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Petrography and chemistry of SiO₂ filling phases in the amethyst geodes from the Serra Geral Formation deposit, Rio Grande do Sul, Brazil

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1. Introduction

Geode and fracture filling by siliceous phases occurs in distinct geological settings all over the world. Among them, deposits of amethyst, the violet variety of quartz, are attractive and important for the precious stone industry. The color of amethyst is attributed to ferric iron incorporation within the quartz structure (Cox, 1976; Rossman, 1994) and can be reproduced in experimental growth of synthetic stones (Balitsky et al., 2002). The conditions of natural amethyst deposits are however not completely understood, in particular the geode filling in basalt flows which probably represents the most spectacular occurrence. The observation of an amethyst-bearing geode raises important questions about the source of silica, the transportation vector, and the factors which control the deposition inside the geode rather than in the fracture framework of the host basaltic rocks.

The deposition temperature is important for the understanding of water–rock interaction processes. However, it does not seem to be a fundamental controlling factor. Indeed, previous studies on south Brazilian geodes reported very different temperatures ranging from 370–420 °C (Thomas and Blankenburg, 1981) down to 50–80 °C (Juchem et al., 1994; Gilg et al., 2003). In all studied occurrences, the geodes frequently exhibit the same organization of silica infilling from the wall to the center of the cavity: (1) a chalcedony rim, followed by (2) colorless quartz commonly displaying a progressive grain size increase and (3) amethyst.

The Serra Geral Formation is a famous site for amethyst production and has been the object of various studies. The geological context and the post-magmatic alteration of the basalts have been studied by Gomes (1996), Scopel (1997) and Schenato et al. (2003), and the vesiculation and formation of the geodic cavities, by Proust and Fontaine (2007a). More recently, Duarte et al. (2009) attributed the origin of the giant cavities to brittle fracturing and hydrothermal dissolution. Theories on the filling process vary from diagenetic reactions (Gilg et al., 2003) to post-magmatic events (Thomas and Blankenburg, 1981). Gilg et al. (2003) interpreted fluid inclusion data as indicative that geode filling occurs at low temperatures, probably less than 50 °C. They proposed the infiltration of meteoric waters through underlying Botucatu sandstone, and further dissolution of the highly reactive interstitial glass of the host basalts as the main mechanism of silica source, transport and deposition. By contrast, Proust and Fontaine...
(2007b) proposed a magmatic/hydrothermal origin of the fluids, based on silica mass balance calculations in the altered and unaltered host basalt and on primary fluid inclusions in the amethyst crystals indicating temperatures between 152 and 238 °C.

In previous studies, a large part of the available data on geodes formation, except the fluid inclusion studies, is related to the basaltic host rock, or accessory calcite locally associated with silica minerals, but not on the SiO$_2$ phases. The present study focuses on these SiO$_2$ phases themselves, using several independent approaches in order to better constrain the process of geode filling. For that, detailed petrography, image analysis, fluid inclusion microthermometry, ICP-MS and Sr isotope analysis, on geode samples from Serra Geral Formation basalts (southern Paraná Basin, Brazil) were performed.

2. Geological setting

The Alto Uruguai region, located in northern Rio Grande do Sul State, is known for its huge amethyst-bearing geode deposits and is described as one of the most important source of amethyst in the world (Bossi and Caggiano, 1974). The mineralization occurs in basaltic rocks of Serra Geral Formation in the Paraná Basin (Fig. 1). This formation comprises continental flood basalts related to the volcanic activity which occurred on the South American platform during the South Atlantic Ocean opening at about 138–127 Ma (Jurassic–Cretaceous transition). Serra Geral magmatism is represented by tholeiitic basalts and basaltic andesites, which are locally overlain by rhyolites and rhyodacites (Peate et al., 1992; Turner et al., 1994). In this area, a 360 m thick sequence of twelve basaltic flows was described (Gomes, 1996). Three zones were identified in each flow: upper and lower vesicular, corresponding to the top and base of the flow, respectively, and a thicker central zone. Alteration processes on this basaltic sequence were discussed by Scopel (1997), who reported celadonite and saponite (C/S) in both vesicular and central zones. C/S is also widespread, showing variation to interstratified chlorite layers from 20% in the inner part of the flow, due to higher porosity and permeability of the rock. The vertical mineralogical variation from the margins to the inner part of the flow was attributed to a conversion from the initially precipitated saponite to C/S in the inner part of the flow, where temperature remained elevated for a longer time. The compositional changes in clay minerals, combined with other mineralogical characteristics, were interpreted as resulting from low-grade metamorphic conditions during the burial process. However, clay mineral distribution in Alto Urugai basalts does not follow the same zoning as described by Schenato et al. (2003). These characteristics can be probably attributed to local discrepancies between both geological settings: Estância Velha basalt directly overlies Botucatu sandstones, representing the first lava flow of a 350 m pile.

The most striking feature of basalts from Alto Urugai is the presence of a macrovesicular level in the central zone, characterized by partially filled geodes. This level was identified by Gomes (1996) in four lava flows of this sequence. Geodes are commonly elongated, ovoid or rounded cavities with sizes ranging from decimetric to metric. The mineralization occurs along the cavity walls as a succession of centimetric layers of different silica mineral varieties. The typical mineralization sequence is composed of microcrystalline quartz (mainly chalcedony) followed by colorless quartz and finally amethyst. Commonly, the geodes contain only two of these mineral phases, or else display a repetition of some of them, with two or more layers of colorless quartz or amethyst. Calcite frequently occurs in association with silica minerals, showing either massive forms or well-formed rhombohedral crystals. Gypsum and, less frequently, barite can also be found crystallized upon amethyst. They probably represent a later depositional event.

Geodes studied in this work come from three different basaltic flows containing distinct mineral associations: (1) silica minerals; (2) silica minerals + calcite and (3) silica minerals + gypsum.

3. Petrography

SEM/EDS analyses performed on a sample of the host rock in contact with the cavity wall show small tabular crystals of pyroxene and plagioclase, and minor quantities of K-feldspar, quartz and acicular Ti-magnetite. A general decrease in grain size near the contact with geodes, and the presence of quartz and K-feldspar patches constituting the mesostasis were previously reported by

![Fig. 1. Localization map. Left: schematic representation of Paraná Basin in South American Platform; right: distribution of Serra Geral Formation volcanic rocks in Rio Grande do Sul State (Brazil), and studied area (Alto Uruguai region), located at the northern extremity.](image-url)
Gomes (1996). Strong dissolution features are observed at the contact between minerals from the host rock and silica minerals inside the geode. This zone is characterized by a mixture of tiny anhedral crystals of igneous pyroxene and Ti-magnetite, and chalcedony (Fig. 2). Based on these general observations, there is no mineralogical clue for the cause of silica deposition inside the geodes.

Hopkinson et al. (1999) reported the occurrence of chalcedony in association with Fe oxyhydroxides in a submarine hydrothermal breccia. The authors suggest that precipitation of chalcedony was catalyzed by ferric compounds, since ferric iron has been described, in similar hydrothermal environments, as a catalyst for silica deposition (Oehler, 1976; Williams and Creer, 1985).

In transmitted light microscopy, chalcedony is characterized by twisted fibers distributed radially and frequently forms spherulites. The fibers are elongated perpendicular to the c-axis and the periodic twisting around the c-axis produces an alternating extinction along the length of the fiber. Thin layers of microcrystalline granular quartz are intercalated with chalcedony at irregular intervals giving rise to the banded structure. Chalcedony is overlain by tiny (few μm) anhedral crystals of colorless quartz lacking preferential optical orientation. From the outer to the inner part of the quartz layer, the size of crystals will increase while their number will decrease (Fig. 2). Frequently, colorless quartz crystals reach cm-size dimensions. The transition from quartz to amethyst may be gradual or abrupt, and is characterized by the presence of well-formed crystals composed of a short prism m and the rhombohedral faces r and z. Amethyst crystals, in general, reach diameters of one cm or more.

SEM images of the geode minerals show the presence of massive calcite in association with chalcedony. The formation of these two minerals seems coeval. Euhedral calcite crystals are also found in the chalcedony layer showing dissolution features at these margins. Small amounts of Mn can be detected in zoned calcite by EDS.

In some samples, celadonite is identified in association with silica minerals and calcite. In the chalcedony layer, collomorphic celadonite is zoned and frequently associated with Fe-oxide/hydroxide, probably goethite (Fig. 2, bottom). EDS analyses performed on zoned celadonite reveal subtle variations in the Fe-content. The relationships between calcite and celadonite suggest that calcite was formed prior to celadonite. Well-formed celadonite crystals associated with Fe-oxide are also identified in a 100 μm cavity inside an amethyst crystal. This feature suggests that celadonite was formed during the whole growth process of silica minerals, since it can be found at different stages in the sequence.

Thin veins of fluorite seal microfractures intersecting the quartz crystals, and can also occur as inclusions in amethyst. However, fluorite seems to have a more restricted or local occurrence, since it was not found in all samples.

4. Image analysis

Previous work on crystal growth has shown the importance of the size and the geometrical arrangement of crystals for the interpretation of the growing process (Grigor’ev, 1965; Eberl et al., 1998; Kile et al., 2000). The variation on both, the number and the size of crystals with the distance from the initial growth surface (substratum), is essential to characterize the growth mechanism of silica minerals in the geodes. This is investigated here using a two-dimensional approach by image analysis of both the texture and the arrangement of quartz crystals in thin section.

Samples were cut parallel to the c-axis of major crystals of amethyst present at the end of the sequence. 150 μm thick doubly-polished sections corresponding to the silica mineral sequence of chalcedony, colorless quartz and amethyst were made. In order to reveal crystal boundaries, digital images were acquired under polarized light at two scales: (i) direct scanning of the sections placed between two polaroid films crossed at 120° and (ii) for a detailed study of the transition from chalcedony to colorless quartz, on a petrographic microscope under polarized light. Quartz and amethyst grain boundaries were highlighted by hand using Adobe Photoshop® software and converted to binary images. The microcrystalline character of chalcedony prevents its individualization as grains and fibers; then, this layer was considered as the substratum from which macrocrystalline quartz nucleated and grew. The

Fig. 2. Upper left: photomicrograph showing contact between chalcedony (top) and colorless quartz (bottom) layers. Chalcedony is well characterized by fibrous habit constituting spherulites. Upper right: BSE image showing contact between basalt and geode. Dissolution features are seen in minerals from the host rock (pyroxene, plagioclase), and a complex aggregate of chalcedony and calcite marks the transition zone. Bottom: two examples of zoned collomorphic celadonite associated with Fe-oxide/hydroxide within the chalcedony layer.
substratum morphology has a strong influence on the distribution and arrangement of grains during the growth process (Rodriguez-Navarro and García-Ruiz, 2000).

To determine the grain distribution as a function of the distance from the substratum, a routine was written and implemented in the Micromorph™ software. Basically, the program starts from two binary images: an image of the chalcedony substratum, and an image of the skeletonized grain boundaries of quartz and amethyst. First, from the image of the substratum, a sequence of equidistant lines was generated by successive dilations of the substratum toward the centre of the geode. From this process, the distance between any points of a given line and the substratum is constant. The distance between two successive lines can be specified according to the required degree of refinement. Second, these lines were superimposed to the grain boundary images, dividing each line into a set of segments. Damaged grains localized at the border of the sample were not counted. From each line, the number and the intersected widths of individual grains were stored in a file.

The changes in crystal frequency versus the distance from the substratum are presented in Fig. 3 for all analyzed samples. To allow a comparison between the curves, the number of crystals was normalized to the number of quartz crystals detected near the substratum for each sample. This diagram shows a progressive decrease in crystal frequency from the chalcedony substratum to the centre of the cavity. This behavior is in agreement with the model proposed by Grigor’ev (1965) for common growth ruled by geometrical selection of randomly oriented crystals. In this model, there is limited amount of space during growth of the first crystallites nucleated on the substratum. As they grow and contact each other laterally, only the crystals with the direction of maximum growth rate oriented perpendicularly to the substratum surface may grow continuously with a supply of nutrients during silica precipitation. Both the decreasing number of crystals and the columnar arrangement of the coarser crystals, which have been measured or observed in the amethyst geodes, are diagnostic features indicated by Grigor’ev (1965) for crystal growth controlled by geometrical selection. It should also be noted that the quantitative results obtained in this study agree fairly well with theoretical modeling of crystal distribution in druse quartz (Rodriguez-Navarro and García-Ruiz, 2000). Other growth mechanisms, such as constant-rate nucleation or Ostwald ripening, would show quite different distributions on both the number and the size of the quartz crystals along a given sequence (Eberl et al., 1998; Kile et al., 2000).

The main result coming from the textural analysis of quartz grains composing the major part of the silica minerals in the geodes is the demonstration that the sequence of quartz layers determined by petrographic analysis (i.e. colorless quartz and amethyst) results from a single nucleation event followed by a single growth process. The textural analysis clearly shows that the observed crystals did not result from dissolution-recrystallisation of previously deposited phases. In absence of textural analysis of the chalcedony layer, there is no evidence for any genetic link between the chalcedony and the quartz layers. However, no traces of dissolution or crystallization of other mineral phases were observed at the interface between chalcedony and the quartz layers. Moreover, the depositional sequence is repeated several times in some geodes. These observations strongly suggest that chalcedony belongs to the same event of silica deposition as quartz.

5. Microthermometry

Microthermometric analyses were carried out on a Chaixmeca stage (Poty et al., 1976). Calibration of the apparatus was performed using synthetic fluid inclusions composed of pure water (ice-melting temperature \( T_{\text{m}} = 0.0 \) °C and bulk homogenization temperature \( T_{\text{h}} \)) into the critical state \( = 374.1 \) °C) and an \( \text{H}_2\text{O} – \text{CO}_2 \) mixture \( T_{\text{m}}\text{CO}_2 = -56.6 \) °C and \( T_{\text{m}}\text{clathrate} = 10.0 \) °C). The accuracy is estimated to be ±0.2 °C at temperature lower than 20 °C and increases up to ±2 °C at 400 °C.

Both colorless quartz and amethyst crystals contain fluid inclusions either distributed in isolated groups or in small trails never crossing any growth zone (Fig. 4a). The later case is most frequent. Both occurrences indicate inclusion contemporaneous with crystal growth.

Fluid inclusions commonly occur as sets of globular, rounded or elongated cavities ranging from 5 to 20 μm in size, and sometimes as irregular cavities reaching 50 μm. At room temperature, most fluid inclusions contain a liquid phase (Fig. 4b). Rare two-phase (liquid + vapor) inclusions (Fig. 4c) occur associated along the same fracture with one-phase inclusions. These two-phase inclusions are often large irregular cavities (20–50 μm diameter) with a variable liquid-to-vapor ratio, but some smaller cavities can also show a vapor phase.

Since most inclusions are initially one-phase, formation temperatures were probably low, generally considered as less than 70 °C (Goldstein and Reynolds, 1994), but possibly as high as 130 °C (Krüger et al., 2009). Different methods were used to nucleate vapor bubbles. First, samples were stored in a refrigerator (at

![Fig. 3. Distribution of quartz crystals from 7 geodes. The diagram shows the decrease in number of crystals with the increasing distance from the substratum (chalcedony), indicating a continuous growth process ruled by geometrical selection.](image-url)
about −5 °C) during two weeks to induce bubble nucleation (Goldstein and Reynolds, 1994). However, very few inclusions showed a vapor bubble nucleation with such a procedure. Second, cooling down to −30 °C on a microthermometric stage was also performed, but was not successful. Finally, nucleation of a vapor bubble was also induced by freezing to −100 °C and rapid warming (about 50 °C/min) up to 0 °C.

All two-phase inclusions were heated up to homogenization, which always occurred to the liquid phase. Considering the very large scatter of measured homogenization temperatures (66–229 °C), we consider that these values have to be disregarded as to post-trapping enlargement of inclusions (stretching) which artificially increases homogenization temperatures.

Measurements of the ice-melting temperature ($T_{mi}$) were made according to the fluid inclusion assemblage (FIA) concept (Goldstein, 2003) and reported with distinct symbols in Fig. 5. In microcracks, $T_{mi}$ was measured only in two-phases inclusions because it can be interpreted in terms of salinity only if measured in the presence of a vapor bubble. Temperatures range from 0 °C to −3.6 °C with most data around −1.4 °C (Fig. 5). Moreover, most values lie between −2 °C and −0.4 °C. The ice-melting temperatures correspond to a liquid of low salinity, ranging from 0.9 to 5.6 wt.% eq. NaCl (Bodnar, 1993), mostly less than 3 wt.% eq. NaCl (Fig. 5). Distribution of $T_{mi}$ within FIAAs seems to reveal at least two different salinities, about 2 and 5.5 wt.% eq. NaCl. An eutectic transition was measured in one sample at −24 °C and indicates a solution dominated by NaCl. Salinity data are in agreement with Gilg et al. (2003), who reported low salinities of about 2 wt.% eq. NaCl.

All-liquid inclusions mostly dominate in the colorless quartz and amethyst crystals. This type of inclusion generally results from the entrapment of fluid of low/moderate temperature in a completely submerged environment. All-liquid inclusions are characteristic of low temperature formation environments, lower than 70 °C (Goldstein and Reynolds, 1994). Moreover, as almost all attempts to nucleate vapor bubbles have failed, temperature was probably below 40–50 °C.

Our results are consistent with data given by Gilg et al. (2003), who suggest amethyst geodes formed at low temperature from a low salinity fluid. Higher formation temperature as given by Proust and Fontaine (2007b) were not found.

Analysis by microthermometry was also performed on fluid inclusions in calcite crystals, co-genetic with chalcedony. Whereas data were very scarce, measurements gave similar results to those for quartz and amethyst. These inclusion studies suggest that the complete mineral sequence, including calcite (and probably chalcedony), colorless quartz and amethyst, formed in a very low temperature environment (less than 40–50 °C), completely submerged in water of low to moderate salinity (0.9–3.0 wt.% eq. NaCl), characteristic of a phreatic zone.

6. Silica chemistry

Chemical analysis of quartz is not easy due to the low element concentrations and the high resistance of quartz to classical acid digestion, but is now feasible with modern in situ techniques (e.g. laser ablation, SIMS). Chemical data for micro- and macrocrystalline quartz from different geological settings have been published in the last decades (Fallick et al., 1985; Perny et al., 1992; Watt et al., 1997; Larsen et al., 2000; Müller et al., 2003). However, chemical analysis of quartz from geodes and cavities associated with volcanic rocks are rare and the genetic constraints for these deposits are still imprecise (Flörke et al., 1982; Merino et al., 1995; Götz et al., 2001).

Silica minerals from Alto Uruguai geode deposits were analyzed with laser ablation ICP-MS in order to evaluate the homogeneity of quartz: (i) from crystal to crystal for a given geode, (ii) from one

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**Fig. 4.** Microphotographs of inclusions in quartz crystals. (A) Plane of pseudosecondary inclusions. (B) One-phase inclusions. (C) One of the two-phase inclusions associated with one-phase inclusions.

**Fig. 5.** Frequency histograms of fluid inclusion microthermometry. Left: $T_{mi}$ data obtained from quartz and amethyst from 6 geodes. Right: Salinity estimates from measured $T_{mi}$ ice.
geode to the next and (iii) from one lava flow to the next. Thirty-three analyses were carried out by using a laser ablation device (CETAT LSX-200, Nd-YAG 266 nm) coupled to a quadrupole ICP-MS Elan 6000 (Perkin Elmer SCIEX, LMTG Toulouse). The elements Al, Ca, Sc, Ti, V, Mn, Fe, Ni, Cu, Zn, Sr, Y, Ba, Ce, Pb and U were above detection limit in chalcedony and quartz (except Cu and Zn for quartz) and have been measured along 3.6 mm long lines on the polished and cleaned samples surface. The concentrations have been calculated for three geodes already analyzed by solution ICP-MS (Fig. 6), using Sr as the normalization element. The data display roughly the same pattern for the three minerals and show that there is no significant variability within a given geode, while a reproducible decrease in concentrations is observed from chalcedony through quartz to amethyst. This feature, also supported by raw data from four more geodes (not shown), can be related to the great differences of structural characteristics between the micro (chalcedony) and macrocrystalline quartz (colorless and amethyst). Chalcedony from different geodes shows significant variations in Al, Fe, Cu and Ba contents. The same heterogeneity in Al, Fe and Ba is observed in quartz, but at lower concentrations.

As mentioned here above, four geodes displaying the complete mineral sequence were selected for further investigation by wet chemistry. Chalcedony, quartz and amethyst from each geode were ground separately and approximately 0.8 g of the powdered samples was dissolved in ultra-pure, concentrated HF/HNO₃ mixture through the combined action of ultrasonic bath and high

Fig. 6. Elemental distribution for chalcedony, quartz and amethyst from 3 geodes representing different mineralized flows. Concentrations were calculated using Sr (also measured by wet ICP-MS) as internal standard.
temperature autoclaves. After silica digestion, residues were dried and then dissolved in 10 ml of distilled HNO₃ (2%) for conventional ICP-MS analyses, using In and Re as internal standards.

Among all of the analyzed elements, we focused on the REE. This family displays progressive chemical properties with particular characteristics for Ce tracing the low temperature oxidation conditions and Eu linked to the occurrence of igneous plagioclase. The REE pattern is here considered as a signature of the source of silica by assuming that REE were not significantly fractionated during the dissolution, transportation and precipitation of silica in the geodes. For a general overview, REE contents were compared to patterns reported in the literature for the host basalt and the regional Botucatu sandstone, which are two possible sources for silica (Gilg et al., 2003). The REE patterns for chalcedony, quartz and amethyst display quite similar V-shaped trends, with a pronounced Eu depletion, but clearly different from the host basalt and the Botucatu sandstone (Fig. 7). Small positive Ce and negative Eu anomalies appeared mainly on quartz and chalcedony patterns. The Ce anomaly is probably due to redox conditions and may be representative of near-surface formation. Indeed the presence of goethite and celadonite are good indicators of oxidizing conditions. The negative Eu anomaly, as well as the slight HREE enrichment, can be assigned to the basalt mesostasis, a likely source for silica. Indeed, the silica-rich mesostasis is the residual liquid after the early crystallization of the pyroxene, opaque minerals and plagioclase phenocrysts and is depleted in Eu and enriched in HREE. As mentioned above, in nearly all samples (Fig. 7) chalcedony has higher REE concentrations than quartz and amethyst. This feature can be related to differences in the crystallization process, since micro (chalcedony) and macrocrystalline quartz (colorless and amethyst) have considerably distinct structural characteristics and therefore different cation acceptances.

Analyses of ⁸⁷Sr/⁸⁶Sr isotopes were performed on one basalt sample (BTO), and on chalcedony, colorless quartz and amethyst from different geodes (Table 1). Sample preparation consisted in acid digestion of approximately 1 g of powdered sample in ultrapure, concentrated HF + HNO₃, with previous carbonate dissolution in HCl. The acidic solution was purified on Sr-Spec resins, using a protocol adapted from Pin et al. (1994). Analyses were carried out on a Micromass VG–Sector 54 mass spectrometer, at the Laboratory of Isotopic Geology at UFRGS, Brazil. After classical mass bias correction, the NBS-987 standard was used for the correction of the ⁸⁷Sr/⁸⁶Sr isotopic ratios measured on this specific thermionization mass spectrometer. The blank level for Sr analysis was lower than 150 picograms. The results show distinct ⁸⁷Sr/⁸⁶Sr ratios for four chalcedony samples (Table 1), with values ranging from 0.709066 to 0.713691, higher than the ⁸⁷Sr/⁸⁶Sr ratio measured in the basalt, (⁸⁷Sr/⁸⁶Sr = 0.706048). Samples of colorless quartz and amethyst were also analyzed, but their very low Sr content precludes any further comment.

### 7. Discussion

#### 7.1. Temperature and salinity of the mineralizing fluid

The temperature at which the silica phases crystallized is indicative of the general context of the geode fillings: either magmatic, post-magmatic, hydrothermal or diagenetic. Our fluid inclusion study is consistent with the data from Gilg et al. (2003) for quartz and amethyst geode from Alto Uruguai, indicating formation temperatures below 100 °C. Higher formation temperatures previously reported by Proust and Fontaine (2007b) were not confirmed and we think that high homogenization temperatures have to be attributed to the stretching process. However, temperature is probably not the key parameter to constrain the process thermodynamically, even if it can help to outline the origin of the mineralizing fluid. The salinity and bulk chemistry (major and trace) of the trapped fluids is a better indicator of their origin. Low salinities reported in Gilg et al. (2003) were based on ice-melting temperatures between −4 °C and +4 °C, measured in the absence of a vapor bubble. In contrast to the investigations of Juchem (1999) and Gilg et al. (2003), and considering the problem of the interpretation of phase transitions in one-phase inclusions (Goldstein, 2001), we focused our study on T⁰ₑₑ measurements made in the presence of vapor in order to estimate salinity more accurately (in absence of a vapor bubble, the internal pressure cannot be properly interpreted in terms of salinity). The higher salinity estimated in the present study suggests that the fluid has a deeper origin than the infiltrated meteoric water proposed by Gilg et al. (2003), or that the infiltrated meteoric waters undergo strong interaction with the host basalt. Two possible fluid sources (e.g. 2 and 5.5 wt.% eq. NaCl) as evidenced by the T⁰ₑₑ distribution within FIAs can have circulated and interacted. Such a high degree of water–rock interaction could have been caused during a deep pathway or an interaction at higher temperature than that recorded by the fluid inclusions in the authigenic quartz. The contribution of a magmatic source for the mineralizing fluid cannot be excluded, according to Proust and Fontaine (2007b), as also stated by Scopel (1997) and Scopel et al. (1998), but the available data do not allow the extent of this contribution to be estimated. According to Gilg et al. (2003) and to this study, it is deemed that a meteoric fluid is the main fluid source.

#### 7.2. Trace-elements and source of silica

The very low content of trace-elements is a peculiar characteristic of quartz in general, attributed by many authors to the configuration of Si–O bonds preventing the incorporation of impurities (Flem et al., 2002; Müller et al., 2003). Only few elements are accepted as structural impurities substituting for Si in the tetrahedra, or as charge-compensating ions in interstitial sites. The most common elements described as structural impurities in quartz are Al,
Li, H, K, Na, Fe, Ti, Ge and P. Other elements like Mg, Mn, U, Rb, Cr, Cu, Ca and REE would rather be concentrated in solid and fluid inclusions. Nevertheless, even if the definition of what is an impurity versus an inclusion is still unclear (Dennen, 1966; Weil, 1984; Maschmeyer and Lehmann, 1983; Monecke et al., 1997), the trace-element pattern is likely a signature of the mineralizing fluid. In the present discussion, we focused on the REE pattern and the Sr isotopic ratio. The studied geodes samples from Alto Uruguay present a slight HREE enrichment relative to LREE, negative Eu anomalies and slight positive Sm anomalies. La/Ce ratios are mostly <1, except for one sample. These characteristics are quite distinct from those presented by Götte et al. (2001), for microcrystalline quartz from northern Rio Grande do Sul.

As mentioned above, these features may be inherited from the mesostasis, which was presumably the most reactive fraction of the basaltic lava flow. This assumption favors the basalt as the source for silica, but the factors controlling the dissolution and precipitation of silica are still unresolved. While microthermometry indicates a low temperature for quartz growth, we have no indications of the temperature at which the source material dissolved. In view of its small grain size and high chemical reactivity, a high temperature is not necessary to drive the interaction between the mesostasis and water.

Strontium analysis performed by Gilg et al. (2003) on silica-associated minerals (calcite and gypsum) and basalt samples from the Alto Uruguai region showed results quite similar to those found here for chalcedony. On different geodes, calcite $^{87}$Sr/$^{86}$Sr ranges from 0.70617 to 0.70893, and from 0.70860 to 0.70872 for gypsum. In the local basalts, ratio varies between 0.70561 and 0.70608, suggesting that the high ratios found in calcite may result from fluid interaction with non-basaltic rocks, like the more radiogenic Botucatu sandstones ($^{87}$Sr/$^{86}$Sr ~ 0.716). However, they seem more in favor of the radiogenic $^{87}$Sr/$^{86}$Sr coming from the leaching of the basalt mesostasis which has an acidic, Rb-rich composition.

The latter hypothesis fits well with our observations both for trace-elements and $^{87}$Sr/$^{86}$Sr measurements on the silica phases themselves ($^{87}$Sr/$^{86}$Sr in chalcedony varies between 0.709 and 0.714). The large isotopic variability observed in chalcedony could be related to the very different Rb and Sr concentrations in the chalcedony samples from one geode to the other (Rb/Sr between 0.24 and 11.0). Depending on the initial Rb and Sr concentrations, the $^{87}$Rb radioactive decay will increase the $^{87}$Sr content differently for each geode, resulting in distinct $^{87}$Sr/$^{86}$Sr. The Rb/Sr for chalcedony samples are also higher than those for the basalt (Rb/Sr ~ 0.08). However, they seem more in favor of the radiogenic $^{87}$Sr/$^{86}$Sr coming from the leaching of the basalt mesostasis which has an acidic, Rb-rich composition.

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The $^{87}$Sr/$^{86}$Sr isotopic evolution with time could be calculated using the $^{87}$Sr/$^{86}$Sr measured in the chalcedony, in order to establish the relationship between these and the host basalt. But, ICP-MS and $^{87}$Sr/$^{86}$Sr analyses of chalcedony were not performed on the same aliquot of material. To overcome this problem, we modelled the $^{87}$Sr/$^{86}$Sr evolution through time of both the basalt and the chalcedony samples. A time gap of about 60 Ma between basalt formation and silica deposition was taken into account, as suggested by Vasconcelos (1998), based on $^{40}$Ar/$^{39}$Ar ages of celadonites. The results showed that the evolution during 60 Ma of chalcedony having an initial $^{87}$Sr/$^{86}$Sr of 0.70586 (calculated at 70 Ma after basalt formation) and present $^{87}$Sr/$^{86}$Sr between 0.706 and 0.7137, can be explained with Rb/Sr ranging from 1.33 to 3.25. These calculated Rb/Sr fall within the broad range found in chalcedony samples (0.22–11.2). Comparable results were obtained by assuming that only the Rb-rich mesostasis is leached 70 Ma after the basalt formation. The main contribution of this hypothesis is to demonstrate that the basalt, or part of it, can effectively be the source for these elements, taking in account all the factors that influence the isotopic distribution and evolution along time. Innocent et al. (1997) use the same assumption in a study on basalts from northern Paraná basin to interpret the observed Sr isotope distribution through a 25 cm alteration profile from a fresh basalt core to an outermost layer of red lateritic soil.

7.3. Thermodynamic constraints on silica growth

Given the low solubility of silica at low temperature, the large amount of silica deposited in the geodes raises the question as to the source and transport mechanism of silica. Previous studies on agate geodes, another form of silica accumulation, suggested a closed-system crystallization from lumps of gel or amorphous silica having a concentration $>1$ g SiO$_2$/cm$^3$ (Wang and Merino, 1990). In the case of the amethyst geodes studied here, image analysis of the crystal textures has demonstrated that growth of SiO$_2$ minerals in the geodes, at least the different crystal habits of quartz and amethyst, frequently results from a single and continuous process in which the size and the arrangement of the crystals are ruled by the principle of geometrical selection. Similar trace-element patterns and similar low temperatures estimated from fluid inclusions on both quartz and co-genetic calcite to chalcedony, corroborate the above interpretations from the textural data, and strongly suggest a common process for geode filling. Silica crystallization is interpreted as due to a continuous supply of aqueous silica likely at constant low temperature. It began by precipitation of chalcedony, which has a higher solubility and lower kinetic inhibition than quartz. The precipitation of quartz is well known to be extremely slow at low temperature, and in diagenetic waters in general, the solubility of silica is assumed to be controlled by chalcedony at temperatures lower than 80 °C (Rimstidt and Barnes, 1980; Bjørkum and Gjelsvik, 1988; Asano et al., 2003). The abrupt change from chalcedony to quartz, commonly observed in geodes and cavities is described by Heaney (1993) as a function of maturation of the parent fluid. Deposition starts from a concentrated aqueous solution, weakly polymerized, that becomes more dilute as polymerization and chalcedony precipitation proceed. When only monomers are present in the fluid, quartz can precipitate. Sequence repetitions are interpreted as successive infiltration of partially polymerized fluids. The observed phase succession reflects, from a thermodynamic point of view, a decrease of the aqueous silica content with time: chalcedony precipitates at first from (highly) supersaturated solution forming a large number of nuclei, then quartz continues to grow more slowly once the aqueous silica concentration has decreased below the chalcedony solubility.

However, some remarks merit attention. At first, and according to obvious competition rules, quartz growth implies that the fluid is undersaturated with respect to chalcedony, the competitor of quartz. Chalcedony under these conditions should dissolve and supply the nutrients for quartz growth following an Ostwald ripening law. Such a growth process was not observed. The main problem with the dissolution–crystallization process is its strong dependence on the accessibility to potentially reactive surfaces. It is clear that the columnar arrangement of crystals resulting from growth controlled by geometrical selection strongly minimizes the surface area of silica phases in contact with the resident solution in the geodes. Silica polymorph transitions in shallow crustal conditions are very slow, even when dealing with geologic time. A point of evidence is the preservation of metastable A and CT opals, but the factors controlling the dissolution and precipitation process are ruled by the principle of geometrical selection. Similar trace-element patterns and similar low temperatures estimated from fluid inclusions on both quartz and co-genetic calcite to chalcedony, corroborate the above interpretations from the textural data, and strongly suggest a common process for geode filling. Silica crystallization is interpreted as due to a continuous supply of aqueous silica likely at constant low temperature. It began by precipitation of chalcedony, which has a higher solubility and lower kinetic inhibition than quartz. The precipitation of quartz is well known to be extremely slow at low temperature, and in diagenetic waters in general, the solubility of silica is assumed to be controlled by chalcedony at temperatures lower than 80 °C (Rimstidt and Barnes, 1980; Bjørkum and Gjelsvik, 1988; Asano et al., 2003). The abrupt change from chalcedony to quartz, commonly observed in geodes and cavities is described by Heaney (1993) as a function of maturation of the parent fluid. Deposition starts from a concentrated aqueous solution, weakly polymerized, that becomes more dilute as polymerization and chalcedony precipitation proceed. When only monomers are present in the fluid, quartz can precipitate. Sequence repetitions are interpreted as successive infiltration of partially polymerized fluids. The observed phase succession reflects, from a thermodynamic point of view, a decrease of the aqueous silica content with time: chalcedony precipitates at first from (highly) supersaturated solution forming a large number of nuclei, then quartz continues to grow more slowly once the aqueous silica concentration has decreased below the chalcedony solubility.
assumption of silica transfer by diffusion through the chalcedony layers, as suggested by Proust and Fontaine (2007b).

The idea of an advective process assuming that the geodic level is an efficient drain for water circulation (also suggested by Duarte et al., 2009) is consistent with some observations made by the local miners that geodes are sometimes partially filled with water, whereas small vacuoles, which are poor drain for fluids, are rarely filled by SiO$_2$ phases. But it does not constrain the source of silica, which may be local or distant: the host basalt or a continental sandstone. The Sr isotopic data did not allow this question to be unambiguously resolved. However, if the Botucatu sandstone is the source of silica, as suggested by Gilg et al. (2003), thermodynamic conditions within these sandstones must be sufficient to increase quartz solubility and generate Si-rich solutions. As an example, the solubility of chalcedony at 20 °C (the first phase of the mineral sequence in the geode) is 8.8 mg/l at near neutral pH. To generate such a solution from quartz dissolution, the temperature of the Botucatu sandstone must have exceeded 35 °C or its pH at 20 °C must have exceeded 10. Assuming 80 °C for the crystallization of chalcedony in the geodes (55 mg/l), the temperature of Botucatu sandstone must have exceeded 105 °C or the pH must have risen by 3 units. These conditions are more consistent with a hydrothermal context than a groundwater context.

The major remaining and unsolved question is why quartz–amethyst deposits are observed only in geodes. Did a precursor promote nucleation and growth there? Does the size of the vacuole play a particular role? The recent paper by Duarte et al. (2009) attributing the origin of the giant cavities to brittle fracturing and hydrothermal dissolution is consistent with the absence of epigenetic filling in smaller and not interconnected vesicles of degassing origin. However, a paper presented by Putnis (2002) recalls that such questions are still open and can be generalized to other porous media.

The second remark is that the observed silica mineral sequence is only valid at the geode scale, and not at the lava flow scale: we did not observe any mineral zoning from chalcedony to amethyst along the lava flow. This implies that the change of fluid chemistry monitored by the mineral sequence occurred at the same time everywhere in the lava flow, and not as a function of the distance from a hypothetical source. This is likely related to the exhaustion of the source rather than the exhaustion of the mineralizing fluid along the pathway. The rare repetition of the complete sequence of silica minerals in geodes suggests that the filling process occurred mainly as a single trapping event. However, in some cases one or more trapping events can induce the crystallization of successive sequences, presenting the same textural characteristics as the former one.

8. Conclusion

In order to account for all of the chemical and physical features, the following scenario is proposed:

- A regional hydrothermal event of high enthalpy mobilizes a large amount of silica. The source of silica is likely to be the mesostasis of the basalt lava flow, but a minor contribution from the regional Botucatu sandstone cannot be excluded.

- Silica precipitates in geodes upon cooling and oxidation of the mineralized fluid. The mineralogy of the deposit changes when aqueous silica concentration decreases, with a final oxidizing stage corresponding to the amethyst growth.

References


