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Physical and chemical properties of some italian opals

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Abstract

The physical and compositional properties of some opals from different parts of Italy have been investigated through several methodologies like optical analysis, specific gravity, refractive indices, XRPD, IR spectroscopy, LA-ICP-MS. The opals show different colors: white, brownish-white, yellowish-white, yellow-/greenish white and grey. Black and metallic inclusions, consisting of todorokite, are sometimes present. Play-of-color have not been observed but some opals show small iridescence zones; opals are inert to the long and short wavelength UV radiation (366 - 254 nm) with the exception of one sample; also phosphorescence is absent. Refractive index and specific gravity values are respectively 1.43 to 1.44 and 2.07 to 2.33 g/cm³ consistent with data available in the literature. XRPD analyses highlighted Italian opals are A, CT and C types, but most of them can be classified as opals-CT. IR spectroscopy data confirmed the opal classification. The most abundant impurities are Mg (between 400 and 900 ppm), Fe (35-400 ppm), Ca (72-96 ppm) and Ni (20-65 ppm). Similarly to what observed in other opals worldwide, Fe appears to be the principal factor that determines the brown to red to orange to yellow colors. Chromophore elements like V, Cr, Cu, Ti, Co are present in very low concentrations and probably do not influence the physical properties of the Italian opals analyzed. Ni is present in more relevant amounts and is probably related to clay minerals. Mn is clearly detected only in two samples and is related to the presence of dendrites. The investigated Italian opals show a rather homogeneous trace element composition which is in the range of worldwide opal's composition, except for their noticeable amount in Ni.

Key words: Italian opals, hyalite, IR spectroscopy, trace elements, XRPD.

Introduction

Although Italian opals feature gemological qualities lower than those from foreign countries,

some specimens are highly prized by gemologists and collectors. In Italy, opals can be found at several sites; the most frequent variety is the common (without any play-of-color) opal, which is an opaque variety colored by iron oxides and hydroxides or by jasper, chalcedony, clay and other minerals (Jerwis, 1873; Hintze, 1915; Fenoglio and Sanero 1943; Mariani and Scaini, 1978). Even if accurate investigations on their modes of formation are lacking, Italian opals are generally considered of hydrothermal origin (see also Ghiara et al., 1999; Cerri et al., 2001; Altaner et al., 2003). Other opal varieties present in Italy are the following (Jerwis, 1873; Hintze, 1915; Fenoglio and Sanero, 1943; Mariani and Scaini, 1978): hydrophane (opaque and very porous variety of opal that becomes translucent or transparent when wet), hyalite (opal with a glassy and clear appearance and a globular surface, that sometimes shows internal play of colors and natural inclusions; it is usually found in volcanic rocks), geyserite (opaline silica usually occurring around hot springs and geysers; botryoidal geyserite is known as fiorite, from Santa Fiora-Amiata Mt. in Tuscany), xyloid opal (also known as wood opal, opalized wood) and diatomite (sedimentary rock almost entirely made up of silica remains of diatoms). Unlike specimens from countries such as Australia, Mexico, Brazil, Peru, Ethiopia, the physical and chemical characteristics of Italian opals have been poorly investigated. These properties can be related to the body color or the luminescence of the opal, and also to the process of formation and the area of provenance. As described in Gaillou et al. (2008), the identification of the chemical and physical properties of opals from a particular geographic area is important for several reasons. For instance, in the gem market, stones coming from specific localities can be more valuable than others. In addition, in the archaeometrical investigation, knowledge of the geographic origin is crucial to reconstruct the ancient trade routes of gem (Giuliani et al., 2000; Gaillou et al., 2008). In this work the physical, mineralogical and chemical properties of opals from different areas of Italy have been investigated through several methodologies, such as optical analysis, specific gravity measurement, refractive indices, X-ray powder diffraction (XRPD), infrared spectroscopy (IR), and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-

MS). The data obtained are discussed and also compared with those of opals from different typologies and from other parts of the world.

Provenance of the investigated samples

Twelve samples of opals from different Italian sites have been analyzed, mostly from the Piedmont region, but also from Sardinia and Emilia Romagna. In particular, the opals investigated in this work come from the following localities:

1) Baldissero Canavese in the Province of Turin, region of Piedmont. The samples were gifted by the "AMI", (Associazione Micro-Mineralogica Italiana).

2) Mount Calvo at Caselette, in the Province of Turin, region of Piedmont. The samples were gifted by the "Museo Don Bosco" of Turin.

3) Mount Maniglia near Bellino, Province of Cuneo, region of Piedmont. The samples were gifted by the "Museo Don Bosco" of Turin.

4) Case Montanini, at Sant'Andrea Bagni (Medesano), Province of Parma, region of Emilia-Romagna. The sample belonged to the personal collection of the first author.

5) Silius in the Province of Cagliari in Sardinia. The sample was offered by the "Museo Don Bosco" of Turin. A comlete list of samples with their properties can be found in Table 1.

Baldissero (Samples 1 to 7). The samples examined come from the town of Baldissero, located in the subalpine area of Canavese; in this area, white, yellowish- and brownish-red opals, sometimes with dendrites of pyrolusite, are found (Hintze, 1915). Also other kinds of opals, with a body color from blue to bluish-grey- and several arborescent inclusions of todorokite, were found in Bettolino, Baldissero and other localities of Canavese (Mariani and Scaini,



Scale: — = 1 cm



Figure 1. Baldissero Samples: a) Sample 4, opal-CT with a white color. b) Sample 6, ; opal- CT with a yellowish-white color and dendrites.

1978). In particular, opals with inclusions of todorokite, such as those investigated in this work, are highly prized by collectors (Figure 1a, b).

Caselette (Samples 8 and 9).

The samples examined originate from the town of Caselette in the Susa Valley; fine specimens of opals are frequently found here, usually in magnesite deposits (Jerwis, 1873; Fenoglio and Sanero, 1943). In particular, opal is still quite abundant, sometimes with samples of appreciable value, in the mine of Mount Calvo in Casellette. The transparency of these opals varies from transparent to semi-opaque and the color from white to brown. Besides Mount Calvo, in the Susa Valley opals have been also found in Val della Torre, in Givoletto and Bussoleno near Cava Tignai (Jerwis, 1873; Fenoglio and Sanero, 1943).

Bellino in Varaita Valley (Sample 10).

The small town of Bellino, in the province of Cuneo in Piedmont, is located in Varaita Valley; opals are present, in particular in the manganese deposits on the Mount Maniglia, located at high altitude (ca 3000 m; Jerwis, 1873).

Case Montanini (Sample 11).

This locality is near Sant'Andrea Bagni (Medesano) in the Province of Parma. Near Case Montanini and in nearby Faieto, there are some quarries with interesting samples of opals: they generally occur as light blue in small veins or quite big spherules and semi-spheres, having a white to intense light blue color, displaying a sericeous (perly) luster and a moderate iridescence (Adorni et al., 2004).

Silius (Sample 12). The analyzed sample is a hyalite from a mine of barite and fluorite located near the village of Silius, in the province of Cagliari in Sardinia. This mine is one of the few still active in Italy. Opals from this site are colorless to milky hyalite with a botryoidal surface and, in some cases, also a considerable thickness. It usually occurs as coatings or incrustations but also nodules, especially in igneous rocks (Figure 2).

Materials and methods

The specimens were examined by standard gemological methods to determine their optical properties, hydrostatic specific gravity (SG), ultra-violet fluorescence (UV) and microscopic features.

Specific gravity and refractive index (RI) measures of opal samples have been carried out



Scale: _____ = 1 cm

Figure 2. Sample 12 from Silius; colorless hyalite opal.

using a Presidium PCS100 Sensible Balance and a Kruss Rifractometer ER6040 equipment, respectively. Detection limits were 1.30 < n < 1.80.

X-Ray Powder diffraction data (XRPD) on samples of opals and the matrix that included them, have been collected with a Philips PW1800 Powder Diffractometer, with CuKa radiation ($\lambda = 1.5418$ Å) and a scan speed of 1°/min, in the range between 2-65° 20.

Mid-infrared spectra (4000-400 cm⁻¹) have been recorded in transmission mode using a Nicolet Nexus FTIR spectrometer, equipped with a 4x beam condenser collector, accumulating 200 scans at a resolution of 4 cm⁻¹. We operated by means of KBr compressed pellets, after a pretreatment of 150 °C and fluxing the sample compartment with gaseous nitrogen.

LA-ICP-MS microanalyses were performed with a double-focusing sector - field ICP-SFMS model Element I, ThermoFinnigan Mat at IGG-CNR of Pavia. Quantification was performed using SiO2 (stoichiometric value) as internal standard and NIST SRM 610 synthetic glass as external standard. Precision and accuracy were estimated by the analysis of a BCR-2 standard (accuracy: 2 sigma), for concentration at ppm level. Opal fragments were mounted on epoxy resin and polished before analyses. Detection limits for each element can be found in Miller et al. (2012).

Gemological properties

The appearance and gemological properties of the investigated Italian opals are reported in Table 1. The opals span a range from colorless, white, brownish-white, yellowish-white, yellowish to greenish white to gravish; four samples are cut in cabochon, and were chosen based on the different kind of color shade; no sample shows a uniform coloration. Luster is described as Vitreous (V) or Greasy (G) and the degree of transparency is defined as translucent (TL) or opaque (O). Investigated opals appear vitreous or greasy, while most of them are generally translucent and only two samples (samples 3 and 5 from Baldissero) are opaque. No samples are perfectly transparent. Samples 1, 2, 3 and 6 (from Baldissero) show the presence of black to dark brown branched and opaque dendrites. Dendrites in opals 2 and 3 are in lower quantity. All samples are common opals, that is, none of them display a play-of-color; only four opals from Baldissero exhibit small iridescence zones (see Table 1). All the samples are inert to long and short wavelength UV radiation (366 - 254 nm respectively), with the exception of the sample of hyalite from Sardinia (n. 12) that shows a typical bright yellowish-green fluorescence that might be attributed to small amounts of uranium, present as uranyl UO₂ (Fritsch et al., 2002; Olmi et al., 2002; Gamboni et al., 1997; 2004; Gaillou et al., 2012). Phosphorescence was never observed. Microscopic observations (observed with a magnification up to 40x) in transmitted and reflected light highlighted the presence of milky microbubbles, gas microfractures, zones, dendrites and iron oxides.

Specific gravities and refractive indices

The average values of measured specific gravity and refractive indices of samples 1, 2, 9

Sample	Origin	Description	Color	Transparence	Luster	Optical effects	Туре
1	Baldissero	rough/cabochon	Yellowish-white with dendrites	TL	V	iridescence	CT (close to tridymite)
2	Baldissero	rough/cabochon	greyish	TL	G	iridescence	CT
3	Baldissero	rough	Yellowish- to greenish- white	0	G	-	СТ
4	Baldissero	rough	white	TL	V	-	CT
5	Baldissero	rough	brownish white	0	G	-	CT
6	Baldissero	rough with dendrites	yellowish white	TL	V	iridescence	CT
7	Baldissero	rough	greyish	TL	V	iridescence	pure C
8	Caselette	rough	yellowish white	TL	V	-	CT
9	Caselette	rough/cabochon	brownish white	TL	G	-	CT
10	Bellino	rough	yellowish white	TL	G	-	А
11	Case Montanini	rough/cabochon	white	TL	V		СТ
12	Silius	rough	colorless	TL	V	-	А

Table 1. Gemological properties of the studied samples.

TL = translucent, O = opaque, V = Vitreous, G = Greasy.

and 11 are reported in Table 2. The specific gravity of opals might be influenced by many factors such as the presence of microcracks, porosity or water content. For this reason, the gravity values have been evaluated only on the most appropriate samples that appeared compact, homogeneous with no presence of empty or recrystallised fractures. In general, the values of specific gravity of the four investigated samples are rather high but in the range of data in literature (2.0-2.25; Klein, 2004). Sample 1 shows higher values most likely due to the presence of dendrites. Similarly, refractive

Table 2. Physical and optical characteristics of the studied gems.

Sample	Cut	Weight	Specific gravity	Refractive index
1	cabochon	0.076 g	2.33 g/cm ³	1.442
2	cabochon	0.752 g	2.07 g/cm3	1.440
9	cabochon	0.096 g	2.07 g/cm3	1.430
11	cabochon	0.078 g	2.07 g/cm ³	1.430

indexes are comparable with the literature data (around 1.39-1.48; O'Donaghue, 2006; Caucia et al., 2009; Simoni et al., 2010).

X-Ray Powder Diffraction (XRPD) on opals

XRPD investigations allow distinguishing the opals into three general groups (Jones and Segnit, 1971; Ghisoli et al., 2010): opal-C (relatively well ordered α -cristobalite), opal-CT (disordered α -cristobalite with α -tridymite-type stacking) and opal-A (amorphous). In the XRPD patterns of the investigated opals, the crystalline part, made up by only cristobalite or by a mixture of cristobalite and tridymite, is generally mixed with the typical amorphous component of the opal (Figure 3 A, B C). The cristobalite versus tridymite ratio was calculated by comparing the position of the characteristic peak in the interval d = 4.04-4.11 Å, whose extremes correspond respectively to the values of pure cristobalite and pure tridymite. In particular, opal-CT shows a peak corresponding to a d value ranging from 4.06 to 4.11 Å, while

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opal C is characterized by a peak between 4.02 and 4.05 Å and by the presence of two other peaks at 3.13 and 2.84 Å (Fritsch et al., 2004: Ghisoli et al., 2010). For the evaluation of the ratio, we used the following equation (Ghisoli et al., 2010):

$$C/T_{XRPD} = \frac{d_{Trid} - d_{measured}}{d_{Trid} - d_{Crist}} = \frac{4.11 \text{ Å} - x}{4.11 \text{ Å} - 4.04 \text{ Å}}$$

XRPD analyses showed that samples 10 and 12 are fully amorphous; sample 1 is a CT type close to pure tridymite (C < 10 % T > 90 %) while sample 7 is a "pure" C type as is almost completely made up by well crystallized α cristobalite. Opals 8, 9 (from Caselette), 2, 3, 4, 5, 6 (from Baldissero) and 11 (Case Montanini) belong to the CT type with a crystalline portion variably composed by C = 43% T = 57%(samples 2 and 9), C = 14% T = 86% (samples 3 and 4), C = 28 % T = 72 % (samples 5 and 8), and C = 71 % T = 29 % (sample 6). In Figure 1 A, B and C, some typical XRD patterns of opals-CT, -A and -C s investigated in this work are reported. In general, opals-C and -CT are of volcanic origin, opals-C being rarer than opals-CT (Jones and Segnit, 1971; Ostrooumov et al., 1999; Fritsch et al., 2004; Simoni et al., 2010). Our results are also consistent with the findings by Elzea and Rice (1996) that opal-C and opal-CT are part of a continuum of disordered intergrowths between end-members cristobalite and tridymite stacking sequences.

X-ray Powder Diffraction (XRPD) on matrix

We analysed two samples of matrix from Caselette, one from Baldissero and one from Case Montanini. Unfortunately, since the material that was possible to collect was very few, these analyses cannot provide complete indication about the mineralogical composition of the host rocks. Anyway they can be very useful to determine the provenance of some trace elements in the opals.

The matrix of opals from Caselette is mostly made up by abundant cristobalite, tridymite and smectite, with few corrensite.

The matrix of one opal from Baldissero is mostly made up by tridymite, lower cristobalite, some todorokite and clay minerals like chlorite/smectite mixed layers. The presence of clay minerals indicate the source rocks underwent extensive alteration, probably due to weathering or hydrothermal processes, that might also be related to the formation of opals.

The matrix of the samples from Case Montanini is mostly made up by Mg Calcite with lower amount of feldspar, chlorite, muscovite, quartz and dolomite.

IR Spectroscopy

We have analyzed through IR spectroscopy the samples n. 1, 3, 9 and 12 (Figure 4A, B, C, D) and the results have been compared with the XRPD data; the combination of these analyses can provide useful information about the composition of the opals. By XRPD, the opals 1, 3, 9 and 12 have been identified as follows : sample n. 1 trydimitic opal-CT (C < 10 %, T > 90 %); samples n. 3 and 9 opal-CT, sample n. 12 A-opal (Table 1).

The samples investigated in this work are characterized by an absorption band in the range $3435 - 3467 \text{ cm}^{-1}$ due to the OH stretching vibration of water molecules as well as the water bending vibration at ~ 1638 cm⁻¹. We also observe three other strong bands at ~ 1105 cm⁻¹, 790 cm⁻¹ and 475 cm⁻¹ that are common to all silicates with tetrahedrally coordinated silicon and are generally assigned to the stretching vibration of Si-O.

In particular, the 1100 and 790 cm-1 bands are generally assigned, respectively, to antisymmetric and symmetric Si-O-Si stretching, whereas the 470 cm⁻¹ band is related to O-Si-O bending vibration (Jones and Segnit, 1971; Farmer, 1974;



Figure 3. XRPD patterns of the investigated opals. A) sample n. 7 (from Baldissero), opal-C; B) sample n. 9 (from Caselette), opal-CT; C) sample n. 12 (from Silius), opal-A. Fritsch et al., 2004; Brajkovic et al., 2007; Caucia et al., 2008; Adamo et al., 2010).

In general C-opals show the absorption bands of well-ordered α -cristobalite, consisting of a peak at about 620 cm⁻¹ and a shoulder at 1198-1200 cm⁻¹ on the 1100 cm⁻¹ absorption band. These absorption bands, in particular the 620 cm⁻¹ sharp peak, are always absent in the FTIR spectra of opal-CT and A, and are therefore diagnostic markers for opal-C (Jones and Segnit, 1971; Farmer, 1974; Caucia et al., 2009; Adamo et al., 2010). Since these bands are not present, our samples can't be classified as C opals.

In general, the band at 790 cm⁻¹ shows the highest value in opal-A (796-801 cm⁻¹), the lowest in opal-CT (788-792 cm⁻¹), whereas opal-C has intermediate value (793-794 cm⁻¹; Adamo et al., 2010). The samples n. 1 (Figure 4A), 3 (Figure 4B) and 9 (Figure 4C) show a band at about 789⁻¹ and can therefore be considered as CT-opals while the sample n. 12 (Figure 4D) shows the band at 801⁻¹, which is typical of A-opal.

In conclusion, IR spectroscopy highlighted that the opals 1, 3, 9 (from Piedmont) can be identified as CT-opals, while the opal n. 12 (from Silius) is an A-opal. The tridymitic opal CT (sample n. 1) cannot be distinguished from the other opals CT. IR spectroscopy analyses therefore confirm the XRPD results.

Laser Ablation ICP-MS Analysis

The opal samples 1, 6, 8, 9 and 12 have been

analyzed through LA-ICP-MS microanalyses for the determination of impurities and trace elements composition, with particular attention to the chromophore elements (Table 3).

It is known that the chemical composition of opals is mostly linked to that of host rocks and influences opal properties like color and luminescence (McOrist and Smallwood, 1997; Gaillou et al., 2008; Caucia et al., 2009; Simoni et al., 2010). The body color is usually related to inclusions of colored minerals while the abundances of some elements determine the color of the opal (McOrist and Smallwood, 1997; Fritsch et al., 2004; Gaillou et al., 2008, and references therein). To the best of our knowledge, analyses on the chemical composition of trace elements in the Italian opals have never been conducted before. Therefore, in this work, the relationships between the color and chemical composition of some Italian opals have been investigated for the first time. The main detected impurities resulted to be Mg (400-900 ppm), Fe (35-420 ppm) and, subordinately, Ca (72-111 ppm) and Ni (20-65 ppm). Mn was clearly detected (about 40 ppm) in the samples 1 and 6 while is absent in the others. Sc and Cr have been detected in all the samples, but in very low amount (4-6 ppm and 4-11 ppm respectively). Ba was detected, in low amount, only in the samples 1 and 6 while is absent in the others. Elements like Ti, V, Co, Pb, Zn, are present only occasionally and in low amounts. REE, U, Rb, Y, Zr, Nb, Cs, Hf, Au, Pb, Sn, Th, As, Ag resulted

Table 3. Trace elements abundances (ppm) for the opals analysed in this work. Columns in bold include chromophore elements.

Samples	Mg	Fe	Ca	Ni	Cr	Sc	Ba	Ti	V	Co	Pb	Zn	Mn	Cu	Li
1	900	250	111	56	7	6	5	2	1	1	10	6	42	3	-
6	880	268	72	52	6	6	4	1	1	1	8	6	43	3	1
8	760	400	96	65	10	5	-	5	2	-	8	2	-	15	-
9	700	421	75	51	10	6	-	5	2	-	-	1	1	28	-
12	400	35	92	20	4	4	-	-	-	-	-	-	-	-	-



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below the detection limits.

Samples 1 and 6 from Baldissero are distinguished by the highest Mg content (around 900 ppm), the appreciable amount of Mn (around 40 ppm) and some Pb, Ba and Zn. Samples 8 and 9 from Caselette differ from the others for the highest Fe content (400 and 421 ppm). Sample 12, which is a hyalite opal from Silius (opal A with botroydal aspect), is characterized by the lowest Mg content (400 ppm), Ni (20 ppm) and especially Fe (35 ppm). In general, we observe that typical chromophore elements like V, Cr, Cu, Ti, Co (columns in grey) are low in all the investigated opals and their presence does not seem related to the color of the gem. Ni is more abundant and can be responsible for the yellowish green color, but no UV -visible absorption spectrum has been acquired to confirm this hypothesis. Conversely, Fe contents are likely related with the color of the opals: the brownish color of sample 9 is due to the highest content of Fe while the lower quantities in opals 1, 6 and 8 determine the yellow tint. Sample 12, which features the lowest Fe content, is the only colorless opal. A clear correlation between Fe content with the color of the gem was also observed in the opals from Bemia in Madagascar (Table 4) (Simoni et al., 2010), from Brazil (Caucia et al., 2009) (Table 5) and other occurrences as well (Gaillou et al., 2008). Fe in opals probably occurs as inclusions of Fe

oxyhydroxides that determine the yellow or orange color (Fritsch et al., 2002, Gaillou et al., 2008). Mn has been detected only in samples 1 and 6 and is due to the presence of dendrites of todorokite: as a matter of fact this mineral has been also detected by XRD investigation on the matrix. Ca and Mg are non-chromophore elements, and are present in relevant amounts; Mg probably derives from the matrix, which is largely formed by Mg rich minerals like smectite, smectite/chlorite mixed laver and corrensite (see also Jerwis 1873; Fenoglio and Sanero 1943). Also, we observe that the Italian opals investigated in this work are characterized by very low amounts of Ba, that are around 5 % or also below the detection limits. According with Gaillou et al. (2008), Ba concentration allow to differentiate sedimentary opals from volcanic ones, as the first feature Ba contents > 120 ppm, while the volcanic opals show lower contents. This is because Ba in the sedimentary opals generally derives from the dissolution, through several weathering cycles, of the detrital feldspars occurring in sedimentary rocks, that is subsequently dissolved into the water from which the opals form. Conversely, feldspars in a volcanic environment are subjected to only one cycle of weathering and, therefore, the Ba content in water is much lower (Fagel et al., 1999; Davidson et al., 2005; Gaillou et al., 2008). The very low Ba values of Italian opals support a

Samples color	Mg	Fe <>	Ca <>	Ni	Cr ⇔	Sc ⊲>	Ti ⇔	V ⇔	Co	Pb <>	Zn	Mn	Cu	Li ⇔
yellowish white	1122	137	1238	1	1	3	54	1	1	1	1	2	1	1
yellow	891	1888	370	5	4	5	62	4	1	1	7	13	2	1
orange	17730	12070	1314	3	6	3	12	2	0.5	6	87	10	2	1

Table 4. Trace elements abundances (ppm) for opals from Bemia, Madagascar (from Simoni et al., 2010).

> = Average value

Samples color	Mg	Fe <>	Ni	Cr	Sc ⇔	Ti ⇔	V ⇔	Co	Mn	Cu	Ba
sky blue	10	3	0.5	0.5	4	2	1	1	0.5	9	4
gold yellow	49	132	1	1	4	16	0.5	-	0.5	13	-
brick red	60	1164	1	1.5	7	86	0.5	0.3	7	29	15

Table 5. Trace elements abundances (ppm) for opals from Piauì, Brazil (from Caucia et al., 2009).

<> = Average value

volcanic origin; this is also demonstrated if we plot our results in the Ca-Ba diagram from Gaillou et al. (2008), that reports the different compositional fields of opals in the world.

It can be interesting to compare the trace element composition of the opals analyzed in this work with that of blue and fire opals from Piauí in Brazil (Caucia et al., 2009; Table 5); fire opals from Bemia in Madagascar (Simoni et al., 2010; Table 4) and other occurrences worldwide (Gaillou et al., 2008), to evaluate differences and similarities.

The most surprising result in our samples is represented by the relatively high content of Ni, as this element is generally present in much lower amount in the opals worldwide (frequently less than one ppm; Gaillou et al., 2008). Large quantities of Ni have been detected only in the green opals from Tanzania and in those from Silesia, where Ni is contained in the structure of pimelite, a Ni rich variety of smectite (Schmetzer et al., 1976; Koivula and Fryer, 1984; Shingley et al., 2009). It is likely that also Ni in our samples is contained in the structure of clay minerals like smectite or mixed layers, that easily incorporate or adsorb transition elements; these mineral have been indeed detected in the samples of matrix from Caselette and Baldissero. Even if the number of analysed samples is quite low, Ni abundance might be therefore used as marker to characterize the Italian opals (especially from Piedmont).

According to Gaillou et al. (2008), Ca is the only element in opals that varies significantly with the geographic origin of the samples and can therefore be useful to determine the provenance. Ca contents in Italian opals are quite low but in the range of the opals worldwide and show a homogeneous composition. Ca contents can be compared with that of opals from Mexico and Honduras (Gaillou et al., 2008) but are lower, or much lower, of that of opals from other regions where this element show concentration of some thousands ppm (for instance, Madagascar; Table 4; see also Gaillou et al., 2008). Concerning Mg and Fe, these elements in opals worldwide can show a large variability, between few units to some thousands ppm, but cannot be related to some specific areas (see Gaillou et al., 2008; Tables 4 and 5). Mg and Fe contents in Italian opals are in the range of opals worldwide and show a homogeneous composition. For instance, we observe that Mg contents in Italian opals are higher than in the opals from Brazil but lower than those from Madagascar (see Tables 4 and 5). Also, Fe in Italian opals is higher than in the sky blue opals, and much lower than the brick red opals from Brazil or the yellow and orange from Madagascar. Lastly, opals from the mentioned foreign localities exhibit a variability larger than that observed in the Italian samples, which appears more limited. Even if the number of samples analyzed in this work is rather limited, it appears that the trace element composition of Italian opals is rather homogeneous, especially in the case of samples of common opal from Piedmont. Sample n. 12, which is the hyalite opal

from Sardinia, partly differs from the others for the even lower content in trace elements.

Conclusions

Italian opals do not have the relevant gemological properties, such as the play-ofcolor, typical of some opals from other countries. However, some samples of Italian opal are aesthetically valuable for their qualities such as iridescence, the presence of metallic inclusions of todorokite and their color variability. As a result, and also for their rarity, Italian opals appear to be well appreciated by collectors. Italian opals analyzed in this work show different colors and variable degrees of luster and transparency; black and metallic inclusions, consisting of todorokite, are often observed. No play-of-colors have been observed, but some opals show the presence of iridescent zones; play-of-colors, as well as iridescence, are appreciated optic qualities in the gem market. Several samples show a typical opalescence and the fracture is usually conchoidal. The values of specific gravity and refractive index of four cut opals are comparable with the range of data in literature. XRPD and IR spectroscopy analyses highlighted Italian opals can be classified as A, CT and C types, but most of them are opals-CT. This composition supports a volcanic origin. The analyses on the matrix of opals from Piedmont also highlighted the occurrence of cristobalite, tridymite, todorokite, clay minerals like smectite, corrensite and chlorite/smectite mixed layers. The presence of clay minerals indicates the source rocks underwent extensive alteration, probably due to weathering or hydrothermal processes; these processes might also be related to the formation of opals.

Impurities and trace element contents in the opals can be, at least partially, related to the color and composition of the matrix of the opal. The most abundant impurities are Mg, Fe, Ca and Ni. Ca and Mg (non chromophore elements) are probably inherited from the matrix; in particular Mg can derive from clay minerals. Ba shows very low content and this would support a volcanic origin of the opals. Chromophore elements like V, Cr, Cu, Ti, Co are present in very low contents and do not seem to influence the physical properties of the Italian opals analyzed. Ni is present in noticeable amounts, might lead to a yellowish-green color of a sample, but does not seem responsible for the coloration of the others: it probably derives from clay minerals. Mn is clearly detected only in two samples and is related to the presence of dendrites of todorokite. As also observed in several opals from other parts of the world, Fe appears to be the main factor that determines the red to brown component. Although the number of analysis performed in this work is limited, it seems that the Italian opals show a rather homogeneous trace element composition which is in the range of composition for opals from other locality, except for their unusual Ni content. Ni could therefore be a useful geochemical tracer to separate Italian opals from opals from other localities.

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