



Luminescence of uranium-bearing opals: Origin and use as a pH record



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ABSTRACT

Fluorescence of minerals has been long used for U exploration. It is proposed here that opal fluorescence can be used as a probe of the pH of the formation solution, bringing constraints for modeling U speciation and sequestration at the Earth's surface. We present a study of fluorescence spectroscopy of U in opals resulting from low-temperature (29 °C) alteration of mineralized rhyolitic lavas (Nopal I U deposit, Sierra Peña Blanca, Mexico). These opals show green fluorescence with a concentric distribution at microscopic scale, which is unambiguously assigned to uranyl groups (oxidized form of U). Spectra appear typical of uranyl in opal as reported in literature for other localities according to peak positions. When considering also the lifetime of fluorescence spectra (with time resolved laser fluorescence spectroscopy), fingerprinting indicates that uranyl occurs either as phosphate or hydroxo-polyuclear complexes trapped onto the opal internal surface. Data are indicative of a pH of opal formation around 8, as derived from both conditions of laboratory experiments and reference to calculated diagrams of speciation. This pH value is consistent with the Nopal geological formations that were potentially in contact with the aquifer involved in the hydrothermal process. In addition, the microscopic zoning of U suggests that the speciation has been stable since opal formation more than 50 ka ago, which allows the record of pH that prevailed at that time.

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1. Introduction

During weathering, reduced U occurring in primary minerals as U(IV) may be released and oxidized to U(VI). In its oxidized form, U is present under two speciations: (i) uranyl UO_2^{2+} groups, which form stable ternary complexes with various anions such as carbonate and phosphate (Langmuir, 1978) and organic groups (Maher et al., 2013 and Altmaier and Vercouter, 2012) (ii) uranate groups, which corresponds to a non-fluorescent speciation as in vorlanite CaUO_4 (Othmane et al., 2013). The strong affinity of uranyl groups for silicic acid in aqueous solution (Moll et al., 1998), for quartz surface (Fox et al., 2006 and Ilton et al., 2012) or for amorphous silica (Zielinski, 1980; Michard et al., 1996; Reich et al., 1998; Sylwester et al., 2000 and Zhang and Tao, 2002), has major environmental consequences as it plays a significant role in the retardation processes of U migration under sub-surface conditions. Several studies showed that the U–opal association was stable at the scale of geological time (Neymark and Amelin, 2008; Nemchin et al., 2006; Paces et al., 2004; Amelin and Back, 2006; Ludwig et al., 1980).

The understanding of mechanisms of U trapping requires getting information at the molecular level. Thus, at the interface between water and synthetic silica, extended X-ray absorption fine structure (EXAFS)

data and numerical models show the presence of mononuclear, inner-sphere, bidentate uranyl complexes at pH values lower than 6, as trimeric $[(\text{UO}_2)_3(\text{OH})_5]^{+}$ and additional polymeric species predominate above pH 6 (McKinley et al., 1995; Reich et al., 1998 and Sylwester et al., 2000). In contrast, studies of U-sequestration in natural nano-divided silica are scarce, and Allard et al. (1999) were the first to determine the formation of uranyl inner-sphere complexes on Si-rich gels during the oxidation of U-mine waters in an acid-mine drainage context.

The bright green fluorescence of uraniferous opals is a well-known property of this mineral that has been related to the presence of U (Gorobets et al., 1977; Fritsch et al., 2001). This fluorescence was proposed as a potential tool for U-exploration or environmental issues (De Neufville et al., 1981). The study of uraniferous, fluorescent opals in Virgin Valley, Nevada, provided a model of U mobility in subsurface conditions that may be useful for exploration (Zielinski, 1982). Opal silica was shown to sequester U, which, together with other reactive phases as, e.g., iron oxides or organic matter, may have real consequences for defining remediation strategies (Massey et al., 2014) and more generally for understanding the behavior of U in mining environments (Allard et al., 1999). Recently, Schindler et al. (2010) and Othmane et al. (2013) investigated the mineralogical and geochemical properties of the uraniferous opals formed during a late oxidizing and low-temperature episode of the U mobilization at the Nopal I

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volcanic-hosted U deposit (Sierra Peña Blanca, Mexico) (Schindler et al., 2010; Calas, 1977; Angiboust et al., 2012). Opals formed 54 ka ago (Pickett et al., 2000) from meteoric seepage waters with a formation temperature of 29 °C according to ^{18}O isotope data (Schindler et al., 2010; Calas et al., 2008) and overlie kaolinite, hematite and uranyl minerals (Schindler et al., 2010; Calas et al., 2008; Cesbron et al., 1993). Schindler et al. (2010), showed that Ca and U occur in a constant atomic ratio of 1:1, suggesting the trapping of Ca–U-containing nanophases or complexes by colloidal silica. Uranophane, although frequent at Nopal deposit, is excluded as a major phase, because its Ca/U ratio is 2. This is consistent with the recent evidence of nanophases of vorlanite, CaUO_4 , a rare uranate mineral, within these opals (Othmane et al., 2013). Nevertheless, Nopal I opals exhibit an intense fluorescence, characteristic of the presence of uranyl groups (Calas et al., 2009). The fluorescence spectra are similar to those already reported in the literature for opals from a wide range of origins and formation conditions (see e.g. Fritsch et al., 2001; De Neufville et al., 1981).

Only fluorescent species, even minor, are detected by fluorescence spectroscopy, so this technique can bring some selected constraints on the U-speciation (Wang et al., 2005a, 2005b). By contrast, fluorescent species can always be considered as markers of conditions of formation such as pH, because the existence of a given chemical species is strongly pH-dependent (see e.g. Moulin et al., 1998). The aim of this study is then to determine the nature of the U species responsible for the fluorescence of U-opals and to use this information as a proxy for the pH that prevailed during the incorporation of U in opal. The pH being a parameter that influences the speciation of elements in solution, it can bring constraints on modeling of U mobility in weathering systems. Because a fluorescent species can be precisely defined according to its spectrum but also to the corresponding lifetime, time-resolved laser-induced fluorescence spectroscopy (TRLFS) was used to determine the nature of the fluorescent complexes in Nopal opals. Data were compared to previous data obtained on uranyl speciation in contaminated water and sediments (Prat et al., 2009; Wang et al., 2005a, 2005b) and in synthetic amorphous silica (Ilton et al., 2012; Gabriel et al., 2001; Kowal-Fouchard et al., 2004). We also show that fluorescence arises from uranyl groups occurring as hydroxo-polynuclear or phosphate complexes sorbed onto the internal surface of opal. In addition, two types of spectroscopic data allow one to consistently constrain a pH value of U-bearing opal formation around 8, which is discussed in terms of geochemical significance.

2. Materials and methods

2.1. Samples

Three opal samples have been used in this study. Sample “yellow opal 1” consists of yellow opal and comes from a stock-pile of high-grade ore in the Peña Blanca mountain, west of the Nopal I mine. Two other samples (“yellow opal 2” and “green opal”) were sampled on the Nopal I U deposit. All samples are X-ray amorphous.

2.2. Sorption experiments

Uranyl species sorbed to amorphous silica were prepared for use as TRLFS references. To minimize the presence of ternary uranyl carbonate complexes, the experiments were carried out in a glove box filled with N_2 atmosphere. All solids were exposed to a N_2 -gas stream for 30 min before being placed into the glove box and water used in all parts of the experiments was Milli-Q deionized water (resistivity: $18 \text{ M}\Omega \text{ cm}^{-1}$) degassed by bubbling deoxygenated N_2 . U(VI) , Ca^{2+} and PO_4^{3-} stock solutions with concentrations of 4.10^{-4} mol/L were prepared by dissolving $\text{UO}_2\text{NO}_3 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and KH_2PO_4 in water, respectively. Six solutions were prepared by mixing 400 mL of water and appropriate amounts of NaNO_3 to fix ionic strength at 0.1 mol/L in Nalgene bottles. A weight of 0.1 g of Merck silica gel 60 (0.015–0.040 mm) was mixed

with each solution and pH was adjusted at 6 and 8 by adding negligible volumes of HCl or NaOH solutions. The pH of solutions was readjusted until it was stable (24 h). At this point, appropriate volumes of stock solutions were added to the solutions in order to have two U(VI) , two $\text{U(VI)}\text{--Ca}^{2+}$ and two $\text{U(VI)}\text{--Ca}^{2+}\text{--PO}_4^{3-}$ solutions with concentrations of 2.10^{-6} mol/L at pH 6 or 8. The pH value was immediately readjusted and the mixtures were shaken for 2 days. Then the final pH was measured. The solution and solid were separated by centrifugation (16,000 rpm for 15 min). The solids were then dried at room temperature in the glove box before being analyzed by TRLFS. Sorption samples are referred as “Si-6”, “Si-Ca-6”, “Si-Ca-P-6”, “Si-8”, “Si-Ca-8” and “Si-Ca-P-8”, with respect to pH values and nature of elements other than Si present in solution.

2.3. Cathodoluminescence

One cross-section of the yellow opal from the inner part of the breccia pipe was examined using a Zeiss Supra 55VP SEM at an accelerating voltage of 25 kV. The X-ray signal was detected by an energy-dispersive silicon-drift detector (model PGT Sahara). The cathodoluminescence signal was collected with an aluminum paraboloidal mirror (Blanc-Perray OPEA™ system) and redirected through an optical fiber towards a spectrometer Jobin Yvon Triax 180 equipped with a 2D CCD camera (Jobin Yvon Spectrum One) and a 300 g/mm grating. The spectral analyses were performed with a wavelength ranging from 900 to 200 nm. The calibration of the wavelengths was made using the YAG standard, a Y–Al synthetic garnet. Spectra were smoothed using a fifth-order Savitzky–Golay algorithm.

2.4. Time-resolved laser-induced fluorescence spectroscopy (TRLFS)

The molecular environment of U(VI) in opals from Nopal I, sorption experiment samples and references (andersonite, $\text{Na}_2\text{Ca}(\text{UO}_2)(\text{CO}_3)_3(\text{H}_2\text{O})_6$ and autunite $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2(\text{H}_2\text{O})_{10}$) were probed by TRLFS at room temperature ($19 \pm 1 \text{ }^\circ\text{C}$). The rock sample was placed on a x–y motorized micrometric stage and illuminated with a pulsed Nd:YAG laser beam at 266 nm and operated at 10 Hz (Minilite, Continuum). The energy was limited to about 3 μJ . The laser beam was focused onto a point close to the surface of the sample to avoid ablation phenomena while keeping the analyzed area smaller than the size of the mineral inclusions. The fluorescence emission of U(VI) was collected by an optical fiber connected to the entrance slit of a spectrograph (Shamrock, SR-303i, Andor) equipped with a 300-groove/mm diffraction grating (500-nm blaze). The fluorescence was recorded by a thermoelectrically cooled time-gated intensified charge-coupled device (iCCD) camera (iStar, DH740-18F-03, Andor). The iCCD was triggered by the laser Q-switch. The delay and width of the acquisition gate were adjusted for every compound in order to have the minimal noise without detector saturation. The fluorescence decay was measured by varying the delay, and fitted with exponential functions in order to determine the characteristic fluorescence decay times. Spectra were smoothed using a fifth-order Savitzky–Golay algorithm.

3. Results

3.1. Cathodoluminescence: the microscopic ring structure

Cathodoluminescence and SEM images (Fig. 1) show alternating bright and dark bands of several micrometers width, that reflect rings of the opal coatings, as described at Nopal (Othmane et al., 2013) and Yucca Mountain (Paces et al., 2004). The resulting spheres have radii of several 10s of micrometers (see also S3 picture in Electronic Annexes). The fluorescent zones correspond to Ca–U enriched opal layers revealed in BSE mode that were shown earlier (Schindler et al., 2010). In addition, apatite domains observed by SEM are not fluorescent as

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