



Physico-chemical characterization of iranian turquoises : a tentative to trace middle-eastern turquoise-bearing artifacts

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**Physico-chemical characterization of iranian turquoises: a
tentative to trace middle-eastern turquoise-bearing artifacts**

**Caractérisations physico-chimiques de turquoises d'Iran:
tentative de traçage d'artéfacts à turquoises moyen-
orientaux**

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INTRODUCTION

Turquoise is an opaque, blue-to-green mineral that is a hydrated phosphate of copper and aluminium. It is rare and valuable in finer grades and has been prized as a gemstone and ornamental stone for thousands of years owing to its unique hue. The main source was Persia (in the mines of actual Iran), it certainly one of the oldest gems. Probably first introduced to Europe through Turkey with other Silk Road gemstones, turquoise did not become important as an ornamental stone in Europe until the 14th century. It is present as settled cabochon in numerous middle oriental artefacts.

The aim of this study is to compare turquoise of various historical mines of Iran (Persia) compared with those from other regional localities in order to potentially find discriminant characteristics allowing the identification of the provenance of turquoise-bearing jewel. Samples were chosen from two different sources; turquoise from Persian mines and turquoise jewelry from the Musée des Arts Décoratifs in Paris (MAD). Turquoise samples of mines were gathered from three major source: Neyshapour, Damghan and Kerman in different color. Selected samples from mines analyzed with different methods; structural analyses such as FTIR and Raman, chemical analyses by XRF and LIBS, and optical absorption analyses. Museum samples were just analyzed by XRF chemical method.

We propose to study of Persian turquoises and to compare them with other turquoise mines especially from ancient times such as Egypt and China. A tentative determination of the origin of the MAD samples according to the result of Persian mines turquoises and bibliography data is part of the purpose of this study.

Moreover, the influence factors on the turquoise color (from blue to green) will be studied via absorption spectroscopy.

The first chapter will present the state of the art of turquoise: its history, its mineralogical and crystallographic characteristics, the various conditions of formations as well as the various geological occurrences. The second chapter presents the various studied samples from Iranian mines as well as turquoise-bearing artefacts from museum. Chapter three presented the different spectroscopic and chemical technics used to characterize the studied samples. The obtained results are presented in the fourth chapter. The main conclusions end this manuscript.

1. TURQUOISE – STATE OF THE ART

Turquoise is a mineral known as **hydrated copper aluminum phosphate** mineral with the chemical $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 5\text{H}_2\text{O}$ formula. Turquoise is classified as a cryptocrystalline mineral and rarely found in crystal form. It is therefore an opaque ornamental stone with waxy luster which is always polished as cabochon. Turquoise can be impregnated by wax or epoxy because it is highly porous. The hardness of turquoise is less than 6 (Mohs scale) and in fact it is a quite soft mineral, between apatite and orthoclase. The variety color of turquoise is from deep blue to yellow green.

Turquoise can be found in pure type, called **ajami** in Persian (means Persian type) described as well as **agaphite** (Fischer, 1818) or **callaïte** (Pelini, Circa 77), from the greek *kallos*, beauty. Turquoise with black, brown or white veins is called spider web turquoise and it is called in Persian **Shajari** (means look likes tree) the term "turquoise matrix" is also often used. Turquoise was called by various names before it was called turquoise. A list of names used turquoise is provided by Gubelin (Gubelin, 1966) and Pearl (Pearl, 1976).

1.1. TURQUOISE HISTORY

According to historical evidence, the world's oldest turquoise, which was cut by human hands, was discovered at a depth of 5-6 meters from the ground, 20 kilometers from Neyshapour, on the belt of a human skeleton of 5500 years old (Zavosh, 1969). From the inscription of the Darius the Great Palace in Shosh, turquoise was called Axsina and was used for decorating the palaces (Zavosh, 1969) and (Sukmar, 1941).

Based on the evidence available, thousands of years ago, the Egyptian pharaohs used turquoise minerals from the Sinai Peninsula and used them in jewelry (Ruska, 1999). It was known as the *mafkat* stone (turquoise chrysocolle) from the Serabit el-Khadim and Timna mines.

Turquoise varieties was described in several ancient books based on its color like The Book Most Comprehensive In Knowledge on Precious Stones *Al-Jamahir-fi-Marefat-al-Jawaher* (Biruni, 1989) , *Tansooghnameh* (Tusi, 1201-1274). The best type of turquoise called *Bu-Eshaghi* which was pure vivid blue.

The term turquoise appears at the 13th century, in The Virtues of Stone *De virtutibus lapidum* from Arnoldus (Saxo.A, 1220-1230): « Turquoise is a blue stone, named since it comes from Turquie ». Turquie was in fact the place where Persian turquoise were sold to Europeans.

The known historical mines from Persia (Iran), Sinai (Egypt) and Uzbekistan (Carò, et al., 2017) are located in Fig. 2.

1.2. TURQUOISE CRYSTALLOGRAPHY

The crystal system of turquoise is triclinic with space group $P1\bar{1}$. The cell parameters (Kolitsch & Giester, 2000) are given in table 1. Turquoise crystalline structure consists of octahedron zigzag chains available in axial direction and with a quadrilateral share with four octahedron aluminum $[\text{AlO}_6]$ linked to tetrahedral $[\text{PO}_4]$, and distorted $[\text{CuO}_6]$ octahedral as shown in the turquoise structure (Fig. 1).

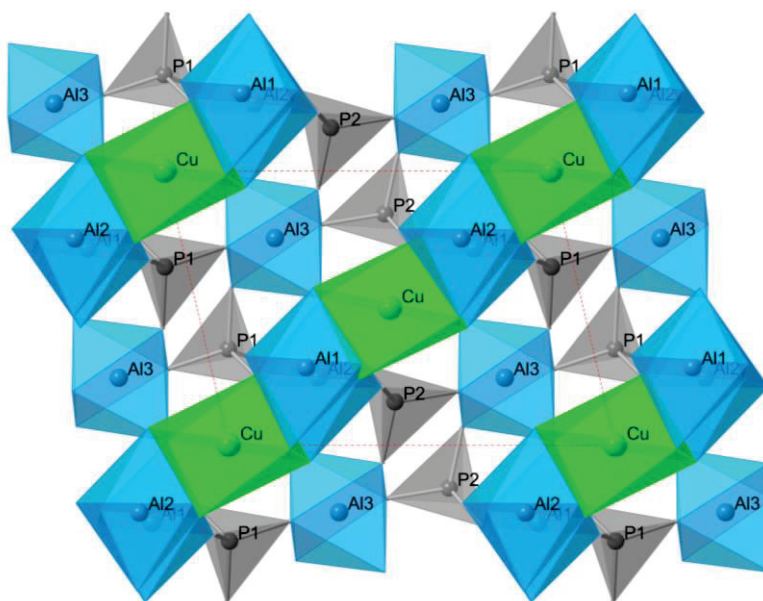
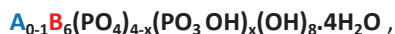


Figure 1 . Crystallographic structure of turquoise $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$ from (Kolitsch & Giester, 2000) $[\text{PO}_4]$ tetrahedra are represented in grey, $[\text{AlO}_6]$ octahedra in blue and $[\text{CuO}_6]$ octahedra in green.

1.3. TURQUOISE GROUP

The chemical formula of turquoise is $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$. It belongs to the turquoise group



where $x = 0-2$ (Foord & Taggart, 1998) (Kolitsch & Giester, 2000).

- In **site A**: Zn^{2+} (faustite), Fe^{2+} (aheylite), a vacancy (planerite) and eventually Ca^{2+} (coeruleolactite, doubtful) can substitute Cu^{2+} .
- In **site B**: Fe^{3+} (chalcosiderite) can replace Al^{3+} , as it can be seen in the turquoise series. (Tab.1).

Table 1. The various minerals of the turquoise group forming continuous series and their cell parameters.

Mineral	Chemical formula	a (Å)	B (Å)	C (Å)	α (°)	β (°)	γ (°)	Ref.
Turquoise	$\text{Cu}^{2+}\text{Al}^{3+}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$	7.410	7.633	9.904	68.42	69.65	65.05	(Kolitsch & Giester, 2000)
Faustite	$(\text{Zn}^{2+}, \text{Cu}^{2+})\text{Al}^{3+}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$	7.419	7.629	9.905	69.17	69.88	64.98	(Kolitsch & Giester, 2000)
Chalcosiderite	$\text{Cu}^{2+}\text{Fe}^{3+}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$	7.653	7.873	10.19	67.57	69.17	64.93	(Giuseppetti, et al., 1998)
Aheylite	$\text{Fe}^{2+}\text{Al}^{3+}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$	7.400	9.896	7.627	110.87	115.00	69.96	(Foord & Taggart, 1998)
Paravauxite	$\text{Fe}^{2+}\text{Al}^{3+}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$	5.240	10.567	6.968	106.82	110.77	72.23	(Gatta, et al., 2014)
"Coeruleolactite" "doubtful"	$(\text{Ca}^{2+}, \text{Cu}^{2+})\text{Al}^{3+}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$	7.529	9.951	7.782	112.51	116.54	68.57	(Foord & Taggart, 1998)

Planerite	$\text{Al}^{3+}_6(\text{PO}_4)_2(\text{PO}_3\text{OH})_2(\text{OH})_8 \cdot 4\text{H}_2\text{O}$	7.505	9.723	7.814	111.43	115.56	68.69	(Foord & Taggart, 1998)
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1.4. TURQUOISE FORMATION

Turquoise is a secondary mineral, which is a hydrated copper-aluminum phosphate. It forms by acidic solutions during weathering and primary mineral oxidation. Turquoise usually found in arid and semi-arid regions. Climate is an important factor of turquoise formation, it is normally found in arid area, typically highly altered volcanic rocks cavities and fractures filling or encrusting with associated limonite and other iron oxides. Typically turquoise mineralization is occur in a shallow depth, less than 20 meters, although it can be found in deeper fracture zones where secondary solutions have greater penetration or the depth to the water table is greater.

Several factors are essential for the formation of turquoise. The first factor is the existence of a **source of a copper**, which exists in limited areas of the earth for example the copper may drives from primary copper sulfide such as chalcopyrite or from the secondary carbonates malachite or azurite. The second factor is the **presence of a phosphate** source which is often the calcium phosphate, apatite. The third is the **source of aluminum** release, which could be provided by feldspars. During deep hydrothermal alteration, feldspar is destabilized and aluminum is released. During this phase, the phosphoric acid is produced by alteration of apatite and copper with is coming with the hot magma penetrating into the host's rock. Copper is easily oxidized near the surface and released with aluminum and phosphate reacts and form turquoise.

Three models of turquoise formation in geology are as follows:

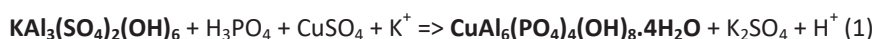
- Turquoise forming with copper-rich porphyry igneous rocks like in the Neyshapour mine in Iran.
- Turquoise formation in metamorphic and sedimentary rocks with igneous intrusions such as Mojave mine in Nevada USA.
- Turquoise without interfering with igneous rocks, is found in sedimentary rocks such as shale and sandstone, such as Turquoise Sinaï Mine in Egypt.

Elements such as iron, calcium, magnesium, manganese, silica and zinc can be replaced in the chemical composition of turquoise. The turquoise paragenes are: chalcociderite (aluminum is replaced by iron) and faustite (zinc is a substitute for copper). Variscite, limonite and silica can be seen with turquoise. Usually, if the amount of copper in the area is low. Variscite $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ is formed instead of turquoise. Silica and limonite yellow are often found in the matrix of turquoise.

In general, a few alteration steps should be performed to make turquoise. In terms of mineralization, there is a definite relationship between the alteration action of kaolinization and the formation of turquoise. Sulfuric acid resulting from the decomposition of pyrite and chalcopyrite. Sulfuric acid, by reacting with apatite, produces phosphoric acid and chloride in the rock. The fluoric acid resulting from this reaction releases aluminum oxide (Al_2O_3) from the available feldspars. Due to the dissolution of aluminum oxide in sulfuric acid which is contain some copper sulfate and phosphoric acid, Turquoise solution is created. This solution is deposited in the cavities and intersecting gaps between the classes or is Substitute to feldspars. The described model is related to porphyry igneous rocks, which are the most important commercial turquoise mines like Neyshapour and New Mexico.

(Taghipour & Noorbehesht, 2007) and (Mackizadeh , et al., 2013) proposed two similar chemical reaction leading to the formation of turquoise during advanced argillic alteration of Darreh-Zerresk and Ali-Abad porphyry copper deposits (Taft-Yazd Province, Central Iran). For these **alunite** and **gibbsite** are the precursor minerals.

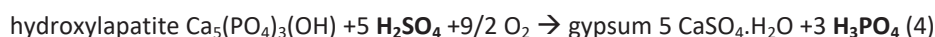
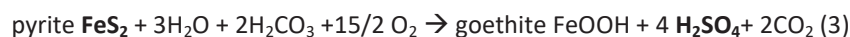




In such context alunite $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ is the weathering product of kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (Gandomani, et al., 2016).



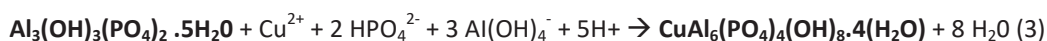
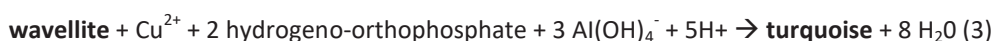
Apatite is considered as the source of phosphorus (H_3PO_4), liberated during H_2SO_4 leaching:



Copper is provided during oxidization of chalcopyrite CuFeS_2 :



Other authors Dilla et al. (1991) proposed other filiations (Nuba Mountains, Sudan), where phosphate minerals (wavellite, crandalite and variscite) are the precursor minerals.



1.5. TURQUOISE DEPOSITS

Four regions have furnished practically the world's supply of turquoise since the beginning of time: the deposits near **Neyshapour in Iran** (Persia), the **Sinai Peninsula** (Egypt), **Uzbekistan**, scarcely known localities in Central Asia (**Tibet and China**) and the southwestern mines portion of the United States of America. Apparently some turquoise was produced in Russian Turkestan as early as the 10th century, Bokhara and Afghanistan. In Europe, turquoise occurs in Germany, France and Spain. Several States in Australia have deposits. In South America, deposits are known in Peru and Chile. Small quantities occur in the States of Zacatecas and Sonora, Mexico (Pogue, 1915) (Fig. 2).

The turquoise occurrences and known historical mines in Eurasia (Egypt, Iran, Uzbekistan and China) are located (Fig.2).



Figure 2. Location map of turquoise deposit of Asia (the known historical mines are indicated by a blue star)

EGYPT

It is believed that turquoise was mined in Egypt before Persia, perhaps around 6000 B.C but evidence shows since 3000 BC, two mines were known in Egypt; *Serabit el-Khadim* « mountain of the servant » and Wadi Maghareh « the cave's valley » mines (Tallet, 2003) . There, the temple of *Serabit el-Khadim* was dedicated to the goddess Hathor, “mistress of turquoise - *mefkat*”. It was the center of a rich mining region exploited from the 2d dynasty for copper, hematites and mainly turquoises (Fig. 3). The ancient Egyptians used gemstones especially turquoise as beads, pendants, amulets, inlays, and seals. All turquoise and some malachite are related to Jurassic time (145.5-199.6 Ma).

Turquoise originating from this region is seen more green, they are less valuable than Persian turquoise, often referred to as Egypt turquoise.



Figure 3. Location and route of Egyptian mines of turquoise (Tallet, 2003)

IRAN / PERSIA

There are several turquoise mines in Iran and for this study we choose 3 major mines and one new deposit: Neyshapour (Khorasan province), Baghu (Damghan province) and Meyduk (Kerman area) turquoise ,old and main mines , Semnan mine is one of the newest examples of Iran turquoise and in a new article it has been discussed (Taghipour, 2014) and it is not a historical mine and is not comparable to the old mines in terms of quality of gemstone and has no place in gem market (Fig 4).



Figure 4. Location of main turquoise mines in Iran: Neyshapour (Khorasan province), Baghu (Damghan province) and Meyduk (Kerman area); Semnan is as well indicated but not considered as an antic mine.

NEYSHAPOUR MINE

The turquoise mine of Neyshapour is the oldest active turquoise mine. Turquoise mine is 55 kilometers northwest of Neyshapour city. Climate of the mining area is moderate and is exploited throughout the year. The rocks contain turquoise mineral are volcanic rocks. (Ghorbani & Mousavipak, 2006). The turquoise Mine of Neyshapour is divided into two types of alluvial or secondary deposit and premium deposited. Mining is done today from the first found located in the mountains. In ancient time, the best quality turquoise was find in Abu-Eshagj cave. This cave has been abandoned for nearly 250 years. The approximate geological age of the region is attributed to Eocene. The rocks of the region in (Fig.5) includes trachyte, hornblende biotite andesite, latite andesite, biotite latite, hornblende latite and volcanic breccia. Of these, trachyte is the main rock unit in the region. Porphyritic texture with trachytic texture in the matrix is common. All volcanic units are more or less affected by silicic and argillic alteration. In some places, due to the severity of alteration, the primary nature of rock is not known and is characterized as altering rocks. (Karimpour & Malekzadeh Shafaroudi, 2011- 2012)

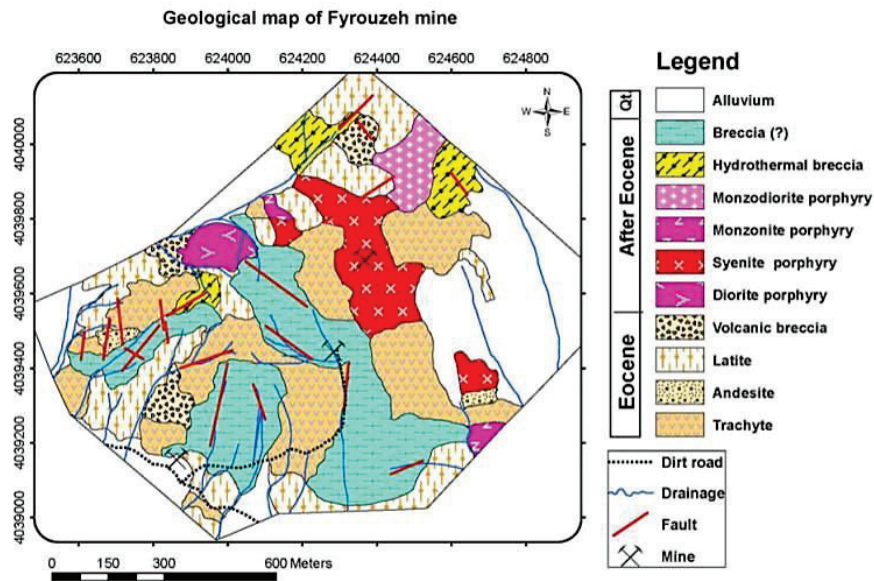


Figure 5. Neyshapour geological map scale 1/100000-(Karimpour & Malekzadeh Shafaroudi, 2011- 2012)

The hydrothermal solutions resulting from the magmatism of the area have deposited copper minerals in fractures and volcanic rocks. In the next step, atmospheric waters, passing through these rocks, washed copper minerals and deposited copper in the form of copper and aluminum hydrophobic phosphates. In 2008, the reserve size is estimated is about 8700 tons and mining is done by underground method. Basement area is in Paleozoic age. The volcanic activity of the region has peaked in the Eocene and usually has gray and reddish-brown color (Karimpour & Malekzadeh Shafaroudi, 2011- 2012). The rock units of the Firoozeh mine area of Neyshapour can be divided into three sections of volcanic units, deep intrusion and different types of breccia. (Ghasemi, et al., 2009).

BAGHU MINE (DAMGHAN)

The mine is located 130 km from Damghan (Fig. 4). In this turquoise mine, turquoise formed near the granodiorite, which can be identified as a source of turquoise mineralization. Turquoise deposit of Baghu include vein mine of Baghu deposit and placery deposit of Baghu's plain. The remains and mining operations in these areas represent the old and ancient history of the mine. There are large remnants of mining in alluvial and northern terraces of Baghu (RashidnejaOmran, et al., 1993). Geologically, the rock outcrops studied are composed of pyroclastic volcanic rocks of the Lutetian age whose formation varies from basaltic, andesitic, dacite to rhyolite, with andesite as main composition. This complex is influenced by the injection of intrusive masses with the dominant granodiorite-diorite component, and the porphyry and Basic Dike have also cut it off. The vein deposit of Baghu consists of one silicon sulfide gold vein which contain tourmaline that has cut off the granodiorite intrusion to microdiorite. The average thickness of this vein is about a few centimeters which cut of the slope N50-60E (incline with Baghu fault) and a 62° to 75° slope to the southwest of the granodiorite rocks to the microdiorite after the Eocene.

The data obtained show that the Baghu deposit is a vein-type hydrothermal deposit which, in hydrothermal classification, can be considered as mesothermal (Babakhani, 1996) to epithermal (Shakeri, 2000). This mine was caused by the derivation of hydrothermal solutions from an intrusive mass of alkaline from acidic to intermediate composition and in the tectonic setting of the active margin. Ions exchange occurred during fluid - rock interaction, while solutions separating, flow through the faults, gaps and voids in the host rock. The above-mentioned solutions are likely to be mixed with superficial waters. Finally, the above solutions react in rocks and alteration zones with copper and aluminum from the decomposition of apatite and form turquois

(Ghorbani, 2008). According to the geological maps of Baghu mine, turquoise beads and veins are created in an area of an intrusive igneous mass that is heavily altered and washed during kaolinization. In terms of age, it can be considered that the andesitic tuffs of this zone probably belong to the upper Eocene or the lower Oligocene (Nadjaran , 2000) . In this mine, there is clearly a complete link between the action of kaolinization and the formation of turquoise

In order to find new mining fronts in Baghu mine, it is necessary to consider the areas where the kaolinization has been carried out. The depth of the turquoise region appears to continue with the groundwater level and reminding to consider its changes (Nadjaran , 2000). Mining in this mine was carried out in 4 tunnels, the activity and extraction of each of the tunnels was followed by turquoise veins. According to 1997 statistics, about 8.05 tons of turquoise are extracted from the deposit and the remaining potential reserve is estimated at 40.6 tons (Khakzad, 1988).

Geology of Baghu mine area

Like the turquoise of Neyshapour, turquoise host rock of Damghan contains a series of volcanic and pyroclastic rocks such as trachyte, trachyandesite, tuff and ignimbrite .The mentioned rocks are influenced by different tectonic phases and have been strongly tectonized and the areas with high crushing intensity generally have the highest concentration of mineralization. These tectonic structures are therefore considered as one of the determining factors of turquoise mineralization (Nadjaran , 2000). The penetration of hydrothermal solutions in the rocks of the region in addition to hydrothermal alteration caused the formation of iron and copper sulfides. Thus, infiltration of atmospheric waters with acidic PH will damage chalcopyrite, pyrite, feldspar, apatite and iron and magnesium mineral structures. Over time, the content of aluminum, phosphorus, iron and copper increases and eventually accumulates in fractures and cracks, lava cavities and suitable spaces that are permeable due to the presence of clay minerals from hydrothermal alteration of the rock. These two main joint systems, in most places associated with turquoise mineralization (Nadjaran , 2000) what is certain is turquoise is the last phase of ore mineralization in the region because the veins and scattered turquoise grains have cut or intertwined all previous mineralization.

MEYDUK MINE (KERMAN)

The Meyduk porphyry copper deposit is located in the Shahr-Babak area in Kerman province. The host rocks mostly consist of volcanic and pyroclastic rocks of Eocene age which are being cross-cutted by many veins of granodiorite (Etemadi, et al., 2011).The most important alterations are potassic, sericitic and propylitic in nature, which were synchronized with the mineralization of the chalcopyrite CuFeS_2 and bornite Cu_5FeS_4 . A supergene zone is widespread in this area and is mostly composed of chalcocite and to a lesser extent covellit CuS . XRF analysis indicated two types of Turquoise in this area: Surface zone turquoise (blue color) which is mainly fracture filling, composed of high amounts of Al_2O_3 , P_2O_5 , CuO and small amounts of Fe_2O_3 (Etemadi, et al., 2011). The other type was formed mainly in the transitional zone (green color) and to a lesser extent in the borders of the supergene zone.

This deposit was exploited since the end of the 19th century (Etemadi, et al., 2011) rediscover in 1967, this area correspond probably to the ancient sites of extraction : Kuh-e-Panj, Sar-Chechmeh and Iju.

UZBEKISTAN

In Uzbekistan, the Muruntau area Qizilqum Desert (Fig. 6) was a source of turquoise since the days of the Silk Road and mined as early as the 4th millennium BC (Carò, et al., 2017). The information about the mine, limited to a presented (Carò, et al., 2017), also the mine has reports on two (Bukanov, 2007) (O'Donoghue, 2006). The

region has huge deposits of turquoise along with gold and arsenic mineralization. The main deposits in Uzbekistan are:

- Bukantau Ore District (Central Kyzyl Kum Region);
- Muruntau gold deposit in the Kyzyl Kum Desert;
- Kalmakyr Mine (Almalyk Mine), in Piskent District, Tashkent (Fig. 6).



Figure 6. Location map of the Uzbekistan and Iranian turquoise deposits (the supposed historical mines are indicated in bold) (modified from Mindat)

Turquoise has been extracted from ancient times in Uzbekistan. According to mindat.org, turquoise has been found in three localities; these regions have huge deposits of turquoise along with gold and arsenic mineralizations (Fig.6).

1. Navoiy
Central Kyzyl-kum Region
Auminzatau Mts, Dzhentuar U deposit
Bukantau Mts, Dzhaman Mn deposit
Uchkuduk area, Altynsai Au occurrences
2. Samarqand
Kara-Tyube Mtn (Kara-Tjube)
3. Tashkent
Piskent District, Kalmakyr Mine (Almalyk region)

The extraction of turquoise began in the 1st cent. A.D. Nowadays, they exploit more than 30 deposits in Qyzylqum (Kyzyl-Kum) Desert, including those in the Bukantau Mts., Auminzatau Mts and other with the volume of extracted rough material up to 14 g/m³ (grams per meter cubed) (Bukanov, 2007) .

In the Toshkent (Tashkent) Region, there are deposits with the volume of extracted rough material up to 95 g/m³. In the region of Olmaliq (Almalyk), there is the copper Kalmakyr-skoye deposit with numerous ancient turquoise mines (Bukanov, 2007).

The deposits of turquoise in Uzbekistan are linked mainly with the zones of oxidation of splintering in black band-carbonate-silica schists (Kalmykar) (Bukanov, 2007). The turquoise of Uzbekistan fine deep blue gem-quality and often shows a green tint (Fig. 7) (O'Donoghue, 2006). It is typical for it bright grass-green color of turquoise, which depends on admixture of V_2O_3 up to 1% (Bukanov, 2007). Chalcosiderite and faustite are found in Uzbekistan turquoise deposits. Chalcosiderite is present on Kyzyl-Kum desert and also in the Bukantau Mts. Faustite is reported in veinlets filling altered shales in the Bukantau Mts. and also at the Kalmykyr deposit, Olmaliq (Almalyk) region (Fig. 7) (Bukanov, 2007).



Figure 7. Rough turquoise gem stone from Almalyk region, Uzbekistan (www.123rf.com).

CHINA

According to ancient literature, turquoise has been known in China for more than 3,000 years. More than 1,000 turquoises were unearthed in 1977, from ruins dating to the Yin Dynasty (about 1300 B.C.) in Anyang, Henan. Most of gemstone quality turquoise are being mined at Yunxian and Zhushan in Hubei Province. (Wang, 1986). China has natural resources and from the point of view of the geologist and gemologist, one could only look at known geological maps of this huge country and speculate on the potential impact that China would have on the world's gem markets if its gem resources were ever developed to their full potential (Wang & Keller, 1986).

The finest Chinese turquoise gemstone is comparable in quality to those from Iran, the Soviet Union, and the southwestern United States (Wang, 1986). Today in China, significant deposits of very fine and quantities of gem-quality turquoise are mined at Yunxian and Zhushan in the Wudang Mountain area of northwestern Hubei Province. Most characteristics of Zhushan turquoise are similar to those samples from elsewhere in Hubei Province (Wang, 1986); (Wang & Keller, 1986); (Chen, et al., 2012).

The turquoise from Yun County is regarded as superior in quality. The output from Yun County (Yunnan province) between 1954 and 1999 totalled more than 800 tonnes, according to data provided by local officials, but its resources are depleting. Also there are Chinese turquoise from the city of Ma'anshan in Anhui Province, Baihe County in Shaanxi Province and the Xichuan area of Henan Province (Chen, et al., 2012) (Fig. 8, Fig.9).

General Properties

In China, gem-quality turquoise is generally found in silicified limestones, primarily in tension fracture zones or in the axial part of folds. The turquoise usually occurs in nodular form on or very near the surface of the ground. Nodules with 1 to 5 cm in diameter (up to 8 cm) are relatively more common (Keller, P.C, 1986; Wang, 1986), and present various structures include pisolitic, botryoidal, or brecciated. Vein deposits may be single or

multiple in the fracture zones; they are usually less than 1 cm in width and more than 1 m in length. Oolitic and grape-like structures are sometimes seen, while turquoise with a nodular texture is of the highest quality (Chen, et al., 2012). It is not unusual to find perfectly homogenous masses, although very fine "spider web" nodules have also been observed (Keller.P.C, 1986). Common associated minerals include quartz, halloysite, allophane, limonite, sericite, variscite, pyrite, and jarosite (Wang, 1986).

Chinese gem-quality turquoises range in various shades of blue to light green. The Zhushan County turquoise (China's Hubei Province) are known since the late 1980s are becoming a significant source of attractive material which located in a mountainous region of central China. More than 100 mine tunnels have been worked, the deepest reaching almost 300 m. The turquoise occurs in the Cambrian age, within thick and thin bedded siliceous and carbonaceous siliceous slates. The slate host rock shows a platy, fine grained crystalloblastic texture. The mineralized zones generally extend northeast-southwest and follow the regional tectonic structure. The turquoise gemstone is found mostly as lenses along faults and as fillings within fractures with a dense texture, mainly occurs as veinlets, blocks, and nodular aggregates (Fig. 10) and an attractive uniform coloration, medium bluish green. Light bluish green, light green, and yellowish green are also fairly common, while "azure" blue is rare (Chen, et al., 2012).

The turquoise is often associated with carbonaceous material, limonite, secondary quartz, kaolinite, allophane, and other clay minerals. The turquoise matrix was composed mainly of carbonaceous material, limonite, and a clay mineral. Secondary quartz is locally present in the matrix as elongate bladed aggregates. Brownish black veinlets/patches and irregular white blebs are typical features of turquoise from Zhushan County (Fig.10). The brownish black areas were identified as carbonaceous material and iron oxides or hydroxides, while the white impurities were formed by quartz and kaolinite (Chen, et al., 2012).

The Zhushan County turquoise samples showed the following properties: RI: 1.61–1.62; Mohs hardness: 5–5½; and SG: 2.57–2.72. Turquoise is normally opaque but is translucent in thin section. Microscopic examination revealed microcrystalline plate like and spherulitic structures (Chen, et al., 2012). Weak greenish yellow fluorescence to both long and short wave ultraviolet radiation, and is tough and compact massive, appearing as a scaly aggregate when observed in the SEM (Wang, 1986). Turquoise production from Zhushan County ranges from 50 to 129 tons annually (Chen, et al., 2012).



Figure 8- This map shows turquoise mines in china and the location of turquoise deposits in Yunxian and Zhushan County, and Hubei Province (modified after (Chen, et al., 2012).



Figure 9. Location of turquoise mines in China (modified from Mindat).



Figure 10. The turquoise occurs as lenses and fracture fillings in a compressed fractured zone between beds of siliceous and carbonaceous-siliceous slates (Right), The Zhushan County turquoise color ranges (Left) (Chen, et al., 2012).

TIBET

The turquoise is so extensively used in Tibet and neighbouring provinces, the northernmost Provinces of India, which lie in close proximity to Tibet, where turquoise has been found and used for centuries; also, a number of the turquoise adorned objects are found in Mongolia (Pogue, 1915).

Turquoise occurrences are reported in the mountains of Derge and Nagari-Khorsum in the east and west of the region respectively (Fig. 11). They present a general green hue.

Turquoise finds wide application in Tibet, in the eighth century the turquoise finds its earliest notice in Tibetan literature, although the mineral was previously known to the people of that country since remote times. Tibetan Turquoise has so long figured in the culture of the inhabitants of this region that it has entered very fundamentally into the traditions and ideas of the people. As jade is the recognized jewel of the Chinese, turquoise is the standard gem of the Tibetans. The early history of Tibet, like all early history, is a mixture of fact and fancy includes many references to the turquoise (Pogue, 1915).

No geological information is available concerning the occurrence of turquoise in Tibet. The native literatures are references designating Tibetan localities where this gemstone has been obtained. The following localities have been mined in the Himalayas:

- 1- The region between Lhasa and the China-Tibetan border; particularly in the vicinity of Lhasa and near Chamdo, a small town of eastern Tibet;
- 2- Djaya (or Draya), the west of Bathang;
- 3- A mine of the Gangs-chan mountains of Ngari-Khorsum in western Tibet;
- 4- Several mountains of the great State of Derge in eastern Tibet (Fig. 11).

The first mentioned locality is probably the most important and it is known the finest quality which Tibetan Turquoise is sourced. Also, the largest turquoise then known in the world on the top of Mount Tag-tse, a few miles north of Lhasa (Pogue, 1915).

The turquoise used in Tibet is usually of mediocre quality, most of the Tibetan turquoise gemstones contain black matrix material, in which turquoise of greenish to bluish color occurs in rounded areas within a dark (Fig.12), iron- colored stone, the whole presenting a mottled appearance when polished (Pogue, 1915).



Figure 11. This map shows the approximation locations of Tibetan localities where turquoise have been mined.



Figure 12- The Tibetan Turquoise Beads are a good example of the colour of Tibetan Turquoise. Notice the Turquoise-blue to green color of the beads; this is very typical of Tibetan Turquoise. It is believed that Tibetans have been making and wearing Turquoise beads for at least 500 years.

USA

It was supposed that the turquoises present in Aztecs and Mixtecs artefacts were extracted from the South-West mines of USA. However, a recent study (Thibodeau, et al., 2015) showed that most of these artefacts have isotopic signatures that differ from turquoise deposits in the American Southwest, but closely match copper deposits and crustal rocks in Mesoamerica. Thus, they conclude that turquoise used by the Aztecs and

Mixtecs likely derives from Mesoamerican sources and was not acquired through long-distance exchange with the Southwest USA.

Turquoise extraction began from 1891 (Chambless & Rayan, 2016)

The best quality turquoise in the United States is found in the Southwest, especially in Arizona, New Mexico, Nevada, Colorado and California (Fig. 13). Even before the discovery of America, turquoise gemstone was sacred to Native Americans. Today most of the old mines are abandoned and only a few are active. Gem quality turquoise mines are hard to find. Most US turquoise comes from Arizona and is discovered as a by-product of copper mining operations. This means that turquoise is part of the "stone trash" and is a by-product of copper mining. The Copper Belt in the United States contains more than 40 mines, with turquoise as a by-product of the mines.



Figure 13. Location map of the turquoise occurrences of the SW of the USA (modified from Mindat)

ARIZONA

Most mines in Arizona such as Bisbee, Morenci, Courtland, Gleeson, Copper Cities (Sleeping Beauty Mine) are emptied of turquoise and are not economically viable to extract. Several mines are important in the area for historical reasons or for the excavation of turquoise. Most Arizona mines are open-pit type. The famous Sleeping Beauty Turquoise was actually re-discovered by accident. The mine was opened to pull copper and gold and it wasn't until relatively recently (**1900s**) that the first turquoise stones were discovered by Anglo miners.

Another Arizona mine is Castle Dome, this mine operated from **1943 to 1953**. Kingman turquoise is famous for its beautiful blue and black matrix. "Sleeping Beauty Turquoise" is light blue in color and has little or no matrix. This mine is still operating, producing beautiful but expensive gem-quality turquoise.

NEW-MEXICO

Burro Mountains (with Azur Mine), Eureka, Oro Grande.

New Mexico is home to 30 turquoise-hosting mines, according to mindat.org. These mines are located in Doña Ana County, Grant County, Hidalgo County, Lincoln County, Otero County, Santa Fe County, and Socorro County. Thus turquoise is found in the mines located in 7 of New Mexico's 33 counties. With the exception of Santa Fe County, these are located in the southern half of the state. The most ancient extraction is from the Hachita turquoise mine from pre-historic times for local use by Native American to **1905**. All other are from the 1990's.

COLORADO

Turquoise deposits in central New Mexico and Colorado have formed via the weathering of Oligocene igneous complexes emplaced or erupted during the early stages of crustal extension along the Rio Grande rift. According to mindat.org, Turquoise has been found in fifteen mines, although four most important turquoise localities are known in Colorado near the towns of Villagrove, Manassa, Leadville, and Creede.

NEVADA

Nevada has been an important source of turquoise since prehistoric time. In Nevada almost 68 separate turquoise mines mentioned. The largest producing areas have been 1- the Copper Basin and Bullion districts in Lander County, 2- the Royston district on the border between Nye and Esmeralda Counties, 3- the Crescent Peak area in Clark County (Morrissey, 1968). Extraction from Crow Springs or Blue Bird mine began in 1909, The No. 8 turquoise mine in **1929**, the Blue Gem mine in **1934**, the Blue Eagle mine in **1940**. All other mines produced turquoise more recently. <http://www.turquoise-museum.com/Nevadatourquoisemines.htm>

It therefore appears that no US turquoise was commercialized before 20's century.

2. SAMPLES

In this study, the analyses of turquoise are divided into two parts:

2.1. ROUGH TURQUOISE FROM IRANIAN MINES

For this study, 52 samples collected from three major mines of Iran and selected for analyses. Of these, 5 samples belong to **Damghan** district, 9 samples from **Kerman** and 38 samples from **Neyshapour** area. The samples were collected in the Neyshapour mine in June 2016 and Kerman mine June 2017 (Fig. 14 and 15). Some samples contain host rock and turquoise mineralization (Fig.16).



Figure 14. Overview of the Neyshapour turquoise mine (gallery and entrance).



Figure 15- Neyshapour turquoise mine entrance.



Figure 16. Host rock and turquoise mineralization.



Figure 17. View of the various samples ready to be polished.

DESCRIPTION

The rocks extracted from the mine are in the form of contiguous masses, called rough stone or crude. After extraction, the lapidary workers cut the turquoise by a wheel made of sand and resin. They brought sand from Badakhshan (Afghanistan) and resin from India (Khajehbidokhti, 2009). Stonemason turns the wheel with the right hand and places the turquoise with the left hand on the wheel. In order not to erode the finger, it is protected with a piece of leather, fabric or wood (Khajehbidokhti, 2009) before using these wheels, they cut the turquoise from the rough stone and the cut methods was based on abrading. During cutting operation the use of cold water reduces the temperature and prevent sparks. Then, the small turquoise is cut the same way. After cutting, the turquoise is polished. The shape of the turquoise cut depends on the size and original shape of the grain and the turquoise piece.

Among different types of shape, two shapes are high quality and common (Fig. 18). One is cabochon, which is a cone, and the other is a flat one that is wide and smooth. When the cabochon has more relief, its peak is steeper and more desirable (Ghorbani & Mousavipak, 2006). Fine turquoise is not used in arrow cuts and they will be cut flat. If it is thick, it will almost cut an oval with a convex shape. The more convex, the more desirable it is (cabochon cut). However, Arabic turquoise market often prefers flat cut which often defective and not

well-colored. As treatment, jewelers and engravers fill the flaws of turquoise, such as white spots with painting, or fill them with gold or acrylic (Khajehbidokhti, 2009). At the end step, the stones polished by leather for being shiny and glossy. Finally, they are ready for going to jewelry markets.



Figure 18. The flat turquoise, sample number BL192 (left) that is wide and the smooth cabochon (right) which is a cone, sample number BL191.

PREPARATION

Samples from the mines were studied as cabochon or cut and polished for analyses. In the first stage, the host rock is separated from the turquoise sample as much as possible, and in the second stage the turquoise gemstone is carved as a cabochon or flat (depending on the mineral conditions) and finally polished and prepared for testing (Fig.19 and 20).

Museum jewelry samples do not require preparation and should only be clean with jewelry napkin, and gloves are used when analyzing to avoid contamination, especially oil.



Figure 19. View of the various sample cutting and polishing processes.



Figure 20. Polished turquoise samples with various color used in this study

2.2. TURQUOISE-BEARING JEWELS (MAD MUSEUM)

Thanks to Mme Posseme, curator of the jewel collection, a selection of 35 turquoise-bearing jewels was chosen from the **Musée des Arts Décoratifs (MAD)** in Paris. All samples are attributed to the **19th century or before**. The origin of all samples are not unknown. The selected jewels have been analyzed at the museum site in Paris. (Fig.21). There are listed in Annex II.

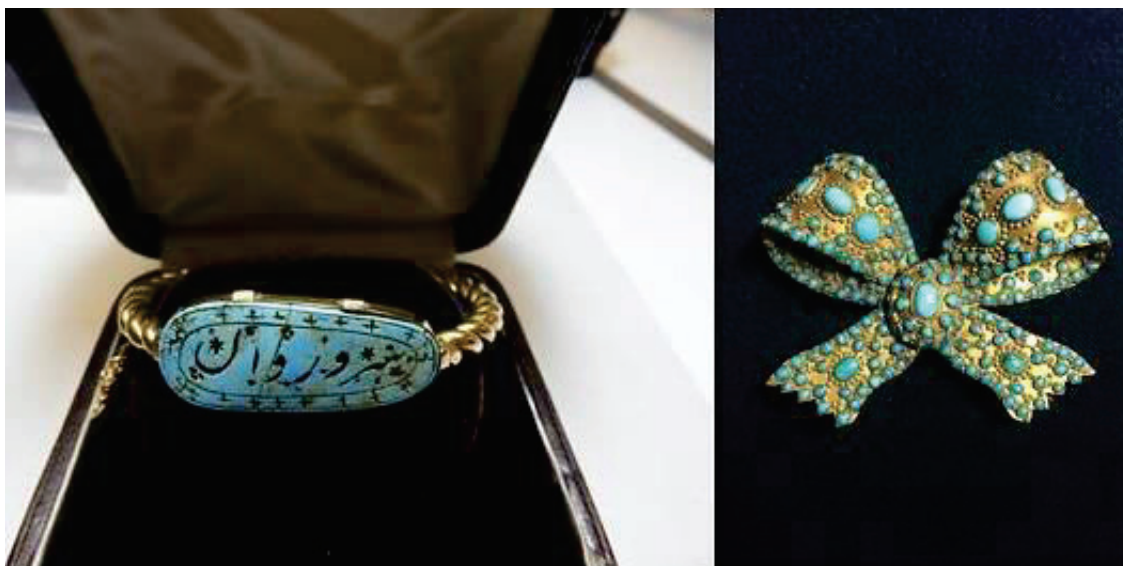


Figure 21. Turquoise-bearing jewels from MAD (Musées des Arts Décoratifs, Paris). Left: Bracelet N°28314 with large turquoise with Persian inscription; Right: Brooch N°34564.B in the shape of a knot.

Since no destructive techniques could be used, these turquoise were analyzed by X-ray fluorescence.

3. METHODOLOGY OF THE STUDY

3.1. STRUCTURAL ANALYSES

Structural analyses of materials can be conducted whether by X-ray diffraction (XRD), infrared absorption (Fourier-transformed IR absorption FTIR) or Raman spectroscopies. While XRD is in conventional mode a destructive method using grained samples into powder, FTIR and Raman can be conducted without powder sample preparation and thus considered as non-destructive methods. They can provide useful information on the structure of the material and other physico-chemical properties via the vibration modes of the various atomic (or molecular) groups and are therefore named vibrational spectroscopies.

FOURIER-TRANSFORMED INFRARED ABSORPTION (FTIR)

Vibrational transitions occur in low energy infrared region of the electromagnetic spectrum and provide the information about the functional groups and bonds of compounds. Vibrational spectroscopy has become an effective tool for the elucidation of molecular structure with the introduction of the Infrared spectroscopy.

Infrared spectroscopy is based on the measurement of the molecular bond vibration compounds, excited by radiation of a suitable frequency, when given the conditions for energy absorption by the molecules. It is an easy way to identify the presence of certain functional groups in a molecule. Also, one can use the unique collection of absorption bands to confirm the identity of a pure compound or to detect the presence of specific impurities. Analysis by infrared spectroscopy is based on the fact that molecules have specific frequencies of internal vibrations. These frequencies occur in the infrared region of the electromagnetic spectrum 200-4000 cm^{-1} (Patel, 2015). Fourier-transform infrared spectroscopy (FT-IR) is a form of vibrational spectroscopy, and particular type and the preferred method of infrared spectroscopy. The Fourier-transform Infrared technique has brought significant practical advantages to infrared spectroscopy. In this transmission technique the user simply places a sample directly into the infrared (IR) beam to determine qualitative and quantitative features of

IR-active molecules in organic or inorganic solid, liquid or gas samples. It is a rapid and relatively inexpensive method for the analysis of solids that are crystalline, microcrystalline, and amorphous. Also, it can be applied to the characterization of gemstones. It is widely used in gemology, as it doesn't damage the sample. The most useful adapter is probably the micro-beam chamber, where a curved mirror focuses the beam down to an area the size of a pinhead. This intense, focused beam can then be passed with relative ease through a very tiny culet or the girdle of a stone to obtain a spectrum. For non-transparent materials, such as turquoise, the diffuse reflectance attachment provides satisfactory spectra, with the beam of energy barely penetrating the surface of the sample, "bouncing" off, and then being collected by a curved mirror before passing to the detector (Fritsch & Stockton, 1987).

FTIR uses changes of the dipole moment of chemical bonds as these interact with infrared light (IR). The frequencies of molecule vibrations coincide with IR wavelengths. Infrared radiation is invisible electromagnetic radiation just below the red color of the visible electromagnetic spectrum between 0.78 and 1000 μm (700 nm to 1 mm). The infrared region is divided into three regions for near, mid and far infrared (table 1). The IR wavenumbers most useful for FTIR lie between 670-4000 cm^{-1} . Usually, the wavelength is measured in "wavenumbers", which have units of cm^{-1} (wavenumber = $1/\text{wavelength in cm}^{-1}$) (Ogiermann.J.C, 2002) (Naseska.M, 2016).

FTIR spectrometer

The FTIR spectrometer used to identify and quantify species in the present study was a **Perkin Elmer GX FTIR Spectrometer** (Fig.23). GX systems are fast and sensitive to the smallest amounts of sample. It uses the technique of a Michelson-Interferometer combined with a Directional-Hemispheric-Reflection (DHR) integrating sphere from the company Labsphere. The basic idea of this spectrometer is to create an interferogram based on two beams which interfere with each other (Stuart, 2008) (Herrmann, 2015). The spectral range is from 1 to 25 μm (10000-400 cm^{-1}). The principles of PerkinElmer GX FTIR Spectrometer are described herein. Ten different interchangeable, bar-coded beamsplitters, a choice of more than nine different detectors, and a built-in filter wheel with many different filters provide optimum performance. Four equivalent output beams allow the greatest available sampling flexibility.

Based on figure 25, the main of this spectrometer is a Michelson interferometer where the basic component consists:

1. an IR source
2. an interferometer
3. a beam splitter
4. a stationary
5. a moveable mirror
6. a detector

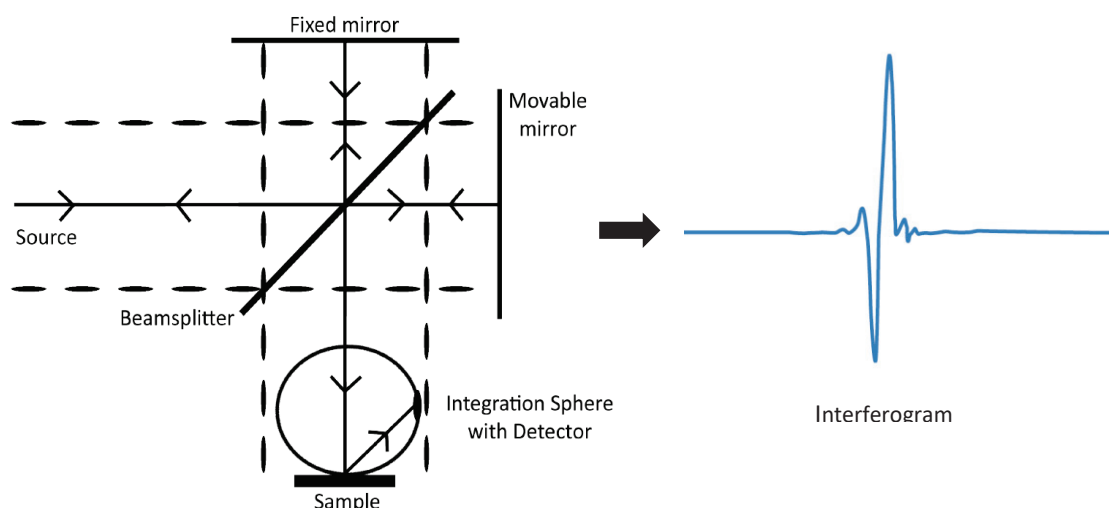


Figure 22. Schematic diagram showing an FTIR instrument, the beam finally passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal (Modified after (Haseeth & Griffiths, 1986) and (Herrmann, 2015)).

The source generates the IR waves of interest. The radiation source is a tungsten halogen lamp for the NIR (750 to 1400 nm) and a wire spool for the mid-and long-wavelength infrared (3000 to 15000 nm). Infrared energy is emitted from a glowing black body source. All the source energy is sent through the interferometer and onto the sample. The light is deflected off of a mirror and directed into an interferometer where the beam is split into two optical beams. The first beam reflects off of a fixed, flat mirror and returns to the interferometer to merge with the second beam. Meanwhile, the second beam reflects off of a flat, movable mirror which oscillates back and forth, then is reflected back to the beam splitter to merge with the first beam. Reflected from the mirrors, the two beams are turned back to the beam splitter where they recombine and are brought to interfere (Haseeth & Griffiths, 1986). Again, the two beams are partially reflected and partially transmitted where the part returning to the source gets lost and is rarely of interest for spectrometry. Only the beam which travels perpendicular to the input beam is detected and measured by the FTIR spectrometer. The moving mirror changes the optical path difference between the interfered beams. If the two beams travel the same distance before reaching the detector, they are in phase and interfere constructively, reinforcing each other (energy maximum). On the other hand, if the two beams are out of phase they interfere destructively (energy minimum) (Stuart, 2008) (Gunzler, 2002) (Herrmann, 2015).

The recombined beam then passes through the sample compartment and is reflected to the detector, the resulting signal is an interferogram (Fig. 22). This interferogram contains all the spectral information, the sample is placed in the beam path and the chemical makeup can be determined from the frequencies at which the infrared radiation is absorbed. When the beam passes through the sample, the infrared radiation causes vibrational and rotational excitation of the molecular bonds in the material. Intensities of vibrations increase when infrared radiation is absorbed. Strong molecular vibrations absorb more energy, producing larger peaks in the resulting spectrum (Naber, 2012).

The interferogram generated by recording the amount of radiation going to the detector for final measurement to convert the signal into a spectrum as a function of the change by the optical path length (Avila & Schiering, 1993). The measured interferogram signal cannot be interpreted directly, so the measured signal is digitized and sent to the computer where the Fourier transformation takes place (Ogiermann, 2002). This transformation is performed by the computer which then presents the user with the desired spectral information for analysis.

The FTIR Spectrum GX spectrometer of the GFZ is modified by an integration sphere which is gold-coated and has a sample compartment hole at the bottom of the sphere (Tab. 2). The interference beam is directed through the top of the sphere directly on the sample on the bottom. The detector is placed at the side of the sphere and measures the whole diffuse reflection of the sample.

The resolution was set to 0.15 cm^{-1} . The resolution is continuously variable up to 64 cm^{-1} . Scan velocities are continuously variable between 0.05 and 5.0 cm/sec.

Table 2- Specifications of the Perkin Elmer FTIR Spectrum GX spectrometer

Technique	Michelson interferometer with beamsplitter
Method	transmission and reflection
HeNeLaser	wavenumber or wavelength calibration
Beam splitter KBr	$7,800 - 370\text{ cm}^{-1}$
Detector	MIRTGS; $10,000 - 220\text{ cm}^{-1}$
OPD Velocity	0.20 cm/s
Scan Time	20 scan/second
Inferogram Direction	Bi-Direction
Single Beam/Ratio	Single

Comparison of FTIR and Raman spectroscopy

As it was said, FTIR and Raman spectroscopy are molecular vibrations; they are often used for similar analytical problems. An important advantage in both methods is the quickness of the analysis. The test itself takes only a few seconds.

Some features and shortcomings of FTIR and Raman spectroscopy mention in table 3.

Table 3. Some advantage and disadvantage of FTIR and Raman spectroscopy.

FTIR	Raman Scattering
Broad linewidths	Narrow linewidths
Good fingerprint; libraries available	Good fingerprint; libraries available
Preparation of KBr pellets	easy sampling, often non invasive
Frequency ($> 350\text{ cm}^{-1}$)	Low frequency modes ($> 50\text{ cm}^{-1}$)
Internally calibrated	Enhancement possible
No generation of fluorescence	Fluorescence of potential luminescent center
Sensible to organic compounds	Sensible to inorganic compounds
Water and hydroxyl absorbs strongly	



Figure 23. Experimental set up of PerkinElmer GX FTIR Spectrometer from Lyon university laboratory.



Figure 24. Grinding turquoise sample and mixing with KBr.

RAMAN SPECTROSCOPY

Spectroscopy technique is an energy sensitive method and often employed in the characterization of molecules and chemical reactions. Vibrational spectroscopic methods use infrared or near infrared (the low energy end of the visible spectrum) to create vibrations (bond stretching or bending) in chemical species. Raman spectroscopy is a vibrational technique and one of the main spectroscopies employed to detect vibrations in molecules is Raman scattering which currently gaining popularity because recent technological advances have made the instrumentation more accessible.

Gemology is a science which is in special demand for non-distractive methods. Classical gemology consisted of mainly taking the specific gravity of a gemstone, studying it in the microscope and taking refractive indicatates. Test which are common in mineralogy, such as hardness test, etching the stones with acids and taking thin sections are not applicable for gemstone. Another quick and non-distractive method for identifying gemstone is the use of Raman spectroscopy. It is widely used to provide information on chemical structures and physical forms, to identify gemstones, and to determine quantitatively or semi-quantitatively the gemstone. The discovery of Raman scattering by Krishnan and Shankar in 1928 is well documented and the phenomenon has been the subject of thousands of research papers.

Raman spectroscopy exposes a sample to a single wavelength of light, usually from a laser in the visible, infrared, or ultraviolet range. The laser light is then scattered by the sample. Scattering simply means that the light particles (photons) are forced to deviate from their straight path by some interaction with the sample, different scattering processes can occur. Two types of scattering are readily identified (Fig.25). The most intense form of scattering, Rayleigh scattering, occurs when the electron cloud relaxes without any nuclear movement. This is essentially an elastic process and there is no appreciable change in energy and consequently the light returns to the same energy state. Raman scattering on the other hand is a much weaker than the intensity of Rayleigh scattering. This occurs when the light and the electrons interact and the nuclei begin to move at the same time. The Raman scattering process from the ground vibrational state m leads to absorption of energy by the molecule and its promotion to a higher energy excited vibrational state (n). This is called Stokes scattering. In the Stokes process the scattered light loses energy $\nu_0 - \nu_m$, due to the recover to a higher energetic state of the phonon than before. Scattering from these states to the ground state m is called anti-Stokes scattering and involves transfer of energy to the scattered photon. In the anti-Stokes process there is an energy gain of scattered light $\nu_0 + \nu_m$ (Leissner, 2014). The resulting scattered light has different wavelengths (because of the energy difference between the incident and scattered photons), corresponding to the energy of vibrational modes. This allows the identification of a variety of species based on their vibrational “fingerprints”.

Raman measurements were conducted using the Thermo Scientific DXR Raman microscope (780 nm laser) as well as by LabRaman Aramis (633 nm laser)(Fig.27). The LabRAM ARAMIS has computer controlled operation for quality control, analytical and research applications alike. The LabRAM series provide the most comprehensive analytical tool available; such as: True confocal Raman microscopy (below) and unique Line Scanning mode for fast Raman mapping with high spectral resolution.

The Raman system consists of four components:

- 1- an excitation source,
- 2- an optical sampling system,
- 3- a wavelength separator,
- 4- A detector.

Raman spectroscopy uses a single wavelength laser source in wavelength visible 633 nm to excite the electrons in a sample; the laser source is aimed at an optical sampling system includes the sample illumination system

and light collection optics (a mirror that directs the beam to a polarizer, ensuring all photons are moving in the same direction for sample excitation). The laser is then sent through a beam expander to ensure the spot size is large enough to produce a strong enough response for measurement. Laser-line rejection devices have the role of preventing the weak scattered Raman light from being overlapped by the intense elastically scattered radiation. The wavelength dispersion devices, separate the wavelengths that comprise the Raman signal and present them to the detector. The most common device used in dispersive Raman spectroscopy is the spectrograph, which is a dispersive polychromator, that contains a diffraction (or dispersion) grating responsible for the angularly separation of the Raman signal into their individual wavelength components, projecting them into the detector which is multi-channel detectors, the charge-coupled device (CCD).

The Thermo Scientific DXR Raman microscope (Fig. 28) with 780 nm was the methodology used in this thesis, where the Raman spectrometer is combined with a standard optical microscope allowing spatial resolution. The lasers, together with the appropriate filters and gratings, lock into place using SmartLock technology for precisely reproducible results. OMNIC™ software recognizes each component, records the serial numbers and checks for compatibility. A convenient storage container is provided for when the components are not in use.

The DXR Raman microscope Expand the capabilities by adding a second or third excitation laser. Minimize fluorescence interference, or enhance sensitivity by up to 10-fold. Components are automatically recognized by Smart technology and pre-aligned so there is no need for a service call.

The use of optical microscopes allows the excitation laser beam to be focused in the sample, creating a micro-spot with small diameters. In addition, it is possible to look at extremely small samples and therefore, despite the fact that Raman scattering is weak, to detect very small amounts of material and also, enable to look for evidence of inclusions or impurities and characterize multi-layer polymer films. The major advantage of the microscope is that any sample or part of a sample that can be aperture optically can also have the Raman spectrum recorded. The use of an X-Y-Z scanning stage allows to perform different mapping techniques, such as X-Y optical sectioning (surface scan), X-Z cross-sectioning (depth profiling or multiple layers of the sample), Z-series (X-Y-Z scan), and surface profiling. Besides that, no preparation of the sample is required, small sample volume measurements are possible, and allows the acquisition of Raman chemical imaging.

According to Figure 26, the pathway of the Raman laser in the Thermo Scientific DXR Raman microscope can be described as follows: the laser beam is reflected in a first mirror and passes through the first pair of lenses and through the bandpass filter into the beamsplitter or dichroic mirror, where half of the beam is transmitted to a second mirror that reflects it into the microscope objective. The light strikes the sample, and is scattered by the sample. The scattered light is collected by the microscope objective at 180° degrees, and passes through the second mirror and the beamsplitter or dichroic mirror, to the filter. The resulted filtered light passes through the second pair of lenses and is reflected by a third mirror to the spectrograph. This dispersive spectrometer contains a grating that diffracts the light and directs it to the cooled CCD detector, connected to a computer for data treatment. The pathway for the portable BWTEK i-Raman pro is similar, except for the fact that the laser needs to pass first through a fibre optic probe, connected to the confocal microscope.

The others advantages and character could be mention for LabRaman Aramis are:

- Full range gratings for complete spectra in one shot, 50 cm^{-1} to 3500 cm^{-1} ,
- 5 cm^{-1} spectral resolution (Spectral range for the 780 nm excitation laser is 50 cm^{-1} to 3300 cm^{-1}),
- High-resolution gratings for difficult to resolve bands, 50 cm^{-1} to 1800 cm^{-1} ,
- Can be done Many organic and inorganic materials are suitable for Raman analysis (solids, liquids, polymers, vapors or gases) without preparation and no water interference – easy to measure aqueous samples,
- Fast multi-wavelength operation,

- SmartLock technology for reproducibly mounting lasers, gratings, filters, fiber port,
- Rapid automated calibration to ensure validity of results,
- Can be done also at high temperatures (e.g. 1000°C) because of detection in the optical regime;

And disadvantages of Raman are low intrinsic cross section, susceptible to fluorescence (can be up to 10⁶ higher; especially coke has a high fluorescence yield), Quantification of Raman intensities is very difficult (even with reference samples, because of possible electronic effects of the substrate); however, there are Ways to improve Raman signal intensity by 1) Resonance Raman (RR) and 2) Surface-enhanced Raman scattering (SERS).

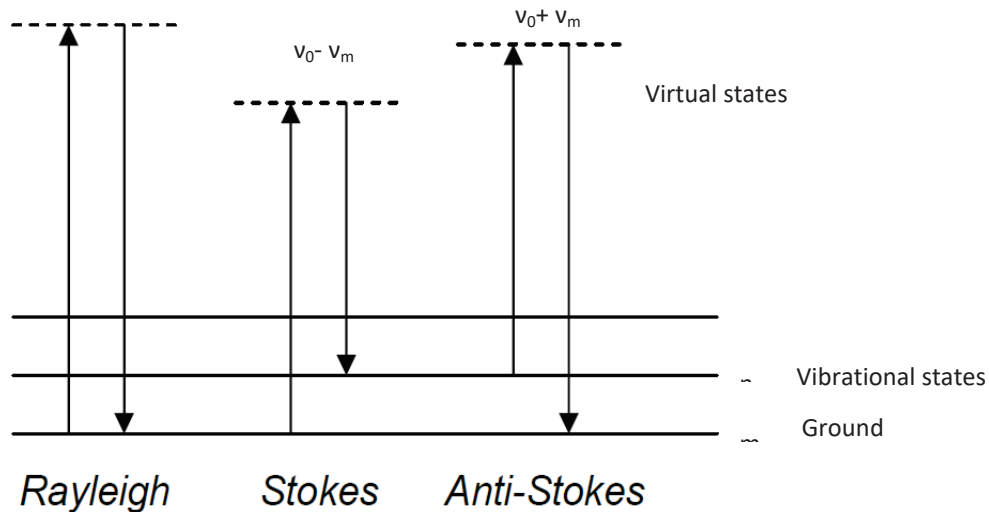


Figure 25- Diagram of the Rayleigh and Raman scattering processes: Stokes and anti-Stokes Raman scattering(adopt from (Smith & Dent, 2005).

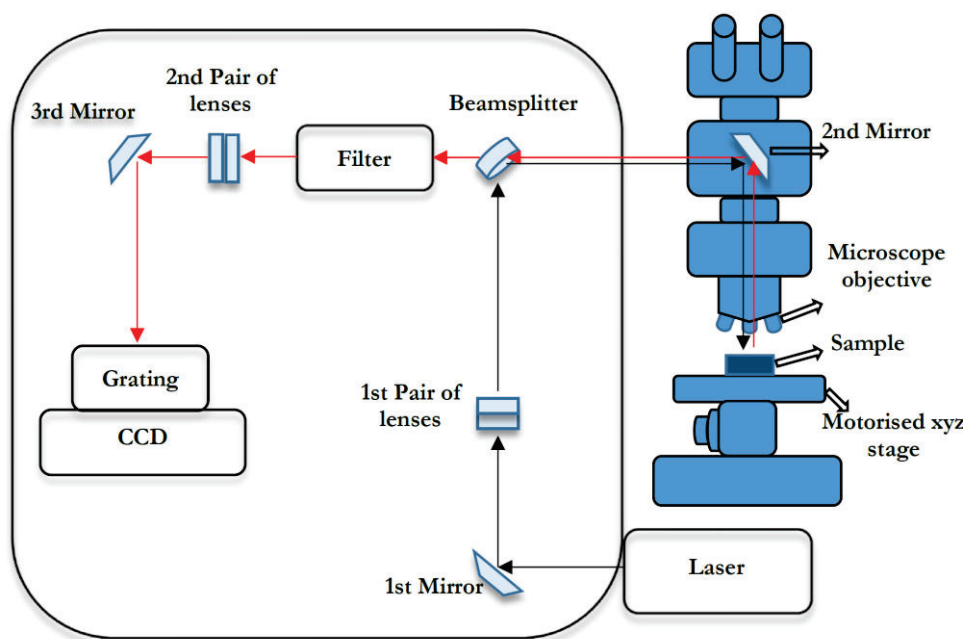


Figure 26. Thermo Scientific DXR Raman microscope (Diogo, 2017).

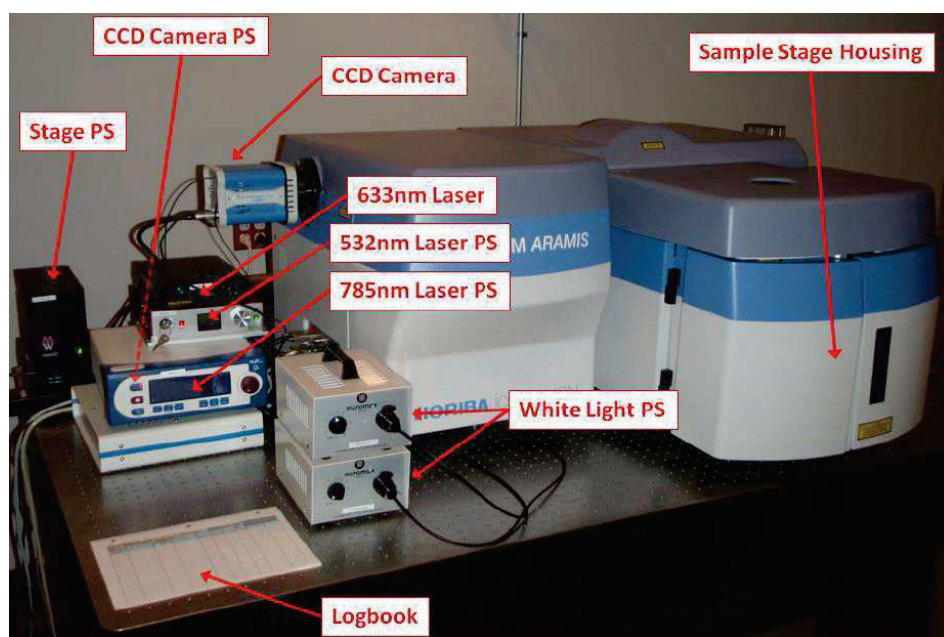


Figure 27. Hardware overview of LabRAM ARAMIS 633nm (ILM, CECOLO center for vibrational spectroscopies, Lyon 1 University).



Figure 28. Thermo Scientific DXR Raman microscope (CECOMO center, Lyon 1 University)

3.2. CHEMICAL ANALYSES

XRF

X-Ray Fluorescence Spectroscopy (XRF) is an elemental analysis method that is important because of the high speed of analysis in some industries. In this method, X-rays are emitted to the specimen and produced by atomic incitement and electron transfer in different layers of the atom, secondary X-ray, which, by determining the wavelength (energy) of the second x-ray that is characteristic of the atom, can be found in the elements in identify the sample.

Using this technique, elemental analysis can be performed qualitatively and somewhat quantitatively, especially in the case of mineral, ancient, geological, minerals, rocks, glass, cement, ceramics and metal alloys, which trace elements from sodium to uranium (Fig.30). Obtained data are more precise for heavy elements.

In XRF, primary X-rays are produced in tungsten tube-molybdenum or chromium. The X-rays exiting the tube, by collision with the sample and its bombardment, release the electrons of the internal circuits of the atom and create empty spaces in the electron shell of the atoms, which are filled with empty electrons, which are placed at a higher energy level. In the transition of electrons from higher energy levels to lower energy levels, secondary X-rays (fluorescence) are produced that characterize the elements in the sample, thus identifying different elements.

The XRF device usually consists of a high voltage power source, an X-ray tube, a sample holder, a spectrophotometer, a sodium fluoride crystal, or other crystals, a spectrophotometer after passing through sodium fluoride crystals, a counting apparatus for measuring X-ray Intensity. Different wavelengths are formed for various elements, a strong recorder and an electron amplifier. Figure 29 shows schematics of an X-ray fluorescence machine.

The specimen is bombarded with an initial X-ray produced in an X-ray tube, and an electron transfer is performed and a secondary x-ray, which is the characteristic beam of the elements in the sample, is generated. This secondary x-ray, after passing through the collimator, is directed toward the crystal in the detector section. The collector consists of several parallel sheets, which, by summing and parallelizing the X-rays, make it move in parallel and collide with a certain angle to the crystal. The crystallite-rays actually have an area of wavelengths, each of which belongs to an element. Therefore, before sending the wavelengths to the detector, they must be separated using a crystal. The analyzer crystal, based on the Bragg relationship, leads to the diffraction of each wavelength at a given angle, and then these dispersed wavelengths are sent to the detector. Since at each angle a particular wavelength is applicable to the Bragg relationship; with a wavelength diffraction, the rest of the wavelengths in the atmosphere around the crystal are dispersed and

destroyed. Then, the X-rays are separated, after passing through the secondary collector, into the detector. The detector and collector are on a circle and the crystal is in the center of it. In the detector, the intensity of the secondary x-ray is determined for each wavelength, and eventually the information is sent to the recorder. Calibrating with proper standard lead to quantitative results.

Chemical composition analyses were done using a Thermo Scientific Niton pXRF XL3T Gold (mining mode) (Fig.29).

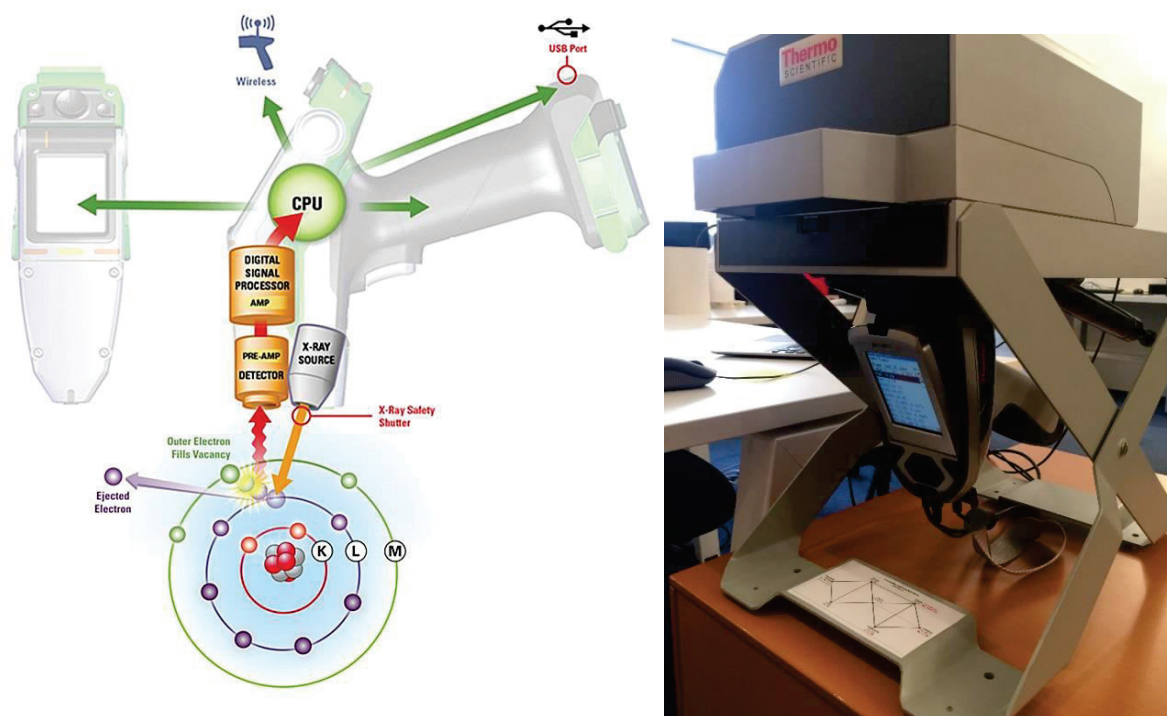


Figure 29. Principle and portable XRF equipment used for turquoise chemical analyses (ILM, CECOLO center for vibrational spectroscopies, Lyon 1 University).

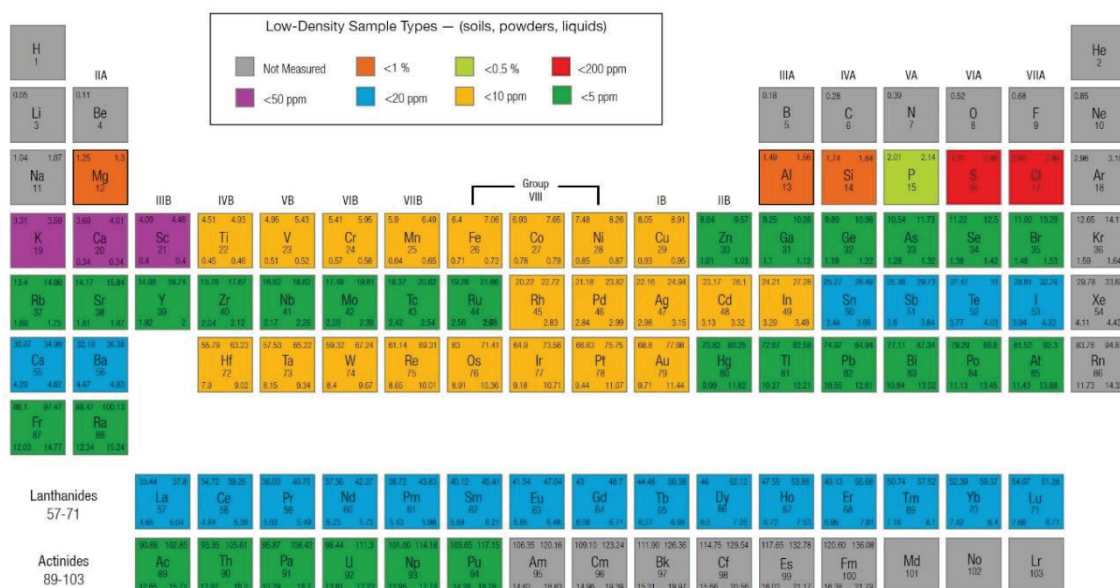


Figure 30. Periodic table with the elements which could be detected by XRF and their approximate limit of detection (The elements in gray cannot be analyzed).

Used filters and X-ray energy:

1. Main range: filter Al@50kV
2. Low range: filter Cu@20kV
3. High range: filter Mo@50 kV
4. Light range: No Filter@8 kV

LIBS LASER-INDUCED BREAKDOWN SPECTROSCOPY

The LIBS experiment was conducted in ILM in Lyon (Moncayo et al., 2018) by using a Nd:YAG laser with a 5 ns pulse duration operating at 100 Hz at the fundamental wavelength (1064 nm)(Fig. 31). The laser beam was focused onto the sample by a 15X magnification objective (LMM-15X-P01, Thorlabs). The sample was placed on a three axes XYZ motorized translation stage, with a travel range of 50 mm in each direction. The LIBS measurements were performed at room temperature under ambient pressure. An autofocus system was used during the analysis to maintain a constant objective-to sample distance. All spectra were obtained using a single laser pulse at each position of the sample, without any accumulation or averaging. The light emitted by the plasma was collected by a quartz lens and then focused onto the entrance of a round-to-linear fiber bundle connected to the spectrometer. This fiber bundle is composed of 19 fibers, each with a 200 μ m core diameter. The entrance slit of the Czerny-Turner spectrometer (Shamrock 500, Andor Technology) was 30 mm. The spectrometer was equipped with a 600 l/mm grating blazed at 300 nm and an intensified charge-coupled device (ICCD) camera (iStar, Andor Technology). In this configuration, a spectral range of 80 nm with a spectral resolution of approximately 0.15 nm was achieved. The ICCD camera was synchronized with the Q-switch of the laser, and the spectrum was acquired with a delay of 500 ns and a gate of 3000 ns in the full vertical binning mode. The laser energy was stabilized throughout the experiment by using a servo control loop consisting of a power meter and a computer-controlled attenuator (ATT1064, Quantum Composers). Finally, homemade software developed in the LabVIEW environment was used to control the entire LIBS imaging

setup, thereby allowing an automatic spectral acquisition of any selected region of interest of a given sample with a pre-set lateral resolution.

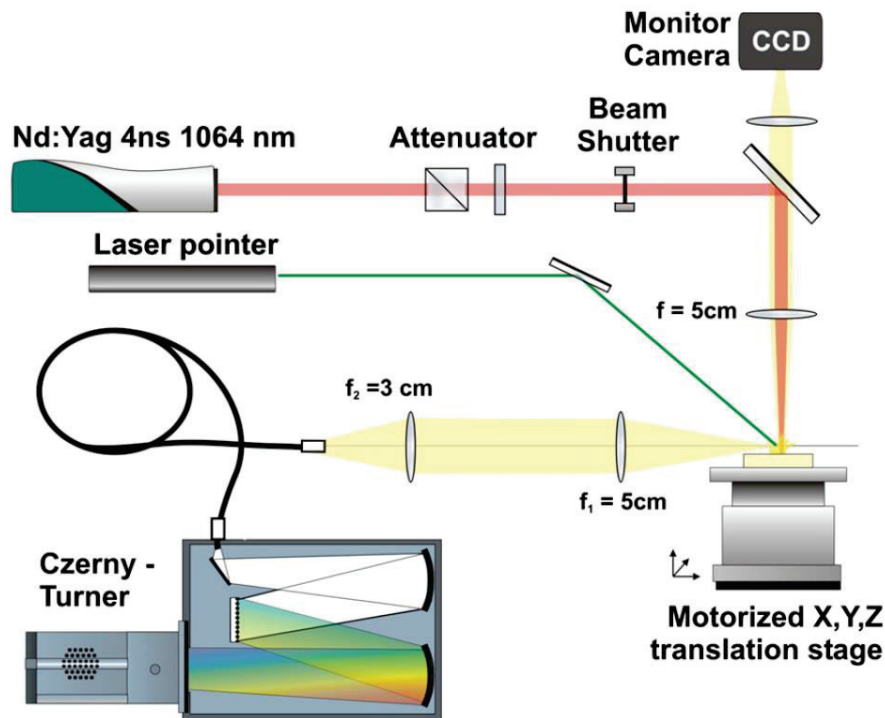


Figure 31. Schematic presentation of the used LIBS experimental setup (Motto-Ros, et al., 2013)

The LIBS image was recorded with a step resolution of 15 mm over a surface area of 468 mm² and represents more than 2 million pixels (1300 by 1600 pixels along the x- and y-axes, respectively). The ablation craters, as observed afterward using optical microscopy, were approximately 8 mm in diameter. Because one LIBS spectrum contains 2048 spectral channels, the whole data set represents a total of 4.2 billion of numerical values. The duration of the LIBS imaging measurement was approximately 6 hours, limited by the laser frequency rate (i.e., 100 Hz). The detection range of the spectrometer was set from 250 nm to 330 nm, covering the main emission lines of all elements of interest, including phosphorus (P I 253.6, P I 255.3 nm), copper (Cu I 324.7, Cu I 327.4 nm), aluminum Al (Al I 308.2, Al I 309.3 nm) and numerous iron lines (for example, Fe II 257.9 and Fe I 302.1 nm). A slight and continuous wavelength drift (lower than 0.05 nm) was observed between the first and last spectra of the dataset. Although this shift was visually negligible, all spectra were recalibrated in wavelength before performing multivariate analysis.

3.3. OPTICAL SPECTROMETRY

OPTICAL ABSORPTION

Gem testing instruments have varying degrees of usefulness. Spectrometer has been tested for gemological applications for the characterization and identification of gems. The optical study of a gemstone may be extremely useful in identification, distinguishing between two gemstones that look alike or in characterization which is why optical properties are often mentioned in gemstone articles.

Optical spectrometry is the technique of measuring the intensity of absorption or emission of radiation in the ultraviolet-visible region of the spectrum. It is a type of spectroscopy where the properties of physical objects are studied based on how the object interacts and emits light. In analytical applications, these measurements are made by exciting, in various ways, transitions of electrons between outer orbitals of atoms, ions or molecular species. In most applications, it is necessary to dissolve the sample before analysis. It's used in the mining and mineral industry to know the concentration of an element.

The Ocean Optics spectrometer is a quick and easy to use instrument for generating spectra in the UV, visible and near- infrared (near-IR) regions of the electromagnetic spectrum. The spectrometer (mirrors, grating, slit and detector) are housed in an optical bench that is small enough to fit into the palm of hand. The spectrometer accepts light energy – either transmitted through an optical fiber or in free space -- and disperses it via a fixed grating across the linear CCD detector. The detector is designed to provide an electronic output for its wavelength range. The output from the detector is then fed into the computer to software, processed, and then displayed in the appropriate units. The spectrum is the result of multiple detector elements being fed into the computer and processed. This happens fast enough to be looking at the spectra generated by the instrument in real time.

Ocean Optics USB2000

Optical absorption spectra were conducted using a compact integration sphere and an Ocean Optics USB2000 spectrometer allowing to record absorption spectra without getting through the samples (Figure 19).

A USB2000 system contains four core elements:

- USB2000 Spectrometer
- OOIBase32 operating software
- Light source
- Sampling optics (varying, depending on application requirements)

The user stores reference and dark measurements to correct for instrument response variables. The light from the light source transmits through an optical fiber to the sample then interacted. Another optical fiber collects and transmits the result of the interaction to the spectrometer. The spectrometer measures the amount of light and transforms the data collected by the spectrometer into digital information and passes the sample information to OOIBase32. OOIBase32 compares the sample to the reference measurement and displays processed spectral information.

The following list explains the movement of light through the optical bench of the USB2000 Spectrometer. The function of each numbered component in the USB2000 Spectrometer diagram (Figure 32).

- 1- The SMA Connector secures the input fiber to the spectrometer. Light from the input fiber enters the optical bench through this connector.
- 2- The Slit is a dark piece of material containing a rectangular aperture, which is mounted directly behind the SMA Connector. The size of the aperture regulates the amount of light that enters the optical bench and controls spectral resolution. The USB2000 can also be use without a slit. In this configuration, the diameter of the fiber connected to the USB2000 determines the size of the entrance aperture.
- 3- The Filter is a device that restricts optical radiation to pre-determined wavelength regions. Light passes through the Filter before entering the optical bench. Both bandpass and longpass filters are available to restrict radiation to certain wavelength regions.
- 4- The Collimating mirror focuses light entering the optical bench towards the Grating of the spectrometer.

Light enters the spectrometer, passes through the SMA Connector, Slit, and Filter, and then reflects off the Collimating Mirror onto the Grating.

- 5- The Grating diffracts light from the Collimating Mirror and directs the diffracted light onto the Focusing Mirror. Gratings have different groove densities, allowing specifying wavelength coverage and resolution in the spectrometer.
- 6- The Focusing Mirror receives light reflected from the Grating and focuses the light onto the CCD Collection Lens.
- 7- The Collection Lens (optional) attaches to the CCD Detector. It focuses light from a tall slit onto the shorter CCD Detector elements.
- 8- The CCD Detector collects the light received from the Focusing Mirror and converts the optical signal to a digital signal.

Each pixel on the CCD Detector responds to the wavelength of light that strikes it, creating a digital response. The spectrometer then transmits the digital signal to the OOIBase32 application.

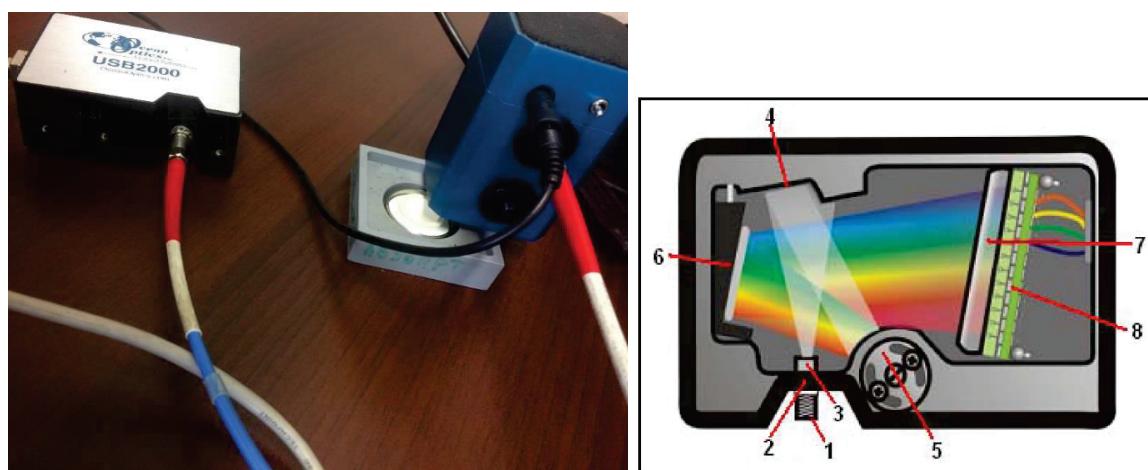


Figure 32. Ocean Optics USB2000 spectrometer and components (1. SMA Connector; 2. Slit; 3. Filter; 4. Collimating Mirror; 5. Grating; 6. Focusing Mirror; 7. L2 Detector Collection Lens; 8. VIS CCD Detector).

4. RESULTS OF THE EXPERIMENTS

4.1. FTIR STRURAL ANALYSES

Only four samples were selected for FTIR analysis, since they had to be grained (destructive). These samples are TN193 to 196, from Neyshapour mine and are representative of different color variation (Tab.4). The samples were grinded in an agate mortar and pressed as a pellet with KBr powder (Fig. 24). IR spectra were collected by Perkin Elmer GX FTIR.

Table 4. Colors of turquoise samples analyzed by FTIR

Sample number	Color
TN193	Blue (B)
TN195	Blue (B)
TN194	Bluish Green (bG)

TN196	Greenish blue (gB)
-------	--------------------

RESULTS

In turquoise, the most important cause for absorption peaks in FTIR are OH, H₂O units and phosphate groups. The FTIR spectrum is from 370 to 4000 cm⁻¹ (Fig.33) and can be divided in two regions. The first region (Fig.34) is from 370 to 1800 cm⁻¹ and it is related to the main structural part of turquoise. The second part (Fig.35) is

from 2700 to 4000 cm⁻¹ and is related to water and OH.

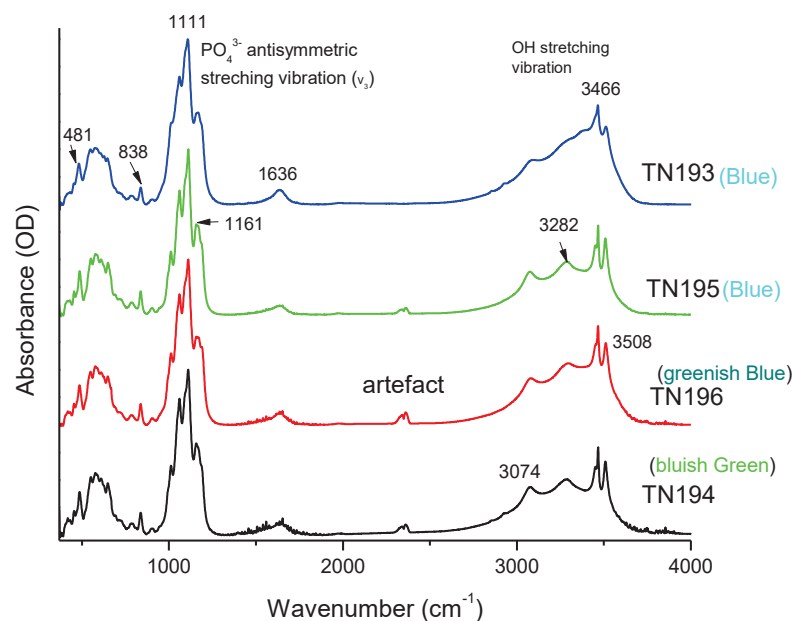


Figure 33. FTIR spectra of four turquoise samples (complete 370-4000 cm⁻¹ range) interpreted according to (Reddy, et al., 2006).

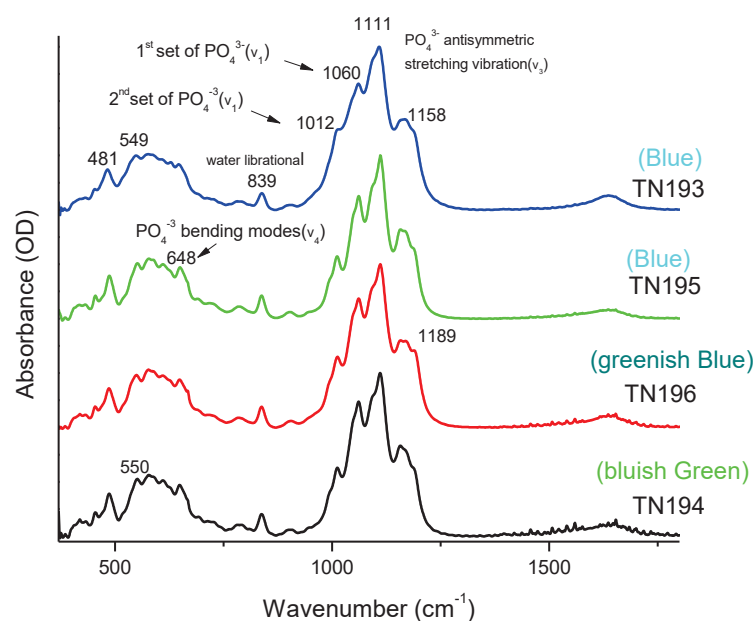


Figure 34. FTIR spectra of four turquoise samples (370-1800 cm^{-1} range) interpreted according to (Reddy, et al., 2006).

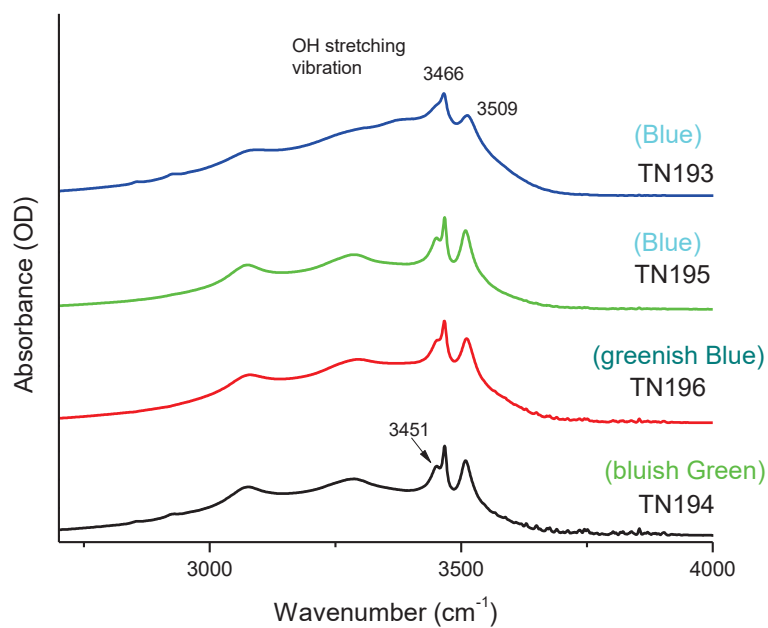


Figure 35. FTIR spectra of four turquoise samples (2700-4000 cm^{-1} OH/H₂O range) interpreted according to (Reddy, et al., 2006).

DISCUSSION

Most OH and H₂O peaks above 3000 cm^{-1} overlap to each other. Phosphate groups peaks are in the range of 900 to 1200 cm^{-1} . Different turquoise samples have at least three peaks in the range of 900 to 1200 cm^{-1} . The absorption peaks with above 3000 cm^{-1} range are related to hydroxyl and water group. The bonds in the range

of 2500cm^{-1} to 4000cm^{-1} are due to the OH bending vibrations of the hydroxyl group and the water (H_2O) molecules in the turquoise structure. A bond in the range of 1500 to 1650 cm^{-1} is related to the bond vibrations of the H_2O molecule. There is also a bond in the 900 cm^{-1} region, which is mainly due to the movements of the tetrahedral and octahedral frameworks of the turquoise unit cell. Octahedral is related to Aluminum and tetrahedral is affiliated to the phosphate. Narrow OH-stretching band at 3608 cm^{-1} , which was assigned to the OH- Fe^{3+} vibrations in the turquoise structure (Reddy, et al., 2006) but this band was not observed in the FTIR spectra of studied samples. Blue turquoise from Neyshapour, sample TN 193 compared to turquoise from Arizona in table 5.

According to (Schwarzinger & Schwarzinger, 2017) , 1034 , 1011 , 990 , 899 and 835 cm^{-1} are related to δ Al-OH and/or δ Cu-OH (Schwarzinger & Schwarzinger, 2017).Turquoise can be easily separated by FTIR from imitations by lack of significant bands in the OH region (3000 - 3500 cm^{-1}). FTIR is a good way to separating treated turquoise especially if the treatment has been done to the surface of the stone. If the stone surface treated by wax, CH bands can be found at 2850 and 2921 cm^{-1} as well as at 1462 cm^{-1} . The band at 1727 cm^{-1} appears when carbonyl groups exist in turquoise and it shows that the wax is already oxidized. Bands at 1742 and 1248 cm^{-1} are related to acrylate treated turquoise. (Schwarzinger & Schwarzinger, 2017).

First region (370 - 1800 cm^{-1}) related to phosphate peaks. Between 2300 to 2500 cm^{-1} artifact can be seen and it is due to exist of CO_2 . Second region is started from 2700 to 4000 cm^{-1} . According to (Reddy, et al., 2006), in the first region peaks from 648 - 725 cm^{-1} are related to PO_4^{3-} bending modes (ν_4). Peaks from 786 - 836 cm^{-1} shows water librations. 2nd set of PO_4^{3-} symmetric stretching vibrations (ν_1) can be seen in peaks from 899 - 1010 cm^{-1} . 1057 - 1085 cm^{-1} peaks related 1st set of PO_4^{3-} symmetric stretching vibrations (ν_1). Second region from 2700 to 4000 cm^{-1} shows water and OH part (water OH stretching vibrations and OH stretching vibrations).

Table 5. Positions and assignments of IR bands (cm^{-1}) in Neyshapour turquoise compared to turquoise from Arizona (Reddy, et al., 2006).

Blue Turquoise from Neyshapour (This work)	Turquoise from Arizona (Reddy, et al., 2006)	FTIR assignments
648	648	PO_4^{3-} bending modes (ν_4)
	725	"
	786	Water librations
838	836	"
	899	2 nd set of PO_4^{3-} symmetric stretching vibrations (ν_1)
	945	"
1012	1010	"
1060	1057	1 st set of PO_4^{3-} symmetric stretching vibrations (ν_1)
3508	1085	"
1111	1109	PO_4^{3-} antisymmetric stretching vibrations (ν_3)
1161	1161	"
1189	1195	"
3079	3068	Water OH stretching vibrations
3282	3281	"
3451	3446	OH stretching vibrations
3466	3465	"
3508	3509	"

FTIR analysis allows to identify the structure of turquoise. However, there is no special differences between the various colors of turquoise. It appears that FTIR is not a convenient method for separating turquoise from different mines. On the other hand, FTIR is a good way to separate turquoise from imitations and treated one by polymer impregnation.

4.2. RAMAN STRUCTURAL ANALYSES

52 samples were analyzed, 3 sample from Damghan, 6 samples from Kerman and 41 samples from Neyshapour as well as 2 synthetic turquoises and 1 treated one.

LATTICE VIBRATIONAL RANGE

Representative Raman spectra in the low frequency lattice vibrational range are shown Fig. 36 and 37.

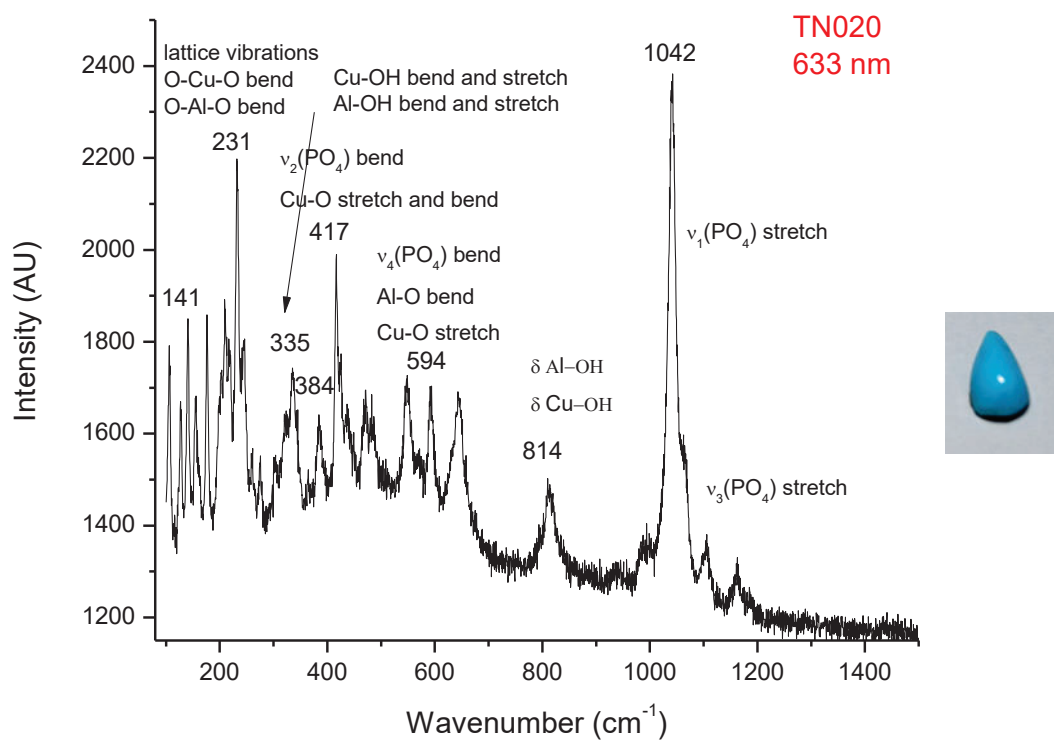


Figure 36. Raman spectrum of pure blue turquoise TN020 (Exc. 633 nm) interpreted according to (Cějka, et al., 2015) .

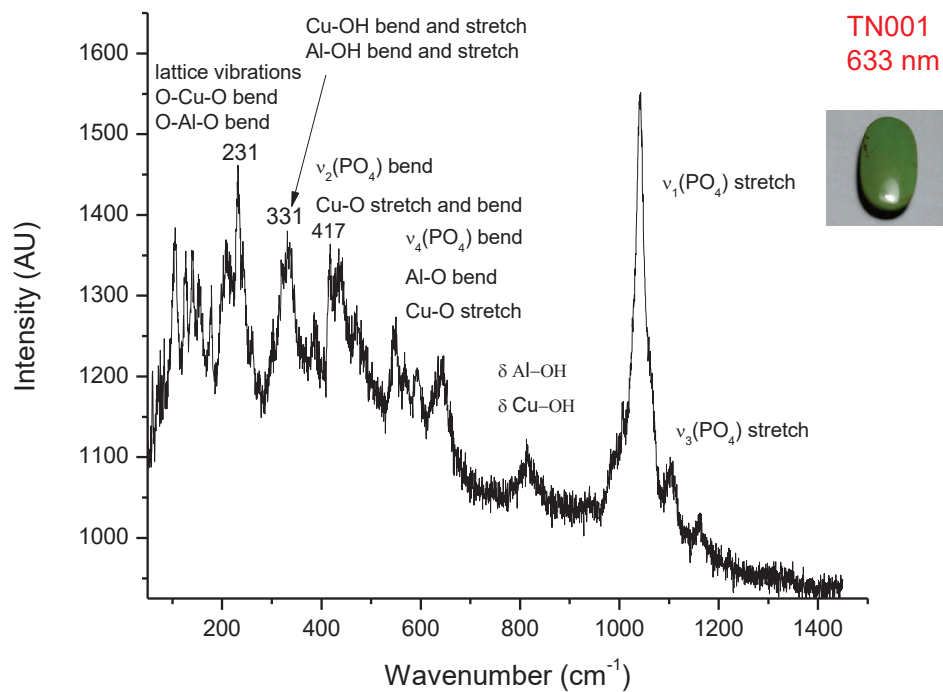


Figure 37. Raman spectrum of pure green turquoise TN001 (Exc. 633 nm) interpreted according to (Čejka, et al., 2015).

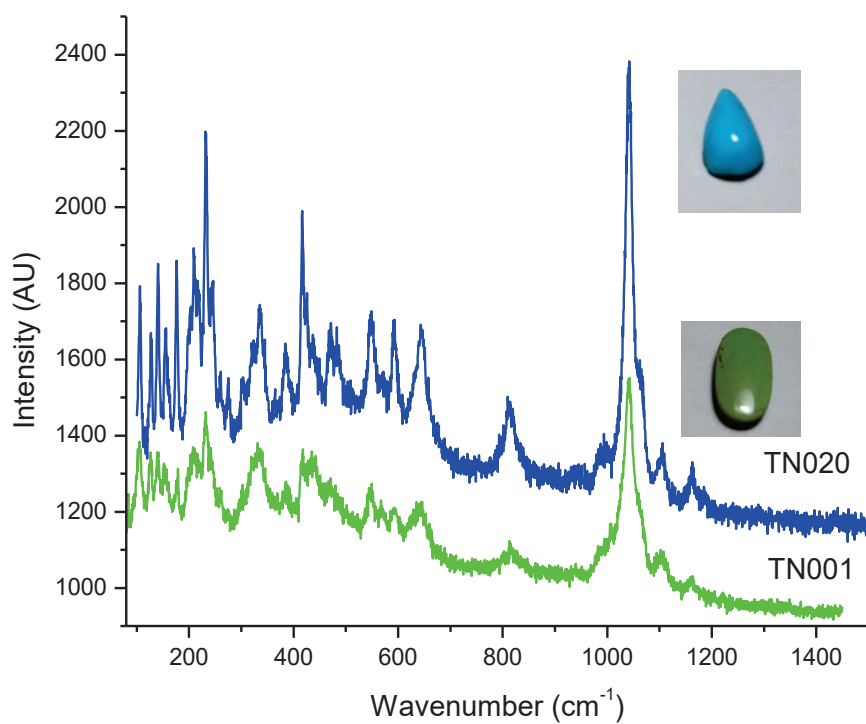


Figure 38. Compared Raman spectra of pure blue turquoise TN020 and pure green turquoise TN001 (633 nm).

As it can be seen comparing two representative Raman spectra of blue and green turquoise samples (Fig.38), the line width of the **blue sample appears much more resolved than of green one. A substitution should have occur inducing a certain disorder.**

OH VIBRATIONAL RANGE

Representative Raman spectra in the high frequency OH vibrational range are shown Fig. 39.

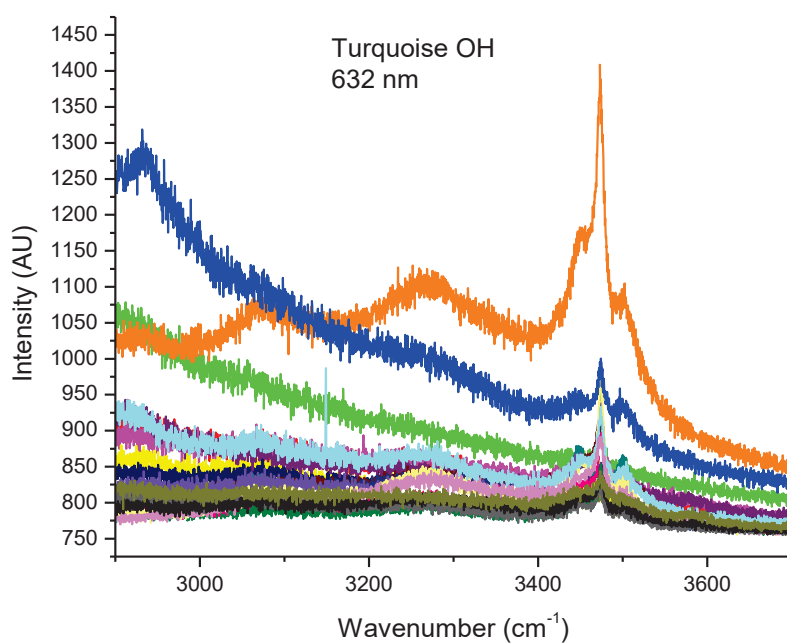


Figure 39. Raman spectra (633 nm) of Neyshapour turquoise samples in the OH/H₂O range.

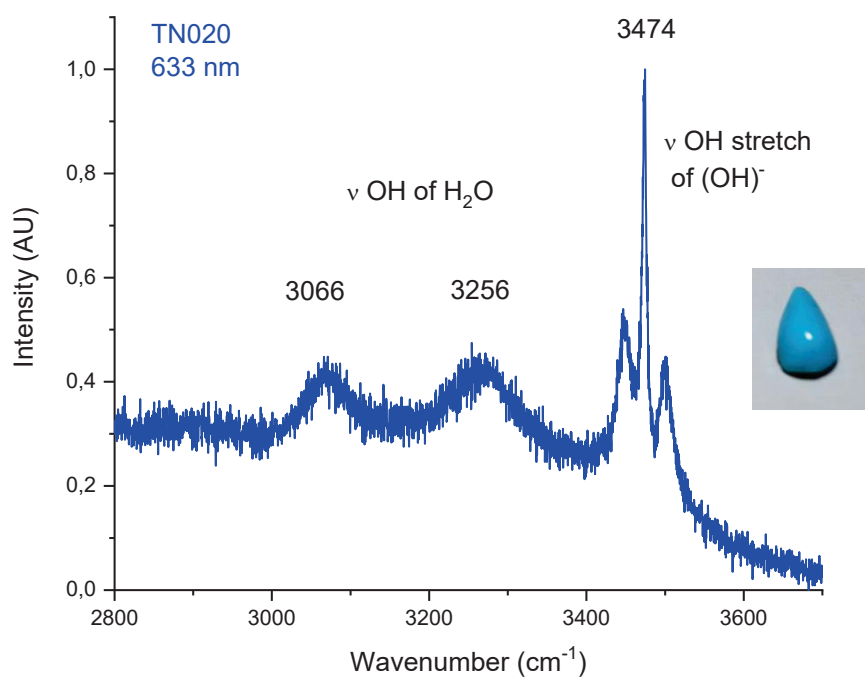


Figure 40. Raman spectrum of pure blue Neyshapour turquoise TN020 (633 nm) in water range interpreted with (Čejka, et al., 2015) .

As it can be seen comparing two representative Raman spectra in the OH range of blue and green turquoise samples (Fig. 40 and 41), **the line width of the blue sample appears much resolved than of green one as noticed for the lattice vibrational modes. Here again, a substitution which have occur induced a certain disorder.**

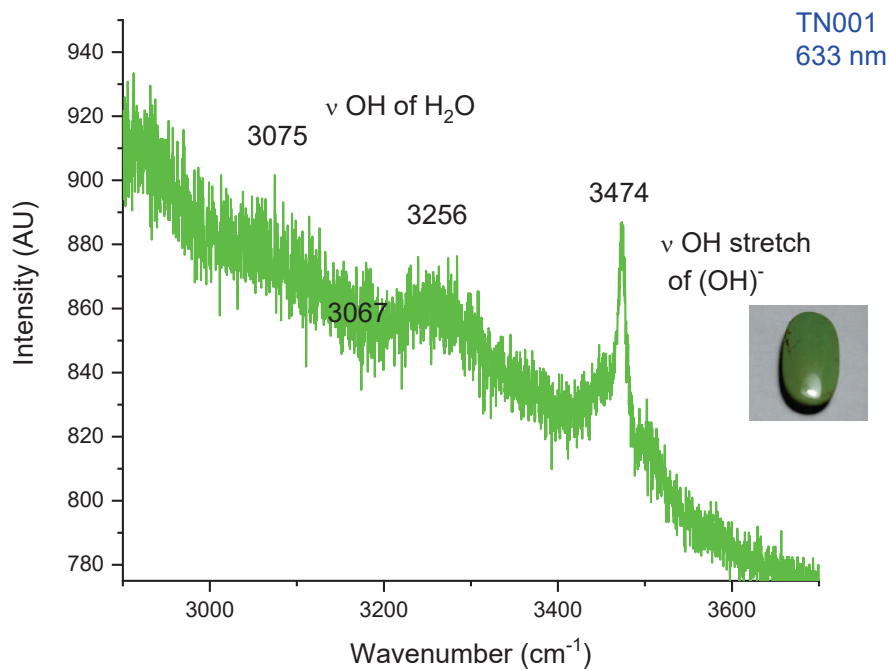


Figure 41. Raman spectrum of pure green turquoise TN001 (633 nm) in water range interpreted with (C̣ejka, et al., 2015).

DISCUSSION

Raman was used for characterization of phosphate minerals specially turquoise (Rossi, et al., 2017) (C̣ejka, et al., 2015) (Frost, et al., 2013) (Reddy, et al., 2006) (Khodabandeloo.P, 2013) (Frost, et al., 2006), separating turquoise from fake turquoise and imitations (Bernardino, et al., 2016).

In this study Raman spectrum was interpreted based on (C̣ejka, et al., 2015) which can be seen in table 6.

The Raman spectrum represents a broad band in the range of 3000 to 3800 cm^{-1} attributed to the bending vibrations of the water molecule (McMillan & Remmele, 1986). There is a broad maximal band in zone 3240 cm^{-1} that is attributed to a tensile state of OH that comprises a network of hydrogen bonds. $\text{Al}(\text{OH})_3$ represents four strong Raman bands in the range of 3520, 3431, 3361 and 3615 cm^{-1} which are attributed to OH tensile vibrations (Black, et al., 2006). The Raman spectrum also represents the other three weak bands at a lower wavelength, the range between 200 and 1200 cm^{-1} containing an $\text{Al}(\text{OH})_3$ deformation and a constant vibration of the $\text{Al}(\text{OH})_3$ network. The Raman spectrum has been determined by the main vibrations specified in 531 and 3692 cm^{-1} , and the range of 3692 cm^{-1} is due to OH vibrations. OH tension bands are observed in the Raman spectrum in the range of 3480 and 3580 cm^{-1} , and bending vibrations of the H_2O molecule in the range of 3372,

3262, and 3405 cm^{-1} , and two OH tension bands in the range of 3588 and 3564 cm^{-1} are observed (Ruan, et al., 2001).

OH tensile region is observed by three different bands in the Raman spectrum at a wave number of 3355 to 3360 cm^{-1} , 3440 to 3455 cm^{-1} and 3535 to 3580 cm^{-1} . Only one single band in the 3471 cm^{-1} wavenumber, FT-IR spectrum, for the OH group is observed (Kloprogge, et al., 2004). The low frequency of $\text{Al}(\text{OH})_3$ in the hydroxyl tensile region between 2800 and 3700 cm^{-1} is coordinated with the low distance between the oxygen atoms of the hydroxyl groups (Ruan, et al., 2001). Spectral vibration in the range of 700 to 2000 cm^{-1} is considered to be a significant evidence of covalent bonding of Al-O bond in $\text{Al}(\text{OH})_3$ system (Ruan, et al., 2001). The deformation modes of the hydroxyl group are observed in Raman spectroscopy in the range of 1091, 980.916 and 1051 cm^{-1} , which is related to the FT-IR spectrum in the range of 914, 969, 1024 and 1060 cm^{-1} (Black, et al., 2006). The deformation modes of the hydroxyl group are observed in Raman spectroscopy in the range of 1091, 980, 916 and 1051 cm^{-1} , which is related to the FT-IR spectrum in the range of 914, 969, 1024 and 1060 cm^{-1} (Black, et al., 2006).

The Raman spectrum in $\text{Al}(\text{OH})_3$ represents 4 strong bonds in the range of 3365, 3435, 3525 and 3618 cm^{-1} , and the tensile region of $\text{Al}(\text{OH})_3$ is in the range of 100 to 1200 cm^{-1} , and the fundamental difference in spectral vibrations of $\text{Al}(\text{OH})_3$ in the range of less than 800 cm^{-1} is attributed to the difference in the symmetry of $\text{Al}(\text{OH})_6$ unit (Black, et al., 2006). The tensile vibration of the phosphate group at 1042 and 1066 cm^{-1} is coordinated with two independent phosphate units in the turquoise structure.

Table 6. Assignment of turquoise Raman bands (C̣ejka, et al., 2015).

Neyshapour TN001 green (this study)	Neyshabur TN020 blue (this study)	Arizona (C̣ejka, et al., 2015)	Raman mode assignment
		3549	ν OH stretch of $(\text{OH})^-$
	3500	3502	"
3474	3474	3473	"
	3446	3450	"
		3397	ν OH stretch of water molecules
3256	3256	3279	"
3075	3066	3077	"
			δ H_2O bends
		1609	"
		1173	$\nu_3(\text{PO}_4)^{3-}$ antisymmetric stretch
1161		1160	"
1107		1105	"
		1065	$\nu_1(\text{PO}_4)^{3-}$ antisymmetric stretch
1042	1042	1042	"
			δ Cu-OH and/or δ Al-OH
1005		1004	"
984	998	985	"
941	938	931	"
			"
813	814	815	δ Cu-OH and/or δ Al-OH
			$\nu_4(\text{PO}_4)^{3-}$ bend and/or Al-(O,OH) bend and/or Cu-O stretch
643	644	643	"
			"
			"
592	594	593	"
568	568	571	"
548	548	550	"
512	508	506	$\nu_2(\text{PO}_4)^{3-}$ bend and/or Cu-O stretch and bend
501			"
480	482	485	"

471	471	471	"
450	449	457	"
435	437	438	"
	425	426	"
417	417	417	"d
404			"
385	389	387	"
345	364		Cu-(O,OH,H ₂ O) and Al-(O,OH,H ₂ O) stretch and bend vibration
331	335	337	"
318	322	321	"
302	301	303	"
273	275	276	Lattice vibration and/or O-Cu-O bend and/or O-Al-O bend
259	261	260	"
252	253		"
241	246	245	"
231	231	233	"
219	219	219	"
210	210	211	"
202	203	200	"
178	176	176	"
157	156	155	"

Three bands observed in the range of 1106, 1161 and 1184 cm⁻¹ are attributed to asymmetric phosphate tensile vibrations. The functional analyses group predicted 6 bands in the range that only three bands were observed due to random degeneration. There are also published spectra on the turquoise mineral (Kloprogge, et al., 2004). Raman spectroscopy of hydrated phosphate minerals has been reported, some minerals containing either hydrated or hydroxylated phosphate or both have been identified. The position of symmetric stretching vibrations of minerals such as turquoise is dependent on the function of the cations and the crystal structure of the minerals. Thus in the turquoise structure there are two distinct sets of water and phosphate vibrations. The network vibrations indicate that the turquoise is composed of 36 internal phosphate vibrations and 12 internal water vibrations which are made up of a total of 162 crystal vibrations. For each hydroxyl there is an active Raman spectrum and an active FT-IR vibration.

In Raman spectroscopy, a band in the range of 900 to 1200 cm⁻¹ of turquoise with the following formula CuAl₆(PO₄)₄(OH)₈·4H₂O and chalcociderite with the following formula Cu(Fe³⁺)₆(PO₄)₄(OH)₈·4H₂O depends on the subunits in the turquoise and chalcociderite structure, namely the phosphate unit, the water unit, and the hydroxyl units. Each of these units shows vibrational bands in the FT-IR Raman spectrum and spectrum. The first observations of the Raman spectrum of the three turquoise minerals are very similar, but there are some variations in the intensity of the observed bands. Secondly, a band of chalcociderite (green turquoise), which is a turquoise type, causes the bands to move to the right, which means a smaller wave number, because in the chalcociderite the substitution of Fe³⁺ instead of Al³⁺ causes the bands to expand and the bands move toward smaller wave number.

Even if tentatively the Fe³⁺/Al³⁺ (chalcociderite/turquoise serie) and Fe²⁺/Cu²⁺ (aheylite/turquoise) substitutions (Tab. 1) were studied by Raman and FTIR, it is not an easy task. The main conclusion is that Raman spectra in the lattice and in the OH and H₂O vibration ranges appears to be much more resolved for blue turquoise samples than for green ones. This suggest without doubt that the occurred substitutions should have induced a crystalline disorder.

4.3. XRF CHEMICAL ANALYSES

XRF ANALYSES OF TURQUOISE FROM THE PERSIAN MINES

Each collected samples from Iranian mines were analyzed by XRF. The chemical compositions are compared to below list and the detail of sample can be seen in Table 7 and Table 8:

- other studies on the same localities in Iran
 - (Khodabandloo.P, 2013) XRF
 - (Sabbaghi, et al., 2015) XRF
 - (Taghipour, 2014) (Etemadi, et al., 2011) EMPA (electron microprobe), XRF
 - (Reddy, et al., 2006) RDX
 - (Shirdam & Aslani, 2016) XRF; as well as
- to turquoise samples over the world:
 - China (Xu, et al., 2011), (Chen, et al., 2012), (Yang, et al., 2003), (Ying & Sun, 2010) EMPA
 - USA (Cejka, et al., 2015), (Othmane, et al., 2015), (Abdu, et al., 2011), (Foord & Taggart, 1998) EMPA, ICP
 - Egypt (Rossi, et al., 2017) EMPA
- And with theoretical compositions.

Important note: It has to be precised, that XRF data provided, during this study, will be compared to other analytical techniques such as EMPA (electron microprobe analyses), EDX-SEM (Energy-dispersive X-ray spectroscopy) and ICP (Inductively Coupled Plasma Mass Spectrometry).

In this study, only the result of one Egyptian turquoise sample was used (Rossi, et al., 2017) due to the lack of access to the mine for sampling as well as the lack of articles and information on XRF analyzes of Egyptian turquoises.

Table 7. Composition and color of turquoise mineral of various origins (Reddy, et al., 2006).

Sample	1 ^a Arizona, blue This work	2 Nishapur, sky-blue	3 Damghan, sky-blue	4 Nishapur, apple-green	5 Damghan, apple-green	6 ^a Senegal, green, This work
CuO	10.0	6.36	8.06	7.60	8.08	10.04
Al ₂ O ₃	47.1	37.40	36.00	36.04	33.90	46.49
Fe ₂ O ₃	1.94	0.38	0.55	1.60	2.72	3.19
P ₂ O ₅	40.96	36.65	33.56	36.26	33.18	40.28
H ₂ O	nd	18.11	19.28	17.88	19.28	nd
Total	100	98.50	97.45	99.38	97.16	100

Table 8. The various samples and chemical data used for PCA analyses (This study and bibliographic data).

Date	Method	Origin	Number of samples	reference
Iran	XRF	Neyshabur	38	This study
Iran	EDX	Neyshabur	2	(Reddy, et al., 2006)
Iran	XRF	Neyshabur	3	(Khodabandloo.P, 2013)
Iran	XRF	Neyshabur	2	(Hassnnezhad, et al., 2013)
Iran	EMPA	Neyshabur	1	(Rossi, et al., 2017)
Iran	XRF	Neyshabur	10	(Sabbaghi, 2018)
Iran	XRF	Kerman	7	This study
Iran	XRF	Kerman	6	(Etemadi, et al., 2011)
Iran	XRF	Kerman	2	(Khodabandloo.P, 2013)
Iran	XRF	Kerman	7	(Shirdam & Aslani, 2016)
Iran	XRF	Damghan	5	This study
Iran	EDX	Damghan	2	(Reddy, et al., 2006)
Iran	XRF	Damghan	3	(Khodabandloo.P, 2013)

Iran	EMPA	Semnan	7	(Taghipour, 2014)
China	XRF	Tibet	1	This study
China		Zhushan	5	(Chen, et al., 2012)
China	EPMA	Zhushan	1	(Xu, et al., 2011)
China	n.d	Zhushan	8	(Ying & Sun, 2010)
China	EMPA	Bambo	2	(Xu, et al., 2011)
China	EMPA	Manshan	1	(Xu, et al., 2011)
China	n.d	Manshan	10	(Yang, et al., 2003)
China	n.d	Yun County	2	(Chen, et al., 2012)
China	n.d	Yun County	2	(Chen, et al., 2012)
Senegal	EMPA	Senegal	1	(C'ejka, et al., 2015)
Senegal	EDX	Senegal	1	(Reddy, et al., 2006)
Senegal	XRF	Senegal	10	(Sabbaghi, 2018)
USA	EMPA	Virginia	1	(C'ejka, et al., 2015)
USA	EMPA	Colorado	1	(Othmane, et al., 2015)
USA	EMPA	California	1	(Othmane, et al., 2015)
USA	EMPA	Nevada	4	(Othmane, et al., 2015)
USA	EMPA	Nevada	2	(Abdu, et al., 2011)
USA	EMPA	New Mexico	2	(Othmane, et al., 2015)
USA	EMPA	New Mexico	5	(Abdu, et al., 2011)
USA	EMPA	New Mexico	2	(Rossi, et al., 2017)
USA	EMPA	Arizona	2	(Othmane, et al., 2015)
USA	EMPA	Arizona	1	(C'ejka, et al., 2015)
USA	EDX	Arizona	1	(Reddy, et al., 2006)
USA	XRF	Arizona	10	(Sabbaghi, 2018)
USA	ICP	Arkansas	8	(Foord & Taggart, 1998)
Egypt	EMPA	Sinai	1	(Rossi, et al., 2017)
MAD	XRF	MAD	39	This study

In figure 42, New Mexico turquoise present the highest amount of Fe_2O_3 . The percentages of iron, copper, and zinc in the various turquoise are shown in figure 43. Most of the percentage of copper oxide is found in Nevada turquoise and the lowest percentage of copper oxide is found in Neyshapour and Damghan turquoise. This table cannot be expressed in terms of divalent iron oxide percentages because it is in most cases not measured or presented, only available in some Chinese samples and samples of this study.

According to the results (Annex II), the higher percentage of copper than iron, lead the color tends to be blue than green.

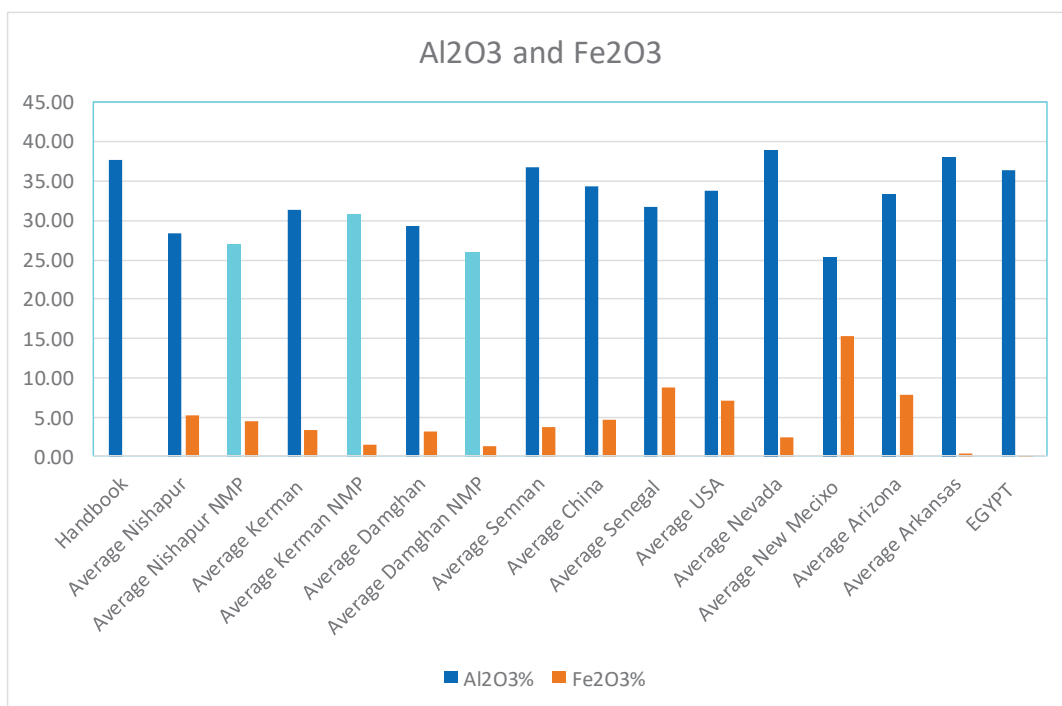


Figure 42. Variations of Al₂O₃ and Fe₂O₃ in turquoise from different mines.

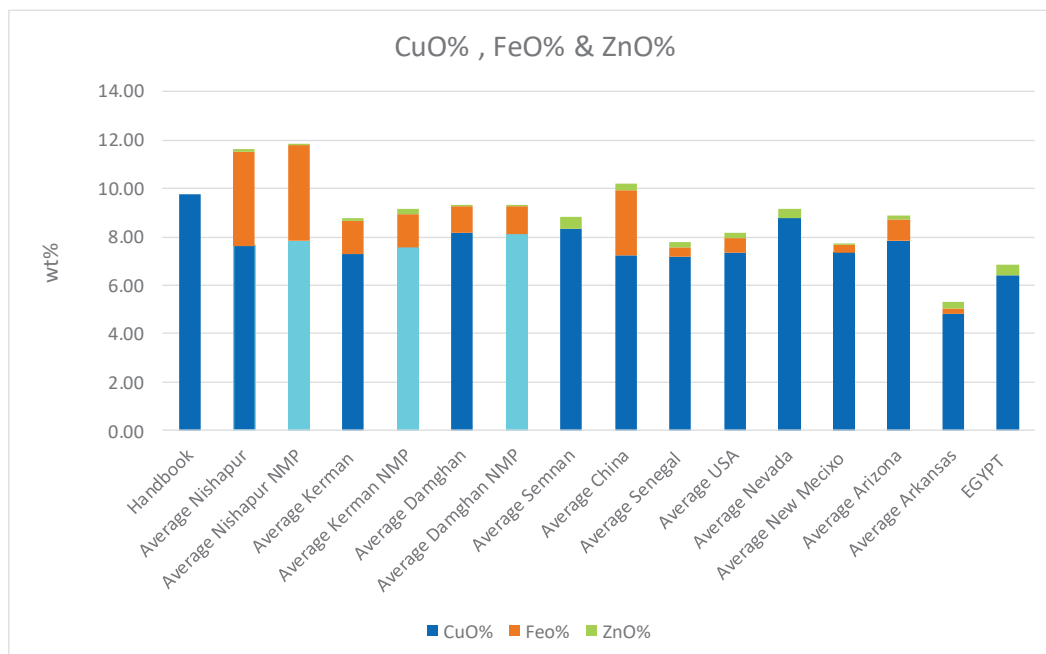


Figure 43. Variations of CuO, FeO and ZnO in turquoise from different mines.

XRF data are collected in ppm which were convert in oxide % for the major elements (Al₂O₃, CuO, P₂O₅, Fe₂O₃), while trace elements are keep in ppm.

XRF ANALYSES OF TURQUOISE-BEARING ARTIFACTS FROM THE MAD MUSEUM

A selection of 34 turquoise-bearing jewels and artefacts were done at the Musée des Arts décoratifs (MAD, Paris). The list is given in Annex I and the report in Annex II.

DISCUSSION

In order to define representative cluster domains, correlation graphs are plotted for mineralogical and jewel samples (logarithmic scale). They were all normalized to Cu, since it is considered as nearly invariable:

- Fe/Cu vs Zn/Cu
- As/Cu vs Zn/Cu
- Ca/Cu vs Zn/Cu
- Ti/Cu vs Zn/Cu

CORRELATION GRAPH: FE VS ZN

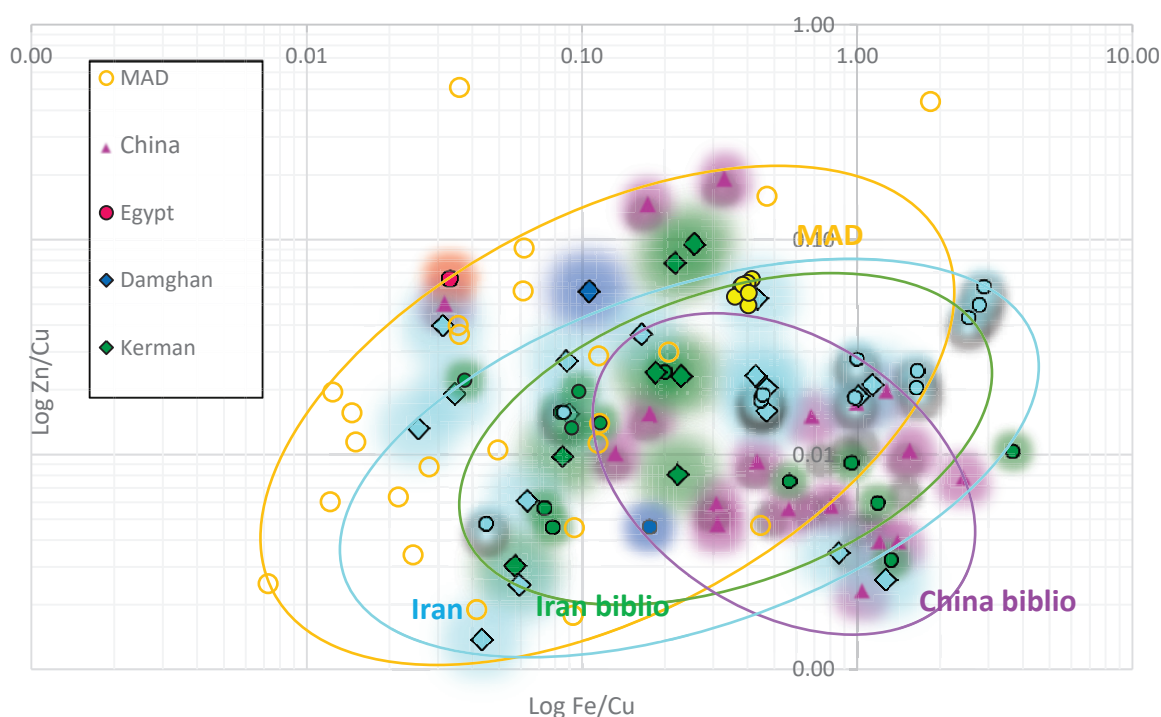


Figure 44. Plot of Zn/Cu ratio versus Fe/Cu (logarithmic scales) of analyzed turquoises from Iran (Neyshapour, Kerman and Damghan), compared to analyzed MAD turquoise-bearing artefacts and data from bibliography (Egypt and China).

As it can be seen localized Fig. 44, define clusters appear:

- **Neyshapour turquoises** (blue diamond symbols) are characterized by a quite well defined Fe/Cu range (0.02 to 1) and Zn/Cu ratio (0,001 to 0,1). Neyshapour turquoise data from bibliography (blue circle) are in similar areas of sample gathered from Neyshapour mine (blue diamond symbols).
- **Kerman turquoises** (Green Diamond symbols) have quite similar Zn/Cu ratios and higher Fe/Cu ratios. Kerman turquoise data from bibliography (green dots symbols) show higher Fe/Cu ratios and lower Zn/Cu ratios.

- **Damghan turquoise** (black diamond symbols) shows similar Fe/Cu ratio and a higher Zn/Cu ratio. Damghan turquoise data from bibliography (black dots symbol) have approximately similar ratios of Fe/Cu but shows lower ratio of Zn/Cu
- Seman samples (yellow dots) as one of minor turquoise mine of Iran shows approximately similar ratios of Fe/Cu and Zn/Cu
- All **MAD** samples (orange circles) **are superimposed on Iran domain.**
- **Egyptian** samples (red dots) appear to have a lower Fe/Cu ratio and higher Zn/Cu than Iranian ones.
- **Chinese** samples (violet triangles) have a quite similar Zn/Cu ratio and a higher Fe/Cu ratio like Kerman samples.

CORRELATION GRAPH: AS VS ZN

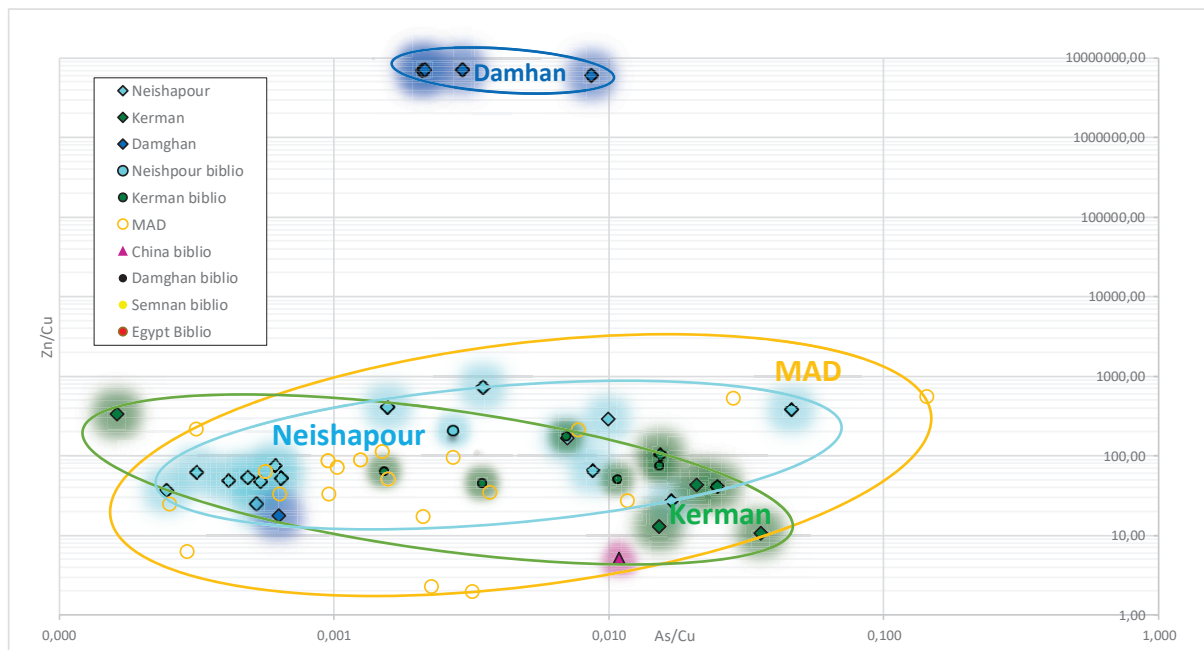


Figure 45. Plot of Zn/Cu ratio versus As/Cu of analyzed turquoise from Iran (Neyshapour, Kerman and Damghan), compared to analyzed MAD turquoise-bearing artefacts and data from bibliography.

As it can be seen localized Fig. 45, define clusters appear:

- **Neyshapour** samples (blue diamond symbols) are characterized by a quite well define Zn/Cu ratio (0,001 to 0,1) and by a wide As/Cu range.
- **Kerman** samples (green diamond symbols) are characterized by a quite well define Zn/Cu ratio, similar to those of Neyshapour, and by a much reduce As/Cu range (0.1 to 0.4). It appears that bibliographic data on Kerman samples (yellow triangle symbols) do not fit to those analyzed during this work. They are superimposed on the Neyshapour domain.
- **Damghan** sample (black diamond symbols) are characterized by extremely low Zn/Cu ratio (no As content), and by a quite well define As/Cu range (0.02 to 0.09).
- All **MAD** samples (yellow circles) **are superimposed on Neyshapour and Kerman domains.**
- Egypt data is not mentioned because of the lack of data.

CORRELATION GRAPH: CA VS ZN

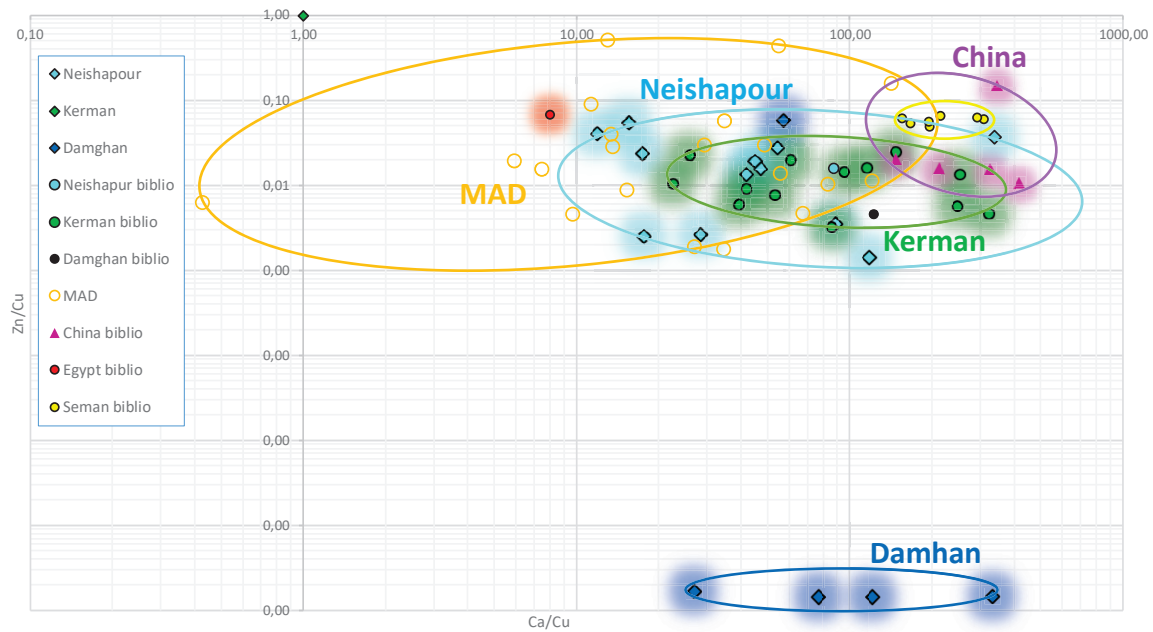


Figure 46. Plot of Zn/Cu ratio versus Ca/Cu of analyzed turquoises from Iran (Neyshapour, Kerman and Damghan), compared to analyzed MAD turquoise-bearing artefacts and data from bibliography (China and Egypt).

Here again MAD samples are more similar to Persian samples mostly from Neyshapour.

As it can be seen localized Fig. 46, define clusters appear as well:

- **Neyshapour** samples (blue diamond symbols) are characterized by a quite well define Zn/Cu ratio (0,001 to 0,1) and Ca/Cu range (10 to 100).
- **Kerman** samples (green diamond symbols) shows the highest ratio of Zn/Cu but with much lower ratio of Ca/Cu (nearly zero)
- **Kerman bibliography** samples (green dots symbols) are characterized by a quite well define Zn/Cu ratio, similar to those of Neyshapour, and by a slight higher Ca/Cu range (20 to 110).
- **Damghan** sample (black diamond symbols) shows similar ratio of Ca/Cu to Kerman and Neyshapour samples but very low in Zn/Cu (nearly no Zn).
- **Damghan bibliography** samples (black dots symbols) are superimposed to Kerman data
- All **MAD** samples (orange circles) **are superimposed on Neyshapour and Kerman domains** (besides one with nearly no Ca).
- **Egyptian** sample (red dots) appears to have a much higher Zn/Cu ratio and lower Ca/Cu than Iranian ones.
- **Chinese** samples (violet dots) on the contrary have a lower Zn/Cu and higher Ca/Cu ratios.

CORRELATION GRAPH: TI VS ZN

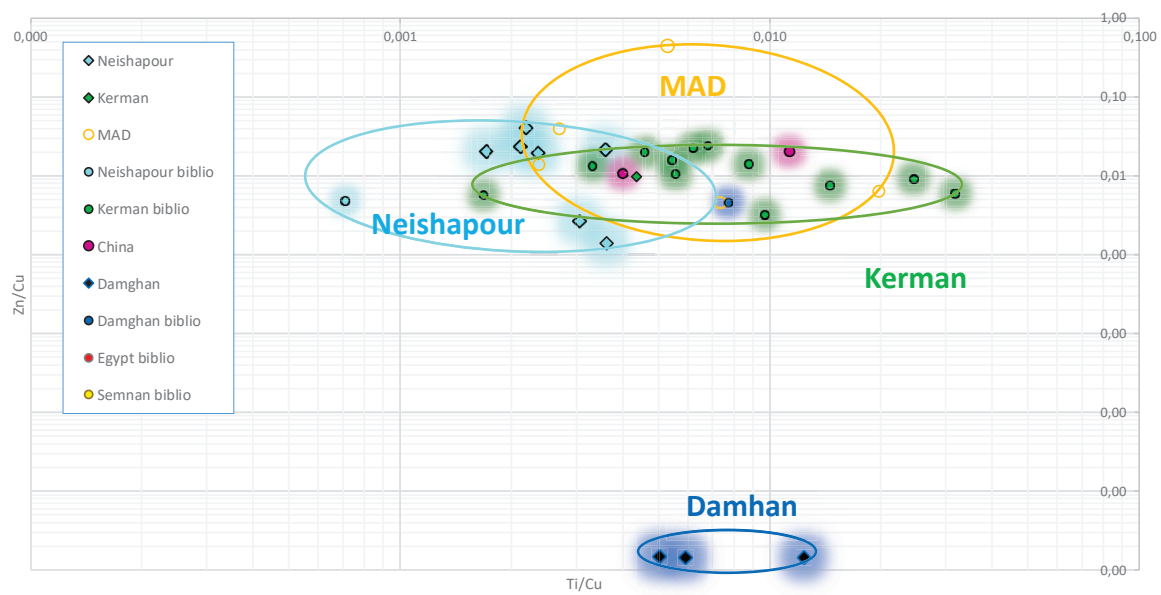


Figure 47. Plot of Zn/Cu ratio versus Ti/Cu of analyzed turquoises from Iran (Neyshapour, Kerman and Damghan), compared to analyzed MAD turquoise-bearing artefacts and data from bibliography.

As it can be seen localized Fig. 47, define clusters appear:

- **Neyshapour** samples (blue diamond symbols) are characterized by a quite well define Zn/Cu ratio (0,001 to 0,1) and Ti/Cu range (0.01 to 0.08).
- **Kerman** samples (Green diamond symbols) and Kerman bibliography samples (Green dots symbols) are similar to those of Neyshapour, with by a slight higher Ti/Cu range.
- **Damghan** sample (Black diamond symbols) present a quite similar Ti/Cu ratio but with much lower Z/Cu (nearly no Zn) value.
- All **MAD** samples (orange circles) are superimposed on Neyshapour and Kerman domains.
- **Chinese** samples (violet dots) are as well superimposed to Neyshapour and Kerman.
- Egypt data is not mentioned because of the lack of analyses.

It appears that MAD turquoise-bearing jewels are superimposed to Iranian Neyshapour and Kerman turquoise domains (Fe/Cu vs Zn/Cu; Zn/Cu vs As/Cu; Zn/Cu vs Ca/Cu). Kerman turquoises do not correspond, as well as Chinese ones.

COMPARAISON OF THIS STUDY WITH PREVIOUS ONES (CARO ET AL., 2017)

Caro et al. (2017) provided XRF analyses of Sinai and Persian turquoises, as well as of Persian, Mesopotamian, and Central Asian artifacts in a non-published report and poster. It was not possible to get their data. In order to try to compare their data with this study, the domains define by Caro et al. (2017) were added in the Cu/Zn vs Cu/Fe (Fig. 49) and the Cu/Zn vs Cu/As (Fig. 51) diagrams.

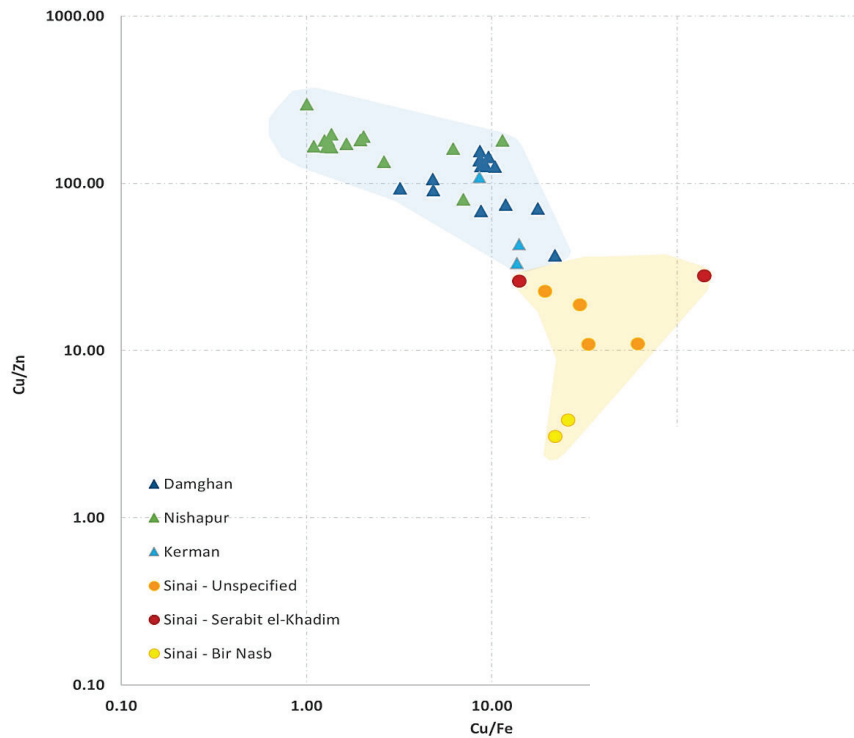


Figure 48. Plot of Cu/Fe ratio versus Cu/Zn of Iranian and Sinai analyzed turquoises of the Metropolitan museum of Art (Carò, et al., 2017)

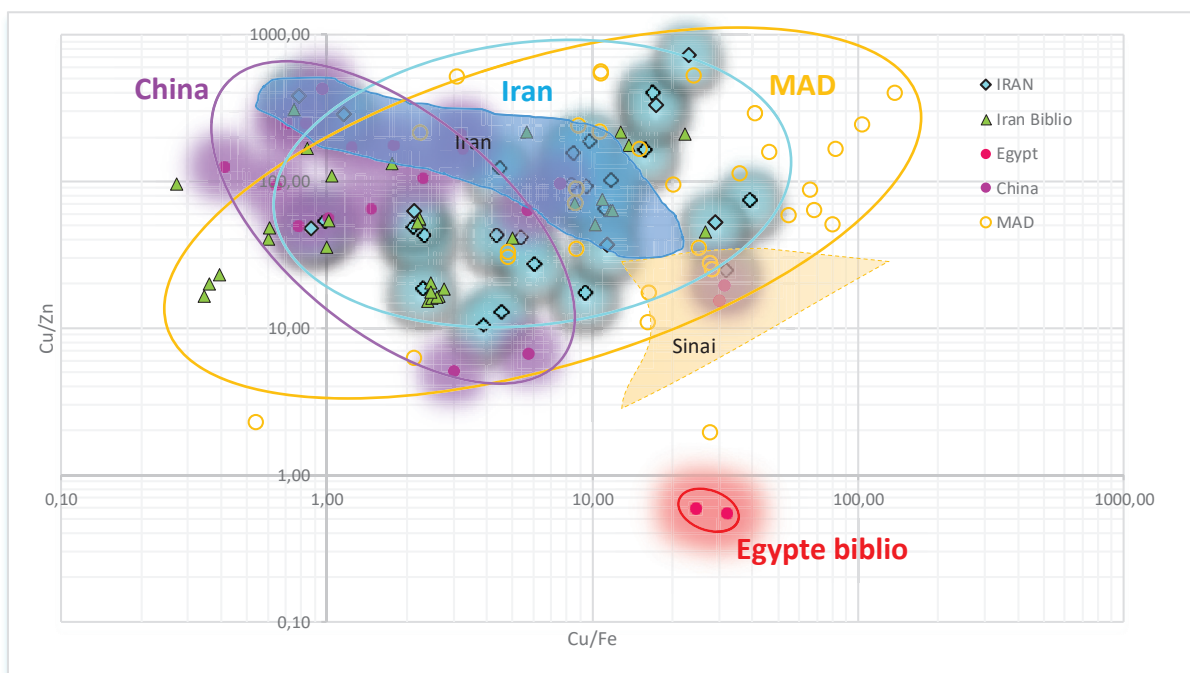


Figure 49. Cu/Zn vs Cu/Fe correlation diagram of Iranian samples (this study), data from bibliography, as well as Sinai domain (Caro et al., 2017). The Iran and Sinai domains of Caro et al. are delimited.

Comparing these results (Fig.49) and the results of the Metropolitan Museum of Art (MET) report (Carò, et al., 2017) (Fig.48), Egypt sample presents a higher ratio of Zn/Cu and lower Fe/Cu from most of Neyshapour samples but in MET result Egypt samples have low Cu/Zn and higher Cu/Fe ratios.

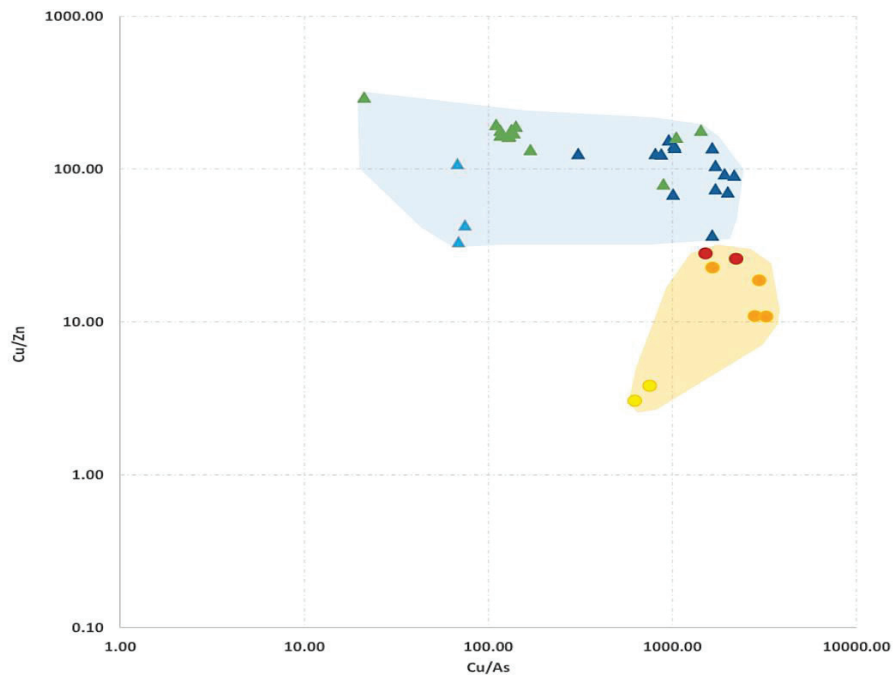


Figure 50. Plot of Cu/Zn ratio versus Cu/As of analyzed turquoises of the Metropolitan museum of Art (Carò et al., 2017)

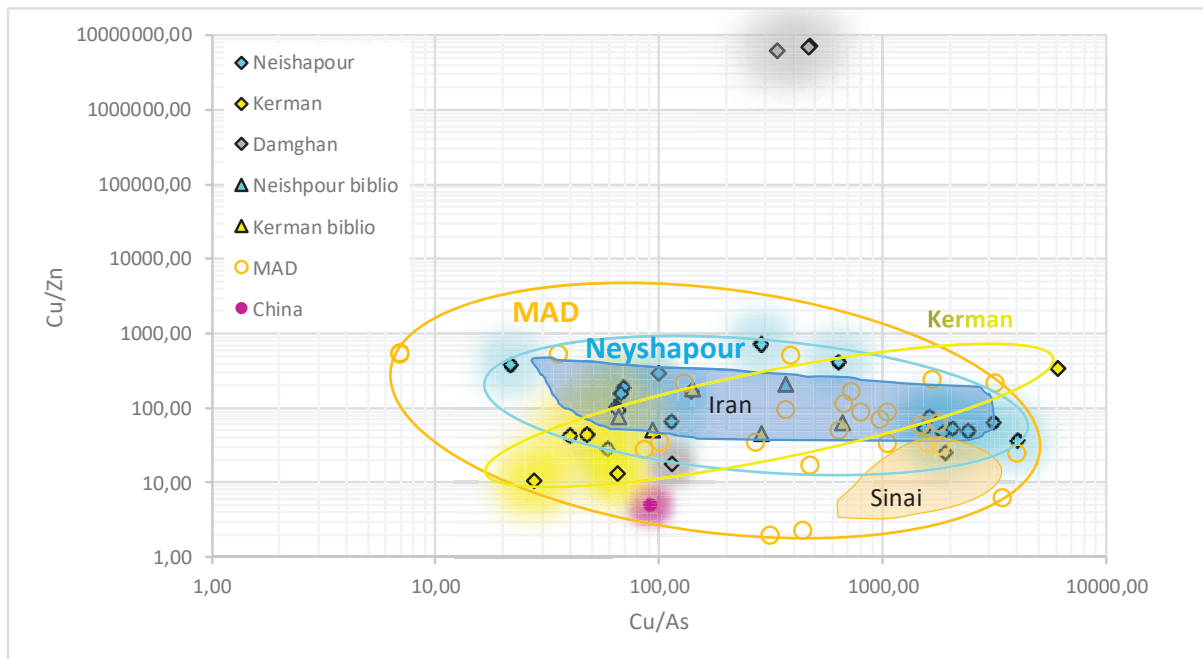


Figure 51. Cu/Zn vs Cu/As correlation diagram of Iranian samples (this study), data from bibliography, as well as Sinai domain (Caro et al., 2017). The Iran and Sinai domains of Caro et al. are delimited.

In MET samples (Fig.50 & 51), Neyshapour turquoises present a lower ratio of Zn/Cu and As/Cu but based on this study, Neyshapour samples approximately have higher ratio in As/Cu and similar ratio in Zn/Cu. Damghan

samples analysed in this study, show high ratio of Zn/Cu compare with Neyshapour and Kerman but in MET samples shows almost similar ratio to those from Neyshapour and Kerman. In this study Neyshapour samples nearly have higher ratio of As/Cu but in MET samples higher ratio is belongs to Damghan samples. . Analyses of some elements are available only for one sample from Egyptian turquoises (Rossi, et al., 2017), therefore the charts are not suitable for comparing Persian and Egyptian turquoises samples.

PRINCIPAL COMPONENT ANALYSES (PCA)

Data for PCA (The technique of PCA is described in Annex V) gathered from Persian Mines and 15 papers including 95 sample from Iran, 32 samples from China, 12 samples from Senegal, 40 samples from USA ,1 sample from Egypt and 39 sample from MAD. Detail of samples can be seen in table 8.

PCA OF MAJOR ELEMENTS (Al_2O_3 , P_2O_5 , CuO , Fe_2O_3)

PCA OF ALL SAMPLES FROM IRAN (THIS STUDY)

49 samples gathered from Neyshapour, Kerman and Damghan mine and the chemical component of main oxides of turquoise (Al_2O_3 , P_2O_5 , CuO , Fe_2O_3) analyzed by PCA (Principal Component Analysis) method. **For Iranian samples there is as attended a strong correlation between Al_2O_3 and P_2O_5 (Tab.9) (Fig.52) and as well as for CuO (F1 factor) and correlation between Fe and Cu (F2 factor).**

Table 9. Correlation of main oxides of turquoise from Iran.

Correlation matrix (Pearson (n)):

Variables	$Al_2O_3\%$	$P_2O_5\%$	$CuO\%$	$Fe_2O_3\%$
$Al_2O_3\%$	1	0.822	0.227	-0.133
$P_2O_5\%$		1	0.193	-0.105
$CuO\%$			1	0.059
$Fe_2O_3\%$				1

Values in bold are different from 0 with a significance level $\alpha=0.05$

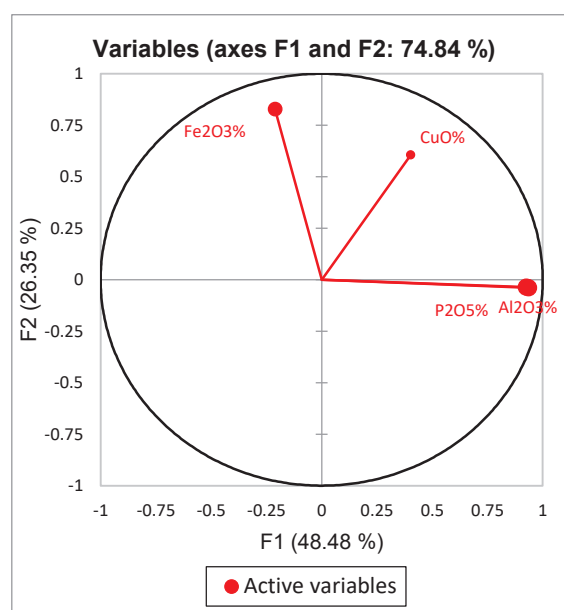


Figure 52. Correlation main oxides (Al_2O_3 , P_2O_5 , CuO , Fe_2O_3) of Iran samples.

PCA OF IRAN SAMPLES FROM BIBLIOGRAPHY

Data for 46 samples were chosen from Neyshapour, Kerman and Damghan mines from literature (table 12). Al_2O_3 is correlated with CuO and P_2O_5 and anti-correlated with Fe_2O_3 . P_2O_5 is correlated with Al_2O_3 and CuO and anti-correlated with Fe_2O_3 . Fe_2O_3 is anti-correlated with Al_2O_3 and P_2O_5 and CuO . (Tab.10) (Fig.53)

Table 10. Correlation of main oxides of turquoise from Iran bibliography.

Correlation matrix (Pearson (n)):				
Variables	$\text{Al}_2\text{O}_3\%$	$\text{P}_2\text{O}_5\%$	$\text{CuO}\%$	$\text{Fe}_2\text{O}_3\%$
$\text{Al}_2\text{O}_3\%$	1	0.581	0.673	-0.872
$\text{P}_2\text{O}_5\%$		1	0.467	-0.697
$\text{CuO}\%$			1	-0.609
$\text{Fe}_2\text{O}_3\%$				1

Values in bold are different from 0 with a significance level $\alpha=0.05$

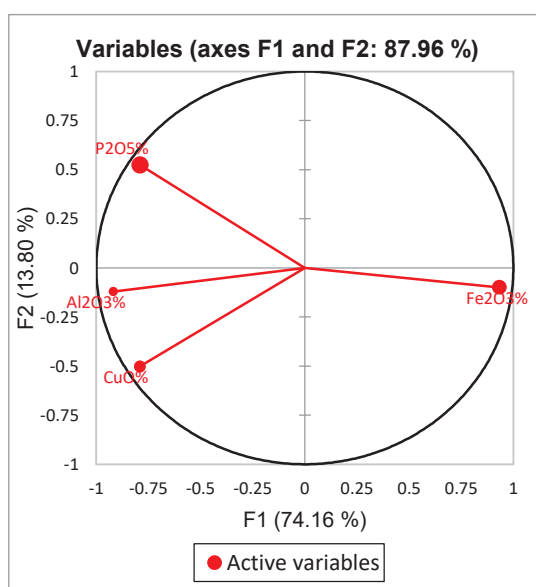


Figure 53. Correlation main oxides (Al_2O_3 , P_2O_5 , CuO , Fe_2O_3) of Iran bibliography samples

PCA OF NEYSHAPOUR SAMPLES (THIS STUDY AND BIBLIOGRAPHY DATA)

56 samples were chosen from Iran Neyshapour mine samples and bibliography (table12). Al_2O_3 is correlated with CuO and P_2O_5 and anti-correlated with Fe_2O_3 . P_2O_5 is correlated with Al_2O_3 and CuO and anti-correlated with Fe_2O_3 . Fe_2O_3 is anti-correlated with Al_2O_3 . (Tab.11) (Fig.54).

Table 11. Correlation of main oxides of turquoise from Neyshapour (Iran + Bibliography)

Correlation matrix (Pearson (n)):				
Variables	$\text{Al}_2\text{O}_3\%$	$\text{P}_2\text{O}_5\%$	$\text{CuO}\%$	$\text{Fe}_2\text{O}_3\%$
$\text{Al}_2\text{O}_3\%$	1	0.604	0.308	-0.267
$\text{P}_2\text{O}_5\%$		1	0.033	0.067
$\text{CuO}\%$			1	-0.133
$\text{Fe}_2\text{O}_3\%$				1

Values in bold are different from 0 with a significance level $\alpha=0.05$

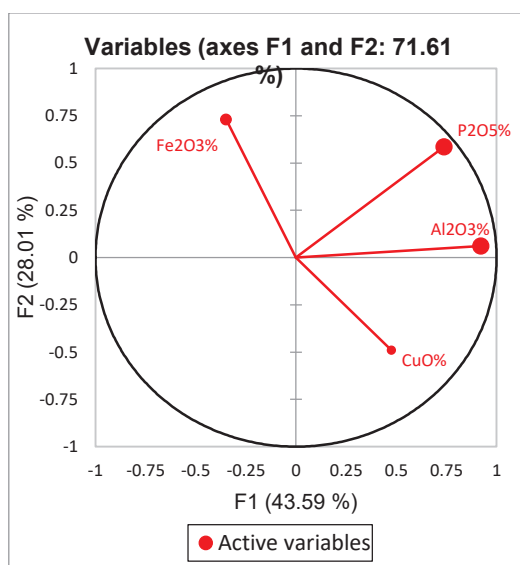


Figure 54. Correlation main oxides (Al_2O_3 , P_2O_5 , CuO , Fe_2O_3) of Neyshapour (Iran + bibliography)

PCA OF KERMAN SAMPLES (THIS STUDY AND BIBLIOGRAPHY DATA)

22 samples were chosen from Iran Kerman mine samples and bibliography (table12). Al_2O_3 is correlated with CuO and anti-correlated with Fe_2O_3 . Fe_2O_3 is anti-correlated with Al_2O_3 and CuO (Tab.12)(Fig.55).

Table 12. Correlation of main oxides of turquoise from Kerman (Iran+ Bibliography)

Correlation matrix (Pearson (n)):				
Variables	$\text{Al}_2\text{O}_3\%$	$\text{P}_2\text{O}_5\%$	$\text{CuO}\%$	$\text{Fe}_2\text{O}_3\%$
$\text{Al}_2\text{O}_3\%$	1	0.339	0.616	-0.603
$\text{P}_2\text{O}_5\%$		1	0.211	-0.110
$\text{CuO}\%$			1	-0.844
$\text{Fe}_2\text{O}_3\%$				1

Values in bold are different from 0 with a significance level $\alpha=0.05$

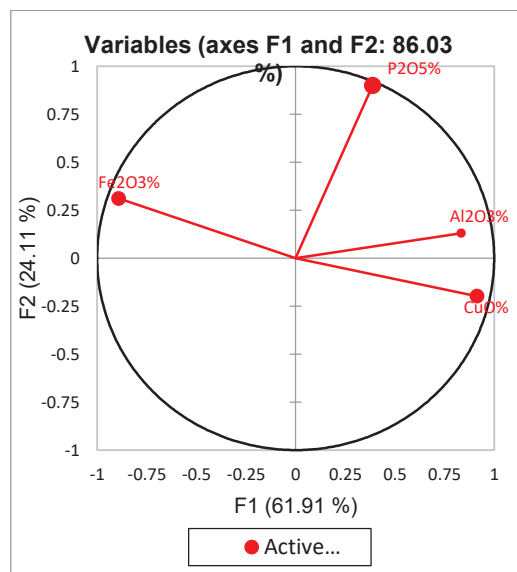


Figure 55. Correlation main oxides (Al_2O_3 , P_2O_5 , CuO , Fe_2O_3) of Kerman (Iran +bibliography)

PCA OF DAMGHAN SAMPLES (THIS STUDY AND BIBLIOGRAPHY DATA)

10 samples was chosen from Iran Damghan mine samples and bibliography (table12). Al_2O_3 is correlated with P_2O_5 . (Tab.13)(Fig.56).

Table 13. Correlation of main oxides of turquoise from Damghan (Iran+Bibliography)

Correlation matrix (Pearson (n)):				
Variables	$\text{Al}_2\text{O}_3\%$	$\text{P}_2\text{O}_5\%$	$\text{CuO}\%$	$\text{Fe}_2\text{O}_3\%$
$\text{Al}_2\text{O}_3\%$	1	0.737	-0.308	-0.227
$\text{P}_2\text{O}_5\%$		1	-0.070	0.280
$\text{CuO}\%$			1	-0.187
$\text{Fe}_2\text{O}_3\%$				1

Values in bold are different from 0 with a significance level $\alpha=0.05$

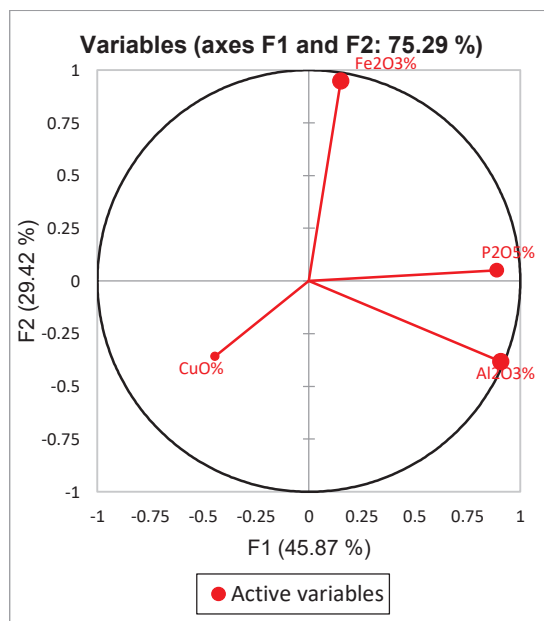


Figure 56. Correlation main oxides (Al₂O₃, P₂O₅, CuO, Fe₂O₃) of Damghan (Iran + bibliography)

PCA OF CHINA SAMPLES BIBLIOGRAPHY

32 samples were chosen from China mine bibliography (table12). Al₂O₃ is correlated with CuO and P₂O₅. P₂O₅ is correlated with Al₂O₃ and CuO (Tab. 14) (Fig. 57).

Table 14. Correlation of main oxides of turquoise from China (Bibliography)

Correlation matrix (Pearson (n)):

Variables	Al ₂ O ₃ %	P ₂ O ₅ %	CuO%	Fe ₂ O ₃ %
Al ₂ O ₃ %	1	0.763	0.518	-0.049
P ₂ O ₅ %		1	0.546	0.261
CuO%			1	-0.098
Fe ₂ O ₃ %				1

Values in bold are different from 0 with a significance level alpha=0.05

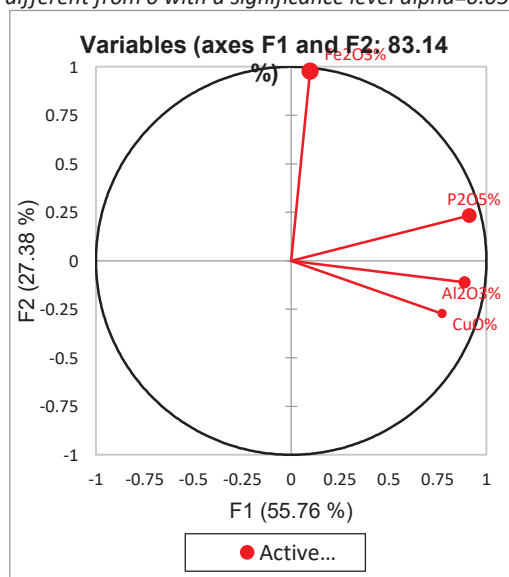


Figure 57. Correlation main oxides (Al_2O_3 , P_2O_5 , CuO , Fe_2O_3) of China (bibliography)

PCA OF MAD SAMPLES

39 samples were tested in Musée des Arts Décoratifs, Paris(MAD) and analyzed by PCA method. Al_2O_3 is correlated with P_2O_5 . P_2O_5 is correlated with Al_2O_3 (Tab.15)(Fig.58).

Table 15. Correlation of main oxides of MAD turquoise samples (Bibliography)

Correlation matrix (Pearson (n)):

Variables	$\text{Al}_2\text{O}_3\%$	$\text{P}_2\text{O}_5\%$	$\text{CuO}\%$	$\text{Fe}_2\text{O}_3\%$
$\text{Al}_2\text{O}_3\%$	1	0.830	0.793	0.147
$\text{P}_2\text{O}_5\%$		1	0.589	0.221
$\text{CuO}\%$			1	0.073
$\text{Fe}_2\text{O}_3\%$				1

Values in bold are different from 0 with a significance level $\alpha=0.05$

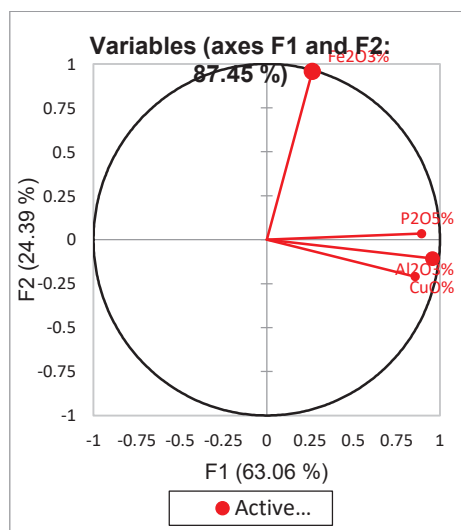
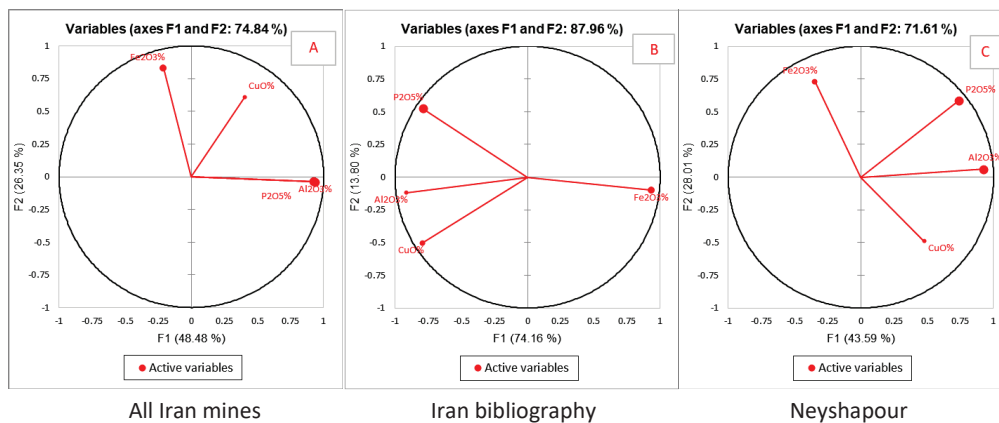


Figure 58. Correlation main oxides (Al_2O_3 , P_2O_5 , CuO , Fe_2O_3) of MAD samples.

DISCUSSION



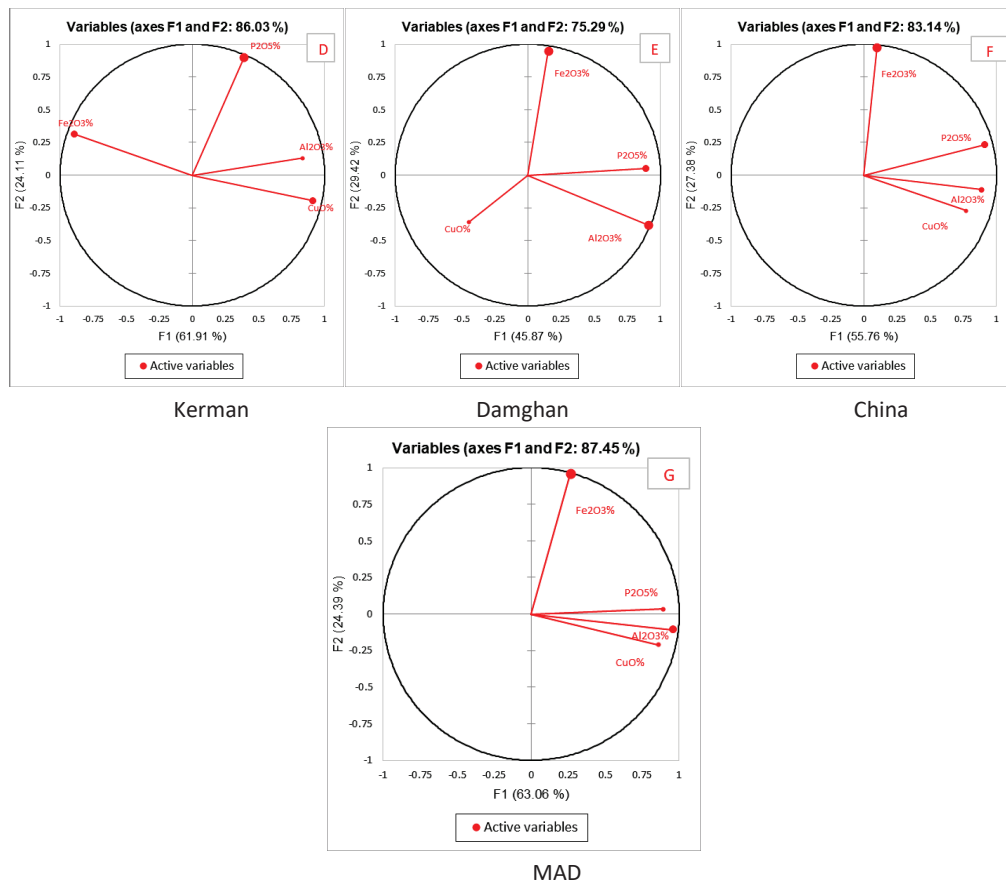


Figure 59. Correlation and anti-correlation of main oxides (Al_2O_3 , P_2O_5 , CuO , Fe_2O_3) of different PCA analyzes result; A: Iran mines sample, B: Iran bibliography samples, C: Neyshapour samples from Iran mine and bibliography, D: Kerman samples from Iran mine and bibliography, E: Damghan samples from Iran mine and bibliography, F: China samples from bibliography and I: samples analyzed in MAD museum.

As it can be seen in (Fig. 59) all samples shows attended a correlation between Al_2O_3 , P_2O_5 and CuO (F1 “turquoise factor”). Part of them a correlation between CuO and Fe_2O_3 (All Iran mines; Neyshapour). The others present an anti-correlation between CuO and Fe_2O_3 (Iran biblio; Kerman). In such case, iron belong to a second factor which could be linked to pyrite FeS_2 phase or other Fe-bearing phase. As it can be seen, MAD samples (G) as unknown origin show more similarity results with Neyshapour pattern (C) and China (F).

PCA OF MAIN ELEMENTS (AL, P, CU, FE) AND TRACE ELEMENTS (ZN, CA, BA, SR, K, TI, SI, S, AS)

In the second step, the main elements and trace elements (Ca, Ba, Sr and Zn) that could replace the Cu^{2+} and also K, Ti, S and As are studied. The correlation matrixes are not represented.

ALL SAMPLES FROM IRAN (THIS STUDY)

49 samples from Persian mines was selected and analyzed, the result as it can be seen (Fig.60) shows that:

- Al is correlated with P and Ba and anti-correlated with Ca.
- P is correlated with Al, Ba and anti-correlated with Si and Ca
- **Cu is correlated with K**
- Fe is correlated with As
- Zn is anti-correlated with Ti

- Si is correlated with K, S and As and anti-correlated with P and Ca. It corresponds to tiny silicate phases.
- Ti is anti-correlated with Zn
- Ca is correlated with S and Si and shows anti-correlation with Al and P
- K is correlated with Cu, Si, S and Ba
- S is correlated with Si, Ca, and K and As
- Ba is correlated with Al, P, K and As
- As is correlated with Fe, Si, S, Ba

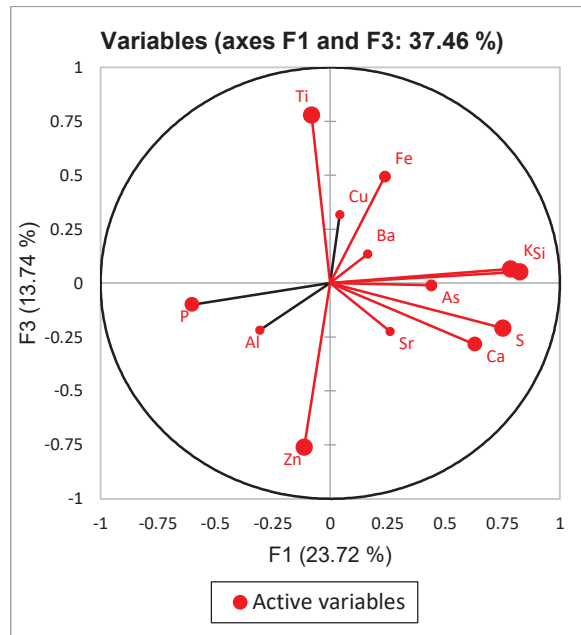


Figure 60. Coordinates of variables of main elements and trace elements of Iran bibliography Samples.

IRAN BIBLIOGRAPHY SAMPLES

46 samples of Persian mines were selected from bibliography, the result as it can be seen (Fig.61) shows that:

- Al is correlated with P and Cu and it is anti-correlated with Fe, Si, K, Sr and Ba
- Fe is correlated with K, Sr and Ba and anti-correlated with Al, P, Cu
- Zn is anti-correlated Si, Ti and S
- Si is correlated to Ti, Ca, K, S and Sr and anti-correlated with Al, P, Cu and Zn
- Ti is correlated to Si, Ca, K, S and Sr and anti-correlated to P and Zn
- Ca is correlated with Si, Ti, S, K and Sr and anti-correlated with P and Cu
- K is correlated with Fe, Si, Ti, Ca, S and Sr and anti-correlated with Al, P and Cu
- S is correlated with Si, Ti, Ca, S and Sr and anti-correlated with Zn and Ba
- Sr is correlated with Fe, Si, Ti, Ca, K and S and anti-correlated with Al, P and Cu
- Ba is correlated with Fe and anti-correlated with Al, P and S

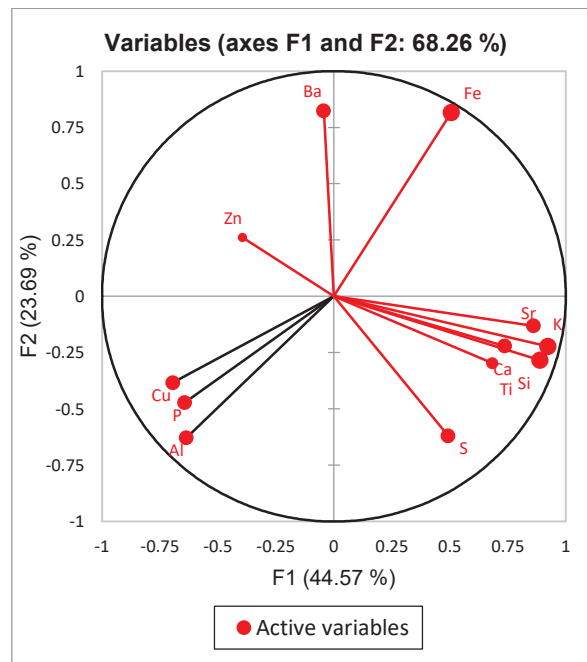


Figure 61. Coordinates of variables of main elements and trace elements of Iran bibliography Samples.

NEYSHAPOUR SAMPLES (THIS STUDY AND BIBLIOGRAPHY DATA)

56 samples were analyzed from Neyshapour mines of this study and bibliography, the result as it can be seen (Fig. 62) and (Tab.18) shows that:

- Al is correlated with P and Cu and it is anti-correlated with Fe, and Ca
- P is correlated with Al and Ba and anti-correlated with Si, Ti, Ca, S, Sr and Ba
- Cu is correlated with Al and Ti
- Fe is correlated with Ba and anti-correlated with Al
- Zn is correlated with Ba anti-correlated Si, Ti, K, S, Sr and As
- Si is correlated to Cu, K, S, Sr and As and anti-correlated with P and Zn
- Ti is correlated to Cu and S and anti-correlated to P and Zn
- Ca is correlated with Si, Sr, S, K and Sr and anti-correlated with Al, P and Ba
- K is correlated with Si, Ca, S and Sr and anti-correlated with zn
- S is correlated with Si, Ti, Ca, K, As and Sr and anti-correlated with P, Zn and Ba
- Sr is correlated with Si, Ca, K, S and As and anti-correlated with P and Zn
- Ba is correlated with P, Fe, Zn and anti-correlated with Ca and S
- As is correlated with Sr, S and Si and anti-correlated with p and Zn

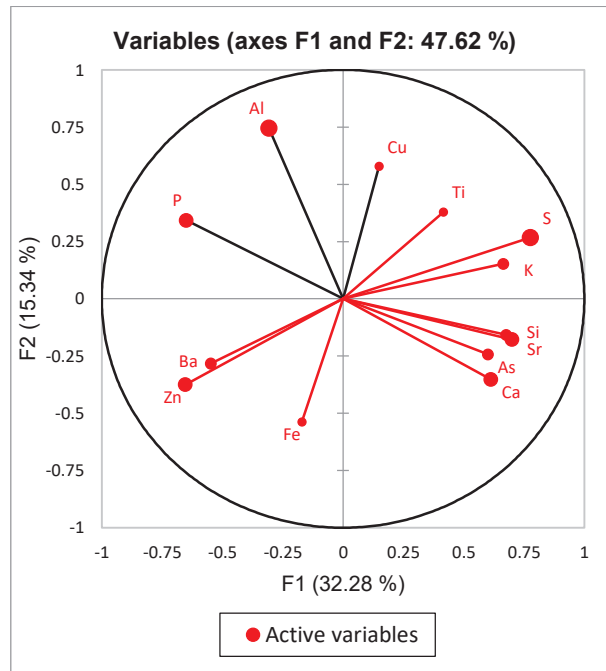


Figure 62. Coordinates of variables of main elements and trace elements of Neyshapour Samples

KERMAN SAMPLES (THIS STUDY AND BIBLIOGRAPHY DATA)

22 samples were analyzed from Kerman mine, this study and bibliography, the result as it can be seen (Fig. 63) and (Tab. 19) shows that:

- Al is correlated with Cu and it is anti-correlated with Fe, Si, K and Sr
- P anti-correlated with Ca, S, As and Ba
- Cu is correlated with Al and anti-correlated with Fe, Si, Ti, Ca, K and Sr
- Fe is correlated with Si, Ti, Ca, K and Sr and anti-correlated with Al and Cu
- Zn is correlated with As
- Si is correlated to Fe, Ti, Ca, K and Sr it shows anti-correlation with Al and Cu
- Ti is correlated to Fe, Si and K and anti-correlated to Cu
- Ca is correlated with Fe, Si, K, S, Sr and Ba and anti-correlated with P and Cu
- K is correlated with Fe, Si, Ti, Ca and Sr and anti-correlated with Al and Cu
- S is correlated with Ca, Ba and As and anti-correlated with P
- Sr is correlated with Si, Ca, K and Fe and anti-correlated with Al and Cu
- Ba is correlated with Ca, S and As and anti-correlated with p
- As is correlated with Zn and Ba and anti-correlated with p

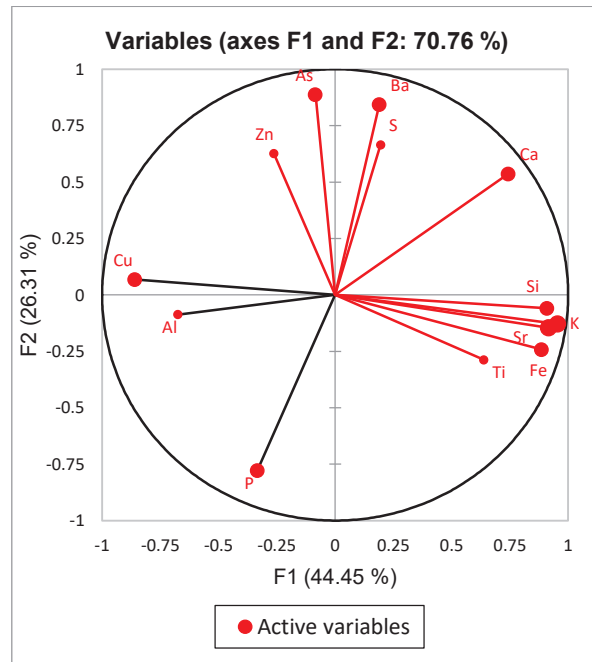


Figure 63. Coordinates of variables of main elements and trace elements of Kerman Samples

DAMGHAN SAMPLES (THIS STUDY AND BIBLIOGRAPHY DATA)

10 samples were analyzed from Damghan mine, this study and bibliography, the result as it can be seen (Fig. 64) and (Tab. 20) shows that:

- Al is correlated with P and it is anti-correlated with S
- P is correlated with Al also anti-correlated with S and As
- Cu is correlated with Ti and anti-correlated with Zn and Ba
- Zn is anti-correlated with Cu
- Ti is correlated to Cu
- Ca is correlated with K, S, Sr, Ba and As
- K is correlated with Ca, Sr and Ba
- S is correlated with Ca, Sr and As and anti-correlated with Al and P
- Sr is correlated with Ca, K, Sr and As
- Ba is correlated with Ca, K, Sr and As and anti-correlated with Cu
- As is correlated with Ca, S, Sr and Ba and anti-correlated with P

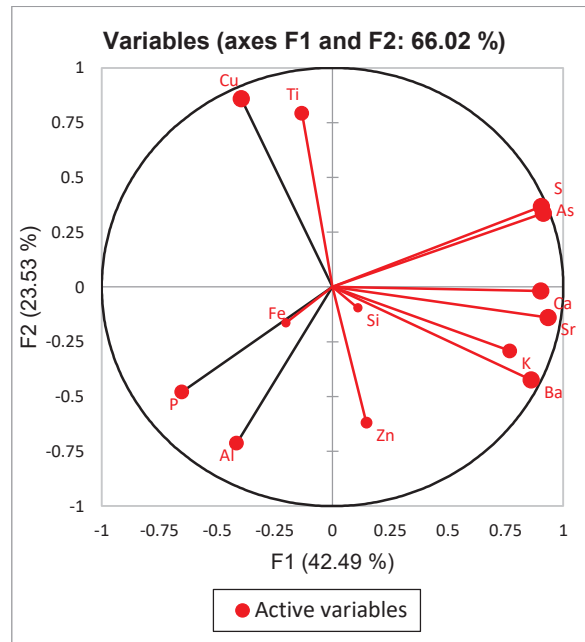


Figure 64. Coordinates of variables of main elements and trace elements of Damghan Samples

CHINA SAMPLES BIBLIOGRAPHY

32 samples of China mines were selected from bibliography, the result as it can be seen (Fig. 65) and (Tab. 21) shows that:

- Al is correlated with P and Cu and it is anti-correlated with Zn
- P is correlated with Al, Cu and S and anti-correlated with Zn and Si
- Cu is correlated with Al and
- Zn is correlated with Si and anti-correlated with Al and P
- Si is correlated to Zn and anti-correlated with P
- Ti is correlated to Ca and K
- Ca is correlated with Ti and K
- K is correlated with Fe, Si, Ti, Ca, S and Sr and anti-correlated with Al, P and Cu
- S is correlated with P

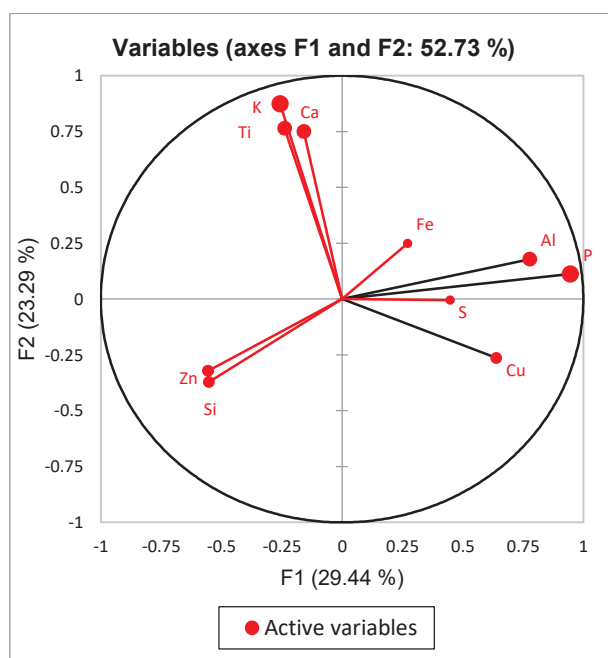


Figure 65. Coordinates of variables of main elements and trace elements of China Samples bibliography

MAD SAMPLES

39 samples were tested in Musée des Arts Décoratifs, Paris(MAD) and analyzed by PCA method, the result as it can be seen(Fig. 66) and (Tab. 22) shows that:

- Al is correlated with P and Cu and it is anti-correlated with Si, Ca and S
- P is correlated with Al and Cu also anti-correlated with Si and K
- Cu is correlated with Al and P
- Si is correlated to Ti, Ca and K also anti-correlated to Al and P
- Ti is correlated to Si, K, Sr and Ba
- Ca is correlated with Si, K and S also anti-correlated with Al
- K is correlated with Si, Ti and Ca and anti-correlated with P
- S is correlated with Ca and anti-correlated with Al
- Sr is correlated with Ti and Ba
- Ba is correlated with Ti and Sr
- As is correlated with Fe and anti-correlated with Al, P and S

Table 16. Correlation of main elements and trace elements of MAD samples

Correlation matrix (Pearson (n):

Variables	Al	P	Cu	Fe	Zn	Si	Ti	Ca	K	S	Sr	Ba	As
Al	1	0.830	0.793	0.147	0.018	-0.332	-0.127	-0.386	-0.305	-0.385	0.205	-0.006	0.059
P		1	0.589	0.221	0.036	-0.396	-0.136	-0.219	-0.405	0.046	0.209	-0.129	0.097
Cu			1	0.073	-0.167	-0.305	-0.161	-0.283	-0.242	-0.160	0.116	0.034	0.194
Fe				1	0.273	-0.083	0.058	-0.160	-0.090	-0.082	-0.062	0.061	0.003
Zn					1	-0.078	0.022	-0.094	-0.083	-0.043	-0.046	-0.100	-0.116
Si						1	0.462	0.601	0.981	-0.065	-0.021	0.073	-0.030
Ti							1	0.278	0.444	-0.065	0.742	0.335	-0.064
Ca								1	0.591	0.435	0.081	0.030	-0.021
K									1	-0.052	-0.027	0.126	-0.029

S										1	-0.027	-0.135	0.101
Sr											1	0.430	-0.026
Ba												1	-0.098
As													1

Values in bold are different from 0 with a significance level
alpha=0.05

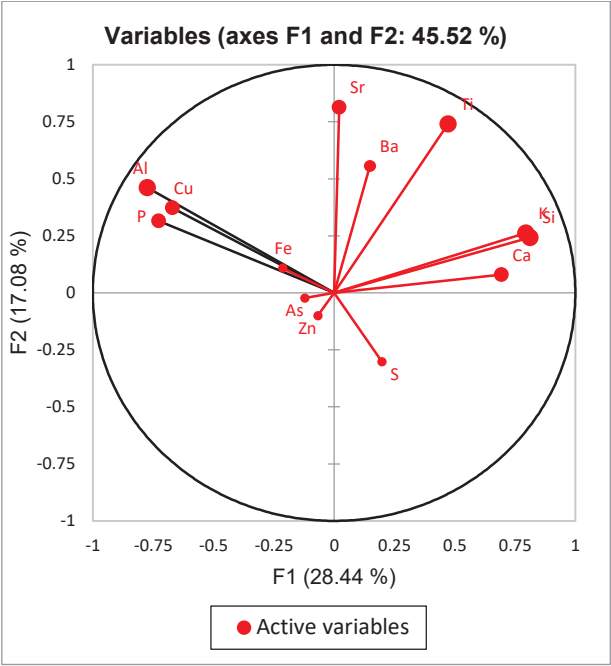
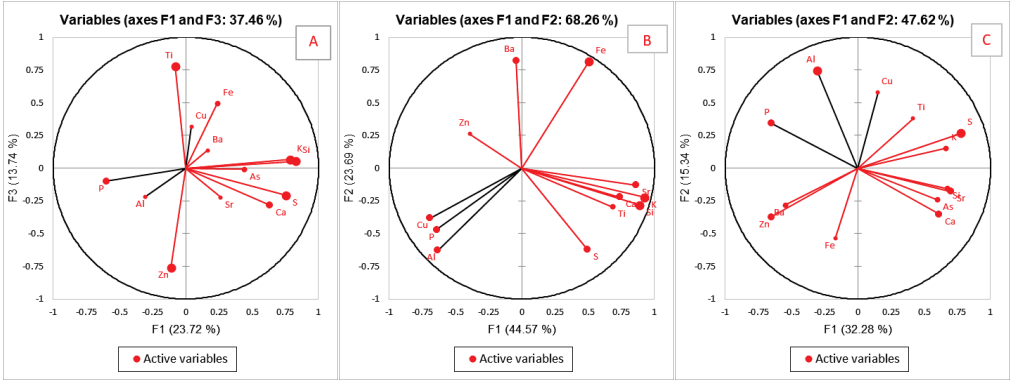


Figure 66. Coordinates of variables of main elements and trace elements MAD Samples

DISCUSSION



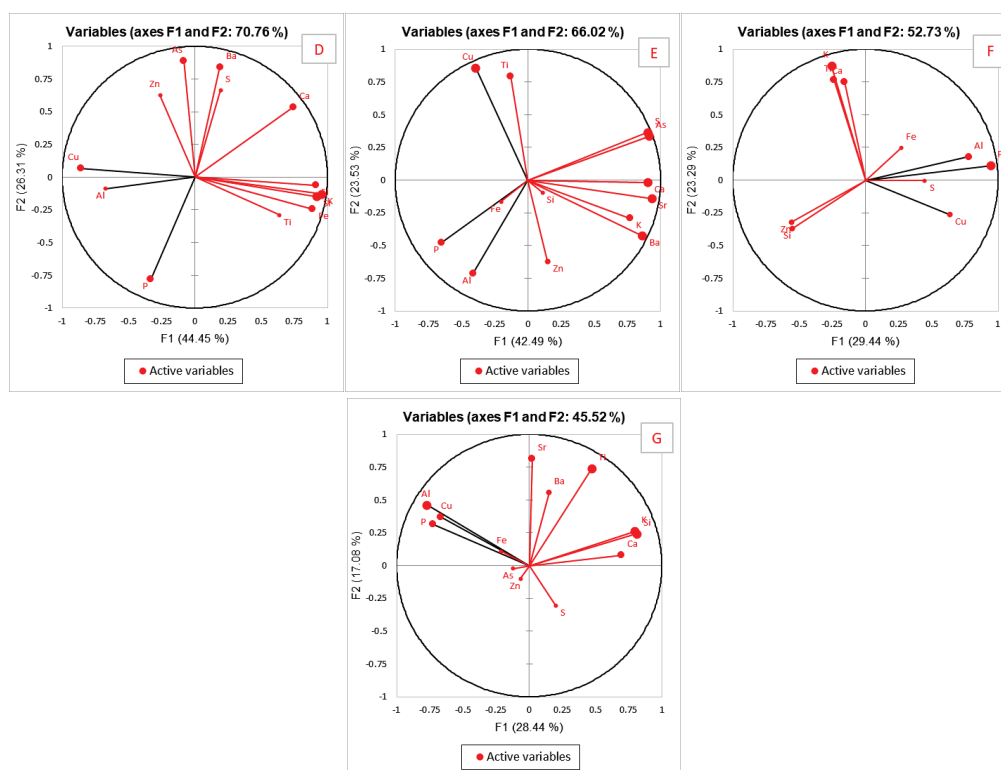


Figure 67. Correlation and anti-correlation of main element and trace elements of different PCA analyzes result; A: Iran mines sample, B: Iran bibliography samples, C: Neyshapour samples from Iran mine and bibliography, D: Kerman samples from Iran mine and bibliography, E: Damghan samples from Iran mine and bibliography, F: china samples from bibliography, G: samples analyzed in MAD museum.

According to the results of the experiment and comparing them and considering that copper and iron are the most important elements affecting the color of turquoise, these two elements are compared in the Table 17 with other trace elements. The results of MAD samples show more similarity to those from Neyshapour.

Table 17. Correlation and anti-correlation of Cu and Fe with other trace elements in different samples.

		Correlated with	Anti-correlated with
Cu	Iran mines samples (this study)	K	
Fe	"	As	
Cu	Iran bibliography samples	Al, P	Fe, Si, Ca, K, Sr
Fe	"	K, Sr	Al, P, Cu
Cu	Neyshapour samples (this study)	Al, Ti	
Fe	"	Ba	Al
Cu	Kerman samples (this study)	Al	Fe, Si, Ti, Ca, K, Sr
Fe	"	Si, Ti, Ca, K, Sr	Al, Cu
Cu	Damghan samples (this study)	Ti	Zn, Ba
Fe	"		
Cu	China samples	Al	
Fe	"		
Cu	MAD samples (this study)	Al, P	
Fe	"		Al

A very recent and similar study by Caro et al. (2017) was conducted on turquoise-bearing Egyptian artefacts and turquoise samples from Egyptian and Iranian localities, using XRF analyses. They use the main results and correlation graphs are presented in **Annex IV**. Their conclusion was that:

1. the Egyptian first millennium B.C. turquoises have a different chemical signature (lower Cu/Fe ratios) than the earlier stones. Their characteristic Cu/Fe, Cu/Zn and Cu/As ratios do not match any of the geological sources considered in this study.
2. Some turquoise from Iranian, Mesopotamian, and central Asian archaeological contexts are consistent with Iranian mines. Others are chemically similar to first millennium B.C. Egyptian turquoises, and do not match any of the analyzed sources. These may derive from as yet unknown source(s) in Iran or Central Asia, such as Uzbekistan and Afghanistan. All are chemically different from Old and Middle Kingdom turquoises.
3. There is an overlapping compositional region where Egyptian and non-Egyptian turquoises have similar Cu/Fe, Cu/Zn and Cu/As ratios. These stones can't be easily differentiated.

4.4. LIBS CHEMICAL ANALYSES

RESULTS

LIBS reveals the characteristic lines of Cu, Al, P, Fe and Si (Fig. 68). The generated maps allow to identify the correlated domains with 1) Cu, Al and P; 2) Fe and 3) Si. Interferences slightly occur between P, Al and Fe (Fig. 69). As well, Cu could be slightly correlated to Fe.

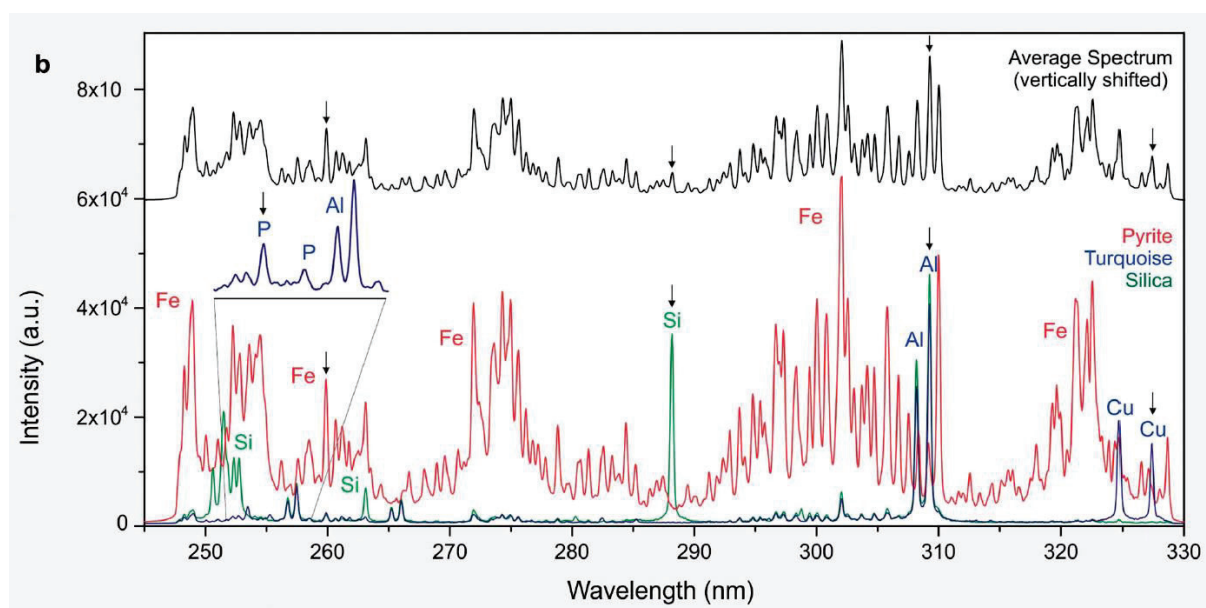


Figure 68. Typical single-pulse spectra from pyrite (red), silicates (green) and turquoise (blue) phases. The mean spectrum of the whole dataset is represented in black. The vertical arrows indicate the line selected for building up the images (see the text for details).

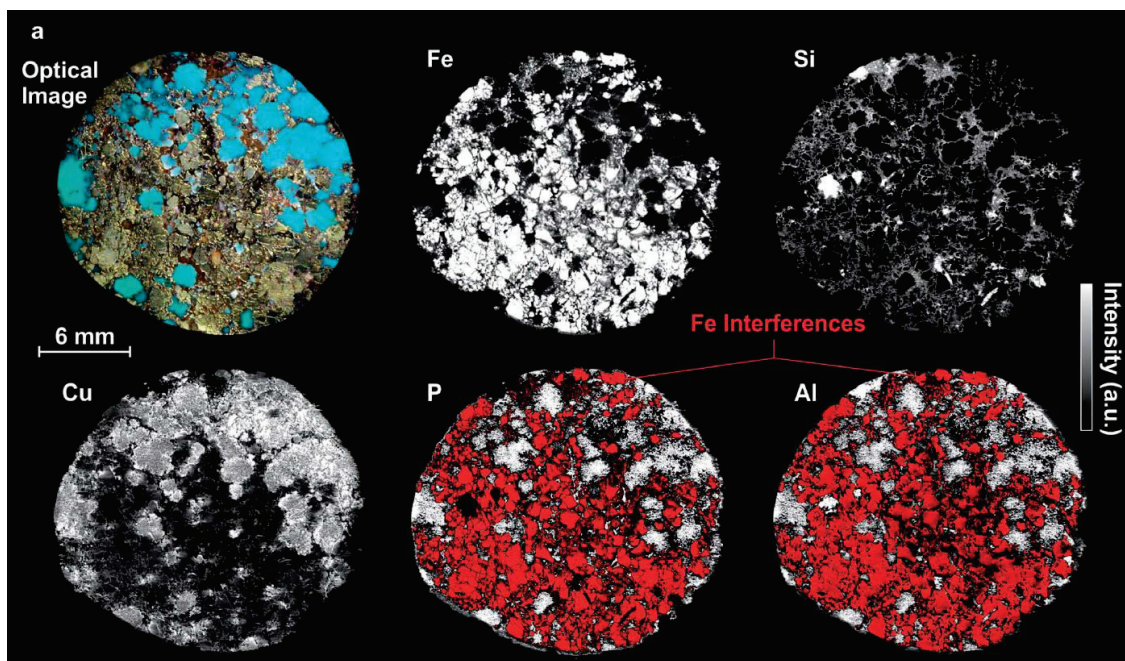


Figure 69. Optical images of the gem stone and five LIBS elemental images Fe, Si, Cu, P and Al in a gray color scale. Red areas show regions rich in P and Al interfered with Fe lines.

DISCUSSION

The generated LIBS map (Fig.70) allow to identify the turquoise phase with correlated Cu, Al and P as well as the pyrite (FeS_2) and silicate ones. Slight interferences between P, Al and Fe reveal the slight substitution of Al by Fe. As well, Cu could be slightly present in pyrite as chalcopyrite CuFeS_2 .

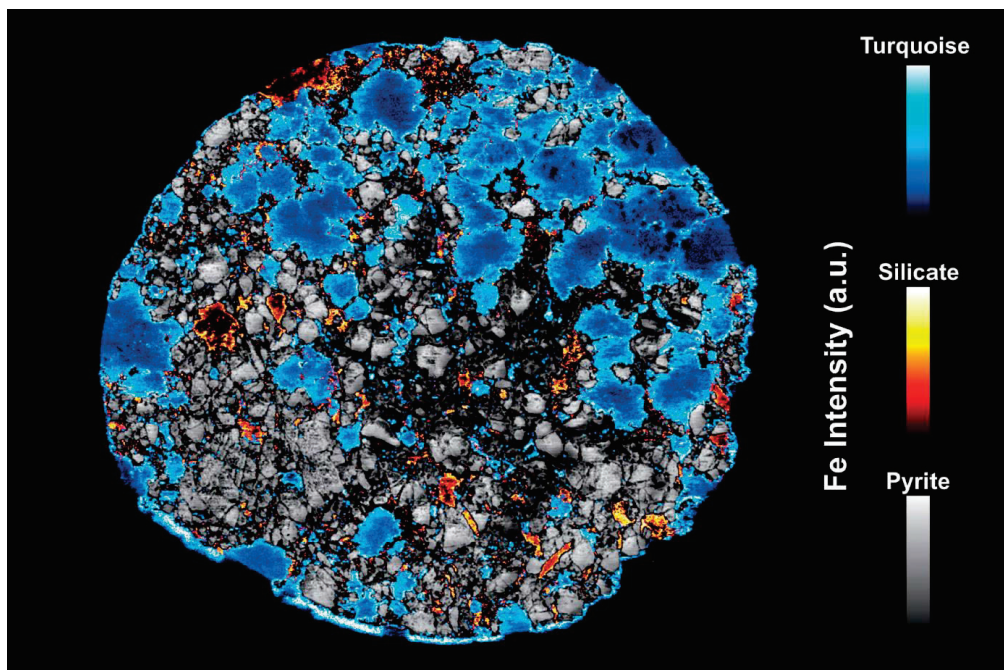


Figure 70. LIBS image of iron (259.939 nm) obtained by merging three images related to the three mineral phases, namely, turquoise, silicate and pyrite. A specific color scale is used for each phase.

4.5. OPTICAL ABSORPTION

RESULTS

The absorption spectra collected from all studied turquoises from Iranian mines present a quite similar shape (Fig. 71). They are characterized by the presence of the broad absorption band in the red-NIR range (650-900 nm) and by the presence of the much narrow line peaking at 428 nm. This peak corresponds to the Fe^{3+} absorption as known from previous optical studies (Fig. 72) such as (Han, et al., 2015) and GGTL (2017). All spectra were normalized in order to get rid of the influence of the size of the samples. As seen in figure 71, the intensity of this Fe^{3+} absorption peak varies quite a lot.

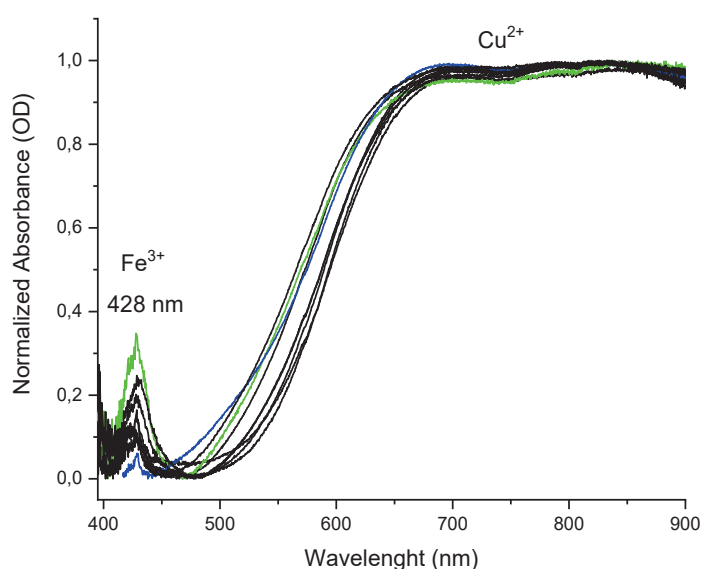


Figure 71. Normalized absorption spectra of various studied turquoise showing the main Cu^{2+} broad band and the narrow Fe^{3+} absorption peak at 428 nm.

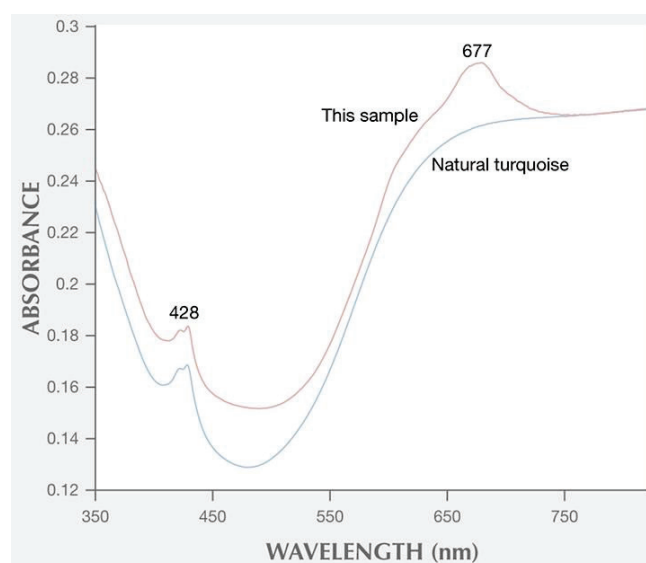


Figure 72. Optical spectra of turquoise (Han, et al., 2015)

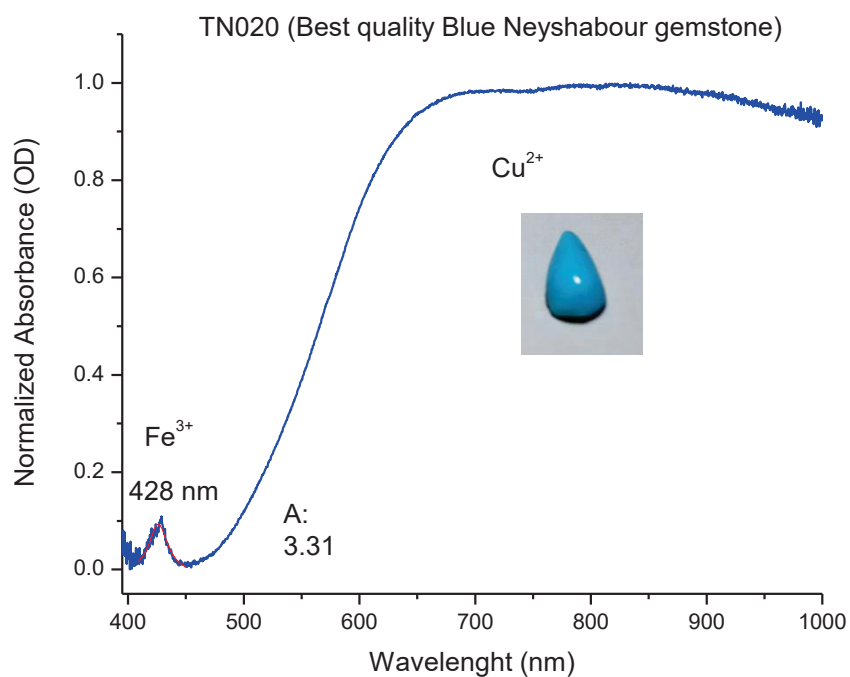


Figure 73. Optical absorption spectrum (normalized) of Neyshapour turquoise TN020 (blue color). A : absorption area of Fe^{3+} .

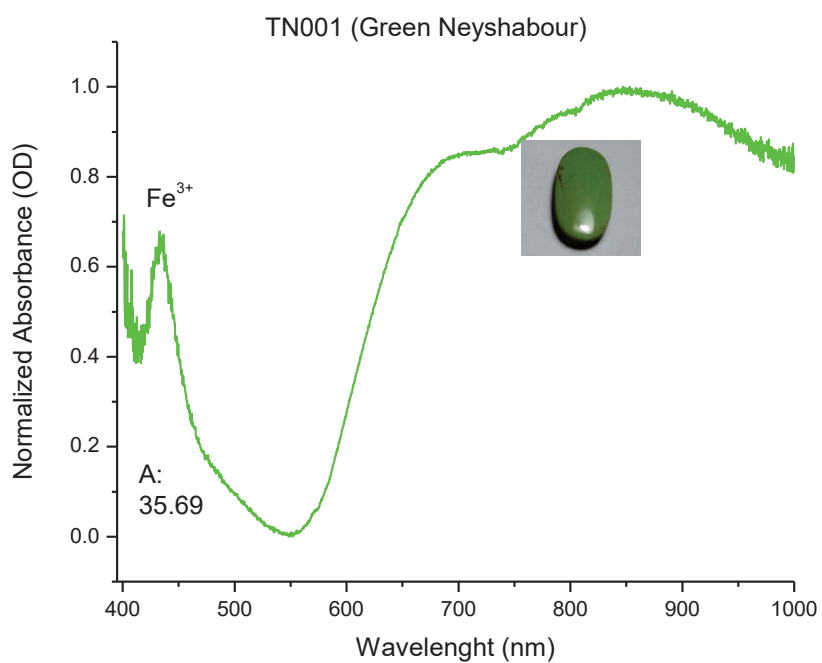


Figure 74. Optical absorption spectrum (normalized) of Neyshapour turquoise TN001 (Apple green color). A : absorption area of Fe^{3+} .

As seen in Fig. 73 and 73, the Fe^{2+} absorption peak appears to be much stronger for green hue samples, while much weaker for the blue ones.

Table 18. Values of estimated Fe^{3+} content (Fe^{3+} absorption area) and measured total Fe content (by XRF) of studied turquoise samples from Neyshapour, Kerman and Damghan Iranian mines.

SAMPLE	Area	Fe^{3+} (Abs area)	Total Fe (% oxide) XRF
TN013	Neyshapour	0,42	7,27
TN012	Neyshapour	0,44	0,15
TN201	Neyshapour	0,49	0,42
TN202	Neyshapour	0,74	1,09
TN022	Neyshapour	1,37	1,68
TN220	Neyshapour	2,15	1,07
TN007	Neyshapour	2,26	0,50
TN199	Neyshapour	2,85	1,17
TN009	Neyshapour	2,93	1,03
TN020	Neyshapour	3,31	2,11
TN016	Neyshapour	3,75	1,03
TN003	Neyshapour	4,18	0,37
TN200	Neyshapour	7,04	0,56
TN015	Neyshapour	8,11	1,99
TN002	Neyshapour	8,30	7,71
TN004	Neyshapour	11,27	4,98
TN017	Neyshapour	11,77	2,14
TN006	Neyshapour	12,03	1,29
TN195	Neyshapour	13,02	3,22
TN205	Neyshapour	13,03	6,01
TN011	Neyshapour	15,52	4,89
TN197	Neyshapour	15,77	3,14
TN194	Neyshapour	18,48	6,75
TN196	Neyshapour	19,63	7,01
TN193	Neyshapour	21,08	5,82
TN001	Neyshapour	35,70	6,61
TN005	Neyshapour	42,13	8,67
TN018	Neyshapour	43,81	5,75
TN021	Neyshapour	49,88	9,38
TK1a	Kerman	4,26	1,34
TK02	Kerman	4,82	0,37
TK04	Kerman	6,10	1,17
TK2a	Kerman	6,83	1,24
TK01	Kerman	12,77	1,47
TK06	Kerman	13,58	0,60
TK05	Kerman	15,47	1,26
TD6a	Damghan	0,99	
TD2a	Damghan	1,91	0,90
TD1a	Damghan	2,11	1,12
Td5a	Damghan	3,17	
TD4a	Damghan	8,67	0,95
TD3a	Damghan	9,53	0,80

44 samples were chosen for correlation, 6 samples from Damghan, 7 samples from Kerman and 31 samples from Neyshapour (Table 18). Most of samples are from Neyshapour because Neyshapour is the most important mine.

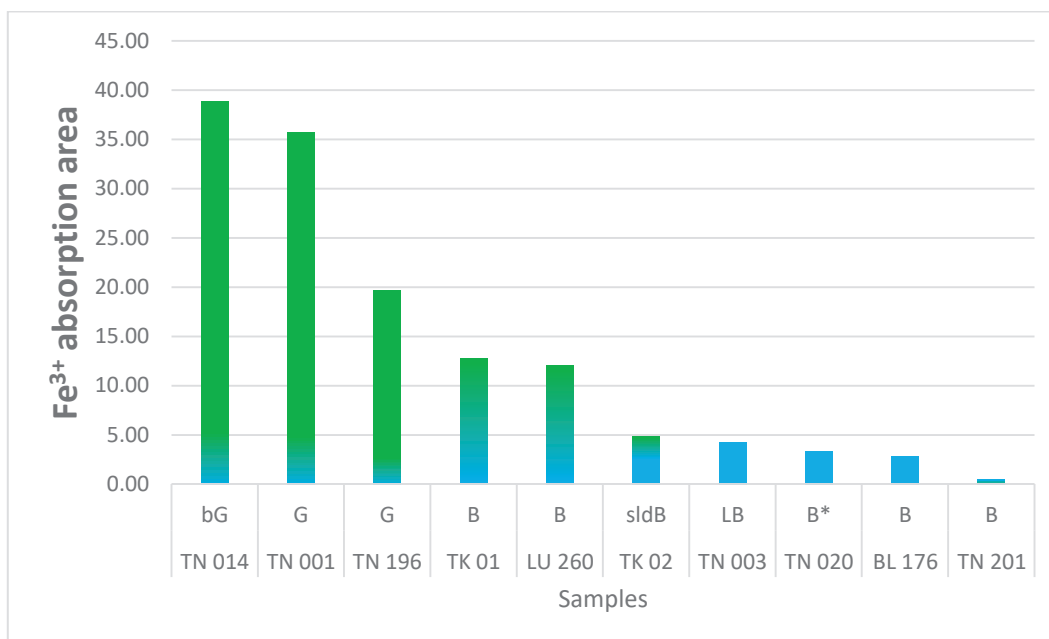


Figure 75. Correlation between (Fe^{3+}) absorption area and color of some selected samples (B: blue, G: green....).

DISCUSSION

INFLUENCE OF THE Fe^{3+} ON THE COLOR OF TURQUOISE

Mossbauer and optical absorption spectroscopy show that with increasing amounts of iron, the color shifts from sky blue to bluish green and then to green (Wang & Keller, 1986) (Keller.P.C, 1986).

The electronic configuration of divalent copper leads to an absorption energy of 14706 cm^{-1} or 680 nm (Fig. 75a). The electronic configuration of trivalent iron leads to a higher absorption energy of 23256 cm^{-1} equivalents to 430 nm (Fig. 75b).

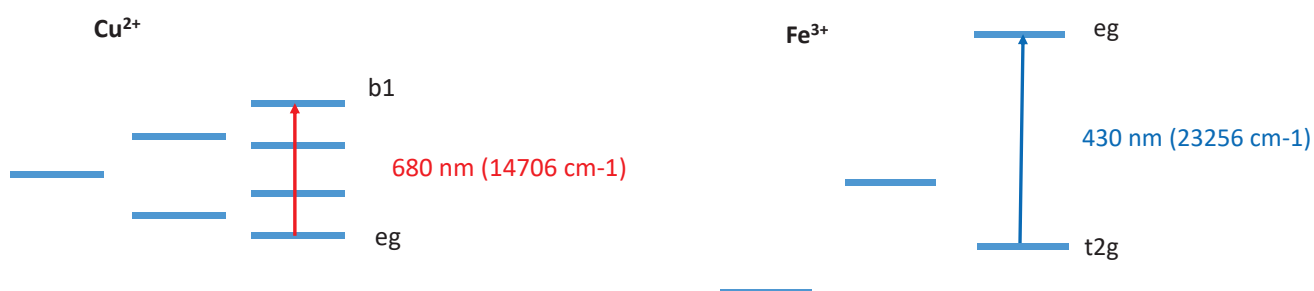


Figure 75. Energy level of a) Cu^{2+} and b) Fe^{3+} and their absorption in octahedral environment.

In general, with an increase in the amount of iron in turquoise, the color changes from blue to green. According to previous data on the optical absorption of turquoise, representative optical absorption spectra (in the visible range) of turquoise show a broad band around 653 nm (Fig. 73) and a doublet pick at 429 nm (Anon., 2017) (Han, et al., 2015).

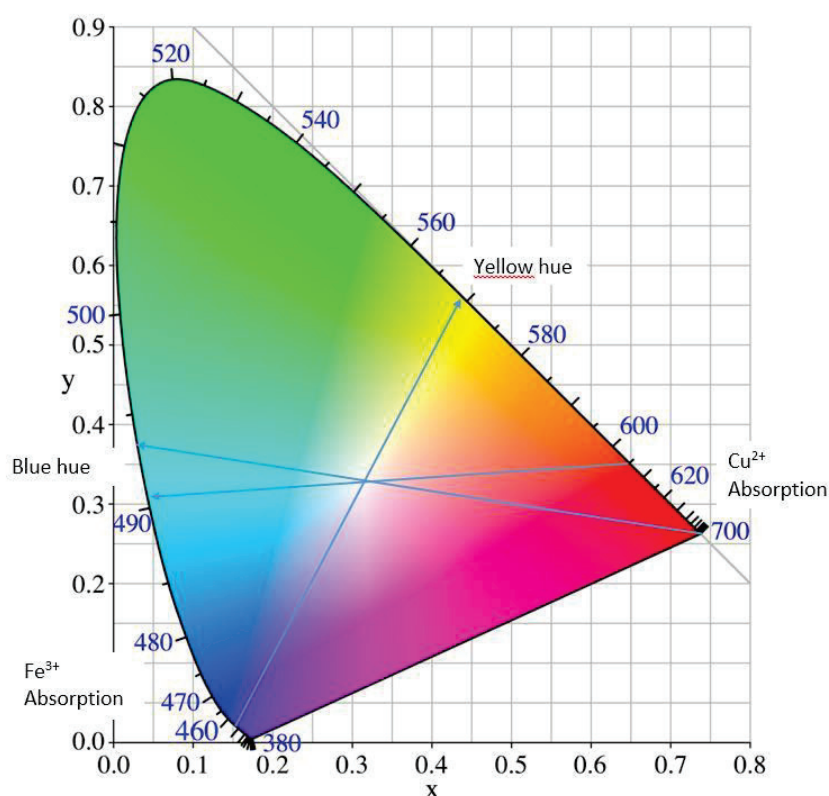


Figure 75. Chromaticity diagram (CIE 1931) showing the effects of Cu^{2+} and of Fe^{3+} absorptions on the color of turquoise.

The comparison of chemical analysis and absorption analysis shows that the increase in iron content will lead to a change in the color of blue to green (Fig.75). As it can be seen, the Cu^{2+} absorption band (605-900 nm) induces a blue hue, while the 428 nm Fe^{3+} absorption peak induces a yellow hue.

XRF analyses allows to determine the total Fe content without possibility to determine if it is present as Fe^{2+} and/or Fe^{3+} . As it was already said, iron can be incorporated in turquoise $\text{Cu}^{2+}\text{Al}^{3+}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$, in two ways: Fe^{2+} can replaces Cu^{2+} and Fe^{3+} can replaces Al^{3+} . Furthermore, Fe^{3+} could substitute Al^{3+} up to complete substitution to the dark green chalcosiderite end-member $\text{Cu}^{2+}\text{Fe}^{3+}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$.

It appears that even the turquoise with the best blue color present a slight Fe^{3+} absorption. This indicates that even in such sample an iron substitution occurred.

According to the optical absorption results, Fe^{2+} has nearly no effect on the color of turquoise. Replacing Fe^{3+} instead of Al changes the color of the turquoise into a green color (Fig.73 - Fig.74).

CORRELATION OF Fe^{3+} ABSORBANCE AND TOTAL FE

Percentage of total iron was measured by XRF Thermo Scientific Niton PXRF XL3T Gold (miming mode). Absorption area, as mentioned, was measured by compact diffuse reflectance sphere and an Ocean optic USB2000 spectrometer

Total iron was measured by XRF method, so it contains both Fe^{2+} and Fe^{3+} . According to the results mentioned, Fe^{3+} is effective in turquoise color. The amount of iron measured by XRF is in ppm scale and it is necessary to convert it to the oxide content first. According to the formula below, the percentage of Fe_2O_3 is raised.

$$\text{Fe (ppm)} * 1.4297 / 10000 = \text{Fe}_2\text{O}_3 (\%)$$

The correlation between absorption area of Fe^{3+} and total iron (XRF) for the Iranian samples shows globally a linear correlation (Fig.78). A trend line (approximately $y=6.2 \cdot x$ with y as Fe^{3+} and x as total Fe) is indicated which corresponds to the cases where the total iron consists in only Fe^{3+} ; below this line, the total iron consists in Fe^{3+} and Fe^{2+} (Fig.78).

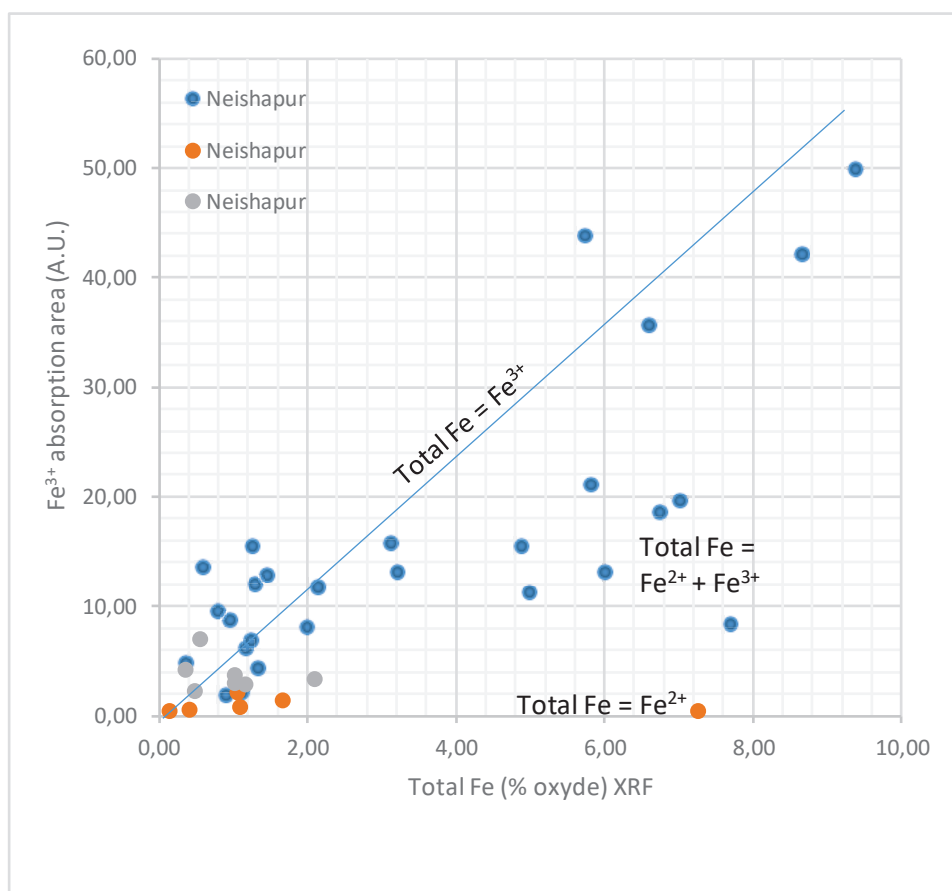


Figure 78. Correlation between Fe^{3+} (absorption area) and total Fe content (XRF).

Our conclusions are not consistent with those of Yin et al. (2010) who considered that Fe^{2+} makes color changed to green, while Fe^{3+} leads to red and yellow tone, for turquoises from Zhushan, Hubei (China). However, we did not quantify the Fe^{2+} concentration and cannot reject absolutely their hypothesis.

CONCLUSIONS

The aim of this study was to compare collected turquoises of various historical mines of Iran (Persia) compared with those from other regional localities in order to potentially find discriminant characteristics allowing the identification of the provenance of turquoise-bearing jewel. Geological samples were collected from Persian mines and analyzed as well as turquoise-bearing jewelry from the Musée des Arts Décoratifs, Paris (MAD).

Vibrational spectroscopies (FTIR and Raman) were tested to characterized these various turquoises. Both, Raman and FTIR allow to identify the structure of turquoise. While FTIR do not show special differences between the various colors of turquoise, Raman analyses of blue and green turquoise samples, show that

linewidth of blue sample appears much more resolved than of green one. This indicates that the lattice and the OH and H₂O vibration modes appear to be sensible to substitutions inducing a relative crystalline disorder.

Absorption spectroscopy reveals that even the turquoise with the best blue color present a slight Fe³⁺ absorption. This indicates that even in such sample an iron substitution occurred. The influence of divalent copper ions and of trivalent iron on the color of turquoise was explicated. According to the optical absorption results, Fe²⁺ has no peculiar effect on the color of turquoise. Replacing Fe³⁺ instead of Al changes the color of the turquoise into a green color.

It was shown that micro **laser-induced breakdown spectroscopy** (LIBS) elemental maps allow to identify rapidly turquoise phase (correlated Cu, Al and P) as well as pyrite (FeS₂) and silicate ones. Slight interferences between P, Al and Fe reveal the slight substitution of Al by Fe.

Non-destructive **chemical analyses** conducted using **XRF**, implement the structural information since it allows to quantify the amount of major (Al, P, Cu) and trace elements (Fe, Zn, As, Ca, Ti). Tentative statistical analyses (PCA) were conducted using measured data as well as bibliographic ones. Even if It appears that MAD turquoise-bearing jewels are superimposed to Iranian Neyshapour and Kerman turquoise domains (Fe/Cu vs Zn/Cu; Zn/Cu vs As/Cu; Zn/Cu vs Ca/Cu). Kerman turquoises do not correspond, as well as Chinese ones. It is therefore possible to suggest that the MAD jewels prior to the 19th century setted turquoise from Persian origin.

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Annex III. Chemical correlation diagrams of Carò et al. (2017) compared with this work

Annex IV. Principal component analysis (PCA) by XLSTAT

Annex V. Mousavipak N. & Panczer G. (2018) Analysis of Iranian turquoise color alteration based on absorption and Raman studies. Poster *EUG Geophysical Research* Vol. 20, EGU2018-1628, Vienna.

Annex VI. Panczer G., Mousavipak N., Mousavipak N & Rionday G. (2018) New trapiche-like sapphires from Hamadan (Iran). Poster *EUG Geophysical Research* Vol. 20, EGU2018-1628, Vienna.

Annex VII. Moncayo S., Duponchel L., Mousavipak N., Panczer G., Trichard F., Bousquet B., Pelascini F. and Motto-Ros V. (2018) Exploration of megapixel hyperspectral LIBS images using Principal Component Analysis., *J. Anal. At. Spectrom.* 33, 210-220.

Annex I. List of the turquoise-bearing MAD jewels (Musée des Arts Décoratifs, Paris)

Numéro d'inventaire	Dénomination	Creation	Location	Pierres	Other associated minerals	Description	Number of Analyses
30863	Bague	16th c.	Italie	turquoise			
30872	Bague d'enfant	16th c.	?	turquoise			
30793	Bague	18th c.	France	turquoise			
30798	Bague de mariage d'homme	18th c.	France	turquoise	Amethyst(?)		2 stones (Red& Brown)
9830	Pendant d'oreille A-B	19th c.	Indes	turquoise	Pearl		2 stones
30119	Bague	19th c.	Chine	turquoise		الله تبارک (tabarak allah)	
30426	Bague	19th c.	?	turquoise			
30818	Bague de mariage	19th c.	Indes	turquoise	Amethyst	Red (Almandine+ spessartine)	2stones
31006	Bague [Serpent]	19th c.	Paris ?	turquoise			
24293 A	Bracelet	1838	Paris	turquoise		Not Turquoise	center stone
28313	Bracelet avec inscription arabe	1838	Paris	turquoise		I am ready to sacrifice myself for you (فدايت سرور)	All 7 stones
28314	Bracelet avec inscription arabe	1838	Paris	turquoise		Elegant tall lady (Sarv e ravan سرور)	2 times analyzed
2004.25.9	Pendant d'oreille	2003	France	turquoise	Diamond/Amethyst	Cartier	2 stones
8294	Plaque de bijou	?	?	turquoise			
9849	Pendant d'oreille A-B	?	?	turquoise	Ruby		3stones
9863	Pendentif	?	?	turquoise	Ruby	top stone wasn't turquoise	2 stones
30080	Bague	?	Indes	turquoise	Pearl/Ruby		2 stones
30755	Anneau [Serpent]	1814-1830	Paris ?	turquoise			
18107	Agrafe de manteau	1865- 1930	?	turquoise			2 stones

24455	Broche pendentif	1878-1900	?	turquoise	Diamond		1 stones
995.19.1	Diadème	1862- 1957	Paris	turquoise	Pearl /Diamond		2 stones
30794	Bague	1934		turquoise	Diamond		
30861	Bague	1934	?	turquoise			
30965	Chevallière	1872	Paris	turquoise			
29028	peigne	1840	?	turquoise	pearl		1 stone
30423	Bague de mariage	17	?	turquoise			1 stone
30665	pendentif	1814-1830	paris?	turquoise			1 stone
30808	Bague	18	germany	turquoise	glass		3 stones(2 t &1 glass)
30864	Bague	16	France	turquoise			
30873	Bague	16		turquoise			
34564B	Broche	19	France	turquoise			3 stones
44434	Peigne à chignon			turquoise		Not turquoise(Amazonite?)	1stone
44653	Collier	19	France	turquoise		Not turquoise	
9867	Pendant d'oreille A-B			turquoise	ruby/pearl/emerald		

Annex II. Rapport sommaire d'expertise gemmologique de bijoux à turquoises du MAD (07/01/2019)

Rapport sommaire d'expertise gemmologique de bijoux à turquoises du MAD effectuée sur site les 18 et 19 décembre 2018 au Musée des Arts Décoratifs par Gérard PANCZER et Niloofar MOUSAVIPAK

OBJET

L'objet de cette étude est d'une part d'effectuer une analyse chimique non destructive par XRF (fluorescence X) des bijoux à turquoises du 16^{ème} au 19^{ème} siècle du MAD, d'autre part d'identifier les quelques simulants de turquoise présents. L'analyse par XRF devrait permettre de mettre en évidence les traceurs chimiques géochimiques caractéristiques des turquoises d'origine persane et iranienne.

LES TURQUOISES

La turquoise, $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$ est un phosphate d'aluminium et de cuivre hydratée. Ce minéral est micro cristallisé et est donc opaque. Les pierres gemmes ornementales sont donc toujours taillées en cabochons et éventuellement gravées.

Les gisements antiques sont ceux de Perse (Iran) et du Sinaï. Les gisements modernes sont ceux du sud-ouest des USA. Les gisements chinois sont ceux de la Province de Shaanxi en Chine centrale. Le nom de turquoise vient de Turquie lieu où se faisait le commerce des turquoises mais la Turquie n'est pas le lieu de production.

Les turquoises les plus recherchées ont une couleur turquoise mais elles peuvent prendre une couleur verte à brune en fonction des substitutions chimiques au sein de la structure : principalement $\text{Al}^{3+} \leftrightarrow \text{Fe}^{3+}$ mais également $\text{Cu}^{2+} \leftrightarrow \text{Fe}^{2+}$, Zn^{2+} ou Ca^{2+} .

BIJOUX ANALYSES

33 bijoux présentant des turquoises ou turquoises supposés ont été analysés (Tab. 1).

Tableau 1. Liste des bijoux analysés et dénomination MAD

Numéro d'inventaire	Dénomination	Création	Lieu
8294	Plaque de bijou	?	?
9830	Pendant d'oreille A-B	19	Indes
9849	Pendant d'oreille A-B	?	?
9863	Pendentif	?	?
18107	Agrafe de manteau	1865- 1930	?
24455	Broche pendentif	1878-1900	?
28313	Bracelet avec inscription arabe	1838	Paris
28314	Bracelet avec inscription arabe	1838	Paris
29028	peigne	1840	?
30080	Bague	?	Indes
30119	Bague	19	Chine
30423	Bague de mariage	17	?
30426	Bague	19	?
30665	Pendentif	1814-1830	Paris ?
30755	Anneau [Serpent]	1814-1830	Paris ?
30793	Bague	18	France

30794	Bague	1934	
30798	Bague de mariage d'homme	18	France
30808	Bague	18	Allemagne
30818	Bague de mariage	19	Indes
30861	Bague	1934	?
30863	Bague	16	Italie
30864	Bague	16	France
30872	Bague d'enfant	16	?
30873	Bague	16	
30965	Chevalière	1872	Paris
31006	Bague [Serpent]	19	Paris ?
44434	Peigne à chignon	1904	Paris
44653	Collier	19	France
2004.25.9	Pendant d'oreille	2003	France
24293 A	Bracelet	1838	Paris
34564B	Broche	1840	France
995.19.1	Diadème	1862- 1957	Paris

RESULTATS

BIJOUX A PIERRES SIMULANTS OU AUTRES QUE TURQUOISES

Tous les bijoux présentent des turquoises véritables à part les bijoux de numéro d'inventaire suivant : 44434, 8294, 9863, 44653.

- Peigne 44434 (Dénomination : Peigne à chignon, 1904, Paris). Les pierres vertes bleuté identifiées correspondent non pas à des turquoises mais à de l'amazonite (Fig. 1). C'est une variété de microcline (feldspath alcalin) de formule intermédiaire $KAlSi_3O_8 - NaAlSi_3O_8$.

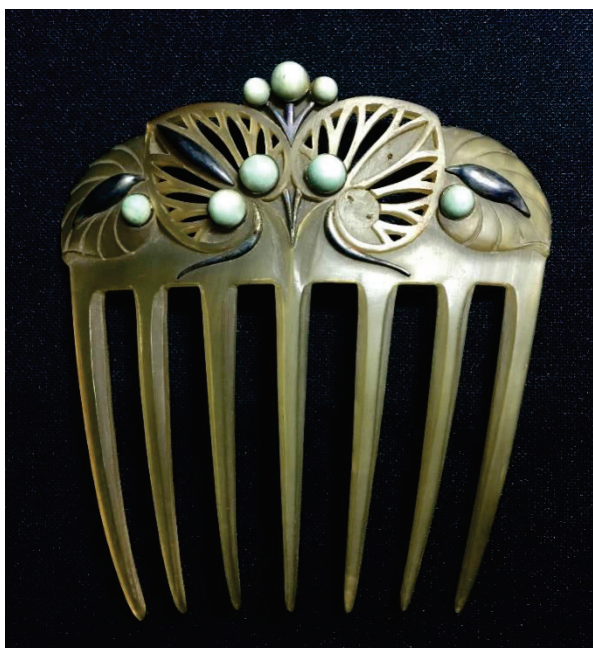


Figure 1. Peigne 44434 en écaille ou en corne serti de cabochons d'amazonite

- Plaque de bijou 8294 (Fig. 2). La pierre bleue apparaît être de la pâte de verre de couleur bleu turquoise imitant une turquoise.



Figure 2. Plaque filigranée à pierre en pâte de verre de couleur bleu turquoise

- Pendentif 9863. La pierre haute (indiquée par une flèche Fig. 3) n'est pas une turquoise. Il s'agit sans doute d'un moulage en plastique imitant et remplaçant une turquoise. Les rubis apparaissent clairement sous illumination UV du fait de leur fluorescence rouge intense. Les autres pierres semblent être de vrais turquoises.

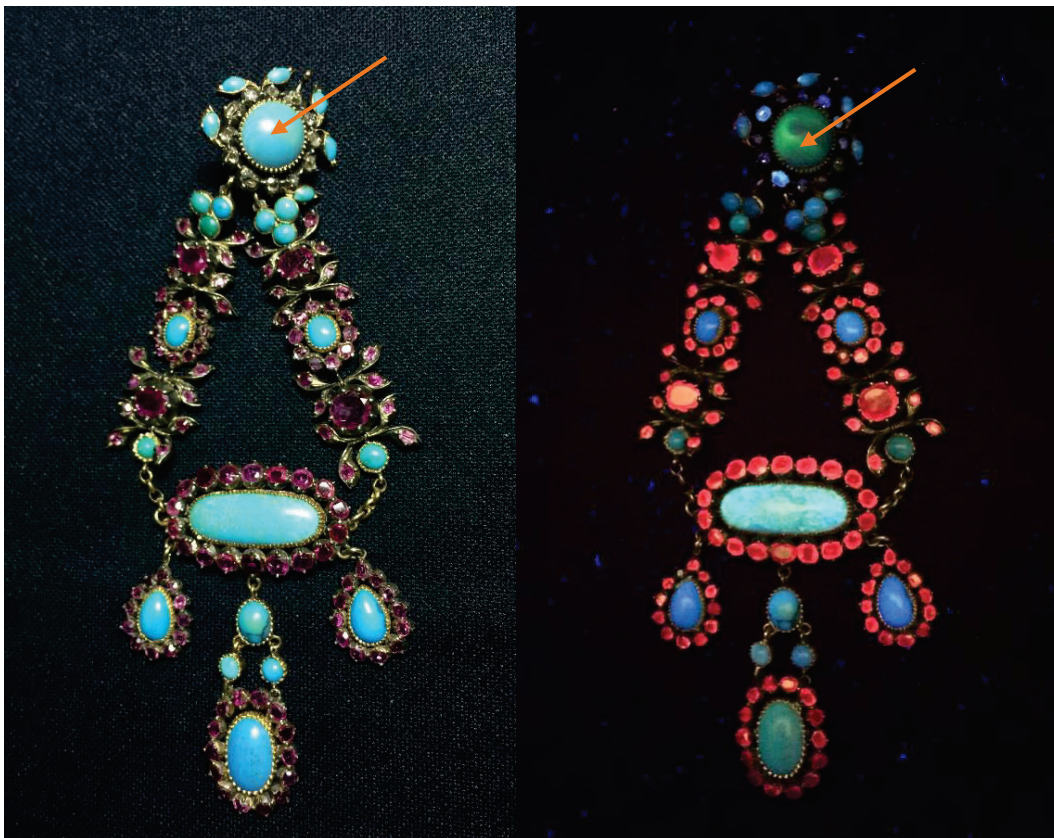


Figure 3. Pendentif 9863 sous lumière blanche et sous UV 365 nm

- Collier 44653 (A vérifier la numérotation !). Les pierres ne sont pas des turquoises mais de la pâte de verre. Les motifs sont moulés avec la pâte de verre imitant de la turquoise et ne représentent pas de texte écrit mais imitent un style persan.



Figure 4. Vues de profil et de dessous des perles du collier 44653 montrant des textures d'écoulement et des bulles de la pâte de verre.

INSCRIPTIONS

Trois bijoux présentent des inscriptions gravées.

- Bracelet 28313 (Dénomination : Bracelet avec inscription arabe, 1838, Paris). La pierre centrale présente une inscription en persan (et non en arabe): « *Fadayat* » فدایت « Je suis prêt à me sacrifier pour toi » ou « Pardonne-moi » (Fig. 6). Les petites pierres de turquoise latérales sont gravées en forme de palmiers et surlignées avec de la peinture dorée.



Figure 5. Vue globale du bracelet 28313

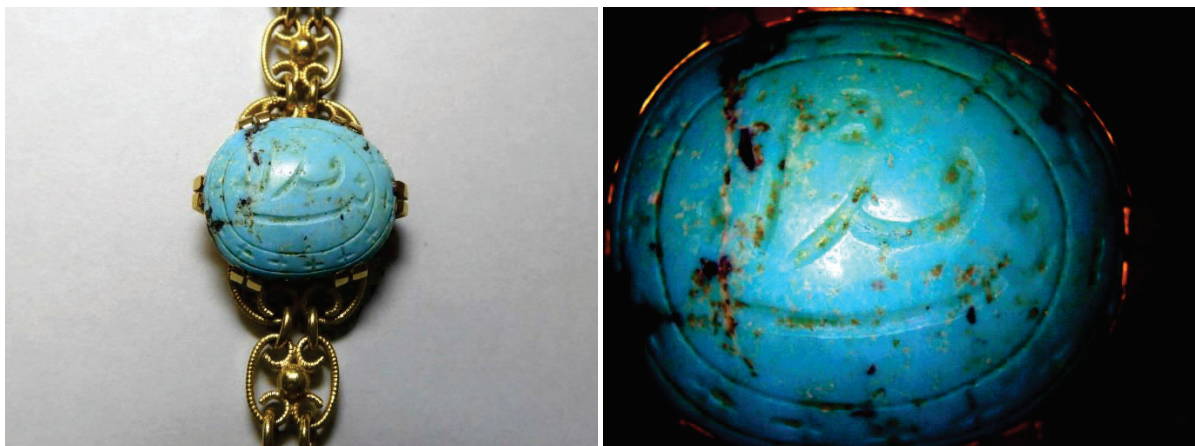


Figure 6. Détail de la turquoise centrale du bracelet 28313 avec l'inscription en persan: « *Fadayat* » فدایت « Je suis prêt à me sacrifier pour toi » ou « Pardonne moi »



Figure 7. Détail d'une des petites pierres de turquoise gravées du bracelet 28313 avec gravure en forme de palmier surlignée avec de la peinture dorée.

- Bracelet 28314 (Dénomination : Bracelet avec inscription arabe, 1838, Paris) Turquoise gravée avec inscription en persan (et non en arabe): « *Sarv e ravan* » سرو روان « A une femme élégante et élancée (comme un if ou un cyprès) » (Fig.8).



Figure 8. Bracelet 28314 avec grande turquoise à inscription en persan « *Sarv e ravan* » سرو روان « une femme élégante et élancée (comme un if ou un cyprès) »

- Bague 30119 (Dénomination : Bague 19^{ème}, Chine) Inscription en persan: « *Tabarak Allah* » تبارک الله « Que Dieu vous bénisse » ou « Quelle création de Dieu ! » (Fig. 9). Cette inscription et le style de la bague font que cette bague n'est sans aucun doute pas originaire de Chine mais de Perse ou d'Iran.

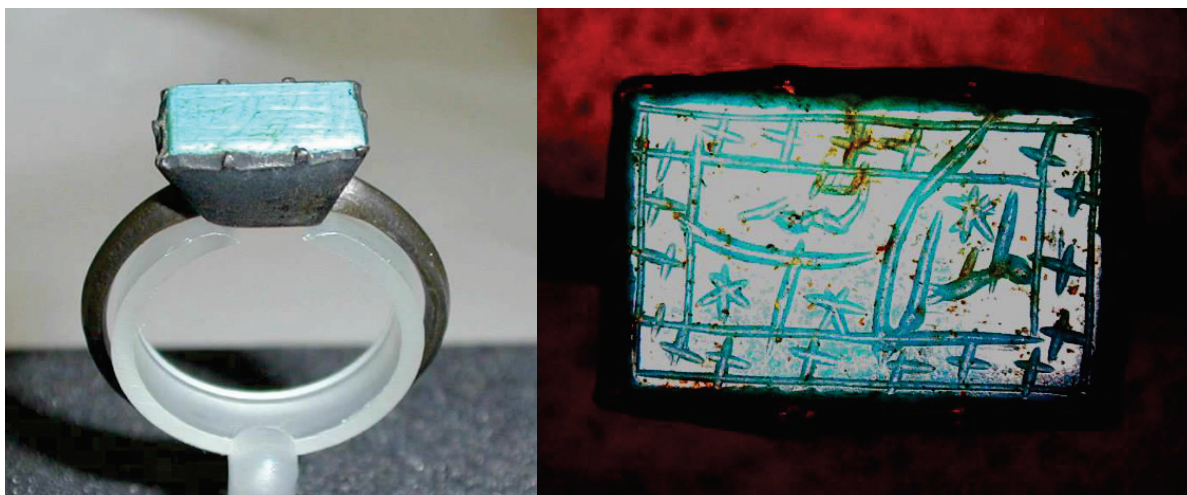


Figure 9. Pierre gravée de la bague 30119 avec inscription en persan « Tabarak Allah » تبارک الله « Que Dieu vous bénisse » ou « Quelle création de Dieu ! »

- Collier 44653 (Vérifier la numérotation !). Les motifs sont moulés avec la pâte de verre et ne représentent pas de texte écrit mais imitent un style persan (Fig. 10).

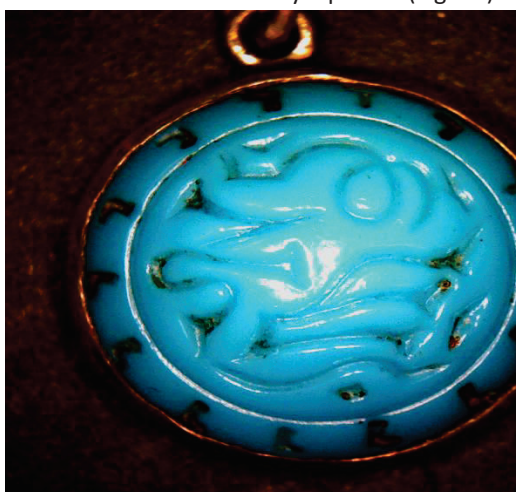


Figure 10. Détail d'une des pierres en pâte de verre moulé du collier 44653. Les motifs ne représentent pas de texte écrit mais imitent un style persan.

Annex III. Chemical correlation diagrams of Carò et al. (2017) compared with this work

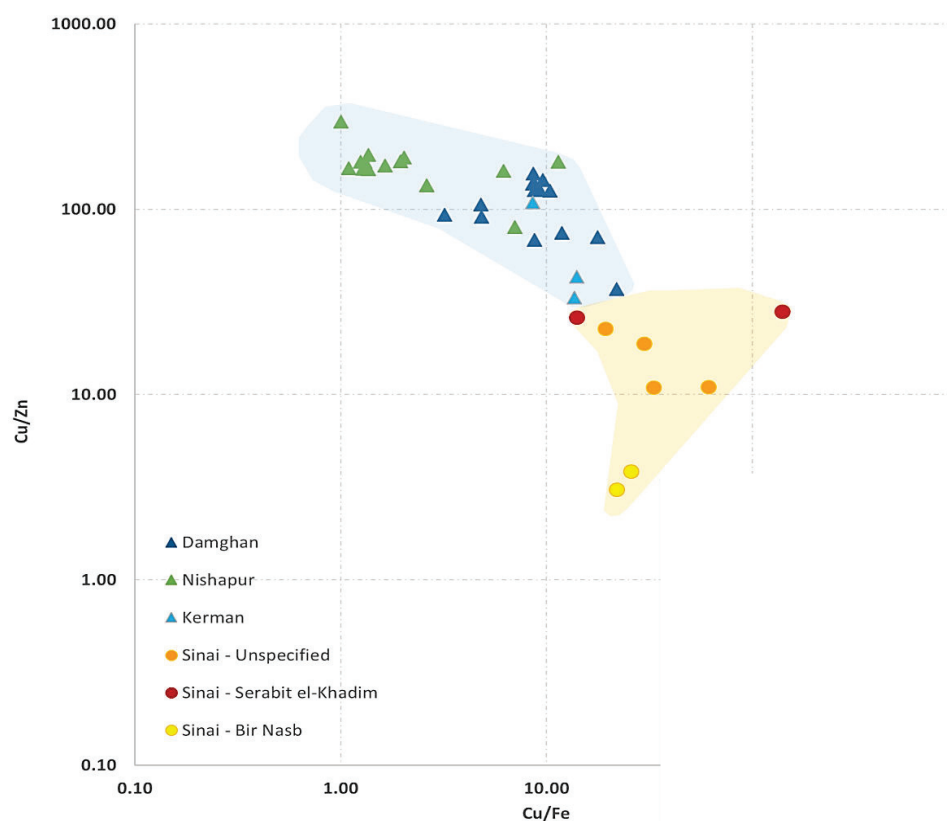


Figure 11. Geological specimens from the Sinai and Iran. Geological specimens plot along a line of variable Cu/Zn, Cu/Fe ratios. Sinai turquoises have low Cu/Zn, high Cu/Fe, and high Cu/As ratios (Carò et al., 2017).

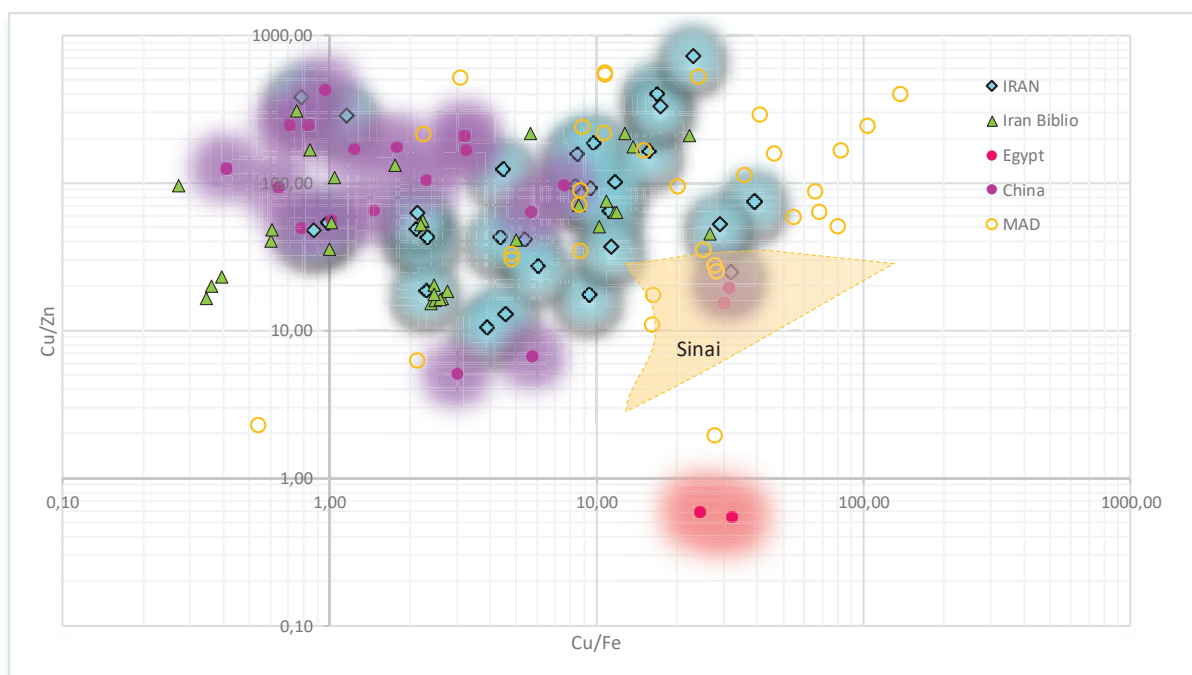


Figure 12. Cu/Fe vs Cu/Zn correlation diagram of Iranian samples (this study), data from bibliography as well as Sinai domain (Caro et al., 2017).

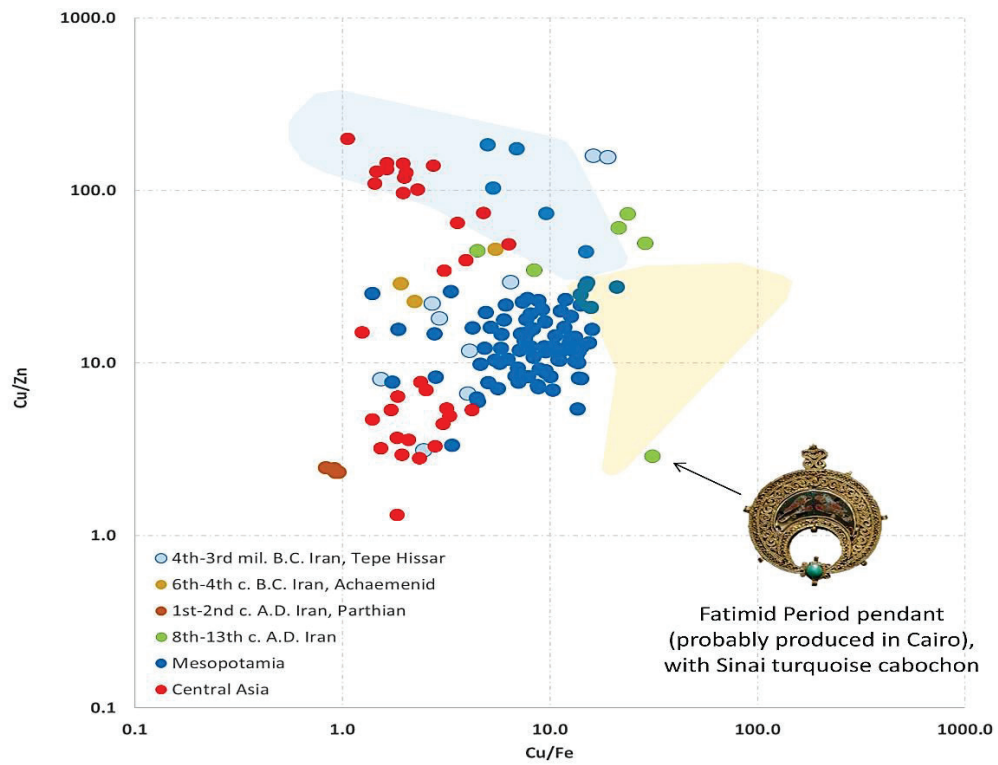


Figure 13. Turquoise from Persian, Mesopotamian, and Central Asian objects are characterized by low Cu/Fe ratios. Some objects have high Cu/Zn ratios consistent with Iranian mines, others do not match any of the analyzed sources (Carò et al., 2017).

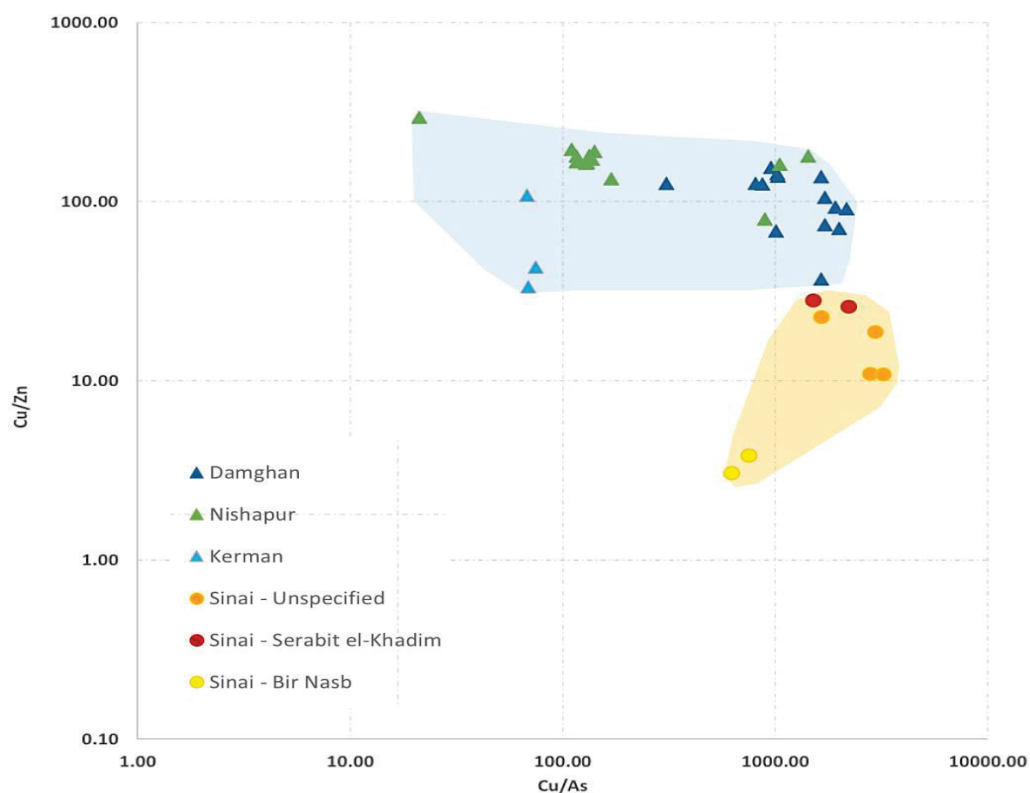


Figure 14. Geological Specimens from the Sinai and Iran. Geological specimens plot along a line of variable Cu/Zn and Cu/As ratios. Sinai turquoises have low Cu/Zn, high Cu/Fe, and high Cu/As ratios (Carò et al., 2017).

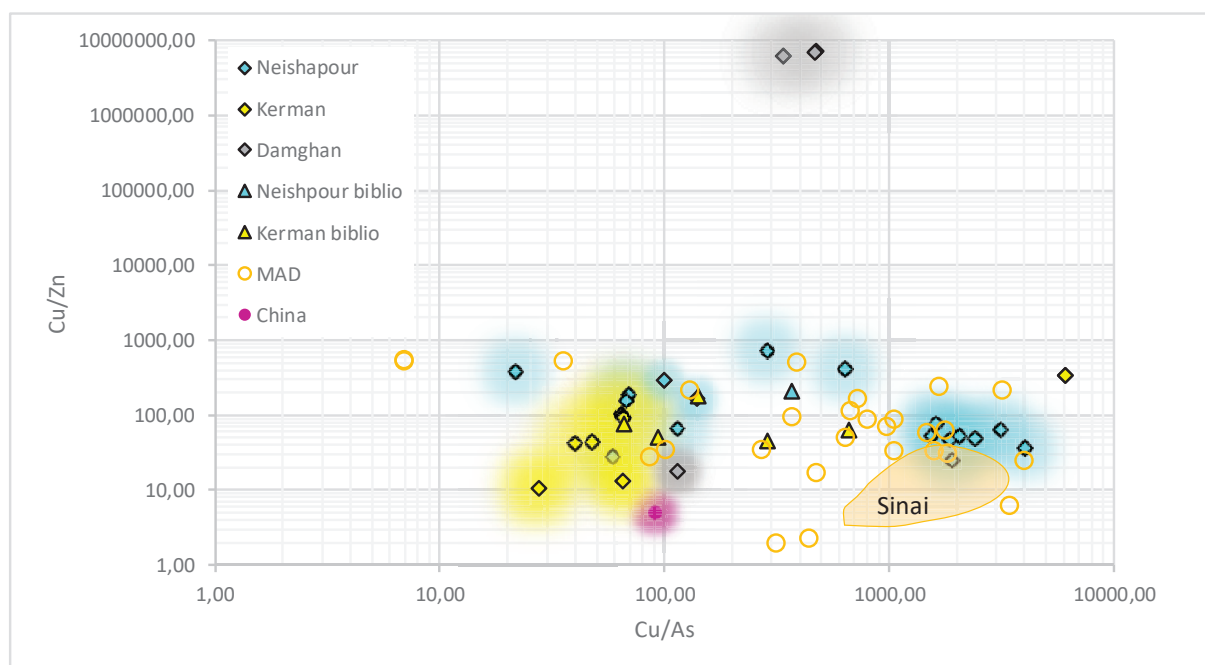


Figure 15. Cu/As vs Cu/Zn correlation diagram of Iranian samples (this study) and data from bibliography.

Annex IV. Principal component analysis (PCA) by XLSTAT

Principal component analysis (PCA) is a technique used to emphasize variation and bring out strong patterns in a dataset. It's often used to make data easy to explore and visualize.

It is a very useful method to analyze numerical data structured in a M observations (samples)/ N variables (chemical composition, elements) table. It allows to:

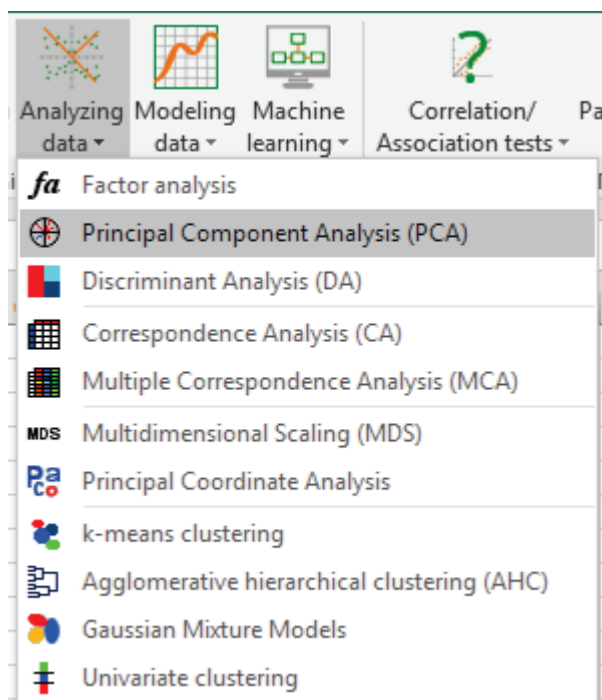
- Quickly visualize and analyze correlations between the N variables,
- Visualize and analyze the M observations (initially described by the N variables) on a low dimensional map, the optimal view for a variability criterion,
- Build a set of P uncorrelated factors

The limits of Principal Component Analysis stem from the fact that it is a projection method, and sometimes the visualization can lead to false interpretations. There are however some tricks to avoid these pitfalls.

Setting up a Principal Component Analysis in Excel using XLSTAT

Selecting the data

Once XLSTAT is activated, select the XLSTAT / Analyzing data / Principal components analysis command (see below).

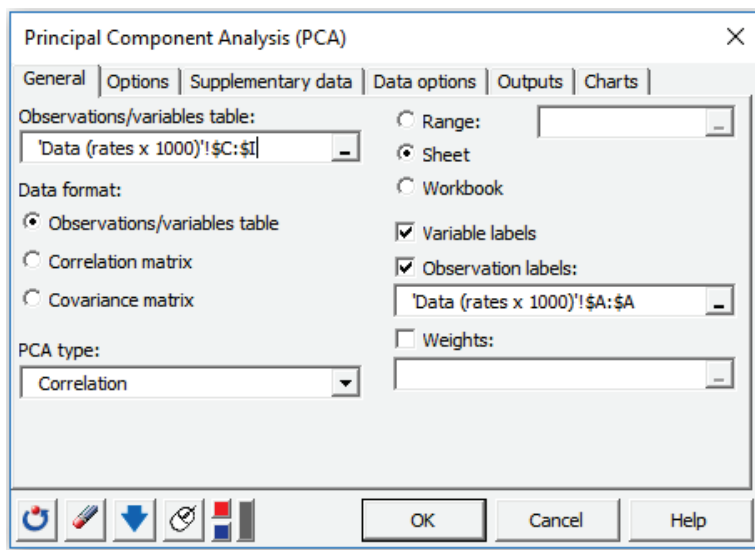


- The Principal Component Analysis dialog box will appear.
- Select the data on the Excel sheet.
- The Data format chosen is Observations/variables because of the format of the input data.

Principal Component Analysis: what type to choose - Pearson or covariance

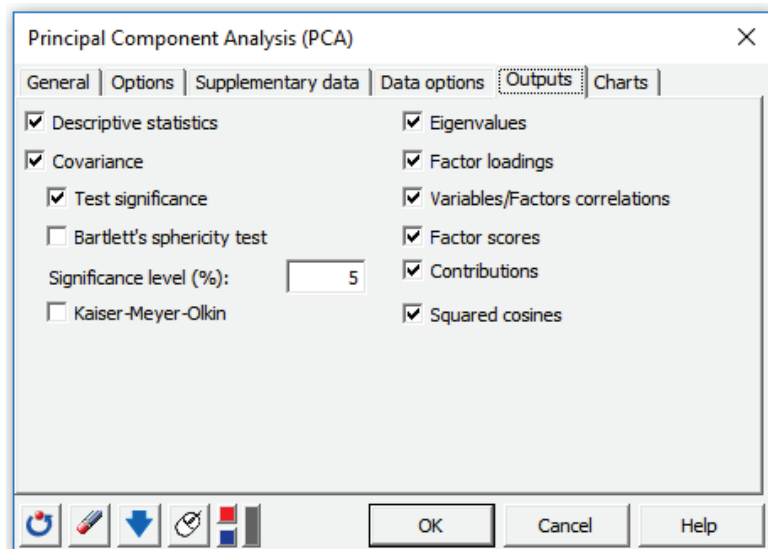
The PCA type that will be used during the computations is the Correlation matrix, which corresponds to the Pearson correlation coefficient. Covariance matrices allocate more weight to variables with higher variances.

Spearman's correlations may be more appropriate when running the PCA on variables with different distributions.



Principal Component Analysis in XLSTAT, configuring outputs and charts

In the Outputs tab, we choose to activate the option to display significant correlations in bold characters (Test significance).



In the Charts tab, in order to display the labels on all charts, and to display all the observations (observations charts and biplots), the filtering option is unchecked. If there is a lot of data, displaying the labels might slow down the global display of the results. Displaying all the observations might make the results unreadable. In these cases, filtering the observations to display is recommended

Principal Component Analysis (PCA) ✕

General | Options | Supplementary data | Data options | Outputs | Charts

Variables | Observations | Biplots

☒ Correlation charts

☒ Vectors

☐ Orientate labels

☐ Colored labels

☐ Color by group

☐ Resize points with Cos2

☐ Filter: Sum(Cos2)

Sum(Cos2) > 0.5

Group variable:

OK Cancel Help

Principal Component Analysis (PCA) ✕

General | Options | Supplementary data | Data options | Outputs | Charts

Variables | Observations | Biplots

☒ Observations charts

☒ Labels

☐ Colored labels

☐ Color by group

☐ Confidence ellipses

Confidence interval (%): 95

☐ Resize points with Cos2

☐ Filter: Sum(Cos2)

Sum(Cos2) > 0.5

Group variable:

OK Cancel Help

Principal Component Analysis (PCA) ✕

General | Options | Supplementary data | Data options | Outputs | Charts

Variables | Observations | Biplots

☒ Biplots

Type of biplot: Correlation biplot

Options for variables:

☒ Vectors

☒ Labels

☒ Supplementary variables

☒ Filter variables

Options for observations:

☒ Labels

☒ Supp. observations

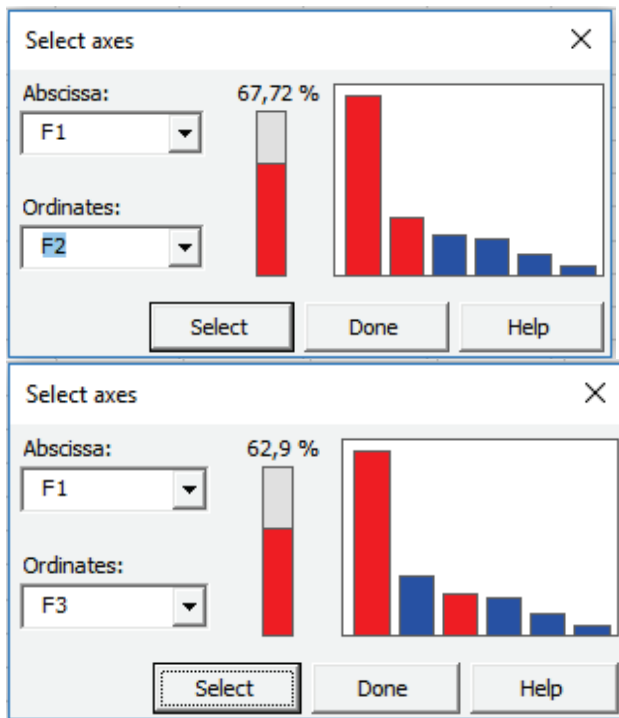
☒ Filter observations

OK Cancel Help

Principal Component Analysis in XLSTAT - launching the computations

The computations begin once you have clicked on **OK**. You are asked to confirm the number of rows and columns.

Note: This message can be bypassed by un-selecting the "Ask for selections confirmation" in the XLSTAT options panel.



Then you should confirm the axes for which you want to display plots

Interpreting the results of a Principal Component Analysis in Excel using XLSTAT

Interpretation of a PCA correlation matrix

The first result to look at is the **correlation matrix**. negatively correlated is presented by $r = -1$. the exact correlation is presented by $+1$.

Matrice de corrélation (Pearson (n)) :

Variables	SiO2 %	Al2O3 %	P2O5 %	CuO %	Fe2O3 %	Zn	Ca	S	Ba	Sr	As	Ga	Mn	Ti	K
SiO2%	1	0.071	0.320	0.080	0.012	0.067	0.068	0.280	0.051	0.032	0.257	0.189	0.073	0.367	0.872
Al2O3 %		1	0.789	0.321	0.156	0.270	0.329	0.094	0.311	0.060	0.140	0.007	0.211	0.081	0.158
P2O5 %			1	0.272	0.090	0.191	0.490	0.178	0.288	0.093	0.049	0.027	0.040	0.020	0.191
CuO %				1	0.101	0.238	0.188	0.145	0.133	0.031	0.148	0.195	0.322	0.195	0.012

Fe2O3 %					1	0.249	0.040	0.031	0.093	0.087	0.377	0.257	0.132	0.030	0.078
Zn						1	0.053	0.087	0.002	0.053	0.087	0.004	0.011	0.384	0.063
Ca							1	0.365	0.121	0.252	0.153	0.035	0.031	0.317	0.005
S								1	0.182	0.172	0.278	0.133	0.083	0.101	0.465
Ba									1	0.235	0.281	0.025	0.098	0.116	0.177
Sr										1	0.001	0.081	0.030	0.161	0.088
As											1	0.205	0.135	0.035	0.213
Ga												1	0.094	0.001	0.188
Mn													1	0.075	0.080
Ti														1	0.402
K															1

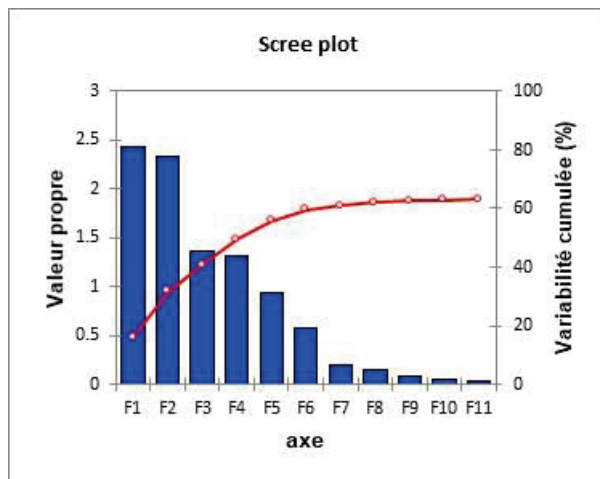
How to interpret Eigenvalues in Principal Component Analysis?

The next table and the corresponding chart are related to a mathematical object, the **eigenvalues**, which reflect the quality of the projection from the N-dimensional initial table (N=15 in this example) to a lower number of dimensions. In this example, we can see that the first eigenvalue equals 2.42 and represents 16% of the total variability. This means that if we represent the data on only one axis, we will still be able to see % of the total variability of the data.

Each eigenvalue corresponds to a factor, and each factor to a one dimension. A factor is a linear combination of the initial variables, and all the factors are un-correlated ($r=0$). The eigenvalues and the corresponding factors are sorted by descending order of how much of the initial variability they represent (converted to %).

Broadly speaking, factor = PCA dimension = PCA axis

	F1	F2	F3	F4	F5	F6	F7
Valeur propre	2.428	2.329	1.362	1.312	0.942	0.575	0.196
Variabilité (%)	16.186	15.525	9.082	8.746	6.282	3.832	1.304
% cumulé	16.186	31.710	40.792	49.538	55.820	59.652	60.956

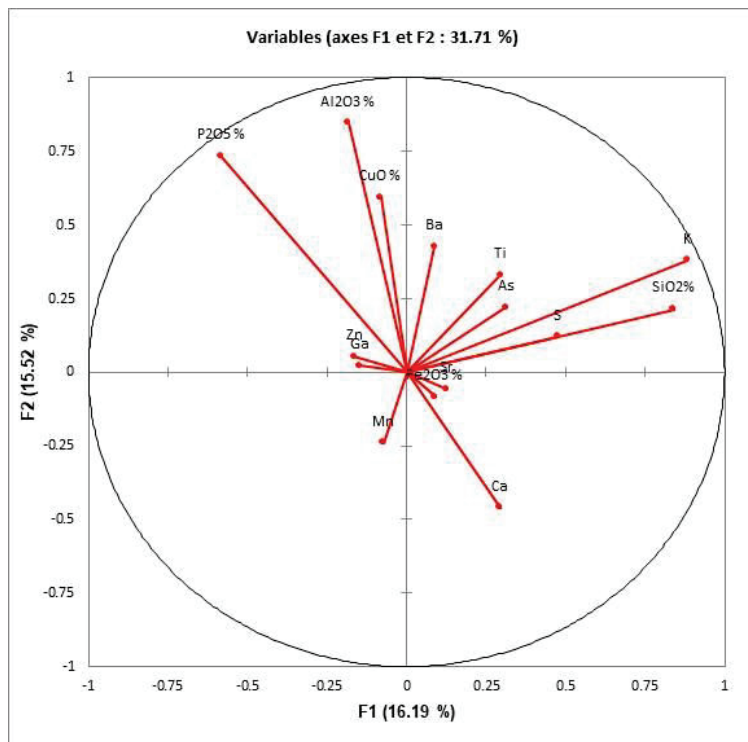


Ideally, the first two or three eigenvalues will correspond to a high % of the variance, ensuring us that the maps based on the first two or three factors are a good quality projection of the initial multi-dimensional table. In this example, the first two factors allow us to represent 31.71% of the initial variability of the data. We can see here that although we initially had 15 variables, the number of factors is 11. The number of "useful" dimensions has been automatically detected.

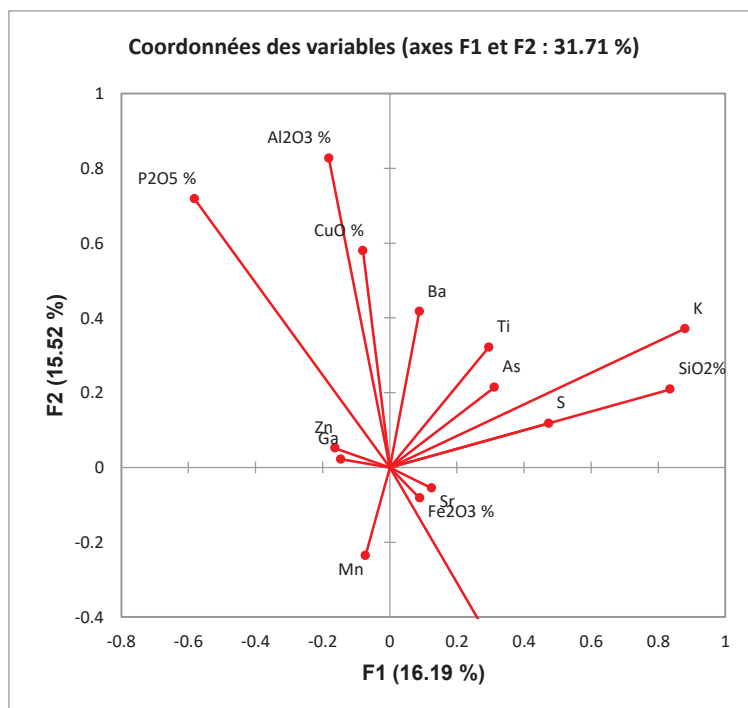
How to interpret results related to variables in PCA?

The first map is called the **correlation circle** (below on axes F1 and F2). It shows a projection of the initial variables in the factors space. When two variables are far from the center, then, if they are: Close to each other, they are significantly positively correlated (r close to 1); If they are orthogonal, they are not correlated (r close to 0); If they are on the opposite side of the center, then they are significantly negatively correlated (r close to -1).

When the variables are close to the center, some information is carried on other axes, and that any interpretation might be hazardous. This can be confirmed either by looking at the correlation matrix or by looking at the correlation circle on axes F1 and F3.

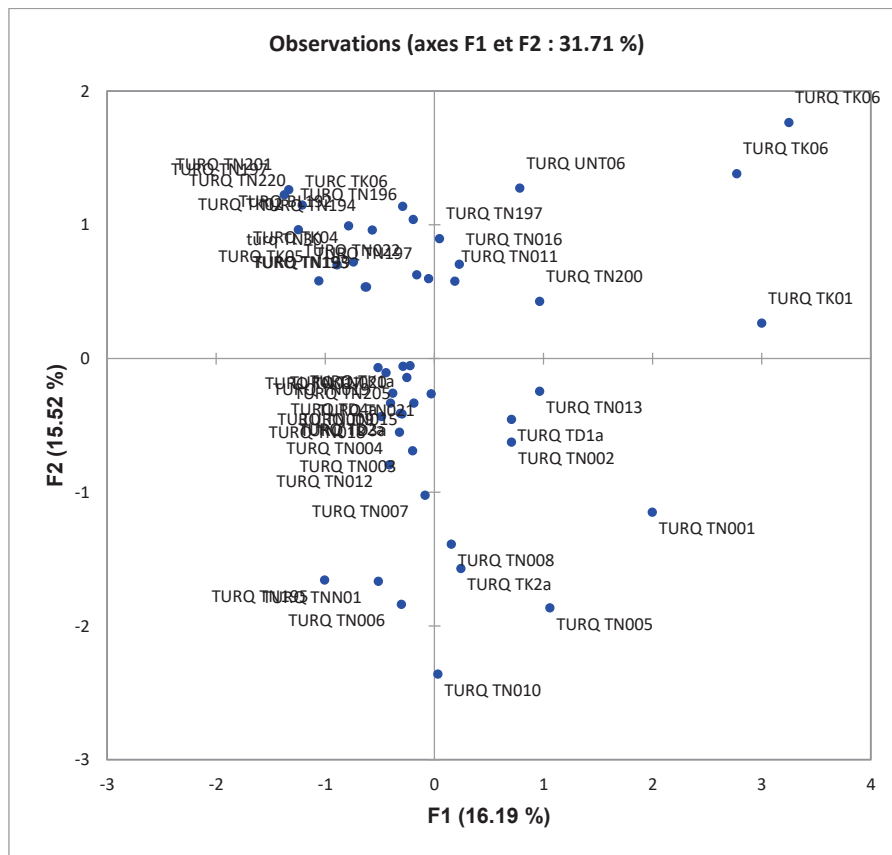


The correlation circle is useful in interpreting the meaning of the axes. These trends will be helpful in interpreting the next map. To confirm that a variable is well linked with an axis, take a look at the squared cosines table: the greater the squared cosine, the greater the link with the corresponding axis. The closer the squared cosine of a given variable is to zero, the more careful you have to be when interpreting the results in terms of trends on the corresponding axis.



How to interpret results related to observations in PCA?

The next chart can be the ultimate goal of the Principal Component Analysis (PCA). It enables you to look at the observations on a two- dimensional map, and to identify trends.



It is also possible to display **biplots**, which are simultaneous representations of variables and observations in the PCA space.

Click to view a 3D visualization on the first three axes generated by XLSTAT-3DPlot.

Note on the usage of Principal Component Analysis

Principal component analysis is often performed before a regression, to avoid using correlated variables, or before clustering the data, to have a better overview of the variables. The number of clusters might sometimes be a simple guess based on the maps.

Going further: adding supplementary variables to the PCA

It is possible to add **supplementary variables** to the PCA after it has been computed. This may help increasing interpretation quality. In XLSTAT, those variables can be selected under the **Suppl. Data** tab of the PCA dialog box. Supplementary variables can be divided into two types:

- **Qualitative supplementary variables:** they allow to color observations on the map according to the category they belong to. In this tutorial's example, we could have added a column defining if a state is mostly republican or mostly democrat.

- **Quantitative supplementary variables:** these variables can be added to see how they correlate with the group of variables that have been used to build the PCA. In the case where PCA is performed before a regression, the explanatory variables can be used to construct the PCA while the dependent variable can be added as a supplementary variable. This may help to roughly detect which explanatory variables could have the strongest effects on the dependent variable.

Generalized multivariate statistic workflow

- **Raw data**

Variable	Observations	Obs. avec données manquantes	Obs. sans données manquantes	Minimum	Maximum	Moyenne	Ecart-type
SiO2%	51	0	51	0.000	17.550	1.933	3.770
P2O5 %	51	0	51	10.310	16.190	13.488	1.397
CuO %	51	0	51	1.490	9.370	7.250	1.494
Fe2O3 %	51	0	51	0.150	13.410	3.650	3.776
Zn	51	0	51	0.000	4989.900	679.913	1087.912
Ca	51	0	51	0.000	3487.270	884.618	917.837
S	51	0	51	481.680	30285.180	3083.292	4281.095
Ba	51	0	51	0.000	4777.610	876.396	925.098
Sr	51	0	51	0.000	3953.480	134.566	552.031
As	51	0	51	0.000	2628.950	610.035	623.579
Ga	51	0	51	0.000	57.710	13.775	21.022
Mn	51	0	51	0.000	792.250	15.534	110.937
Ti	51	0	51	0.000	872.370	195.896	232.038
K	51	0	51	0.000	7036.240	902.993	1602.344

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M.F. Gazley1, 2. K. (2015). Application of principal component analysis and cluster analysis to mineral exploration and mine geology. *AusIMM New Zealand Branch Annual Conference* . New Zealand .

Introduction

Turquoise CuFe₂(PO₄)(OH)₂·H₂O is mined for more than 4000 years in Iran. Neighbouring Fathabad, a village of the oldest iron and lead known occurrence on the world, is famous for turquoise. In this study, the turquoise mines in Iran and the best gem-quality turquoise in the world, there is several turquoise mines in Iran and for this study we choose 3 major mines: Neyshabour (Khorasan province), Baghoo (Kerman province) and Chah Firoozeh (Danglman area) turquoise mines (Fig. 4). Blue colour in turquoise is due to Cu²⁺ and can be strongly modify by other substituted elements such as Fe²⁺, Zn²⁺ and specially Fe³⁺ in this study we analyzed this variation by optical absorption as well as by Raman methods and compared different color of turquoise from the blue (B) to the green (G) range of these three mines. The turquoisees used in this study have low to excellent qualities.

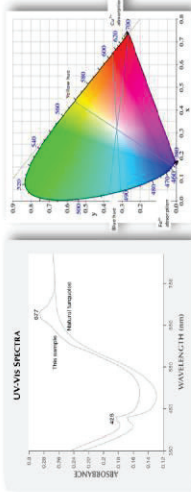


Figure 1. Optical spectra of turquoise (Han et al., 2015)

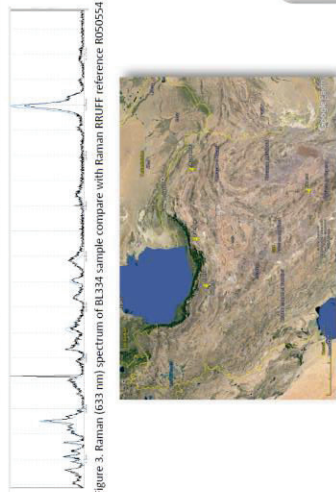


Figure 4. Location of the three main turquoise historical mines (Damghan, Kerman and Neyshapour) in Iran.

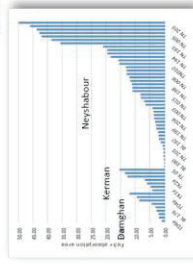


Figure 5. Percentage of iron oxide (XRF) of the studied samples.

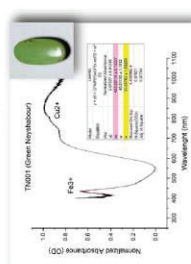


Figure 7. Optical spectrum of Neyshabour green turquoise (TN001) and Fe^{3+} absorption area

Theoretical	Yinch Solids, Virginia, USA	DANGHAN MEAN TC	MEAN TC (KEMAN)	MEAN TC Meyersburg
P205	34.9	34.13	30.28	32.19
Al2O3	37.6	36.5	36.36	34.51
CaO	9.78	9	8.38	7.26
SiO2			1.72	1.86
Fe2O3	0.21		1.74	0.52
SO3			1.36	1.23
CaO			0.18	0.03
ZnO			0.08	0.69
NO estimated	17.72	20.12	20.30	20.00

Chart 1. XRF mean analyses of turquoise samples.



Jegheh egret from Qajar dynasty (19th c.) made during the reign of Nasruddin Shah (Central Bank of Iran)

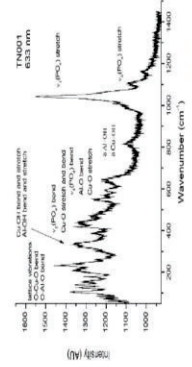


Figure 10 Raman spectrum of pure green tiranulose TN001 (633 nm)

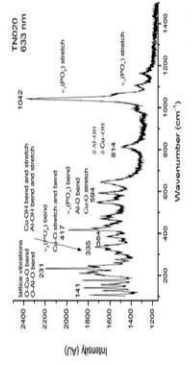


Figure 11. Raman spectrum of pure blue turquoise TN020 (633 nm)

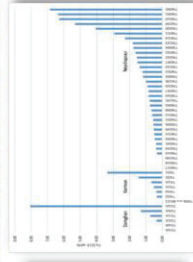


Figure 6. Area of Fe^{3+} absorption band of the studied samples.

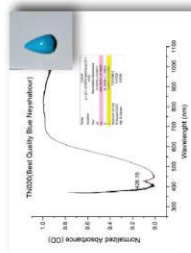


Figure 8. Optical spectrum of blue Neyshabour turquoise (TN020) and Fe^{3+} absorption area.



Figure 12. Energy levels of Cu^{2+} and Fe^{3+} and their absorption in various structural environment

Raman analyses

Raman measurements were conducted using two different laser excitations: 780 (near infrared) and 633 nm (red). Raman spectra under 780 nm were recorded using the Thermo Scientific DXR spectrometer from 100–1500 cm^{-1} allowing to record the lattice Raman modes. Raman spectra under 633 nm were recorded using the LabRAM ARAMIS spectrometer in the range 50–1500 cm^{-1} allowing to record the lattice vibration modes and in the range 2900–3700 cm^{-1} allowing to record the vibration modes of OH and H₂O.

XRF analyses

Chemical composition analyses were done by Thermo Scientific Niton PXRF XL3t Gold (miming mode). Result of oxide analyses of turquoise sample is shown in chart 1. The percentage of iron oxide present in the samples is shown in fig.5.

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Conclusion

Absorption spectra of turquoise disclose the broad absorption band corresponding to Cu^{2+} (600–800 nm) as well as the absorption line corresponding to Fe^{3+} (428 nm) which present an intensity correlated to the amount of substituted iron. As it can be seen the amount of iron (Fe^{3+} area) is higher in green turquoise samples than in blue turquoise ones. It appears that even the turquoise with the best blue color present a slight Fe^{3+} absorption. This indicates that even in such sample a iron substitution occurred. Complementary analyses are undergone to tentatively trace historical turquoise.

New trapiche-like sapphires from Hamadan (Iran)

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Introduction

A new sapphire deposit has been discovered in Iran. This is the first deposit for this gem in the country. Resulting from a fortuitous discovery, the discoverer kept the secret until now. The exploitation of the deposit could begin in the coming years. The operating area, accessible only by 4x4, is located away from the city of Hamadan (or Hamadan) (Fig. 1). It is one of the main cities of Iran in the western and mountainous region of the country on the border of Iranian Kurdistan (Fig. 2).



Figure 1. Location of the Hamadan region



Figure 2. Aerial image of the Hamadan region

Geological context

These sapphires (Fig. 4) are associated with the pegmatitic formation of Alvand (Fig. 3) closely related to regional magmatic rocks and associated with low pressure metamorphism and partial melting (Sepahi et al., 2009). Local saturation in aluminum explaining the crystallization of corundum (Shekhi and Hadi, 2015). They have a relatively dark blue-gray hue probably related to a high iron and titanium content.



Figure 3. Outcrops



Figure 4. Rough sapphires

Gem-quality sapphires

While some of the samples appear to be gem quality and can be used in jewelry (Fig. 4 and 5), they are mostly dark blue in color and mostly opaque. Their originality consists in the fact that a high rate of sapphires in this deposit has a "trapiche-like" texture.

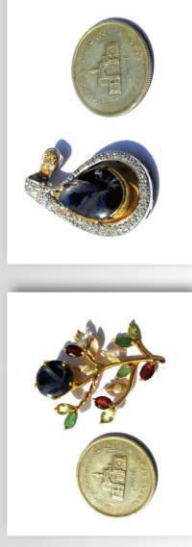


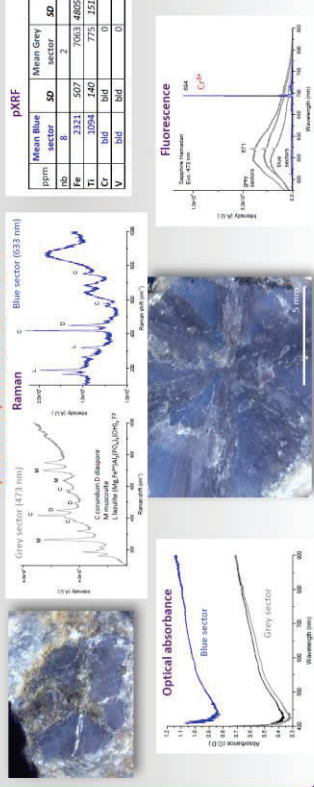
Figure 4. Trapiche-like sapphire cabochon on a brooch

Figure 5. Trapiche-like sapphire cabochon on a pendant

Other trapiche-like sapphire occurrences

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- Tasmania (Verriest et al., 2016)

Spectroscopic characterizations



Conclusion

The sapphires of the Hamadan area are characterized by their dark color, a high percentage of trapiche-like structure and a high concentration of iron (>2000 ppm) and titanium (>1000 ppm). The blue corundum sectors present a high amount of diaspore (and lazulite ?) while the grey ones have numerous muscovite inclusions. Those associated phases could have crystallized with corundum and/or generated during alteration. Thermal treatments will be conducted to improve the sapphire transparency and color. If this treatment will be efficient, it may be a chance for the gem trade in Iran.

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Exploration of megapixel hyperspectral LIBS images using principal component analysis†

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Laser-Induced Breakdown Spectroscopy (LIBS) has achieved promising performance as an elemental imaging technology, and considerable progress has been achieved in the development of LIBS over the last several years, which has led to great interest in the use of LIBS in various fields of applications. LIBS is a highly attractive technology that is distinguished by its table top instrumentation, speed of operation, and operation in ambient atmosphere, able to produce megapixel multi-elemental images with micrometric resolution (10 μm) and ppm-scale sensitivity. However, the points that limit the development of LIBS are undeniably the expertise and the time required to extract a relevant signal from the LIBS dataset. The complexity of the emission spectra (e.g., elemental responses, structure of the baseline), the high dynamic range of measurement (i.e., possibility to image major to trace elements), and the large number of spectra to process require new data analysis strategies. Such new strategies are particularly critical for multi-phase materials. In this paper, we report a new methodology based on the well-known Principal Component Analysis (PCA) approach for the multivariate hyperspectral analysis of LIBS images. The proposed methodology is designed for large, raw, and potentially complex series of LIBS spectra, that allows various and exhaustive levels of information to be extracted (including the characterization of mineral phases, assessment of the measurement and identification of isolated elements) and facilitates the manipulation of such hyperspectral datasets.

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rsc.li/jaas

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) imaging has been demonstrated to be a suitable technique to perform multi-element imaging analysis, thus arousing great interest among researchers in several areas of science.^{1–10} In LIBS, a laser beam is focused onto the sample surface to generate a hot plasma. The optical emission, resulting from the electronic relaxation of excited atoms and ions, is collected by adequate optical components and is then analyzed by an optical spectrometer to generate an emission spectrum characteristic of the elemental composition of the sample.^{11,12} In imaging mode, the sample surface is scanned, pixel by pixel, in a raster scan mode using a computer-controlled motorized translation stage. Plasma emission (i.e., spectrum) is obtained at each position of the

mapping sequence following the raster scan pattern. The spectral dataset is then processed with the aim of extracting the relevant elemental intensities before generating elemental images.¹³ This approach has many advantages, such as high speed of operation, ease of use, multi-elemental capabilities, accessibility to a wide spectral range and operation at atmospheric pressure. LIBS enables the imaging analysis of all types of samples (e.g., rocks, alloys, biological tissues) without any size restriction (up to several tens of cm^2).^{1,14} Such advantages, coupled with reachable spatial resolution of approximately 10 μm and limit of detection on the order of ppm, make LIBS-based imaging highly attractive for many fields of applications, with a great potential of development in both academic and industrial fields.

In homogenous matrices (i.e., similar physical properties of the sample surface), several cases of study have already been reported in the literature (e.g., speleothems,^{1,9,15} crystals,⁷ catalysts,^{10,16,17} or biological tissues^{18,19}), thus demonstrating the maturity of the technique. In this type of sample, knowledge of the spectral structure of the matrix (main emission lines) allows selection of the emission lines free of the interferences associated with the elements of interest, thereby providing fast and reliable data extraction. This approach is what we call standard data processing.¹³ In contrast, when complex samples that contain several phases and thus different matrices are screened,

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data analysis becomes much more challenging. This multi-phase analysis is particularly difficult and time-consuming when one or several phases are associated with elements that present complex spectral structures with hundreds or thousands of emission lines, such as iron (Fe) or titanium (Ti). In such cases, selecting an appropriate spectral lines requires the analyst's expertise and a rigorous case-by-case evaluation of the spectral dataset. Occasionally, it is even impossible to find specific lines for the elements of interest. The standard data processing approach has other weaknesses. First, manual line selection leaves behind no possibility of full data interpretation. Second, the study of the association between elements is not straightforward. Moreover, considering the current speed of analysis and instrumentation, it is easy to obtain daily spectral data sets with several millions of spectra; as a result, the data processing step becomes the bottle neck of the analysis. In this sense, more sophisticated extraction approaches must be developed to streamline the process.

In this paper, we propose a new data processing methodology, based on the hyperspectral images (HSI) analysis of the large LIBS dataset (*i.e.*, millions of pixels spread on thousands of wavelength channels) by Principal Component Analysis (PCA). This methodology allows the exhaustive characterization of the dataset under analysis without any spectral pre-processing or prior knowledge of the sample composition. The present work has been conducted on a megapixel dataset (~2 millions of LIBS spectra) obtained by measuring a blue Iranian turquoise hosted in pyrite and silicate matrices. As mentioned above, this type of mineralogical analysis represents a real challenge for performing LIBS data analysis because of the complex spectral structure, spectral interferences, and high dynamic concentration ranges as well as the added difficulty of line saturation. The hyperspectral analysis coupled to PCA has been largely used in numerous imaging techniques, such as Raman,^{20,21} Maldi,^{22,23} FT-IR^{24,25} and LIBS.^{26,27} Herein, our approach focuses on the exploration of raw data, without any further consideration or pre-processing. To the best of our knowledge, this is the first time that such a methodology has been applied to megapixels images containing millions of pixels and thousands of spectral channels (wavelength). This paper introduces the use of PCA in the hyperspectral analysis of a LIBS dataset as a new exploration tool for the analysis of complex and heterogeneous materials; this novel tool opens new perspectives for LIBS-based imaging measurement.

2. Experimental methods

2.1 Sample description

The turquoise sample was obtained from the Nishâpur turquoise deposit (Iran). A thin section bloc was prepared and polished for LIBS imaging. This sample is composed of three main mineral phases: turquoise, pyrite and silica (mainly quartz). Turquoise, $\text{Cu}^{2+}\text{Al}^{3+}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$, is a microcrystalline copper aluminum phosphate mineral that occurs as a secondary phase in the alteration zone of hydrothermal porphyry copper deposits or during the weathering of aluminous igneous or sedimentary rocks. Turquoise is often

associated with pyrite FeS_2 and chalcocopyrite CuFeS_2 . Turquoise can present a continuous series with chalcociderite $\text{Cu}^{2+}\text{Fe}^{3+}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$, faustite $(\text{Zn}^{2+}, \text{Cu}^{2+})\text{Al}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$ and aheylite $(\text{Fe}^{2+}, \text{Zn}^{2+})\text{Al}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$. Therefore, Fe is often identified in turquoise, whether substituted as Fe^{2+} to copper ("aheylite") or as Fe^{3+} to aluminum ("chalcociderite"). In addition, the presence of Zn is associated with its substitution to Cu ("faustite"). The precise spatial distribution of Fe and Zn is therefore a challenge because it is a precious indication of its genetic condition of formation. In the present work, we focus only on the iron distribution.

2.2 Experimental setup and data acquisition

The LIBS instrumental setup was based on a homemade optical microscope. The methodology used in the present work for LIBS data measurement and the advantages of using advanced experimental conditions have been previously described.^{1,14} Briefly, the experiment was conducted by using a Nd:YAG laser with a 5 ns pulse duration operating at 100 Hz at the fundamental wavelength (1064 nm). The laser beam was focused onto the sample by a 15× magnification objective (LMM-15X-P01, Thorlabs). The sample was placed on a three axes XYZ motorized translation stage, with a travel range of 50 mm in each direction. The LIBS measurements were performed at room temperature under ambient pressure. An autofocus system was used during the analysis to maintain a constant objective-to-sample distance. The system can control the vertical position of the plasma emission by compensating for any flatness variation of the sample surface *via* a feedback loop operating at high repetition rate.^{1,28} All spectra were obtained using a single laser pulse at each position of the sample, without any accumulation or averaging. The light emitted by the plasma was collected by a quartz lens and then focused onto the entrance of a round-to-linear fiber bundle connected to the spectrometer. This fiber bundle is composed of 19 fibers, each with a 200 µm core diameter. The entrance slit of the Czerny-Turner spectrometer (Shamrock 500, Andor Technology) was 30 µm. The spectrometer was equipped with a 600 l mm⁻¹ grating blazed at 300 nm and an intensified charge-coupled device (ICCD) camera (iStar, Andor Technology) defined by 2048 × 512 pixels. In this configuration, a spectral range of 80 nm with a spectral resolution of approximately 0.15 nm was achieved. The ICCD camera was synchronized with the Q-switch of the laser, and the spectrum was acquired with a delay of 500 ns and a gate of 3000 µs in the full vertical binning mode. The laser energy was stabilized throughout the experiment by using a servo control loop consisting of a power meter and a computer-controlled attenuator (ATT1064, Quantum Composers). Finally, home-made software developed in the LabVIEW environment was used to control the entire LIBS imaging setup, thereby allowing an automatic spectral acquisition of any selected region of interest of a given sample with a pre-set lateral resolution.

The LIBS image was recorded with a step resolution of 15 µm over a surface area of 468 mm² and represents more than 2 million pixels (1300 by 1600 pixels along the *x*- and *y*-axes, respectively). The ablation craters, as observed afterward using

optical microscopy, were approximately 8 μm in diameter. Because one LIBS spectrum contains 2048 spectral channels, the whole data set represents a total of 4.2 billion of numerical values. The duration of the LIBS imaging measurement was approximately 6 hours, limited by the laser frequency rate (*i.e.*, 100 Hz). The detection range of the spectrometer was set from 250 nm to 330 nm, covering the main emission lines of all elements of interest, including phosphorus (P I 253.6, P I 255.3 nm), copper (Cu I 324.7, Cu I 327.4 nm), aluminum Al (Al I 308.2, Al I 309.3 nm) and numerous iron lines (for example, Fe II 257.9 and Fe I 302.1 nm). A slight and continuous wavelength drift (lower than 0.05 nm) was observed between the first and last spectra of the dataset. Although this shift was visually negligible, all spectra were recalibrated in wavelength before performing multivariate analysis.

2.3 PCA of a LIBS dataset

The spectral data set is a 3-D structure, also known as a hyper-spectral cube, that simultaneously contains all the spatial and spectral information (*cf.* Fig. 1). It is formed by two spatial

dimensions (m and n), where m and n are the numbers of pixels (spectra) along the x - and y -axes, respectively, and one spectral dimension (λ).²⁹ In the present case, each pixel (x - y coordinate) was related to a LIBS spectrum of 2048 values corresponding to the signal intensity at each wavelength (z -values). The PCA calculation was performed on the unfolded dataset X corresponding to a 2-D matrix of dimension N ($m \times n$) by 2048 (*i.e.*, the number of wavelength λ).

PCA is one of the most flexible and effective chemometric methods for exploratory data analysis applied to hyperspectral imaging. In PCA, the unfolding spectral data matrix X ($m \times n$, λ) is decomposed into a scores matrix T ($x \times y$, a), a loadings matrix P (a , λ) and a residual matrix E ($x \times y$, λ), where a is the number of principal components considered, following eqn (1):³⁰

$$X = TP + E \quad (1)$$

The loading vector of each principal component (PC) is a direction in the original wavelength space. The loading vector represents a new set of variables calculated by linear combination of the original variables along the direction of maximal

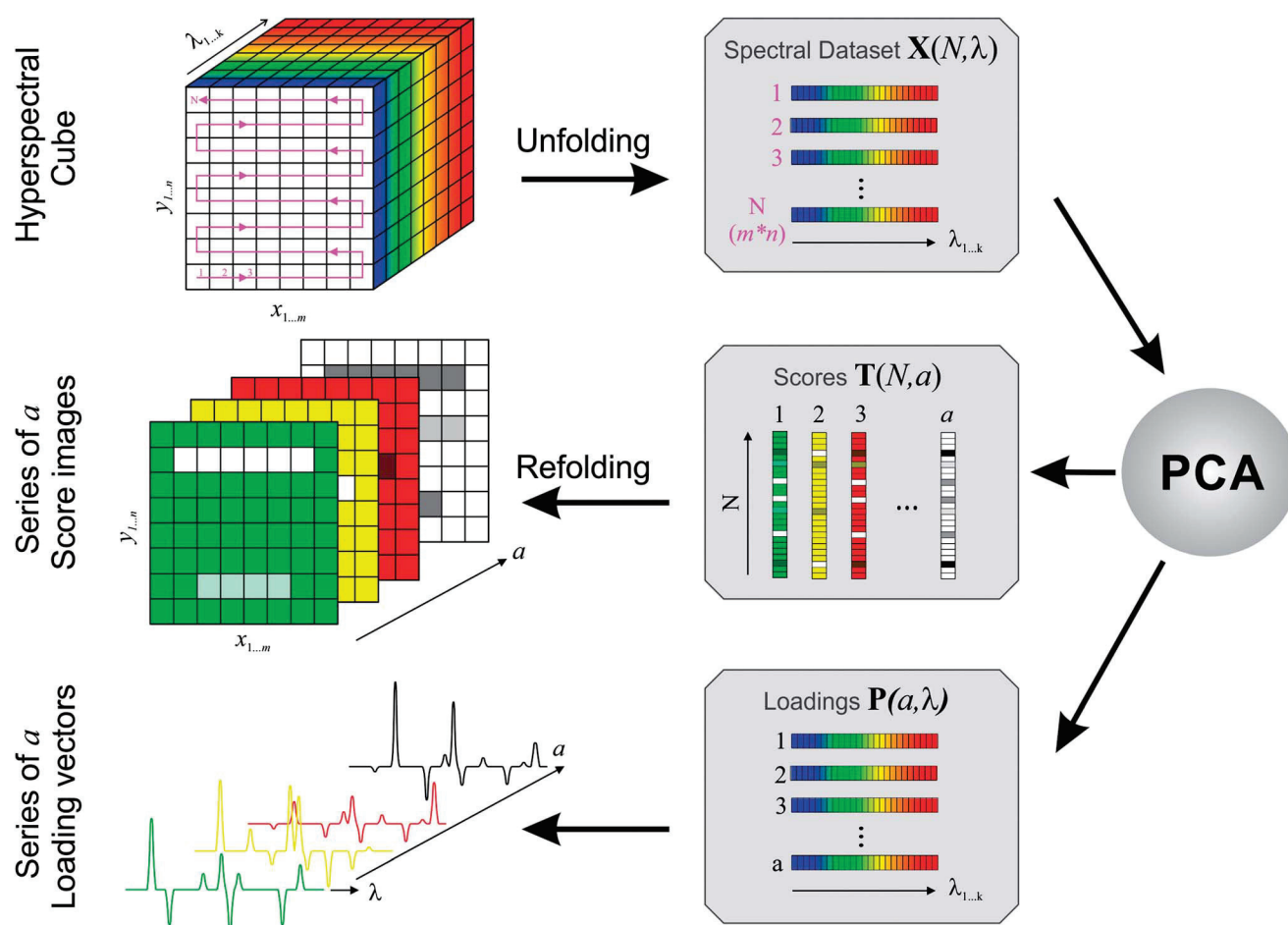


Fig. 1 Flow chart of hyperspectral LIBS imaging coupled with PCA analysis. The hyperspectral data cube is composed of two spatial dimensions, x and y , corresponding to the image pixels and one spectral dimension (λ), where each cell of the cube represents a single-shot LIBS spectrum. The unfolding of the hyperspectral data cube generates successive N spectra ($x \times y$). PCA is applied to generate the score and loading matrices with dimensions of N by a and a by λ , respectively, where a is the number of selected PCs. A scores matrix can be refolded for each PC to generate the scores image associated with its corresponding loading vector.

variance. The corresponding scores represent the projection of all spectra (pixels of the image) onto these new axes, allowing observation of the similarities and differences between the original spectra. After the PCA transformation, the score matrix is refolded considering the *x* and *y* coordinates of each pixel, displaying the results in a so-called score image or score map. The score image displays the contribution for each principal component of the original hypercube, thus allowing the distribution of the different elements within the surface to be visualized, considering the main sources of variability.

Because the turquoise stone was embedded in a polymeric resin for fixation, the LIBS spectra associated with the pixels related to resin were not considered for the PCA calculation. For this purpose, a mask index (matrix representing the spectrum index of all pixels associated with the turquoise stone) was used. The mask index was obtained by integrating the emission spectrum for each pixel (*i.e.*, global signal) and then using a threshold value to discriminate between pixels related to the resin and pixels related to the stone. Following this procedure, a total of approximately 1 200 000 spectra was used as the input to the PCA model. Before applying PCA, the raw data cube was mean-centered, which caused all of the spectral variables to have a zero mean. This data-centering step is generally used to increase the differences between pixels.²⁵ All PCA calculations were performed in the Matlab 2016b environment.

3. Results and discussion

3.1 Conventional data analysis

The proposed dataset was first processed by the conventional univariate method, which has been described elsewhere.^{1,14} This methodology is optimal for revealing the heterogeneous distribution of major and/or trace elements in samples with a unique and homogenous matrix. In this case, the mean spectrum (computed with the whole spectral dataset) provides a good overview of the spectral structure dataset, identifying the main elements by matching the observed emission lines with an atomic spectra database. The knowledge of the matrix composition enables the selection of the lines, free of interference from the element of interest. Next, an algorithm extracts the net intensity of the lines by retrieving their intensity and subtracting the baseline for each selected line in every single spectrum to generate a 2-D matrix (*i.e.*, relative abundance image). This procedure is rather fast, with a megapixel dataset typically analyzed in less than 10 minutes. However, for multi-phase material (*i.e.*, the present case), this procedure is not well adapted; nevertheless, it is still important to apply it first to highlight the encountered issues and evaluate the potential of PCA.

The optical image of the gem stone analyzed and univariate LIBS images of Fe II (line at 259.939 nm), Si I (288.158 nm), Cu I (327.395 nm), P I (253.399 nm), and Al I (309.271 nm) that were extracted following the conventional procedure are represented in Fig. 2a. The lines selected to generate these images were carefully chosen to fulfill two criteria; (i) the line must present one of the highest intensities in the detection range, and (ii) the line must be as isolated as possible with regard to other

emission lines of different phases of the sample. Because of the complex spectral structure of the sample, only the iron line met the line selection criteria. The presence of multiple mineral phases indeed makes the conventional data extraction tricky to perform and inaccurate. This is clearly visible in Fig. 2a (red regions of the image), where Cu and P are strongly affected by spectral interferences from iron.

Fig. 2b shows three single-shot spectra associated with each mineral phase: pyrite in red, silicates in green and turquoise in blue; the average spectrum of the whole dataset is in black. The similarity between the average spectrum and the pyrite spectrum is due to the strong emission of iron and the sample composition containing a larger area of pyrite phase compared to the areas of the other mineral phases. The presence of iron lines produces a complex spectral structure that hinders the line selection for all elements. This is critical for P and Al lines, for which no line can be extracted by following the selection criteria. In the present case, the average spectrum does not allow elements to be identified, except for the iron associated with the pyrite phase. As a result, new strategies for data analysis must be developed and PCA appears to be a powerful tool for extracting elemental information from millions of spectra potentially with interference among the different sample phases.

3.2 PCA data exploration

In PCA of megapixel-scale images, the maximum number of principal components that can be potentially calculated is equal to the number of spectral variables included in the data structure. However, in the present case, only the first 10 PCs were extracted, explaining 99.86% of the total variance. As mentioned above, each principal component was associated with an eigenvalue (and, by extension, an explained variance) and a score column matrix (generating a 2-D scores image when re-folded). Scores can be read in exactly the same manner as any other variable and can thus be plotted and interpreted in many different ways. If desired, the scores can be plotted as score images, considering the spatial coordinates of the pixels, as shown in Fig. 3. Pixels with similar values of score are similar in terms of what the components represent, as defined by the loading vectors. Scores can be positive or negative. The loading vector defines the linear combination of the variables represented by a particular component. In our case, the loading vectors provide correlations among the emission lines of the elements present in the same mineral phase. For interpretation of the loading vectors, the emission spectra were simulated using the Kurucz database³¹ for a typical LIBS plasma temperature and electron density (8000 K and $5 \times 10^{17} \text{ cm}^{-3}$, respectively).

The following results and discussion are organized with regard to the type of information obtained by PCA. This information includes the sample characterization (*i.e.*, identification of the different mineral phases), the diagnosis of the LIBS measurement, and the identification of new low concentration elements associated with isolated pixels. A special Look Up Table (LUT, false color scale) was applied to represent each

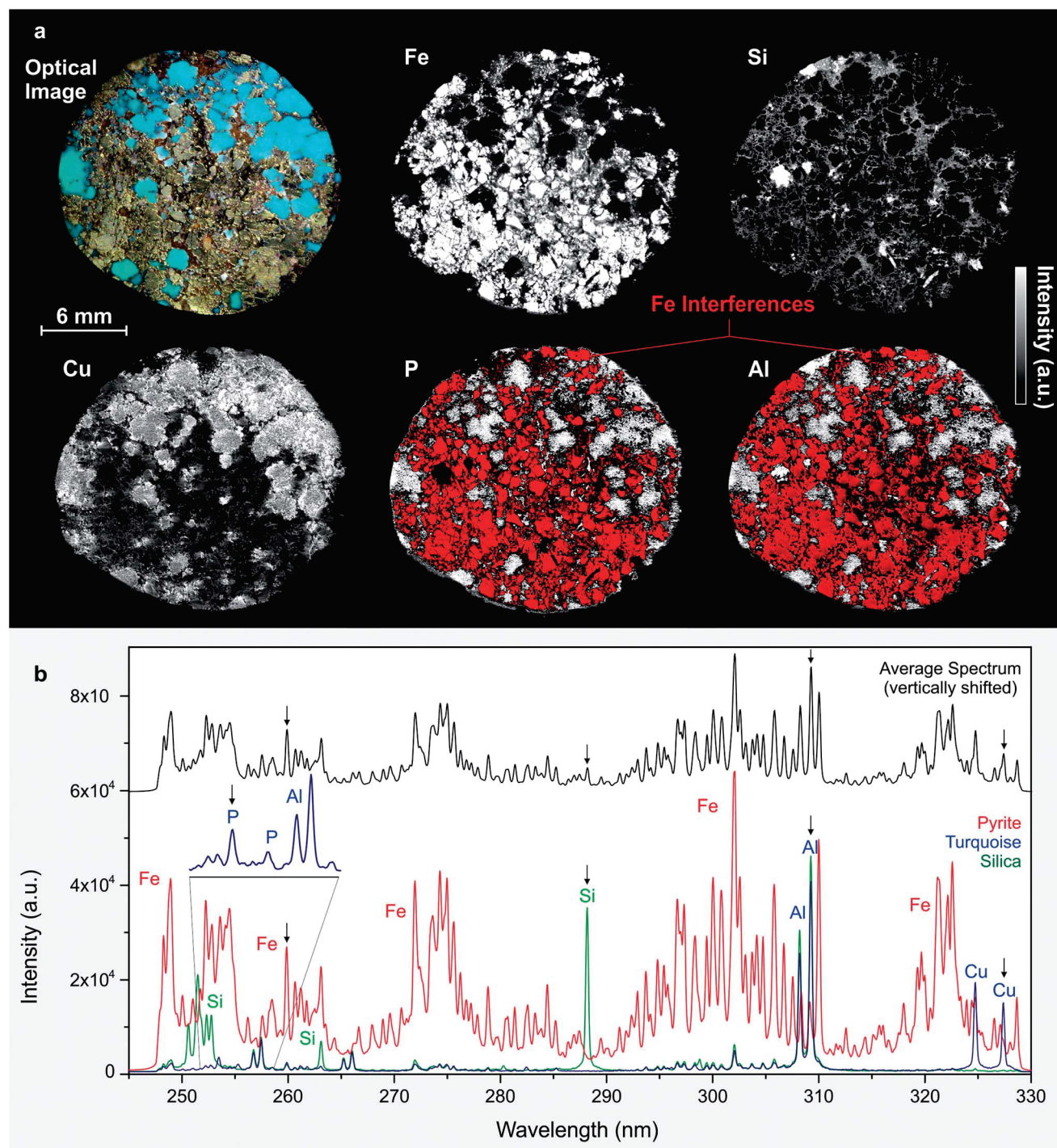


Fig. 2 (a) Optical images of the gem stone and five LIBS elemental images Fe, Si, Cu, P and Al in a gray color scale. Red areas show regions rich in P and Al interfered with iron lines. (b) Typical single-pulse spectra from pyrite (red), silicates (green) and turquoise (blue) phases. The mean spectrum of the whole dataset is represented in black. The vertical arrows indicate the line selected for building up the images (see the text for details).

score image. This LUT was generated by coupling two standard color scales (*i.e.*, yellow and reversed blue). The black to yellow scale represents the positive values of the scores, and the black to cyan scale represents the negative ones. The black color is used for zero or very small score values (*i.e.*, insignificant ones).

3.2.1 Identification of mineral phases. Fig. 3 shows the images of the first, second and fourth principal components (PCs) and their associated loading vectors. The first PC (PC1) represents 95.45% of the total variance; *i.e.*, almost all of the variation of the raw data is explained by this component.

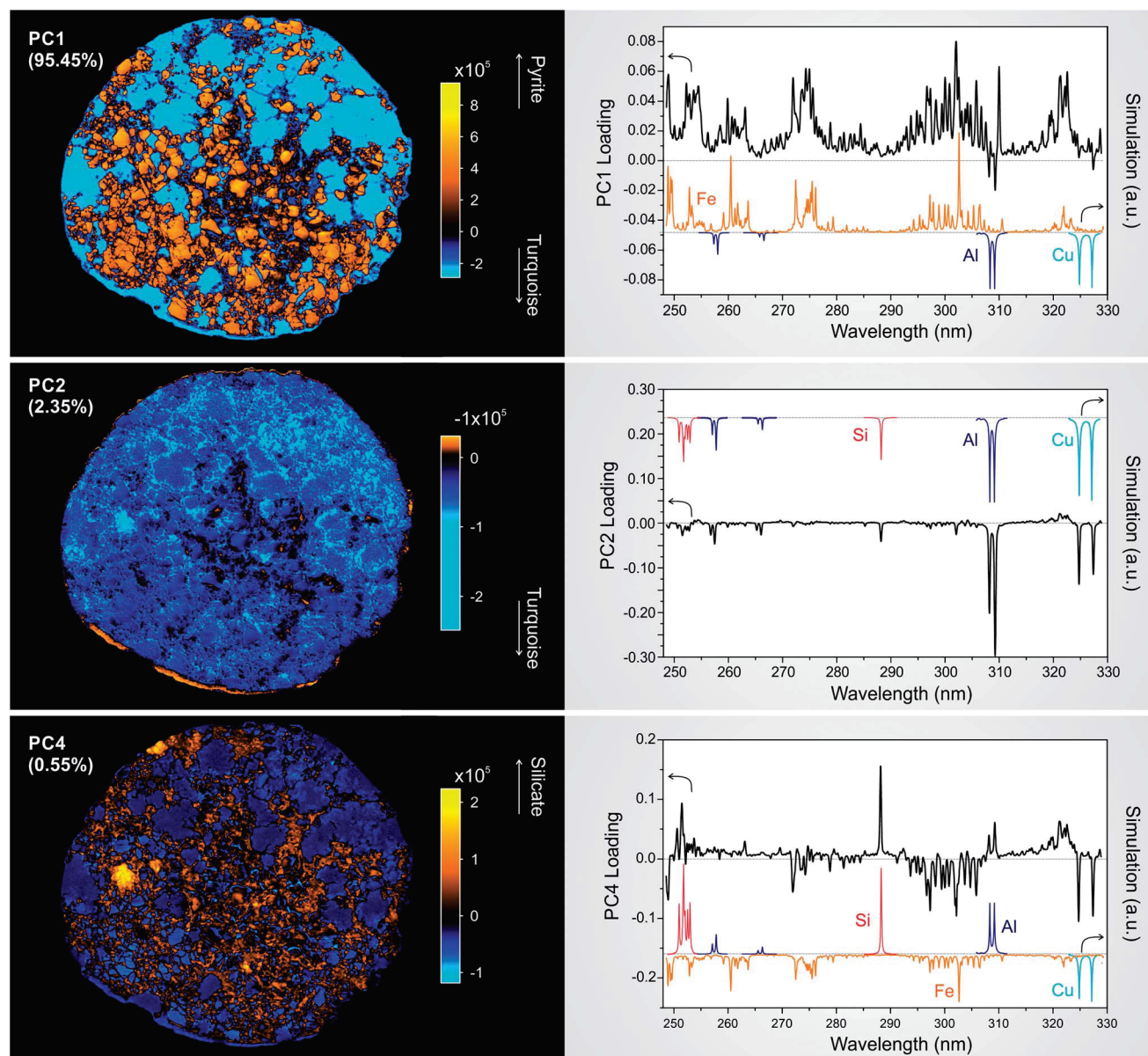


Fig. 3 Score images calculated for PCs 1, 2 and 4. The score values are represented in a false color scale, revealing three mineral phases: from PC1, turquoise (blue) and pyrite (orange) and from PC4, silicate (orange). The corresponding loadings associated with each component are shown on the right of the figure, and the simulated LIBS spectra of Fe, Al, Cu and Si are displayed to aid in the interpretation of the loadings.

Examining the corresponding loading vector, it can be clearly seen that the positive contributions in the first PC correspond with the LIBS spectrum of iron, whereas the negative ones seem to be associated with Al and Cu emission lines. Simulated LIBS spectra related to Fe, Al, and Cu are also shown in the graph of loadings (vertically shifted with arbitrary unit) to facilitate interpretation. Thus, the score image of PC1 displays the spatial distribution of the pyrite (orange) and turquoise (blue) phases. The second PC (PC2), which represents 2.35% of the total variance, shows in negative the presence of Al, Cu and Si, with a small contribution of Fe. These results may be related to both the turquoise and silicate phases. The interpretation of the positive contribution is more difficult because it is weak and not easily related to any spectral structure. In light of the score image,

positive scores appear to be related to edge effects, probably because of the sample preparation and holes in the surface of the sample. The fourth PC (PC4), representing only 0.55% of the total variance, is clearly associated with Si and Al, as supported by the simulated spectrum allowing the identification of the silicate phase. A perfect match can be observed when comparing the phases obtained by PCA with the optical image (Fig. 2a).

3.2.2 Experimental diagnostic. In addition to compositional information, PCA provides details on the experimental issues affecting the LIBS imaging measurement. For example, some matrix effects are illustrated in the score image of the third PC (PC3) displayed in the top panel of Fig. 4. Indeed, the corresponding loading vector (black trace) displayed on the right side of the figure indicates the presence of ionic and

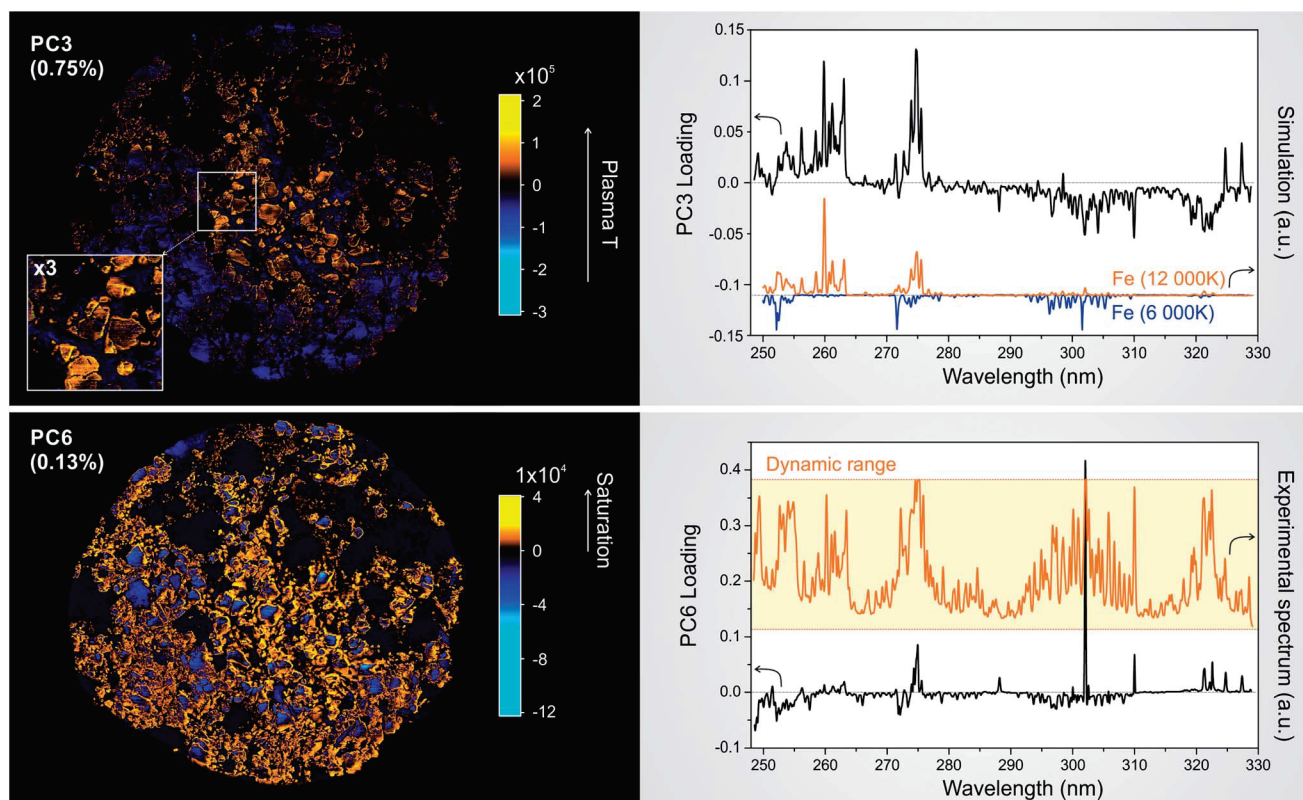


Fig. 4 Score images calculated from the LIBS hyperspectral data cube for PCs 3 and 6. The score values are represented in a false color scale to reveal various instrumental distortions. The corresponding loading associated with each component is shown in the right. Simulated LIBS spectra of iron are shown in the top figure for 2 different plasma temperatures. An experimental single-shot spectrum is shown in the bottom figure to illustrate the saturation effect and dynamic range of the measurement.

atomic lines of Fe with positive and negative values, respectively. This can be highlighted by the spectral simulation of the iron at two different temperatures: at low temperature (*i.e.*, 6000 K), only atomic lines are observed, whereas at high temperature (*i.e.*, 12 000 K), the main contribution of Fe emission results in ionic lines. Therefore, the score image of PC3 shows the balance between atomic and ionic lines of iron, revealing different physical conditions of laser-matter interaction that induce different plasma temperatures and electronic densities. These differences may be due to local variations in the hardness of the sample that result in variations of the LIBS spectra, which may be considered matrix effects. Here, this PC only expresses 0.75% of the total variance; *i.e.*, this aspect has little implication with respect to the original data. The bottom panel of Fig. 4 shows the score image of the sixth PC (PC6). This component represents only 0.13% of the total variance and can be related to a saturation effect. Positive lines in the loading of PC6 are associated with saturated lines. Together with the loading vector (black trace), a typical experimental spectrum affected by saturation (gold trace) is also shown with its dynamic range superimposed. The interpretation of this PC is risky, considering the elemental composition of the sample; however, this component provides a clear warning of when saturated signals could generate artefacts in the scores image, with neither physical nor chemical meaning.

3.2.3 Detection of low concentration compounds. The last type of information accessible by PCA concerns the identification of low-concentration compounds that are present in a very small number of pixels that somehow present an “unusual” structure compared to those with the highest percentage of variance. Finding a few isolated pixels associated with one or several elements is definitely not an easy task, considering the size of the spectral hypercube. With PCA, some pixels linked to a compound of interest can be highlighted in principal components with a low percentage of variance. Fig. 5 shows the score images and the loading vector of the seventh and eighth PCs (PC7 and PC8), which only represents 0.07% and 0.05% of the total variance, respectively. These results show two typical cases of elemental identification of isolated pixels. The results for PC7 clearly indicate the variation in the composition of the silicate phase compared to PC4 (*cf.* Fig. 3). This principal component emphasizes a correlation between Si and Cu and an anti-correlation between Si and Al. Moreover, magnesium (Mg), which was not observed previously, is also found in the loading vector. The loading vector for PC8 is related with the presence of titanium and is clearly distinguishable in the positive contribution. The associated scores image hence shows the distribution of Ti (orange) within the sample. In spite of the high number of Ti lines present in the investigated spectral range, no Ti lines were identified either in the raw data or from the

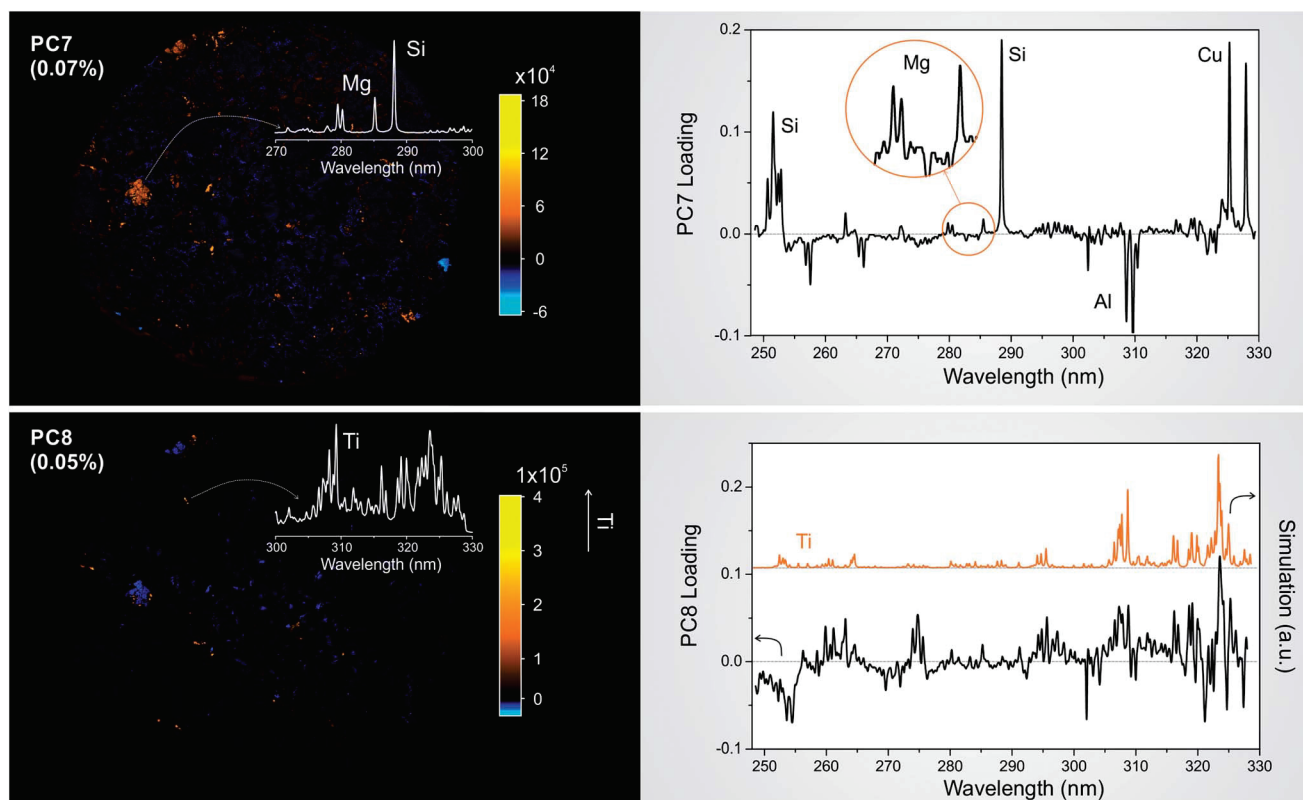


Fig. 5 Score images for PCs 7 and 8. The score values are represented in a false color scale. The corresponding loading associated with each component is shown on the right. The simulated LIBS spectrum of Ti is shown in the bottom figure.

average spectrum. The hyperspectral analysis of LIBS dataset by PCA allows trace elements such as titanium or magnesium to be detected. Although observed in principal components with very low explained variance, these elements can be identified mainly *via* the good signal-to-noise ratio of the data set.

Finally, although only the first ten principal components were modeled, after eight components, no more meaningful information was observed (*cf.* ESI†).

3.3 Advanced data manipulation

The reduction of dimensionality by PCA opens other possibilities in the data processing of such a large dataset involving both PCA and conventional extraction. Instead of plotting the scores as images (only one score is considered at a time), it is also possible to represent them in scatter plots, one score *vs.* another (*i.e.*, conventional PCA representation). Using basic software tools, it is then possible to select different clouds of points and observe their corresponding spatial distribution. In this way, all pixels (*i.e.*, spectra) associated with each phase of the sample can be retrieved and then represented in a mask form. A mask image is a logical matrix of 0s and 1s, denoting unselected and selected pixels, respectively. In Fig. 6a, an example of a scatter plot illustrating PC1 *versus* PC4 scores shows that there seem to be certain groupings in the data. These two components were chosen with regard to Fig. 3 because they appear to be the most discriminative with regard to the sample composition. This type

of representation allows the similarities and differences among samples to be assessed in terms of the raw data. Fig. 6b shows mask images associated with the three main phases; pyrite, turquoise, and silicate in red, blue, and green, respectively. Another region, named “intermediate”, can be obtained from points between groups in the score plot. These points (in yellow) correspond to pixels separating different phases, with a composition being a mixture of them. This region is represented by the mask in yellow color and is not considered in the following. Using all spectra associated with each cloud of points, it is straightforward to estimate the average spectrum of each phase, as shown in Fig. 6c. Then, the conventional data extraction can be applied to generate the classical elemental images for each of the 3 phases independently.

As an example of the results, Fig. 7 shows the spatial distribution of iron in the 3 mineral phases. A different color scale was chosen to represent the variation of Fe in each phase independently; grayscale for pyrite, cyan hot for turquoise and red hot for silicate phase. Fig. 7 was generated by merging all of the images. This type of representation displays a wide dynamic range of Fe concentration (several orders of magnitude) from the pyrite phase, where Fe is a major element, to the turquoise and silicates phases, where trace or minor amounts of Fe are contained. This representation is likely affected by matrix effects; hence, it is questionable to compare the Fe concentration between phases because it is not possible to join the scale from one phase to another. In addition, the heterogeneous

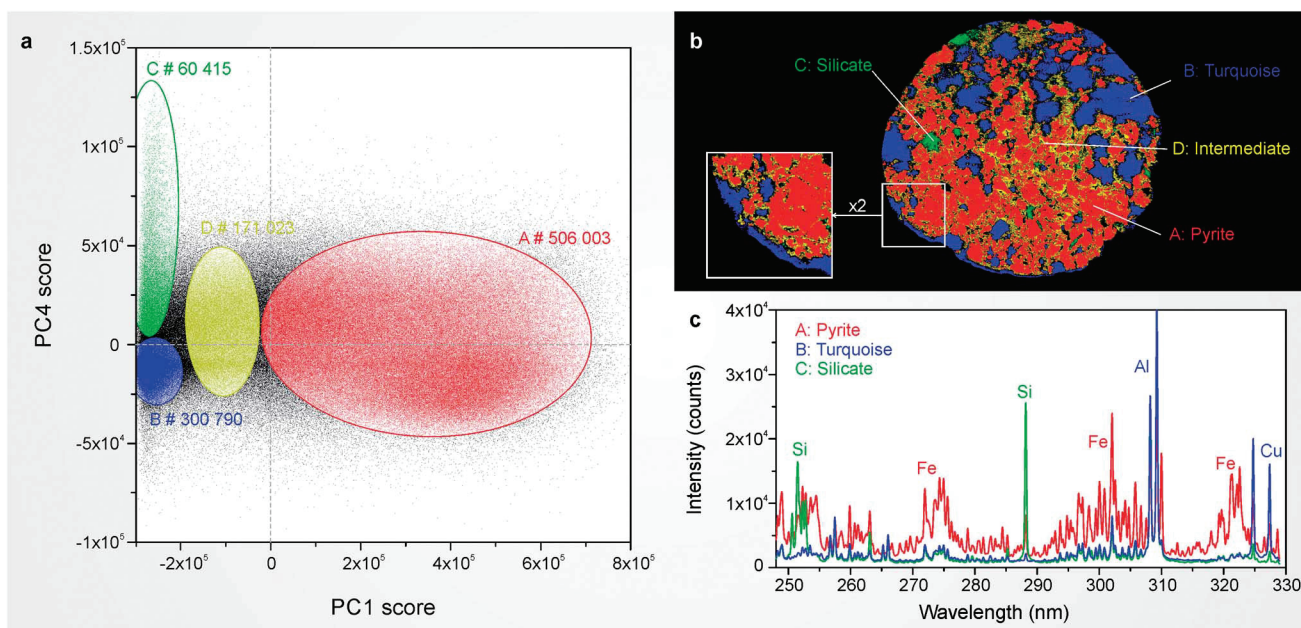


Fig. 6 Example of advanced data manipulation. (a) Scatter plot of PC4 versus PC1 scores with 4 different clouds. For each selected cloud, the number of corresponding spectra is indicated. (b) Mask images associated with the 4 selected clouds. (c) Average spectra for (A) red mask – pyrite, (B) blue mask – turquoise and (C) green mask – silicate.

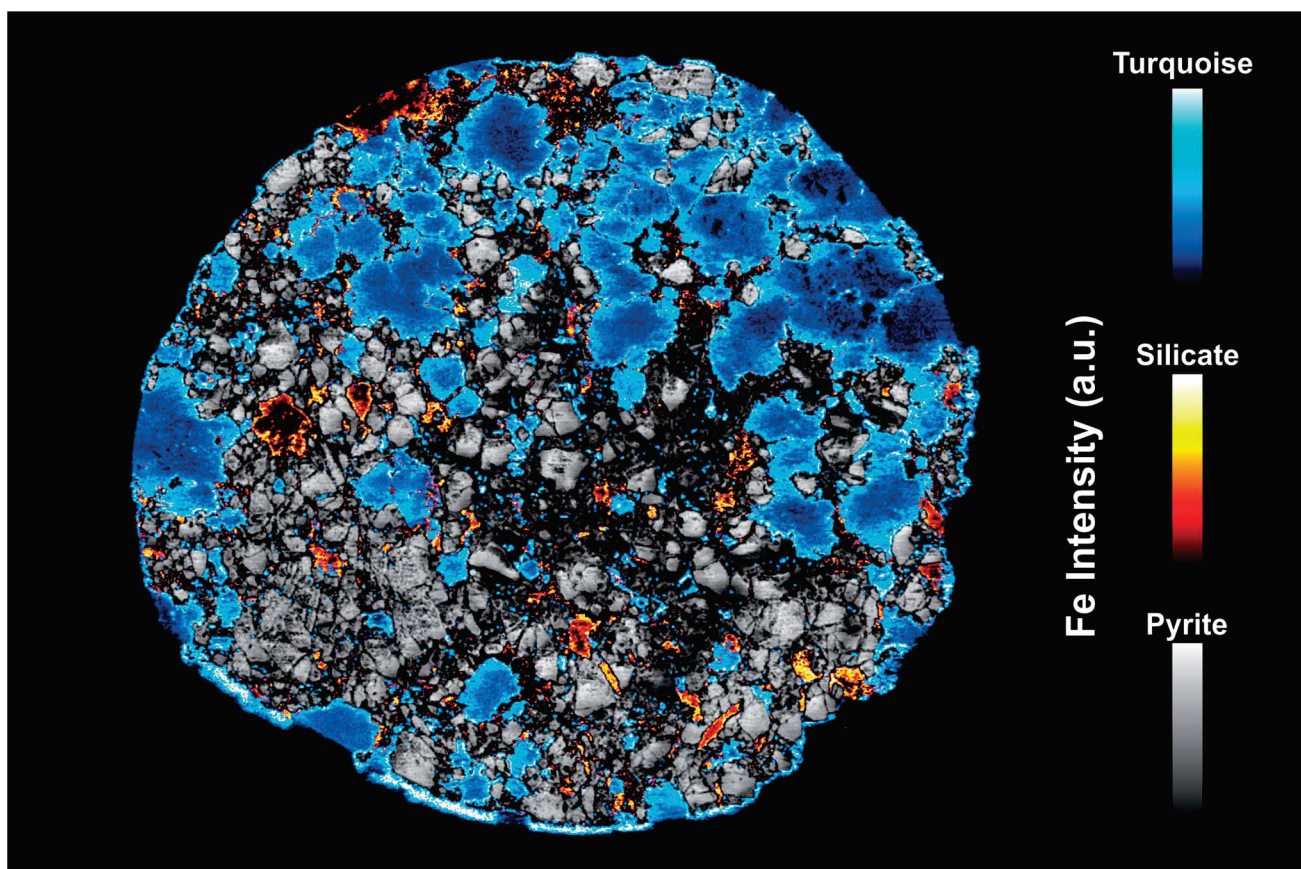


Fig. 7 LIBS image of iron (259.939 nm) obtained by merging three images related to the three mineral phases, namely, turquoise, silicate and pyrite. A specific color scale is used for each phase.

distribution of Fe within the turquoise is noticeable. This effect is produced during the crystallization of the turquoise, where the Fe coming from the pyrite is substituted for Al or Cu, thereby modifying its properties. From the mineralogical point of view, Fig. 7 is able to display the replacement between Fe^{2+} and Fe^{3+} from the pyrite phases to produce a solid solution with Al^{3+} and Cu^{2+} , respectively. The images obtained by LIBS are in accordance with mineralogical studies, highlighting the very slight substitution of Al^{3+} by Fe^{3+} in the turquoise structure $\text{Cu}^{2+}(\text{Al}, \text{Fe}^{3+})_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$. A complete substitution would have reached the chalcociderite end-member.

3.4 Discussion

As mentioned above, analyzing a megapixel LIBS dataset is not an easy task and requires the development of specific tools. It is impossible to observe and analyze each individual spectrum of such a large dataset. In such a case, and considering, for example, 30 seconds of analysis per spectrum, the analyst would require approximately 1 year to process a dataset of 1 megapixels in size. This slow data processing is obviously not acceptable when the experiment is able to provide several megapixel series a day. Although the conventional method of data extraction can be rather efficient in simple sample cases, it is clearly not well adapted for “real world” samples. This paper demonstrates that the use of PCA is highly desirable in such cases. The results presented show that PCA analysis can provide an exhaustive characterization of such large datasets, without prior knowledge of the sample. This characterization includes the determination of the mineral phases (*i.e.*, matrices) in terms of both the spatial distribution and the composition, the assessment of the experiment (such as matrix and saturation effects) and the identification of minor compounds in isolated pixels. In addition, PCA represents an efficient methodology to reduce data dimensionality, which greatly facilitates the manipulation (*e.g.*, processing, observation) of such hyperspectral data. Once the PCA calculation is complete, the observation and analysis of PCA data are rather fast and efficient. Note that spectroscopic expertise is still required to interpret the PCA results. However, instead of considering row datasets (and a huge number of spectra), the analyst's job consists only of interpreting few loadings.

In addition, the processing of such a large amount of data in PCA only requires a high computing power combined with, in particular, a large amount of Random Access Memory (RAM) (*i.e.*, ~256 GB). This computing power is actually necessary when the calculation must be conducted on the entire megapixel-scale dataset. However, several tricks can be applied to reduce the requirement of computing power: binning the wavelengths, reducing the spectral range, and/or processing only a certain percentage of spectra (and then building up the PCA model for all pixels). In such a manner, we were able to process the same dataset (data not presented here) with an office computer (*i.e.*, ~32 GB RAM). We obtained very similar results and conclusions. In addition, no prior knowledge of the sample was required. Overall, these results appear highly attractive for LIBS-based imaging and open new perspectives for the development of this technology.

4. Conclusion

The main objective of this work was to evaluate PCA processing for the analysis of a megapixel LIBS dataset. As a proof of concept, we examined the potential of multivariate data analysis applied to the study of minerals. PCA has been demonstrated to be a powerful tool that is capable of identifying mineral phases by finding relationships between variables, manifesting experimental issues and detecting low concentration compounds, and PCA has many possible applications. The interpretation of principal component images enables a deeper understanding of the sample, highlighting very delicate ion substitution in a mineral lattice. This paper critically examined the basic concepts of the possible use of PCA in extracting information from megapixel-scale LIBS imaging. Based on the results provided by the present study, we are convinced that multivariate methods applied to megapixel LIBS images may be applied to any type of sample.

Conflicts of interest

There are no conflicts to declare.

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