

A new interpretation of round embayments in quartz crystals

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Abstract

The surfaces of quartz crystals that were partially dissolved in superheated, H₂O-saturated rhyolite melt are covered with hemispherical embayments; each embayment is judged to have formed where a gas bubble in the melt approached the crystal. 'Flux-line attack' and 'upward-drilling' of the refractory lining of glass tanks are analogous processes. As a bubble nears a dissolving solid it enters a compositional boundary layer in the melt, resulting in melt of variable surface tension surrounding the bubble. This unstable situation results in small-scale convection of the melt about the bubble (Marangoni convection) which can cause locally enhanced dissolution rate of the solid. It is suggested that this mechanism could cause round embayments to form in quartz phenocrysts in acid volcanic and sub-volcanic rocks. Criteria by which embayed phenocrysts formed by dissolution can be distinguished from those formed by unstable growth are reviewed briefly.

KEYWORDS: quartz, magmatic dissolution, embayment, crystal-liquid interface, surface tension, Marangoni convection.

Introduction

PHENOCRYSTS and xenocrysts in volcanic and sub-volcanic rocks sometimes have surfaces that are embayed. The embayments have traditionally been interpreted in one of two ways: some petrologists hold that they result from unstable *growth* (e.g. Heddle, 1896; Holmes, 1930; Drever and Johnston, 1957; Gutmann, 1977), while others maintain that they are a consequence of dissolution in melt (e.g. Judd, 1883; McMahon, 1889; Bain, 1925; Larsen *et al.*, 1936, 1938; Varne, 1968; Harris and Anderson, 1984). Compelling petrographic evidence in support of a growth origin was provided by Laemmlein (1930). More recently, experimental growth of minerals from silicate melts has demonstrated repeatedly that unstable growth, brought about by large degrees of supersaturation, does indeed encourage embayments to form (e.g. Donaldson, 1976; Lofgren, 1980). Experiments have also demonstrated that as minerals resorb in superheated silicate melts they become progressively rounded and typically develop a smooth, embay-

ment-free interface with the melt (e.g. Kuo and Kirkpatrick, 1985; Donaldson, 1985; Tsuchiyama, 1986). Yet some petrologists still incline to the dissolution interpretation.

We report here the result of a new dissolution experiment in which quartz crystals, partially resorbed in superheated, H₂O-saturated rhyolite melt, have developed distinctive, well-rounded embayments on their surfaces. The likely origin of these embayments introduces to petrology a new concept in the transport of material in the melt, and offers an explanation for the development of round embayments on crystals undergoing resorption.

Experimental methods

Rhyolite from Glen Coe, Scotland, was fused dry at 1 atm., quenched to form a clear glass (Table I) and ground to a fine powder. 0.3 g of the powdered glass was loaded into an Au capsule, together with three faceted crystals of quartz from the Llallagua mine in Bolivia (Donaldson, 1985, Table III) and about 5 wt. % of deionised water. The welded

Table 1. Composition of rhyolite starting material and analysed glasses

	1	2 ^b	3	4 ^b	5 ^b
SiO ₂	73.1	75.1	71.8	75.0	72.4
TiO ₂	0.2	0.2	0.2	0.2	0.2
Al ₂ O ₃	14.4	14.3	13.7	12.1	13.3
Fe ₂ O ₃ (total)	1.0	1.0	0.9	0.7	0.7
MgO	0.2	0.2	0.2	0.3	0.2
CaO	0.6	0.6	0.5	0.6	0.5
Na ₂ O	4.8	3.9 ^a	3.7 ^a	3.1 ^a	3.5 ^a
K ₂ O	4.7	4.5	4.3	4.2	4.4
Total	99.0	99.8	95.35	95.85	95.25

1 XRF analysis of powdered Glen Coe rhyolite.

2 Electron probe analysis of glass prepared by fusing rock at 1300°C for about 2 hours in an atmospheric pressure, gas-mixing furnace. Note the Na₂O loss and SiO₂ gain, as compared with the rock.

3 Analysis 2 recalculated as if 4.5 wt.% H₂O is present.

4 E.P. analysis of glass 10 μm from crystal.

5 E.P. analysis of glass 300 μm from crystal.

^a These are minimum values, owing to the fact that Na migrates in the glass under the heating of the electron beam.

^b Obtained with St Andrews University JEOL Superprobe, using mineral standards, accelerating voltage of 15 kV, sample current of 20 nA, counting time of 20s on peak, 5s on background; for Na 2s on peak to minimize loss of count rate.

capsule was held in a cold-seal bomb at 850 ± 10 °C and 0.83 kbar for 197 hours before quenching. These conditions are approximately 100 °C above the H₂O-saturated liquidus temperature for this

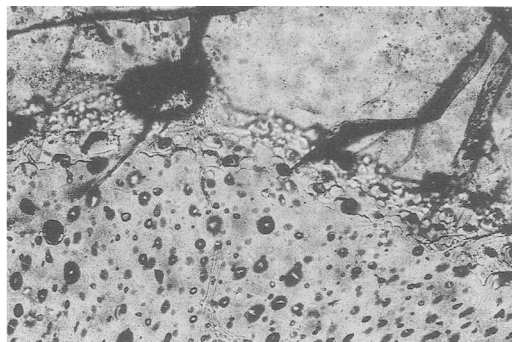
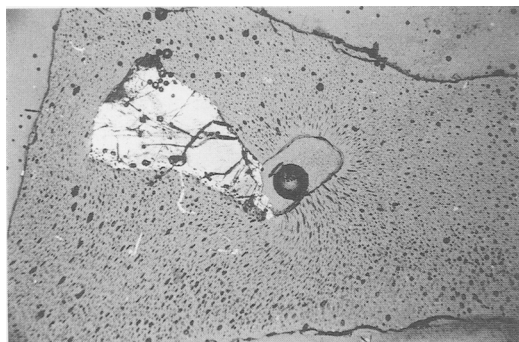
melt (interpolated from data of Tuttle and Bowen, 1958), causing the quartz crystals to dissolve. The computed viscosity for the bubble-free melt is 2.3×10^6 poise, using the method of Shaw (1972).

The capsule released gas upon opening and the glassy charge was densely vesicular throughout, indicating that there was gas present during the experiment [4–4.5 wt. % H₂O is needed to saturate the melt at the run pressure used (Tuttle and Bowen, 1958, fig. 27)]. A portion of the charge was prepared as a polished thin section, while the remainder was steeped in dilute hydrofluorosilicic acid for twelve hours to dissolve the rhyolite glass and expose the quartz crystals. [Quartz is extremely resistant to this acid (Chapman *et al.*, 1969), as was confirmed by steeping some quartz crystals in the acid for twelve hours, with no etching being detected.] Once released from the glass, the quartz crystals broke along conchoidal fractures into several pieces; the surface appearance of some of these pieces was examined with a scanning-electron microscope at magnifications up to $\times 700$.

Observations

Fig. 1 illustrates the run product in thin section. Two touching crystals of quartz (one has plucked from the section) are surrounded by clear, highly vesicular glass. Many of the vesicles are discoidal in shape and hence have an elongate, aligned appearance in section; this is probably due to crumpling of the capsule during quenching of the experiment. On one side of the larger quartz crystal the glass and crystal have a scalloped junction (Fig. 2), with the crystal indented by curved cavities.

The pieces of crystal examined with the scanning-electron microscope are bounded partly by irregularly fractured surfaces and partly by cellular



FIGS. 1 and 2. FIG. 1 (left). Transmitted light view of a portion of charge. In the centre a piece of quartz has been plucked from the section. (Partially crossed polars; field of view 6 mm). FIG. 2 (right). Close-up of part of the quartz-glass interface along top side of the crystal in fig. 1 (PPL; field of view 1 mm).

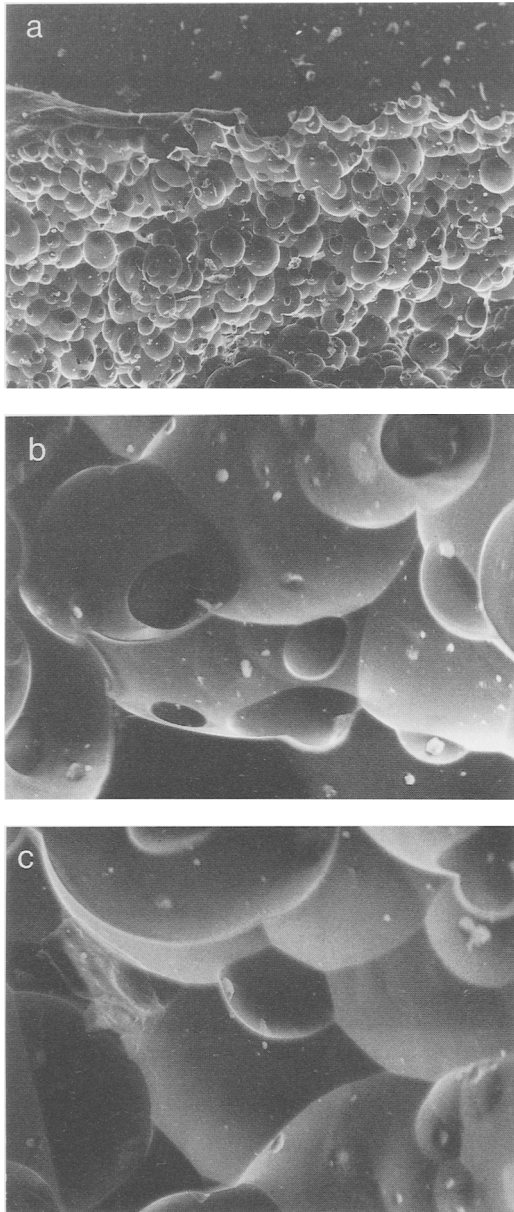


FIG. 3. (a-c) SEM views of the glass-free surface of two fragments of quartz crystals. Width of views 1.1, 0.15 and 0.12 mm, respectively.

surfaces. The latter are covered with perfectly smooth, curved pits (Fig. 3a), resembling the frothy interior of a popular British chocolate bar. Some of the pits have smaller pits within them (Fig. 3b), and the cusp formed where several pits meet may be the site for a new pit to develop (Fig. 3c). The largest

pits are 100 μm in diameter and the smallest 20 μm . (For comparison, the vesicles in the glass range in diameter from 10 to 70 μm .) Notice that the crystal surfaces in Figs. 3a-c are saturated with pits.

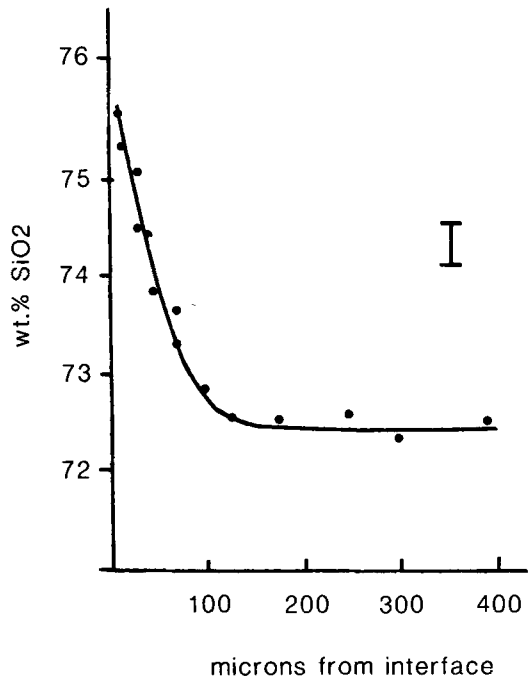


FIG. 4. Variation in SiO_2 content of glass adjacent to the quartz crystal in Fig. 1, as measured in a series of 'spot' analyses. (Bar shows precision 2σ).

Electron microprobe analysis reveals the existence of an approximately 150 μm -thick composition gradient in the glass adjacent to crystals (Table 1, Fig. 4). The interface glass composition and the bulk composition of the rhyolite glass are projected into the normative quartz-albite-orthoclase triangle in Fig. 5, on which are also shown the 850 $^{\circ}\text{C}$ isotherms at 0.5 and 1 kbar $P_{\text{H}_2\text{O}}$ in the quartz-saturated phase field. The diagram suggests that melt (composition 4) near to quartz crystal is less silica-rich than the supposed equilibrium composition (i.e. it does not plot where the 850 $^{\circ}\text{C}$ isotherm for 0.83 kbar must lie). This could be an indication that interface-detachment kinetics has contributed to limiting the dissolution rate (estimated at approximately 0.2 $\mu\text{m}/\text{hour}$). Alternatively, insufficient time may have elapsed to achieve surface equilibrium (i.e. a transient condition may be recorded).

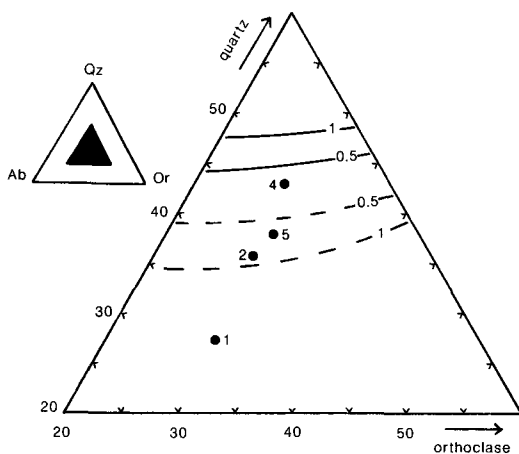


FIG. 5. Normative compositions of original rhyolite (1), fused rhyolite (2), and of glass near (4) and far from (5) partially dissolved quartz crystals (Table 1). Projection onto part of the plane albite-orthoclase-quartz. 850 °C isotherms (solid lines) and quartz-feldspar boundary curves (dashed lines) for the system at $P_{\text{H}_2\text{O}} = 1$ and 0.5 kbar are redrawn from Tuttle and Bowen (1958).

Discussion

Mechanism of dissolution. Dissolution of the quartz involved transport of solute through the silica-enriched boundary layer of melt that forms about each crystal. The approach to surface equilibrium suggests that the principal control on dissolution rate was solute diffusion, rather than the rate of release of solute from crystals.

The hemispherical pits on one side of the quartz crystal in Fig. 1 point to an unusual dissolution behaviour having operated locally. The pits are distinct from the well-known faceted kinds that form when quartz is etched with acids (e.g. Frondel, 1962). Furthermore, pitting does not occur when this quartz is dissolved in dry rhyolite melt (Donaldson, unpubl. data). This fact, together with the shape and size of the pits, leaves no doubt that the origin of the pits is related to the existence of the bubbles in the melt. Bubbles may have nucleated on imperfections and projections on the surface of crystals (Fig. 3c), or have been attracted to crystals by surface tension, or have floated up under crystals. This final suggestion could account for the apparent absence of bubbles from two sides of the crystal in Fig. 1. Irrespective of their origin, it is certain that where a bubble contacted a crystal, dissolution locally accelerated, and this must be the result of faster transport of solute in the vicinity of bubbles.

Accelerated dissolution of solid in a solution containing gas bubbles is a notable problem in the

glass industry (e.g. Flint and Payne, 1926), for the refractory lining of a furnace containing molten glass is preferentially corroded at the interface between the melt and the ambient atmosphere (so-called 'flux-line attack'). Preferential corrosion also occurs where bubbles collect in the horizontal joints between refractory bricks or on downward-facing surfaces of the furnace, leading to carious corrosion caused by preferential upward dissolution of the refractory surface (so-called 'upward drilling'). The textural resemblance between refractory corroded in this manner (Preston and Turnbull, 1941, Plate 1) and the quartz crystals described in the present paper is extremely striking.

In a simulation of upward drilling Busby and Barker (1966) have investigated the accelerated dissolution of crystals of ice and of halite in a methanol-H₂O solution: when bubbles of air or nitrogen were injected into the solution below the downward-facing, horizontal faces of crystals, upward drilling caused cavity formation adjacent to bubbles. Cavities formed in the ice crystals elongated with time, whereas those in halite were hemispherical, with a small, central lump in each (Busby and Barker, 1966, Fig. 8).

The explanation given by Preston and Turnbull (1941) for the enhanced dissolution of furnace refractory above bubbles is that a component of the molten glass, suggested to be Na, which has the effect of reducing the surface tension of the melt, concentrates on the surface of bubbles, forming a melt composition in which the solid is more readily dissolved. Thus, where a bubble approaches the furnace lining it locally corrodes the lining to form a cavity. It is suggested that the product melt is denser and has a higher surface tension than the bulk melt and so flows out of the cavity to be replaced by more of the sodium-enriched melt creeping along the surface of the bubble to maintain the surface tension.

Busby and Barker (1966) offer a simpler explanation, based on the fact that a gas bubble approaching a dissolving solid will encounter a large compositional gradient (boundary layer) in the melt adjacent to the solid, assuming that the dissolution rate is limited by mass transport in the melt. Once in the gradient, the bubble will be surrounded by melt of non-uniform composition and surface tension: in the case of a dissolving quartz crystal the part of the bubble nearest the crystal will be in contact with the most siliceous melt, and probably that with the largest surface tension. As the excess pressure in the bubble is given by twice the ratio of the surface tension to bubble radius, the non-uniform surface tension of the melt about the bubble will cause instability. In the vicinity of the bubble, motion will begin in an attempt to homo-

genize the melt in contact with the bubble. Turbulent fluid motion of this kind, caused by difference(s) in surface tension, was observed by Busby and Barker (1966, p. 445) in their experiments: it is known as Marangoni convection (Wilcox, 1983). Should the bubble closely approach the crystal, the convection will remove the SiO_2 -rich melt at the interface more readily than from adjacent areas of the crystal surface, and replace it with less siliceous, more undersaturated melt. The dissolution rate must, therefore, rise next to the bubble.

Petrographic relevance. To the best of our knowledge, there are no records in the literature of quartz crystals with surface textures like that produced in the experiment reported here, i.e. *saturated* with *small* curved embayments. A superficially similar, but different, texture which is due to preferential dissolution along dislocations in quartz has been described by Sunagawa and Sugibuchi (1986). While a search among products of explosive volcanic eruptions might reveal examples of the same texture, vesicles in rocks tend to be larger and less closely spaced than those in the experiment; consequently, individual crystals are more likely to be contacted by far fewer and much larger bubbles. Here may be an explanation of the numerous descriptions and illustrations in the literature and petrography textbooks of sectioned quartz crystals with faces penetrated by isolated, round, or often somewhat elongated, embayments, some of which may appear to be totally enclosed groundmass inclusions (e.g. Fig. 6, and see Joplin, 1964, Figs. 45B, 46B, and 47B; Moorhouse, 1964, Figs. 117B, 118A, and 120A; Eichelberger, 1978, Fig. 2A; and MacKenzie *et al.*, 1982, Fig. 30).

The problem that has existed in explaining these embayments as being of dissolution origin is that there has been no means of accounting for the local accelerated dissolution rate needed. As pointed out in the introduction, dissolution experiments with minerals in silicate melts do not result in formation of embayments. Indeed, this negative observation is only to be expected, because the compositional gradient in melt about a dissolving crystal will be less inside an embayment than outside, due to the larger ratio of crystal surface area to melt volume inside compared to outside (cf. Berg, 1938; McLachlan, 1978; Flemings, 1974). Consequently, the crystal dissolves more slowly inside the embayment. The corollaries are that an embayment should be an unstable feature on the crystal surface, and indeed ought never to form spontaneously on a crystal that lacks embayments.

This objection to the formation of round embayments by resorption is overcome by the mechanism of 'upward drilling' described here, because any vapour bubble that temporarily contacts a dissolv-

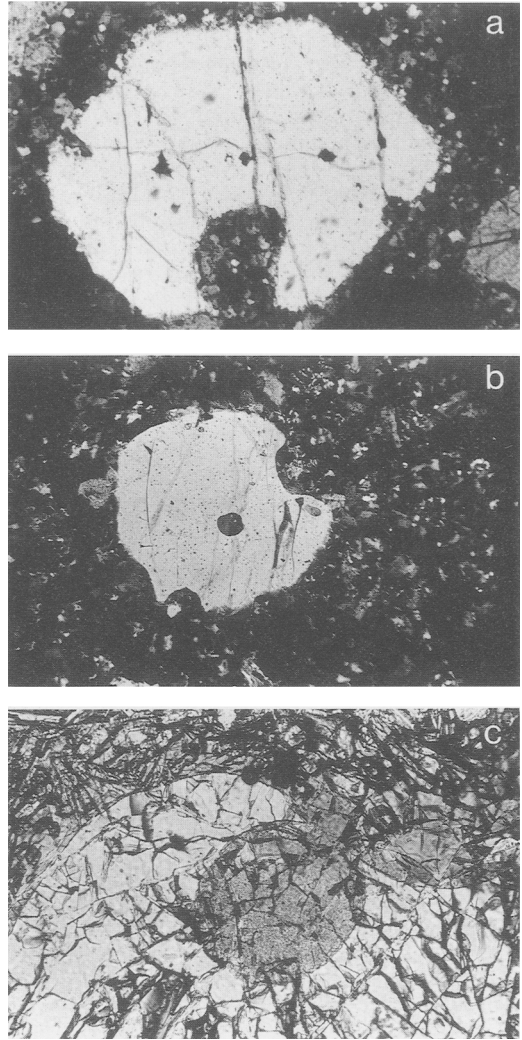


FIG. 6. Quartz crystals with round embayments. Widths of views 2.5, 3 and 0.5 mm, respectively. (a) Microgranite Tibchi complex, Nigeria (courtesy of P. Bowden). (b) Dacite porphyry, Isle of Eigg. Note the round inclusion. (c) Quartz basalt, Lassen Park, California. Detail of junction between quartz xenocryst and groundmass; glass occupies the curved embayment on the upper side of the crystal and the adjoining circular inclusion (middle of view).

ing quartz crystal will direct a continuous flow of more undersaturated liquid into the film of melt that separates bubble from crystal. Situations in which acid magma in a chamber is reheated, resulting in crystal resorption and exsolution of gas from the melt, are described by Sigurdsson and Sparks (1981) and Bacon (1986), amongst others,

and involve emplacement of hotter, heavier, basic-intermediate magma beneath the acid magma. Resorption in the presence of bubbles can continue until the crystal-liquid mixture is quenched by eruption (Fig. 7), or until cooling of the acid magma is re-established and bubbles re-dissolve. The same explanation can also be offered for the occurrence of embayed quartz crystals in hybrid basic-intermediate rocks, regardless of whether the quartz crystals are derived from wall-rock assimilation or by mixing of basaltic magma with a quantity of quartz-phyric rhyolite magma (e.g. Larsen *et al.*, 1936, 1938; Wilcox, 1944; Kanaris-Sotiriou and Gibb, 1986).

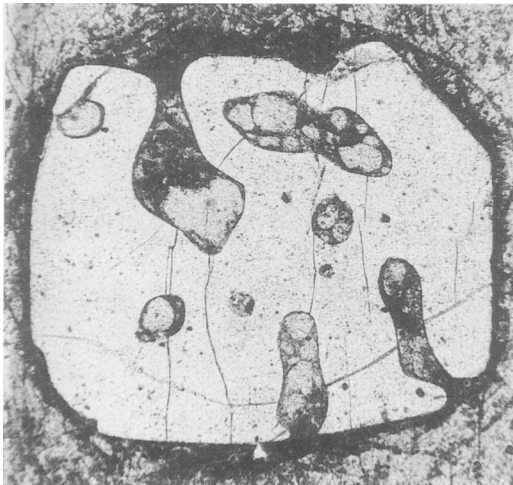


FIG. 7. Quartz phenocryst in flow-banded pitchstone, Suregei Plateau, N. Kenya. The glass in the embayments contains vesicles. Note the rounding of the crystal edges, consistent with resorption. Width of view 1.6 mm.

In thin section, embayments may appear considerably elongate and even sinuous. While this appearance is probably often the effect of oblique sectioning of a hollow, it might also in part result from a bubble moving up the surface of the crystal and scouring a groove.

Conclusion

Now that a suitable mechanism for explaining the occurrence of round embayments by dissolution is available, it becomes apparent that cavities can form during *both* dissolution and growth. Distinction between the two processes requires additional textural evidence: crystals with round

corners and edges, with or without round faces, are likely to have been partially dissolved (cf. Tsuchiyama, 1986), whereas those with sharp corners and edges are of unstable growth origin. Another criterion indicating embayment formation during unstable growth is provided by solid- and fluid-inclusion trains, or zones, which are deflected adjacent to the outline of an embayment (Laemmlein, 1930; Blackerby, 1968); if the trains or zones are not deflected but are merely cut through by the embayment, then the dissolution origin is correct.

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References

- Bacon, C. R. (1986) *J. Geophys. Res.* **91**, 6091–112.
 Bain, G. W. (1925) *Am. Mineral.* **10**, 435–41.
 Berg, W. F. (1938) *Proc. Roy. Soc. Lond. A* **164**, 79–95.
 Blackerby, B. A. (1968) *Am. Mineral.* **53**, 954–62.
 Busby, T. S., and Barker, J. (1966) *J. Am. Ceramic Soc.* **48**, 441–6.
 Chapman, S. L., Syers, J. K., and Jackson, M. L. (1969) *Soil Sci.* **107**, 345–56.
 Donaldson, C. H. (1976) *Contrib. Mineral. Petrol.* **57**, 187–213.
 — (1985) *Mineral. Mag.* **49**, 683–93.
 Drever, H. I., and Johnston, R. (1957) *Trans. Roy. Soc. Edinb.* **63**, 289–315.
 Eichelberger, J. C. (1978) *Nature*, **275**, 21–7.
 Flemings, M. C. (1974) *Solidification Processing*, McGraw-Hill, New York.
 Flint, F. C., and Payne, A. R. (1926) *J. Am. Ceramic Soc.* **9**, 613–17.
 Frondel, C. (1962) *Dana's System of Mineralogy, III, Silica Minerals*. New York: Wiley. 158–62.
 Gutmann, J. T. (1977) *Am. J. Sci.* **277**, 833–61.
 Harris, D. W., and Anderson, A. T. (1984) *Contrib. Mineral. Petrol.* **87**, 120–8.
 Heddle, M. F. (1896) *Trans. Geol. Soc. Glasg.* **10**, 80–95.
 Holmes, A. (1930) *Petrographic Methods and Calculations*. Van Nostrand, New York.
 Joplin, G. A. (1964) *A Petrography of Australian Rocks*. Sydney: Angus and Robertson.
 Judd, J. W. (1883) *Q. J. Geol. Soc.* **39**, 444–64.
 Kanaris-Sotiriou, R., and Gibb, F. G. F. (1986) *Geol. Mag.* **123**, 569–79.
 Kuo, L.-C., and Kirkpatrick, R. J. (1985) *Am. J. Sci.* **285**, 51–90.
 Laemmlein, G. (1930) *Z. Kristallogr.* **75**, 109–27.
 Larsen, E. S., Irving, J., Gonyer, F. A., and Larsen, E. S. 3rd (1936) *Am. Mineral.* **21**, 679–701.
 — (1938) *Ibid.* **23**, 227–57.

- Lofgren, G. E. (1980) In *Physics of Magmatic Processes* (R. B. Hargraves, ed.) Princeton Univ. Press, 487-552.
- MacKenzie, W. S., Donaldson, C. H., and Guildford, C. (1982) *Atlas of Igneous Rocks and Their Textures*. London: Longman.
- McLachlan, D. (1978) *Can. Mineral.* **16**, 415-25.
- McMahon, C. A. (1889) *Mineral. Mag.* **8**, 10-14.
- Moorhouse, W. W. (1964) *The Study of Rocks in Thin Section*. New York: Harper and Row.
- Preston, F. W., and Turnbull, J. C. (1941) *Am. J. Sci.* **239**, 92-106.
- Shaw, H. R. (1972) *Ibid.* **272**, 870-93.
- Sigurdsson, H., and Sparks, R. S. J. (1981) *J. Petrol.* **22**, 41-81.
- Sunagawa, I., and Sugibuchi, A. (1986) *J. Japan. Assoc. Min. Pet. Econ. Geol.* **81**, 348-58.
- Tsuchiyama, A. (1986) *J. Volcanol. Geoth. Res.* **29**, 245-64.
- Tuttle, O. F., and Bowen, N. L. (1958) *Geol. Soc. Am. Mem.* **74**, 153 pp.
- Varne, R. (1968) *J. Petrol.* **9**, 169-90.
- Wilcox, R. E. (1944) *Geol. Soc. Am. Bull.* **55**, 1047-80.
- Wilcox, W. R. (1983) *J. Crystal. Growth*, **65**, 133-42.

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