

THE GENESIS OF AGATES AND AMETHYST GEODES

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ABSTRACT

Practically all aspects of agate genesis generate debate. The time is ripe to clarify the most important enigmas concerning the environments of formation of agates and the related famous amethyst geodes of Brazil and Uruguay. Agates form over a wide range of temperatures, from those of basaltic and andesitic melts (about 1100 °C) down to about 50 °C, and at rather low pressures. Their formation in liquid mafic magmas is indicated by a correlation between (1) the orientation of amygdulites and the inclination of onyx banding in them and (2) the attitude of amygdulites in the lava flow layers. The correlation arises because lava moves at a different rate close to and far from the upper and lower rims of a flow. The alkaline supercritical fluid fills gas vesicles in lavas and dissolves silica, mainly, from ambient lava or rock to produce a silica sol. If the pressure on the fluid causes percolation of water from amygdulites, the sol coagulates on the walls of the vesicle to form a concentric lining. If the pressure in amygdulites falls below the maximum osmotic pressure of a sol (about 0.1 MPa for a silica sol), percolation of fluid stops, and coagulation leads to the formation of horizontal onyx banding. Multiple repetitions of precipitation of various gel layers can be caused by overlapping fresh flows upon the cooling older agate-bearing lava flow. In a submarine setting, phase separation of the fluid and the formation of a film of gel between vapor (or diluted solution) and brine stimulate the osmotic processes, which result in growth of hollow membrane tubes and branching moss-like arrays at the bottom of amygdulites. Some agates exhibit numerous channels as a result of repeated extrusion of fluid or gel from inner zones to the periphery of amygdulites that were compressed under the burden of new flows. Previously, such channels were interpreted to be feeding channels for silica supply in amygdulites. Periodic compression of amygdulites after percolation of fluid from them requires no additional supply of silica because the volume of the amygdulites is reduced in proportion to the loss of fluid. The concentric and horizontal banding and mossy textures of agates from the lithophysae of felsic volcanic rocks were created during active volcanism as well. The agates from dissolution-induced cavities in carbonate rocks and the famous amethyst druses of Brazil and Uruguay formed at the moderate temperatures associated with low-grade burial metamorphism, as indicated by the lack of moss textures and onyx banding.

Keywords: vesicles, amygdulites, agate texture, microglobulites, volcanism, colloids, silica minerals, osmotic pressure, extrusion channels, moss textures, lithophysae, amethyst geodes.

INTRODUCTION

The genesis of agates invariably brings into focus some hotly debated issues. Among these are: (1) the participation of colloidal solutions (sols and gels) in their formation, (2) the presence or absence of a temporal gap between the formation of gas vesicles in volcanic rocks and their mineral infilling, (3) the temperature (high or low?) and pressure of formation, (4) the role of internal channels in the formation of the agate filling, (5) the cause of a textural shift from concentric lining to horizontal (onyx) banding, (6) the

conditions of formation of microtubular and mossy structures, (7) the timing and mechanism of introduction of silica into amygdulites, (8) the mechanism of agate formation in lithophysae in felsic rocks, (9) the mechanism of agate formation in sedimentary rocks, and (10) the environment of formation of giant amethyst geodes. These issues are revisited here.

THE ROLE OF COLLOIDS IN AGATE FORMATION

The term “agate” refers to the variously shaped banded arrays of silica minerals filling cavities in

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volcanic and, less commonly, sedimentary rocks. Agates form as a result of the rhythmic coagulation of silica sol in cavities that were gas bubbles in lavas and solid volcanic rocks or dissolution-related cavities in limestones. Agates contain opal and the products of its recrystallization and transformation (cristobalite, tridymite, chalcedony, and quartz). In addition, agates may contain other minerals that formed later, including celadonite, calcite, siderite, aragonite, hematite, goethite, zeolites, chlorites, gypsum, and todorokite, among others. These late minerals may replace the silica minerals or fill the cavities. Many publications devoted to the structure and conditions of formation of agate have appeared, including remarkable and well-illustrated monographs, for example *Agate* (Godovikov *et al.* 1987) and *Agates* (Zenz 2009, 2014). New textural analyses of agate specimens and of photos published recently have led to refinements or modifications of earlier interpretations of agate genesis. The new information has challenged some views published recently concerning the timing of agate formation.

It is the author's opinion that the beautiful and highly variable textures of agates are invariably related to gels, which are the products of coagulation of sols, *i.e.*, colloidal solutions. Professor D. Grigor'ev (1953), a pioneer in the ontogeny of minerals (Grigor'ev 1961) and his followers, Dymkov (1960, 1966), Stepanov (1970), and Zhabin (1979) among others, including Roedder (1968), have denied any participation of colloids in mineral formation. They considered all colloform aggregates to be the products of the collective crystallization of spherulites of various minerals. Even Godovikov *et al.* (1987) failed to recognize the participation of a silica gel in the formation of agate.

A voluminous literature is devoted to mineral colloids and metacolloids: Chukhrov (1955) and Lebedev (1965) provided impressive reviews. Iler (1979) documented the importance of colloids in his treatise on the chemistry of silica. The participation of colloids in the formation of minerals in general has been demonstrated (Kigai 1974), with "wood tin" (metacolloidal cassiterite) as an excellent example. The conclusions of that article were never challenged. The participation of colloids in the formation of agate is shown by the common presence of relics of opal-A (X-ray amorphous silica) in the banded texture of agate. The direct transformation of silica gel into opal has been documented in studies of natural silica gels in areas of recent volcanism (Naboko & Sil'nichenko 1957).

The recrystallization of opal to cryptocrystalline cristobalite + tridymite (opal CT), later to chalcedony or quartzine (optically length-fast chalcedony), has been established by many investigators of agates (*e.g.*,

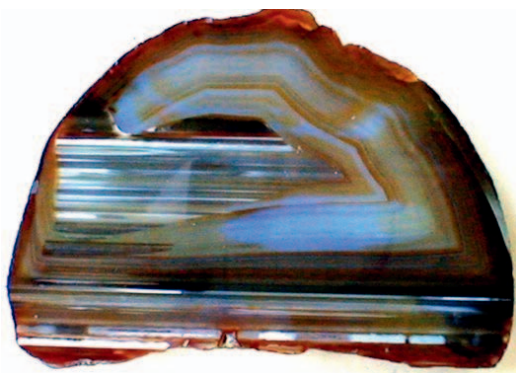


FIG. 1. Agate from Brazil with concentric and horizontal (onyx) banding composed completely of SiO₂ minerals. Sample is 10 cm wide.

Pilipenko 1934, Leonov & Chekalova 1972, Kastner *et al.* 1977, Yusupov 1982, Plyusnina 1983, Lange *et al.* 1984, Lynne & Campbell 2003, Eckert *et al.* 2015). Chalcedony and quartzine commonly also grow independently in agate in the form of spherulites, and quartz appears in druses in geodes. Chalcedony was found to be microcrystalline fibrous silica composed of very fine intergrowths of quartz and moganite (Heaney & Post 1992).

In a specimen of agate from Rio Grande do Sul, Brazil (Fig. 1), the concentric and horizontal bands are composed entirely of various textural and mineralogical types of silica minerals. The patches of late opalization (bluish color) contain very thin-fibered aggregates of cristobalite and chalcedony. In the portion showing onyx banding, the milky-white bands are dehydrated layers of cristobalite–chalcedony, and the transparent bands are hydrous layers of the same composition. All types of silica polymorphs can be seen in the thin section cut from this sample (Fig. 2); note the presence of a triple junction of texturally distinct domains. The vertical band of opal-CT with the common festoon-like boundary is a part of a thin (3–4 mm thick) outer border of the amygdule. The horizontal onyx banding consists of alternating bands of microgranular and microglobular low cristobalite (with 20 to 60 µm grain size) and variously fibrous chalcedony. The chalcedony bands show repeated crystallization, with each layer of spherulites starting their growth with a shape-preferred orientation of fibers. The horizontal bands of chalcedony in the thin section are a part of the onyx banding, but a vertical band is a part of the concentric (wall-lining) banding of chalcedony.

From treatises on colloid chemistry, one knows that a silica sol consists of a dispersion medium; suspended



FIG. 2. Photomicrograph of a thin section from the extreme right end of the agate sample shown in Figure 1. Three types of silica polymorphs are visible: the vertical band on the right is an assemblage of small opal-CT spherulites composing the outer 3–4 mm thick brown envelope of the agate sample; the horizontal band at the bottom of the section is microgranular (20–60 μm) and partly microglobular cristobalite aggregate; the upper part is fibrous chalcedony spherulites in horizontal and vertical bands, each having a basic zone of shape-preferred orientation initial growth. Nicols are crossed. FOV 2.5 mm wide.

in it are micelles of silica from 1 to 100 nm in size. The dispersion medium is the ionic-molecular true solution saturated with silica. Its mutual relations with the micelles are analogous to the equilibrium between a solution and crystals (Alexander *et al.* 1954, Krauskopf 1956, Iler 1979).

Under room conditions, the formation of gel in hydrophilic colloidal solutions such as silica sol can occur *via* a rapid one-time transformation of all of the mass into gel. For this reason, Liesegang (1915) believed that an amygdale fills with silica gel quickly by overall gelation; then, in his opinion, there is a structural evolution of the gel to form banding, which becomes visible by the diffusion of pigment impurities into the gel and their rhythmic precipitation. Such diffusional banding is sometimes encountered in agates, but it formed later. It occurs obliquely and cross-cutting relative to concentric and onyx bands and can in some cases be simply recognized. Three examples of likely diffusional

Liesegang-type banding in agates are shown in Zenz (2014, p. 62, photo 2, p. 141, photo 4, and p. 584, photo 3). The first two samples are from Baumholder, Germany, and the third is from Sidi Sahal, Morocco. However, as a textural analysis of many agates shows, the formation of silica gel in them at an elevated temperature actually proceeds by a rhythmic precipitation of small portions of gel as successive thin layers. Under room conditions, such a style of gel formation, named flocculation, is typical of hydrophobic sols, for example, of sulfide sols. But at high temperatures, it evidently occurs in hydrophilic silica sols as well.

The micelles and their aggregations form microglobules from 10 nanometers to several dozens of microns in size with a round shape, which is energetically most favorable for liquid and ductile substances. Non-crystallized soft globules could easily agglutinate with the formation of rods, 3D lattice structures, disks, and fibers, as has been demonstrated by Maleev (2016), with HRTEM applied to examples of microglobular opal, goethite, hematite, and other minerals from Bulgaria.

The microglobules are almost invariably found to contain opal-CT in agates. Initially, the cristobalite and rarer tridymite, usually found in agates of all geological epochs, most likely belonged to high-temperature varieties, but they were converted into low-temperature types during cooling. And the low cristobalite retains a microglobular structure and water inherited from the opal-A to be preserved over hundreds of million years (Moxon & Rios 2004).

The harmonic texture of agate can be repeatedly broken by processes of late opalization (Fig. 1). Opal-A can replace not only wall lining and onyx banding, but also aggregates of quartz and other minerals. The temperature range of the opalization process is fairly broad. For example, Stepanov (1959) described the metasomatic formation of opal in the weathering crust of a tungsten deposit in central Kazakhstan at the expense of such a high-temperature mineral as topaz. A requirement for the formation of agates is an aqueous fluid ($\pm$ salt) present in an open space in a silicate melt or rock, or in a carbonate rock; in the latter, the disseminated silicate substance can be mobilized by the introduction of formation water into the dissolution cavity.

In a classification of agates relative to the environment of formation, three types can be considered: (1) agates in basic volcanic rocks (basalts, andesites), (2) agates in lithophysae of felsic volcanic rocks (rhyolites, dacites and ignimbrites), and (3) agates in sedimentary rocks, mainly in limestones.

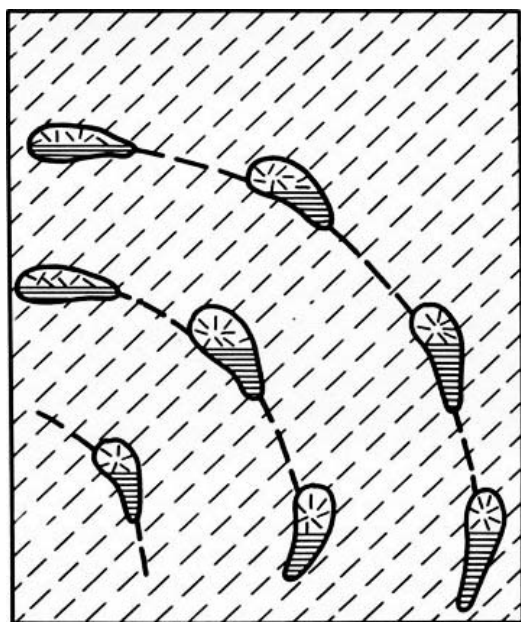
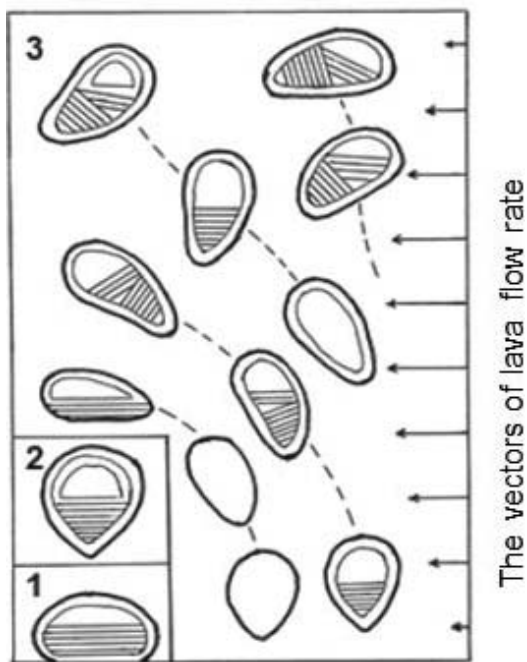


FIG. 3. Scheme of transformation of shape, inclination, and onyx layering of agate amygdules in a lava flow from the Brazilian traps, after Freyberg (1927). See text for details.

THE EVOLUTION OF THE SHAPE AND INTERNAL TEXTURE OF VESICLES IN A LAVA FLOW

The reasons for the transformation of the shape of a gas bubble in lavas have been described using samples from Scotland (Heddle 1901) and Brazil (Freyberg 1927). If the basaltic or andesitic lavas flow into a water basin or aquifer, the water or brine (in the case of ocean water) in the bottom sediments can be expected to evaporate. The supercritical fluid can be expected to rise into the melt and, unlike descending rain drops, will have a rounded top and a pointed lower termination. During movement of the lava, a transformation in the shape and orientation of the vesicles takes place: they become narrower and gradually re-orient in order to bring their elongation parallel to the direction of the lava flow (Fig. 3). Furthermore, they will have a flat lower side and a convex upper side. The transformation of the bubbles is caused by differential rates of flow close to and far from the lower and upper solid rims of the flow. The lava close to both the bottom and top rim is cooler, more viscous, and more slowly moving, and the bulk of the flow away from the rims moves more rapidly. As a result, the bubbles near the bottom of the flow tend to tilt in the direction of the lava flow, with the vesicles in the upper part of the flow tilting to become oriented parallel and toward the lava flow.

The upper crust of a lava flux



The bottom crust of a lava flux

FIG. 4. Schematic evolution of shape, orientation, and zoning of agate amygdules ascending in a lava flow. 1 – at the bottom of very viscous lava, 2 – in low-mobility liquid lava, after Heddle (1901), 3 – in a full vertical section of the liquid lava flow (Kigai 2017).

The sketch of Freyberg (1927), shown as Figure 3, fits the observations in the lower half of the lava flow only. In the upper half, the shape of the amygdules and the orientation of the onyx lamination (where present) should be the mirror opposite, as shown in Figure 4. The orientation of the amygdules parallels the flow layering, with their round ends oriented toward the direction of lava flow. Striking examples of such amygdules located in the upper half of a lava flow (Fig. 4) can be seen at the entrance to the adit at Idar-Oberstein, Germany (Zenz 2014, p. 121).

The onyx banding is a typical geoptetal indicator, being initially invariably oriented horizontally. Owing to the change in inclination of an amygdule, onyx banding formed at different angles indicates the possible formation of such precipitates during tilting of an amygdule while ascending in a moving lava or as a result of folding of the host volcanic rocks.

Especially convincing is the specimen of agate from Brazil (Fig. 5) in which the rather flat left side indicates that the initial change in the shape of the



FIG. 5. Vertical section of a Brazilian agate showing the change in its shape and variously oriented silica banding during ascent of the vesicle from the base to the upper crust of a moving lava flow. Sample is 13 cm long. See text for explanation.

amygdule occurred when it inclined to the left in the lower part of the lava flow. The concentric banding was most likely created at that time, thus preventing further transformation of the amygdule's shape. The major part of the onyx banding in this amygdule was likely created when it had a vertical orientation during ascent through the midstream of thick lava. The inclination and opening of a fan of the later onyx banding, however, directed to its convex side, indicate that the infilling of the amygdule with later horizontal layers of onyx terminated when the amygdule was lifted to the thin upper border of the lava flow. There the amygdule already had been forced to tilt to conform to the flow direction (see Fig. 4, the second row from the top). The total change of the amygdule's inclination amounts in this case to approximately 50–60°. As the agate-bearing Early Cretaceous Paraná trap formations of Brazil lie almost horizontal and have not been involved in folding (Fig. 6), one can conclude that the amygdule was filled with concentric and onyx-layered precipitates when the basaltic lava containing it was still partially liquid and could move.



FIG. 6. Agate mining at Salto do Jacui (Rio Grande do Sul state, Brazil), confined to a flat agate-bearing lava flow. Photo by Andre Simao, 2003, from Johann Zenz.

ON TEMPERATURE AND PRESSURE CONDITIONS OF AGATE FORMATION

The range of compositions and P - T - X parameters of the fluids that created agates in various deposits is very wide. The amygdules in basaltic lavas form at temperatures close to 1100 °C, and agates in rhyolitic volcanic rocks form at lower temperatures, but still above 800 °C. The temperatures of formation of agate minerals in solid volcanic rocks are lower still. In the course of his studies of fluid inclusions in agates from 16 deposits in the Southern Ural Mountains and Kazakhstan, Yusupov (1982) documented the presence of many minerals: silica gel (in all zones of amygdules), cristobalite (as walls of membrane tubes 1–2 mm thick), tridymite, native copper, cuprite, zincite, hematite, goethite, carbonates, zeolites, chlorite, and kaolinite. Quartz from geodes was found to contain inclusions of an aqueous solution of NaCl and CaCl₂, with concentrations from 3–10 to 32 % NaCl equiv., that provide clear evidence of boiling. Temperatures of homogenization to a liquid phase were found to attain 320 °C, and to the vapor phase, from 320 to 470 °C. Earlier minerals in agate of these deposits would have formed at even higher temperatures. On the basis of the multiphase state of the inclusion fluids, the temperatures of homogenization of inclusions probably do not require a pressure correction and can be taken as trapping temperatures. In late growth-zones of smoky quartz in agate geodes from the Sartmola deposit in Kazakhstan, the multiphase inclusion undergoes a gas-to-liquid homogenization at 386 °C, and the halite crystal disappears at 396 °C (Yusupov 1982). According to the experimental data for such inclusions (Becker *et al.* 2008), these findings correspond to a pressure about 20 MPa. This corresponds to a depth of formation of the late

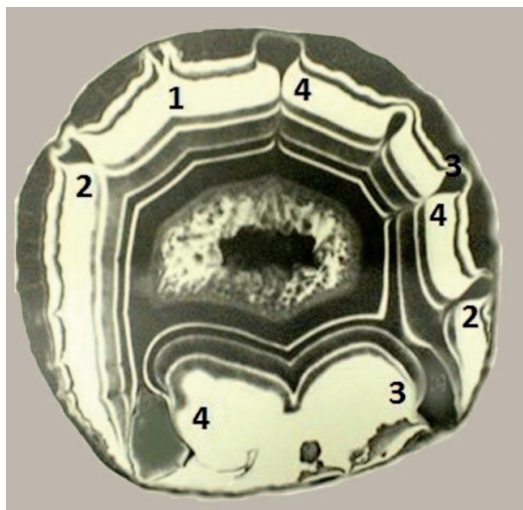


FIG. 7. Agate with channels of four-fold squeezing of gel from internal layers. After Shaub (1955); the origin and size of the sample were not reported.

minerals in agate at Sartmola of about 2 km, *i.e.*, an environment of low-grade burial metamorphism. On the other hand, agates and opal replacing corals and tree trunks or filling chambers in ammonites and dissolution-induced cavities in limestone occur at temperatures below 100 °C at a rather lower pressure than that quoted above.

THE ROLE OF INTERNAL CHANNELS IN AGATE GENESIS

The concentric lining that is rhythmically precipitated on walls of agate vesicles is inferred to have remained a soft gelatinous substance for a fairly long time. The repeated extrusion of fluids or gel away from central cavities to the amygdule border led to the formation of channels of various shapes that cross-cut the concentric banding. Some of the channels are thin and are accompanied by orbicular bulbous terminations; others are wide, with a cylindrical shape and blunt terminations. The concentric layers of agate near the channels are invariably bent outward, progressively thinned, and pinched out, as seen in Figure 7. The channels never reach the outer boundary of the amygdule. This observation, along with the pattern of deformation next to the channels, rules out the possibility that the channels were paths of inflow (feeding channels) for silica-bearing solutions, as proposed Liesegang (1915) and Pilipenko (1934). Rather, they were the paths of extrusion of gel or fluid toward the external parts of the amygdules as they were being squeezed, as inferred by Shaub (1955).



FIG. 8. Fortification agate from Brazil. 6.5 cm long. Photo by Jerry Schaber.

Shaub (1955) attributed this extrusion of material to compression due to pressure exerted by the lava; it is more likely, in my opinion, due to the arrival of new overlying flows. This assumption is supported by deformation of concentric and horizontal bands with the formation of festoon-like or lace structures turned with their convex part inside the amygdules (Fig. 7). Festoons formed in this way should not be confused with similar textures created in agates by gel precipitates covering an uneven surface composed of spherulites and other crystal aggregates, resulting in the formation of so-called “fortification agates” (Fig. 8).

Any significant compression of amygdules could only occur in the presence of liquid lava and only in high-temperature agate; however, extrusion without compaction of amygdules could also occur in agates that are still soft within the solidified lava as a result of repeated volcanic eruptions that led to a temperature and pressure increase inside the agate.

WHY IS THERE AN INTERCHANGE BETWEEN CONCENTRIC AND HORIZONTAL BANDS?

Nacken (1917) attributed the change from concentric lining to horizontal (onyx) banding in agates to the heterogenization (unmixing) of a supercritical fluid. Such an explanation cannot be accepted as being universal for two reasons. Firstly, from a detailed study of mutual relations between onyx and concentric banding, it is clear that some bands of these two types were deposited simultaneously, with concentric banding repeatedly alternating with pure onyx banding (Fig. 9). Secondly, if the agates formed in basaltic and andesitic lavas having a solidus temperature close to 1100 °C, the temperature of a fluid in the amygdules should be considerably higher than the critical temperature of water and salt brines of a concentration typically encountered. The maximum concentration of natural brines cannot exceed 26.4 wt.% NaCl equiv., which corresponds to the solubility of NaCl in water under room conditions. At such a salt content, the



FIG. 9. Agate from Brazil with multiple alternations of concentric and synchronous horizontal (brown) bands with dehydrated (milky-white) pure onyx layers. 9 cm long.

critical temperature of the fluid is equal to 700 °C, and the critical pressure is 1237 bar, or 123.7 MPa (Sourirajan & Kennedy 1962). As a result, the fluid will invariably be in a supercritical vaporous state, and its unmixing cannot be reached at any pressure.

At the same time, the pressure in the amygdules cannot be very high, even if the initial pressure of the fluid before its entrance into the lava flow was much higher than the pressure in the lava. In basic lava possessing a rather low viscosity, the gas bubble will expand until the internal pressure is equilibrated with the pressure in the lava or only slightly exceeds it. During expansion the gas bubbles can increase in volume a thousand times. Confirmation of this can be seen in the huge amethyst geodes of Brazil, which can be several meters high and wide (Hartmann *et al.* 2015).

During an eruption, a lava loses most of its dissolved H₂O by degassing. Microporous basalt and pumice are characteristic of the upper horizons of effusive rocks. The eruption of basic lavas into any water-filled basin with wet sediments or upon an aquifer provides a favorable environment for agate formation, as there is a ready source of water to fill gas vesicles. The fluid in the vesicle at the temperature of the lava will be supercritical and alkaline (Kigai & Tagirov 2010), and thus can extract SiO₂ from the adjacent lava as it cools and crystallizes, to create the silica sol.

At first glance, it might seem strange that in basaltic lava, only silica gel and silica minerals are found in amygdules, without amphiboles and feldspars. According to the principle of acid–base interaction of Korzhinskii (1960, 1976, 1978), an increase in the alkalinity of the fluid should increase the activity of all bases. The increase in alkalinity of the fluid in the amygdules will lead to a leaching of only the most acidic component, SiO₂, from the melt

into the amygdules, leaving basic (K, Ca, Mg) and amphoteric components (Fe, Al) in the melt. As a result, there is no possibility to use silica to form amphibole and feldspar in the amygdules at temperatures typical of lava, which accounts for the presence of only pure silica minerals.

Experiments on the ultrafiltration of sols through walls of collodion test tubes by Duclaux (1929) showed that if the sol pressure inside the tube exceeds the pressure of the surrounding solution by the value of the maximum osmotic pressure of the sol (which for silica sol is about 0.1 MPa), the sol dispersion medium percolates through the outside walls of the tube, and the micelles coagulate to a gel that forms a concentric lining on the walls. If the pressure of the sol is below the indicated value, the gel only precipitates at the bottom of the tube as horizontal strata.

These experiments shed light on the nature of the interchange between concentric and onyx bandings in agate. The collodion test tubes used in Duclaux (1929) have pores from 1 to 10 nm across. A typical size of colloidal micelles is from 1 to 100 nm. The pores of metamorphic rocks are mostly less than 100 nm in size (Ovchinnikov *et al.* 1955). The channels in the spongy quasicrystalline structure of silicate melts and the pores in solid volcanic rocks can have the same dimensions. Therefore, unlike an ionic–molecular solution of a dispersion medium, the micelles of sol, having sizes in the range 1–100 nm, cannot filter collectively through pores of the surrounding melt or rock having the same or narrower dimension. Thus, the micelles agglutinate and coagulate to form the gel. If the pressure inside the amygdules does not exceed the pressure in the surrounding lava or rock by a value equivalent to the maximum osmotic pressure of silica sol, the sol cannot percolate from the amygdules toward the outside. It will flocculate in the cavity, with precipitation of horizontal onyx layers at the bottom of the amygdules. This could occur, as the fluid is in a supercritical state in the amygdules.

But what about the formation of agate in lavas that have already cooled to temperatures far below the solidus of the melts? The deposition of horizontal layers of onyx in agate can be caused by unmixing of the fluid, as proposed by Nacken (1917), or by a simple pressure decrease of the fluid below that required for percolation. In both cases, the periodic alternation of concentric layers and onyx banding in agate can be related to a continuation of volcanism, creating an episodic rise of temperature and pressure of the fluid inside the amygdules within the older lava flows.

Upon the appearance of the initial packet of onyx layers, the formation of the following concentric layers can be accompanied also by continuation of simulta-



FIG. 10. Asymmetric structure of concentric layering in an agate amygdule from Timan, Russia, likely related to unilateral percolation of sol.

neous growth of horizontal layers, as long as the onyx packets are composed of porous fresh gel that does not interfere with fluid percolation. In the case of a non-uniform permeability of the walls of an amygdule, the concentric layers can precipitate asymmetrically (Fig. 10). Clear evidence of such an interpretation can be seen in a photo from Zenz (2014, page 32), in which a significant condensation of fluid bubbles extruded from the amygdule into the host rock, mostly along the side of the amygdule where the wall lining is thicker.

THE ENVIRONMENT OF FORMATION OF MOSSY AND TUBULAR MYELINE TEXTURES

So-called mossy textures are commonly developed in agates generated in lavas that were erupted underwater, for example in the Idzhevan agate deposit in Armenia (Fig. 11). A sketch illustrating the formation of such textures is shown in Figure 12. In essence, the process is rather straightforward. If the solution inside the amygdules contains dissolved salts, then following its unmixing at a low pressure, a marginal semipermeable film can be created between a steam phase and a liquid solution of brine. The film can be composed of a gel of silica or some other substance (for example, oxides of iron and manganese or celadonite). Then, the vapor phase should, according to the laws of osmosis, percolate through the semipermeable film of gel into the brine, raising the pressure there. Under the influence of osmotic pressure, the film of gel, owing to its non-uniform surface tension, should protrude and create tubular or treelike structures with empty channels inside.



FIG. 11. Agate with mossy textures at the bottom of the amygdule. Sample from the Idzhevan deposit, Armenia. 10 cm in size.

Such an origin for moss agates was proposed by Gergens (1858), Liesegang (1915), and Chukhrov (1955), who named them “membrane structures”. In the biophysical literature in English, they are known as “myeline forms”. In such a way, picturesque mossy, tubular, and plume-like aggregates form at the bottom of agate amygdules. These attractive membrane tubes are well developed in agate from Chihuahua, Mexico (Fig. 13). Such tubes and mossy aggregates offer direct evidence that colloids participate in the formation of agates. The growth of mossy aggregates is driven by osmosis rather than gravity, in the same way that the growth of plants is due to osmotic intracellular pressure (turgor). Thus, the morphological similarity of mossy aggregates in agate to plants is quite expected.

If the fluid returns to a supercritical state after formation of myeline aggregates or if the salt concentrations in the fluids below and above the film of gel become equal, growth of the mossy aggregates will stop. Furthermore, depending on the internal pressure of the amygdules, the usual growth of concentric or onyx layers can proceed. In some cases, empty channels in moss agate may be filled with later-formed opal, whereas the walls of myeline structures remain as opal-CT, for example in agate of the southern Urals and Kazakhstan (Yusupov 1982). If bubbles in lavas are filled with fresh water rather than

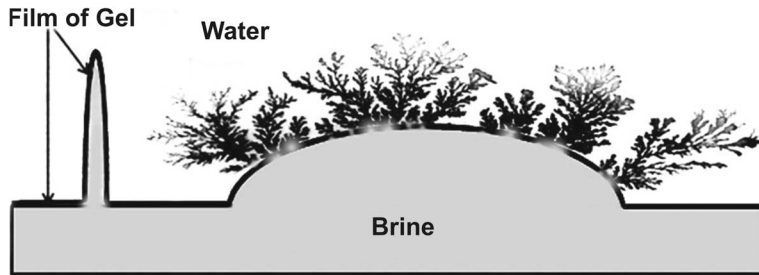


FIG. 12. Scheme of osmotic formation of membrane tubes and moss textures (myeline forms) in agate (Kigai 2017).

brine, the mossy structures cannot form because the osmotic pressure of sols is much less than that of brines and is insufficient to form myeline aggregations.

THE PROBLEM OF SILICA BALANCE IN AGATE

When a basic lava flows into a water-filled reservoir, bubbles of water or brine expelled from the wet sediments will rise into the lava. At high temperature, the small bubbles will at first possess a pressure much higher than the pressure of the lava; therefore, the bubbles in the lava will increase in size until the pressure inside of the bubbles approximates the pressure in the lava or surpasses it only slightly. The fluid in the bubbles will be supercritical and alkaline, as discussed above. Such a fluid is able to dissolve much silica from the melt and be converted to a silica sol, which is saturated relative to micelles. Until the internal pressure of the vesicles exceeds that of the enclosing lava, the dispersion medium of the sol will be filtered through the semipermeable envelope of the vesicles, which will result in a concentric lining of gel in the amygdules.

If a cooled agate-bearing lava flow is covered by new flows of hot lava, the underlying earlier flow will undergo an increase in pressure. This will compress the agate amygdules, which have lost some solution owing to percolation. As a result, some concentric and onyx layers may become warped (Figs. 7, 14). The heat from the new flows will cause the temperature and pressure to rise in the amygdules of the older flow, and the process of sol percolation can be renewed. The compression of the amygdules and the extrusion of gel or fluid from the internal parts of the amygdules under the burden of the new lava flows will end as soon as the internal and external pressures equilibrate. That is why the channels of extrusion never extend outside the agate boundaries.

In view of the periodic repetition of the processes indicated to occur in molten lava, there is no need to propose an additional input of silica into the amygdules after the initial creation of the sol, because

the volume of the amygdules will continually be reduced in proportion to the loss of solvent.

After crystallization of the agate-bearing volcanic rocks, the volume of the amygdules cannot be reduced significantly. Thus, the loss of solvent by percolation will lead to the formation of residual drusy cavities in agate. The silica and other substances required for the replacement of agates by pseudomorphs and for the filling of drusy cavities within them by late minerals can be supplied by migrating hot solutions responsible for hydrothermal alteration of the host volcanic rocks. These late solutions would presumably be entirely ionic-molecular rather than colloidal in nature.

A MECHANISM FOR AGATE FORMATION IN LITHOPHYSAE OF FELSIC VOLCANIC ROCKS

A mechanism of formation that differs from that described for agate in basalts can be proposed for the round lithophysae (so-called “thunder eggs”) found in felsic rocks (rhyolites, dacites, ignimbrites). The lithophysae represent spherical concretions with a massive concentrically zoned texture, found in rhyolitic vitrophyres and welded tuffs and composed of



FIG. 13. Agate from Chihuahua, Mexico, with white membrane tubes. Photo by Ian Meltzer.



FIG. 14. Agate from Mashatu, Botswana, with concentric layers crumpled due to amygdule contraction. Sample is 6.5 cm wide. Photo and collection of Johann Zenz.



FIG. 15. Lithophysa with a shadow flow layering and some arching above the agate core. 10 cm wide sample from Tarbal'dzhey area, Transbaikalia, Russia. Collection of Fersman Mineralogical Museum, Moscow, photo by A. Evseev.

microcrystalline cristobalite, tridymite, and sanidine (Richthofen 1860, Iddings 1887, Godovikov *et al.* 1987, Bretkrenz 2013). Inside the lithophysae, there is an agate filling of variable shape and size. The absence in felsic volcanic rocks of agate-filled amygdules typical of basic lavas is, undoubtedly, related to the high viscosity of felsic melts, which prevent the introduction of gas bubbles into lavas from underlying water-bearing rocks. The intrinsic volatiles that had exsolved from the magma are lost to the atmosphere from upper horizons of the lavas by degassing during eruption, leaving fine-pored pumice.

Richthofen (1860) provided the first explanation for the genesis of cavities in agate-bearing lithophysae; he coined the term 'lithophysa', although he used it to refer to the cavities rather than to the concretions as a whole, as it is used today. He related their formation to the expansion of the gas expelled from glass during devitrification. The formation of anhydrous minerals such as feldspar and polymorphs of silica at the expense of congealed hydrous felsic magma must inevitably result in the release of water.

To understand the genesis of agate in felsic volcanic rocks, it is important to realize that agates only appear inside lithophysae and never directly in the groundmass of the rocks next to the lithophysae or in primary spherulites. The devitrification of glass in the lithophysae is thus a prime source of water for agate formation, as Richthofen (1860) had proposed. Gas pockets of comparable size are lacking outside the lithophysae. The lithophysae in felsic lavas thus represent bubbles of the vapor phase that could not escape owing to the viscosity of the lava. It is possible that the aqueous vapor phase interacts with the

enclosing lava and acts as an inoculant to form clouds of amorphous glass around bubbles. Where the bubbles are numerous, the lithophysae in lavas may form rather tight clusters and combine in complex botryoidal assemblies.

The internal structure of such assemblies differs from structures arising from the interference between adjacent spherulites or oolites during their mutual growth, and these assemblies show no plastic deformation due to the "collision" of soft gel ovoids, as has been demonstrated for wood tin (Kigai 1974). As a result, an assumption can be made about the initial glassy state of the concretions and the formation of complex clusters of concretions during their initial solidification at separate sites in a lava or tuff, rather than after the full solidification of individual concretions. The creation of a ball of glass seems to have occurred without distortion of lava-flow structures or tuff banding. If this were not the case, it would be impossible to explain the preservation of vestiges of lava-flow texture and tuff banding in some lithophysae (Fig. 15), described from one Australian deposit (Bryan 1954).

The formation of cavities in lithophysae could involve contraction related to cooling, with the formation of arcuate cavities and radial cracks, as well as dissolution. Without dissolution, it is impossible to imagine the formation of some lithophysae with agate-containing cavities comprising more than 80% of their total volume, with preservation of the integrity of peripheral layers (Fig. 16). The matter removed by dissolution of a lithophysa could be used directly *in situ* to form its agate filling.



FIG. 16. Lithophysa with a large agate filling from the Baker egg mine, Deming, New Mexico. ~8 cm long. Photo by Don Roach.

In a specimen from the Khapcheranga area, in Transbaikalia, Russia (Fig. 17), it is possible to find a lithophysa in which the concentric lining was blown out by a fluid phase, and the lava-flow lamination is oriented transverse to the onyx banding. The rhyolites of the Early Cretaceous Akkuin suite in the basin of the Onon River, from which the specimen was taken, have not been involved in folding. The only possible explanation for the sharply differing orientation of onyx banding and lava flow in this specimen is the formation of onyx banding in the lithophysa when it was being transported in magma in the feeder channel. As a result of the eruption of the lava at the Earth's surface, the lithophysa changed its orientation and was covered by layers of lava. Such layering is not typical of subvolcanic extrusions. For example, Khoseyni & Rusinov (1999) described spherical concretions in unlayered dacites from a vertical cylindrical channel in an extrusive dome at Tarom Mountain in northwestern Iran.

The appearance of agate in lithophysae occurs with the formation of concentric banding, horizontal onyx banding with changing inclination of different layers, typical channels of extrusion of substances, and, more rarely, mossy textures (Fig. 16). These features indicate that all agate-bearing lithophysae were created during emplacement of molten lavas or hot ignimbrites.

THE RELATIVE AGE OF AGATES AND THEIR HOST VOLCANIC ROCKS

The filling of amygdulites to form agate could be a long-term process, just as is the hardening of lavas.

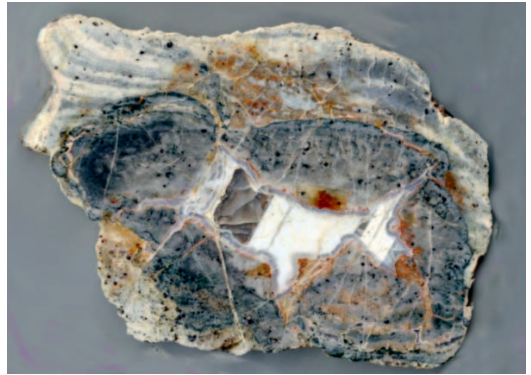


FIG. 17. Lithophysa (blown up by fluid) with onyx banding and nearly perpendicular flow layering of rhyolite—evidence of formation of onyx banding prior to lava eruption. Khapcheranga district, Transbaikalia region, Russia. 16 cm long.

Although solid crusts of lava flows form rather quickly, their interior may cool down very slowly. Daly (1933) estimated that a flow with an initial temperature of 1100 °C would cool to 750 °C in 12 days for a flow 1 m thick, in three years for a flow 10 m thick, and in 30 years for a flow 100 m thick. The rate of cooling increases considerably if the lava is erupted on the seafloor. On the basis of the logic outlined above, formation of the Mesozoic agates of Brazil and Transbaikalia was likely synchronous with the host volcanic rocks. Therefore, it is possible to challenge the conclusion of some investigators (*e.g.*, Ostashchenko & Rozhkova 1987, Spiridonov *et al.* 2000, 2001, Moxon 2014) that agates are considerably younger than their host volcanic rocks by amounts ranging from several million to up to hundreds of million years.

The problem in establishing the time of formation is that the early minerals formed in agate, represented by various silica minerals, do not contain a sufficient concentration of elements of use for dating (K-Ar, Rb-Sr, U-Pb, Sm-Nd). Consequently, their age has not been defined yet. By means of K-Ar and Rb-Sr dating, only the age of such late minerals as mordenite, apophyllite, and calcite (Ostashchenko & Rozhkova 1987, Spiridonov *et al.* 2000) has been determined. However, these minerals could be the products of much younger hydrothermal events and metamorphic processes totally unrelated to the period of primary filling of agate amygdulites with the silica minerals.

The presence of such minerals as fayalite, garnet, and topaz in agates (Iddings 1885, Cross 1886), the relationships of the orientation of the amygdulites with the layers of lava flows described above, and the

existence of substance-extrusion channels in agates all conflict with the opinion of Spiridonov *et al.* (2001) that agates form many millions of years after solidification of their host volcanic rocks and under an environment of low-grade burial metamorphism in the zeolite facies.

Agate deposits are generally spatially related to stratovolcanos (Yusupov 1982, Yurgenson 1995), but do not occur in them directly, because only the bottom layers of volcanic units that were laid down on water-bearing sedimentary rocks (aquifers) or on submarine sedimentary and volcanic rocks are favorable for agate creation. The fact that agates are found mainly in volcanic suites older than Cenozoic, as pointed out by Spiridonov *et al.* (2001), can be explained as follows: the upper and intermediate horizons in older volcanic piles have been removed by erosion, which renders accessible their agate-bearing bottom layers. These are commonly inaccessible for inspection in younger volcanic units.

In any case, the agates mined from metavolcanic rocks in Mexico are known to be of Neogene age, and a modern agate with chalcedony and mossy textures composed of iron hydroxides has been documented in the area of black smokers in the TAG hydrothermal mound, 26°N Mid-Atlantic Ridge (Hopkinson *et al.* 1998). Considering the data offered above, the gap between the age of agate minerals determined by some geologists and the age of their host volcanic rocks simply points out the termination of a very long history of mineral formation in an agate, not the late filling of empty vesicles created long ago in volcanic rocks by much younger minerals.

CONDITIONS OF FORMATION OF AMETHYST GEODES IN BRAZIL AND URUGUAY

The well-known amethyst-lined geodes of Brazil and Uruguay come from the basic traps of the Paraná volcanic formation, of Early Cretaceous age. They have a geometry ranging from prolate and cigar-shaped to oblate, like a round loaf of bread (Fig. 18). Extended prolate geodes are reported to be found in strongly hydrothermally altered basalts, whose losses of ignition (LOI) are >5% H₂O, whereas the oblate geodes are said to occur where the basalt is less strongly altered, with a LOI of less than 5% (Duarte *et al.* 2011, Hartmann *et al.* 2015). On this basis, those authors proposed a formational mechanism involving percolation of fluid from an aquifer horizon through mechanically weakened hydrothermally altered volcanic rocks. However, the assemblage of alteration minerals described by them is of low-temperature smectite type, not minerals expected from the deuteric modification of basalt during cooling, such as epidote,

chlorite, or amphibole (Duarte *et al.* 2011). In other words, alteration of the basalts occurred at conditions close to surficial weathering, whereas the minerals composing the amethyst geodes formed at higher temperatures.

According to Gilg *et al.* (2014), the agate geodes of Brazil were filled with mineral substances in four stages. In stage I, celadonite, chalcedony, and pyrite formed under reducing conditions due to the biogenic reduction of sulfate by organotrophic bacteria, which is suggested by the low $\delta^{34}\text{S}$ value of pyrite (–25 to –32‰). During subsequent stages, the fluids became more oxidizing and produced amethyst, goethite, and anhydrite (stage II); early calcite (stage III); and baryte, late calcite, and gypsum (stage IV). The temperature of the fluids responsible for the mineralization of the first stage remains undetermined because fluid inclusions are absent in the relevant fine-grained minerals. Minerals of stages II–IV contain single-phase liquid inclusions with concentrated chloride-sulfate solutions and formed under oxidizing conditions at less than 80–90 °C; calcite crystallized with gypsum below 45 °C.

Agates with concentric banding may be found beside the amethyst geodes (Fig. 19). It is quite reasonable to propose that the internal pressure of the fluids increased during their formation. But this pressure, most likely, was lithostatic, caused by the burden of the overlying column of volcanic rocks. It is unlikely that a cavity three to four meters high could form in a solid like the hydrothermally altered rocks. The mechanism of cavity formation in volcanic rocks proposed by Duarte *et al.* (2011) and Hartmann *et al.* (2015) thus seems unfeasible. High values of $\delta^{34}\text{S}$ reported in anhydrite and baryte, from 7.5 to 9.9‰, suggest that sedimentary brines from the deeper parts of the Guarani aquifer system were responsible for the amethyst mineralization in Brazil. The Catalanes pile of andesite in Uruguay, with its amethyst-bearing cavities, lies directly over the Botucatu Formation, also an aquifer (Duarte *et al.* 2011).

It is quite likely that the cavities for agate geodes were created by injection of fluids into the molten lavas, as suggested by Macdonald (1972), and thus long before the incrustation of cavities by minerals. Such an injection was favored by the eruption of the first flows of trap lavas of the Paraná Formation on top of the water-rich horizons of the Guarani aquifer. Water expelled from this aquifer as the result of the sudden heating behaved explosively, and its pressurized bubbles were forcefully injected into the melt and expanded to form enormous cavities.

The general thickness of the Paraná trap formation containing agate and amethyst geodes amounts to two kilometers. The amethyst-bearing horizons lie at its



FIG. 18. Amethyst geodes from Brazil with giant prolate and small oblate geometries.

bottom and agate-rich horizons lie at higher levels, although frequently in the same areas, but produced from different mines (Zenz 2014). It is known that the amethyst-producing Veia Alta flow in Brazil has a thickness of 30 m. Its amethyst-bearing intermediate bed of massive structure is located between its thin-layered bottom and top crusts (Duarte *et al.* 2011) which were, undoubtedly, the crusts formed as the lava flowed.

Considering the enormous size of some amethyst geodes and their rather thin wall-lining bands of mineralization, one can assume that the lower 30-meter flow of the Paraná traps solidified long before eruption of the overlapping new flows. As a result, the giant gas bubbles in the earlier flow were not subjected to compression. The absence of moss textures and onyx banding in the amethyst geodes suggests a two-step history. First, during the slow burial of bubble-bearing volcanic rocks under the younger flows and sediments, the cavities were filled with silica-rich formation waters derived from the underlying aquifers. Later, once the volcanic rocks had become depressed into a zone of low-grade burial metamorphism, they were subjected to limited compression, which raised the pressure in the bubbles and forced silica sol to percolate into the host rocks, with the formation of a thin concentric layer with chalcedony and celadonite on the walls of the geode. After that, the walls of the cavities were covered with druses of amethyst and other minerals from components leached from the host volcanic rocks by retrograde metamorphic fluids. During the entire process, the solutions did not undergo any great variations in pressure, nor any unmixing, which resulted in the absence of horizontal onyx banding and moss textures in the amethyst geodes.



FIG. 19. Agate from Brazil (with only concentric banding) connected to a larger amethyst geode. Collection of S.M. Mironov, on display in the Vernadsky Geological museum, Moscow, Russia. Photo by A. Evseev.

AGATES IN SEDIMENTARY ROCKS

The agates found in calcareous sedimentary units form by the mobilization of silica disseminated in rocks by formation waters and its redeposition in dissolution-induced cavities. Such agates are found in limestones of Carboniferous age near Moscow. I had the opportunity to study the collection of agates from the limestones of the Golutvin district assembled by my colleague L.M. Lebedev. These agates are of low-temperature origin and contain no mossy aggregates (the products of brine unmixing), no onyx banding, and no channels of substance extrusion, which could indicate a periodic rise of pressure in the amygdulites. These agates, like the amethyst geodes of Brazil, have only a concentric lining, composed in this case of metacolloidal silica minerals. It was possible to entirely fill such dissolution-induced cavities with the low-temperature silica sol, which coagulated on their walls (Fig. 20). The pressure needed for the filtration of the solution from the cavities into the surrounding rock, necessary for sol percolation and coagulation, could be provided by the limited compression of the rocks and the cavities in them by lithostatic pressure after these rocks found themselves in the zone of low-grade burial metamorphism.

CONCLUSIONS

The major conclusions of this study of the main problems of agate genesis listed in the Introduction are as follows:

- (1) A detailed analysis of the evolution of the shape and internal wall-lining and onyx banding of agate amygdulites inevitably leads to the conclu-

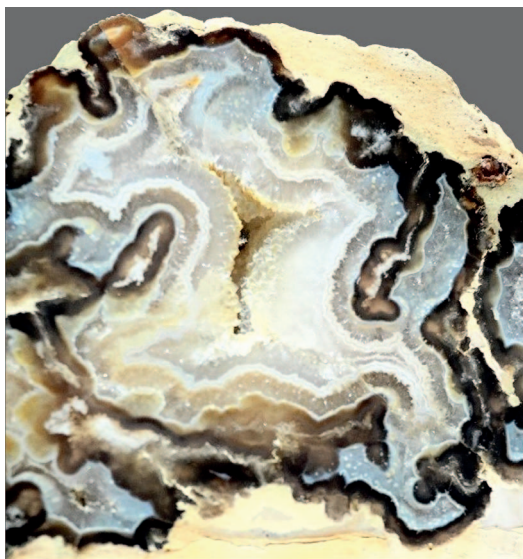


FIG. 20. Agate with only concentric banding from the limestones of the Golutvin area, Moscow region, Russia. 15 cm in size. Collection of Fersman Mineralogical Museum, Moscow, photo by A. Evseev.

sion that they formed through silica gel precipitation at magmatic temperatures in the enclosing lavas. High-temperature SiO_2 gels are unfamiliar because industry has not, to date, found it necessary to produce such gels at magmatic temperatures. But there are at least four geologic and experimental studies on the stability of SiO_2 gel at high temperatures.

- (a) At Kawah Ijen stratovolcano (Java), Indonesia, Lowenstern *et al.* (2018) found xenoliths of magmatic rock with the feldspar phenocrysts replaced by microgranular amorphous silica gel in fresh, non-altered dacite. The authors proposed several different explanations, but the last one, relating the gel replacement to the action of subsurface acid waters *after* capture of older rock inclusions by dacitic magma and its solidification, seems less favorable. Their first suggestion, that the “opaline materials are likely to be encountered by rising magma at a variety of locales within the volcanic edifice” is more realistic because the micro-agate inclusion in the altered feldspar phenocryst shown in their photomicrograph (Fig. 2c in Lowenstern *et al.* 2018) could not form from simple subsurface acidic alteration. The formation of

vuggy agate infill with concentric banding within the earlier formed opaline material can be realized only under the influence of enclosing magma. The high temperature of the magma promoted dehydration of the gel material in the feldspar phenocryst and raised the pressure of the released water for exfiltration of the sol. The exfiltration is necessary to produce gelation on the walls of the vug, as in the case discussed earlier of agates in lithophysae of felsic volcanic rocks.

- (b) According to Bogoevski's (2000) experiments, the silica gel composed of microgranular fractal (framboidal) aggregates of silica gel particles of nanometric size was amorphous after heating for 10 hours at 1100 °C.
 - (c) In studies of SiO_2 gel films, Fardad (2000) found “dramatic effects on the porosity, optical quality, shrinkage, thickness, and structural evolution during thermal treatment” of amorphous gel films at different temperatures up to 1000 °C, but no crystallization effects during the heating were reported.
 - (d) Nguyen *et al.* (2008) executed a profound theoretical simulation of changes of Si-O stoichiometry in core and peripheral parts of amorphous SiO_2 nanoparticles in the temperature range from 7000 to 350 K with 700 K steps. The particles were considered to be amorphous upon cooling the material from the melting temperature of bulk SiO_2 (1460 °C) until solidification to glass or solid opal.
- (2) The described “conmagmatic” genesis of early silica gel infilling in agates contradicts previous suggestions about the formation of silica minerals in vesicles only after solidification and cooling of host volcanic rocks.
 - (3) The temperatures of agate formation have a wide range, from the melting temperature of host lavas (>1100 °C) to those of low-grade burial metamorphism (<200 °C) and perhaps to 100–50 °C for the formation of agate infillings in ammonites. The pressure of agate formation is generally low, being dependent in volcanic rock on the burden of overlapping new lava flows and on burial metamorphism.
 - (4) The internal channels in agates are treated here as extrusion channels rather than silica feeding paths, as was suggested previously. The extrusion of material was attributed by Shaub (1955) to compression of amygdules due to pressure

exerted by the lava but, in our opinion, it is more likely due to the arrival of new lava flows. This conclusion is supported by the patterns of change in the layers next to the channels and by the termination of all channels within the boundaries of all agates.

- (5) The cause of a textural shift from wall lining to horizontal (onyx) banding is related, with reference to the experiments of Duclaux (1929), to a change in internal pressure in agate from higher to lower than the maximum osmotic pressure of silica sol (about 0.1 MPa). It is shown that Nacken's concept (1917) relating this phenomenon to heterogeneous fluids can be valid only for agate formation at subcritical temperatures.
- (6) The formation of hollow tubular and mossy structures in agates has been related by Gergens (1858), Liesegang (1915), and Chukhrov (1955) to osmotic processes in brine and water systems containing gel film membranes. This idea is confirmed and expanded in the article by analysis of the behavior of such structures at various environments and fluid compositions.
- (7) Subsequent to the first formation of SiO_2 in amygdules after the appearance of water fluid bubbles in lava flows, the additional filling of agate with SiO_2 is unnecessary, because the soft amygdules are compressed and diminish their volume proportionally to water loss due to exfiltration.
- (8) Textural analysis of agates in lithophysae in felsic volcanic rocks shows their genesis in liquid lavas or in the feeding channels of eruptions. These agates suffered recurrent changes in fluid pressure and aggregate state of the fluid (unmixing of supercritical solutions). Therefore, they possess both concentric or onyx banding and mossy and tubular textures.
- (9) The problem of the formation of giant amethyst geodes in Brazil and Uruguay is simplified by the absence of onyx banding and mossy or tubular textures. Therefore, there is no evidence of fluid unmixing or oscillation of pressure. Such a simple environment could take place during low-grade burial metamorphism of volcanic rocks with the giant gas bubbles filled with silica sol. The bubbles could avoid compression because the enclosing lava flow was solidified long before it was covered with overlapping new lava flows.
- (10) Agates in sedimentary rocks and other low-temperature agates, like amethyst geodes, are devoid of moss textures and onyx banding.

Therefore, their formation may also be related to processes of low-grade burial metamorphism.

The formation of primary filling of agate amygdules is related to the rhythmic coagulation of silica sol in various cavities that were gas vesicles in liquid lavas and in solidified volcanic rocks, or dissolution-induced cavities in limestones. The entire formation of agates, starting with the filling of cavities with the silica gel (with its transformation into opal-A, opal-CT, and chalcedony) and terminated by late low-temperature pseudomorphs and druse-lining minerals, can be spread over many millions of years.

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