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Uranium and uranyl luminescence in agate/chalcedony

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ABSTRACT

A systematic investigation of agates from different occurrences in Europe, Northern and Southern America reveals that macrocrystalline quartz and chalcedony within them have an unusually high uranium content. Whereas agates may contain >70 ppm of U, quartz from magmatic and metamorphic rocks as well as pegmatite quartz commonly exhibit U concentrations at sub-ppm levels. Spatially resolved trace-element analyses by laser ablation inductively coupled plasma mass spectrometry show that the distribution of U within the agate samples is heterogeneous and coincides with the structural banding. The results indicate that U is incorporated into agate as uranyl ions. These ions, which are bound to the silica surface, are interpreted to originate from the parallel accumulation of Si and U by alteration processes of surrounding host rocks during agate formation.

The uranyl ion is the cause of greenish photoluminescence (PL) in agate, which can only be excited by short wavelengths (<300 nm). The green PL is due to the electron transition from an excited to a ground state of the uranyl ion and is shown by a typical emission line at ~500 nm accompanied by several equidistant lines. These are due to the harmonic vibration of oxygen atoms along the uranyl axis. Luminescence can be detected in samples with a U content down to the 1 ppm level.

KEYWORDS: luminescence, green photoluminescence, uranium, uranyl, agate, chalcedony, quartz.

Introduction

BANDED chalcedony is known as agate and this spectacular product of nature commonly occurs in volcanic rocks, both SiO_2-rich (rhyolite, rhyodacite) and SiO_2-poor (andesite, basalt). Many authors conclude that the formation of volcanic agates is associated with late- or post-volcanic alteration or weathering of these rocks (e.g. Walger, 1954; Harder, 1993; Holzhey, 1995; Moxon, 1996; Pabian and Zarins, 1994; Möckel and Götze, 2007; Götze, 2011). Additionally, agates may occur as hydrothermal veins in fissures and fractures of crystalline rocks, or form from low-temperature SiO_2-rich solutions in pores and cavities of sedimentary rocks (Götze, 2011).

Apart from its characteristic appearance (e.g. typical agate banding) and micro-structure, chalcedony and macrocrystalline quartz within agates possess chemical and physical properties that are very different from those of quartz in crystalline rocks, such as trace-element composition and luminescence behaviour (Moxon, 2009; Götze, 2011).

Quartz is one of the minerals in the Earth's crust that typically has very low trace-element concentrations. However, in agates, elements such as Al, Ca, Fe, K, Na, Ge, B and U can be present in higher concentrations (Götze *et al.*, 1999, 2001, 2012*a*). These elements are mobilized from surrounding host rocks during late- and post-volcanic alteration processes, transported and

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accumulated together with SiO_2 during agate genesis (Götze, 2011).

In particular, uranium is one of the elements that is normally present at very low concentrations in quartz. Most quartz crystals in magmatic and metamorphic rocks as well as in pegmatites have a U content far below 1 ppm (e.g. Gerler, 1990; Blankenburg *et al.*, 1994; Götze *et al.*, 2004; Götze, 2009). The typically small U content in quartz is due to the fact that the crystal-chemical properties of uranium ions (in particular ion size) prevent a substitutional incorporation into the quartz structure. Therefore, observed high concentrations of U within some agates and chalcedony are surprising. Previous geochemical investigations on 14 agates from different host rocks and of contrasting ages yielded U concentrations of <0.1–4.2 ppm for macrocrystalline quartz and <0.1–21.3 ppm for chalcedony, respectively (Götze *et al.*, 2001).

Another remarkable feature of agates is the greenish luminescence emitted under UV excitation (Fig. 1), which is uncommon in quartz of magmatic and metamorphic rocks. There are only a few studies of UV-excited green luminescence in opal and chert that have elevated uranium concentrations (e.g. Lyons *et al.*, 2003; Matteson *et al.*, 2005; Gaillou *et al.*, 2008). Gorobets and Rogojine (2002) concluded that the green luminescence in silica minerals is caused by uranyl ions $(UO_2)^{2+}$ in the SiO_2 host.

The aim of the present study is to determine the origin of the green photoluminescence (PL) in agate/chalcedony. Spatially-resolved trace-element analyses of 13 agate samples from different locations are used to quantify the uranium content and the local distribution of uranium in the agate structure. These results clarify the mechanisms of U accumulation and incorporation into the agate structure. This knowledge can provide additional arguments concerning general aspects of agate genesis and the behaviour of chemical elements during geological processes of rock alteration.

Materials and methods

The sample material comprises 13 agates from selected occurrences around the world (Table 1). Most of the agates are from acidic volcanic rocks, but the sample set also includes agates from basic volcanic rocks, hydrothermal veins and sedimentary rocks. The agates were examined regarding their luminescence properties under UV-B excitation (280–315 nm) using a commercial UV lamp (KRANTZ). Samples exhibiting a greenish photoluminescence (PL) were selected for further spectral luminescence measurements and chemical analyses. Details of the specimens analysed in the present study are compiled in Table 1.

In situ chemical analyses by means of laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) were obtained along profiles across the agate banding or as point analyses in separate sample parts with chalcedony or macrocrystalline quartz. For profile analysis, a section perpendicular to the agate banding was cut, polished and fixed with epoxy resin in a 1" diameter ring, which fits in the sampling cell of the LA-ICP-MS device. Measurements were performed at the VSEGEI (St. Petersburg, Russia) on a system with a Thermo Finnigan Element 2 mass spectrometer, linked to a DUV 193 laser ablation system including optics and viewing by New Wave Research/Merchantek Products. The ArF excimer laser operates with a wavelength of 193 nm and an energy output of 50–200 mJ. The spot size was chosen to be between 150 and 250 μm. The two accredited standards, NIST 611 and NIST 612, were used for calibration procedures (Hollocher and Ruiz, 1995). Calibration was undertaken at the beginning and at the end of each measuring cycle, and after analysing five spots, mainly in order to remove memory effects. To minimize errors, the measurements of all elements were repeated 20 times on each spot. Details of the procedure are given in Möckel *et al.* (2009).

Additional analyses with conventional ICP-MS were performed on separated chalcedony and quartz parts of the agates. 400–500 mg samples were hand-picked under a stereo microscope and milled to a grain size of <30 μm using a pre-cleaned agate mortar. The powdered sample was digested in a glassy carbon vessel with 5 ml concentrated HF and 3 ml concentrated HNO_3 at 50ºC (35 min). Rhenium solution (1 ml of 100 μg/l concentration) was added as an internal standard for the ICP-MS measurements. The analysis was performed using a Perkin Elmer Sciex Elan 5000 quadrupole instrument with a cross-flow nebulizer and a rhyton spray chamber. The precision and accuracy of the ICP-MS measurements were evaluated by analysis of the glass sand reference material UNS-SpS (Monecke *et al.*, 2000). The relative standard deviations for all analyses were <10%.

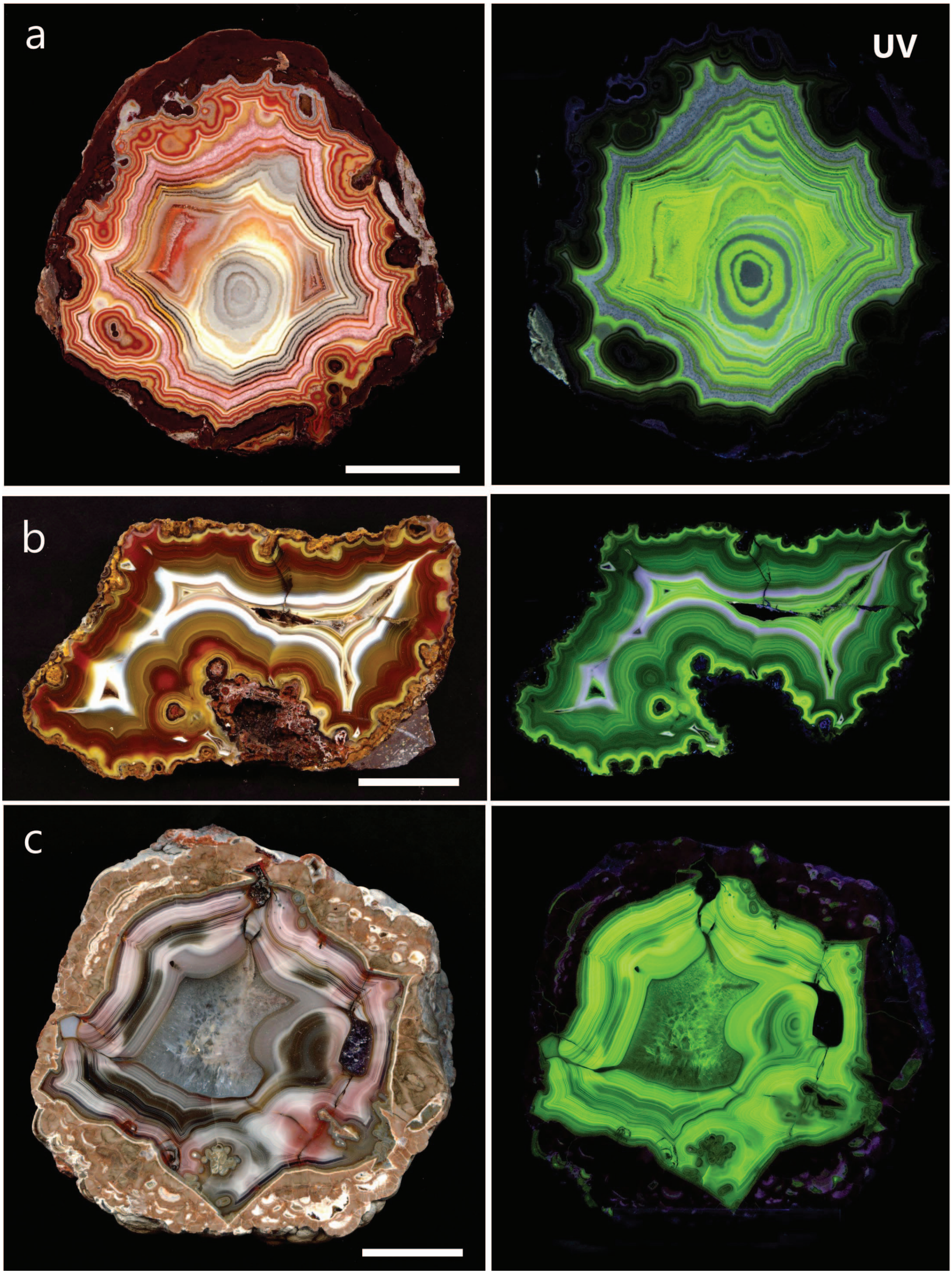

FIG. 1. Agates from different occurrences in normal light (left) and under UV excitation (right) showing the typical greenish luminescence: (*a*) sedimentary Dryhead agate from Prior Mountains, Montana (USA); (*b*) agate in andesitic rocks from Ojo Laguna, Chihuahua (Mexico); (*c*) agate in ignimbrites from the Baker Egg Mine near Deming, New Mexico (USA). Scale bar is 2 cm.

TABLE 1. Uranium contents (in ppm) of the agate and quartz samples investigated (related U profiles are shown in Figs 2 and 3).

Sample	Location	Type	ICP-MS single measurement	LA-ICP-MS profile
CH1	Chemnitz-Furth Saxony, Germany	Agate in ignimbrite		<0.01–1.01 (13)
ChemACh	Chemnitz-Altendorf Saxony, Germany	Vein agate	0.23 (chalcedony)	
Chemwood	Chemnitz-Hilbersdorf Saxony, Germany	Silicified wood in ignimbrite	9.32 (chalcedony)	
HoE	Hohenstein-Ernstthal Saxony, Germany	Agate in ignimbrite	2.81 (quartz) 8.98 (chalcedony)	
HE1	Hohenstein-Ernstthal Saxony, Germany	Agate in ignimbrite		8.32–18.09 (6)
StE1	St. Egidien Saxony, Germany	Agate in ignimbrite		<0.01–7.16 (20)
AStE	St. Egidien Saxony, Germany	Agate in ignimbrite		5.79–17.10 (4)
Z1	Zwickau-Planitz Saxony, Germany	Agate in melaphyre		<0.01–0.86 (31)
ZwiCh	Zwickau-Planitz Saxony, Germany	Agate in melaphyre	0.40 (chalcedony)	
AGeh	Gehlberg Thuringia, Germany	Agate in rhyolite	2.80 (quartz) 4.37 (chalcedony)	
ALag	Ojo Laguna Chihuahua, Mexico	Agate in andesite	4.21 (quartz) 16.20 (chalcedony)	
NK1	Novy Kosciol Poland	Agate in rhyolite		<0.01–3.37 (12)
M1	Dryhead area Montana, USA	Sedimentary agate		1.93–71.99 (33)

Numbers in brackets give the number of analytical points

The experimental setup for laser-induced time-resolved luminescence measurements consists of three main units: laser excitation source, gated spectrometer and computer for system synchronization and data treatment. An optical parametric oscillator (OPO, OPOLET) laser was used with 250 nm wavelength and pulses of 5–10 ns duration, which were synchronized by iStar equipment (ANDOR V). The equipment enables spectral measurements to be acquired in certain time windows, which are determined by delay time, i.e. the time between the end of the laser pulse and the beginning of the measurement, and gate width, i.e. the time between the beginning and the end of the measurement. The number of pulses is determined according to the signal/noise ratio and depends on luminescence intensity. A delay time of 1 µs and a gate width of 200 µs were selected for uranyl luminescence measurements. The specific luminescence decay times have been measured by a kinetic series of different delay and gate settings to prevent any interference from closely spaced spectral features.

Results

Concentration and distribution of U in agate

The trace-element studies showed a wide scatter of U concentrations in agates from different localities, ranging from <0.1 ppm up to >70 ppm (Table 1). The U concentrations in agates are thus up to two orders of magnitude higher than those of paragenetic calcite in agates (0.2–0.8 ppm, Götze *et al.*, 2001).

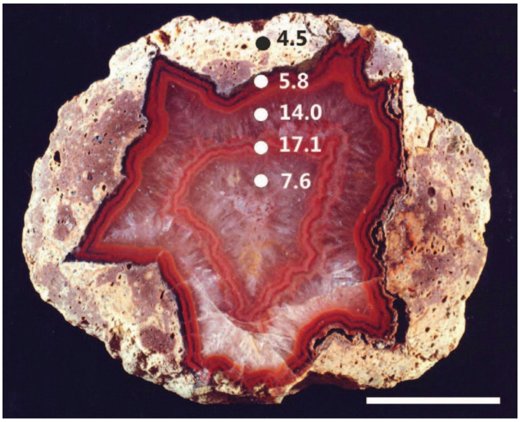

FIG. 2. Agate sample from St. Egidien, Germany showing the range of U contents (in ppm) in different agate zones; note that the U concentration in agate is higher than in the surrounding host rock. Scale bar is 2 cm.

Point analyses of separate chalcedony and macrocrystalline quartz parts within the agates as well as U concentration profiles across the agate banding (Figs 2 and 3) have revealed that the distribution of U is very heterogeneous with no apparent compositional trend from the agate margin to the centre. The concentration of uranium and the majority of other trace elements is mostly higher in parts of agates containing chalcedony than macrocrystalline quartz. However, certain samples, such as an agate from St. Egidien, Germany (Fig. 2), show the opposite behaviour. It is noteworthy that the concentration of U in agate can exceed the Clarke value of 2.5 ppm (average U concentration in the Earth's crust – Clarke and Washington, 1924) and sometimes the concentration of uranium in the host rock (Fig. 2).

The highest U concentrations were measured in the sedimentary Dryhead agate from Montana, USA (Table 1). In contrast to generally low concentrations of most trace elements in the Dryhead agate (Götze *et al.*, 2009), U concentrations range from 5 to 71 ppm (average of 9.8 and 21.3 ppm for quartz and chalcedony, respectively). Although the highest U contents in the investigated agate samples were often found in red/dark chalcedony bands, U contents in points along the trace-element profile do not exhibit a correlation with Fe contents (Götze *et al.*, 2009). Therefore, U appears to be transported and

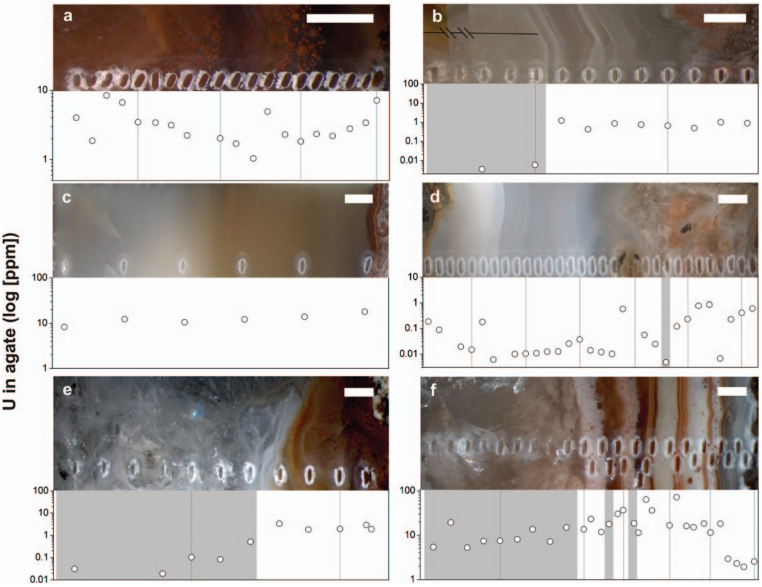

FIG. 3. Distribution of U in profiles perpendicular to the agate banding in selected samples (contents are given in log ppm): (*a*) St. Egidien; (*b*) Chemnitz; (*c*) Hohenstein-Ernstthal; (*d*) Zwickau (all Saxony, Germany); (*e*) Nowy Kościół, Poland; (*f*) Dryhead Area, Montana (USA); note the scatter of the U concentrations independent of chalcedony or macrocrystalline quartz (grey zones). Length of the scale bars is 1 mm, errors of measurements within the symbol sizes; missing data points are due to values below the limit of detection (0.01 ppm).

accumulated together with Fe compounds, but is not bound directly to Fe oxides/hydroxides.

Luminescence

A conspicuous feature of many agates under UV excitation is a visible bright green luminescence (Fig. 1). The greenish PL can only be excited by short wavelengths (<300 nm). The visual luminescence pattern follows both the agate banding and the distribution of macrocrystalline quartz and chalcedony.

Agate samples with high U content mostly exhibit a high luminescence intensity, but there is no quantitative correlation between U content and luminescence intensity. This observation points to an interaction between luminescence activator (U) and possible quenchers (e.g. Fe). In addition, the green luminescence is even detectable in samples with a U content in the sub-ppm level (Fig. 4). This fact emphasizes the extreme sensitivity of the relevant luminescence centre concerning excitation with the laser beam.

Spectral measurements of the visible green luminescence emission show a multi-line spectrum with the main emission line at ~500 nm accompanied by several equidistant lines (Fig. 4). The greenish luminescence with the typical multi-line spectrum is characteristic for the uranyl luminescence in mineral species at room temperature (Gorobets and Rogojine, 2002). Laser-induced luminescence measurements with a delay time of 1 μs and gate of 200 μs provided two different luminescence lifetimes of $\tau_1 = 2$ μs and $\tau_2 = 25-105$ μs, respectively.

Discussion

Accumulation and incorporation of U in SiO$_2$

Trace elements can be incorporated into the quartz structure by substitution of Si and in interstitial positions, or may be present as inclusions of fluids and other minerals. The structural incorporation is limited due to the small number of ions that have similar ionic radii and valence and can substitute for Si^{4+} in the

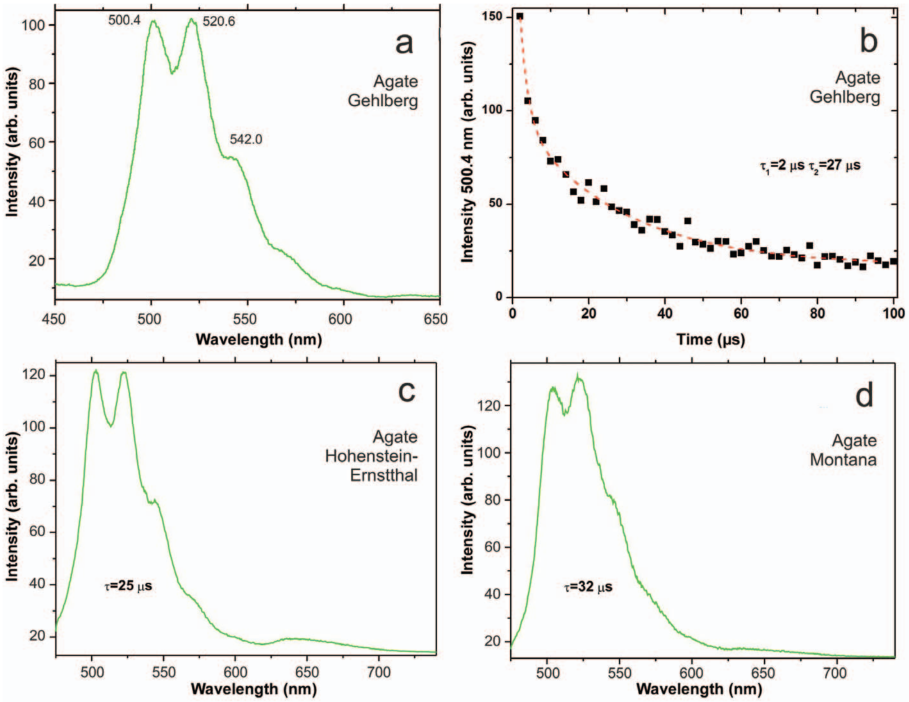

FIG. 4. Selected luminescence emission spectra upon excitation with 250 nm laser light measured with a delay time *D* of 1 μs and a gate *G* of 200 μs; the spectra show typical uranyl multi-line spectra with the main emission line at ~500 nm accompanied by several equidistant lines; (*a*) agate from Gehlberg, Germany (sample AGeh); (*b*) luminescence decay behaviour of the luminescence of sample AGeh shown in (*a*) (τ = decay time); (*c*) agate from Hohenstein-Ernstthal, Germany (sample HE1); (*d*) Dryhead agate from Montana, USA (sample M1).

crystal structure (e.g. Al^{3+}, Ga^{3+}, Fe^{3+}, Ge^{4+}, Ti^{4+}, P^{5+}).

In the case of agates, several geochemical studies have shown that chalcedony and macrocrystalline quartz can be enriched in Al, Fe, Ca and Na, which originate from alteration processes of the volcanic host rocks and the associated release of chemical elements (e.g. Holzhey, 1995; Götze, 2011). It is assumed generally that the formation of agates is associated with the alteration or weathering of surrounding host rocks and the transport of released silica by residual magmatic fluids (H_2O, but also CO_2 or HF) and/or heated meteoric water (Götze, 2011). Such processes are evidenced by the chemical composition of the agates and the association with typical secondary minerals such as clay minerals, zeolites or iron oxides.

The observed high concentrations of U (>70 ppm) in some of the agates of the present study are surprising and suggest the operation of specific processes of mobilization, transport and accumulation, which result in concentrations of U in quartz and chalcedony that can exceed the Clark concentration and sometimes the concentration of U in the surrounding rocks (compare Fig. 2).

The mobility of U during the alteration of volcanic rocks was investigated by Zielinski (1979), who observed a parallel accumulation of Si and U. Based on the premise that the transport of chemical compounds is mainly realized by diffusion processes in aqueous fluids (e.g. Si as monomeric silicic acid $Si(OH)_4$), Porter and Weber (1971) inferred for the uranyl ion a complex with monomeric silica $UO_2SiO(OH)_3^+$. However, the appearance of certain paragenetic minerals (e.g. calcite, fluorite) and the concentration of certain elements (e.g. U, Ge, B) in agates indicate that volatile fluoride (and chloride) compounds can also play a role in the alteration of volcanic rocks as well as the mobilization and transport of SiO_2 and other chemical compounds (Götze et al. 2012*a*). The presence of volatile compounds such as SiF_4, UO_2F_2, GeF_4 and BF_3 that facilitate element transport may present an additional alternative to explain agate formation, because transport accomplished in these gaseous phases is very efficient. A possible transport mechanism to produce hydrothermal veins could occur when the gaseous phase forms an aqueous solution (Schrön *et al*., 1988).

Condensation processes cause the bridging of molecules of monomeric silicic acid and the formation of polymeric silicic acid as well as discrete silica particles (sol). Uranium can be adsorbed from the solution of any concentration due to the high adsorption area of natural silica compounds (0.5 m^2/g for quartz and up to 20 m^2/g for opal). Silica colloids (sols) dispersed in aqueous solution have an overall negative charge, which allows the adsorption of positively charged ions such as Na^+ or uranyl. The UO_2^{2+} ions are fixed on the surface of dispersed SiO_2 particles by means of two or three water molecules forming water-uranyl complexes (Glinka and Krak, 1995). An equilibrium between solution and sorbent is achieved immediately, and the accumulated uranium content is independent of anion composition, pH of solution or the reaction time (Kobyshev, 1961). Further polycondensation can result in a three-dimensional silica network, which is responsible for trapping the uranyl ion (and other ions with high affinity to silica colloids such as Fe^{3+}) in a stable matrix (Lopez and Birch, 1996).

A substitution of Si^{4+} in the quartz structure is unlikely due to the size of U ions. Therefore, the incorporation may occur as fluid and/or mineral inclusions or involve the adsorption of the uranyl complex. Fluid inclusions in agates (in particular in chalcedony) are rare, so that significant accumulation of U in fluid inclusions is considered unlikely. The spatial distribution of uranyl luminescence within the agate bands is also inconsistent with a preferred concentration of U in fluid inclusions, as such a mechanism would result in brightly luminescent spots. Moreover, detailed investigations by scanning electron microscopy and Raman spectroscopy revealed no uranium- or thorium-bearing micro-inclusions, which challenges the role of mineral micro-inclusions as a host for U. Instead the evidence points to a physical adsorption process of uranyl ions by active-surface centres with negative charge, and it can be assumed that there is a co-precipitation of dissolved U together with amorphous silica (Zielinski, 1982).

Origin of the green luminescence

Additional evidence for the chemical speciation of U in agates is provided by means of luminescence spectra. Uranium-bearing minerals can incorporate two different structural types leading to completely different spectroscopic properties (Gorobets and Rogojine, 2002). The incorporation of U^{4+}, U^{3+} and U^{2+} ions results in an electronic structure and spectra similar to the rare-earth ions. In most minerals, however, uranium is present as U^{6+} forming the uranyl complex UO_2^{2+} (Marfunin, 1979). Uranyl is a linear oxycation O–U–O, which is symmetrical relative to the arrangement of the two oxygen ions.

Uranyl is responsible for the yellow colour of most uranyl compounds and the resulting green luminescence when viewed under UV light. Micro- and non-crystalline silica minerals (chalcedony, opal) sometimes show a greenish PL under excitation with short wavelength (<300 nm) radiation. The characteristic equidistant emission lines in natural silica minerals are similar to emission lines of uranyl adsorbed by synthetic silica gel in the form of aqua complexes $UO_2^{2+}\cdot nH_2O$ (Kobyshev, 1961). Therefore, it was assumed that the uranyl luminescence in silica minerals is caused by separate aqua complexes of uranyl groups in the SiO_2 host (Gorobets and Rogojine, 2002). This structure results in visible greenish PL at room temperature, and a luminescence lifetime τ of 170–500 μs was reported (DeNeufville *et al*., 1981).

The fact that two distinct decay times were measured in the agate samples investigated is probably due to the presence of two different emissions. The shorter one is associated with the luminescence of so-called ‘water-organic complexes’ with a very broad emission band and very short decay time, whereas the longer decay is produced by the uranyl luminescence. The measured decay time is relatively short compared to previous studies, in which the shortest decay time was reported to be ~150 μs (DeNeufville *et al*., 1981). However, the decay time is strongly dependent on many parameters, including the luminescence centre concentration and temperature. High U concentrations may lead to shorter decay times because of concentration quenching. In addition, the measurements reported here were performed at 300 K, where decay is usually shorter than at 77 K.

The ground state of uranyl is $^1\Sigma_g^+$, a singlet with a total spin of 0 and a centre of symmetry (Marfunin, 1979). The excited state is split by electron-phonon interaction creating vibrational sublevels due to the vibration of oxygen atoms in uranyl. The absorption of photons by uranyl causes electron transitions from the upper filled orbital $1\pi_g^4$ to one of the excitation levels of the empty orbitals $1\delta_u$ and $1\varphi_u$ with vibrational sublevels. The electron transition back $1\varphi_u^1(1\delta_u^1) \rightarrow {}^1\pi_g^3$ (zero-phonon electron transition) results in the emission of photons with an energy of about $k_0 \approx 2\cdot10^4\ cm^{-1}$ (~500 nm) accompanied by equidistant lines, which are due to the harmonic vibration of oxygen atoms along the uranyl axis (Gorobets and Rogojine, 2002).

The present study shows that uranyl is a very effective luminescence activator, and successful excitation is possible with U content as low as the ppm level. Marfunin (1979) stated that quenchers for uranyl luminescence are similar to those for the *REE*, i.e. they include Fe, Cu, Mn, Pb and Bi. The sensitivity of uranyl luminescence in this study confirms results of Gaillou *et al.* (2008), who reported a general green luminescence in common and gem opals from various locations around the world with U contents ⩾1 ppm (and Fe <1000 ppm).

Uranium and agate genesis

The results of the present study provide additional arguments concerning general ideas about agate genesis and agate structure. First, the assumed processes of uranium transport and accumulation support the idea of agate genesis *via* a ripening process: silicic acid → silica sol → amorphous silica → chalcedony → quartz (e.g. Landmesser, 1984). Alteration processes associated with a release of Si and certain chemical elements (including U), the transport as aqueous complexes (e.g. $UO_2SiO(OH)_3^+$; $FeSiO(OH)_3^{2+}$ Porter and Weber, 1971), and the accumulation and fixation of these chemical compounds in silica colloids best explain the observed chemical signature and structure of agates.

The idea that U in agates is adsorptive and not fixed structurally is also supported by the fact that U in silica is relatively mobile and can be removed by secondary (e.g. hydrothermal) alteration processes. Silicified wood from Chemnitz, Germany shows an average U content of ~10 ppm (compare Table 1). However, hydrothermal processes are interpreted to have mobilized uranium locally, resulting in U concentrations below 1 ppm (Matysova *et al*., 2013).

Another interesting point is the mode of incorporation of uranium into the agate structure. The incorporation of the large uranyl ion should be not possible in the ideal quartz structure and is only realized in silica minerals with a strong local structural disorder. In fact, chalcedony and quartz with elevated U concentrations are characterized by high amounts of E'_1 defects (electron defects related to an oxygen vacancy), which also reflect local damage and radiation induced defects (Götze *et al.*, 1999).

In this context, the first detection of radiation haloes in agates from Mali is noteworthy (Götze *et al.*, 2012*b*). Radiation haloes indicate a considerable amount of structural damage and are commonly produced by micro-inclusions of radioactive minerals (e.g. Owen, 1988; Krickl *et al.*, 2008). However, in the absence of U- or Th-bearing micro-inclusions, it is difficult to account for the radiation haloes. One possible explanation is the presence of clusters of trace elements, which produce luminescence-active defects or local amorphization in the immediately surrounding silica matrix. In the centre of one of the radiation haloes an increased Raman background was measured, but there was no Raman signal that could be attributed to a crystalline mineral or hydrocarbon phase (Götze *et al.*, 2012*b*). Considering the results of the present study, the origin of the radiation haloes could probably be explained by a localized accumulation of uranyl ions, which produced radiation damage in the surrounding micro-volume.

Last but not least, an elevated U content in agates can influence the colour of macrocrystalline quartz in these specimens. An intensive natural irradiation can produce defects in the crystal structure and activate colour centres in quartz (Lehmann and Bambauer, 1973). The presence of U and the related internal radiation could explain the occurrence of amethyst and smoky quartz in agates of several occurrences (Götze, 2011).

Conclusions

The present trace-element and luminescence study has revealed that U is a common trace element in agates from occurrences around the world. Although U concentrations can vary widely between agates from different localities and even within one sample (<0.1 to >70 ppm), the average values are higher than for most of the other trace elements (Götze *et al.*, 2001; Götze, 2011). Assuming an origin of U in agates from alteration processes of surrounding host rocks, the different U contents mainly reflect the local geochemical speciation of the agate-bearing region.

Luminescence spectroscopy has shown that U is mainly incorporated in form of the uranyl complex in chalcedony and macrocrystalline quartz. The visible greenish luminescence in agates is characterized by a typical emission line at ~500 nm accompanied by several equidistant lines due to the harmonic vibrations of oxygen atoms in the uranyl complex. The mechanism of the uranyl luminescence is very effective and can be detected in agates with U contents as low as 1 ppm.

The investigations concerning the mode of incorporation of U into chalcedony and macrocrystalline quartz of agates provide additional arguments concerning agate genesis and the properties of SiO_2 modifications and varieties. The suggested transport by aqueous complexes and adsorptive fixation of uranyl to the silica surface is consistent with the idea that agates have an amorphous precursor. Furthermore, structural damage to agate quartz, occurrence of radiation haloes as well as amethyst and smoky quartz in agates can be explained by elevated contents of incorporated uranium. Thus, it can be concluded that agates are an important geochemical indicator for the reconstruction of geological processes.

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