NOTES AND NEWS

ZONING IN SPHERULITES

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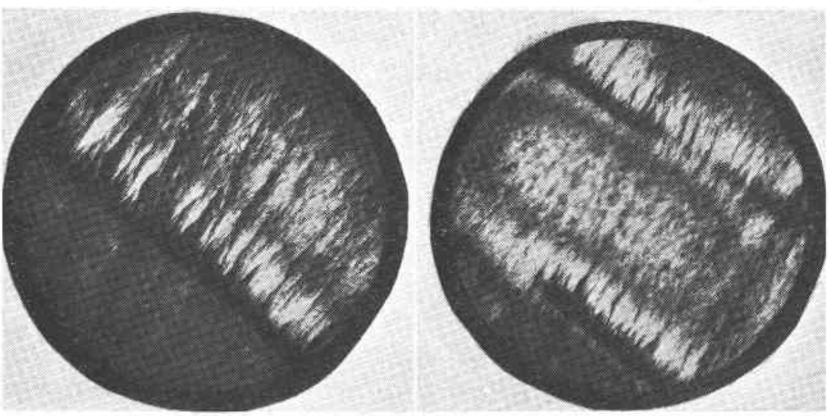
Introduction

In studies of artificial spherulites, the author has observed the development of a peculiar type of zoning (Figs. 1 and 2). A similar phenomenon has been observed in nature by Whitman Cross in the spherulitic rhyolites of the Rosita Hills in Custer County, Colorado. So far as the writer is aware, Cross neither described nor illustrated this phenomenon in any of his own reports. Unfortunately, too, his original thin sections are no longer available. However, one of Cross' photographs of this structure appears in Iddings' *Igneous Rocks* (2nd edition, John Wiley and Sons, New York, 1920, p. 233) and is herewith reproduced as Fig. 3. The present paper is an inquiry into the origin of this zonal structure.

Description of Zoning

The zoning consists of concentric shells of the crystallizing substance, but the transition from the outer surface of one shell to the next is peculiar. At some distance from the center of the menthol spherulite the radiating crystal fibers terminate to form a complete compact spherulite. On the surface of this spherulite other relatively thick crystal fibers appear at evenly distributed but scattered points. These fibers become more



Figs. 1 and 2. Multiple zoning in menthol spherulites under crossed nicols. The core of the spherulite is to the lower left. Magnification about 24×.

slender outward and branch and ramify until they again form a massive, compact shell. From this surface the transition to still another shell may take place (Figs. 1 and 2). Iddings (*op. cit.*, pp. 232–233) in discussing Cross' illustration states that the photograph represents "a section across a large spherulite at a spot where a spheroidal surface, or zone, terminating closely parallel prismoids, minutely branched, is succeeded by a growth of larger, branched crystals. These in turn become slender and more nearly parallel to one another."

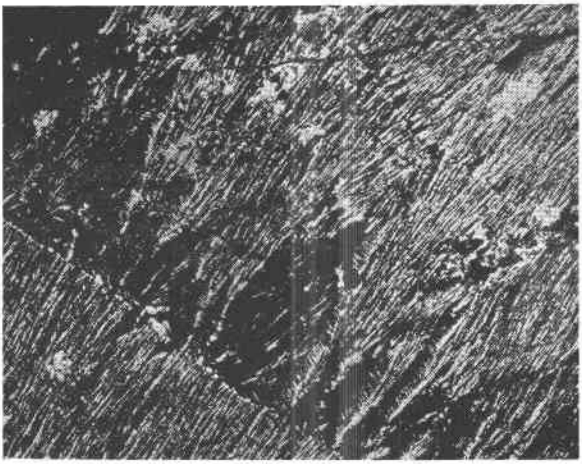


FIG. 3. Zonal boundary in spherulite from Rosita Hills, Colorado. (Cross, U. S. Geological Survey.)

ORIGIN OF ZONING

Iddings attributes the variation in the crystallization of the radiating crystals shown in Fig. 3 to "changes in saturation in the liquid magma arising from the rapidity of crystallization of the prismoid minerals." He suggests that "a sudden rush of crystallization may liberate sufficient heat to reduce the saturation of the surrounding liquid and even stop the separation of solid material until the diffusion of the heat permits saturation to rise again." He further notes that "a pulsation of crystallization in rapidly solidifying liquids can be observed in the laboratory under favorable circumstances."

In the explanation offered below for this type of zoning the writer makes use of the concepts of metastable and labile conditions in supercooled liquids. According to the more widely accepted of the two versions concerning the rate of crystallization in a supercooled liquid (Fig. 4), namely that of Tammann,[1] and later Doelter,[2] crystallization in a slowly cooling, supersaturated[3] solution will for some time take place slowly (metastable condition) from a few scattered loci, resulting in the growth of scattered large crystals. With continued fall in temperature the limit of supersaturation for the solution is finally reached, and copious crystallization from many centers results (labile condition). This may be the explanation for some porphyritic structures. The zoning described in this paper is more readily understandable on the basis of the curve subscribed to by Tammann and Doelter. Dr. Bowen[4] writes that he is not entirely convinced that crystallization can take place under both metastable and

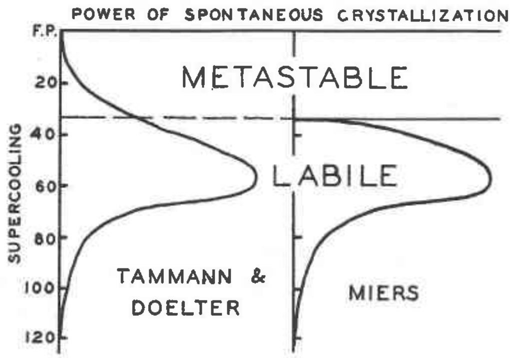


FIG. 4. Two concepts of the effects of supercooling on crystallization. Although Tammann experimented with organic substances and Doelter with rock-forming minerals, their conclusions were similar. The left-hand curve illustrates Doelter's results with augite. Miers' conclusions were based on experiments with salt solutions. The views of Tammann and Doelter are believed to more nearly represent conditions in magma. (From Harker's *Natural History of the Igneous Rocks*. Slightly modified.)

labile conditions. In his opinion crystallization under one set of conditions may preclude crystallization under the other. If this view should prove to be correct the explanation for zoning offered in this article would require revision. It is interesting to note that Mourant,[5] in discussing a type of zoning characterized by concentric areas of silica and feldspar, has likewise employed the concepts of metastable and labile crystallization.

[1] Tammann, Gustav, *Kristallizieren und schmelzen,* J. A. Barth, Leipzig, 148–156 (1905).

[2] Doelter, Cornelius, *Physikalisch-chemische-mineralogie,* J. A. Barth, Leipzig, 111–112 (1905).

[3] Both "supersaturation" and "supercooling" imply retarded crystallization. The former term, however, is best limited to solutions, whereas the latter includes simple melts.

[4] Bowen, N. L., Personal communication.

[5] Mourant, A. E., The spherulitic rhyolites of Jersey: *Mineral. Mag.* and *Jour. Mineral. Soc.* London, **23** (No. 139), 227–238 (1932).

Rate of cooling is probably the controlling factor in determining whether a compact or zoned spherulite will appear from solution. If the cooling is sufficiently rapid, the solution in the neighborhood of a center of crystallization may not linger at any temperature sufficiently long to permit all the material in excess of the saturation point for that temperature to crystallize out. In other words crystallization of the solute in excess of the saturation point for a given temperature may not yet be complete when an additional supply, representing the excess for the next lower temperature, begins to appear. Precipitation in this case will be continuous, and compact spherulites can be expected. If, however, the rate of cooling is slow, the solution may, under the conditions described later, periodically rid itself of the solute in excess of the saturation point for certain temperatures. The zoning described above is probably a result of such rhythmic precipitation.

The degree of saturation within cooling lava undoubtedly varies from point to point. If the cooling is slow enough, parts of the lava may become supersaturated. According to the experiments of Doelter who worked with rock-forming minerals (Fig. 4), crystallization would begin at a few scattered centers and its rate would be slow (metastable condition). When the limit of supersaturation was reached, the rate of crystallization would accelerate to a maximum and then diminish as rapidly (labile condition). The rapid extraction of solute would soon impoverish the solution around the crystallizing body, and crystallization would cease. The earlier formed crystals would thus be insulated from the rest of the magma by an envelope of barely saturated solution.

The features to be explained in zoned spherulites are the compact core and the successive concentric shells. On the assumption of an initial period of slow and scattered crystallization (metastable condition) the center of the core might be expected to show thick and widely spaced crystal fibers. If the central fibers in menthol spherulites are thicker than the outer ones, it is not readily apparent. Certainly they are not widely spaced. However, conditions at the core of a spherulite are necessarily peculiar; crystallization in the outer shells takes place over a spherical surface of large radius, whereas this area diminishes toward a point at the center of the spherulite. Hence, no matter how little material crystallizes out under metastable conditions at the center of the core, there is so little room that it completely occupies the space available. A relatively large amount of solute can hardly be expected to crystallize from scattered centers in the restricted area at the center of a spherulite. Hence, the metastable crystallization at the center may not be distinct from the succeeding, more rapid, labile crystallization of the outer part of the core.

The rapid labile crystallization may impoverish the magma in contact with the spherulite of the constituents needed for further growth. The saturation of the surrounding solution may also be lowered by an increase in temperature due to the heat of crystallization and also, in the case of solutions, by the relative increase in water due to extraction of the solid phase in the growth of the spherulite. It is probable, therefore, that the solution immediately surrounding the spherulite at this stage is no longer supersaturated. Crystallization will then cease, and the compact core of the spherulite will terminate in a spherical surface.

Crystallization will not be resumed until the immediately surrounding solution again becomes supersaturated. Later crystallization will also take place under metastable and labile conditions. From the solution surrounding the compact core crystallization will start at scattered loci[6] on the earlier formed spherulite front (metastable condition). As the temperature falls, the solution will pass slowly through the metastable phase with crystallization slowly increasing in volume as reflected in the fan-like branching of the feldspar fibers (Fig. 3). When the temperature falls sufficiently, the solution will reach the limit of supersaturation, and here crystallization will be spontaneous (labile condition). This is reflected in the spherulite by the more rapid branching of the feldspar fibers to give for the second time a solid spherulite front. This process, involving periodicity of crystallization, may continue until a multi-zoned spherulite results.

Acknowledgments

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[6] Viscosity may explain the failure of the earlier formed crystals to inoculate the enveloping solution and cause spontaneous crystallization.