First direct evidence for natural occurrence of colloidal silica in chalcedony-hosted vacuoles and implications for ore-forming processes

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ABSTRACT

Different forms of abundant silica (e.g., quartz and chalcedony) are closely associated with many types of ore deposits in igneous, metamorphic, and sedimentary environments. Occurrence of quartz and metal-bearing minerals together strongly indicates that silica is an important component in hydrothermal fluids transporting and concentrating economic metals to the ore grade, however chemical and physical characteristics of such ore-forming media remain debated. Understanding of the environment in which chalcedony forms is largely hampered by the lack of chalcedony-hosted fluid inclusions. Our study reports for the first time fortuitously preserved, large-sized (up to 150 μm) fluid inclusions in chalcedony from the Gonchak deposit of optical calcite in the Early Triassic basalts belonging to the Siberian large igneous province. The application of microthermometric methods, scanning electron microscopy with cathodoluminescence, and laser Raman spectroscopy to the fluid inclusions and their host chalcedony recognized the formation of chalcedony from a colloidal suspension. The fluid inclusions represent a gel-like saline aqueous fluid that is residual after precipitation of spherulitic chalcedony aggregates with numerous H_2O-bearing and H_2O-poor layers. We propose that the colloidal nature of fluids forming chalcedony lends strong support to the natural existence of experimentally predicted "silicothermal fluids". Such fluids can be instrumental in mobilizing and transporting large quantities of both silica and nano- and micro-particles of ore minerals, followed by efficient separation of the latter from coagulating silica gel into ore-rich zones and bodies.

INTRODUCTION

Understanding the formation of orthomagmatic mineralization requires building knowledge about magmatic fluids that are both a source and a transporting medium of ore-forming components. Silica in the form of quartz and chalcedony is one such component and commonly most abundant in porphyry, mesothermal, and epithermal environments, where it occurs with economic minerals (e.g., sulfides, native gold, etc.) in ore bodies and associated alterations halos. However, given the low solubility of SiO_2 in aqueous solutions (e.g., Kennedy, 1950; Rimstidt, 1997; Shmulovich et al., 2006), "unreasonably large volumes" of hydrothermal fluid (Wilkinson et al., 1996, p. 1061) are required to explain quartz-rich orthomagmatic deposits. As an alternative to true solutions with low solubility of silica and metals, hydrothermal fluids may be represented by a viscous, dense, and highly metal-charged substance that is essentially colloidal in origin.

Concentric, colloform, and porcelain textures, spherulitic quartz and chalcedony, septarian structures, and "syneresis" shrinkage cracks are commonly observed in hydrothermal ores and provide support for the crystallization of an amorphous silica gel (e.g., Herrington and Wilkinson, 1993; Sander and Black, 1988; Saunders, 1990, 1994). This point of view is strongly supported by numerous experimental works at the conditions of hydrothermal mineralization (<3 kb, <750 °C) in the systems involving SiO_2, H_2O, carbonate, alkali elements, and halogens (e.g., Fournier, 1985; Kotel'nikova and Kotel'nikov, 2010; Oehler, 1976; Smirnov et al., 2012; Thomas et al., 2000, 2011, 2014; Wilkinson et al., 1996). The synthesized "silicothermal fluid" (Wilkinson et al., 1996), "supercritical silicate-rich fluid" (Thomas et al., 2000), and "hydrosilicate liquid" (Smirnov et al., 2012; Thomas et al., 2014), "more closely resembling a gel than a conventional melt" (Thomas et al., 2011, p. 326), have been considered a novel medium in a range of geological environments, enabling extreme concentrations of

ore-forming elements, especially at the magmatic-hydrothermal transition. The exact compositions of such fluids have proved extremely difficult to document and understand, largely because of their metastable, transient, and reactive qualities. Nevertheless, silica gel–like fluids compositionally similar to those formed in experiments are being increasingly documented among inclusions in hydrothermal minerals such as quartz, topaz, and sanidine (e.g., Fulignati et al., 2011; Kamenetsky and Kamenetsky, 2010; Kamenetsky et al., 2004; Sirbescu and Nabelek, 2003; Thomas and Davidson, 2008, 2012; Williamson et al., 1997, 2002).

Chalcedony, a cryptocrystalline form of silica abundant in many types of hydrothermal deposits, is the best candidate for identifying a gel-like amorphous precursor in nature (Sander and Black, 1988), but has been largely overlooked in conventional studies of fluid inclusions because the latter were not large enough for genetic constraints (Bodnar et al., 1985). In this work, we report abundant, large-sized inclusions of colloidal silica in the chalcedony from the Iceland Gonchak deposit in the Triassic flood basalts of the Siberian large igneous province and make implications for occurrence and evolution of "silicothermal fluids" (Wilkinson et al., 1996) in natural environments.

SAMPLES AND METHODS

The sample in this study is chalcedony (Fig. 1A) from the Gonchak deposit of optical calcite ("Iceland spar") in southeastern Siberia (Nizhnyaya Tunguska River) (see the GSA Data Repository[1]). The hydrothermal mineralization is located within Early Triassic amygdaloidal
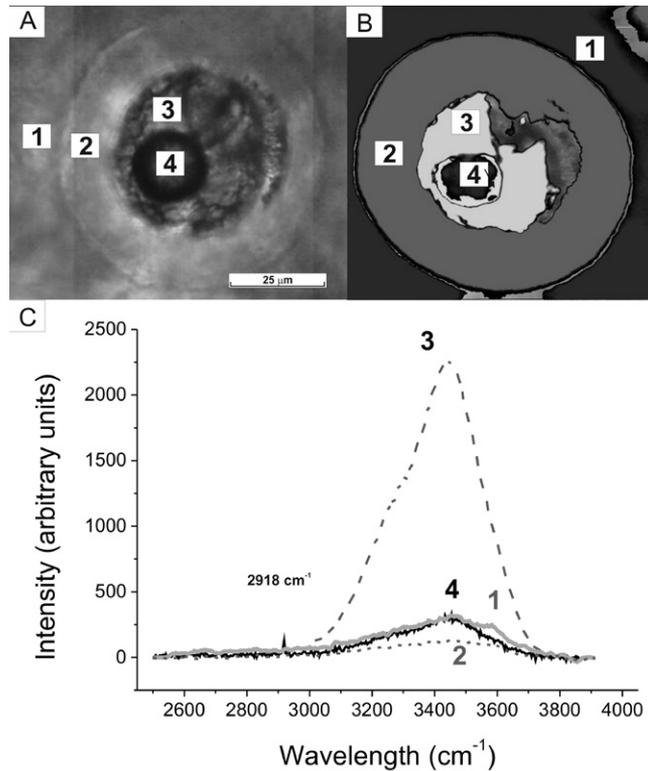
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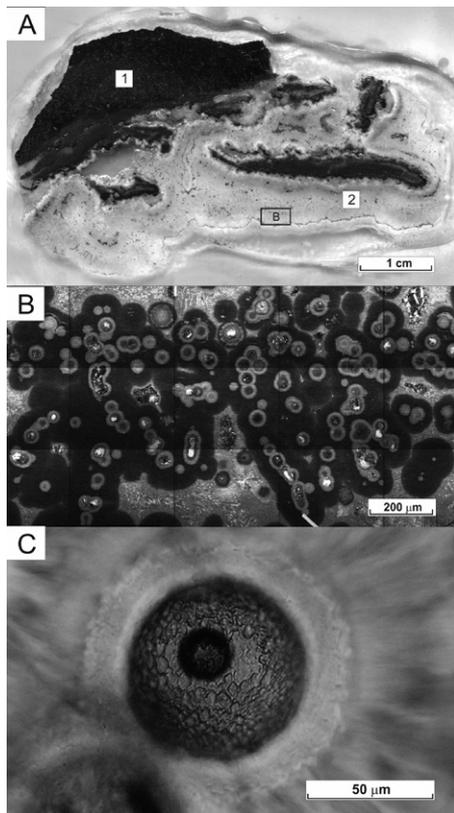
Figure 1. Optical (A,C) and panchromatic cathodoluminescence (B) images showing polished section of chalcedony (1) in basalt (2) and occurrence of chalcedony-hosted fluid-filled vacuoles. Box in A shows location of B.

Figure 2. Optical image (A), Raman map (B), and part (2500–3900 cm⁻¹) of Raman spectra (C) of a single vacuole in chalcedony showing (1) H_2O-bearing outer chalcedony layers (dark in Fig. 1B), (2) H_2O-poor inner bands around the vacuole, (3) aqueous fluid, and (4) methane-bearing shrinkage bubble.

basaltic pillow lavas with thickness up to 50 m. The mineral association of optical calcite and chalcedony in amygdules and veins includes mordenite, heulandite, analcime, chlorite, montmorillonite, apophyllite, saponite, and pyrite.

Chalcedony is generally colorless and transparent, milky-white in places, with very fine texture represented by fibrous intergrowths of cryptocrystalline silica, commonly with radiating and spiral-like filiforms. The studied chalcedony is characterized by numerous near-spherical, dumbbell- and spindle-shaped vacuoles up to 150 μm in diameter, commonly arranged in clusters with up to six to eight vacuoles and showing coalescence (Fig. 1B). The individual vacuoles are enclosed in distinctively layered chalcedony (Fig. 1C) and contain transparent fluid and a gas bubble (Figs. 1C and 2). Unlike for typical fluid inclusions in hydrothermal quartz (e.g., Roedder, 1984), the surfaces of the vacuoles are not smooth but are covered by randomly oriented quartz crystals of variable size (Figs. 1C and 3).

The content of the vacuoles and their host chalcedony were studied using the following methods and equipment: Linkam THMSG-600 cooling/heating stage (IGEM, Russia); Linkam TS1500 heating stage (Centre of Excellence in Ore Deposits [CODES], University of Tasmania); and Renishaw inVia micro-Raman spectroscopy system with StreamLineHR and XYZ stage, FEI Quanta 600 MLA scanning electron microscope with a cathodoluminescence (CL) detector, and Hitachi SU-70 Schottky field emission scanning electron microscope (all in Central Science Laboratory, University of Tasmania). The Raman spectra were recorded, using a diode-pumped solid-state laser at 532 nm with a power output of 25 mW at the sample, 50× objective (NA 0.75), high confocal mode, 1 s exposure time (0.1 s for three-dimensional volume maps), and a 600 l/mm grating giving a spectral range of 100–3910 cm⁻¹.

RESULTS

Concentrically layered chalcedony around the vacuoles, clearly visible in transmitted light on the optical microscope (Fig. 1C), shows optical continuity and may reach 45% of the vacuole's diameter at mid-plane. However, the CL study depicts much more significant volume (90%–95%) of chalcedony that forms rings and bands around the vacuoles (Fig. 1B). The immediate surroundings of the vacuoles are characterized by alternating chalcedony bands that are variable in CL brightness. The outer, volumetrically most significant layers are invariably dark (black) in CL (Fig. 1B). The overlapping outer bands of the individual vacuoles together with concentrically zoned inner layers are responsible for a distinctive "spherulitic" texture of the studied chalcedony (Fig. 1B), reminiscent of textures observed in felsic volcanic rocks (e.g., Breitkreuz, 2013).

The fluid content of the vacuoles was recognized by Raman spectroscopy as liquid water (a broad peak in the water stretching region, 3050–3750 cm⁻¹) using a two-dimensional mapping of the vacuole at 50 μm below the sample surface (Fig. 2). The exact composition of the vapor bubble in the vacuole is uncertain, however a small peak at 2918 cm⁻¹ indicates the presence of methane. The Raman study also detected the presence of water in the outer (dark) chalcedony band, whereas the inner layers adjacent to the vacuole are almost water free (Fig. 2).
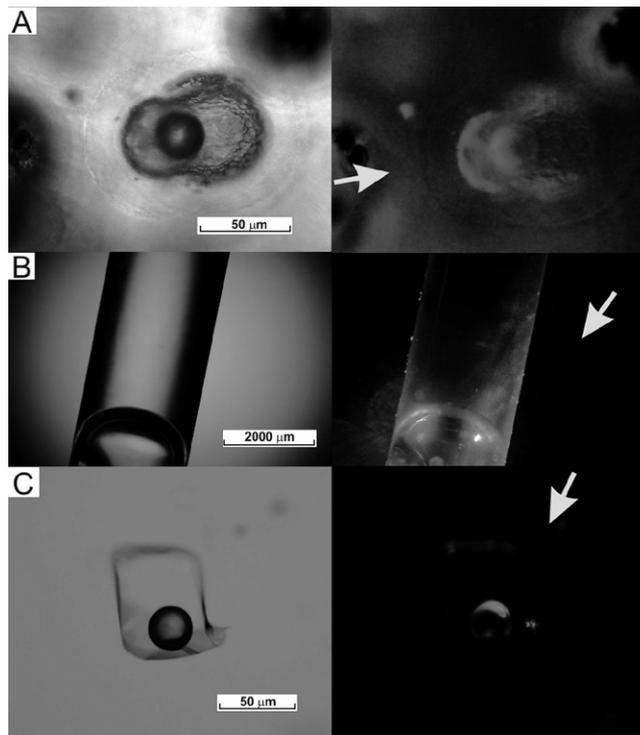
Microthermometric experiments with the fluid inside the vacuoles showed its unusual behavior compared to typical quartz-hosted aqueous inclusions. During cooling the fluid freezes and becomes opaque at −60 to −80 °C (Fig. 3B). Consecutive heating produces a liquid within the temperature interval of −60 to −35 °C. Such low temperatures of ice thawing may correspond to the eutectic temperatures (Fig. 3C) of aqueous systems containing chlorides of Na, Ca, and Fe (e.g., Borisenko, 1977). The ice melts completely at temperatures from −18.9 to −9.6 °C, thus indicating concentrations of salts corresponding to 13.5–21.6 wt% eq. NaCl (Brown, 1989). With further heating the vapor bubbles diminish in size and disappear at temperatures of 70–250 °C (Figs. 3D and 3E). Such a range in homogenization temperatures for the fluid in neighboring vacuoles may indicate different internal pressure and argue against the conventional mechanism of parental fluid entrapment in a growing mineral (Roedder, 1984). Unusual behavior of the fluid in the vacuoles is also
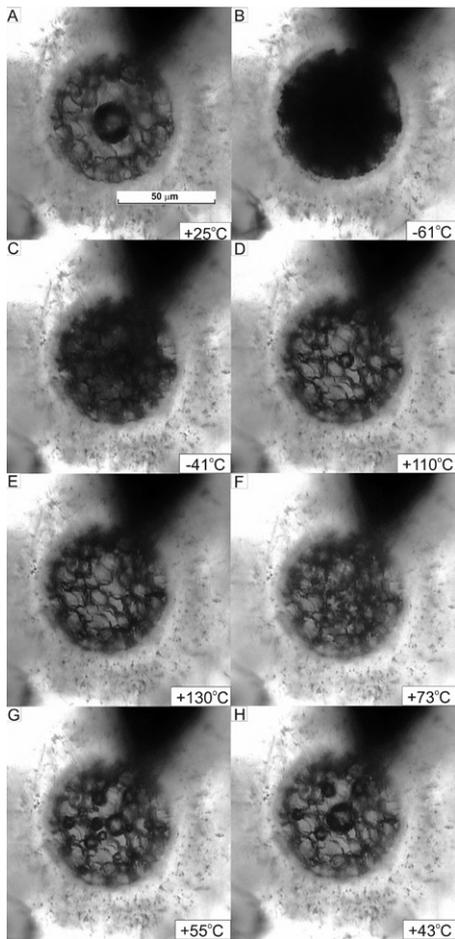
Figure 3. Snapshots in plane-polarized transmitted light showing phase transformations inside typical vacuole in chalcedony at room temperature (A), during experimental cooling (B, F–H), and heating (C–E).

Figure 4. Scattering of light (laser pointer, direction of illumination is shown by arrows) inside chalcedony-hosted vacuole (A), artificially made sol of silicic acid in glass capillary (B), and low-salinity aqueous fluid inclusion in hydrothermal quartz (C). Left-hand images were obtained in plane polarized light; right-hand images obtained by side laser beam illumination.

recorded during post-homogenization cooling when numerous small bubbles simultaneously appear throughout the whole volume of the fluid (Fig. 3F). The initial small bubbles gradually coalesce at constant temperature into bigger ones that continue to merge into a single bubble over several minutes to several hours (Figs. 3G and 3H). Coarsening of the bubbles also appears to occur through dissolution of smaller bubbles. Importantly, the resulting bubble has the same size as the original one, but may reside in a different location inside the vacuole.

Experimenting with a laser beam through the vacuoles' content shed additional light on the nature of the fluid hosted in the studied chalcedony. We used a laser pointer with a 657 nm wavelength as a source of light scattering (e.g., Van de Hulst, 1957) to illuminate the vacuoles in chalcedony. It is observed that significant light scattering occurs in the whole volume of the fluid except in a "shadow" zone behind the vapor bubble, which appears to strongly absorb light (Fig. 4A). For comparison, an artificially made sol of silicic acid, stored in a glass capillary,

shows exactly the same light-scattering effects (Fig. 4B). In contrast, a quartz-hosted aqueous saline two-phase inclusion (8.2 wt% eq. NaCl) is not illuminated by the laser beam, whereas light scattering can only be seen locally at the liquid-gas interface (Fig. 4C).

DISCUSSION

The main result of this study is recognition of large-sized fluid inclusions in chalcedony that was deposited in amygdules and fractures in a common basaltic rock. Several petrographic and compositional features of the studied inclusions make them distinct from aqueous solutions that are typically present in hydrothermal quartz. Firstly, the content of the fluid-filled vacuoles in chalcedony is clearly related to the volumetrically substantial chalcedony bands around every vacuole (Figs. 1B and 1C). Secondly, these concentric bands are structurally and compositionally variable, as shown by their CL brightness (Fig. 1B) and water abundance (Fig. 2). Thirdly, quartz crystals like those projecting into the fluid-filled vacuoles at the interface with chalcedony (Figs. 1C and 3) have never been observed in other studies of fluid inclusions. Finally, the appearance of numerous vapor bubbles during post-homogenization cooling of the fluid in the vacuoles and their sluggish coalescence (Fig. 3) testifies to a highly viscous environment that is atypical of true aqueous solutions. The results of the microthermometric experiments suggest that the content of the vacuoles is likely a sol of silicic acid. Formation of a hydrosol (mixture of a colloidal solution of polysilicic acids) relates to the presence of reactive silanol groups

SiOH in an aqueous medium that undergo polycondensation. If this is the case, relatively large molecules of polysilicic acid in such solution are surrounded by oriented water molecules to form electroneutral micelles that hinder adhesion of the vapor bubbles (Figs. 3G and 3H). In alkaline environments, such a hydrosol is thermodynamically stable and can exist for millions of years without coagulation. Our conclusion about the colloidal nature of the vacuoles' content is seemingly supported by the experimental laser beam scattering (Fig. 4).

We envisage that the studied chalcedony formed from post-magmatic aqueous fluid containing significant abundances of dissolved silica. Cooling of such fluid resulted in the silica solubility being reduced, followed by separation of colloidal silica that was mainly responsible for the spherical aggregates (layered chalcedony with central vacuoles; Figs. 1B and 1C). Notably, their spherical shape suggests that the gel-like substance was immiscible and formed prior to solidification of chalcedony in the amygdule. The studied vacuoles filled with a silica hydrosol together with banded chalcedony around them (Figs. 1B and 1C) appear to represent one entity that evolved through layered deposition of water-bearing chalcedony inwards (dark in CL in Fig. 1B; region 1 in Fig. 2), followed by increasing H_2O abundances in the closed system. The residual aqueous fluid with a shrinkage bubble, residing in the central parts (vacuoles) of each spherical aggregate (Figs. 1C and 3), is still characterized by distinctive "silica-gel" properties (Fig. 4A), whereas the adjacent bands of chalcedony are significantly dehydrated (region

2 in Fig. 2) possibly due to water extraction into the central cavity.

In conclusion, this paper documents silica textures and properties in an analogous system (cooling volcanic rocks) and thus provides implications for ore-forming systems, in particular epithermal ores that are important precious-metal producers worldwide. The colloidal silica appears to be instrumental in stabilizing colloids of sulfides and native metals, promoting their transport and accumulation in ore-forming systems (e.g., Hannington et al., 2016; Herrington and Wilkinson, 1993; Saunders, 1990, 1994; Saunders and Schoenly, 1995). The colloidal nature of fluids forming natural chalcedony also confirms experimentally predicted "silicothermal fluids" (Wilkinson et al., 1996). The previously overlooked or neglected role of hydrothermal colloidal silica should be revisited for many quartz- and chalcedony-hosted ore deposits in igneous, sedimentary, and metamorphic rocks.

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