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The geochemistry of gem opals as evidence of their origin

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ABSTRACT

Seventy-seven gem opals from ten countries were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) through a dilution process, in order to establish the nature of the impurities. The results are correlated to the mode of formation and physical properties and are instrumental in establishing the geographical origin of a gem opal. The geochemistry of an opal is shown to be dependant mostly on the host rock, at least for examples from Mexico and Brazil, even if modified by weathering processes. In order of decreasing concentration, the main impurities present are Al, Ca, Fe, K, Na, and Mg (more than 500 ppm). Other noticeable elements in lesser amounts are Ba, followed by Zr, Sr, Rb, U, and Pb. For the first time, geochemistry helps to discriminate some varieties of opals. The Ba content, as well as the chondrite-normalized REE pattern, are the keys to separating sedimentary opals (Ba>110 ppm, Eu and Ce anomalies) from volcanic opals (Ba<110 ppm, no Eu or Ce anomaly). The Ca content, and to a lesser extent that of Mg, Al, K and Nb, helps to distinguish gem opals from different volcanic environments. The limited range of concentrations for all elements in precious (play-of-color) compared to common opals, indicates that this variety must have very specific, or more restricted, conditions of formation. We tentatively interpreted the presence of impurities in terms of crystallochemistry, even if opal is a poorly crystallized or amorphous material. The main replacement is the substitution of Si^{4+} by Al^{3+} and Fe^{3+}. The induced charge imbalance is compensated chiefly by Ca^{2+}, Mg^{2+}, Mn^{2+}, Ba^{2+}, K^{+}, and Na^{+}. In terms of origin of color, greater concentrations of iron induce darker colors (from yellow to "chocolate brown"). This element inhibits luminescence for concentrations above 1000 ppm, whereas already a low content in U (≤1 ppm) induces a green luminescence.

1. Introduction

Opal is an amorphous (opal-A) or poorly crystalline (opal-CT) hydrated silica, $SiO_2 \cdot nH_2O$ (Jones and Segnit, 1971). The mode of formation of gem opal has been the subject of much speculation. Surprisingly, only a few detailed geochemical analyses have been conducted, mainly on Australian material (Bartoli et al., 1990; McOrist et al., 1994; McOrist and Smallwood, 1995, 1997). Furthermore, those analyses were performed only on opal-A, and not on opal-CT which are more widely distributed around the world.

The main objective of this study is to understand the mode of formation of gem opals on the basis of their trace element chemistry. Secondly, the gemological objective is to identify the geographic and geologic origin of such gems. Sellers want to know where gems come from as some localities are more valuable than others (for example, fire opal from Mexico is better known, and hence more valued, than any other fire opal in the world), and depending on this, some gems are thus easier to sell. The knowledge of the geographical origin is also useful for archaeometry, to study ancient routes of gem trade (i.e., Giuliani et al., 2000). Finally, we consider the influence of geochemistry on some physical properties such as color or luminescence. With this goal in mind, 77 opals from 10 different countries were characterized (using laser Raman spectroscopy, scanning electron microscopy and luminescence spectroscopy), then analyzed for their trace elements using inductively coupled plasma-mass spectrometry (ICP-MS). The host rocks from Mexico and Brazil were also analyzed (ICP-MS, ICP Atomic Emission Spectrometry) in order to understand the mobilization of elements during opal deposition.

2. Background

Several classifications of opal are useful for our purposes. The first is based on its appearance: precious ("play-of-color" or "noble") opals

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Table 1
Characteristics of opal samples in this study (Abbreviations: Qr, Queretaro; Jal, Jalisco; Nay, Nayarit; C, common opal; P, precious opal; Luminescence: G-Y, greenish yellow; B, blue)

Sample	Country, state, mine	Colour	C/P	Raman	Luminescence
Peru					
620	Acari	Blue	C	CT	G-Y
QOP3	Acari	Pink	C	CT	G-Y
Mexico					
643	Durango, Mapimi	Pink	C	CT	G-Y
267	Durango, Mapimi	White	C	CT	G-Y
267	Durango, Mapimi	White	C	CT	G-Y
799	Qr, Olimpia	"Fire"	P	CT	No
730	Qr, Olimpia	Yellow	C	CT	G-Y
801	Qr, Guacamaya	"Fire"	C	CT	No
767B	Qr, Guacamaya	Red	C	CT	No
768A	Qr, Iris	Milky white	C	CT	No
768B	Qr, Iris	"Fire"	C	CT	No
770	Qr, Carbonera	Red	C	CT	No
771	Qr, Cerro Viejo	Yellow	C	CT	No
626	Qr, Cerro Viejo	Milky white	C	CT	No
627	Qr, Cerro Viejo	Fire	C	CT	No
628	Qr, Cerro Viejo	Red	C	CT	No
798	Qr, La Fe	"Fire"	C	CT	No
747	Qr, La Fe	Milky white	C	CT	G-Y
Jal2S	Jal, Los Laureles	Red	C	CT	No
Jal2D	Jal, Los Laureles	Opaque orange	C	CT	G-Y
800	Jal, Los Laureles	"Fire"	P	CT	No
629A	Jal, Los Laureles	Yellow	C	CT	No
629B	Jal, Los Laureles	Uncoloured	C	CT	No
630	Jal, Los Laureles	Red	C	CT	No
772	Jal, Lupita	Light yellow	C	CT	G-Y
774	Jal, Lupita	Red	P	CT	No
773	Jal, San Martin	Yellow	C	CT	No
769	Jal, San Martin	Brown	C	CT	No
631	Jal, San Martin	Red	C	CT	No
765	Nay, Guadalupa	Cream	C	CT	G-Y
623A	Nay, Guadalupa	Chocolate	C	CT	No
623B	Nay, Guadalupa	Brown	C	CT	No
624	Nay, Guadalupa	Fire	C	CT	No
625	Nay, Guadalupa	White	P	CT	B
Ethiopia					
580		Chocolate	C	CT	No
581		Cream	C	CT	G-Y
726		Uncoloured	C	CT	G-Y
727		Contraluz	P	CT	G-Y
584		White	C	CT	G-Y
617		Chocolate	P	CT	No
618		Yellow	P	CT	G-Y
619		Yellow	C	CT	G-Y
Honduras					
632A		Milky white	C	CT	B
632B		White	C	CT	B
633		White	P	CT	B
634		Light yellow	C	CT	No
635		Uncoloured	C	CT	G-Y
787		White	C	A	G-Y
791		White	C	A	G-Y
Brazil					
621		Yellow green	C	CT	G-Y
622	Rio Grande do Sul	Yellow	C	CT	No
761	Para	Yellow	C	CT	No
762	Para	White	C	CT	G-Y
763	Piaui, PedroII	Milky white	P	A	G-Y
766	Piaui, PedroII	Milky white	P	A	G-Y
Australia					
827	NSW, Lightning Ridge	Grey	P	A	G-Y
234	NSW, Lightning Ridge	Grey	C	A	B
234	NSW, Lightning Ridge	Grey	P	A	B
847	SA, Mintabie	Grey	C	A	B
839	SA, Quilpie	White	P	A	B
832	SA, Coober Pedy	White	P	A	B
835	SA, Coober Pedy	White	P	A	B
844	SA, Andamooka	Cream	C	A	B
818	WA, Norseman	White	C	CT	B

Table 1 (*continued*)

Sample	Country, state, mine	Colour	C/P	Raman	Luminescence
Australia					
387C	NSW Tintenbar	Brown	C	CT	B
387N	NSW, Tintenbar	Brown	P	CT	B
Slovakia					
204.2		Orange	C	A	No
650		Brown	C	CT	No
Kazakhstan					
107		"Fire"	C	CT	No
652		"Fire"	C	CT	No
653		"Fire"	C	CT	No
Tanzania					
793		Yellow	C	CT	No
794		Green	C	CT	No
USA					
795	Oregon, Owyhee	Blue	C	CT	No
796	Oregon, Opal butte	White	C	CT	No
797	Oregon, Opal Butte	"Fire"	C	CT	No

are more valuable than "common" opals, which do not display this optical phenomenon. The play-of-color is due to diffraction of visible light on a perfect network of silica spheres having the adequate diameter, between 150 and 300 nm (see e.g., Sanders, 1964). Common opals can still be very valuable as gems for their transparency and their body color which spans a large spectrum. Another classification is based on X-ray diffraction (Jones and Segnit, 1971), and depends on opal "crystallinity". It distinguished three varieties of opals: opal-A for amorphous, opal-CT for disordered α-cristobalite with α-tridymitic stacking, and opal-C for α-cristobalite (with only a small amount of α-tridymite). Elzea and Rice (1996) postulated that opals-CT and -C form a continuous series. This is why we chose to restrict our notation in this study to opal-A and opal-CT, abandoning the term opal-C. At present, the distinction between these two varieties can be done non-destructively with Raman spectroscopy (Ostrooumov et al., 1999).

Opal forms either in volcanic or sedimentary deposits. It is believed to come from the weathering of silicic rocks (rhyolite or sandstones for example), followed by precipitation from a SiO_2-enriched liquid in cavities (e.g., Des Cloizeaux, 1862; Lacroix, 1896; Koivula et al., 1983; Gübelin, 1986; Payette, 1999; Smallwood, 1999; Horton, 2002). Opal is not a pure form of silica as it contains water as a component, and some impurities and trace elements can also enter its structure. The most common impurity is aluminum, which substitutes for silicon (Bartoli et al., 1990). Australian opals are the best studied (Bayliss and Males, 1965; McOrist et al., 1994; McOrist and Smallwood, 1995, 1997), probably because they represent 95% of world production (e.g., Horton, 2002; Pewkliang et al., 2004). Some other opals have been analyzed semi-quantitatively, e.g., from Opal Butte, Oregon, USA (Holzhey, 1997) and Brazil (Bartoli et al., 1990). From these data, one can establish that "impurities" (i.e., elements present at concentrations above 500 ppm) are Al, Ca, K, Mg, Fe and Na. Elements at concentrations below 500 ppm are named "trace elements". These are mainly Ba, Sr, Rb, Mn, Ti, and sometimes U or Nb (the latter is typical of Somali and Ethiopian opals; Johnson et al., 1996; Kinnaird and Jackson, 2000). In some deposits, the U concentration in opals is high enough (around 100 ppm) to determine ages of alteration, as in the Virgin Valley or Yucca Mountain, Nevada deposits (Zielinski, 1982; Neymark et al., 2000).

The influence of trace element chemistry on the physical properties of opal such as color or luminescence has been partially studied. The body color of opal is usually due to colored mineral inclusions (e.g., Fritsch et al., 1999). Not all opals are fluorescent, and two types of luminescence have been recognized. The first has a green color, is attributed to uranyl groups (Fritsch et al., 2001, 2003) and is believed