ROEDDER, Edwin, 1970, Laboratory studies on inclusions in the minerals of Ascension Island granitic blocks, and their petrologic significance: in Problems of petrology and genetic mineralogy, Sobolev's volume II, P. 247-258 (in Russian with English abstract). Note: This title and abstract are given here as originally submitted for publication. The English title and abstract in the published version (p. 258) were erroneous. The English text is reproduced here because interest has been expressed in seeing the new data here that have not appeared in English previously. (Editor)

Quartz and alkali feldspar from vuggy ejected granitic blocks found in trachytic breccias at Ascension contain large numbers of fluid inclusions of three main compositional types, I, II, and III, presumably the homogeneous fluids. These fluids were I—silicate melt; II—dense aqueous-saline fluid with 50-70 weight percent NaCl; and III—dense water-rich steam or vapor, with CO₂. In addition, a number of mixed type I-II inclusions were trapped, providing verification of the existence, at depth, of immiscible droplets of aqueous-saline fluid in the silicate magma from which the granite crystallized.

Homogenization temperatures and devitrification experiments on the inclusions indicate that the solid granite was hot at the time it was broken and erupted as blocks, and place some limits on the possible rates of cooling of the blocks. The inclusion studies also have bearing on the problems of the validity of the decrepitation method, the pressure during crystallization of the granites, the change in shape of inclusions after trapping, and the possibility of leakage of inclusions in nature. (Author's abstract).

Introduction

In view of Prof. Sobolev's extensive studies in mineralogy and petrology, it seems appropriate to review here the petrologic significance that may be attached to some laboratory studies made on inclusions, both aqueous and glassy, in the minerals of some granitic rocks from Ascension Island. Although most of this work is part of a larger study of the inclusions in these rocks (Roedder and Coombs, 1967), the present paper includes new data and extends the discussion in some areas. The reader is referred to the earlier paper for a fuller account of the geologic setting, the mineralogy and petrography of the rocks (particularly the feldspars), other types of inclusions, and a more extensive bibliography.

Geologic setting

Although the dominant lavas on Ascension Island are basaltic, there are some trachytic breccias, as well as numerous other rock types. The granitic blocks used in the present study are angular fragments, generally less than 30 cm in size, lying loose at the surface, among a litter of trachytic breccia fragments, particularly on the slopes immediately below the Five Mile Post on the road up Green Mountain. There is no evidence that these blocks were ever embedded in liquid trachyte, as no lava has been found coating them; they are evidently accidental blocks torn from the walls of the volcanic conduit by an explosive blast.
Petrography

Individual granitic blocks vary rather widely in mineralogy and texture, but all are irregularly miarolic, porous and friable, quartz-alkali feldspar rocks. Most of the mineral grains are in the range of one to five mm, and only a few of the blocks are porphyritic. The miarolic cavities are generally small and exceedingly irregular in shape, and grade into intergranular porosity throughout the rocks. This characteristic indicates that a volatile phase was present during crystallization, as the miarolic cavities require the former existence of a fluid phase (gas or liquid) of a composition sufficiently soluble or volatile that all traces of it are subsequently lost to the atmosphere or groundwater, leaving the crystal lining exposed. Such cavities thus represent "fluid inclusions" that have leaked and have been flushed of all readily soluble minerals. Smaller fluid inclusions, trapped in strong and presumably impermeable single crystals rather than polycrystalline, permeable rocks, give us samples of these previously existing fluids and provide evidence for the environment of formation as discussed below.

The feldspars vary widely from one block to another, from an irregular, patchy perthite (monoclinic potassic phase of about Or67 to Or74, and twinned, low-albite of approximately Or3-5) to essentially single-feldspar sanidine rocks (Or35-Or55) showing only slight traces of heterogeneity optically or by X-ray.

Some of the blocks contain the rare potassium zirconium silicate, dalyite (van Tassel, 1952), and most show peralkaline affinities, as seen by the presence of aegirine, arfvedsonite, and aenigmatite (totaling five-ten percent), as prisms and needles as much as 4 mm long. In addition to dalyite, the most common accessory minerals are zircon and pyrochlore. The rocks are high in Cl, F, and Zr, low in Ca, and have several percent acmite in the norm.

The inclusions and their behavior in the laboratory

Sections made from the granite blocks show very large numbers of inclusions in all minerals. In particular, much of the feldspar is crowded with as many as $10^{10}$ inclusions per cubic centimeter.\footnote{Estimated by counting the inclusions in minute volumes of the feldspar in apparently typical areas.}

Although some of these could be called primary, many are of the indeterminate origin. A number of different types of inclusions are found in the samples, indicating a very complex history, but the great bulk of the inclusions fall into three groups. Inclusions from all these groups have been found coexisting in single grains of both quartz and feldspar from every granite block studied, regardless of the degree of exsolution of the feldspar phases. All the inclusions in quartz are in the form of rounded to sharply faceted negative crystals, but those in the feldspar are much more irregular in shape. The samples contain few of the very flat inclusions and none of the long tubular inclusions so useful in precise phase-ratio measurements.

Type I - Glass plus small, low-pressure gas bubble
Such inclusions are common in any igneous rock that has been cooled rapidly, and represent merely parts of the silicate melt or magma. In the Ascension blocks they are rare in the feldspar, but common in the quartz. The glass has an index of refraction of 1.500 +0.002 and occasionally shows a slight granularity in strongly collimated lighting, presumably indicating slight devitrification. Examination on a crushing stage (modified from that of Decha, 1950) proves the bubble to be nearly a complete vacuum. A number of the larger type I inclusions have a small isotropic daughter crystal tentatively identified as fluorite (also present in the glass of mixed type I-II inclusions, see Figs. 1 and 2). The bubble (formed by shrinkage) amounts to only a few volume percent (Fig. 1). A variety of heat treatments were tried on such glass inclusions. Fluorite daughter crystals formed when the inclusions were held at 710°C for 32 days, and dissolved when held at 800°C for 43 hours.

In each of the experiments of this type reported here, the time given represents the arbitrarily chosen length of the experiment, before reexamination of the sample. Shorter time might yield identical results.

A sample with clear glass inclusions was given a sequence of heat treatments: the inclusions showed no change after 19 hours at 250°C, but 25 hours at 415°C resulted in a mat of birefringent needles (unidentified) in all but the smallest glass inclusions. Following this, 96 hours at 650°C caused visible coarsening of the needles, and after 32 days at 710°C most of the needles had dissolved in the glass. An additional 43 hours at 800°C eliminated most the remainder. Separate samples, each reheated for 24 hours, showed devitrification and growth of crystals at 400°, at 500°, and at 600°C, but none at 700°C. Heating (for two hours) at 1050°C apparently was adequate to cause homogenization of these glass inclusions, as might be expected. This is based on the fact that many of the smaller glass inclusions contain no bubble after such a heat treatment if it is followed by rapid quenching (approximately one second). By contrast, type I inclusions as small as 4μ in diameter had (or developed?) shrinkage bubbles after quenching in four seconds from 995°C.

Type II - Large halite crystal plus saturated water solution plus gas bubble ± minor phases.

The gas bubbles in these inclusions range from about 20 to a maximum of about 50 volume percent. The halite crystal may occupy more than 30 volume percent of the inclusion, corresponding to original homogeneous fluids with as much as 70 weight percent NaCl (see inclusions marked II in Fig. 2). The identification as halite was based on its index of refraction and on observations of its reaction.

Type II inclusions are so abundant in some of the feldspar that single crystal X-ray diffraction photographs of these crystals show diffraction lines for the three strongest reflections from halite.
with the liquid to form the birefringent compound NaCl.2H₂O on cooling below +0.1°C. On subsequent heating, this hydrate melts incongruently to form liquid plus NaCl crystal (Roedder and Coombs, 1967, Plate 1, Figs. G-J). Many of the larger type II inclusions also contain a second isotropic cube (probably KCl), small amounts of liquid CO₂, a small, highly birefringent grain (possibly calcite), and an opaque grain.

The homogenization temperature of type II inclusions, both primary and secondary, was determined to be generally between 590° and 612°C, and occurred in the liquid phase (type I homogenization of Ermakov (1950)). Solution of the last of the halite crystal occurred slightly below the temperature of elimination of the vapor bubble. Although the platinum/platinum-10 percent rhodium thermocouple of the heating stage (Richter and Abell, 1953) was calibrated, simultaneously with the actual runs, at the melting points of very pure tellurium (449.5°C) and antimony (630.5°C), no great precision can be claimed

/ Minute slivers of these elements were sealed, in vacuum, in individual short sections of fused silica capillary tube, <1 mm in diameter, and placed beside the sample grain.

for these homogenization temperatures, as severe thermal gradients were evident. The experimental uncertainty is thus at least ±25°C.

Crushed grains of quartz and of feldspar were heated to determine the decrepitation characteristics of type II inclusions. Grains of quartz of 0.1 - 0.5 mm diameter showed no loss of fluid from their inclusions after 24 hours at 700°C. Some quartz grains as small as 0.1 mm retained their type II inclusions during two hours at 1050°C and even two hours at 1200°C. Most type II inclusions in grains of feldspar of similar size were unaffected by 16 hours at 600°C, but were emptied during 16 hours at 710°C or two minutes at 865°C. As the samples were mostly < 1 mg. in minute platinum foil capsules, the time to reach furnace temperature was only a few seconds. To obtain fast air quenching, the capsules were jerked out of the horizontal tube furnace by a thin platinum wire.

Type III - Dilute water solution plus very large gas bubble containing some CO₂.

This type normally contains about equal amounts of gas and liquid (see Fig. 2 inset). Under ordinary lighting these may seem to be opaque, or empty. As the liquid forms a thin layer around the large bubble, it is difficult to observe with the collimated lighting of a heating stage, and hence the homogenization temperatures (probably in the gas phase) are undetermined. The conditions for leakage or decrepitation for type III were about as for type II. Examination on the crushing stage verified the presence of gas under pressure; examination on the cooling stage showed the formation of the clathrate compound CO₂.53H₂O and little evidence of salts in solution. Type II and type III inclusions of apparently primary origin occur in close proximity but randomly distributed with respect to each other, and are frequently only a few microns apart. A number of curving healed fractures were also found, however, outlined by dozens of obviously
secondary or pseudosecondary inclusions of sharply faceted negative crystal shape. These consisted of both types II and III, in random array relative to each other.

Type I-II, an uncommon but particularly significant mixed type.

In addition to the three main types, there were a number of examples of inclusions containing silicate glass, and saline liquid, with a halite crystal and vapor bubble. Figs. 2-6 show several of these, and Roedder and Coombs (1967, Plate 2) show six others. These are difficult to photograph /\, but show generally a large "bubble" in a

/ Many other similar inclusions were found which were unsuited for photography, but showed the same phases quite adequately when several different settings of lighting and focus were used.

glass inclusion, too large to have formed by normal shrinkage on cooling. Each such bubble" contains crystals, liquid, and vapor. The inside of the "bubble" is either lined with a layer of wet salt crystals surrounding the vapor phase, or has a single large isotropic cube and other smaller isotropic and birefringent crystals, a liquid, and a vapor bubble. The ratio of (gas + liquid) to glass varies widely. After rapid quenching in the experimental runs, the lining of tiny wet crystals on the surface of the bubble (for example, Fig. 4a) might be easy to confuse with the rather common feature of solid daughter crystals in some glass inclusions giving the appearance of sticking to the bubble (presumably due to preferential nucleation on the interface). However, when the mixed type I-II inclusions are given a moderate heat treatment, such as two hours at 60°C, the tiny salt crystals recrystallize through the liquid to form a few larger ones (Fig. 4b).

A number of these mixed inclusions were examined on the heating stage. The salt crystals, vapor, and liquid in them homogenized to a single fluid at about 600°C, simultaneously with the homogenization of adjacent type II inclusions, but no effect was seen on the glass phase or the occasional daughter crystals found in the glass. Higher temperatures, up to 105°C, showed no permanent effects. For example, the inclusion in Fig. 3 is only 16μ below the surface of the grain, and has been held at 1050°C for two hours, with no evidence of leakage. A small grain of quartz, less than 0.3 mm thick and containing a number of mixed type I-II inclusions (mostly less than 30μ from the surface), was given the following sequence of heat treatments, with quenching and optical examination after each: 710°C for 32 days; 800°C for 72 hours; and 990°C for 17 hours. There was no change in any of the inclusions; all showed a layer of wet salt crystals lining the bubble. The photomicrographs shown in Figs. 1, 4a, and 6a happen to have been taken after this sequence of heat treatments, but the inclusions looked the same before and after. The grain was then heated to 1105°C for 42 hours and quenched in approximately two seconds. Now each mixed type inclusion showed three phases (Figs. 5 and 6b): silicate glass (unaffected except for some increase in volume by solution of the walls); a clean, clear vapor
bubble, and a round, solid globule of mainly isotropic salt crystals with a granular surface and interior. Within each such salt globule another vapor bubble is now visible.

From this evidence it is presumed that at 1105°C, the salt was present as fused globules, immiscible with the hydrous silicate melt, and all the water was in solution in the melt. On cooling the melt shrunk and formed new vapor bubbles, essentially free of salt. The salt globules crystallized while the glass was still soft, and shrunk to form another vapor bubble in the interior of each. A second heating to 1105°C, followed by slow cooling, caused most of the inclusions to return to their original appearance, with a single "bubble."

Significance of data and conclusions

Although the results of this work apply strictly to only the materials studied, some petrologically significant conclusions may be drawn from them.

A. Overheating of inclusions (above their homogenization temperatures) and geologic thermometry by decrepitation.

As the bulk of the inclusions of types II and III in quartz grains even as small as 0.1 mm could be taken to 100°C above their homogenization temperature for a month without decrepitation or leakage, and some could be taken as much as 600°C higher for hours, decrepigrams made of such samples could be very misleading. This is perhaps expectable, as inclusions with a high temperature of homogenization exhibit a much smaller change in the rate of pressure increase with temperature rise at the point of homogenization than do lower temperature inclusions of the same composition.

B. Silicate melt-hydrous saline fluid immiscibility in granitic magmas.

The common occurrence of individual inclusions of both types I and II in any sample would merely indicate the existence, at unspecified times, of each of these types of fluid. Many crystals of quartz, and a very few of feldspar, contain apparently primary inclusions of both types, implying simultaneous existence of the two immiscible fluids: silicate melt, and dense hydrous saline fluid or "melt" (density about 1.4 g/cm³). Far more convincing evidence of immiscibility is found in the mixed type I-II inclusions. These indicate the existence, and trapping, of globules of dense hydrous saline fluid immersed in a silicate melt.

One alternative possibility that might be considered is that a homogeneous silicate melt was originally trapped, and that the salts and water have exsolved from it on cooling to form the mixed type I-II inclusions. Although this possibility in itself would indicate immiscibility, at lower temperatures and pressures, several facts preclude it. One of the strongest points of evidence is the fact that the ratio of (gas + liquid) to glass varies widely, and cannot be explained by simple necking down and compartmentalization of elongated multiphase inclusions, yielding a variety of ratios (the "beading" described by Lemmllein, 1929)). Another is that most of the glass inclusions (even in the same grain) have only the normal, small size bubble, with no evidence of exsolved salts or water. Lastly, the behavior of the mixed inclusions on heating is not explicable in terms of a homogeneous, hydrous, silicate-saline fluid. This is seen in the fact that on heating to 1105°C an obviously immiscible droplet of fused salts formed in the silicate melt. As this is well above the probable formation temperature
of the rock, this behavior indicates that a homogeneous silicate melt, containing salt and water in solution, could not be responsible for the mixed type I-II inclusions.

The tremendous concentration of type II inclusions in the feldspar is believed to be merely a result of preferential wetting; although the feldspar grew essentially from the silicate melt, the globules of saline fluid in this melt apparently adhered preferentially to the growing feldspar surface and thus were enclosed in large numbers, even though they were not the fluid from which the crystal was actually growing. Such a phenomenon could also lead to differentiation by flotation of the crystals.

C. Boiling of the saline fluid.

The simultaneous presence of apparently primary inclusions of both types II and III in the same sample is permissive evidence of boiling, particularly as the distributions of salts and of CO₂ between the two types of inclusions are as expected for "liquid" and "vapor" phases in the system H₂O-CO₂-NaCl/ (Sourirajan and Kennedy, 1962; Takenouchi and Kennedy, 1965).

/ Only rare examples of mixed type II-III were found.

The common occurrence of these two types of inclusions outlining the same healed fracture is difficult to explain except by the trapping of a boiling solution, perhaps early in the eruption of the blocks, and the pressures involved are geologically reasonable. The relative abundances and distributions of the two types preclude necking down of elongated inclusions as an explanation. Such boiling places some limitations on the pressure, and hence depth, at which type III inclusions were trapped. Sourirajan and Kennedy (1962) have shown that the vapor phase in equilibrium with a saturated solution of NaCl at 600°C (the homogenization temperature of the inclusions) has a pressure of only 392 bars, and contains only 0.04 percent NaCl. Thus it is feasible that these granites crystallized at rather shallow depths.

D. Nucleation and crystallization of glass inclusions and the cooling rate in nature.

Except for the possibility of some at present unknown hysteresis effects, the fact that 24 hours heating at 400°, 500°, or 600°C caused crystallization of formerly clear glass inclusions requires that in nature these blocks were cooled from about 600° to under 400°C in less than 24 hours. Data on the exsolution rate and composition of coexisting feldspar phases (Roedder and Coombs, 1967) seem to be in conflict with this conclusion, but may still be explicable. The evidence seems to point to original crystallization of the minerals of the blocks at or above about 650°C, relatively rapid quenching (less than one day) to just below 400°C, presumably by eruption, maintenance of temperatures just below 400°C for a period, and subsequent quenching, or at least cooling into a range where further reaction was insignificant.

E. Decrepitation of inclusions in feldspar and the temperature of eruption.

The fact that the type II inclusions in feldspar (also type III, probably) are emptied by two minutes heating at 865°C, and by 16 hours (or less?) at 710°C, requires that these blocks were erupted at temperatures under 865°C, and probably under 710°C. (As the blocks are friable they are assumed to have no significant tensile strength.) Such temperatures are not unreasonable for accidental blocks in a trachytic volcanic breccia with no lava.
F. Recrystallization and the change in shape of inclusions.
Most of the inclusions in these samples, including many obviously secondary inclusions outlining healed fractures, are equant, faceted negative crystals. As it is almost impossible for secondary inclusions to have this shape at the time of trapping, it must be assumed that they have changed shape after trapping. Such changes in inclusions shape, as first described by Lemnlein (1929), probably occur in all cases where (1) the host mineral has a finite solubility in the trapped fluid; (2) the shape at the time of trapping does not represent the lowest energy configuration, i.e., the minimum surface energy; and (3) there has been adequate time for recrystallization to occur. It is thus surprising to see inclusion shapes in general, and negative crystal shapes in particular, used so commonly in the literature as criteria for a primary origin for inclusions. The difference between two groups of inclusions in a given sample, one irregular and the other negative crystals, may be empirically related to secondary vs. primary origin in some given locality, but such a relationship is far from regular, and in fact it is frequently found to be reversed.

G. Leakage of fluid inclusions in quartz.
If fluid inclusions have commonly leaked under natural pressure gradients, letting material in or out, their usefulness in geologic studies would be greatly reduced. Although a more extensive laboratory study minimizing the general problem of leakage in fluid inclusions is to be reported in a separate paper, it should be noted here that many of the heating experiments show that quartz is relatively immune to leakage of aqueous fluids, even at elevated temperatures. / Heating to the

/ Although the Ascension Island samples have probably cooled through the $\alpha$-$\beta$ quartz inversion temperature rapidly, other quartz samples have cooled through this range at extremely slow rates. This would be very difficult to duplicate in experimental runs, but the possibility that much more rapid leakage might take place during the transition should be considered (oral communication, P.B. Barton, Jr., 1967).

/ homogenization temperature of 600°C develops pressures in the inclusions up to 392 bars along the three-phase curve (Sourirajan and Kennedy, 1962), and lower salinities or higher temperatures would result in still higher pressures. Yet 32 days at 710°C, plus 11 more days at temperatures of 800° to 1105°C, failed to produce any visible evidence of leakage of a large number of mixed type I-II inclusions (and a few plain type II inclusions), even though many were less than 30µ below the surface of the grain. Similarly, some type II and type III inclusions within 20µ of the surface showed no evidence of leakage after two hours at 1200°C.
References


Captions for figures

Fig. 1  Group of mixed type I-II inclusions in quartz. Each contains a thin layer of salt crystals and water inside the bubble, in an amount that is a function of the bubble size. Although the two inclusions marked 'look in this illumination like normal type I inclusions, with small bubbles, heat treatment showed that they were actually mixed type I-II (see Fig. 5). The inset shows a type I inclusion, with vapor bubble (v) and fluorite daughter crystal (f) in glass (g). Sample As 51.3.

Fig. 2  Grain of quartz from sample As 51.14 showing several probably primary type II inclusions, and one large mixed type I-II inclusion. The latter is a sharply faceted negative crystal cavity filled with glass (g), containing a small daughter crystal presumed to be fluorite (f), and a large "bubble" containing a single cube of halite (h) and a wet mass of smaller crystals of soluble salts, plus a vapor bubble (v). The inset shows two type III inclusions in quartz from the same sample, each with liquid (l) and a large vapor bubble (v).

Fig. 3  Mixed type I-II inclusion in quartz showing two isotropic cubes (presumably halite, h, and sylvite, s), in a liquid film (l) lining "bubble" in glass (g).

Fig. 4  Mixed type I-II inclusion, showing wet mass of small salt crystals lining "bubble" in glass, from rapid quenching of sample (a); and the results of recrystallization to a small number of larger crystals after holding for two hours at 60°C (b). Sample As 51.3.

Fig. 5  Same area as Fig. 1, after heating for 42 hours at 1105°C and rapid quenching. Each mixed type I-II inclusion now consists of a granular globule (h) of salt crystals (an immiscible liquid droplet at 1105°C) and a separate vapor bubble (v), in the glass (g).

Fig. 6  Enlargements of another inclusion in same grain as Fig. 5, before (a) and after (b) heating to 1105°C. Letter identifications as in Fig. 5. The globule of salt crystals is seen to contain a small shrinkage cavity (V').