

Formation of coagulated colloidal silica in high-temperature mineralizing fluids

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ABSTRACT

Recent experimental studies have suggested that colloidal silica can form in high-*T* (300 to >700°C) hydrothermal fluids (Wilkinson *et al.*, 1996). Natural evidence in support of this was found by Williamson *et al.* (1997) who proposed a colloidal (gel) silica origin for <50 µm irregularly-shaped inclusions of quartz contained in greisen topaz from southwest England. Confocal and microprobe studies, presented here, strengthen this argument although rather than forming a gel in the hydrothermal fluid, it is suggested that the colloidal silica aggregated as a viscous coagulated colloid, with much of its volume (<10 to 30 vol.%) consisting of metal (mainly Fe) -rich particles. This is evident from the largely solid nature of metal-rich shrinkage bubbles contained at the margins of the inclusions of quartz which shows that the material forming the inclusions contained much less liquid than would be expected in a silica gel. These findings may have important implications for models of ore formation since the precipitation of a coagulated colloid could inhibit hydrothermal fluid transport and cause co-deposition of silica and entrained ore-forming elements. The mode of formation of the colloidal silica and further implications of the study are discussed.

KEYWORDS: silica, colloid, hydrothermal, ore genesis, supercritical fluids.

Introduction

THE formation of colloidal silica has been widely discussed in low-*T* (<200°C, Saunders, 1990; Hopkinson *et al.*, 1998, 2000) and, rarely, medium-*T* (<400°C) hydrothermal systems (e.g. Herrington and Wilkinson, 1993). Until recently, there has been much less direct natural or experimental evidence for the formation of colloidal silica in higher-*T* (>450°C) hydrothermal fluids. Williamson *et al.* (1997) suggested a colloidal silica (gel) origin for irregularly shaped inclusions of quartz, containing metal-rich multiple shrinkage bubbles, found in greisen topaz from southwest England. At about the same time as the greisen studies, Wilkinson *et al.*

(1996) presented experimental data in the system K₂O-CO₂-SiO₂-H₂O (300 to >750°C, <200 MPa). An immiscible K-Si-rich (~90 wt.% SiO₂) fluid was found to coexist with alkaline aqueo-carbonic fluids and quartz. The silica-rich fluid was trapped as synthetic fluid inclusions in quartz. These inclusions have irregular ‘plastic’ morphologies, due to being trapped as a viscous fluid, which are remarkably similar to the natural inclusions (now composed of quartz) studied by Williamson *et al.* (1997).

In the current paper we present additional textural and geochemical evidence for the formation of colloidal silica in greisens within the Hensbarrow topaz granite stock, Cornwall, and discuss the consequences for the hydrothermal transport of ore-forming elements. Throughout the paper the following definitions for colloidal silica and silica gel will be used, taken from Iler (1979); ‘colloidal silica’ is ‘stable dispersions or sols of discrete particles of

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amorphous silica'; "silica gel" is a 'coherent, rigid three-dimensional network of contiguous particles of colloidal silica'; "coagulation" is 'where the particles come together into relatively close-packed clumps in which the silica is more concentrated than in the original sol, so the coagulum settles as a relatively dense precipitate'.

Geological setting and petrography

The geological setting and petrography of the Hensbarrow topaz granite of southwest England are detailed in Bray and Spooner (1983) and Williamson *et al.* (1997), and references contained therein, and a short summary of this is presented below. Greisens in the Hercynian Hensbarrow topaz granite mainly occur as <10 cm wide alteration zones at the margins of tourmaline-quartz and mineralized veins. They mainly consist of quartz and mica with topaz and tourmaline and were largely formed as a result of the flow along fractures of acid high temperature post-magmatic fluids (rich in F, B and Li) which reacted with granite wall rocks. They often contain cassiterite, wolframite and a range of copper and copper-tin sulphide minerals. Topaz in the greisens contains up to 30 to 40 vol.% of a varied suite of fluid and mineral inclusions, including quartz, albite, K-feldspar, zinnwaldite, muscovite, columbite, apatite, zircon, ilmenorutile, qitianlingite [(Fe,Mn)₂(Nb,Ta)₂WO₁₀] and varlamoffite [(Sn,Fe)(O,OH)₂].

Aqueous fluid inclusions in the topaz show liquid-vapour homogenization temperatures of 300 to >500°C and are highly saline (23 to 30 wt.% NaCl equivalent), some showing critical homogenization behaviour (Williamson *et al.*, 1997). The homogenization temperatures and moderate to high salinity are typical of early, granite-derived, hydrothermal fluids in the Cornubian batholith (Rankin and Alderton, 1985; Alderton and Harmon, 1991). These initially formed at pressures greater than ~1 kbar (e.g. Alderton and Rankin, 1983; Yucheng, 1989). With this composition and under these conditions the hydrothermal fluid would have existed as a supercritical, single-phase fluid (Sourirajan and Kennedy, 1962). In greisen quartz, fluid inclusions show generally lower homogenization temperatures (150 to 450°C, at pressures of ~250 bar), a much wider (trimodal) distribution of salinities compared with those in the topaz, and vapour-rich inclusions associated with higher-

salinity inclusions, interpreted as evidence of boiling (Yucheng, 1989; Yucheng *et al.*, 1989). From this, and from textural evidence, it is likely that the quartz formed later than the topaz, below the critical point at lower pressures and temperatures and during episodes of boiling.

Previous evidence for colloidal silica formation in greisens from SW England

Williamson *et al.* (1997) showed that topaz from the greisens at Hensbarrow contains a high proportion of inclusions of quartz, identified as such from electron probe micro-analysis (EPMA) and laser Raman microspectroscopy. Such inclusions of quartz have not to our knowledge been documented in other, non-greisen or quartz-topaz rock, geological settings. The inclusions largely consist of what appears to be a single crystal of quartz and are generally <50 µm in size, and rarely up to 100 µm. They show bottle, wisp and bleb-shape morphologies and contain dark brown multiple shrinkage bubbles, usually at their margins (Fig. 1a). The inclusions may form closely-spaced masses, occasionally in equal proportions to surrounding topaz, or isolated, randomly distributed single inclusions within topaz. They are often concentrated in bands at the margins of topaz grains. From EPMA of the shrinkage bubbles and laser ablation ICP-AES analyses of the entire inclusions of quartz, the shrinkage bubbles are known to be rich in Sn, Fe, Mn, S and Cl. Some of this material has similar compositions to varlamoffite, which often forms a major (up to 90%) component of the mineralized veins of the area. Other solids contained within the inclusions are likely to be pyrrhotite from their chemical composition (Williamson *et al.*, 1997) and morphology. Rare inclusions of quartz contain, or are attached to, euhedral crystals of albite, K-feldspar or stannite (Cu₂FeSnS₄), which are commonly up to 40 µm in size.

Inclusions which appear identical to those of quartz in topaz have been described by Eadington and Nashar (1978) in quartz-topaz rocks from the New England Batholith, Australia, and interpreted as silicate melt inclusions. According to Williamson *et al.* (1997), the Hensbarrow topaz-hosted quartz inclusions cannot have originated from a Si-rich melt since production of a quartz melt would require temperatures far in excess of those consistent with post-magmatic greisen-forming fluids (~500°C). The wisp and bleb-like morphologies were interpreted as indicating

formation from material which was once plastic in nature. In the absence of any other known viscous

Si-rich material in high-*T* hydrothermal fluids, the inclusions of quartz were interpreted as having crystallized from silica gel which was trapped within the topaz host. This theory was also used to explain the presence of the metal-rich multiple shrinkage bubbles in that silica gels have open structures which may trap a variety of chemical species (Saunders, 1990). During crystallization of this material to quartz, incompatible elements would be partitioned to grain margins to form the multiple shrinkage bubbles (Williamson *et al.*, 1997).

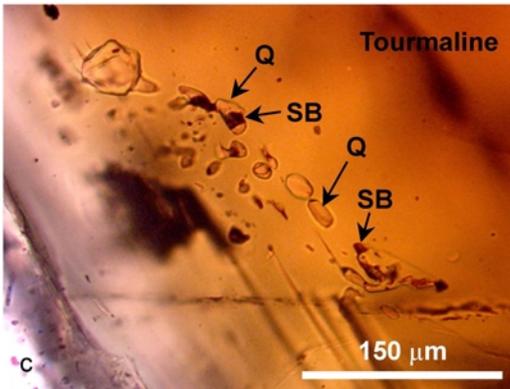
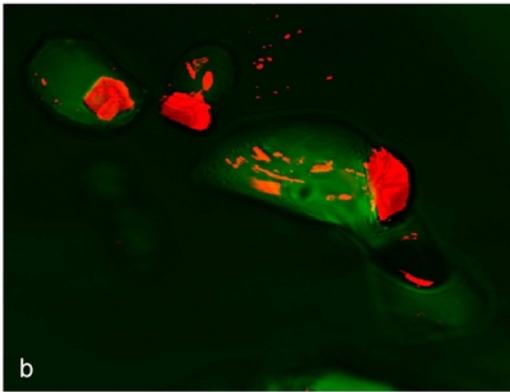
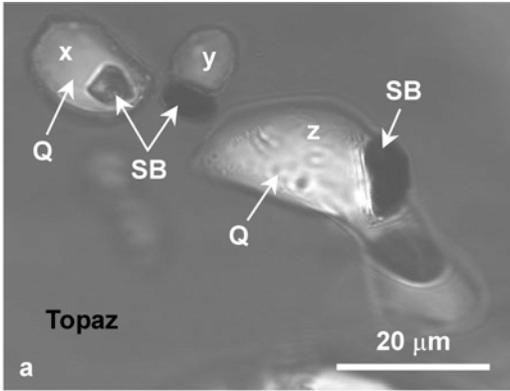


FIG. 1. High-power photomicrographs of inclusions of quartz (labelled x, y and z) in topaz in (a) transmitted light and (b) by laser confocal microscopy. (c) Photomicrograph of inclusions of quartz in tourmaline from massive quartz-tourmaline rocks at Roche. Q = inclusion of quartz, SB = shrinkage bubble.

Analytical methods

Quantitative EPMA of the quartz inclusions for low levels of Al (Fig. 2) and other elements was carried out on an automated WDS Cameca SX50 microprobe at an accelerating voltage of 20 kV, a beam current of 40 nA and a spot size of ~1 μm. For Al, a corundum standard was used which yielded a theoretical detection limit (d.l.) of 0.006 wt.% (Fig. 2). For Fe, the only other element detected, the theoretical detection limit was 0.002 wt.%, using an olivine standard. Inclusions >20 μm in size and depth were analysed to ensure no penetration of surrounding or underlying phases, respectively. Qualitative analysis for mineral inclusion identification was carried out using an Hitachi S2500 SEM with Link AN10000 energy-dispersive analyser. Confocal images were obtained using a Carl Zeiss Laser Scanning Microscope, Model 410. The inclusions of quartz in Fig. 1a were imaged in 3-D by stacking up horizontal 2-D images

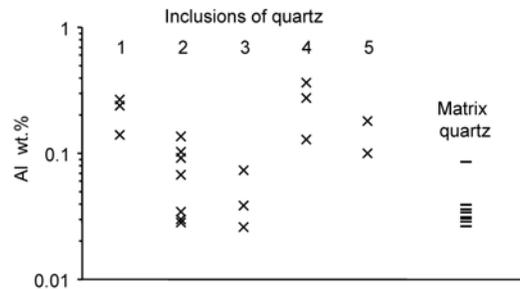


FIG. 2. Al concentrations in five inclusions of quartz in topaz compared with Al concentrations in greisen matrix quartz from Hensbarrow, southwest England. Detection limit for Al in quartz was 0.006 wt.%, estimated as $\frac{3}{M} \sqrt{\frac{CR_b}{CT_b}}$, where M = counts/second/% element on the standard, CR_b = count rate on background and CT_b = count time on background on sample.

taken at different depths below the surface of a doubly-polished rock wafer (see composite image in Fig. 1*b*).

Results

From EPMA studies of the inclusions of quartz, the main element consistently and significantly above detection limits was Al. Aluminium in natural quartz may be present in concentrations from <0.0013 to 1.5 wt.% (Smith and Steele, 1984). The inclusions of quartz show highly variable and generally larger (<0.4 wt.%) concentrations of Al compared with the greisen matrix quartz (Fig. 2). Individual inclusions show a relatively restricted range of Al contents. However, there are major differences between inclusions. Iron was the only other element detected, 0.005 to 0.04 wt.% in the inclusions of quartz and <0.027 wt.% for matrix quartz. There was no significant difference in the spread of Fe contents between the inclusions of quartz and matrix quartz, with both having average Fe contents of ~0.015 wt.%.

From confocal imaging, the shrinkage bubbles at the margins of the inclusions are opaque and appear to be solid in nature. The volume fraction of fluid to metal-rich material and to quartz in the inclusions is impossible to estimate with any certainty, and varies greatly between inclusions. However, from observations of a large number of inclusions of quartz, the dark brown material usually does not exceed more than ~10 to 30 vol.%. If present, and none has been positively identified, the volume fraction of fluid would appear to be less than a few percent, although this is very difficult to judge given the complex distribution of metal-rich material in the shrinkage bubbles.

The confocal image in Fig. 1*b* also reveals the distribution of metal-rich material within the inclusions. In inclusion z, it is mainly concentrated at one end, forming a series of stacked dish-shaped layers, which conform to the rounded end of the inclusion. Parallel to the long axis of inclusion z, are linear, thin trails of opaque metal-rich material, <5 µm wide. Inclusions x and y also contain platy material, although this appears to show different orientations with respect to the long axes of the inclusions, compared with inclusion z.

The confocal 3-D image in Fig. 1*b* was rotated using computer software to confirm the platy nature of the solids in the multiple shrinkage bubbles and to confirm that the inclusions of

quartz are not related to annealed microfractures, as would be suggested by the presence of secondary fluid inclusion trails.

Discussion and conclusions

One of the most important considerations in establishing the presence of colloidal silica in the hydrothermal fluid is whether the material in the inclusions of quartz crystallized post-trapping within the topaz host. If it did, then in the absence of any other likely silica-rich fluid during greisen formation, the material in the inclusions must have crystallized from colloidal silica. If post-trapping crystallization cannot be proven then the possibility remains that the inclusions represent trapped mineral phases, or co-precipitated minerals, although this is considered unlikely since they would be expected to be trapped with fluids similar to those found in primary aqueous inclusions, rather than the metal-rich material found within the multiple shrinkage bubbles (Williamson *et al.*, 1997).

From the confocal image in Fig. 1*b*, the metal-rich material in inclusion z can be seen to be platy and dish-shaped, conforming with the rounded end of the inclusion. An incidental mineral inclusion would not be expected to have taken on such a shape. The metal-rich material must have crystallized *in situ* and after trapping. Too little aqueous fluid was trapped within the inclusion of quartz for the Fe-rich material to have possibly crystallized from this. The presence of the Fe-rich material cannot be circumstantial, e.g. as a composite mineral inclusion, as it is associated with countless numbers of such inclusions of quartz within the greisens.

That the quartz in the inclusions of quartz crystallized after trapping is evident from the thin trails of opaque material smeared out along the length of inclusion z. The trails are interpreted as being orientated parallel to the direction of crystal growth of the silica phase (now quartz), from the left hand end to the right hand end of the inclusion. As crystal growth advanced through the inclusion, so deposition/crystallization of incompatible metal-rich material occurred in parallel along the walls of the inclusion. The bulk of incompatible material was then deposited at the end of the inclusion (right hand side) as the metal-rich shrinkage bubble.

No textural evidence can be found within the quartz of the inclusions for a former colloidal precursor, such as the chalcedonic spherules and

spheroidal inclusion-rich quartz cores found in mesothermal quartz veins (see Herrington and Wilkinson, 1993). As explained later, this is probably due to the quartz having crystallized from cristobalite which itself crystallized directly from the gel precursor, with no lower-order polymorph intermediate phases. The trace element composition of the quartz, however, does support a colloidal precursor, although it cannot provide unequivocal proof. From the microprobe studies, the inclusions of quartz show higher and variable Al contents compared with greisen matrix quartz. This, together with earlier fluid inclusion and textural evidence (Williamson *et al.*, 1997), suggests that the inclusions of quartz are an earlier generation compared with the greisen matrix quartz. The variable and relatively high Al contents are consistent with an origin from a heterogeneous and rapidly-formed colloidal silica precursor. Heterogeneities could result from differing conditions of polymerization and variations in density of the colloidal silica (variably open structure) resulting in different levels of incorporation of contained (non-silica) elements.

A wide variety of evidence has now been presented here, in Williamson *et al.* (1997) and Wilkinson *et al.* (1996) for the formation of colloidal silica in high-*T* hydrothermal fluids. We believe that no other known process or processes can explain the textures observed in the inclusions of quartz.

Clues as to the nature of the colloidal silica can be derived from the confocal imaging and light microscopy. Williamson *et al.* (1997) considered that due to the 'plastic' morphologies of the inclusions, the colloidal silica is likely to have formed a gel prior to trapping in the topaz. However, the estimated few vol.% of fluid component in the inclusions of quartz, from the imaging studies, is less than would be expected in a gel. Gels may contain between 25 vol.% pore space (fluid phase), for densely packed gels, and 95 vol.% or more for gels with an open structure (Iler, 1979). The most likely explanation for the small volume of fluid in the multiple shrinkage bubbles is that the gel aggregated, expelling much of the remaining aqueous fluid, to form a coagulated colloid (termed a "dense gel" by Saunders, 1990). Much of the pore space in the coagulated colloid would have been filled by amorphous or crystalline metal-rich particles of varying size (rather than aqueous fluid) represented by the <10 to 30 vol.% metal-rich material

in the inclusions of quartz. The aqueous fluid from which the coagulated colloid separated may have been trapped in adjacent fluid inclusions.

The crystallization of coagulated colloid, with concomitant partitioning out of incompatible elements to the margins of the inclusion, is likely to have involved at least one phase transformation. Detailed experimental studies on the decomposition of feldspars by acid solutions via reactions such as: $3\text{KAlSi}_3\text{O}_8$ (microcline) + 2H^+ = $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ (muscovite) + 6SiO_2 (amorphous) + 2K^+ (between 300 and 600°C, 1 kbar), showed that the first phase to crystallize from the amorphous silica was cristobalite, which is metastable and is rapidly recrystallized to quartz (Zaraiskii, 1999). Alteration of granite feldspar during greisen formation is ubiquitous in the Hensbarrow granite. Within the inclusions of quartz, the common occurrence of the multiple shrinkage bubbles at one apex suggests that the cristobalite nucleated at the opposite side, and progressively crystallized outwards from this point through the rest of the inclusion. Recrystallization to quartz from the more open structure of cristobalite would have led to a further partitioning out of incompatible elements. Where an inclusion of quartz contains several multiple shrinkage bubbles distributed within it (e.g. Fig. 2c in Williamson *et al.*, 1997), there may have been multiple cristobalite nucleation sites. The direct crystallization of cristobalite from amorphous silica, with no lower-order silica polymorph intermediate phases, explains the lack of other textural evidence for a gel precursor.

Why quartz inclusions of this type have not been more widely reported is difficult to say with certainty. They may have been overlooked or could be difficult to recognize due to the mineralogy of vein and replacement deposits being dominated by quartz, the inclusions being virtually invisible or disappearing altogether during recrystallization. The identification of metal-rich shrinkage bubbles, similar to those described here, may indicate their presence. It is also possible that at least some of the matrix quartz in such greisens may have crystallized from colloidal silica and therefore inclusions of quartz would not be present at all.

Rare inclusions of quartz, similar to those found in the topaz, have now been identified in tourmaline from southwest England (Fig. 1c). They are, however, fairly rare in tourmaline and do not seem to occur in other greisen minerals. This may be due to these phases being unable to

preferentially trap coagulated colloidal silica or that the colloidal silica was only present in the hydrothermal fluid during the crystallization of certain phases.

The discovery of inclusions of quartz in tourmaline may be of interest in mineral exploration since tourmaline is associated with many types of ore deposits, including some of the largest copper porphyry systems. If present, the characterization of material contained within their multiple shrinkage bubbles could yield information on the nature and ore-forming capacity of hydrothermal fluids at different structural levels or during different stages of ore deposit evolution. For example, due to its viscous nature and high density, the metal-charged coagulated colloid is likely to be rapidly deposited compared with any likely fluid component (depending on flow rate). This would provide an efficient mechanism for co-deposition of silica and ore-forming metals and the process may inhibit further fluid flow in hydrothermal conduits.

Non-geological applications

The formation of colloidal silica in high- T hydrothermal fluids is not only important geologically, but may also have unforeseen industrial applications. Colloidal silica has many low- T industrial uses, for example as catalysts and in the manufacture of superconductors, high-purity glasses and ceramics (Jones, 1989). The use of supercritical colloidal fluids has yet to be explored although any applications are likely to be relatively specialized due to the increased manufacturing costs in this type of environment. Possible future applications may be as sealants for high- T joints, where glass-ceramic frits are currently used, as they are likely to be more penetrative and homogeneous than current, higher-viscosity sealants. This may be of particular interest in the aeronautic and space industries. Also, the preparation of colloidal particles in supercritical fluids is of current interest from a safety and environmental viewpoint. Supercritical fluids make excellent solvents which, if aqueous in nature, rather than being organic-based, produce no toxic fumes and are considerably less volatile.

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