

Genesis of banded, fibrous, and twisted quartz by 'catalysis,' unstable crystallization fronts, and substitution: self-organization in agates

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Introduction

Agates from basalts display bands consisting of chalcedony fibers with low-trace-element content that repeatedly alternate (Wang and Merino, 1990) with bands consisting of twisted, very fine fibers high in trace elements. This association of repetitive features is a striking case of self-organization, a class of processes in which the system generates its features through its own dynamics (Nicolis and Prigogine, 1977). We summarize here a new crystal growth model that accounts for the genesis of each texture and composition, their association, and their systematic alternation. Petrographic, microstructural, chemical, isotopic, and other agate data are given by Michel-Lévy and Munier-Chalmas (1892), Correns and Nagelschmidt (1933), Frondel (1962, 1978), Fallick *et al.*, (1985), Harris (1989), Flörke *et al.*, (1984), Cady *et al.*, (1993), Heaney (1993), and others.

Proposed Mechanisms of Agate Growth

The model contains three hypotheses: that quartz growth is enhanced, or 'catalyzed,' by some cations (of which there are experimental hints, e.g., Kastner *et al.*, 1977; Hosaka and Taki, 1981); that fibrous textures are produced by crystallization fronts that were morphologically unstable; and that fine fibers grow *twisted* by substitution of cations for silicon along their peripheries. These mechanisms are modelled quantitatively (Wang and Merino, 1994; Merino *et al.*, 1994) with continuity equations coupling diffusion, growth rate, concentrations of silica and 'catalysts,' and the curvature and surface energy of the growth front, and with geometric constraints.

Inward crystallization of agate starts at the margin from a medium containing water, cations (one of which 'catalyzes' quartz growth), and silica. As quartz grows, the 'catalyst' segregated just ahead of the front accelerates quartz growth — hence its own further accumulation. This

feedback causes the silica and trace-element concentrations at the front (and thus the content of cations incorporated by the quartz — see below) to oscillate.

Simultaneously, the front becomes morphologically unstable (Sekerka, 1973): incipient bumps on the crystallization front grow longer, become fingers, and generate other fingers just beyond a threshold distance. The fingers constitute a coherent fibrous *texture*. The condition for morphological instability, $grad$ (growth rate) > 0 , links growth kinetics to fibrous habit.

Each finger becomes a fiber by accretion of conical sleeves (Langer, 1980) of quartz. As each conical sleeve of quartz forms, it crosses decreasing trace-element concentration profiles generated at the front by the 'autocatalytic' instability: the rim of the sleeve has to take up more trace elements than its tip does. Thus, fibers become richer in trace elements along their peripheries than along their centers. Ion-probe analyses (Merino *et al.*, 1994) indicate that Al enters the quartz fibers in substitution for Si. Al-O bonds being longer than Si-O bonds, the fiber is forced to grow twisted to accommodate the larger peripheral Al content.

Implications of model

The conditions for the system of equations to have oscillatory solutions (which are necessary for the model to represent self-organization in agates) are: (1) The 'catalyst' needs to be carried to the growth front by the silica; this is possible if the silica species were polymeric and the 'catalyst' were attached to the polymers. (In turn, polymeric silica would be viscous, and difficult to transport through solid basalt, which suggests that the silica was somehow in place to begin with, and that agate growth is closed system.) And (2) repeated oscillatory banding requires that silica diffusivity in the initial medium be very low, which also would be true for polymeric species.

Linear analysis of the morphological instability of the crystallization front yields a dispersion equation that brings out factors favoring (high growth rate constant and 'catalysis') and impeding (surface tension and solubility) the genesis of fibrous textures in general. For agates, the equation gives a 'preferred' fiber thickness of a few micrometers, as observed. The equation also links the genesis of fibrosity to the oscillations in silica and cation concentrations produced by 'autocatalysis' at the front. Under the two conditions outlined above, this linkage is responsible for the predicted association of oscillatory bands, fiber sizes, fiber twist periods, and trace element concentrations, a series of predictions that exactly match observations.

Evidence

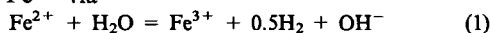
Closed-system growth is confirmed by trace-element, petrographic, and rare field evidence. In a fresh agate quarry in the Paraná basalt at Rio Jacuí, Rio Grande do Sul, no channels are visible coming into or leaving hundreds of in-situ agates in a 13-metre-thick flow. All vesicles are near the top of the flow, and all are empty. The agates only occur in the flow's lowermost 3 meters.

Ion-probe analyses of agate confirm the oscillatory profile predicted by the model. Minima in Al, Fe, and K exactly correspond to layers consisting of untwisted fibers, and maxima to layers consisting of twisted fibers, as predicted. The agate quartz also contains Mn, Na, H (not shown), and, notably, Ni.

Plagioclase laths in the basalt mesostasis adjacent to the agate occasionally are tangent to it, but are randomly oriented farther away. This suggests that siliceous lumps formed and collected (perhaps by immiscibility) while the basalt was still liquid, and after the laths had crystallized. The occurrence of Ni (unaccompanied by Mg) in the agate quartz also points to an igneous origin of the silica lumps.

Other predictions

The model also predicts (correctly): (1) The systematic genesis (by annealing of twisted fibers) of dislocations and of a new low-symmetry polymorph, reported by Flörke *et al.*, (1984), Cady *et al.*, (1993), and Heaney (1993). (2) The systematic inward switch from concentric bands of length-fast fibers to a layer of coarse length-slow quartz, and the occurrence of a central void. (3) The systematic inward self-oxidation of Fe^{2+} to Fe^{3+} via



(which is driven by the rises in Fe^{2+} and H_2O concentrations produced by removal of silica), and the increase in Fe^{3+} content of many agates, which makes the quartz increasingly darker purple, and causes goethite to crystallize within the quartz. (4) The systematic inward decrease in ^{18}O of the quartz (Harris, 1989). (5) The association of agates with zeolites, whose growth is promoted by the high pH produced by reaction (1). And (6) the alteration of surrounding basalt to a film of (dark green) Ni layer silicates; the alteration is driven by nickel-bearing water escaping from the agate's central void.

Conclusions

The combination of the self-organizational model's internal requirements with field, petrographic, and trace-element evidence points to agates growing from pre-existing silica lumps, as part and parcel of the igneous phenomenon of basalt generation. Detailed trace-element and isotopic analyses will help to check this. Experiments are needed to detect if very-high-temperature immiscibility in basaltic magmas is possible (Navrotsky, 1992), and to study cation-enhancement of quartz growth. If the mechanisms invoked here (quartz growth rate enhancement by cations, genesis of fibrous textures by unstable fronts, and fiber twisting by substitution) are confirmed by additional work, the model will have remarkable implications for the origin of agates, crystal growth, quartz crystal chemistry, the behavior of basaltic magmas, and the geochemical interpretation of authigenic textures.

References

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