the Dogger aquifer and fall in the range 0.34 µmol/l (V95-5) to 0.56 µmol/l (V96-4). In the Infra-Toarcian aquifer, the Sr content is close to 1.4 µmol/l. These values are comparable to those measured in deeper groundwater samples collected from the boreholes (Table 2): 0.18–0.31 µmol/l in the Dogger aquifer and 0.68–1.25 µmol/l in the Infra-Toarcian aquifer. Sr contents in water from the crystalline basement varied greatly from 0.19 µmol/l in sample V98-108 (Glane granite batholith) to around 2.5 µmol/l in samples V97, V98-15 (Abzac diorite batholith) and V97, V98-103 (gneiss from Ansac batholith). This range in Sr contents from groundwaters samples from different batholiths agree with previous work on groundwaters sampled from granitic rocks in France (Sarazin et al., 1976; Meybeck, 1986; Négrel, 1997, 1999).

In the springs and rivers draining the sedimentary covers, the $^{87}Sr/^{86}Sr$ ratio ranges from 0.70923 to 0.71055 in the Dogger and the $^{87}Sr/^{86}Sr$ ratio is 0.71160 for the Infra-Toarcian. These Sr values are in the same range as those measured in water samples collected from deeper levels of the aquifer systems (Table 2) where samples from the Dogger range from 0.70971–0.71016 and for the Infra-Toarcian range from 0.71057 to 0.71221.

The large range in Sr isotope compositions for the remaining samples from the Availles and Glane batholiths, is clearly greater than for samples from other watersheds on granite and gneisses in France

Table 2
Uncorrected and corrected data for Sr content and $^{87}Sr/^{86}Sr$ ratios in deep groundwaters from the Vienne granitoids

Sample	Bedrock	Z (m)	Percent deep groundwater	Sr, uncorrected data (μmol/l)	$^{87}Sr/^{86}Sr$	Sr, corrected data (μmol/l)	$^{87}Sr/^{86}Sr$
CHA113							
113-T3-F5	granite	263	75	13.7	0.70815	17.5 (2.9)	0.70807
CHA115							
115-T3-F15	granite	275	98	11.4	0.70775	11.6 (1.0)	0.70774
115-T3-F16	granite	250	98	11.4	0.70786	11.6 (1.0)	0.70786
115 (90802)	granite	240	98	10.3	0.70797	10.5 (0.8)	0.70796
115 (90816)	granite	280	98	11.3	0.70770	11.5 (1.0)	0.70769
CHA117							
117-T1-S63	granite	293.9	40	6.3	0.70943	12.1 (6.5)	0.70926
117-T1-F65	granite	240	65	22.3	0.70915	32.9 (4.3)	0.70911
117-T1-F66	granite	370	55	25.8	0.70894	44.9 (6.2)	0.70889
CHA212							
212-T2-S23	granite	573.6	75	92.4	0.70804	122.5 (15.5)	0.70802
212-T18-S48	granite	571.8	84	67.1	0.70808	79.4 (5.1)	0.70806
212-T18-F3	granite	356.2	85	44.9	0.70825	52.4 (3.6)	0.70824
212-T21-S2	granite	368	95	9.1	0.70832	9.5 (1.2)	0.70830
212-T21-F4	granite	402.2	98	10.0	0.70842	10.5 (0.9)	0.70840
212-91930	granite	360	95	51.0	0.70812	53.6 (2.3)	0.70812
212-91937	granite	406	95	11.4	0.70833	11.9 (1.3)	0.70831
212-91244	granite	570	95	87.0	0.70806	91.4 (4.1)	0.70806
CHA107							
107-T2-F2	granite	375	30	6.6	0.70848	16.5 (10.0)	0.70796
107-T2-F4	granite	375	40	18.3	0.70831	42.1 (9.1)	0.70817
107-T2-F5	granite	375	67	22.8	0.70831	32.9 (4.1)	0.70825
CHA106							
106-T1-F1	granite	430	40	30.8	0.70842	73.4 (12.0)	0.70834
106-T1-F2	granite	560	40	27.4	0.70847	64.9 (11.1)	0.70839
106-T1-F3	granite	400	75	60.5	0.70820	79.9 (5.9)	0.70819
106-T1-F4	granite	580	70	50.2	0.70832	70.7 (5.9)	0.70829
106-T2-F17	granite	270	90	75.5	0.70827	83.7 (4.9)	0.70827
106-T2-F18	granite	300	95	91.3	0.70821	96.0 (5.2)	0.70821
106-T2-F19	granite	416	95	89.2	0.70824	93.8 (5.1)	0.70823
CHA115							
115-T1-S4	Dogger	58.9	98	1.3	0.71016	1.2 (0.2)	0.71016
115-T2-S6	Infra-Toarcien	122.6	98	3.5	0.71221	3.6 (0.5)	0.71224
CHA312							
312-V0-S1	Dogger	45	98	0.7	0.70971	0.7 (0.5)	0.70969
312-T2-S10	Infra-Toarcien	132.95	98	3.2	0.71179	3.2 (0.5)	0.71182
312-T7-S1	Infra-Toarcien	153.95	33	2.1	0.71057	1.4 (1.0)	0.71262
312-T7-S9	Infra-Toarcien	153.95	46	3.3	0.71069	4.4 (3.1)	0.71114

Analytical errors and uncertainty within the correction of potential contamination by cleaning waters (see text) can be taken into consideration by a progression of errors according to the general Gauss formula (Kloppmann et al., 2001). Values in parentheses associated with corrected data represent the propagate errors.

(Négrel, 1997, 1999), ranging from 0.707064 in sample V97-13 (Availles) to 0.717303 in sample V98-108 (Glane).

4.1.2. Rainwater input correction

Mass-balance calculations (e.g. Velbel, 1985; Mast et al., 1990) can be used to interpret the geochemical processes in surface water from watersheds. The mass-balance approach involves determining input–output budgets for dissolved constituents in surface waters.

Some solutes of rainfall can constitute an important fraction of dissolved species appearing in surface waters (Meybeck, 1983). The aim of the atmospheric input correction is to quantify and subtract the portion of the elements carried by rainwater in the chemical composition of the surface water. The quantification of atmospheric input due to rainwater requires knowledge of the chemical composition of the rainfall over the total watershed (Likens et al., 1977; Meybeck, 1983; Négrel et al., 1993; Grosbois et al., 2000). For this purpose ; a rainwater sampler was operated at Tours during each rain event from September 1996 to January 1998, the results presented in Grosbois et al. (2000). Briefly, the Sr concentration ranged from 0.012 to 0.04 μmol/l with a weighted mean of 0.016 μmol/l. The $^{87}Sr/^{86}Sr$ isotope ratios ranged between 0.70901 and 0.71060 with a mean of 0.70943 weighted by the percent of rainfall.

Chloride ions behave conservatively through the hydrological cycle (Meybeck, 1979) so they can be used as a reference of atmospheric inputs in many unpolluted hydrosystems (e.g. Meybeck, 1983; Négrel et al., 1993; Négrel and Deschamps, 1996; Gaillardet et al., 1997; Négrel, 1999; Grosbois et al., 2000). Therefore, for any element Z in the river, the correction for an atmospheric contribution to a river is estimated by reference to the Cl concentration, called $(Cl)_{ref}$, multiplied by the Z/Cl ratios of rainwater (Meybeck, 1983; Négrel et al., 1993).

Chloride ions in the atmosphere originate from sea salt and from a wide range of human activities (Sherwood, 1989; Meybeck, 1986; Roy et al., 1998; Grosbois et al., 2000). The release of significant Cl due to rock weathering has not been demonstrated clearly except in the weathering of rock salt (Meybeck, 1979; Négrel et al., 1993; Gaillardet et al., 1997). For the mass balance equations, the highest concentrations of Cl ions derived from rainwater $(Cl)_{ref}$, had to be determined. The $(Cl)_{ref}$ was calculated with the mean weighted chloride at Tours multiplied by the concentration factor F resulting from evapotranspiration. Its value for the region is approximately 1.5 giving a maximum value of 118 μmol/l of Cl_{ref}, which represent the highest chloride concentration from the rainwater to the river. When the chloride content measured in the dissolved load of the river and springs (Table 1) was lower than the $(Cl)_{ref}$, the entire chloride content of the river was assigned to atmospheric origin. When the chloride content measured in the dissolved load of the river was higher than the $(Cl)_{ref}$, the atmospheric correction was applied with $(Cl)_{ref}$ as the rainwater input. The residual chloride $(Cl)_{res}$ in the river was attributed to human activities.

One groundwater sample (V95-11, Table 1) obviously derives its total Cl content from rainwater input. All other groundwater samples have been affected by anthropogenic addition. Twelve groundwater samples exhibit a Cl contribution from rainwater that is close to or less than 25–27% in samples V98-14 and V98-104 (Dogger aquifer) and 18–26% in samples V95-13 and V98-110 (Esse granite). Nine groundwater samples have a Cl contribution from rainwater higher than 40%. The maximum percentage of atmospheric contribution is found in sample V95-11 from the groundwater associated with the Esse granite with 100% of Cl derived from rainwater while a 42% contribution is observed for the groundwater sample V98-109 from the microgranite bordering the Esse granite.

The Sr input from rainwater ranges from 1% (V98-103, emerging from gneiss) to 11% (V98-108, lake draining the Glane granite). Within this range, the mean Sr input by rainwater is close to $3 \pm 2\%$. The input of NO_3 from rainfall is generally difficult to calculate using a mass-balance approach because the NO_3 content is high relative to Cl in rainwater, sometimes resulting in negative values reflecting an over correction. In this study, the large NO_3 content in water was used as a possible estimate of rainwater input. In most cases, less than 10% of NO_3 is calculated to have originated from rainwater. When the NO_3 content of the water is low, either by possible denitrification (V98-110) or from a low

anthropogenic input, the rain correction led to high NO_3 percentage, up to 50%.

4.1.3. Evidence of anthropogenic influence on the $^{87}Sr/^{86}Sr$ ratio

Because the release of chloride ions due to rock weathering has not been demonstrated clearly excepted in the weathering of salty rocks (Meybeck, 1979), the residual chloride concentrations in water samples, after correction for atmospheric input, may reflect Cl derived from of human activities like agricultural (mineral fertilisers, carbonate amendments, etc.) and human activity (deicing salts, etc.). Deicing salts are a mixture of KCl (K = 1.7–2.9%) and varying amounts of NaCl and $CaCl_2$ (Ca = 9%), these salts originate from the "Potasse d'Alsace" (*Alsace Potash*) in the east of France. Mineral fertilisers include total fertilisers (N–P–K) where chloride mainly takes the form of KCl (K = 1.6%) and carbonate amendments (47% Ca, 15% Mg). The use of fertilisers in the basin may have an impact on the chemical constituents in waters (Van Der Weijden et al., 1978; Négrel and Deschamps, 1996; Négrel, 1997, 1999; Roy et al., 1998; Grosbois et al., 2000) and the general trend observed between the residual Cl contents and the rain corrected NO_3 contents (not shown) confirm the agricultural origin of the residual Cl in waters.

Both fertilisers and deicing salts contain very large amounts of Cl (up to 1%) and varying amounts of Sr (range 3–1500 ppm), the isotopic ratio of deionised water-soluble Sr measured in three different fertilisers shows a range from 0.70794 to 0.70830 (Négrel, 1999). Carbonate amendments have Sr contents of 250–1500 ppm with a $^{87}Sr/^{86}Sr$ ratio of around 0.7087 (Négrel, 1999). The ratio for deicing salts is 0.7095 with a Sr content of around 1500 ppm (Négrel, 1999). Anthropogenic disturbance through agricultural and other human activity induces an input of Sr that may be important to the Sr content of the groundwater samples studied as these inputs have a range of Sr contents (3–1500 ppm) with an isotopic ratio ranging from 0.70794 to 0.7095.

After correcting the data for atmospheric inputs, the effect of human activities on the chemistry of the sampled waters can be examined by means of multivariate regressions between element/Sr ratios and $^{87}Sr/^{86}Sr$ ratios (Négrel and Deschamps, 1996). Indeed, the input of fertilisers demonstrably leads to variable levels of chemical species depending on the kinetic effects of dissolution of the elements. When plotted vs. Cl/Sr, the $^{87}Sr/^{86}Sr$ ratio discriminates several groups of points (Fig. 4). Four groups show fluctuations of the $^{87}Sr/^{86}Sr$ ratios—from 0.707 to 0.7185—associated with Cl/Sr ratios lower than 500. The values of the $^{87}Sr/^{86}Sr$ ratio are close to 0.7075, 0.709 and 0.711 for the first three groups, respectively. The highest values (V98-107 and 108) are close to 0.7165 and 0.7185, respectively. The fourth group, including most of the water emerging from the Dogger aquifer, exhibits a $^{87}Sr/^{86}Sr$ ratio in the range 0.710–0.711 and an increase in Cl/Sr ratios from 500 to around 1000. One sample emerging from the Dogger aquifer (V98-14) is excentred with a high $^{87}Sr/^{86}Sr$ ratio (around 0.7115) and a Cl/Sr close to 1500.

As can be seen in Fig. 4, the Vienne District surface waters plot inside a mixing field defined by three end-members. One end-member is clearly related to anthropogenic inputs and has a range in $^{87}Sr/^{86}Sr$ ratios from 0.7079 to 0.7095 and a Cl/Sr > 1000 (Négrel and Deschamps, 1996; Négrel, 1997; Martin and McCulloch, 1999). If we extrapolate the Cl/Sr ratio to 0 (i.e. we assume no chloride is derived from the rock matrix and a variable amount of Sr is derived from WRI), the large range in $^{87}Sr/^{86}Sr$ ratios reveals two extreme WRI end-members: the first one is characterised by a low $^{87}Sr/^{86}Sr$ ratio close to 0.707, while the second one is characterised by the highest $^{87}Sr/^{86}Sr$ ratio (close to 0.722). These two extreme signatures reflect the potential interaction of water with the different Sr isotope ratios of the suite of rocks (granites, diorites, etc) forming the bedrock of the studied area.

4.2. Deep groundwaters

The data from deep groundwaters includes samples collected from boreholes located either in the granitoids or in the two overlying sedimentary aquifers together with samples collected from the outlet of the Availles–Limousine mineral springs. In waters collected by boreholes in the granitoids (Table 2), the Sr content ranges from 9.1 μmol/l (CHA212/330-406) to more than 90 μmol/l (CHA212/562-585, CHA106/300) whereas Sr in

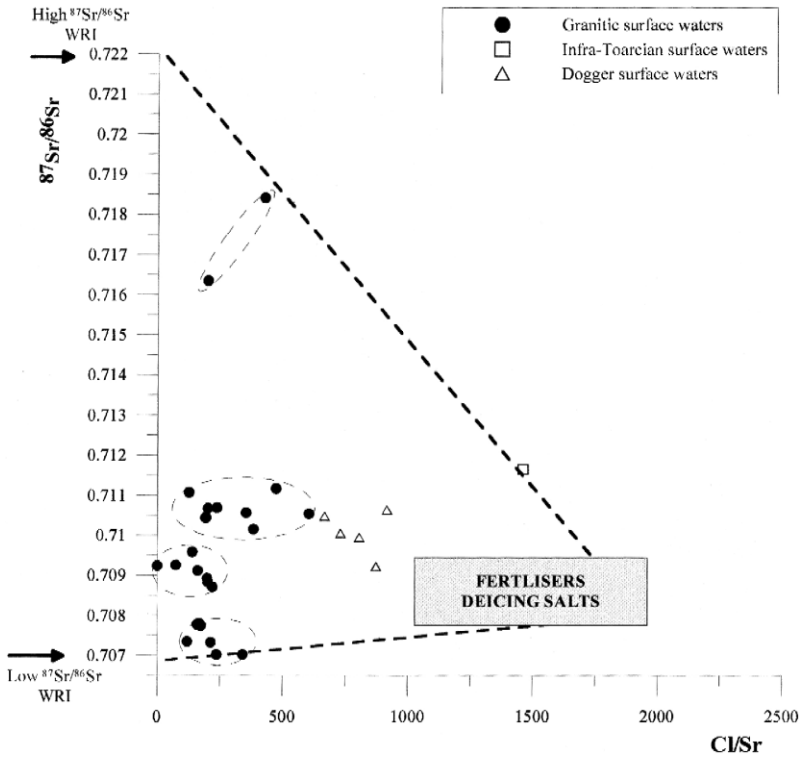


Fig. 4. Plot of the $^{87}Sr/^{86}Sr$ vs. Cl/Sr ratios in surface waters draining the different types of granitoids in the regional framework (see Fig. 1).

samples collected from the Availles-Limouzine spring ranged from 49 to 154 μmol/l. The $^{87}Sr/^{86}Sr$ ratios are in the range 0.70769–0.70926 (CHA115/280 and CHA117/189-399, respectively) for borehole samples while the ratios reach 0.71275 in samples from the Availles-Limouzine spring (Table 1).

In waters collected from boreholes into the two overlying sedimentary aquifers, slightly higher Sr contents are found associated with $^{87}Sr/^{86}Sr$ ratios similar to those observed in the surface waters (see Section 4.1.1).

4.2.1. Influence of cleaning water: methodology of correction

While the drilling process is thought to have no influence on the chemical and isotopic composition of the groundwater samples measured, (material used for drilling contains Sr less than 0.5 μmol/l), the water used for cleaning the boreholes may have contaminated the samples. Thus, the chemical and isotopic data require a correction for this potential contamination as illustrated by Kloppmann et al. (2001). This can be done by means of a binary mixing equation (Faure, 1986) which includes the Sr contents, the isotopic compositions, the percentage of groundwaters and the percentage of drilling fluids determined by tracer experiments (Matray et al., 1998; Kloppmann et al., 2001).

Eight samples were used to characterise the waters used for cleaning operations, Cleaning waters were estimated to have a Sr content of 2.6 ± 0.3 μmol/l, while the isotopic composition of three samples suggested an average $^{87}Sr/^{86}Sr$ ratio of around 0.70999 and a Sr content of $0.2.4 \pm 0.3$ μmol/l. The Sr content estimated from the three samples used for isotopic determinations is similar to that obtained from eight samples and so is thought to be suitably representative of the cleaning waters.

As one sample of deep groundwater may correspond to the mixing of several end-members, numer-

ous samples were taken to help constrain the effects of different potential end-members on the $^{87}Sr/^{86}Sr$ ratio of the samples. Twenty-six representative samples of deep groundwater were taken and the sampling strategy (packered pumping test and individual sampling, Matray et al., 1998) was noted. Corrected data are presented in Table 2 and when compared with uncorrected data. The mean uncertainty (i.e. propagate error) on the Sr content resulting from the correction method is 17% and the influence of cleaning fluids appears to represent 5–60% of the Sr contents, without any relation to the salinity of the water. Notwithstanding the propagate errors on the Sr isotope data (0.004), the difference in the isotopic ratios is always weak between the uncorrected and corrected ones with a mean value of $5 \pm 3 \times 10^{-5}$. Therefore, each $^{87}Sr/^{86}Sr$ ratio is representative and sign a deep groundwater, it can be used to reconstruct the history of deep groundwaters in the Vienne granitoids.

4.2.2. Strontium isotope systematics in deep groundwaters

A first approach to characterise deep groundwaters in granitoids is to consider the average values and coefficient of variation (%) of Sr contents in water samples from each borehole. Five average values and associated coefficient of variation are available from Table 3. Large variations in the mean values can be observed from the different boreholes. The lowest mean Sr content (11.3 μmol/l) is found from borehole 115 associated with a low coefficient of variation (5%). Borehole 106 has the highest mean Sr content of 80.3 μmol/l with a relatively small coefficient of variation (14%). Similar mean Sr contents are observed in boreholes 117 and 107 (30.0 and 30.5 μmol/l, respectively) but the coefficient of variations are very high, close to 55% and 43%, respectively. Samples from borehole 212 yielded an intermediate mean Sr content of 53.9 μmol/l but with very high coefficient of variation (78%).

The $^{87}Sr/^{86}Sr$ ratios for all borehole samples range from 0.70781 ± 0.00012 (borehole 115) to 0.70909 ± 0.00019 (borehole 117). However, between these two extremes values, the $^{87}Sr/^{86}Sr$ obtained for the other boreholes are quite similar and ranged from 0.70807 (borehole 113, one value) and 0.70827 ± 0.0001 (borehole 106). Within a single borehole, a weak variability of the $^{87}Sr/^{86}Sr$ is generally observed, as evidenced by the standard deviation, which ranges from 0.0001 (borehole 106) to 0.00019 (borehole 117). The limited range of $^{87}Sr/^{86}Sr$ ratios contrasts with relatively large dispersion in Sr contents previously described. Moreover, there is no evidence of a direct link with the geological character of the bedrock: calc-alkaline granitoids for boreholes 113 and 212, sub-alkaline granitoids for boreholes 106, 113, 107, 115 and 117. For example, the extreme values of the $^{87}Sr/^{86}Sr$ ratios, from borehole 117 on one hand and boreholes 106, 107, 115 on the other hand, came from the same geological unit. Through this descriptive study, we thus have evidenced large variations in the Sr contents of deep groundwaters in the granitoids (mean values in the range 11.3–80.3 μmol/l) together with three different $^{87}Sr/^{86}Sr$ ratios. One group of ratios, in the range 0.70807–0.70827 ($n = 19$) in boreholes 106, 107, 113 and 212, the two other groups characterised by higher $^{87}Sr/^{86}Sr$ ratios (borehole 117) and lower $^{87}Sr/^{86}Sr$ ratios (borehole 115).

The Sr contents of deep groundwaters in granitoids and the overlying sedimentary aquifers are plotted vs. depth in Fig. 5. A gradual increase in the Sr content of waters derived from the sedimentary aquifers towards deep groundwaters from the granitoids is apparent. The deep groundwaters in the granitoids quickly reach the Sr content observed in the Availles-Limouzine mineral springs (this study) and in the saline groundwaters studied by Beaucaire et al. (1999) in the granites from the Chardon mine, few tenth of kilometres north of the Vienne granotoids.

Table 3
Average values and associated standard deviation for deep groundwaters from the Vienne granitoids

Borehole	Sr (μmol/l)	Coefficient of variation (%)	$^{87}Sr/^{86}Sr$	Standard deviation
106	80.3	14	0.70827	0.0001
107	30.5	43	0.70813	0.00014
115	11.3	5	0.70781	0.00012
117	30.0	55	0.70909	0.00019
212	53.9	78	0.70819	0.00014

All samples in boreholes 106, 115, 117, 212 were averaged. Borehole 113 cannot be averaged because only one sample of water was collected.

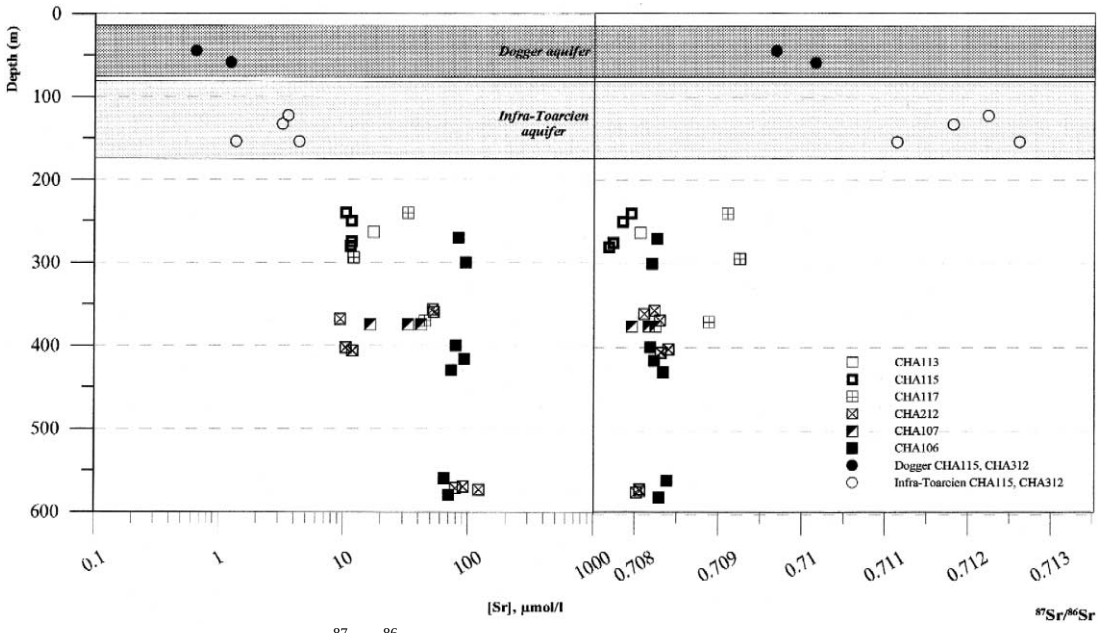


Fig. 5. Plot of the corrected Sr contents and $^{87}Sr/^{86}Sr$ ratios of deep groundwaters sampled from granitic and sedimentary rocks overlying aquifers vs. the depth at which they were sampled.

In Fig. 6, the $^{87}Sr/^{86}Sr$ ratios vs. depth are plotted. The $^{87}Sr/^{86}Sr$ ratios are higher in the Infra-Toarcian aquifer than those observed in the Dogger aquifer but deep groundwaters in the granitoids show lower $^{87}Sr/^{86}Sr$ than in the sedimentary aquifers. The $^{87}Sr/^{86}Sr$ ratios of deep groundwaters in granitoids vary slightly with depth, except for the samples from borehole 117. One major feature is the lack of intermediate $^{87}Sr/^{86}Sr$ ratios between the three zones, which suggests that only very weak water interaction/exchange occurs between the different formations, if any.

4.2.3. Mixing processes

The $^{87}Sr/^{86}Sr$ ratios are mainly used as tracers of WRI (Moldovani et al., 1993; Bottomley et al., 1994; Négrel et al., 1997a,b). When coupled with Sr concentrations, Sr isotope systematics can be used to investigate mixing of different groundwaters (Stueber et al., 1993; Négrel et al., 1997a,b).

Fig. 6 illustrates the relationship between $^{87}Sr/^{86}Sr$ ratios and Sr content in deep groundwaters from granitoids. The samples are scattered amongst five groups and the lack of a direct linear relationship between any of the samples implies the existence of more than two end-members. Groundwaters from borehole 115 form one group with relatively low $^{87}Sr/^{86}Sr$ and low Sr content. Samples from boreholes 117 have a higher $^{87}Sr/^{86}Sr$ and a large range in the Sr content. The third group encompasses the groundwaters from boreholes 106, 107 (excepted one sample) and five samples from borehole 212. Two samples from boreholes 113 and 107 plot closely and from the fourth group. The last group is formed by samples from borehole 212, which plot above the samples from borehole 115 reflecting higher $^{87}Sr/^{86}Sr$ ratio.

4.2.4. Rock water interaction and geochemical modelling

The Sr isotopic composition of groundwaters is constrained by Sr supplied by chemical weathering of Sr-bearing phases from the host rock (Franklyn et al., 1991; Zuddas et al., 1995; Brantley et al., 1998). The dissolved Sr content also depends on the dissolution of these Sr-bearing phases and the formation of new Sr-bearing phases (Seimbille et al., 1998). Amongst the minerals typically found in granitic rocks, apatites, feldspars (plagioclase and potassic feldspar) and micas (biotite and muscovite) are the

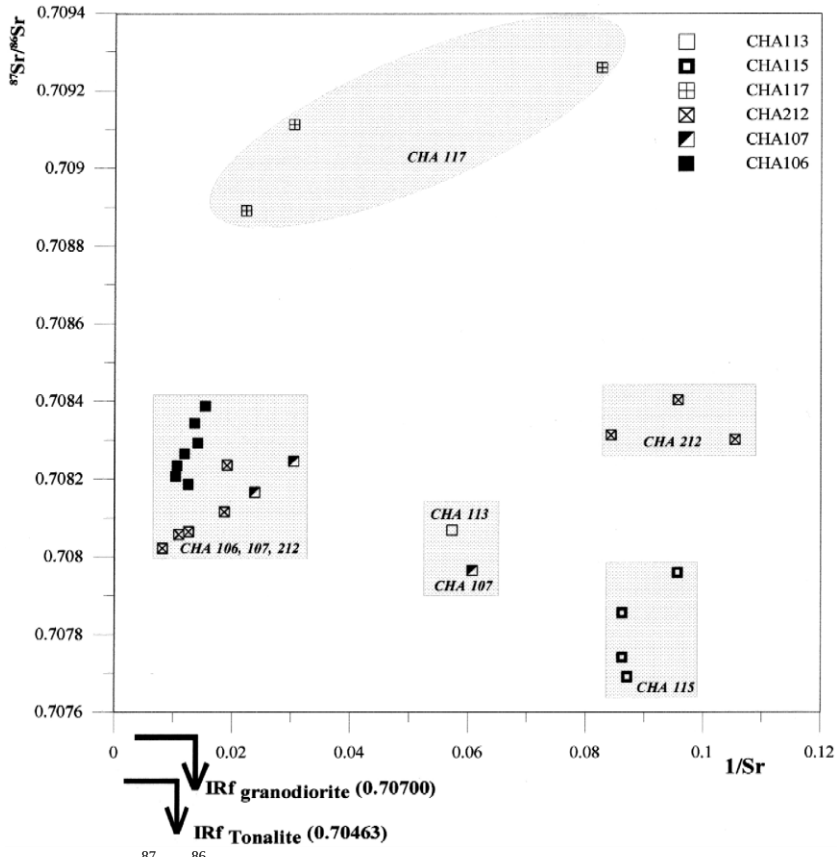


Fig. 6. Plot of $^{87}Sr/^{86}Sr$ ratios vs. 1/Sr in the deep groundwaters sampled from the granitoid.

minerals that most commonly contain significant amount of Rb and/or Sr. The Rb/Sr ratio increases from plagioclase to biotite and therefore the $^{87}Sr/^{86}Sr$ ratio increases. Moreover, Sr-bearing phases with high Rb content will have an $^{87}Sr/^{86}Sr$ ratio that increases with time while the $^{87}Sr/^{86}Sr$ ratio of a mineral with poor Rb content will not.

In rock–water interactions involving granitoids, the dissolution of plagioclase is supposed to progress significantly more rapidly than the dissolution of other Sr-bearing phases such as K-feldspar and micas (Lasaga, 1984). Therefore, in open fluid systems, the time for the reaction between plagioclase and water will be short and, thus, the Sr isotopic signature of the fluids will reflect the dissolution by hydrolysis of plagioclase with low $^{87}Sr/^{86}Sr$ ratio rather than dissolution of the whole host rock (Franklyn et al., 1991; McNutt et al., 1987, 1990; Smalley et al., 1988). However, clearly radiogenic strontium from weathering of biotite or feldspars may be effectively removed from various granitic weathered systems (Blum et al., 1994; Blum and Erel, 1997; Zuddas et al., 1995; Bullen et al., 1997; Brantley et al., 1998). K-feldspar and biotite have high Rb contents and hence, high $^{87}Sr/^{86}Sr$ ratios. As K-feldspar and biotite become involved in dissolution processes, fluids that have derived most of their Sr from the hydrolysis of these minerals must have high $^{87}Sr/^{86}Sr$ ratios. Until recently, the dissolution of K-feldspars and of Rb-rich phases (biotite) has not been considered as significant. The dissolution of highly radiogenic phases may affect the Ca-rich plagioclase signature imposed on the water.

We have developed a model to determine the $^{87}Sr/^{86}Sr$ ratio of water after interaction with granite. This model is based on that of Fritz et al. (1992),

Bullen et al. (1997) and Probst et al. (2000) with the assumption that Sr was derived from three minerals: plagioclase, K-feldspar and biotite as developed by Fritz et al. (1992) and Zuddas et al. (1995) for studying natural and/or experimental granitoid-fluid interaction. Furthermore, we assumed that the newly formed phases would contain Sr in isotopic equilibrium with their parent solutions (Seimbille et al., 1998). If dissolution is stopped after the formation of new phases, the initial Sr content of fluid is modified by the formation of these phases but the $^{87}Sr/^{86}Sr$ ratios will not be modified. The $^{87}Sr/^{86}Sr$ ratio (IR_f) of the water after equilibration with the minerals of a granitoid is given by the following equation:

$$IR_f = m_w * IR_w / m_w$$

where m_w is the mass of Sr provided by mineral weathering. It corresponds to the sum of the masses of Sr provided by the dissolution of the three minerals considered in the weathering processes: plagioclase ($m_w$pl), K-feldspar (m_wf) and biotite (m_wb). This mass of Sr provided to the system is given by the product of (1) the proportion of each mineral in the rock, (2) the average Sr concentration of each mineral and (3) the weatherability of each mineral (Blum et al., 1994; Blum and Erel, 1997; Zuddas et al., 1995; Seimbille et al., 1998; Probst et al., 2000).

IR_w corresponds to the $^{87}Sr/^{86}Sr$ ratio of Sr provided by the weathering (and chemical erosion) of the three minerals. It corresponds to the sum of each mass of Sr provided by the dissolution of plagioclase ($m_w$pl), K-feldspar (m_wf) and biotite (m_wb) multiplied by the corresponding $^{87}Sr/^{86}Sr$ ratio IR_{pl} (plagioclase), IR_f (K-feldspar) and IR_b (biotite).

The weatherability of each mineral, i.e. the ratio of mineral/mineral weathering rates shows fluctuation. The rate of plagioclase weathering is considered as the reference. Hence, the ratio of plagioclase to K-feldspar weathering rates ranges from 1/5 (Blum et al., 1994; Blum and Erel, 1997) to 1/10 (Zuddas et al., 1995; Seimbille et al., 1998). In our model, we assume that plagioclase and K-feldspar have comparable surface areas per unit mass (Blum and Erel, 1997). In the case of plagioclase to biotite weathering rates, the range is from 1/2.5 to 1/5 (Blum et al., 1994; Zuddas et al., 1995; Blum and Erel, 1997; Seimbille et al., 1998). In our calculation, we used ratios of 1/4 and 1/10 for the weathering rate of plagioclase to biotite and K-feldspars, respectively.

The model can be verified by comparing the IR_f calculation for given conditions of Sr abundance and isotopic characteristics of separate minerals with the $^{87}Sr/^{86}Sr$ ratio of water that has interacted with the rock. Such a validation method was applied to seven granitoids: Soultz-sous-Forêts, France (Zuddas et al., 1995; Pauwels, 1997), Chirac, France (this work), Coudes and Clermont-Ferrand, France (Stetller, 1977), Wind River Mountains, USA (Blum and Erel, 1997), Merced watershed, USA (Bullen et al., 1997) and Sierra Nevada, USA (Blum et al., 1994) and two basalts in the Massif Central, France (Chauvel, 1982; Négrel and Deschamps, 1996; Négrel, 1997).

A comparison of the results shows agreement between the calculated IR_f and the observed $^{87}Sr/^{86}Sr$ ratios in five granitoids and in the two basalts. A sensitivity analysis of the model was investigated in these granitoids and basalts by testing different weatherability ratios for the selected minerals (i.e. 1/5–1/10 for K-feldspars, 1/2.5–1/5 for biotite). The difference in the computed $^{87}Sr/^{86}Sr$ is always lower than 1×10^{-4}. However, two granitoids (Soultz-sous-Forêts, France and Wind River Mountains, USA) show higher $^{87}Sr/^{86}Sr$ ratios in waters than in the model calculation and so an additional source of Sr is required.

The calculated IR_f ratio of water after equilibration with the Sr derived from minerals was calculated for monzogranite and tonalite. Data of separate primary minerals are given in Table 4. Plagioclase and apatite have the lowest $^{87}Sr/^{86}Sr$ ratios (0.70450–0.70679). In the tonalite, plagioclase and apatite have similar $^{87}Sr/^{86}Sr$ ratios whereas in the monzogranite, the $^{87}Sr/^{86}Sr$ ratio of apatite is higher. Biotites have high $^{87}Sr/^{86}Sr$ ratios, reflecting higher Rb/Sr ratios (0.73428 in the monzogranite and 0.75491 in the tonalite). Potassic feldspars, only measured on the monzogranite have a relatively low $^{87}Sr/^{86}Sr$ ratio (0.70884). The abundance of plagioclase reaches 62% in the tonalites and 40% in the monzogranites. The abundance of biotite ranges between 7% and 10% in monzogranites and tonalites, respectively. Potassic feldspar abundance reaches 17% in the monzogranites but occurs in only trace amounts in the tonalites (close to 1%). Whole rock

Table 4
Strontium data from separate minerals (Plagioclase, KF, Biotite) used for the weathering model (see text)

Separate minerals	Abundance (%)	Sr (ppm)	$^{87}Sr/^{86}Sr$	Sr (ppm)[a]	$^{87}Sr/^{86}Sr$[a]
Tonalites					
Apatite	Trace amount	954	0.70451		
Plagioclase	62	930	0.70450		
K-feldspar	0.01	751	0.70880		
Biotite	10	61.2	0.75491		
Whole rock[b]		590	0.70503	582–778	0.70507–0.70605
Monzogranites					
Apatite /Plagioclase	40	990	0.70679		
Biotite	7	178	0.73428		
K-feldspar	17	750	0.70800		
Whole rock[b]		540	0.70704	418–588	0.70571/0.70822

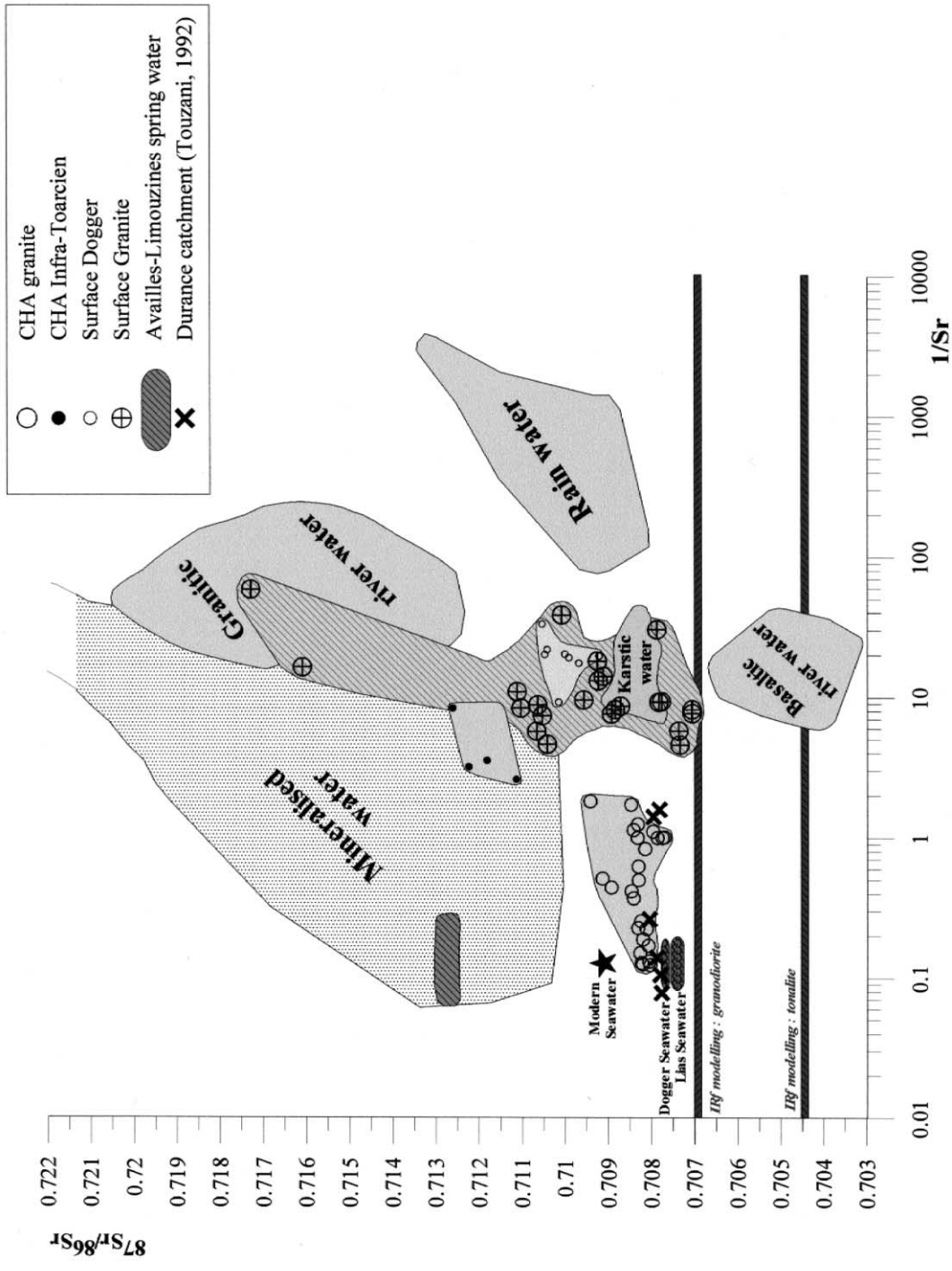
[a]Whole rocks; data from Zevenhuisen (1996) and Cuney et al. (1999).
[b]Recalculated using separate minerals.

data, recalculated from mineral abundance and individual mineral measurements (Table 4) are in agreement with that given by Zevenhuisen (1996) and Cuney et al. (1999).

Results of the Ir_f ratio calculations yield a low $^{87}Sr/^{86}Sr$ ratio for the tonalite (0.70463) and a higher one for the monzogranite (0.70704). When compared to Fig. 6, the results of the IR_f calculation (arrows) indicate that the deep groundwaters analysed within the Vienne hydrosystem cannot be directly linked with the weathering of tonalite and monzogranite. Clearly higher $^{87}Sr/^{86}Sr$ ratios are measured in water samples than the calculated $^{87}Sr/^{86}Sr$ ratios using the weathering model described above. This indicates that the water–rock interactions calculated are unable to predict the measured Sr values and so an additional source of Sr is required to model the system accurately.

It may be argued, as White et al. (1999) demonstrated, that disseminate calcite within the rock matrix could play an important role in controlling the Ca budget (and by analogy the Sr one). However, in the case of the Vienne granitoids, two arguments do not support this hypothesis. First, as Cuney et al. (1999) evidenced, the presence of calcite as replacment of plagioclases and biotites in the matrix is not important and the calcite amount is never higher than 1%. Secondly, as Kloppmann et al. (2001) have shown, after correction of contamination, the Ca/Sr ratio of the groundwaters is always lower than 100, which is not compatible with the dissolution of calcite. Recent work by Probst el al. (2000) demonstrate that the Sr isotopic budget in granite weathering is supported by weathering of three minerals (i.e. plagioclase, K-feldspar and biotite). One can supposed that the role of disseminate calcite in granite weathering is "site specific" and the presence of calcite in the matrix should be tested before computing a weathering model that use only primary minerals from the granite.

Fig. 7. Investigation of the strontium isotope systematics in waters from the Vienne district plotted in an expanded $^{87}Sr/^{86}Sr$ vs. 1/Sr diagram. Reported in this figure are the data of mineralised water in the Massif Central and the Pyrenees (Michard et al., 1976; Stetller, 1977; Stettler and Allègre, 1978; Krimissa, 1995; Négrel, unpublished data; Négrel, 1999; Négrel et al., 1997a,b, 2000; Pauwels et al., 1997). Rain waters in the Massif Central (Stettler and Allègre, 1978; Négrel and Roy, 1998), in the Morvan east of the Massif Central (Négrel, unpublished data) and in the north of the Vienne district (Grosbois et al., 2000), karstic waters and rivers draining sedimentary areas of Jurassic in the South of France (Hérault catchment, Petelet et al., 1998, and Durance catchment, Touzani, 1992), river waters draining granitic terrains in the south of the Massif Central (Négrel et al., 1997a; Négrel, 1999; Petelet et al., 1998) and in the Morvan east of the Massif Central (Roy, 1996; Roy et al., 1998), river waters draining volcanic areas from the Massif Central (Négrel and Deschamps, 1996; Négrel et al., 1997b). The mean Sr isotope composition for ocean water (Hodell et al., 1990; Dia et al., 1992) and for past ocean waters, the Dogger (Veizer and Compston, 1974; Burke et al., 1982) and Liassic oceans (Faure et al. 1978; Burke et al., 1982; Jones et al., 1994) are also recorded.


CHA granite
CHA Infra-Toarcien
Surface Dogger
Surface Granite
Availles-Limouzines spring water
Durance catchment (Touzani, 1992)
Granitic
River water
Rain water
Mineralised water
Karstic water
Basaltic River water
Modern Seawater
Dogger Seawater
Lias Seawater
IRf modelling : granodiorite
IRf modelling : tonalite
87Sr/86Sr
1/Sr
0.722
0.721
0.72
0.719
0.718
0.717
0.716
0.715
0.714
0.713
0.712
0.711
0.71
0.709
0.708
0.707
0.706
0.705
0.704
0.703
0.01
0.1
1
10
100
1000
10000

4.3. Comparison between surface and deep groundwaters

Distinct groups of waters can be distinguished on the basis of their strontium isotope systematics in an expanded $^{87}Sr/^{86}Sr$ vs. 1/Sr diagram (Fig. 7). A first field is defined by deep groundwaters from the Vienne district, with a variable Sr content and $^{87}Sr/^{86}Sr$ ratio (Fig. 6 and Section 4.2.3).

Mineralised water from springs emerging from granitic bedrock in the Massif Central (Michard et al., 1976; Stettler, 1977; Stetller and Allegre, 1978; Négrel, unpublished data; Négrel, 1999; Négrel et al., 1997a,b; 2000; Pauwels et al., 1997) and the Pyrenees (Krimissa, 1995) form a second field. The mineral spring waters from the Massif Central show $^{87}Sr/^{86}Sr$ ratios, in the range 0.713–0.718, and slightly variable Sr contents whereas mineral spring waters from the Pyrenees show more radiogenic $^{87}Sr/^{86}Sr$ ratios (range 0.71058–0.7395, Krimissa, 1995) and lower Sr contents. There is evidence of two extreme types of $^{87}Sr/^{86}Sr$ ratios in waters from granitic areas, one less radiogenic than the other, which reflects differences in the type of granitoid interacting with waters. The samples from Availles spring plots in this field revealing an intermediate Sr isotopic signature.

Different fields of surficial waters are reported in Fig. 7: Rain waters (Stetller and Allegre, 1978; Négrel and Roy, 1998; Négrel, unpublished data, Grosbois et al., 2000), karstic waters and rivers draining sedimentary areas of Jurassic (Petelet et al., 1998; Touzani, 1992), river waters draining granitic terrains (Négrel et al., 1997a; Négrel, 1999; Petelet et al., 1998; Roy, 1996; Roy et al., 1998), river waters draining volcanic areas (Négrel and Deschamps, 1996; Négrel et al., 1997b). The mean Sr isotope composition for ocean water (Hodell et al., 1990; Dia et al., 1992) and for past ocean waters, the Dogger (Veizer and Compston, 1974; Burke et al., 1982) and Liassic oceans (Faure et al. 1978; Burke et al., 1982; Jones et al., 1994) are also recorded in Fig. 7.

Large shaded areas mark some of the water populations. For example, rainwaters are delimited by a domain encompassing isotopic ratios from 0.708 to 0.712 and from 100 to more than 1000 for the 1/Sr ratio. River waters draining volcanic terrains are located in a restricted domain with regard to their $^{87}Sr/^{86}Sr$ and 1/Sr ratios (around 0.704 and 10, respectively). River waters draining granitic terrains show fluctuations in the 1/Sr ratios from 10 to 100 and a large range in the $^{87}Sr/^{86}Sr$ ratios (from 0.712 to 0.720). Three domains are located within the centre of this figure, namely the karstic waters in the Hérault catchment, and waters from the Dogger and Infra-Toarcian aquifers in the Vienne District. The shallow groundwaters from the Infra-Toarcian and Dogger aquifers have relatively high Sr isotopic ratios (0.70971 and 0.71179, respectively) supported by a low Sr content with a 1/Sr ratio close to 3.5 for the Infra-Toarcian aquifer and 17 for the Dogger aquifer. Surficial waters draining diorites and granites in the Vienne District occupy a vertical zone in Fig. 7 characterised by small fluctuations in Sr contents and larger ones in the $^{87}Sr/^{86}Sr$ isotopic ratios. They mostly range from the top of the basaltic water field (Négrel and Deschamps, 1996; Négrel et al., 1997b) to the middle of the granitic water field (Négrel et al., 1997a; Négrel, 1999; Roy, 1996; Roy et al., 1998; Petelet et al., 1998).

The meteoric input by rainwater is very dilute with respect to strontium and shows a $^{87}Sr/^{86}Sr$ ratio that is close to the range observed from karstic waters from the Hérault catchment (draining Jurassic deposits) to that of the Infra-Toarcian aquifer. The shallow groundwaters from the Infra-Toarcian may represent interaction between rainwater and rocks. This is suggested by contemporaneous increases in both Sr content and $^{87}Sr/^{86}Sr$ ratio with increased rainwater input. However, the increase in $^{87}Sr/^{86}Sr$ ratio cannot solely reflect weathering of the Jurassic sedimentary cover because this process should result in a $^{87}Sr/^{86}Sr$ ratio close to that of the Jurassic sediments (i.e. 0.708, Burke et al., 1982). Such an increase is exemplified in the karstic waters sampled from the Hérault catchment (Petelet et al., 1998), but may involve the weathering of the base of this sedimentary series composed of silicates (arkosic sediments). The Sr signature of the shallow groundwaters from the Dogger aquifer may result from interaction between rainwater and rocks plus anthropogenic disturbances due to the use of fertilisers (see Fig. 3 and related text). The increase of Sr content compared to rainwater is accompanied by a roughly similar Sr isotopic ratio and may reflect either

weathering of the Jurassic sedimentary cover ($^{87}Sr/^{86}Sr$ ratio close to 0.708, Burke et al., 1982) or the influence of fertilisers that have a $^{87}Sr/^{86}Sr$ ratio close to 0.708 (Fig. 4, Négrel, 1999).

Deep groundwaters are not covered by the field for mineral spring waters from the Massif Central and the Pyrenees or by any other field. Only the Sr contents of deep groundwaters are similar to the most concentrated mineralised waters in the Massif Central and Pyrenees. Moreover they have $^{87}Sr/^{86}Sr$ ratios clearly higher than that expected from the Ir_f modelling results of water–rock interaction with either tonalite or granodiorite, which would provide another source of Sr in these waters. These supplementary sources have $^{87}Sr/^{86}Sr$ in the range of the Mesozoic seawaters (Veizer and Compston, 1974; Faure et al. 1978; Burke et al., 1982; Jones et al., 1994) and actual seawater and are in virtual agreement with paleoseawater. Furthermore, a close resemblance can be seen between the $^{87}Sr/^{86}Sr$ ratios of deep groundwaters from the Vienne District with those from surficial drainage of Toarcian and Callovo–Oxfordian marine deposits (Touzani, 1992). This surficial drainage shows high Sr contents reflecting a high solubility of the Sr-bearing phases in these deposits associated with a Sr isotopic composition in the range of the ocean at the time of formation of the deposit (Veizer and Compston, 1974; Faure et al. 1978; Burke et al., 1982; Jones et al., 1994).

From Fig. 7, it appears that the deep groundwaters from the Vienne district plot away from the fields for mineral spring waters from granites and are almost identical in their $^{87}Sr/^{86}Sr$ ratios to paleoseawater. Larger geochemical investigations on deep groundwaters in the Vienne granitoids were carried out (Matray et al., 1998; Michelot, 1999; Casanova et al., 2001). As exemplified by Négrel et al. (1999) and Casanova et al. (2001), the Cl–Br data plot on a dilution curve between marine and dilute meteoric water end-members and fully agrees with a marine origin for the saline waters without evolution from seawater. As demonstrated by Négrel et al. (1999) and Casanova et al. (2001), the combined use of $\delta^{11}B$, Cl, B, Br, Sr contents and $^{87}Sr/^{86}Sr$ ratios makes it possible to define and quantify a mixing model between marine and crustal end-members in order to explain the origin of the deep groundwaters. Casanova et al. (2001) assume that the deep groundwaters from the Vienne district originated from marine incursions during the Jurassic and have been diluted by mixing with groundwaters produced by WRI with surrounding granitoids. Similar origin was stated by Beaucaire et al. (1999) for the saline waters in the Chardon mine, located north of the Vienne granitoids.

5. Conclusion

Sr isotope data from surface waters and shallow and deep groundwaters sampled from granitoids of the Vienne District (France) are presented in this paper. The surface waters delineate three different fields on a plot of electrical conductivity and pH with a clear influence from components of rainwater, weathering of carbonate rocks and silicate basement (granite and diorite). Moreover, Cl and NO_3 from some of the surface waters are clearly related to agricultural activities.

The Sr contents are in agreement with previous data published on waters derived from granitic and sedimentary rocks in France and a large range in $^{87}Sr/^{86}Sr$ ratios is observed. A rainwater input correction allows the Sr isotope systematics from rock weathering to be investigated along with anthropogenic disturbance. After correction, the waters plot within a mixing field defined by three end-members, one is anthropogenic (low $^{87}Sr/^{86}Sr$ and high Cl/Sr ratio) whereas the others are characterised by low Cl/Sr ratios and represent two extreme WRI $^{87}Sr/^{86}Sr$ signatures (0.707–0.720).

For deep groundwaters, a correction for the Sr introduced by cleaning fluids is necessary for the $^{87}Sr/^{86}Sr$ ratio and Sr contents. The lowest mean Sr content is found in borehole 115 ([Sr] = 11.3 μmol/l) associated with a low coefficient of variation (5%). Borehole 106 has the highests mean Sr content ([Sr] = 80.3 μmol/l) with a relatively low coefficient of variation (14%). Similar mean Sr contents are observed in boreholes 117 and 107 (30.0 and 30.5 μmol/l, respectively) but the coefficient of variations are close to 55% and 43%, respectively. Samples from borehole 212 yielded an intermediate mean Sr content ([Sr] = 53.9 μmol/l) but with a large coefficient of variation (78%).

A model to determine the $^{87}Sr/^{86}Sr$ ratio (Ir_f) of water after interaction with granitoid was developed based on the assumption that Sr was derived only from the three minerals: plagioclase, K-feldspar and biotite. Results of the Ir_f ratio calculations yielded a low Irf value for the tonalite (0.70463) and a higher Irf value for the monzogranite (0.70704) indicating that the deep groundwaters analysed within the Vienne hydrosystem cannot be directly linked with the weathering of tonalite and monzogranite as considered in the model. The measured $^{87}Sr/^{86}Sr$ ratios are clearly higher than the calculated $^{87}Sr/^{86}Sr$ ratios based on simple water-rock interaction and so an additional Sr source must be invoked. It is assumed that the deep groundwaters from the Vienne district originated from marine incursions during the Jurassic and have been diluted by mixing with groundwaters produced by WRI with the Vienne granitoids.

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Rare earth elements, neodymium and strontium isotopic systematics in mineral waters: evidence from the Massif Central, France

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Abstract

Rare Earth Elements (REEs), and Sr and Nd isotope distributions, have been studied in mineralized waters from the Massif Central (France). The CO_2-rich springs are characterized by a neutral pH (6–7) associated with total dissolved solids (TDS) from 1 to 7 g l^{-1}. The waters result from the mixing of very mineralized water pools, thought to have equilibrated at a temperature of around 200°C with superficial waters. These two mineral water pools evidenced by Sr isotopes and dissolved REEs could reflect 2 different stages of water–rock interaction and an equilibrium with different mineral assemblages.

The concentrations of individual dissolved REEs and total dissolved REEs (ΣREE), in the mineral waters examined, vary over several orders of magnitude but are not dependent on the main parameters of the waters (TDS, T°C, pH, Total Organic C). The dissolved REE concentrations presented as upper continental crust normalized patterns show HREE enrichment in most of the samples. The time evolution of REE patterns does not show significant fluctuations except in 1 borehole, located in the Limagne d'Allier area, which was sampled on 16 occasions over an 18 month period. Ten samples are HREE-enriched, whereas 6 samples show flat patterns.

The aqueous speciation of REEs shows that CO_3^{2-} complexes dominate (>80%) over the free metal, F^-, SO_4^{2-} and HCO_3^- complexes. The detailed speciation demonstrates that the fractionation of REEs (i.e. the HREE enrichment) in CO_2-rich and pH neutral fluids is due essentially to the predominance of the CO_3^{2-} complexes.

The Sr isotopic composition of the mineral waters in the Massif Central shows different mixing processes; in the Cézallier area at least 3 end-member water types exist. The most dilute end-member is likely to originate as poorly mineralized waters with minimal groundwater circulation. Two other mineralized end-members are identified, although the link between the geographical location of spring outflow and the mixing proportion between the 2 end-members is not systematic. The range in $\epsilon_{Nd}(0)$ for mineralized waters in the Massif Central correlates well with that of the known parent rocks except for 4 springs. One way to explain the $\epsilon_{Nd}(0)$ in these instances is a contribution from drainage of volcanic rocks. The isotopic systematics help to constrain the hydrogeological models for this area. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The study of rare earth elements (REEs) in natural waters initially involved an examination of their occurrence and behavior in seawater and coastal waters such as estuaries (Fleet, 1984; Elderfield et al., 1990; Bertram and Elderfield, 1993; Sholkovitz, 1995). Since the 1980s, REE geochemistry has been applied to continental waters such as rivers (Keasler and Loveland, 1982; Hoyle et al., 1984; Gaillardet, 1995; Gaillardet et al., 1997), lakes and groundwaters (Fee et al., 1992; Johannesson and Lyons, 1995; Johannesson et al., 1996). Alkaline mineral waters, all discharging from a granitic area, have been investigated in the Massif Central (Michard et al., 1987a,b; Sanjuan et al., 1988) and in the Pyrenees (Alaux-Négrel, 1991; Alaux-Négrel et al., 1993), whereas acidic natural waters have been largely investigated by Johannesson and Lyons (1995) and Johannesson et al. (1996), and references therein.

The process of weathering causes rocks with different chemical characteristics and ages to release Sr into water. Faure (1986) has shown that $^{87}Sr/^{86}Sr$ ratios vary according to Rb/Sr ratios and the age of the weathered material. Because Sr isotopes are not fractionated by any natural process, the measured differences in the $^{87}Sr/^{86}Sr$ ratios are due to the mixing of Sr derived from various isotopically different sources. The $^{87}Sr/^{86}Sr$ ratio variations within a hydrosystem can provide information about the sources of Sr and the different mixing processes involved (Albarède and Michard, 1987; Palmer and Edmond, 1992). If, in a given hydrosystem, Sr comes from 2 components with distinct isotopic compositions, the proportion of Sr derived from each component can be determined (Négrel et al., 1988, 1993). The Sm–Nd isotopic systematics are also related to radioactive decay, where the $^{143}Nd/^{144}Nd$ ratio varies according to the Sm/Nd ratio and the age of the weathered material. The Sr and Nd isotopic ratios would, in any case, not be altered by terrestrial processes and thus lead to a clear indication of the source material.

The isotopic composition of Nd and Sr are well established within the ocean basins (Piepgras et al., 1979; Piepgras and Wasserburg, 1980; Palmer and Edmond, 1989). On continental areas, large rivers have been investigated to constrain the Sr budget of the ocean (Wadleigh et al., 1985; Palmer and Edmond, 1992; Pande et al., 1994; and references therein) and to study weathering processes of the continental crust (Négrel et al., 1993; Allègre et al., 1996). However, Nd isotopic knowledge of waters draining the continental crust is meagre or lacking. Goldstein and Jacobsen (1987) determined the isotopic composition of Nd in the dissolved load of rivers from North America, Australia, Japan, the Philippines and Venezuela. Their data were mainly used to characterize the behavior of Nd during weathering and river transport and to increase knowledge of the Nd isotopic mass balance in the oceans. More recently, Andersson et al. (1992) reported Nd and Sr values in rivers and in the Baltic sea in order to characterize mixing between river and seawater in large estuarine areas.

Although the Sr isotopic data are better documented globally than are Nd isotopes in surface (Palmer and Edmond, 1992) and groundwaters (Stueber et al., 1993), few studies concerning the Sr isotope composition of waters of the French Massif Central have been carried out. Stettler (1977) and Stettler and Allègre (1978) used $^{87}Sr/^{86}Sr$ ratios in mineral waters from a geothermal area in the Cantal (Massif Central) to identify the different rock types through which the waters percolate. Michard et al. (1976) used Sr isotopes to study the chemical composition of a thermal reservoir in the Vichy basin. More recently, Négrel et al. (1997a, b, c) have used the Sr isotopic composition in selected areas of the Massif Central to investigate the discharge of mineral waters, and in particular from those issuing springs.

The current study analyzes the concentrations of Sr and REEs, and the isotopic composition of Sr and Nd in mineral waters from the Massif Central (France). The CO_2-rich springs are characterized by a neutral pH associated with a total dissolved solids (TDS) concentration of 1–7 g l^{-1}. The waters result from the mixing of very mineralized waters, thought to have equilibrated at a temperature of around 200°C (Fouillac, 1983; Berthier et al., 1982; Michard et al., 1987a,b), with near-surface waters. The aim of this study is to use Sr and Nd isotopes, and REE patterns, to characterize the sources and fluid paths of the mineralized spring waters, and the mixing processes within the crystalline bedrocks. Where the authors' previous studies in the Massif Central showed the potential of Sr isotopes for deconvoluting mixing in small areas (Négrel et al., 1997b, c), it is the intent here to expand this with a more detailed study of a larger area in the Massif Central.

Among the different parameters which can be used to characterize the REE patterns, the focus here is on: the La/Yb and Pr/Yb normalized ratio represented by $(La/Yb)_N$ and $(Pr/Yb)_N$ and the Ce and Eu anomalies represented by Ce/Ce^* and Eu/Eu^*. The $(La/Yb)_N$ and $(Pr/Yb)_N$ ratios are defined by the ratio La_{sample}/Yb_{sample} to the ratio La_{UCC}/Yb_{UCC} and Pr_{sample}/Yb_{sample} to the ratio Pr_{UCC}/Yb_{UCC}. UCC refers to Upper Continental Crust and data are from Taylor and McLennan (1985). The Ce and Eu anomalies after De Baar et al. (1985) are defined as $Ce/Ce^* = 2Ce_N/[La_N + Pr_N]$ and $Eu/Eu^* = 2Eu_N/[Sm_N + Gd_N]$. Ce_N, La_N, Pr_N, Eu_N, Sm_N and Gd_N correspond to the UCC normalized concentrations.

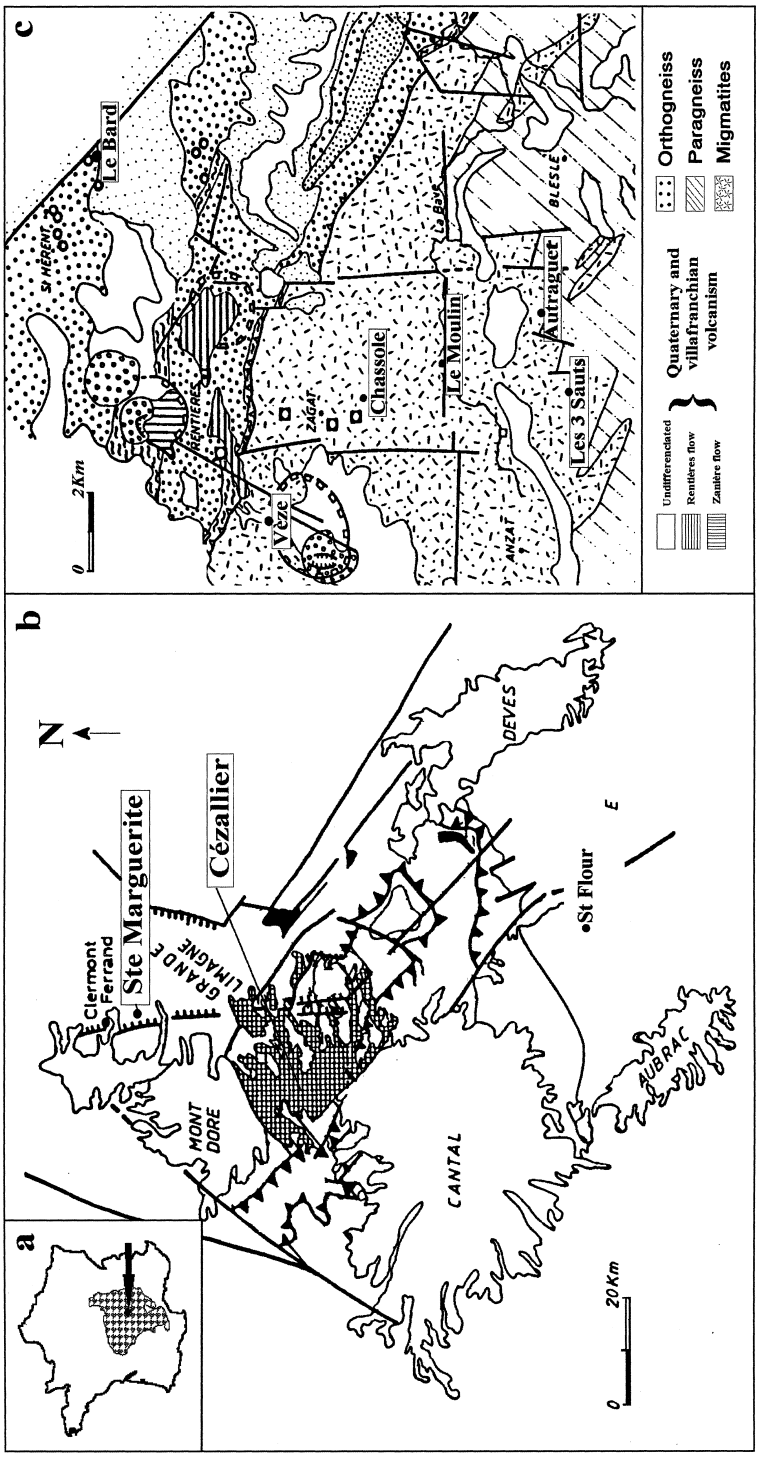

Fig. 1. (a and b) General location map of the study area and regional geological framework of the French Massif Central. (c) Regional geological framework of the Cézallier area in the Massif Central.

2. Hydrogeological settings

The Cézallier, Limagne d'Allier and Margeride areas are located in the French Massif Central (Fig. 1a and b). Granitoids and gneiss are the main lithologies. The Massif Central granitoids, generally medium-grained, range from leucogranite to quartz-diorite in composition; gneiss include ortho- and paragneiss. Both have been investigated for REE data, as well as Nd and Sr isotope systematics.

In the Limagne d'Allier area (namely Grande Limagne in Fig. 1b), the calc-alkaline monzonitic Viseen granite (327 M.a., Aubert et al., 1982) has an average composition of ~25% quartz, 39% plagioclase, 19% K-feldspar and 15% biotite. The REE patterns are LREE enriched with $(La/Yb)_N$ ranging from 0.80 to 1.92 (Downes and Duthou, 1988), and an Eu anomaly ranging from Eu/Eu* of 0.54 to 0.75. The granitoids in the Limagne d'Allier have $^{87}Sr/^{86}Sr = 0.71603–0.71746$ and an $\epsilon_{Nd}(0)$ of −8.2/−9.3 (Stettler, 1977; Downes and Duthou, 1988; Pin and Duthou, 1990).

A detailed description of the *Cézallier* area was given by Feuga (1987). It mainly comprises metamorphic Variscan basement (Fig. 1c), subdivided into ortho- and paragneiss, amphibolites and migmatites. Volcanic deposits occur on the lava plateau (Fig. 1c, Feuga, 1987). The orthogneiss are medium- to fine-grained and contain quartz, K-feldspar, oligoclase, biotite, apatite and zircons. Accessory minerals include garnet, corundum, rutile, sphene and illmenite. Few REE data are available on the Cézallier metamorphic rocks. However, in the Massif Central near the Cézallier area, Downes and Duthou (1988) and Barbey and Cuney (1987) show flat to HREE-enriched patterns with an $(La/Yb)_N$ ranging from 0.39 to 0.98 for the gneiss. All patterns have a strong negative Eu anomaly ranging from Eu/Eu* close to 0.23 to 0.36. The granitoids have flat to LREE-enriched patterns with an $(La/Yb)_N$ ranging from 0.80 to 2.63 and an Eu anomaly ranging from Eu/Eu* of 0.37 to 1.11. Few Nd isotope data are available on the Cézallier metamorphic rocks. However, in the Massif Central near the Cézallier area, Downes and Duthou (1988) give a range in the whole rock $^{87}Sr/^{86}Sr$ ratios of the granitoids from 0.71603–0.8622. For the whole gneiss (orthogneiss) collected elsewhere in the Massif Central, the $^{87}Sr/^{86}Sr$ ratio ranges from 0.73255 to 0.8689 and the $\epsilon_{Nd}(0)$ ranges from −6.3 to −9.

The Margeride massif consists of light and dark granite facies, average mineral compositions are around 37% quartz, 30% oligoclase, 23% K-feldspar and 10% biotite (light facies, Marchand et al., 1985) and 31% quartz, 30% andesine, 20% K-feldspar and 19% biotite (dark facies). In the Margeride granites (Cocherie, 1984; Williamson et al., 1996), the REE patterns are flat to HREE-enriched with a $(La/Yb)_N$ ranging from 0.64 to 1.06. The patterns have an Eu anomaly ranging from 0.52 to 2.83, attributed to the decreasing amount of K-feldspar (Cocherie, 1984). In the Margeride area, Couturié et al. (1979) reported whole rock $^{87}Sr/^{86}Sr$ ratios in the range 0.7211 to 0.7704. Downes and Duthou (1988) give a leucogranite whole rock $^{87}Sr/^{86}Sr$ ratio of 0.76846 ± 0.00003 and monzogranite whole rock of 0.72006–0.75115. A complementary study (Couturié and Vachette-Caen, 1980) on leucogranite intruding this granite gives whole rock $^{87}Sr/^{86}Sr$ ratios of 0.722–1.981. The $\epsilon_{Nd}(0)$ ranges from −4.8 for the leucogranites (Williamson et al., 1996) to −9.5 for the granite (Pin and Duthou, 1990).

In the Massif Central area, the mineralized waters are characterized by neutral pH (6–7), high CO_2 concentrations corresponding to $0.1 < PCO_2 < 1.0$ bar, with high concentrations of Fe and Al. Most of the sampled waters represent natural springs with the exception of a shallow borehole in the Limagne d'Allier area (Négrel et al., 1997a). The Na–Cl–HCO_3 springs in the Limagne d'Allier (Fig. 2b) emerge from granitic bedrock (Fouillac et al., 1975; Stettler, 1977), while the borehole in the Sainte-Marguerite area is located in the granitic body (Négrel et al., 1997a). Two water emergences were collected in 2 places (SM23D and G, SM51 and SM51G).

Around 50 CO_2-rich Na–HCO_3 cold springs (mean temperature: 10.2°C), generally accompanied by travertine deposits, have been inventoried in the Cézallier area (Fig. 2a, Criaud and Fouillac, 1986a, b). The springs emerge with a low flow rate (i.e. few l/min) from the intensively fractured basement, and have been classified into 4 groups (Michard et al., 1987a,b; Vuataz et al., 1987; Criaud and Fouillac, 1986a, b; Beaucaire et al., 1986) with regard to chemical ratios and stable isotopes (Fig. 2a). The different groups are the north group (6 springs), the centre group (12 springs), the south group (12 springs) and the southwest group (3 springs).

Few studies have considered the springs in the Margeride area (Fig. 2c). The Na–HCO_3 springs here emerge with a low flow rate near the occidental fault of the massif. Three springs are located in the vicinity of Le Mazel (spring Le Mazel, FB1 and FB2) and 2 near Le Ranc (Ranc1 and 2).

3. Sampling and analytical methods

3.1. Sampling

Water samples for REEs, Nd and Sr isotopic determination were collected in acid washed polyethylene bottles after filtering through pre-washed 0.2 μm Sartorius cellulose filters in cleaned teflon apparatus under

N_2. Samples were acidified with ultra pure HNO_3 to pH < 2. The pH was measured on-site using an Ingold electrode and an Orion 250 pH-meter previously calibrated using standard buffers. The electrical conductivity was measured with a microprocessor conductivity meter WTW LF96 standardized to 20°C.

3.2. REE concentrations and isotopic measurements

The determination of REE concentrations by inductively coupled plasma mass spectrometry is now a useful method (Smedley, 1991; Fee et al., 1992; Stetzenbach et al., 1994; Johannesson et al., 1994, 1996; Johannesson and Lyons, 1995). At the joint BGRM-INSU-LPS Laboratory at Saclay, a VG Plasma Quad 2plus spectrometer was used (ICP-MS, peak jumping mode). During the course of this work, direct measurements of REE were used (samples collected in 1994 and 1995, see Tables 1–3) and specific protocols involving REE preconcentration on cation exchange resin (10- to 20-fold preconcentration on AG 50WX8, Stetzenbach et al., 1994), for samples collected in 1996 (see Tables 1–3), or with $Fe(OH)_3$ co-precipitation (10- to 20-fold preconcentration, Piepgras et al., 1979) for samples collected in 1997 (see Tables 1–3), were applied to improve the detection limits for many samples containing low REE contents.

The analytical procedure used ^{139}La, ^{140}Ce, ^{141}Pr, ^{146}Nd, ^{147}Sm, ^{151}Eu, ^{157}Gd, ^{159}Tb, ^{163}Dy, ^{165}Ho, ^{167}Er, ^{169}Tm, ^{172}Yb and ^{175}Lu REE isotopes to minimize the effects of interference. Oxide and hydroxide interferences were corrected after analysis of pure solutions of

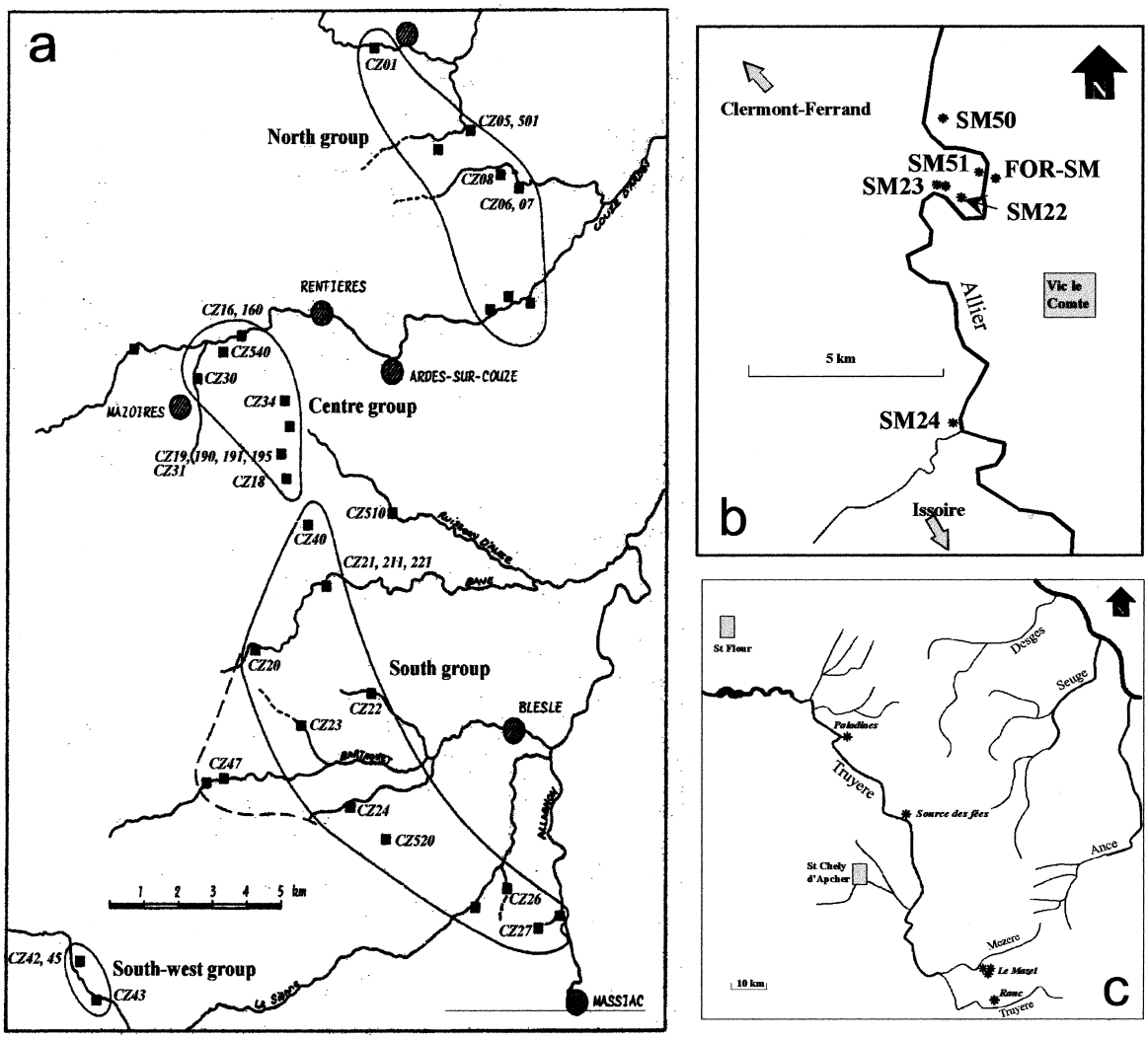

Fig. 2. Location and nomenclature for the mineralized springs in the Cézallier (a), Limagne d'Allier (b) and Margeride (c) areas.

Table 1
Data from the mineral water springs in the Limagne d'Allier region[a]

Sample	Date	T (°C)	C (μS/cm)	pH	La (ng l^{-1})	Ce (ng l^{-1})	Pr (ng l^{-1})	Nd (ng l^{-1})	Sm (ng l^{-1})	Eu (ng l^{-1})	Gd (ng l^{-1})	Tb (ng l^{-1})	Dy (ng l^{-1})	Ho (ng l^{-1})	Er (ng l^{-1})	Tm (ng l^{-1})	Yb (ng l^{-1})	Lu (ng l^{-1})	ΣREE (ng l^{-1})	$^{87}Sr/^{86}Sr$	Sr (mg l^{-1})	1/Sr	$^{143}Nd/^{144}Nd$	$\pm 2\sigma$ (M)	$\epsilon_{Nd}(0)$	1/Nd	Ce/Ce*	Eu/Eu*	La/Yb_N	Er/Nd_N
SM50	10/03/95	14	6760	6.42	39	15	< 5	< 15	31	21	55	< 5	27	< 5	23	< 5	35	< 5	< 286	0.713356	6.64	0.15	nd		–	–	–	2.44	0.08	–
SM22	10/03/95	23.6	6810	6.51	nd	52	9	35	33	22	65	6	13	< 5	22	7	30	< 5	< 332	0.713374	7.84	0.13	nd		–	–	0.01	2.06	–	27.63
SM24	10/03/95	11	3210	6.22	194	111	17	91	43	19	65	7	44	9	31	5	20	8	664	0.713609	3.27	0.31	0.512212	0.000005	−8.27	0.011	0.39	1.30	0.71	20.61
SM23	17/11/94	17.9	7010	6.43	25	31	11	45	64	28	51	7	36	10	32	9	30	10	389	0.713420	7.25	0.14	0.512451	0.000028	−3.61	0.022	0.41	2.88	0.06	32.89
SM23	17/11/94	15.9	4970	6.58	507	194	121	442	110	32	108	10	43	13	44	8	42	9	1683	0.713337	5.89	0.17	nd		–	–	0.18	2.24	0.89	4.11
SM23	10/03/95	12.4	6850	6.57	47	29	11	72	72	29	57	7	43	11	54	9	45	12	498	0.713260	6.64	0.15	nd		–	–	0.29	2.87	0.08	55.49
SM23	10/03/95	10.1	6780	6.66	57	47	13	85	86	21	80	11	45	13	57	10	52	14	591	0.713341	6.51	0.15	nd		–	–	0.39	1.87	0.08	49.57
SM51	17/11/94	13	6950	6.88	22	33	7	46	68	27	75	10	43	10	40	11	51	11	454	0.713365	7.02	0.14	nd		–	–	0.60	1.99	0.03	64.00
SM51	10/03/95	9.6	7560	6.99	38	15	10	65	58	20	75	8	39	11	40	10	43	10	442	0.713366	7.77	0.13	nd		–	–	0.18	1.35	0.06	45.22
SM51	10/03/95	6.7	6870	7.60	36	19	12	55	61	24	82	10	36	12	25	8	43	8	431	0.713390	6.59	0.15	nd		–	–	0.21	1.82	0.06	23.55
FOR.SM	15/12/93	18	7560	6.66	480	176	26	85	23	25	71	15	35	< 5	37	7	30	6	1016	0.713366	9.21	0.11	nd		–	–	0.28	2.39	1.17	16.09
FOR.SM	11/01/94	18	7170	6.60	387	194	30	94	32	27	88	13	52	9	32	10	52	7	1027	0.713361	7.79	0.13	nd		–	–	0.35	2.03	0.55	12.06
FOR.SM	11/04/94	nd	nd	nd	nd	6382	716	2190	73	31	205	23	68	14	41	8	57	11	9819	0.713356	13.73	0.07	nd		–	–	0.55	1.00	–	0.65
FOR.SM	28/07/94	nd	7510	nd	595	109	19	75	39	29	61	10	31	11	30	8	50	7	1074	0.713361	7.55	0.13	nd		–	–	0.15	2.67	0.87	17.85
FOR.SM	18/08/94	18.7	7500	6.41	149	125	12	86	18	30	70	8	37	5	28	9	22	5	604	0.713352	7.28	0.14	nd		–	–	0.59	3.04	0.50	26.38
FOR.SM	19/09/94	15.5	7850	6.42	465	189	25	70	36	15	76	8	31	6	38	8	36	6	1009	0.713375	7.47	0.13	nd		–	–	0.31	1.22	0.95	17.18
FOR.SM	05/10/94	17.6	7560	6.33	119	121	22	51	20	31	60	11	29	7	28	9	35	6	549	0.713357	7.57	0.13	nd		–	–	0.54	3.48	0.25	14.39
FOR.SM	29/10/94	17.5	7510	6.45	130	105	13	79	50	18	82	7	43	7	42	7	26	10	619	0.713360	7.65	0.13	nd		–	–	0.53	1.25	0.37	36.52
FOR.SM	17/11/94	17.2	7440	6.38	52	116	17	77	63	26	60	11	20	7	38	9	30	9	535	0.713442	7.85	0.13	nd		–	–	0.88	1.98	0.13	25.27
FOR.SM	16/12/94	16.6	7010	6.40	50	108	17	78	38	24	84	13	47	6	35	7	32	10	549	0.713448	7.40	0.14	nd		–	–	0.83	1.79	0.11	23.27
FOR.SM	17/01/95	15.9	7320	6.49	43	104	13	66	49	29	93	9	52	6	19	7	33	7	530	0.713480	7.71	0.13	nd		–	–	1.00	1.86	0.10	16.52
FOR.SM	06/03/95	15.4	7540	6.43	377	166	82	276	91	29	129	12	42	6	42	7	27	8	1294	0.713419	7.44	0.13	nd		–	–	0.22	1.22	1.02	5.79
FOR.SM	06/04/95	17.5	7030	6.48	45	98	15	72	58	23	89	11	44	< 5	29	10	61	8	563	0.713385	7.53	0.13	nd		–	–	0.85	1.44	0.05	21.86
FOR.SM	12/05/95	16.4	7540	6.48	82	104	14	74	55	26	72	9	46	5	41	8	35	8	579	0.713438	7.76	0.13	nd		–	–	0.69	1.90	0.17	33.11
FOR.SM	15/06/95	20.3	7350	6.56	< 5	7	< 5	< 15	< 15	16	33	< 5	< 10	< 5	< 15	< 5	18	< 5	< 74	0.713352	6.48	0.15	nd		–	–	–	–	–	–
FOR.SM	07/07/95	17.7	7680	6.52	45	111	14	81	46	36	59	15	40	5	32	7	30	6	527	nd	7.47	0.13	nd		–	–	1.00	3.18	0.11	25.84
FOR.SM	02/08/95 9 h	19.2	7460	6.43	48	101	16	67	58	27	64	7	47	6	23	9	28	7	508	nd	7.74	0.13	nd		–	–	0.82	2.06	0.13	16.25
FOR.SM	02/08/95 15 h	nd	nd	nd	49	100	14	73	62	36	73	10	44	< 5	26	9	24	9	529	nd	nd	–	nd		–	–	0.87	2.48	0.15	20.99

[a] Physico-chemical parameters measured in the field: temperature T (in °C), electrical conductivity C (in µS/cm standardized to 20°C) and pH. REE concentrations in ng l^{-1}, $^{87}Sr/^{86}Sr$ ratios and Sr concentrations in mg l^{-1}, $^{143}Nd/^{144}Nd$ ratios and $\epsilon_{Nd}(0)$, Ce and Eu anomalies and La/Yb_N and Er/Nd_N ratios (see text for calculations).

Table 2
Data from the mineral water springs in the Cézallier region (North group, Center group, South group and Southwest group)[a]

Sample	Date	T (°C)	C (μS/cm)	pH	La (ng l^{-1})	Ce (ng l^{-1})	Pr (ng l^{-1})	Nd (ng l^{-1})	Sm (ng l^{-1})	Eu (ng l^{-1})	Gd (ng l^{-1})	Tb (ng l^{-1})	Dy (ng l^{-1})	Ho (ng l^{-1})	Er (ng l^{-1})	Tm (ng l^{-1})	Yb (ng l^{-1})	Lu (ng l^{-1})	ΣREE (ng l^{-1})	$^{87}Sr/^{86}Sr$	Sr (mg l^{-1})	1/Sr	$^{143}Nd/^{144}Nd$	±2σ (M)	$\epsilon_{Nd}(0)$	1/Nd	TOC (mg l^{-1})	Ce/Ce*	Eu/Eu*	La/Yb_N	Er/Nd_N
North group																															
CZ1	03/95	7.2	4660	6.43	nd	417	82	378	94	26	96	9	71	5	40	6	40	9	1600	0.716236	3.65	0.27	0.512141	0.000007	−9.66	0.03	nd	–	1.28	–	1.20
CZ501	03/95	10.8	1650	5.66	nd	43	13	72	67	10	58	12	73	22	80	15	93	21	600	0.716359	1.22	0.82	0.512264	0.000006	−7.26	0.014	nd	–	0.75	–	12.56
CZ6	03/95	11.0	5870	6.59	36	9	5	16	38	20	51	< 5	27	6	22	11	54	8	295	0.716155	4.54	0.22	0.512154	0.000048	−9.40	0.063	nd	0.15	2.08	0.05	15.54
CZ7	03/95	13.7	5520	6.98	61	41	16	72	60	70	146	17	107	24	85	14	98	13	811	0.716188	4.43	0.23	0.512143	0.000018	−9.62	0.014	nd	0.30	3.07	0.05	13.35
CZ5	07/95	14.6	6000	6.97	37	97	16	68	24	18	67	< 5	34	7	< 15	7	39	6	414	0.716409	4.15	0.24	0.512245	0.000025	−7.63	0.015	2.68	0.87	1.78	0.07	–
CZ8	07/95	11.4	4650	6.20	14	23	8	30	24	49	56	6	44	9	40	9	31	7	343	0.716187	3.61	0.28	0.512244	0.000026	−7.65	0.033	2.16	0.45	5.55	0.03	15.07
CZ7	03/97	13.3	5700	6.45	54	21	42	27	11	17	39	11	84	19	59	8.4	51	8.4	406	0.716138	3.45	0.29	0.512179	0.000013	−8.91	0.037	nd	0.27	3.04	0.08	24.70
Center group																															
CZ18	04/94	8.0	5100	6.42	41	57	19	58	39	22	51	17	58	22	66	20	65	19	535	0.716773	2.30	0.44	nd		nd	0.017	nd	0.44	2.26	0.05	12.86
CZ19	04/94	6.0	4390	6.19	42	63	12	61	56	17	86	8	64	15	48	12	64	9	548	0.716723	3.00	0.33	nd		nd	0.016	nd	0.64	1.10	0.05	8.90
CZ31	04/94	5.2	2210	6.16	229	441	64	291	85	33	86	22	102	22	74	16	65	15	1530	0.715541	3.35	0.30	nd		nd	0.003	nd	0.83	1.81	0.26	2.87
CZ190	04/94	6.8	2170	6.59	29	43	12	49	48	19	33	11	30	10	35	10	34	8	363	0.716705	3.34	0.30	nd		nd	0.020	nd	0.51	2.23	0.06	8.07
CZ191	04/94	4.4	3180	6.54	16	13	9	52	39	11	37	8	31	7	38	8	30	11	299	0.716715	3.72	0.27	nd		nd	0.019	nd	0.23	1.36	0.04	8.26
CZ195	04/94	4.5	5250	6.01	20	21	9	48	42	12	49	10	52	14	64	10	58	11	409	0.716748	3.02	0.33	nd		nd	0.021	nd	0.34	1.23	0.03	15.07
CZ18	09/94	10.9	4900	6.48	58	55	13	29	23	15	70	5	25	9	51	10	47	9	410	0.716759	3.34	0.30	nd		nd	0.034	nd	0.46	1.45	0.09	19.88
CZ19	09/94	14.2	4340	6.33	262	84	13	55	33	23	91	9	73	17	51	12	59	14	782	0.716715	3.02	0.33	nd		nd	0.018	nd	0.25	1.67	0.33	10.48
CZ190	09/94	13.9	3090	6.91	62	84	9	32	< 15	13	36	< 5	14	< 5	< 15	< 5	12	< 5	< 262	0.716669	1.52	0.66	nd		nd	0.031	nd	0.79	–	0.38	–
CZ191	09/94	nd	3470	6.52	60	14	5	15	11	19	32	< 5	12	< 5	< 15	< 5	11	< 5	< 179	0.716721	2.08	0.48	nd		nd	0.067	nd	0.16	3.97	0.40	–
CZ195	09/94	nd	5100	6.58	320	98	69	268	86	29	83	13	81	24	78	15	87	14	1251	0.716743	3.49	0.29	nd		nd	0.004	nd	0.15	1.61	0.27	3.29
CZ160	03/95	6.1	3810	6.71	106	103	19	104	65	35	79	10	68	16	54	11	55	11	725	0.716723	2.29	0.512768	0.000009	2.57	0.010	1.46	0.52	2.26	0.14	5.87	
CZ18	03/95	7.9	4800	6.68	67	81	15	55	30	29	58	8	54	11	62	11	72	11	553	0.716752	3.20	0.31	nd		nd	0.018	nd	0.58	3.01	0.07	12.74
CZ19	03/95	6.1	4400	6.20	217	70	< 5	43	44	24	96	9	63	15	74	13	46	9	714	0.716754	3.18	0.31	0.512267	0.000007	−7.20	0.023	1.92	0.28	1.56	0.35	19.45
CZ31	03/95	4.9	2360	6.15	74	136	18	80	< 15	16	47	< 5	37	< 5	14	< 5	41	< 5	< 463	0.716515	1.45	0.69	0.512572	0.000008	−1.25	0.013	3.24	0.85	–	0.13	1.98
CZ195	03/95	3.8	5120	6.27	44	68	15	57	20	21	58	11	65	14	64	13	66	6	516	0.716762	3.57	0.58	nd		nd	0.018	2.43	0.59	2.42	0.05	12.69
CZ16	07/95	12.0	3750	6.31	19	19	7	64	41	22	49	8	34	9	37	8	27	8	344	0.716705	2.62	0.38	0.512329	0.000018	−5.99	0.016	nd	0.37	2.27	0.05	6.54
CZ30	07/95	15.1	3150	6.17	19	30	< 5	< 15	< 15	18	33	< 5	< 10	< 5	20	< 5	19	6	< 139	0.716476	2.38	0.42	0.512128	0.000006	−9.91	–	1.41	–	–	0.07	–
CZ195	07/95	13.6	5300	6.52	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.716756	nd	–	0.512160	0.000006	−9.29	–	nd	nd	nd	nd	nd
CZ191	07/95	14.7	4120	6.44	21	34	< 5	15	11	15	46	< 5	19	< 5	22	10	43	8	236	0.716728	2.86	0.35	0.512216	0.000011	−8.19	0.067	1.98	–	2.34	0.04	16.58
CZ540	07/95	14.6	4500	6.13	41	62	12	65	24	18	68	6	43	10	40	10	49	6	448	0.716679	2.86	0.35	0.512331	0.000050	−5.95	0.015	2.20	0.63	1.76	0.06	6.96
CZ34	12/95	4.0	5040	6.76	34	43	7	27	7	1	19	5.4	51	17	65	12	72	14	361	0.716746	2.06	0.49	0.512227	0.000032	−7.98	0.037	nd	0.62	0.34	0.03	27.21
CZ510	12/95	9.0	2700	6.29	99	76	14	54	13	2	24	5	41	12	42	8	46	8	435	0.718496	0.72	1.39	0.512216	0.000029	−8.19	0.019	nd	0.45	0.40	0.16	8.79
CZ18	03/97	9.4	4790	6.80	20	9	14	7	2	1	7	4	29	6	23	3	30	5	140	0.716743	2.53	0.39	0.512317	0.000015	−6.22	0.152	nd	0.31	0.64	0.06	39.39
CZ30	03/97	14.9	3160	6.21	22	7	11	4.7	1.40	0.3	3.50	nd	nd	2	7.7	1.2	9.40	1.4	61	0.716422	1.77	0.56	0.512464	0.000024	−3.36	0.213	nd	0.26	0.55	0.17	18.52
South group																															
CZ20	12/95	4.7	3300	6.23	382	543	84	322	67	21	68	9.7	61	14	39	5.7	34	5.5	1650	0.717215	0.91	1.10	0.512348	0.00004	−5.62	0.003	nd	0.69	1.46	0.82	1.37
CZ24	03/95	8.8	2080	6.16	95	50	8	32	11	15	29	< 5	19	< 5	20	< 5	15	5	< 294	0.717097	1.41	0.512246	0.000009	−7.61	0.031	nd	0.36	3.38	0.46	7.07	
CZ26	03/95	8.6	4450	6.31	185	281	50	219	64	28	132	22	147	40	136	23	156	25	1483	0.716965	3.24	0.31	0.512282	0.000004	−6.91	0.005	nd	0.66	1.30	0.09	7.02
CZ27	03/95	10.0	1630	6.38	185	357	48	202	92	21	104	26	195	51	182	29	208	34	1700	0.716321	1.07	0.93	0.512293	0.000007	−6.69	0.005	nd	0.86	1.00	0.07	10.19
CZ21	07/95	12.1	4120	6.41	17	33	11	16	17	< 5	22	7	39	13	61	10	293	0.718055	2.58	0.39	0.512188	0.000018	−8.74	0.063	1.31	0.49	0.61	0.02	27.55	
CZ211	07/95	13.4	3560	6.75	70	141	23	89	62	12	105	21	128	32	112	27	128	21	950	0.717715	2.29	0.44	nd		nd	0.011	1.26	0.79	0.66	0.04	14.23
CZ221	07/95	11.7	3850	6.13	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	–	0.718124	nd	–	0.512188	0.000010	−8.74	–	1.07	–	–	–	–
CZ22	07/95	15.5	4100	6.57	13	17	26	19	34	6	48	< 5	17	< 5	< 15	< 5	32	7	< 212	0.718796	1.94	0.52	0.512289	0.000024	−6.77	0.053	nd	0.13	0.68	0.03	–
CZ23	07/95	14.2	3250	6.29	12	14	< 5	< 15	25	7	44	< 5	12	< 5	26	< 5	44	< 5	< 184	0.718637	1.94	0.52	0.512243	0.000018	−7.67	–	1.47	–	0.93	0.02	–
CZ40	07/95	14.6	5410	6.51	12	14	7	< 15	16	14	42	< 5	11	< 5	34	6	22	7	< 178	0.717792	3.00	0.33	0.512139	0.000009	−9.69	–	1.85	0.32	2.18	0.04	–
CZ520	07/95	14.3	4390	6.42	51	29	7	38	< 15	13	38	< 5	24	7	45	9	58	11	< 319	0.716826	3.07	0.33	0.512221	0.000009	−8.10	0.026	nd	0.34	–	0.06	13.39
CZ47	12/95	6.9	4830	6.42	27	39	6	19	5	1	7.8	1.8	13	4.5	18	3.9	26	5.4	172	0.717355	2.20	0.45	0.512158	0.000032	−9.32	0.053	nd	0.72	0.81	0.08	10.71
CZ21	03/97	11.2	4100	6.52	24	22	3.2	19.00	6.60	1.50	21.00	8.10	75	19	66	12.00	81.00	13.00	358	0.718068	1.86	0.54	0.512175	0.000013	−8.99	0.053	nd	0.55	0.49	0.02	39.27
CZ22	03/97	9.6	3870	6.70	21	10	1.3	6.30	1.40	0.90	6.50	nd	nd	3.3	12	2.1	16.00	2.90	81	0.718793	1.53	0.65	0.512161	0.000052	−9.27	0.159	nd	0.35	1.01	0.10	21.53
CZ23	03/97	10.0	3520	6.35	31	11	1.4	5.50	0.70	0.20	3.60	nd	nd	1.8	8	1.3	9.30	1.50	73	0.718672	1.40	0.72	0.512295	0.000008	−6.65	0.182	nd	0.28	0.41	0.24	15.42
Southwest group																															
CZ42	03/95	11.4	3130	6.44	nd	35	6	< 15	< 15	19	37	< 5	< 10	< 5	13	< 5	24	< 5	nd	0.716773	1.70	0.59	0.512623	0.000015	−0.25	–	nd	–	–	–	–
CZ45	03/95	11.3	1830	6.52	15	13	6	44	35	21	33	< 5	32	7	19	7	24	7	< 256	0.716050	1.03	0.97	nd		nd	0.023	nd	0.30	2.90	0.05	4.88
CZ43	07/95	11.3	3430	6.35	98	275	35	106	51	19	53	< 5	26	< 5	18	< 5	17	< 5	< 698	0.716338	1.59	0.63	0.512247	0.000027	−7.59	0.009	0.72	1.05	1.71	0.42	1.92

[a] Physico-chemical parameters, Rare Earth Elements, $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios as in Table 1.

Table 3
Data from the mineral water springs in the Margeride region[a]

Sample	Date	T (°C)	C (μS/cm)	pH	La (ng l^{-1})	Ce (ng l^{-1})	Pr (ng l^{-1})	Nd (ng l^{-1})	Sm (ng l^{-1})	Eu (ng l^{-1})	Gd (ng l^{-1})	Tb (ng l^{-1})	Dy (ng l^{-1})	Ho (ng l^{-1})	Er (ng l^{-1})	Tm (ng l^{-1})	Yb (ng l^{-1})	Lu (ng l^{-1})	ΣREE (ng l^{-1})	$^{87}Sr/^{86}Sr$	Sr (mg l^{-1})	$^{143}Nd/^{144}Nd$	±2σ (M)	$\epsilon_{Nd}(0)$	1/Nd	Ce/Ce*	Eu/Eu*	La/Yb$_N$	Lu/La$_N$	Er/Nd$_N$
Mazel	09/94	9.5	2170	6.60	123	261	37	171	74	23	96	14	72	19	71	16	73	15	1065	0.713149	1.41	nd	–	–	–	0.006	0.83	1.25	0.12	0.00	45.56
FB1	09/94	9.8	3950	6.61	27	23	12	53	58	21	67	12	60	18	63	14	65	17	510	0.712968	3.76	nd	–	–	–	0.019	0.28	1.56	0.03	0.00	130.42
FB2	09/94	8.7	4020	6.58	50	33	20	78	57	26	73	15	67	17	72	20	99	19	646	0.713029	3.83	nd	–	–	–	0.013	0.24	1.85	0.04	0.00	101.28
Source Fées	09/94		339	6.77	17	12	7	30	25	7	43	6	21	5	30	8	38	6	255	0.716906	0.10	nd	–	–	–	0.033	0.25	0.94	0.03	0.00	109.72
Mazel	05/95	9.7	2200	6.54	23	26	6	45	42	24	40	6	32	11	24	7	35	7	328	0.713167	1.95	0.512247	0.00004	−7.59	0.022	0.37	2.75	0.05	0.00	38.52
FB1	05/95	9.2	3800	6.69	42	16	6	30	48	13	54	7	43	12	62	11	66	15	425	0.712968	4.76	0.512059	0.000025	−11.26	0.033	0.19	1.19	0.05	0.00	226.75
FB2	05/95	9.8	3020	6.50	53	46	12	62	74	22	58	7	55	12	35	12	54	8	510	0.712954	3.94	0.51215	0.000012	−9.48	0.016	0.36	1.58	0.07	0.00	61.94
Ranc1	05/95	23.2	1580	6.56	39	26	10	56	60	23	46	6	36	9	39	5	39	10	404	0.715965	0.44	0.512051	0.000013	−11.41	0.018	0.26	2.05	0.07	0.00	76.41
Ranc2	05/95	8.6	2580	6.79	30	10	< 5	< 15	< 15	10	25	< 5	< 10	< 5	< 15	< 5	< 10	< 5	–	0.716360	0.28	0.512078	0.000045	−10.88	–	–	–	–	–	–
Paladines	05/95	8.4	1630	6.55	9	11	< 5	< 15	< 15	< 5	< 20	< 5	< 10	< 5	< 15	< 5	< 10	< 5	–	0.716241	0.02	nd	–	–	–	–	–	–	–	–

[a] Physico-chemical parameters, Rare Earth Elements, $^{87}Sr/^{86}Sr$ and $^{143}Nd/^{144}Nd$ ratios as in Table 1.

Ba, Ce, Pr, Nd, Sm, Eu, Gd and Tb at 100 μg l^{-1}. Instrumental drift was monitored and corrected using ^{115}In and ^{187}Re, where both internal standards were used according to an interpolation procedure.

The calibration was performed using a SPEX standard solution at 10 μg ml^{-1}: a series of 8 dilutions of this standard permitted the construction of a calibration curve (range 0.02–100 μg l^{-1}, extrapolated to 0 after blank correction). A blank correction was applied to all samples and standard solutions. Sample, standard and blank solutions were acidified in HNO_3 2% suprapur acid. Pure water (18 MΩ, alpha-Q Millipore) was used for sample dilution, standard solutions and blanks. The precision of the REE measurements ranged between 5 and 10% for concentrations around 100–1000 ng l^{-1}. The detection limits for direct measurements on natural water are: 1–5 ng l^{-1} (Pr, Tb, Ho, Tm, Yb, Lu), 2–10 ng l^{-1} (La, Ce, Eu) and 5–15 ng l^{-1} (Nd, Sm, Gd, Dy, Er), calculated at 3σ.

The Nd isotopic compositions were determined for 37 water samples following the method used for seawater (i.e. Jeandel, 1993). Nd was extracted from 1–4 l of water using $Fe(OH)_3$ coprecipitation (Piepgras et al., 1979). Ten milligrams of ultrapure Fe was added to each liter of acidified sample. The pH was then brought to 7.5 by using concentrated ultrapure NH_4OH. After vigorous shaking for 1 day, flocculation occurred over the course of 1 week. More than 95% of the Nd was recovered in the precipitate, whereas major cations remained in the supernate. After extraction of the supernate followed by several centrifugation steps, the precipitate was dissolved with 2.5 N HCl and evaporated to dryness. Neodymium was then separated using classical cation exchange followed by HDEHP reverse chromatography (White and Patchett, 1984). Total procedural blank was less than 100 pg.

The Nd isotopic ratios were measured using a Finnigan MAT 262 multiple collector mass spectrometer with samples loaded on double Re filaments. The $^{143}Nd/^{144}Nd$ ratios were normalized to an $^{146}Nd/^{144}Nd = 0.7219$ and then adjusted to the value of 0.511860 of the La Jolla standard. Repeated measurements of the La Jolla international standard during the period of analysis yielded a mean $^{143}Nd/^{144}Nd$ of 0.511826 ± 0.000011 (2σ, n = 33). The $^{143}Nd/^{144}Nd$ ratios are expressed as $\epsilon_{Nd}(0)$ which represents the deviation in parts per 10^4 (ε units) from $^{143}Nd/^{144}Nd$ in a chondritic reservoir with a present day CHUR value of 0.512636 (De Paolo and Wasserburg, 1976).

Standard cation exchange chemistry was adopted for chemical separation and mass spectrometry for Sr (Négrel and Deschamps, 1996). Mass spectrometry analyses of Sr were performed on a Finnigan MAT 262 multiple collector mass spectrometer on a single W filament with a Ta activator. $^{87}Sr/^{86}Sr$ ratios were determined for all water samples. The total blank for

Sr was less than 0.5 ng for the entire procedure (sampling, filtration, storage and chemical separation). The $^{87}Sr/^{86}Sr$ ratios were normalized to an $^{86}Sr/^{88}Sr$ ratio of 0.1194. The in-run precision of the $^{87}Sr/^{86}Sr$ ratio is generally better than $\pm 10 \times 10^{-6}$ (2σ m). The reproducibility of $^{87}Sr/^{86}Sr$ ratio measurement was tested by replicate analyses of the NBS 987 standard, with the mean value obtained during this study being 0.710227 ± 0.000017 (2σ, $n = 70$).

4. Results and discussion

Because of the similarity in their physical and chemical properties, the REEs behave as a coherent chemical group in terrestrial surface processes and in granite-gneiss rocks. They are associated with feldspars and micas as trace elements and as major constituents in accessory minerals (Henderson, 1984). The mobilization of REEs during water–rock interaction depends on different factors, such as the abundance of REEs in parent rocks, the distribution of REEs in the primary bearing minerals (most important), and the stability of these minerals with regard to weathering processes (Nesbitt, 1979; Humphris, 1984). It is generally agreed that the light REEs (LREEs) are less mobile than the heavy REEs (HREEs) such that the LREEs are enriched in the solid residual (Braun et al., 1990).

4.1. Dissolved REE concentrations

The concentrations of individual dissolved REEs, and total dissolved REEs (ΣREE) in the investigated mineral waters, vary over several orders of magnitude. In the Limagne d'Allier area (Table 1), where 7 springs were analyzed, the dissolved ΣREE concentrations range from <256 ng l^{-1} (SM50) to 1683 ng l^{-1} (SM23). In the Cézallier area (Table 2), ΣREE varies from 295 ng l^{-1} (CZ6) to 1584 ng l^{-1} (CZ01) in the north group (7 springs). In the centre group where 25 springs were analyzed, some on several occasions, the range of ΣREE is 61 ng l^{-1} (CZ30) to 1530 ng l^{-1} (CZ31). In the south group where 13 springs were analyzed, some several times, the ΣREE ranges from 73 ng l^{-1} (CZ23) to 1700 ng l^{-1} (CZ27). In the southwest group (3 springs), the ΣREE varies from <256 ng l^{-1} (CZ45) to <698 ng l^{-1} (CZ43). In the Margeride area (Table 3), where 5 springs were analyzed, the ΣREE ranges from 255 ng l^{-1} (SDF) to 1065 ng l^{-1} (Mazel). The REE contents obtained in the present study agree with previous investigations carried out in the Massif Central by Michard et al. (1987a,b) and Sanjuan et al. (1988).

The variation in concentration of individual dissolved REEs can be illustrated by Nd. The Nd concentrations ranged from 5 to 378 ng l^{-1} in the Cézallier where all groups evidenced a similar range. The Nd concentrations fall in the same range in the Limagne d'Allier, whereas in the Margeride, the Nd concentration only reaches 170 ng l^{-1} (Mazel). By comparison, Alaux-Négrel (1991) found Nd concentrations around 100–160 ng l^{-1} in mineral waters from the Pyrénées, whereas Sanjuan et al. (1988) and Michard et al. (1987a,b) observed Nd concentrations of 7–15 ng l^{-1}.

The lack of a clear relationship between either ΣREE or the individual dissolved REE concentrations and the TDS seems to indicate that the dissolved REE concentrations in mineral waters are not initially related to the salinity of the water. Likewise, as shown by Michard et al. (1987a,b) and Sanjuan et al. (1988), the concentration of individual REEs are not temperature dependent, especially in regards to water collected from the spring surface, and by drilling at Chassole (Fig. 2).

Several workers have shown that pH can play an important role in REE concentrations. All relevant data published thus far (Goldstein and Jacobsen, 1987; Elderfield et al., 1990; Keasler and Loveland, 1982; Fee et al., 1992; Johannesson et al., 1994; Dupré et al., 1996) suggest an inverse relationship between pH and ΣREE. That is, higher REE concentrations correspond to lower pH values. Such a correlation is observed in surface waters collected in the Margeride area (waters from rivers adjacent to the springs studied here) with a correlation coefficient of 0.92 (Négrel, unpublished data). This kind of relationship is generally attributed to colloidal control or to adsorption processes. Of all the mineral waters from the Massif Central (Cézallier, Limagne d'Allier and Margeride), there is no evidence of this type of relationship either between pH and ΣREE ($R = -0.26$), individual REE, or Er/Nd. This may be due to the low pH variations in the mineral waters (mean value 6.48 ± 0.26) and these results agree with the previous work on CO_2-rich waters by Michard et al. (1987a,b) and Sanjuan et al. (1988), which have shown that REE concentrations are not affected by the degassing of CO_2 at the spring outcrop and therefore are not pH dependent.

The existence of large concentrations of organic matter in surface waters may be responsible for this effect (see Dupré et al., 1996, for a review). In some mineral waters sampled during this work, total organic C (TOC) ranges from 0.72 mg l^{-1} (CZ43) to 3.24 mg l^{-1} (CZ31). However, there is no relationship between the TOC and the dissolved REE concentrations ($r = 0.01$), implying that organic matter does not play a significant role in controlling the dissolved REE concentrations in mineral waters.

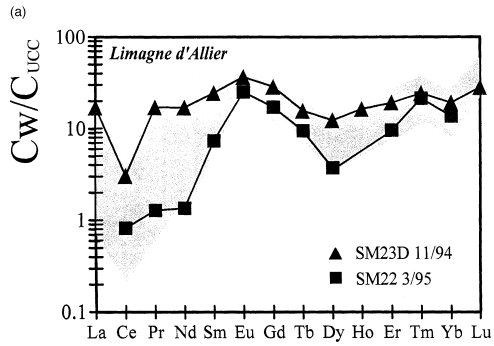

Fig. 3a. Dissolved REE patterns Cw normalized to the Upper crust (C_{UCC}) of the mineralized springs in the Limagne d'Allier.

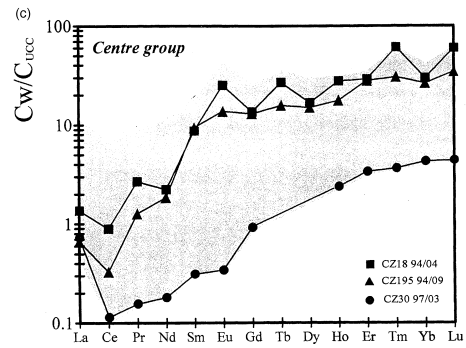

Fig. 3c. Dissolved REE patterns Cw normalized to the Upper crust (C_{UCC}) of the mineralized springs in the center group of the Cézallier area.

4.2. Dissolved REE patterns

4.2.1. General observations

Dissolved REE concentrations are presented as Upper Continental Crust (UCC, Taylor and McLennan, 1985) normalized patterns in Fig. 3. The UCC was chosen as being more representative of the bedrocks from which the mineral waters emerge. The dissolved REE patterns in Fig. 3 are plotted with respect to each region (Limagne, Cézallier and Margeride) and within the Cézallier district, and are reported for each of the spring groups. In the Limagne, north, centre and south groups of the Cézallier, all dissolved REE patterns are included in a shaded area and the most representative springs (i.e. historical springs, higher salinity, larger flow ...) of the area are illustrated.

In the Limagne d'Allier (Fig. 3a, Table 1), the dissolved REE exhibited relatively uniform patterns with enrichment in heavy REEs (HREEs) relative to the light REEs (LREEs). The springs SM22 and SM23D were chosen as the most representative springs of the area. Their $(La/Yb)_N$ and $(Pr/Yb)_N$ ratios range from 0.09 to 0.89. Spring SM22 is HREE enriched, whereas SM23D (and also SM24, Table 1) have a relatively flat pattern with regard to their $(La/Yb)_N$ and $(Pr/Yb)_N$ ratios. All patterns have a negative Ce anomaly with Ce/Ce^* ranging from 0.01 to 0.18 and a positive Eu anomaly around 2.1–2.2.

In the *north group* of the Cézallier area (Fig. 3b, Table 2), springs CZ6 (Gallo-roman spring) and CZ7 (larger flow) were chosen as the most representative springs. Their dissolved REE patterns show HREE enrichment $\{(La/Yb)_N = 0.05, (Pr/Yb)_N = 0.03–0.05\}$, as for the other springs included in the shaded area. The Ce anomaly is always negative with $Ce/Ce^* = 0.15–0.30$ in CZ6 and 7 and 0.87 in CZ5 (Table 2). The Eu anomaly is close to 2.1–3.1 in CZ6 and 7. This anomaly is more variable than in the Limagne d'Allier spring waters with Eu/Eu^* reaching 5.6 in CZ8 (Table 2), and 1 spring has a negative Eu anomaly (0.75, CZ501, Table 2). In the *centre group* (Fig. 3c, Table 2), springs CZ18 (19th century spring), CZ195

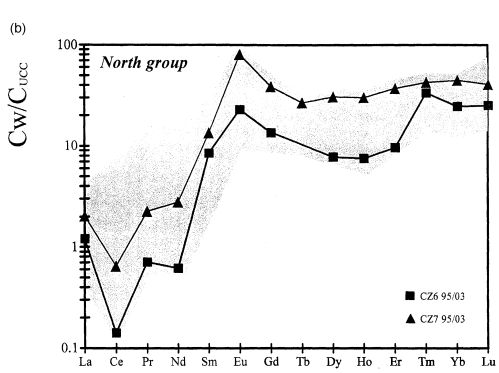

Fig. 3b. Dissolved REE patterns Cw normalized to the Upper crust (C_{UCC}) of the mineralized springs in the north group of the Cézallier area.

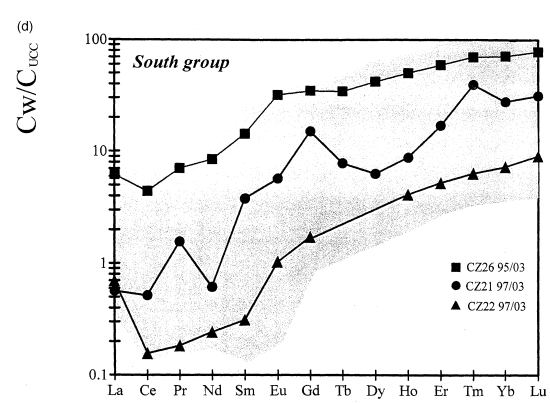

Fig. 3 d. Dissolved REE patterns Cw normalized to the Upper crust (C_{UCC}) of the mineralized springs in the south group of the Cézallier area.

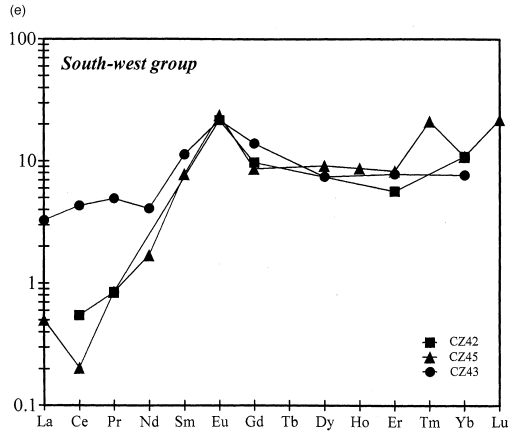

Fig. 3e. Dissolved REE patterns Cw normalized to the Upper crust (C_{UCC}) of the mineralized springs in the southwest group of the Cézallier area.

(higher salinity) and CZ30 (larger flow) were chosen as the most representative springs. Their dissolved REE patterns are HREE-enriched {$(La/Yb)_N = 0.05–0.27$, $(Pr/Yb)_N = 0.04–0.25$}. The Ce anomaly is always negative ($Ce/Ce^* = 0.15–0.44$). The Eu anomaly is positive: 1.6 and 2.3 in CZ195 and 18 and up to 3.9 in CZ191 (94/09, Table 2), but in CZ50 the Eu anomaly is <1 (0.55), as in 3 other springs (Table 2). In the *south group* (Fig. 3d, Table 2), springs CZ21 (larger flow), CZ22 (larger diffusive emergence) and CZ26 (19th century spring) were chosen as the most representative springs. Their dissolved REE patterns show HREE enrichment {$(La/Yb)_N = 0.02–0.10$, $(Pr/Yb)_N = 0.01–0.10$}. The Ce anomaly is always negative {$Ce/Ce^* = 0.35–0.66$}. The Eu anomaly fluctuates greatly, with negative anomaly (0.49 in spring CZ21) as for 3 other springs (Eu/Eu^* in the range 0.41–0.68, Table 2), and positive anomaly (1.01–1.3 in springs CZ22 and 26) as also in 3 other springs (Eu/Eu^* in the range 1.3–3.4). In the *southwest group* (Fig. 3e, Table 2), the dissolved REE patterns are HREE-enriched {$(La/Yb)_N = 0.05–0.4$, $(Pr/Yb)_N = 0.08–0.64$}. The Ce anomaly is negative in 2 springs ($Ce/Ce^* = 0.07–0.3$) and slightly positive in 1 spring ($Ce/Ce^* = 1.04$). The Eu anomaly is positive with Eu/Eu^* (1.7 and 2.9).

In the Margeride area (Fig. 3f, Table 3), the dissolved REE patterns are HREE-enriched {$(La/Yb)_N = 0.03–0.12$, $(Pr/Yb)_N = 0.03–0.16$}. Europium shows a slight positive anomaly with Eu/Eu^* ranging from 1 to 2.8, whereas Ce shows a negative anomaly with Ce/Ce^* ranging from 0.19 to 0.83.

The conclusion of this descriptive REE study is that most waters are characterized by HREE enrichment {$(La/Yb)_N < 0.4$, $(Pr/Yb)_N < 0.6$} and large positive $(Er/Nd)_N$ values (Tables 1–3). Similar REE patterns occur in the Vichy basin and Vals les bains (Michard et al., 1987a,b; Sanjuan et al., 1988) and in the Pyrenees (Alaux-Négrel, 1991).

4.2.2. Time evolution of dissolved REE patterns

During this work, some mineral spring waters were collected several times in order to investigate the potential for dissolved REE variation with time.

In the Limagne d'Allier, springs SM23 (D and G) and SM51 were sampled twice; 1 borehole (FOR.SM, Fig. 1b) in the Sainte-Marguerite area was investigated for major element concentrations and Sr isotopes from

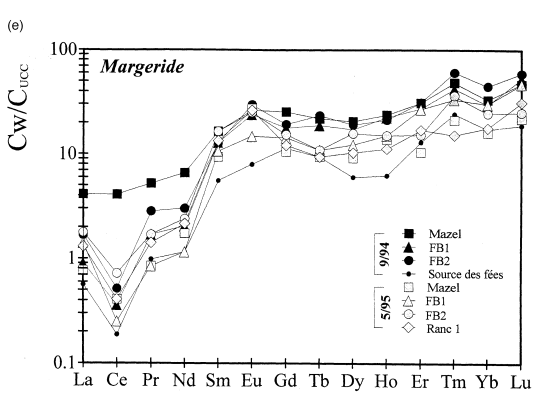

Fig. 3f. Dissolved REE patterns Cw normalized to the Upper crust (C_{UCC}) of the mineralized springs in the Margeride.

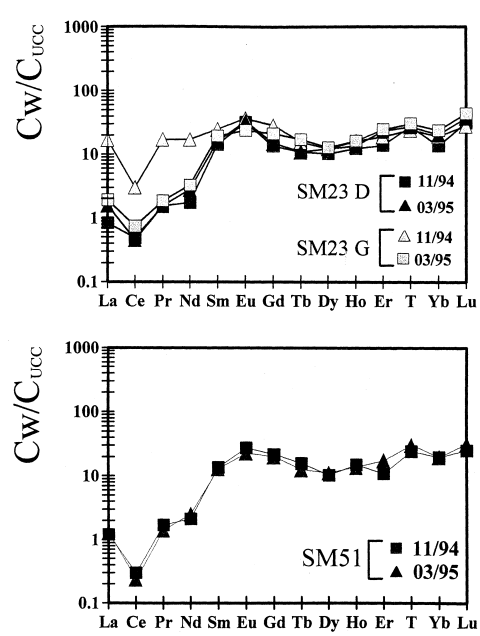

Fig. 4. Dissolved REE patterns Cw normalized to the Upper crust (C_{UCC}) of the mineralized springs SM23 and SM51 in the Limagne d'Allier collected at different periods.

January 1994 to August 1995 (Négrel et al., 1997a), for a total of 17 times in all. In the *north and south groups* of the Cézallier area, springs CZ7 and CZ21 were sampled twice. In the *centre group*, 5 springs were sampled several times. No springs in the *southwest group* were sampled more than once. In the *Margeride area*, 3 springs were sampled twice. All dissolved REE patterns are very similar, illustrated by the patterns of springs SM23 and SM51 (Fig. 4) which do not differ from the general representation of REEs in Fig. 3a. However, it is noteworthy that SM23G collected in November 1994 exhibits higher LREE than the 3 other springs, inducing a flatter pattern for this sample.

One important feature in the previous study of the borehole FOR.SM is the constancy of Cl concentrations in the water during the sampling period (Négrel et al., 1997a). Chlorine is a mobile element which, unlike most other elements, is not controlled by dissolution–precipitation processes. The constancy of the Cl concentration reflects the lack of dilution–concentration effects in mineral waters through climatic variations over the year. Moreover, in the Cézallier region, a slight but significant variation in the dissolved $^{87}Sr/^{86}Sr$ ratios reflects the existence of at least two mineral pools with similar chemistry, but different Sr isotopic signatures (Négrel et al., 1997b).

The dissolved REE concentrations for repetitive sampling of borehole FOR.SM are presented in Table 1 along with UCC normalized patterns in Fig. 5. In spite of variations in the elemental abundances, as illustrated, for example, by the Nd variations from 51 ng l^{-1} to 276 ng l^{-1}, 15 REE patterns are HREE-enriched, with $(Pr/Yb)_N < 0.3$ and 2 samples have patterns with $(Pr/Yb)_N$ values >0.9. There is no relationship between the $(Pr/Yb)_N$ ratio (and, therefore, the REE profile) and time. The dissolved REE pattern reflects a single behavior in water from borehole FOR.SM. Europium always exhibits a positive anomaly, with Eu/Eu* ranging from 1.0 to 3.5.

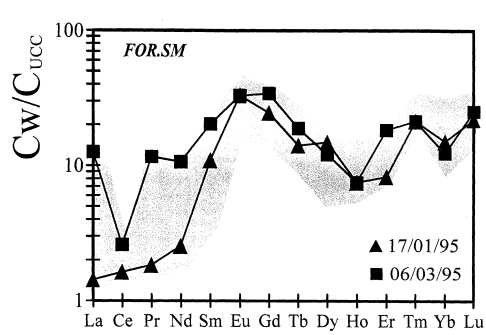

Fig. 5. Dissolved REE patterns Cw normalized to the Upper crust (C_{UCC}) of the mineralized water in the borehole FOR.SM in the Limagne d'Allier collected at different periods.

4.2.3. Comparison between host rocks and waters

The REE patterns in the mineral waters are completely different to those of rocks known to be in contact with the water. The REE patterns in the dissolved load are generally defined by the aquatic chemistry, including the nature of the reaction between the dissolved REE and the secondary phases. It is generally accepted that the HREEs are preferentially released into solution during the water–rock interaction and that LREEs are preferentially adsorbed at particle surfaces according to adsorption/equilibria reactions (Braun et al., 1990). The supergene alteration of granite generally yields evidence of strong depletion of LREEs and slight depletion of HREEs (Anderton et al., 1980), although 50% of the REEs are in major mineral phases, and 50% in accessory minerals. This leads to the HREE-enriched patterns in mineral waters as predicted thermodynamically (see Fig. 6 and following text).

Moreover, 2 of the REEs (Eu and Ce) may develop anomalies due to changes in their oxidation states. The most stable oxidation state of REEs is the III form, but under oxidizing or reducing conditions, Ce^{4+} and Eu^{2+} represent the other geochemically important oxidation states for Ce and Eu, respectively.

The reduction of Eu, and, therefore, a positive Eu anomaly, is thought to occur in magmatic rocks (Henderson, 1984) and hydrothermal systems (Michard and Albarède, 1986). If soluble Ce^{3+} is oxidized to Ce^{4+}, the Ce precipates from the solution as the very insoluble CeO_2 (cerianite). Consequently, the solution shows a negative Ce anomaly. However, the occurrence of cerianite in nature has rarely been reported (Braun et al., 1990) and Ce depletion may be controlled by the preferential removal of Ce^{4+} by Fe and Mn oxides. Most of the Eu anomalies in the waters studied are positive, with the exception of 7 samples that have negative anomalies. The positive Eu anomalies indicate either the predominance of dissolved Eu without removal and/or the preferential alteration of feldspars (Cullers and Graf, 1984; Sverjensky, 1984), whereas negative anomalies indicate removal by oxides or carbonates. With the exception of 2 positive samples, the Ce anomalies are negative, which is consistent with the oxidation of waters at the outcrop (Beaucaire et al., 1986) and the preferential removal by Fe oxides.

4.3. Aqueous speciation of REEs

Experimental measurements (Mironiv et al., 1982; Cantrell and Byrne, 1987; Lee and Byrne, 1992, 1993; Gammons et al., 1996) and theoretical computations (Wood, 1990a, b; Millero, 1992; Haas et al., 1995) of the complexation constants of REEs with inorganic ligands show the strong tendency of the REEs to form stable aqueous complexes even at room temperature.

Therefore, high concentrations of REEs in shallow and hydrothermal fluids can be attained. The effect of aqueous complexation on the REEs mobility can be evaluated by speciation calculations.

4.3.1. Thermodynamic data of inorganic REE complexes

Wood (1990b) extrapolated room temperature stability constants to 350°C using a hybrid approach, combining the methods of Helgeson (1967) and Mesmer (1985). He concluded that REE-Cl^- complexes should be insignificant relative to F^-, phosphate, and CO_3^{2-} complexes in many hydrogeological systems. However, Haas et al. (1995) have derived a set of high temperature stability constants for REE inorganic complexes using the revised HKF approach (Shock et al., 1992). Their values for REE-Cl^- complexes are orders-of-magnitude higher than those estimated by Wood (1990b) at high temperatures. More recently, Gammons et al. (1996) experimentally determined that the stability constants are higher than those estimated by Wood (1990b) and Haas et al. (1995). A consensus does, however, seem to have been achieved for values at ambient temperatures.

REEs only form some stable complexes with inorganic ligands (OH^-, Cl^-, F^-, HCO_3^-, CO_3^{2-}, SO_4^{2-}, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}). Fig. 6 shows that OH^- (pH), F^- and CO_3^{2-} ligands are potentially very powerful REE fractionating agents in aqueous fluids. Precedent works using the available thermodynamic data to compute REEs speciation in seawater (pH ~ 8) (Cantrell and Byrne, 1987) and in cirumneutral pH (7–9) groundwaters (Johannesson et al., 1995a, b, 1996) have confirmed this tendency. Consequently, the geochemical behavior of the REEs is strongly influenced by solution chemistry, meaning that the specific composition of weathering fluids needs to be taken into account.

In the present study, the authors have used the extended database of Haas et al. (1995) with all aqueous complexes (Fig. 6) to compute the aqueous speciation of dissolved REEs in CO_2-rich fluids. These data are introduced in the DATA0.COM database of EQ3NR (Wolery, 1992). In order to illustrate species of REEs taken into account in the speciation calculation, the following complexes are considered: $LaCl^{2+}$, $LaCl_2^+$, $LaCl_3$(aq), $LaCl_4^-$, LaF^{2+}, LaF_2^+, LaF_3(aq), $La(OH)^{2+}$, $La(OH)_2^+$, $La(OH)_3$(aq), $La(OH)_4^-$, $LaNO_3^{2+}$, $LaHCO_3^{2+}$, $LaCO_3^+$, $LaH_2PO_4^{2+}$, and $LaSO_4^+$. Similar complexes of all other REE species are taken into account.

4.3.2. REE aqueous species

The aqueous speciation of REEs have been computed in 6 fluids (Fig. 7). In the Na–HCO_3–H_2O fluids of the Massif Central, more than 80% of REEs are

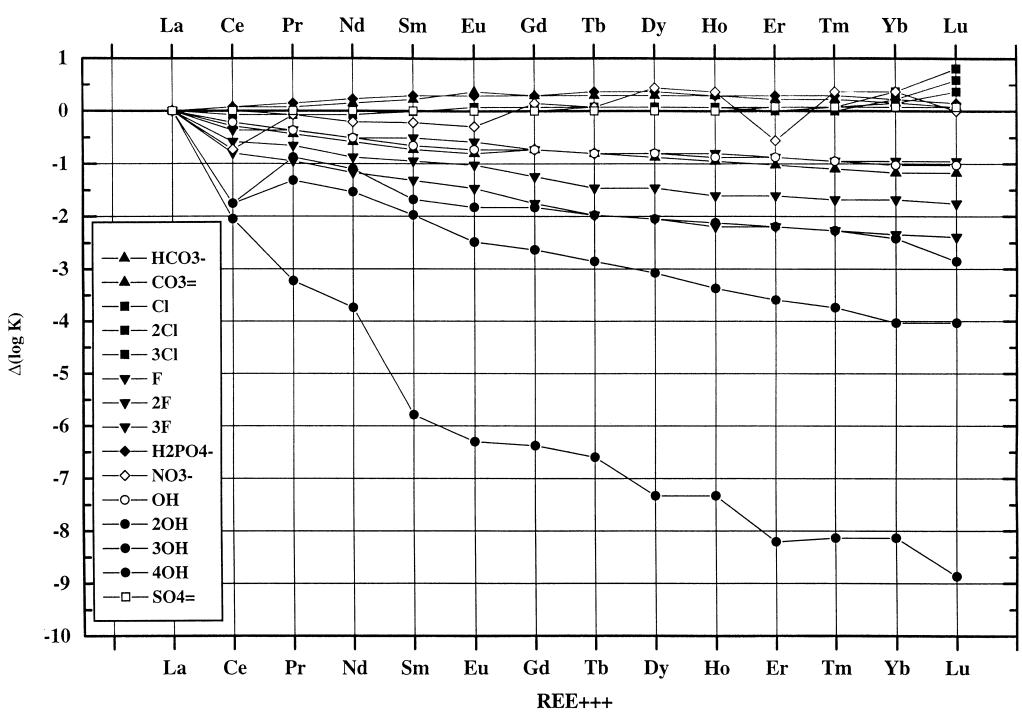

Fig. 6. REE fractionation potential of inorganic ligands expressed as Δ log K (of REE complexation reactions) relative to log K(La−L) where L represents an inorganic ligand (e.g., Cl, OH, etc.) at 25°C and 1 bar.

complexed by carbonates in the form of REE–HCO_3^{++} and especially REE–CO_3^{+}. Consequently, these fluids have a very high REE-mobilizing capacity. As shown in Fig. 7, and in accordance with predictions of Fig. 6, carbonate-rich fluids of the Massif Central are potentially REE-fractionating fluids. The CO_3^{2-} ligand has a tendency to enhance the relative abundance of aqueous REEs in the following order: HREEs > MREEs > LREEs. This pattern is also clearly observed in normalized curves (Figs. 4–6). The concurrence between CO_3^{2-}, SO_4^{2-}, and F^- ligands has no effect on the fractionating behavior.

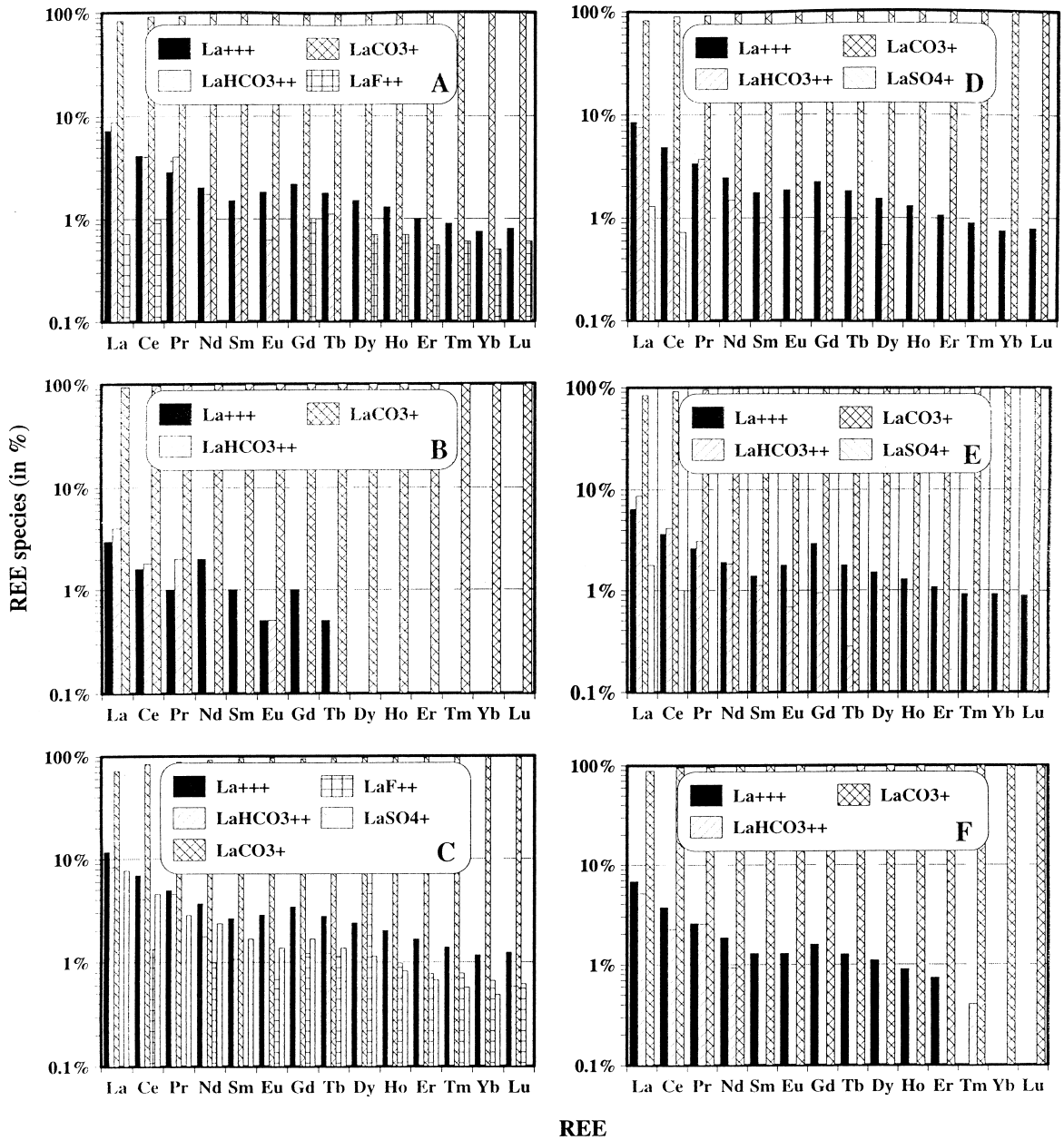

Fig. 7. Aqueous speciation of REEs in CO_2-rich water from the Massif Central (France) as % metal. Some characteristics of these fluids are given hereafter. **A** (North group): pH = 6.45; T = 13.3°C; P_{CO_2} = 0.505 bar. **B** (Center group): pH = 6.8; T = 9.4°C; P_{CO_2} = 0.24 bar. **C** (South group): pH = 6.35; T = 10.0°C; P_{CO_2} = 0.34 bar. **D** (Southwest group): pH = 6.44; T = 11.4°C; P_{CO_2} = 0.34 bar. **E** (Limagne): pH = 6.51; T = 23.6°C; P_{CO_2} = 0.54 bar. **F** (Margeride): pH = 6.6; T = 9.5°C, P_{CO_2} = 0.18 bar.

The calculations show that the CO_3^{2-} complexes dominate (>80%) over the free metal, F^-, SO_4^{2-} and HCO_3^- complexes. The detailed speciation demonstrates that the fractionation of REEs in CO_2-rich and pH neutral fluids is due, essentially, to the predominance of the CO_3^{2-} complexes.

4.4. Sr and Nd isotopic variations

4.4.1. Strontium isotopes

Strontium isotopic data are presented in Tables 1–3. Strontium isotopic data from mineral waters in the Limagne d'Allier and parts of the Cézallier areas have been presented elsewhere (Négrel et al., 1997a, b) and are also included in this table.

The Sr isotopic composition of the mineral waters in the Massif Central range from around 0.7134 in the Limagne d'Allier and for some springs in the Margeride areas to 0.7187 in the Cézallier area. The Sr isotopic ratios appear to fall into different groups. Mineral waters from the Limagne d'Allier have the lowest Sr isotopic signature (Négrel et al., 1997a and this work), as do 3 springs in the Margeride area (Mazel, FB1 and FB2), which display $^{87}Sr/^{86}Sr$ ratios of 0.71296. Mineral waters from the south Cézallier group have the highest $^{87}Sr/^{86}Sr$ (around 0.7187), whereas mineral waters from the north and southwest groups have $^{87}Sr/^{86}Sr$ ratios from 0.7162–0.7165. The centre group exhibits $^{87}Sr/^{86}Sr$ ranging from 0.7158 to 0.7185.

It appears that the lowest $^{87}Sr/^{86}Sr$ ratios are observed in mineral waters that circulated within granitic areas (Limagne d'Allier and Margeride), whereas highest ratios are observed in the gneissic Cézallier area. However, 4 mineral waters from the Margeride (Ranc1, 2, Paladines and Source des fées) have higher $^{87}Sr/^{86}Sr$ ratios than the other springs emerging from the same granitic bedrock.

Mixtures of two components having different $^{87}Sr/^{86}Sr$ ratios and also Sr contents yield a hyperbola in coordinates of $(^{87}Sr/^{86}Sr)_{mixture}$ and $(Sr)_{mixture}$. This hyperbola can be transformed into a straight line by plotting $(^{87}Sr/^{86}Sr)_{mixture}$ vs $1/Sr_{mixture}$ and, therefore, water mixing and end-member water compositions have been largely studied by using this classic diagram (Faure, 1986).

4.4.1.1. Interpretation of the granite-derived waters: Limagne and Margeride. Surface waters in the Margeride district (Négrel, 1999) show a binary mixing trend in terms of $^{87}Sr/^{86}Sr$ vs 1/Sr for unpolluted surface water samples flowing on the granite bedrock (Fig. 8). This mixing trend is consistent with 2-component mixing between a low radiogenic and concentrated end-member, and a higher radiogenic and lower concentration end-member. The first end-member in the mixing line may be related to baseflow, whereas the second end-member may be related to stormflow.

Fig. 8 illustrates this linear relationship, where the 1/Sr scale is expressed in logarithmic units for easier viewing. The curve corresponds to the mixing line and the equation of the regression line is $0.71546 + 0.0002x$, $r = 0.98$. It appears that 4 mineral springs (Paladines, S des Fées, Ranc1 and 2) plot on this mixing line and correspond to an isotopic signature and Sr content from the shallow groundwater end-member. The Paladines spring contains the most diluted water, whereas the two springs from the Ranc are the most concentrated waters. The other springs from the Margeride area (Mazel and FB1 and 2) plot with mineral waters from the Limagne area, albeit with a lower Sr content, but similar $^{87}Sr/^{86}Sr$ (0.7129 for springs FB1 and 2 in

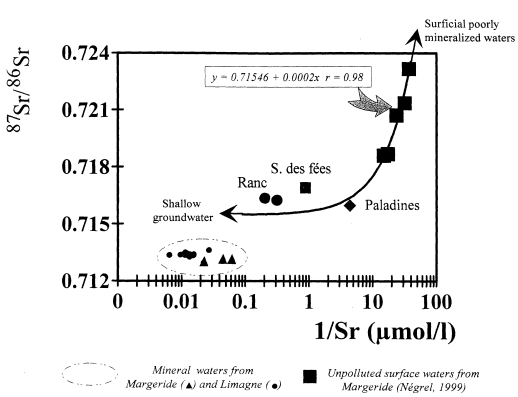

Fig. 8. Relationship between the $^{87}Sr/^{86}Sr$ ratios and 1/Sr ratios for unpolluted streams flowing over granite in the Margeride (Négrel, 1999). The samples of mineralized waters from Margeride are also represented. Note that the Sr concentration in the 1/Sr ratios are expressed in µmol/l.

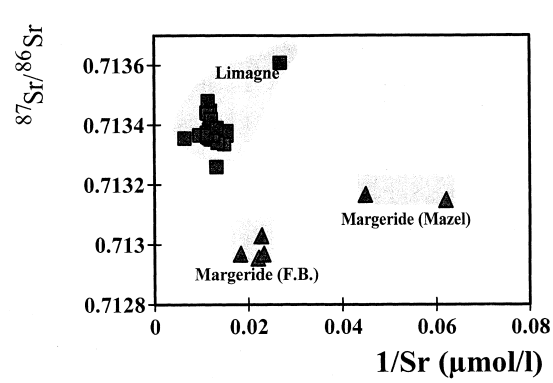

Fig. 9. A discrimination diagram, in terms of $^{87}Sr/^{86}Sr$ vs 1/Sr, for the mineralized waters from Margeride and Limagne d'Allier. Note that the Sr concentration in the 1/Sr ratios are expressed in µmol/l.

the Margeride area compared to 0.7136 in the Limagne area).

Fig. 9 illustrates the compositional variation ($^{87}Sr/^{86}Sr$ vs 1/Sr) of the mineralized springs from the Limagne area (Négrel et al., 1997a), and the Mazel, FB1 and 2 springs from the Margeride area. Three fields corresponding to the Limagne, the Mazel spring and the FB1 and 2 springs can be discriminated. The springs from Limagne are clearly more radiogenic than the springs from the Margeride region. For the latter, in spite of the proximity of the Mazel and FB springs (a few 10s of m) in the margeride area, both the $^{87}Sr/^{86}Sr$ ratios and the Sr contents differ. The Mazel spring waters have the lower Sr content and higher $^{87}Sr/^{86}Sr$. This slight, but significant, difference could be related to different stages of interaction between groundwater and the local granitic body (i.e. depth of water circulation, water–rock ratio ...).

There is evidence of 3 main types of waters in the granitic area. The more radiogenic and less mineralized water from the Margeride area may correspond to a shallow groundwater end-member that originates by a rapid and sub-superficial water circulation in the granitic bedrock. In this reservoir, the water interacts with the most altered part of the granite, which includes the most radiogenic mineral phases (i.e. biotite). Conversely, concentrated waters with lower $^{87}Sr/^{86}Sr$ ratios, observed in the Margeride area, may reflect deeper circulation with a water–rock interaction constrained by equilibrium with Sr-bearing phases with low $^{87}Sr/^{86}Sr$ ratios. For the Limagne d'Allier area, the waters display a clearly higher $^{87}Sr/^{86}Sr$ ratio that reflects equilibrium between water and a granite matrix different than that of Margeride.

4.4.1.2. Interpretation of the gneiss-derived waters: Cézallier. Some of the mineral spring waters from the center group were investigated using Sr isotopic systematics (Négrel et al., 1997b). Binary mixing trends were observed with one of them involving mixing between gneissic mineral water and gneissic surface water. The $^{87}Sr/^{86}Sr$ ratio of the mineral water end-member was estimated to be 0.71675 and its Sr content was approximately 2.4 mg l^{-1}. The second end-member was poorly mineralized near-surface groundwater with $^{87}Sr/^{86}Sr = 0.71507$ to 0.71615, and an Sr content of 0.05–0.07 mg l^{-1}.

Fig. 10 illustrates the differences amongst Cézallier mineralized waters in terms of the $^{87}Sr/^{86}Sr$ ratios vs 1/Sr. The scatter of points can be explained by 3 end-member compositions. The most dilute end-member (hereafter referred to as EM1) is compatible with the poorly mineralized waters of surficial origin described by Négrel et al. (1997b), whose characteristics are summarized above. The 2 mineralized end-members have very different isotopic compositions and Sr concentrations. The less mineralized end-member, hereafter referred to as EM2, is characterized by an Sr concentration close to 5–7 mg l^{-1} and a low $^{87}Sr/^{86}Sr$ (0.715–0.7155). The most mineralized end-member (hereafter referred to as EM3) is characterized by a more radiogenic signature ($^{87}Sr/^{86}Sr = 0.719$–0.720) and a lower Sr concentration (~1.5–2 mg l^{-1}).

Most of the samples from the north group plot along the trend between EM2 and EM3, near EM2. Some points from this group are shifted towards lower Sr concentrations associated with a slight decrease in $^{87}Sr/^{86}Sr$. Mixing with diluted EM1 waters can influence this shift. Following increasing $^{87}Sr/^{86}Sr$ ratios along the trend EM2-EM3, some of the mineralized

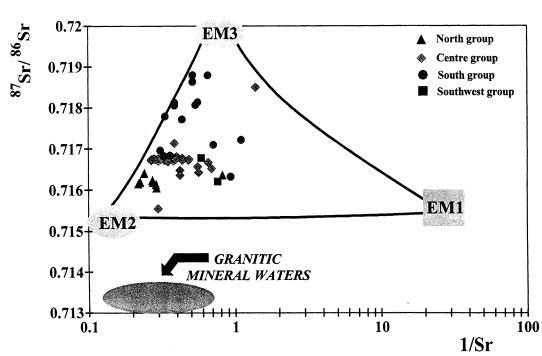

Fig. 10. Relationship between $^{87}Sr/^{86}Sr$ and 1/Sr for the mineralized springs from the Cézallier area. Mineralized waters from Margeride and Limagne d'Allier, "granitic waters" are also represented in the shaded field. The 1/Sr scale is expressed in logarithmic units for easier viewing.

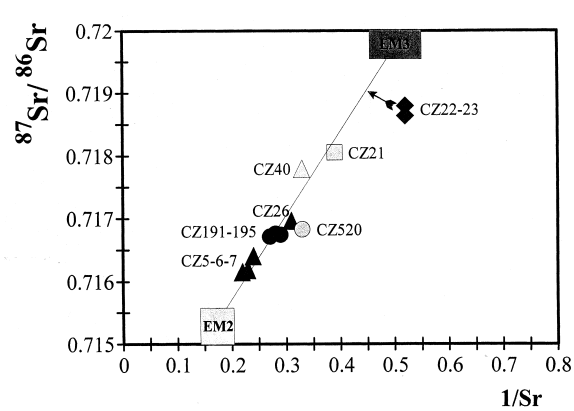

Fig. 11. Relationship between $^{87}Sr/^{86}Sr$ and 1/Sr for selected mineralized springs from the Cézallier area which illustrate the mixing between the end-members EM2 and EM3 (see text). For easier viewing and clarity, note that symbols are different than that of Fig. 10.

waters from the center group also plot along the mixing line. But most of the points are shifted towards lower Sr concentrations and decreasing $^{87}Sr/^{86}Sr$ ratios. This secondary mixing trend also encompasses 1 sample from the north group, samples from the southwest group and 5 samples from the south group. Other springs from the south group plot near the end-member EM3 and are also consistent with a shift resulting from dilution by less mineralized water (EM1 type). These variations imply a complex water circulation in the fractured basement.

Notwithstanding the effect of the poorly mineralized waters, it is obvious that at least 2 end-members constrain the Sr concentrations and the $^{87}Sr/^{86}Sr$ ratios in this area, as illustrated by Fig. 11. Samples plot along the straight line between EM2 and EM3, with EM2 contributing 60% of the Sr to the north group, 40% of Sr to the center group, and 30% to the south group. However, south group samples exhibit complexity, in that the spring CZ26, which is compositionally similar to the center group, contains 30% of Sr derived from EM2 and is located on the south-eastern limit of the south group (Fig. 2a). South group springs CZ21 and CZ40 have 15–25% of EM2 and are located at the top of the group. The springs CZ22 and CZ23 show a dilution by EM1, and after translation onto the mixing line, they have around 5% of EM2 Sr. These springs, which are mostly influenced by the end-member EM3, are located in the middle of the south group (Fig. 3).

Sr isotopic systematics are very useful for defining mixing processes in the Cézallier area. Two mineralized end-members are identified, but the links between the geographical location of the springs' outflow, and the mixing proportion of the 2 end-members, are not clear.

4.4.2. Neodymium isotopes

In contrast to Sr isotopes, Nd isotopes have not been extensively employed in hydrogeological studies. Some data are available on riverine (Goldstein and Jacobsen, 1987; Martin and McCulloch, 1999) and hydrothermal fluid compositions (Michard et al., 1987a,b), but very little information is available regarding spring waters. Because various minerals in silicate rocks weather differently, it is possible that Nd isotopic compositions may not reflect the bulk parent rock. In their study of Nd isotopes in major rivers around the world, Goldstein and Jacobsen (1987) found small differences between $\epsilon_{Nd}(0)$ of both the dissolved and suspended phases within the same rivers. In rivers draining igneous and metamorphic rocks, preferential dissolution of silicate minerals (plagioclase, pyroxene, amphibole, and garnet) may be more important and may induce the weak shift in $\epsilon_{Nd}(0)$. However, the Nd isotopic composition mainly appears to be a good indicator of the weathered parent rock (Martin and McCulloch, 1999).

The isotopic composition of neodymium in the mineral waters ranges from $\epsilon_{Nd}(0) = -12$ to $+2.6$. The $\epsilon_{Nd}(0)$ in the Limagne d'Allier springs are -8.3 and -3.6, whereas in the Margeride springs, the range of $\epsilon_{Nd}(0)$ is -11.4 to -7.6. In the Cézallier mineral waters $\epsilon_{Nd}(0)$ is -9.9 to $+2.6$, with the widest range observed in the center group (-9.9 to 2.6), compared to the north group (-9.6 to -7.3), the south group (-9.7 to -5.6) and the southwest group (-7.6 to -0.25).

Fig. 12 illustrates the range in $\epsilon_{Nd}(0)$ for mineralized waters in the Massif Central along with the range for parent rocks (granites and gneisses). Waters fall in the range $+4$ to -12 for $\epsilon_{Nd}(0)$ while 75% of the mineralized waters have an $\epsilon_{Nd}(0)$ ranging from -6 to -10, which is in complete agreement with the range for parent rocks. Some springs from the Margeride area have $\epsilon_{Nd}(0)$ slightly lower than the measured values of the parent rock, and springs from the Cézallier have $\epsilon_{Nd}(0)$ slightly higher than the range given for the parent rocks. Four springs with $\epsilon_{Nd}(0)$ higher than -4 are outside the range of parent rocks. One way to explain these high values of $\epsilon_{Nd}(0)$ is to consider a contribution from volcanic rocks. Basalts in the Cézallier area have an $\epsilon_{Nd}(0)$ ranging from $+2.7$ to $+6.8$ (Chauvel, 1982) which has the potential to shift the Nd isotopic signature of the mineralized waters.

When plotted on a classical mixing diagram ($\epsilon_{Nd}(0)$ vs 1/Nd), the data from the Cézallier springs appears to fall into 3 different domains (Fig. 13). Four springs have very low Nd concentrations and therefore have a 1/Nd higher than 0.14. Three of these have $\epsilon_{Nd}(0)$ in the range of the parent rocks and 1 an $\epsilon_{Nd}(0)$ that is more radiogenic. Two other springs also have an $\epsilon_{Nd}(0)$ with a value > -2, but with a high Nd concentration (1/Nd around 0.015). The third domain is characterized by an $\epsilon_{Nd}(0)$ in the range of the parent rocks ($-5.5/-10$) and 1/Nd < 0.08. In this domain, the lowest $\epsilon_{Nd}(0)$ is observed for springs from the south group, whereas the highest $\epsilon_{Nd}(0)$ correspond to springs from the north group. Two springs from the center group varied in their plotted position depending on the time of year, fluctuating either in their $\epsilon_{Nd}(0)$ or in both their $\epsilon_{Nd}(0)$ and Nd concentration.

4.5. Relationship between $^{87}Sr/^{86}Sr$ and $\epsilon_{Nd}(0)$

The isotopic composition of Sr is plotted in Fig. 14 vs the isotopic composition of Nd for the mineral waters from the Margeride, the Limagne and the Cézallier areas. From this figure, it is evident that there is no general relationship (linear or curvilinear) between these 2 parameters. The lack of general relationship between $^{87}Sr/^{86}Sr$ and $\epsilon_{Nd}(0)$ reflects the discrepancy between Sr and Nd in crustal

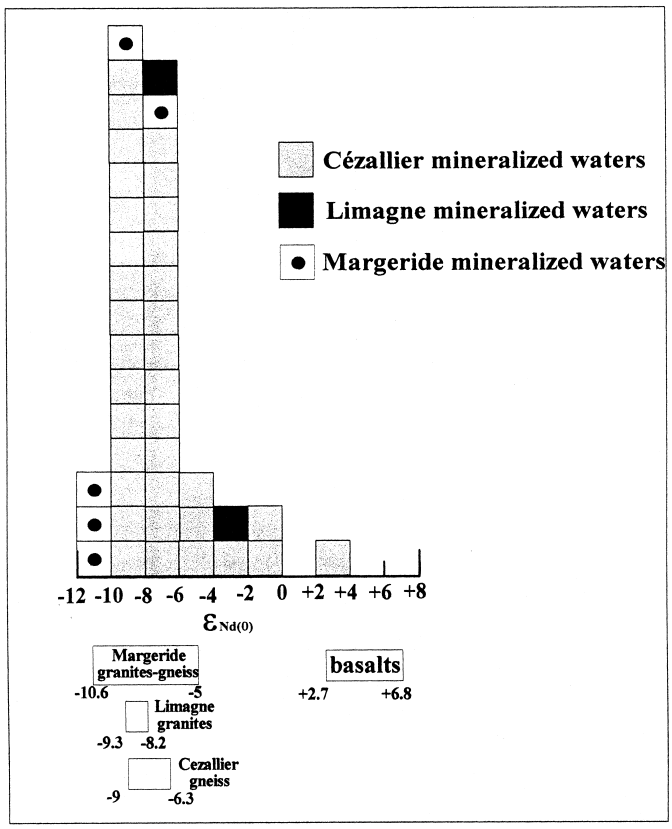

Fig. 12. Histogram of the $\epsilon_{Nd}(0)$ for the mineralized waters collected in the Massif Central. The range of parent rocks is also represented (see text).

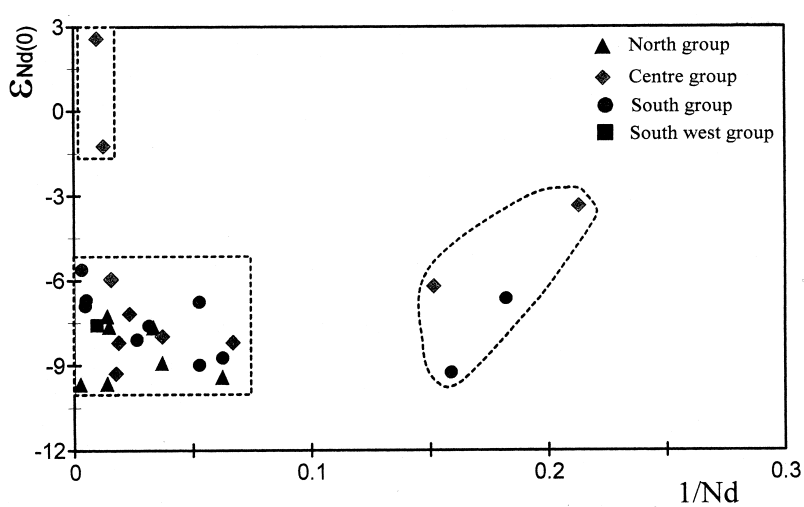

Fig. 13. Relationship between the $\epsilon_{Nd}(0)$ and 1/Nd ratios for the mineralized springs from the Cézallier area.

material exposed to weathering, and the lack of simple mixing of waters with different $^{87}Sr/^{86}Sr$, $\epsilon_{Nd}(0)$ and Nd/Sr ratios.

Within the Cézallier area, samples from the north group display similar $^{87}Sr/^{86}Sr$ ratios but varying $\epsilon_{Nd}(0)$ (−7 to −10). With the exception of CZ510, those of the center group show a slightly larger variation in Sr isotope signatures but a very wide range of $\epsilon_{Nd}(0)$. In contrast, the south group have less variation in Nd isotope signature but a much greater range of more radiogenic $^{87}Sr/^{86}Sr$ ratios. Only basaltic rocks are available in the known surface geology to induce a shift in $\epsilon_{Nd}(0)$ (Fig. 12). However, one surprising feature is the lack of Sr isotopic shift, because basalts contain $^{87}Sr/^{86}Sr$ ratios of around 0.703–0.704 (Chauvel, 1982).

One explanation can be found in the concentration fluctuations. Granitic and gneissic basements contain average Sr and Nd concentrations of ~250 and 50 mg l^{-1}, respectively (Stettler, 1977; Downes and Duthou, 1988; Pin and Duthou, 1990; Couturié et al., 1979), whereas basaltic basement contains 40 mg l^{-1} of Nd and 800 mg l^{-1} of Sr (Chauvel, 1982). Superficial drainage of basalts yields Sr concentrations of around 0.05 mg l^{-1} (Négrel and Deschamps, 1996; Négrel et al., 1997b; Négrel, 1997) and around 5–20 ng l^{-1} for Nd (Gaillardet, 1995). The mineralized waters with high $\epsilon_{Nd}(0)$ have Nd concentrations ranging from 5 to 104 ng l^{-1}, and Sr concentrations ranging from 1.45 to 2.62 mg l^{-1}. A factor of 10^6 can be seen between Nd and Sr concentrations. The Nd concentrations in superficial waters are of the same order of magnitude as those of mineralized waters, whereas for Sr, the concentration in superficial waters is lower by a factor of 40 to 80 when compared to the concentrations in mineralized waters. This implies that weathering of volcanic basement yields a larger proportion of Nd in solution than Sr and, therefore, induces an increase in $\epsilon_{Nd}(0)$.

No relationship appears in the Margeride and the Limagne d'Allier areas. One point of the Limagne springs clearly plots outside the range of parent rocks and could be explained by drainage of volcanic lithologies.

4.6. Summary of mixing processes in the mineral spring field of the Massif Central

The following conclusions may be drawn from the Sr and Nd isotope investigations:

- Using Sr isotopes, 3 end-members were in evidence in the Cézallier mineralized water field. One end-member is poorly mineralized and the other 2, which are mineralized, define a good mixing trend. The main spring emergences from the 3 main groups (Michard et al., 1987a,b) plot along this mixing trend. There is no direct link between the signature of waters emerging in the granitic area (Limagne and Margeride) and those emerging in the gneissic area (Cézallier).
- The Nd isotopes in mineralized waters contain $\epsilon_{Nd}(0)$ signatures similar to those of parent rocks, which have no large fluctuations. One exception is when the circulation of the water in its drainage area encompasses volcanic rocks, resulting in a positive shift in the $\epsilon_{Nd}(0)$. This is clearly shown for the springs CZ16 and CZ160 which emerge throughout a basaltic lava flow, and for the spring CZ30 which is located near the Mazoires-Veze volcano (Figs. 1c and 2c).

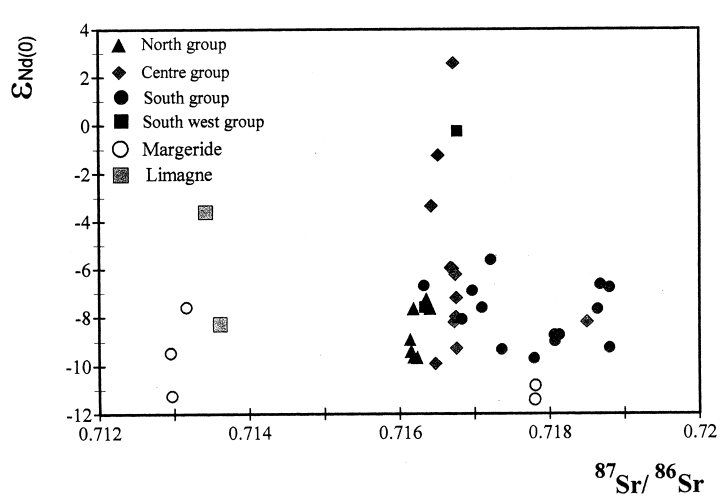

Fig. 14. Relationship between the $\epsilon_{Nd}(0)$ and $^{87}Sr/^{86}Sr$ for the mineralized springs from the Massif Central.

The hydrogeological model of Berthier et al. (1982) maintains that the amphibolite basement is the main focus of deep groundwater circulation through microfracture networks that are highly connected. However, this is not supported here by the Sr isotope data, because springs from the center group, which emerge within the amphibolite basement, do not have isotopic end-member characteristics (CZ195, CZ18, CZ19). The data from spring CZ26, emerging from the same basement underlain by the gneiss in the Blesle-Massiac zone (Fig. 2), plot near the other points of this group.

The hydrogeological model can account for the 2 end-members EM2 and EM3. The north group of mineralized waters emerge within the anatectic metamorphic rocks, and correspond to EM2. The hydraulic fluxes were previously proposed to originate from SE or NE (?) (Berthier et al., 1982). The $^{87}Sr/^{86}Sr$ ratios do support SE circulation, but it must be limited within the anatectic basement. Greater interaction with anatectic rocks would require an NE circulation component originating in Limagne, which is not consistent with the $^{87}Sr/^{86}Sr$ data from the Limagne area (Fig. 10).

One problem is to explain the unusual isotopic signature of the springs CZ22 and CZ23. The $^{87}Sr/^{86}Sr$ data do not specifically identify a parent lithology, because anatectic rocks, amphibolites and gneiss (Blesle-Massiac zone) are all present within the sub-surface circulation path of these springs. The weathering of gneiss in the Blesle-Massiac zone (Fig. 2) could explain the high $^{87}Sr/^{86}Sr$ value. In this way, Négrel (1999) showed that surficial drainage of gneiss in Margeride could provide $^{87}Sr/^{86}Sr$ values higher than 0.718. Consequently, some local water circulation through the gneiss from the Massiac anticlinal may increase the $^{87}Sr/^{86}Sr$ ratios of mineralized waters. In contrast, the springs CZ21 and CZ40, which drain the 3 lithologies (anatectic rocks, amphibolites and gneiss), have intermediate $^{87}Sr/^{86}Sr$ ratios which are consistent with contributions from all 3 rock types, rather than gneiss alone.

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