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Gemological, physical and chemical properties of prase opals from Hanety Hill (Tanzania)

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ABSTRACT

Chemical, physical and gemological properties of some green “prase” opals from Hanety Hill in Central Tanzania were investigated. The color of the opals ranges from clear green to apple green, diaphaneity from translucent to semitransparent, luster is vitreous, and all result inert to UV lamp radiations. Specific gravity values are between 2.11-2.13, refractive indices between 1.439 and 1.458. XRD and FTIR analyses show the opals belong to the CT type, with prevailing tridymite. SEM observations revealed a mammillary structure formed by spherules with a diameter around 10-12 μm , on their turn composed of silica microspheres. The opals show a homogeneous chemical composition with very high contents of Ni and lower of Mg, Ca, Fe and transition elements like Zn, Cr and Co. Al and K are nearly absent. The chemical composition of the opals reflects that of serpentine rocks. Because of its abundance, the chromophore element responsible for the green color is Ni. Prase opals may have formed through the process of low temperature metamorphism, which generated the serpentinite from a magmatic ultrafemic rock.

Keywords: Opal; Tanzania; XRPD; SEM; trace elements; spectroscopic analyses.

INTRODUCTION

Opals usually form through precipitation from silica-rich solutions, generally inside cavities or fractures, in both volcanic and sedimentary environments. With passing of time the fluid in the cavities dries or filters out and, consequently, the deposition of the opal occurs. Under favorable conditions, opals can develop a texture formed by an aggregate of close-packed spheres that show the typical diffraction colors. In the sedimentary environment, silica-rich solutions are formed during the process of weathering of silicic rocks, such as rhyolite and sandstone; typical examples of sedimentary opals are those from Australia (Smallwood et al., 2008). Conversely, in the volcanic setting the silica-rich fluids usually form during the last hydrothermal stages of the cooling of magma; when the system is open, the fluids can also alter the surrounding lithologies and this would lead to an enrichment of different trace elements. Volcanic opals deposited at a temperature higher than that of sedimentary opals. Typical opals considered of volcanic origin are those from Mexico,

California, Indonesia, Honduras, Japan, Faroe, some parts of Australia (Fritsch et al., 1999; 2004; Brajkovic et al., 2007; Caucia et al., 2008; 2009; 2012 a,b; 2013 a,b; Gailloeu et al., 2008 a,b; Smallwood et al., 2008).

This article describes the chemical, physical, and gemological properties of some green “prase” opals from Hanety Hill, north of Dodoma, Central Tanzania. This typology of opal was found in 1962 and outcrops into a strongly weathered serpentinite together with chrysoprase, thus being easily confused with it (Koivula and Fryer, 1984; Kinnunen and Malisa, 1990; Shingley et al., 2009; Graetsch, 2011). Both chrysoprase and prase opal from Tanzania have a beautiful green color that is due to inclusions of nickel-bearing minerals and are well appreciated in the markets; their quality ranges from low-opaque material to high-quality translucent jewels, but the prase opal tends to be more translucent and gemmy. The majority of the production from this deposit is concerned with chrysoprase, while the prase opal is rarer. As well as in Tanzania, nickel colored green opals and chrysoprases

have been collected also from other parts of the world like Australia, Peru and Poland (Schmetzer, 1976; Koivula and Fryer, 1984; Hatipoğlu and Yardımcı, 2014). The term “prase opal” was used for the first time by Johann Georg Ludwig Meinecke (1805) to indicate the minerals with bright green color, caused by the presence of nickel. In literature some studies on the chrysoprases from Tanzania can be found, but few investigations have been conducted on prase opals (Koivula and Fryer, 1984; Shingley et al., 2009) that are instead the subject of this paper. In particular, new data on trace elements obtained through LA-ICP-MS analyses are discussed that are meaningful as very few have been conducted on these prase opals before.

GEOLOGICAL SETTING OF THE MINING AREA AND GENERAL FEATURES OF CHRYSOPRASE AND PRASE OPALS

Information about the mine and surrounding geological setting are reported in the papers of Kinnunen and Malisa (1990) and Shingley et al. (2009). The mine is located near the top of a hill of the Iyobo Mountains, at an elevation of 1,452 m, not far from the villages of Haneti and Itiso. The Iyobo Mountains are aligned in a northwesterly direction, following the orientation of a regional fracture/shear zone. The rocks that host chrysoprase and opals are mainly ultramafic, silicified and ferruginized serpentinite of Archean Age, belonging to the Dodoma Formation. The lithologies are cut by numerous veins of magnesite and asbestos (gedrite). Although similar in color and appearance, the chrysoprase and the common prase opal can be distinguished by the refractive index, which for the first is of about 1.55, while for the second is around 1.45, and the specific gravity: 2.6 to chrysoprase, 2.11 for the common opal (Shingley et al., 2009). The real nature of the nickel compounds that provides the green color to the mineral is still subject of debate; some studies consider the nickel occurs in the form of oxides (gaspeite), other instead as silicates (kerolite, willeimite) or within the structure of clay minerals like garnierite, lizardite, saponite (Heflik et al., 1989; Rossmann, 1994; Nagase et al., 1997; Sachambinski et al., 2001; Sojka et al., 2004; Shingley et al., 2009). According with Graetsch (2011), the green color in the chrysoprase from Tanzania is caused by the incorporation of gaspeite in the structure of microcrystalline quartz. In some cases also small amounts of Fe^{3+} can be present and modify the color into more yellowish. The light scattering deriving from microdefects and small particles can turn the color into a more bluish green, when observed in reflected light (Sachambinski et al., 2001). Both the minerals are found in discontinuous veins up to several centimeters thick and several meters long in the weathered host rock. The quality of opals is variable, from high-quality translucent to low-opaque. The best samples of chrysoprase occur in veins surrounded by red clay or soil, while poorer-quality material

is found where the vein is enclosed by yellowish material. The best-quality prase opal is found in veins within very brittle host rock. Chemical analyses by Kinnunen and Malisa (1990) revealed the chrysoprase have high Ni contents (0.50 wt%), low Co and Cr (120 and 1 ppm respectively) and REE contents close to chondritic values, suggesting that an enrichment from serpentinites took place during the process of weathering. X-ray diffraction analyses highlighted the chrysoprase are made up by alpha quartz with some CT opal. Microscope observation showed the chrysoprases are made up by disordered and concentric spherules with diameter ranging from 40 to 77 μm , composed of bipyramidal quartz, chalcedony, quartzine and opal, while the spherules of prase opals are an order of magnitude smaller (around 6 μm). Fluid inclusions in the quartz are monophasic, of low-temperature type. These features would indicate the chrysoprase formed through evaporation of surface waters connected with the silification of the serpentinites, due to the intense weathering (Kinnunen and Malisa, 1990).

MATERIALS AND METHODS

Three gemstones from rough samples were fashioned as cabochon of various shapes and one as emerald cut (Figure 1 and Figure 2). The opals derive from the personal collection of the first Author and Mr. Carlo Cerutti.

The gems were examined by standard gemological methods to determine their optical properties, hydrostatic SG, UV fluorescence (366-254 nm) and microscopic features. Specific gravity and refractive index measures have been carried out using a Presidium PCS100 Sensible Balance and a Kruss Refractometer ER6040 equipment, respectively. Detection limits of the refractive index were $1.30 < n < 1.80$.

Powder X-ray diffraction data (XRPD) have been collected with a Philips PW1800 powder diffractometer, with $\text{CuK}\alpha$ radiation ($\lambda=1.5418 \text{ \AA}$) and a scan speed of $1^\circ/\text{min}$, in the range between $2-65^\circ 2\theta$. XRPD investigations allow distinguishing the opals into three general groups (Jones and Segnit, 1971; Fritsch et al., 2004; 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). The cristobalite vs. tridymite ratio was calculated by comparing the position of the characteristic peak in the interval $d=4.04-4.11 \text{ \AA}$, where 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 \AA , while opal C is characterised by a peak between 4.02 and 4.05 \AA and by the presence of two other peaks at 3.13 and 2.84 \AA (Fritsch et al., 2004; Ghisoli et al., 2010).

For the evaluation of the ratio cristobalite vs. tridymite the following equation was used (Ghisoli et al., 2010):

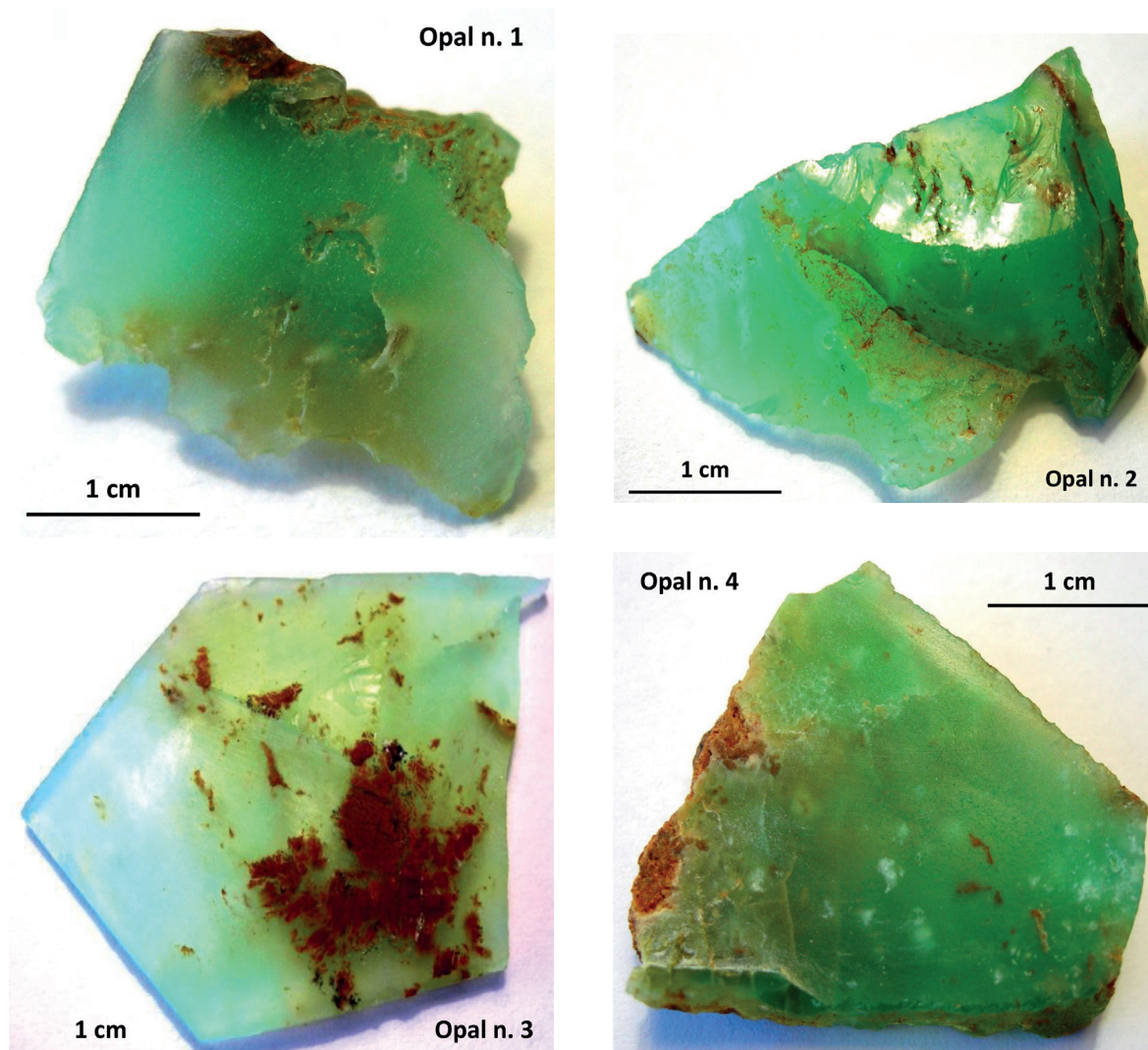


Figure 1. Pictures of the raw samples of the opals analysed in this work (n.1, 2, 3 e 4).

$$C/\text{TXRPD} = \frac{d_{\text{Trid}} - d_{\text{measured}}}{d_{\text{Trid}} - d_{\text{Crist}}} = \frac{4.11 \text{ \AA} - x}{4.11 \text{ \AA} - 4.04 \text{ \AA}}$$

Mid-infrared spectra (FT-IT; 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 pre-treatment of 150 $^{\circ}\text{C}$ and fluxing the sample compartment with gaseous nitrogen.

Laser Ablation - Inductively Coupled Plasma - Mass Spectrometry (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 SiO_2 (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 and resulted better than 5 and 10%, respectively, for concentration at ppm level. Opal fragments were mounted on epoxy resin and polished before analyses. The investigations have been conducted on 4 samples, analyzing three different spots on each sample and using a spot size of 40 μm ; the data presented for each sample are an average of the analyses on all spots. The detection limits for each element are reported in Miller et al. (2012).

The samples were analyzed through the AvaSpec-2048 spectrometer, a CCD (Charge Coupled Device) based



Figure 2. Pictures of the faceted gemstones (n. 1 oval cabochon, ct 3.49; n. 2 pear cabochon, ct 3.93; n. 3 emerald cut, ct 1.63; n. 4 oval cabochon, ct 12.30).

instrument able to acquire electromagnetic waves spectra with wavelengths from 400 to 1000 nm i.e. visible and near infrared. The instrumentation to acquire spectra from gems also include a halogen light source, an integrating sphere placed above a sample holder and fiber-optic conductors cables. All the studied samples were not cooled before being subjected to the light beam and the measurements were therefore conducted at room temperature (Leone et al., 2015).

Textural observations of opal samples were carried out with Evo 40 (Zeiss) type scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (Oxford Energy), using an electron-beam energy of 40 electronvolts and a focal spot of about 5 nm. The samples were mounted on carbon adhesive tabs and were carbon coated (Agar Carbon Coater) before analyses.

GEMOLOGICAL PROPERTIES

The appearance and gemological properties of the investigated Tanzanian prase opals are reported in Table 1. The opals show a color that ranges from clear green to apple green, diaphaneity varies from very translucent to semitransparent and luster is vitreous. All showed conchoidal fracture and resulted inert to UV lamp radiation. The specific gravity values are between 2.11-2.13 and refractive indices between 1.439 and 1.458. The most evident macroscopic features are botroidal blackish agglomerates and whitish masses, containing brown matrix bodies. The light microscopy observations revealed the presence of several diagnostic features like microfractures, cloudy color distributions, veinlets, whitish dots and, in the sample pear cabochon, brownish spots of host rock. In the sample 1 we also found arboreous inclusions.

X-RAY POWDER DIFFRACTION

According with XRPD analyses, the opals analysed in this work belong to the CT type. Cristobalite vs. tridymite ratios vary from 30/70 to 0/100; in three samples also low amounts of quartz have been detected. No amorphous (A) opal was found. A low intensity, and broad, peak between 2 and 10°2θ indicates the presence of low amount of clay minerals. In the sample n. 4 we found the presence of willemseite, a mineral of the group of talc that contains Ni and Mg.

The most significant XRPD patterns are shown in Figure 3 while C/T ratios are presented in Table 2.

FTIR DATA

The infrared spectrum of the investigated sample (opal 1, Figure 4) is characterized by a multicomponent broad absorption band centered at about 3470 cm⁻¹, due to the OH stretching vibration of water molecules, as well as the water bonding vibration at ~1640 cm⁻¹. The other three strong bands at ~1100, 790 and 480 cm⁻¹ are common to all silicates with tetrahedrally coordinated silicon and are related to the fundamental Si-O stretching vibration. In particular, the 1100 and 790 cm⁻¹ bands are generally assigned, respectively, to antisymmetric and symmetric Si-O-Si stretching, whereas the 480 cm⁻¹ band is related to O-Si-O bending vibration (Zarubin, 2001 and references

Table 1. Gemological features of the investigated samples.

Sample n.	Color	Diaphaneity	RI	G	Weight (ct)	Internal features
1	Green	translucent	1.448	2.12	3.49	Arboreous inclusions
2	Apple green	translucent	1.458	2.13	3.93	Brownish spots of host rock
3	Light green	translucent	1.450	2.12	1.63	Microfractures
4	green	translucent	1.439	2.11	12.3	Microfractures

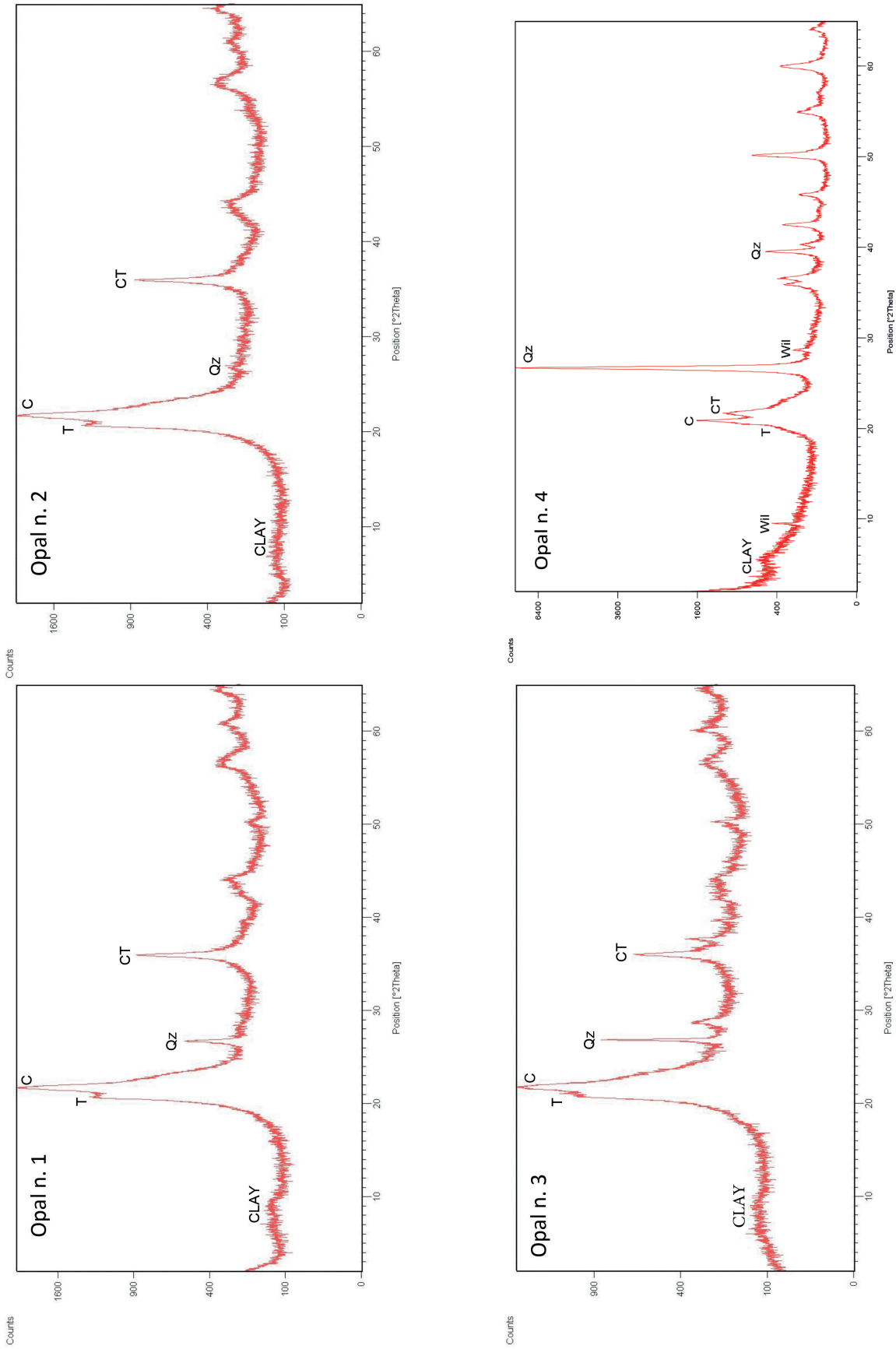


Figure 3. XRPD patterns of the samples.

Table 2. C/T ratio in the Haneti Hill opals evaluated through XRPD.

Samples n.	d (Å)	C/T (%)
1	4,11	0/100
2	4,10	15/85
3	4,09	30/70
4	4,10	15/85

therein; Fritsch et al., 2004; Brajkovic et al., 2007; Caucia et al., 2008; Adamo et al., 2010). The peaks at around $\sim 3700\text{ cm}^{-1}$, and $\sim 690\text{ cm}^{-1}$ indicate the presence of smectite (Farmer, 1974; Van der Marel and Beutelspacher, 1976). The spectra of opals analysed in this work are very similar to that of tridymite (Figure 4). The peak at $\sim 620\text{ cm}^{-1}$, typical of C opals, is not present. The band centered at $\sim 1100\text{ cm}^{-1}$ is wider than the corresponding band in the spectra typical of C opals. In conclusions FTIR data support the XRPD results and show our opals are CT with tridymite higher than cristobalite.

LA-ICP-MS DATA

In each investigated sample (Table 3) the most abundant trace element is Ni (between 3800 and 20300 ppm). All the other elements are present in much lower amounts; their total sum is approximately 1000 ppm, a value relatively low when compared to that of many other opals in the world (Gaillou et al., 2008a; Caucia et al., 2012a; 2013 a,b; 2015).

Other elements in significant quantities are Mg (around 500 ppm), Ca and Zn (around 100 ppm), Cr (around 80 ppm), Co (around 40 ppm), Fe (between 6 and 30 ppm) and Na (around 10 ppm). It is noteworthy that elements such as Al, Na and K which are often present in high amounts in the opals worldwide, appear instead very low or virtually absent in the Tanzanian opals. Al is frequently the most abundant impurity in opals, and substitutes locally for silicon; the imbalance of charge is compensated by the ingress of monovalent or divalent cations such as Na^+ , K^+ , Ba^{2+} , Mg^{2+} , Ca^{2+} (Gaillou et al., 2008a and references therein). In the prase opals from Tanzania Al and K are very scarce or absent; these low values reflect the composition of the serpentine rocks that do not contain these elements. In particular, K and Al in opals usually derive from the alteration of feldspars. The very small presence of Al also suggests that there is a low amount of clay minerals in the body of the opals, as also observed by XRPD analysis. It therefore appears unlikely that the high contents of Ni in Tanzanian opals are mostly contained within clay minerals, and this element is more probably diffused within the body of opal, in the form of oxides.

Also the presence of Mg, Ca, Fe and transition elements like Ni, Zn, Cr, Co in the prase opals reflects the composition of the surrounding serpentine rocks that commonly host these elements. In general in the serpentines, the precursor mineral that contains these elements (in particular Ni) is olivine (Trescases, 1997, and references therein). Our analyses also confirm that chromophore elements in opals from Tanzania are especially represented by Ni and, with minor importance, Fe, Co and Cr.

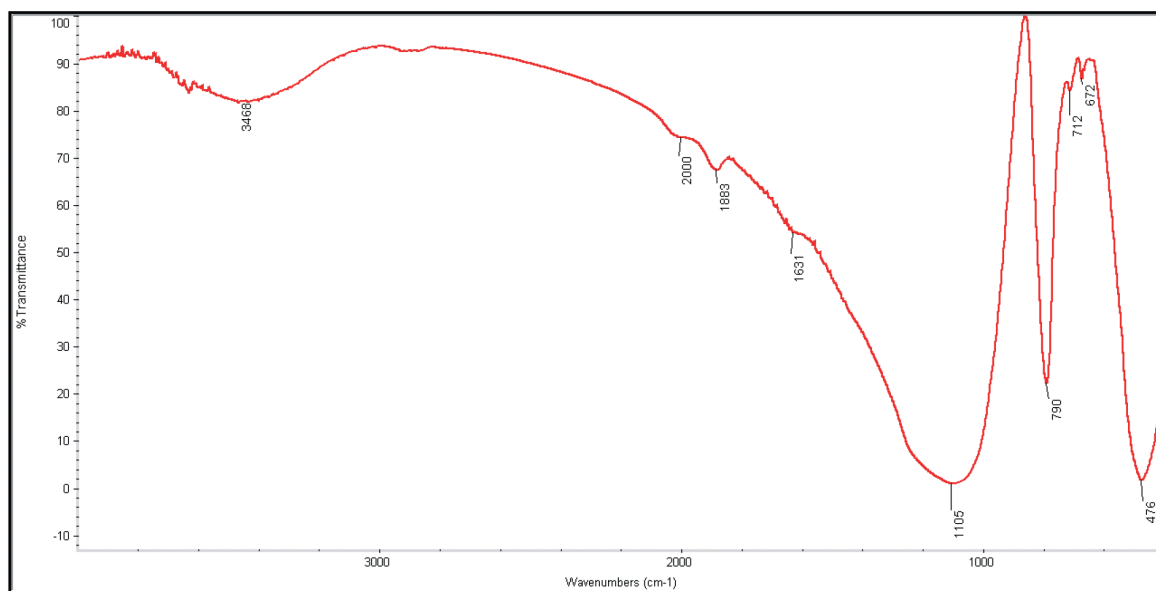


Figure 4. FTIR spectrum of sample n. 1. The assignments of the infrared bands are the following: band at 3468 cm^{-1} : "OH" stretching; bands at 2000, 1883, 1105, 790 and 475 cm^{-1} : "Si-O" stretching vibration; band at 1631 cm^{-1} : "OH" bending of molecular water.

Table 3. Trace element composition of the opals investigated in this work, obtained through LAM analysis. The elements that resulted below the detection limits are not reported; detection limits are reported in Miller et al., 20012.

Element (ppm)	n. 1	n. 2	n. 3	n. 4
Be	3	3	4	4
Na	10	11	6	7
Mg	587	84	551	532
Al	4	1	2	3
P	1	4	8	5
K	7	1	3	3
Ca	125	116	92	99
Sc	4	4	3	4
Ti	2	1	1	1
V	1	1	1	2
Cr	80	9	69	72
Co	44	7	45	45
Ni	20307	3833	18174	19256
Zn	109	21	115	122
Mn	3	1	4	3
Fe	30	10	6	7
Cu	3	1	2	3

Ca in the opals worldwide is the only element that varies significantly with the geographic origin of the samples (Gaillou et al., 2008a). Ca contents in our opals are quite low (around 100 ppm) when compared to opals worldwide and show a homogeneous distribution: Ca contents can therefore be used as marker for these opals, when not contaminated.

AVASPEC RESULTS

Spectrometer analyses have been conducted on all the samples of green opal (Figure 5). The absorption spectra are similar for all the samples and show an absorption band at 650 nm related to octahedral coordinated Ni²⁺ (Sachanbiński et al., 2001). The absorption bands at about 415 and 450 nm in the blue-green region of the spectra are

related to the presence of Fe³⁺ (Sachanbiński et al., 2001). These bands are more evident in the sample n. 1, probably for the presence of iron oxyhydroxides.

The range of the light transmission responsible for the specific color of green opal occurs between the absorption bands at 400 nm and 650 nm. Their absolute and relative intensities determine the hue and saturation of the green color of the samples.

The presence of Fe³⁺ in some of the samples results in yellowish hue of their color and it overlaps the blue-green region of the spectra (400-450nm). Ferric iron may also occur in Ni-bearing clay minerals.

SEM OBSERVATIONS

In general CT opals are made up of spherical aggregates of plate-like crystallites of cristobalite, called lepispheres in a matrix of amorphous silica (Graetsch, 1994; Gaillou et al., 2008b and references therein). The green opals from Tanzania (Figure 6 a,b,c,d) show a mammillary structure formed by spherules with a diameter around 10-12 μm, that are on their turn composed of silica microspheres. The size of the spheres is of the same order of magnitude as those reported in the work of Kinnunen and Malisa (1990). The spherules are much smaller than those reported for the Tanzanian chrysoprase, but are anyway too large to cause any play of color effect (Kinnunen and Malisa, 1990).

DISCUSSION AND CONCLUSION

Our XRPD investigations highlighted the Tanzanian opals are all CT type, as already pointed out by previous research (Kinnunen and Malisa, 1990; Shingley et al., 2009). FTIR Spectroscopy results are in agreement with the XRPD data, as the frequencies of the bands at 1100 cm⁻¹ in sample n. 1 (Figure 4) is compatible with the CT typology (Adamo et al., 2010). The SEM investigations show a mammillary structure; we suggest a series of formation events: at the beginning there was the formation of growth plans and, later, the mammillary structure made up by silica spherules (Figure 6).

The influence of trace elements on opal properties like color and luminescence has been investigated by several authors. In general, the color is related to inclusions of colored minerals and to the abundance of chromophore elements (McOrist and Smallwood, 1997; Fritsch et al., 1999; Gaillou et al., 2008a; Simoni et al., 2010; Caucia et al., 2009; 2012a; 2013 a,b). In the green and blue-green opals from Acari mine in Peru, the most important chromophore element is represented by Cu that occurs in form of submicroscopic inclusions of chrysocolla and plancheite (Koivula and Kammerling, 1991; Fritsch et al., 1999; Brajkovic et al., 2007; Caucia et al., 2015). In the green Peruvian opals from Lily Mine, the color is due to the abundant presence of iron that is contained in the structure

of clay minerals (Ghisoli, 2008). In the green opals from Silesia and Kazakhstan, the chromophore element is Ni (Schmetzer et al., 1976; Sachabinski et al., 2001) while in the green chrysoprase from the Biga-Cankale region from Turkey the color is determined especially by Ni and also Fe and Cr (Hatipoglu and Yardimci, 2014).

The chemical composition of prase opals analysed in this work is somewhat different from the few analyses reported in literature, since in these last analyses, apart from Ni, the most abundant elements resulted to be Co, Zn, Fe (Kinnunen and Malisa, 1990; Shingley et al., 2009).

Tanzanian opals show a homogeneous chemical composition with very high contents of Ni and lower Mg, Ca, Fe and transition elements like Ni, Zn, Cr and Co. Because of its abundance, the chromophore element responsible for the green color appears to be the nickel. By XRPD we found very low amount of willemseite, a mineral that contains Ni and Mg, which was considered a carrier for Ni also in the green opals from Silesia. (Schmetzer et al., 1976). Willemseite is believed to derive from the weathering alteration of ultramafic rocks (Brindley et al., 1977).

In general the brighter color allows differentiating these opals from the green opals of Brazil, Australia and Turkey, which have darker colors due to Cr (Bank et al., 1997; Hatipoğlu and Yardımcı, 2014). A distinctive character of our Tanzanian opals resulted to be the absence of Al and K that are usually abundant in opals worldwide. The chemical composition of Tanzanian opals globally reflects the

general composition of serpentine ultrabasic rocks and their weathering products that are devoid of Al and rich in Mg, Ni and transition elements (Trescases, 1997, and references therein). The carrier for Ni and other elements may be partly represented by clay minerals and willemseite, but we think most of Ni occurs in the body of the opal as oxide. To better understand the pattern of formation of these opals, it would be necessary to conduct a thorough petrographic and field investigation. We think that, as described for the chrysoprase, the origin of Tanzanian prase opals might be sedimentary, related to laterization processes on serpentine bedrocks, a process widely described in literature (Trescases, 1997). Anyway we cannot discount also a low temperature metamorphic (hydrothermal) origin: in this case the silica, together with the serpentine and other minerals like magnesite may be generated through the transformation of peridotitic ultramafic rocks. This last hypothesis would be supported by the CT composition with high tridymite: as a matter of fact, CT opals are found in volcanic hydrothermal environment, while A opals are typical of both sedimentary (the most widespread) or hydrothermal environments (Gaillou et al., 2008a; Ghisoli et al., 2010).

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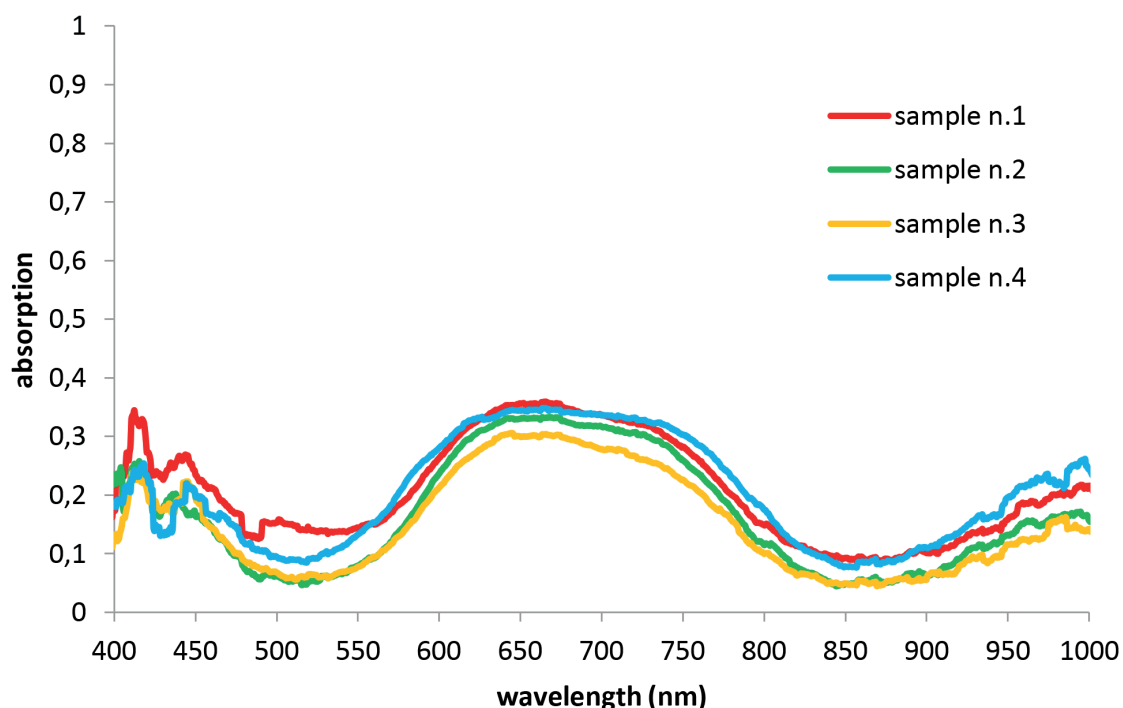


Figure 5. Absorption spectra of green opals.

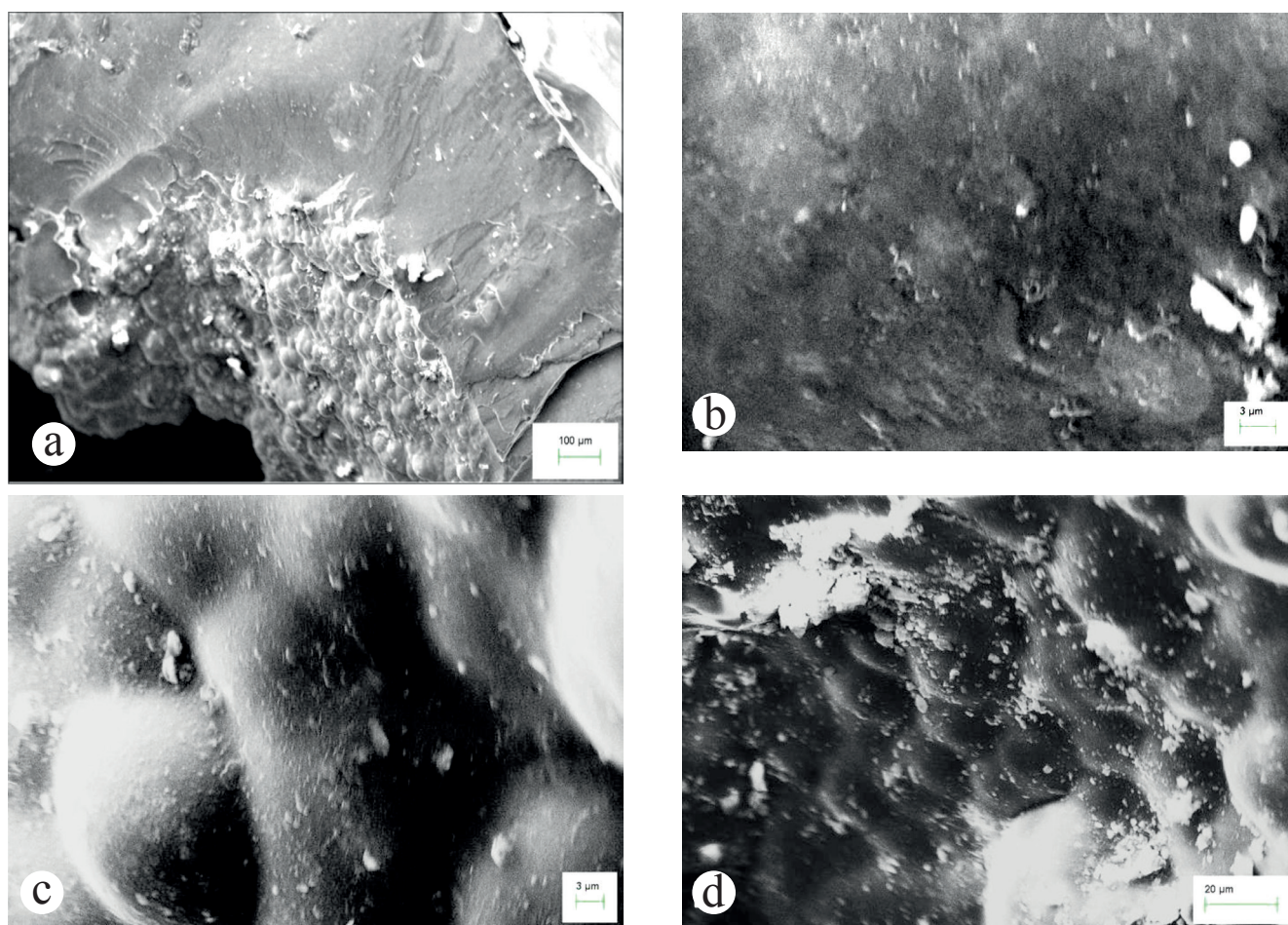


Figure 6. SEM observations on the sample of opal n. 1. a: growth plans with homogeneous structure interspersed with wide zones having a mammillary structure; b: magnification of the previous image (a) in which we observe the silica microspherules forming a dense assemblage c: magnification of the A image showing the mammillary structure formed by spherules around 10-12 μm of diameter; d: magnification of A showing the silica microspheres.

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