

EDWIN ROEDDER

Occurrence and significance of magmatic inclusions and silicate liquid immiscibility

ABSTRACT: This paper reviews work on magmatic (particularly silicate-melt) inclusions in terrestrial and extraterrestrial samples and evaluates its significance. Particular attention is given to silicate liquid immiscibility, as it is frequently a cause for both the trapping of inclusions, and for confusion in their interpretation. This includes a discussion of immiscibility in the synthetic system $K_2O-FeO-Al_2O_3-SiO_2$, and in lunar and terrestrial basalts. For ordinary inclusions, formed during normal magmatic differentiation by crystal fractionation, this review details the trapping mechanisms, the three main changes that may occur within inclusions after they have been trapped (separation of an immiscible fluid phase, crystallization, and leakage), and the five main types of useful data available from such inclusions (temperature of trapping, temperatures and sequence of phase changes during cooling, constraints on maximum minimum cooling rates, bulk composition and the liquid line of descent, and the volatile content). Other inclusions in magmatic rocks are trapped and have their composition determined by a variety of types of fluid immiscibility.

INTRODUCTION

The study of silicate melt inclusions got its start early in the history of petrography with the keen observations of Sorby (1858), Vogelsang (1867), and especially Zirkel (*e.g.* 1866, 1873). Sorby (1858) first recognized the similarity between glassy inclusions in lava and those found in the minerals of metallurgical slag. Fouqué & Michel-Lévy (1879, 1881), made important observations on the resemblance of melt inclusions in synthetic minerals formed by fusion processes to those found in fresh igneous rocks. After these papers, little was published anywhere on melt inclusions for many years, until Tuttle (1952) made an important observation on the origin of granite, based on the lack of glass inclusions. Then, Barrabé & Deicha (1956—1957) and Barrabé & *al.* (1957) homogenized melt inclusions by heating spheres of volcanic quartz from Guadeloupe. Subsequently Kalyuzhnyi (1961, 1965) studied

inclusions in phenocrysts in dacites, and since then, interest in such studies has rapidly increased. Much of this later work is in Russian literature and has been reviewed by Sobolev & Kostyuk (1975). The recent extensive French work on magmatic inclusions has been thoroughly reviewed by Clocchiatti (1975). One interesting aspect of this last work is the use of inclusions in detrital volcanic materials to clarify the provenance and processes involved in their origin.

This paper will review the status of magmatic inclusion study from the following five aspects: (1) mechanisms of trapping of melt inclusions; (2) the significance of "normal" melt inclusions (as used by Sobolev & Kostyuk 1975, those representing samples of the homogeneous melt trapped during normal magmatic differentiation by crystal fractionation); (3) inclusions originating from various types of magmatic immiscibility; (4) inexplicable and enigmatic inclusion types; and (5) the future promise for inclusion study.

TRAPPING MECHANISMS

Inclusions are generally trapped within crystals growing in a magma as a result of some irregularity in growth conditions (Text-fig. 1). Numerous quantitative experimental studies have been made in recent years of the nucleation, growth rate, and morphology of crystals growing in various silicate melts (e. g. Lofgren & Donaldson 1975, Kirk-

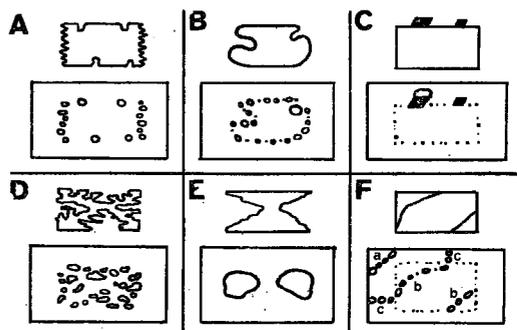


Fig. 1

The six most common mechanisms for trapping silicate melt inclusions: A — Rapid skeletal growth, B — partial dissolution yielding deep reentrants, C — Enclosure of other phases, D — nucleation and growth from highly supersaturated melt E — Tabular growth, F — Fracturing or re-growth ("a" — secondary; "b" — pseudosecondary; "c" primary)

patric 1976). As some of the textures, formed reproducibly under given conditions, result in the trapping of specific types of inclusions, these experiments may add a new dimension to the interpretation of natural melt inclusions, but the multiple variables in the natural systems result, in considerable ambiguity.

Actual examples of these various trapping mechanisms are as follows. Quartz phenocrysts from lava frequently have negative cavities or have flat reentrants on the faces (Pl. 1, Figs 1 and 2) that may

cause the trapping of large inclusions. Such inclusions in igneous quartz often develop radial cracks on cooling because of the sudden 1% volume decrease of the quartz when it inverts from the high-temperature β form to the low-temperature α form at a temperature where the glass inclusion is rigid. Deep reentrants at the terminations of quartz phenocrysts are not uncommon (Pl. 1, Fig. 3) and may lead the trapping of a series of inclusions.

I have found some leucite phenocrysts that have an almost spherical internal shell of 24 inclusions, one for each face of a tetrahedron (Pl. 1, Fig. 4). As happens so frequently in observational studies, I discovered later that Zirkel (1873) had already described these, more than 100 years ago.

Generally, inclusions in phenocrysts of olivine are relatively large (Pl. 1, Fig. 5), but those in pyroxene or plagioclase may be small or rare, and I really do not know why. Where inclusions do occur in pyroxene or plagioclase, however, they are commonly in zones and may be very numerous (Pl. 1, Fig. 6). A classification of such zonal inclusions by Sobolev & Kostyuk (1975) into "zonal", and "regenerated pseudosecondary" inclusions differs, however, from that used in the Western world.

Solid inclusions are a very common cause of trapping of melt inclusions, *e. g.*, when growth of olivine crystals encloses spinel (Pl. 1, Figs 7 and 8). Not uncommonly, the direction of growth of the host crystal can be determined from such composite inclusions, because the silicate melt inclusion will generally be on the side of the solid inclusion toward the outside of the host crystal. Such evidence is of more than trivial importance as it may help to distinguish between solid inclusions and daughter crystals, as mentioned below. In aqueous inclusions, recrystallization of the host mineral via diffusion through the fluid phase after trapping can eliminate such evidence, but such recrystallization is generally minor in melt inclusions.

"NORMAL" MELT INCLUSIONS

"Normal" melt inclusions are here defined as those that are trapped during classical magmatic differentiation by crystal fractionation. Much of the past work has been on this type of magmatic inclusion. The major importance of "normal" melt inclusions to petrology is that give us actual samples of melt from the line of liquid descent, as well as well as information on the composition, temperature, and sequence of various stages in the process.

CHANGES WITHIN INCLUSIONS AFTER THEY HAVE BEEN TRAPPED

SEPARATION OF AN IMMISCIBLE FLUID PHASE

In order to use melt inclusions intelligently, one must first understand the changes that may take place in them after they have been trapped. The most common change is the formation of a separate immiscible fluid phase. Normally this phase is merely a vapor cavity or bubble, formed because the shrinkage on cooling of the included melt is much larger than that of the enclosing "crystal bottle", as described long ago by Sorby (1858). Partial crystallization of the included melt after it has been trapped also adds to the bubble volume (see, e.g. Anderson 1974). The bubble may be essentially a vacuum if the vapor pressure of the melt is low, but as most volatile species such as water or CO₂ will be strongly partitioned into the new fluid phase, it can consist of a dense gaseous fluid at high pressures. On cooling, the melt can also become saturated with respect to an iron sulfide melt and precipitate a globule of that fluid.

The nucleation of a vapor bubble does not always take place, because metastability — of many types — is even more common in silicate melt inclusions than in their aqueous counterparts. Inclusions of melts rich in volatile materials usually nucleate a bubble on cooling, but many melt inclusions do not, for three reasons: (1) lacking an effective nucleus for heterogeneous nucleation; (2) statistical probabilities of homogeneous nucleation in such tiny systems (e.g. a small inclusion may contain only $\sim 10^7$ molecules of a minor constituent); and (3) the surface energy for a bubble with small radius may be so high that the lowest energy state would be for the melt to remain somewhat stretched at a lower density than it would have if it were free to shrink (Roedder 1971 a, b).

As a result of these three factors, generally only the larger inclusions in any given sample will have bubbles (Pl. 1, Fig. 9). Because nucleation of any new phase is also a rate phenomenon, the more viscous the melt and the faster the cooling, the larger the inclusion that will remain without a bubble. The change in viscosity of silicate melts with temperature is such that relatively large silicic glass inclusions without bubbles are commonly found in crystals from crystal tuffs and similar volcanic rocks of explosive origin (Pl. 2, Fig. 1). However, crystals in such a tuff could have inclusions with bubbles, inherited from an earlier slow-cooling episode.

CRYSTALLIZATION OF NEW PHASES ("DAUGHTER MINERALS")

The term "daughter minerals", from aqueous inclusion usage, and referring to the formation of new phases from the trapped material in the inclusion, is equally applicable here, but perhaps "daughter phases" should be used to describe non-crystalline phases such as vapor or sulfide melt. Crystallization of the host mineral from the melt onto, or reaction of the melt with, the walls of the inclusion produces a special type of "daughter mineral".

Several typical features of daughter-phase formation are well illustrated by inclusions in olivine phenocrysts from the lunar mare basalts (Text-fig. 2). Some lunar (and terrestrial) melts precipitate an immiscible sulfide globule even when trapped as 5 μm inclusions that are too small to form a vapor bubble (Text-fig. 2A). The sulfide globule generally nucleates on the wall and adheres to it; thus many become partially enclosed (Pl. 2, Fig. 2). In contrast, a vapor bubble,

although also generally nucleating at the wall, apparently has a contact angle near zero: therefore, the olivine can continue to grow beneath it and push it into the remaining melt. As a result, vapor bubbles in olivine rarely appear to be embedded in the walls. Such is not true for the vapor bubbles in some other minerals (e.g. quartz, as shown by Zinkel 1873, Fig. 22).

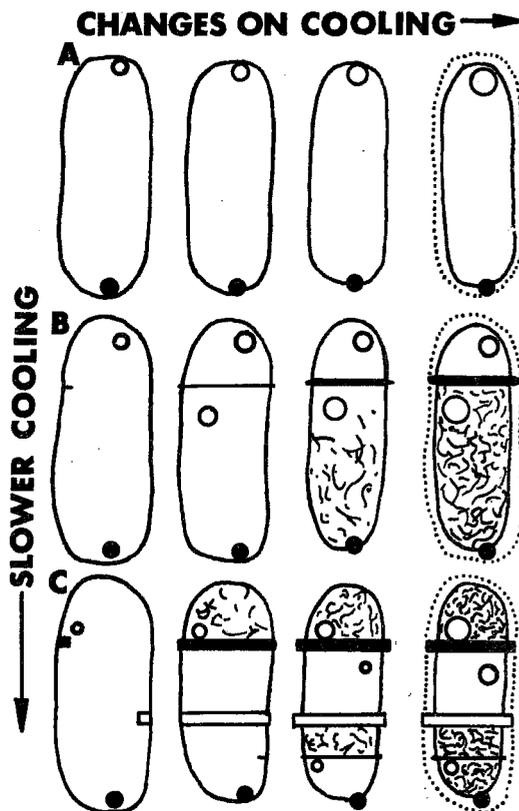


Fig. 2

Changes within inclusions after trapping — crystallization of new phases (i.e., "daughter minerals")

The zone of precipitated olivine, the so called "border of cognate substance" in the Russian literature, is in crystal continuity with the host crystal and may go unnoticed except when such features as the buried sulfide globule are recognized for what they are. Minor differences in index can sometimes be detected, e.g. in topaz (Vozyak & Kalyuzhnyi 1974b).

Sometimes, an opaque daughter crystal of ilmenite has nucleated on the olivine walls in epitaxial orientation. (Text-fig. 2B). The resulting flat plate of ilmenite is always parallel to (100) of the enclosing olivine, forming a bulkhead that effectively divides the inclusion into two isolated parts that subsequently each have their own nucleation and growth history. Continued precipitation of olivine causes the ends of the plate to become embedded. Pyroxene may nucleate and form a mass of feathery crystals in one or more of the isolated parts, crystallizing dendritically (and presumably rapidly) from a strongly supersaturated melt. In larger inclusions, several plates of ilmenite and/or epitaxial plates of anorthitic plagioclase may form (Text-fig. 1C), which results in multiple isolated chambers. The above phase changes (Text-fig. 1) may be observed in actual melt

inclusions in olivine from the lunar samples (Pl. 2, Figs 2—6). A 4 μm glass inclusion contains a bubble and has the daughter ilmenite and sulfide phases well embedded in the walls, (Pl. 2, Fig. 2), and a 7 μm inclusion contains only glass, bubble, and sulfide. (Pl. 2, Fig. 3). Note that the bubble size relative to the amount of melt is so large that it cannot result from simple shrinkage; it probably indicates crystallization of considerable olivine on the walls after trapping (Roedder & Weiblen 1971). Another example may be presented (Pl. 2, Fig. 4), showing the significant crystallization of olivine on the walls after growth of the epitaxial ilmenite daughter plate. Note also that this inclusion is approximately half the size of the host olivine. (Lunar olivine is not always easy to distinguish from pyroxene, because of the absence of alteration effects, and the presence of such epitaxial ilmenite in the inclusions is sometimes a convenient indicator and criterion for recognizing rare olivine grains, as in Pl. 2, Fig. 4). An example shows how such inclusions may look, (Pl. 2, Fig. 5), in both reflected and

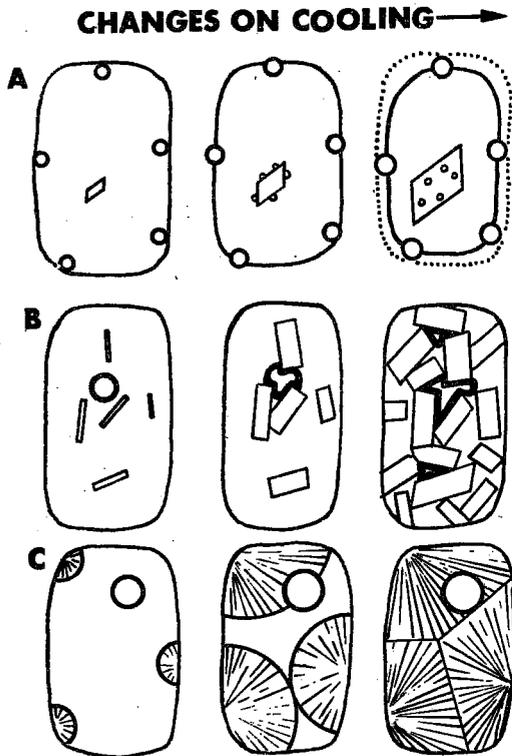


Fig. 3

Diagram showing development of types of vapor phase position and shape

transmitted light, when the aggregate of feathery pyroxene and residual glass is almost opaque; an early bright ilmenite daughter plate, a thick plate of plagioclase (dark here in reflected light), and feathery pyroxene in residual glass. (Pl. 2, Fig. 6) fill another inclusion. Note the later crystallization of olivine on the walls around the ilmenite but not around the plagioclase.

Additional types of change are seen in various specimens (Text-fig. 3). The part A depicts the nucleation of multiple bubbles on the walls and on a daughter mineral. These features are common in viscous silicic melts but are only rarely seen in basaltic inclusions (Pl. 2, Fig. 7).

Growth of daughter crystals can deform the vapor bubbles into irregular shapes (Text-fig. 3B) that are difficult to recognize in an almost opaque, all-crystalline inclusion.

If early cooling is fast and later cooling is slow, fine feathery radial or spherulitic crystals may form (Text-fig. 3C). The included glass is essentially a solid at this stage, so the bubble remains round, although enclosed in crystals.

LEAKAGE

Leakage includes movement of material into or out of the inclusion. Most crystals are essentially impermeable to most substances. Hydrogen, however, can diffuse through many substances with relative ease. Most hydrogen in magmas is present, in effect, as water in solution. Whether this water is dissolved in the melt or has partitioned into the vapor bubble, some disproportionates into hydrogen and oxygen. If hydrogen activity decreases in the surrounding environment, *i.g.* the environment becomes more oxidizing, either in nature or in the laboratory, hydrogen will diffuse out, particularly at elevated temperatures. Oxygen, however, diffuses much more slowly and is left behind, causing auto-oxidation of any variable-valence elements, *e.g.* iron, in the melt, or in the host crystal walls.

When a sample containing a water-bearing inclusion is heated in air, hydrogen should diffuse. The only real question is the rate. In some of the Russian literature, this matter has been discussed and discarded as insignificant, on the basis of experiments that in part do not really address the problem. Anderson & Sans (1975, and *personal communication*) studied highly hydrous silicate melt inclusions (*i.e.* containing 8–12 wt. % H₂O) in olivine and pyroxene from Mt. Shasta, California. When sufficiently iron-rich samples ($> \text{Fa}_{17}$ or $> \text{Fs}_{12}$) are heated in vacuum in the laboratory, they form an anomalously birefringent, brownish halo in the walls of the inclusion within hours (Pl. 2, Fig. 8) and lose their water in 18h. These and other facts suggest loss of hydrogen and auto-oxidation of ferrous to ferric iron in the host olivine or pyroxene. More experiments are required, particularly with controlled hydrogen activity. If hydrogen (or water) does indeed diffuse during original cooling or in the laboratory heating runs, it may be necessary to reevaluate much of the earlier high temperature work on hydrous inclusions. Studies in vacuum or in inert atmospheres are not free of doubt, as these do not preclude diffusion of hydrogen. Such diffusion, perhaps taking place mainly in nature before laboratory heating, may also explain some of the exceptionally high homogenization temperatures reaching a maximum 1600°C, reported in many modern Russian papers on melt inclusions (see abstracts in Roedder, 1968–1979; and particularly Volokhov 1975, Sobolev & Kostyuk 1975, pp. 213–214, and Sobolev & *al.* 1976).

Another form of "leakage" is that partial decrepitation. When the differential between the internal pressure of an inclusion and the external pressure on the host crystal becomes sufficiently large, the walls will crack. This cracking principally results from a lowering of the external pressure during eruption but can also result from heating in the laboratory. An 18 μm inclusion of basaltic melt, now crystallized, (Pl. 2, Fig. 9) was trapped at high pressure, along with a globule of dense high pressure CO₂ fluid. During eruption, such inclusions may break the crystal apart and free CO₂ bubbles into the magma. However, if the size of the inclusion is small relative to the crystal, as it is in this sample, it may cause only cracking of the walls. Volume expansion reduced the pressure far enough

to prevent further propagation of the crack. The inclusion constituents — melt and gas — flowed out into the crack and caused recrystallization and trapping of a halo of new secondary inclusions. Both the old and the new inclusions have a lower density and pressure of fill than the old inclusion had originally. Similar phenomena have been described in some aqueous inclusions (Larson & *al.* 1973; Voznyak & Kalyuzhnyi 1974a).

Still another kind of leakage results from the addition of water, which may alter silicate-melt inclusions to clay where a crack intersects an inclusion; examples can be seen in many basalts. Unfortunately, the cracks are sometimes nearly invisible and I fear that more than one mistake has been made in the interpretation of such altered inclusions. Such zones of alteration can be rendered conspicuous by etching the surface for about 10 s. with concentrated HBF_4 at room temperature, and then viewing in reflected light with Nomarski interference contrast illumination (Anderson, Jr., *personal communication* 1978). It has been suggested (Takenouchi & Imai 1975, p. 756) that some of the devitrification of glass inclusions in silicic igneous rocks associated with ore deposits in Japan has come about as a result of the later hydrothermal activity. However, since these authors point out the "remarkable" effect of inclusion size in this devitrification (only the larger inclusions are devitrified, p. 751), I suspect that this effect is essentially a nucleation phenomenon.

TYPES OF DATA AVAILABLE FROM "NORMAL" MELT INCLUSIONS

TEMPERATURE OF TRAPPING

The use of melt inclusions to obtain the temperature of trapping is perhaps the most obvious of all the possible uses, in view of the extensive use of aqueous inclusions for this purpose. By the temperature of trapping I mean, of course, the temperature of crystallization of the host mineral at that point. This temperature is usually assumed to be given by the temperature of homogenization of the inclusion contents — gas, glass and crystals — to a uniform single melt phase, when the sample is heated in the laboratory. In theory, a pressure correction should be added to the homogenization temperature to obtain the true trapping temperature, as in aqueous inclusions, but the relative incompressibility of silicate melts, however, and the generally low pressures of most of the igneous environments involved in melt-inclusion studies make such corrections negligible at this time, particularly when compared with several much larger errors in the opposite direction discussed below.

It is generally assumed in aqueous-inclusion studies that if, on heating, the gas and liquid phases homogenize at a lower temperature than of the disappearance of daughter crystals, the difference between these two temperatures represents a minimum pressure correction. Although this is a generally valid concept, there are practical problems in making use of it, particularly when inclusions containing coarse daughter phases are involved.

If the homogenization run is of too short duration, time may be insufficient for re-resolution of daughter crystals and of material crystallized on the inclusion walls. Perhaps even more important but much less obvious (and frequently ignored) is the problem adequate time for diffusion leveling of the concentration gradients caused by the dissolution of such phases. The resulting compositionally zoned melts can temporarily show apparently "reversible" phase behavior, simula-

ting equilibrium. Additional problems are present when inclusions contain much water, and when they yield particularly viscous melts. In all these examples, the final "homogenization temperature" determined will be too high, perhaps by 100°C or more, if these diffusion-limited rate problems are not eliminated. Longer runs, however, tend to cause external oxidation, which makes the sample opaque. Longer runs also exacerbate the possible problems of hydrogen diffusion and hence may cause a gross rise in homogenization temperature. Obviously, equilibration problems will be reduced by the use of smaller inclusions, thus reducing the diffusion distances within the melt, but observational problems pose a limit here.

Multiphase inclusion samples can be held at various temperatures for specific times and then quenched and examined (*e.g.*, Roedder & Weiblen 1970). This procedure was very tedious but consumed a minimum amount of material (important in lunar studies), and provided useful data (Roedder & Weiblen 1970, 1971) with minimum ambiguity. If material were plentiful, groups of grains could be heated, each to a given temperature, and examined. Such a procedure is particularly appropriate for studies of silicic melt inclusions that require long time to achieve equilibrium (see, *e.g.*, Takenouchi 1972, and Takeuchi & Katsura 1972). Although even this procedure is relatively slow, it minimizes the possible loss of hydrogen and poses few experimental problems. Such experimental problems are much more severe in the seemingly more straightforward and far more common procedure of using a heating microscope stage and watching the phase changes take place on slow heating.

The microscope heating stage itself presents some considerable problems. When measuring the temperature of an inclusion under microscope, it is not too difficult to achieve good precision, but it is extremely difficult to obtain good accuracy. Many models of high-temperature microscope heating stages have been described, particularly in the extensive Russian literature. In any such design, there have to be rather large thermal gradients within the hottest area, because heat must be flowing rapidly by conduction, convection and radiation, from the hottest central areas into the colder surroundings close by, and hence there almost certainly are thermal gradients within the sample. When any such designs are used, a carefully standardized procedure can lead to a reasonably high precision of measurement, and the effect of thermal gradients on a measurement can, in theory, be eliminated by calibration procedures. This ideal is realized only if the calibration runs have the identical technique and thermal regime (including thermal transmissivities and emissivities) used in the running of the unknown sample. It is difficult to set up a truly valid calibration of this type; hence the accuracy of such measurements is difficult to assess.

All the foregoing may give the false impression that I believe it is impossible to obtain a temperature determination by homogenization of a melt inclusion that is free of suspicion. Careful homogenization studies, particularly on inclusions with low volatile contents, can produce valid data on the crystallization temperatures of the host mineral. However, I suggest caution in evaluating the data obtained on hydrous inclusions until experiments having appropriate external atmospheres have been performed on that specific mineral. In particular, one should remember that the three major sources of possible error in such determinations — inadequate time for equilibration, loss of hydrogen or water, and thermal gradients in the stage — generally will all tend to yield high results.

TEMPERATURE AND SEQUENCE OF PHASE CHANGES DURING COOLING

Inclusions provide data on the temperatures of the liquidus, the solidus, and the phase sequences on crystallization. Here we once again encounter the nemesis of many inclusion studies, metastability. Once a melt inclusion is trapped within a mineral, it is isolated from all other solid phases that might have been

present in the same magma. Obviously, because the inclusion is trapped within a crystal, one can never determine the true liquidus for that magma; however, one can sometimes determine the temperature at which the melt within the inclusion became saturated, on cooling, with respect to additional phases. Metastable supercooling precludes simple watching of a homogenized inclusion during a cooling cycle. If, however, the inclusions already contain crystals of the phase or phases of interest, nucleation is no longer a problem. The temperature of disappearance of these phases on reheating will be the temperatures at which they could have crystallized, at equilibrium, on cooling.

This procedure is best illustrated by inclusions in lunar olivines from Apollo 11 and 12 that originally contained crystals of pyroxene, plagioclase, and ilmenite. When these inclusions were given sequential heatings to higher and higher temperatures (Roedder & Weiblen 1970) and were quenched and examined after each heating, the data indicate that in the original magma, ilmenite started to crystallize at 1210°C, pyroxene at 1130°C, plagioclase at 1105°C, and that the last liquid crystallized below 1065°C. Note that these temperatures are for olivine-saturated melts, because the experiment was run in an "olivine bottle".

CONSTRAINTS ON MAXIMUM AND MINIMUM COOLING RATES

Now let us examine briefly some of the data available on relative cooling rates and some of the constraints on the absolute cooling rates that can be obtained from melt inclusions. Inclusions in lunar olivine show that the phases present are mainly a function of cooling rate and inclusion size (Text-fig. 4). Because random nucleation processes are involved, averages of many inclusions must be used and highly precise result cannot be expected. When cooling is fast, only glass will be present. Slightly cooling may permit nucleation of a sulfide globule, a bubble, or epitaxial ilmenite and plagioclase. Still slower cooling, maintained through a lower temperature range, permits nucleation and growth of feathery pyroxene, and presumably of more plagioclase and ilmenite, from the remaining liquid.

Nucleation is volume-dependent as well, so the smaller the inclusion, the less likely a given phase will nucleate. When cooling is very fast, all sizes of inclusions will consist solely of glass. When cooling rates are intermediate, the larger inclusions will, on the average, contain more phases than the smaller ones. When cooling is very slow, only the very smallest inclusions will still contain glass. These differences must be based on averages. For example, of the two small adjacent inclusions in the same olivine grain (Pl. 3, Fig. 1), one nucleated epitaxial ilmenite and plagioclase, plus pyroxene, whereas the other, of the same size, contains only ilmenite and vapor in glass. By establishing a sequence of more-or-less objective categories based on observable differences such as the presence or absence of epitaxial ilmenite or plagioclase, or of random crystals, one can plot the number of inclusions having a given assemblage versus a measure of the individual inclusion volume, the maximum inclusion length (Text-fig. 5). Inclusions in these three lunar samples showed significant differences, suggesting a range of cooling rates.

The epitaxial daughter mineral plates of ilmenite and plagioclase in these lunar olivines provide an interesting scientific anecdote. Although many people had studied basalts over the years, to my knowledge, no one had ever reported such inclusions in terrestrial samples, so when I found them in both Apollo 11 and 12, I began to wonder why they did not occur in terrestrial lavas. When

I looked at some old slides of Hawaiian rocks that had been around the U.S. Geological Survey for years, I found that such inclusions were plainly visible. Thus, for instance, a single 1 mm diameter Hawaiian olivine phenocryst contains three inclusions, each with its black ilmenite and transparent plagioclase plates, and even sulfide globules (Pl. 4, Fig. 4). We simply had to go to the moon to open our eyes to what was plainly visible on earth.

As a result of this discovery of epitaxial daughter crystals in terrestrial as well as lunar samples, a comparison is desirable. When I compared the silicate melt inclusions in Apollo 11 and 12 samples with those from several Hawaiian samples, I found there was a great similarity, but I could not be sure whether the differences were due to melt composition or cooling rate.

Laboratory heating of natural glassy inclusions, or previously homogenized ones, also permits us to place some constraints on the absolute cooling rates in the natural cooling cycle. Thus, if inclusions that were originally glass nucleate crystals during a given laboratory cooling cycle, the natural cooling cycle must have been faster than the laboratory one. Similarly, ilmenite nucleates as random crystals at one laboratory cooling rate and as epitaxially oriented plates at a slower rate, as in a formerly homogeneous glass inclusion (Pl. 3, Fig. 2) in which several epitaxial plates of ilmenite formed during laboratory cooling from 1120 to 1020°C over an 11-day period.

BULK COMPOSITION AND LIQUID LINE OF DESCENT

One of the most important uses of melt inclusions in petrology is to provide data on the compositions along the liquid line of descent of the magma. Once again, one must remember the differences between that which occurs within the

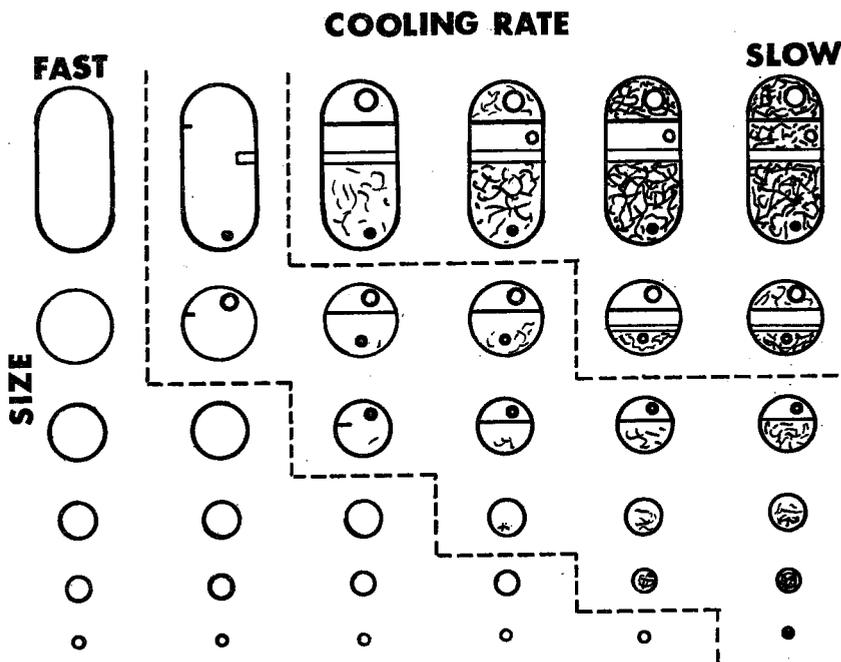


Fig. 4. Diagram showing the effects of cooling rate and size on the nucleation and growth of phases in inclusions in lunar and terrestrial olivines

crystal bottle containing an inclusion and that which occurs outside the crystal in the main mass of magma.

Knowledge of the true composition of the melt that was trapped in an inclusion would be exceedingly valuable to petrology. Barring local disequilibrium effects, for example, from fast crystallization, a melt inclusion represents a real point on the liquid line of descent for that magma, rather than those inferred points obtained from analyses of apparently genetically related rocks believed to represent a series. Such compositions might also reveal the existence of magma mixing. As in so much geological research, however, things are never quite as simple as they may seem at first.

The electron microprobe has provided petrology with a powerful tool matched perhaps only by that of Sorby's introduction of the petrographic microscope 120 years ago. The electron microprobe and its relatives, the ion microprobe and the scanning electron microscope, permit analyses that were simply not even dreamed of earlier.

As in the application of several other new analytical tools to geochemical problems, however, major difficulties generally lie not in the tools themselves, but in the selection of truly appropriate samples for analysis. One of the most serious problems in the analysis of melt inclusions is the gross sample heterogeneity caused by daughter phases. Superimposed on this is the difficulty of obtaining a valid broad-beam analysis from a coarse-grained mixture (Albee & *al.* 1977).

After an inclusion is trapped, the host mineral generally continues crystallizing onto the walls, as is sometimes indicated by the apparent embedding of daughter crystals in the walls. If the host is a solid-solution series such as olivine, there should be either continuous reaction if the included melt and the crystal, if diffusion permits attainment of equilibrium, or continuous fractionation, if it does not. One way of investigating this problem is to examine the inclusion/host crystal interface, by making electron microprobe traces across it. Since the electron beam, even though small, excited a sample volume of much larger radius, considerable care must be used in interpreting such data (Roedder

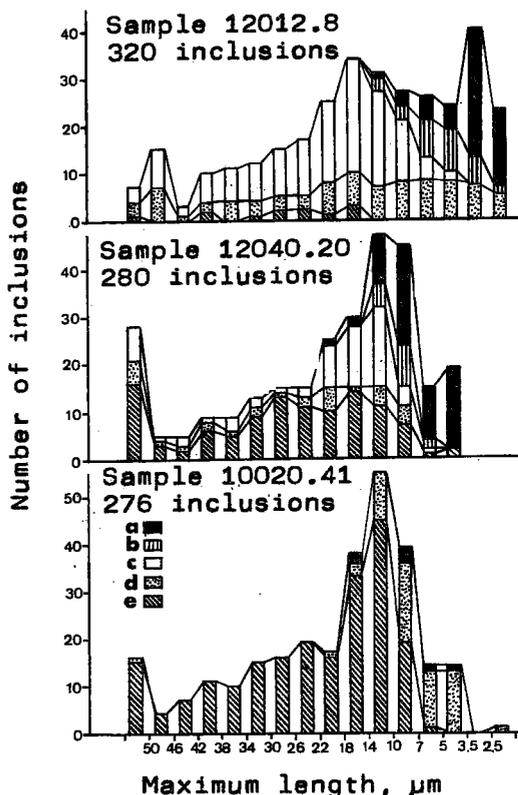


Fig. 5

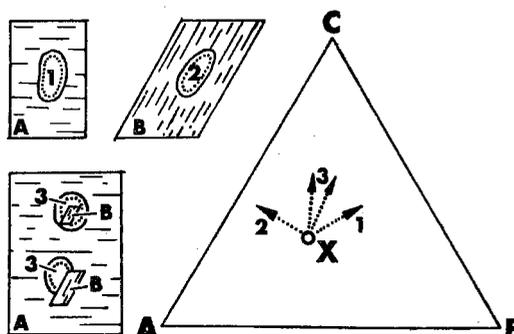
Frequency of occurrence of various assemblages in primary melt inclusions in three different lunar olivines, plotted against maximum inclusion length (Roedder & Weiblen 1971); a — all glass, b — few random crystals, c — many random crystals, d — epitaxial ilmenite and plagioclase

1979b). Anderson (1974) has shown that calculating the composition of the melt that was originally trapped in an inclusion in which there has been crystallization on the walls is not a trivial matter. One method that avoids many (but not all) of these problems involves homogenizing the inclusions in the laboratory before quenching and sectioning for analysis (Roedder & Weiblen 1971). An interesting version of this procedure involves examining the crystal/melt interface after the inclusion has been heated to various temperatures (Potter 1975). At low annealing temperatures, iron is enriched in the wall of the inclusion; at high temperatures, it is depleted, suggesting that these inclusions were trapped at some intermediate temperature.

Any analysis of an inclusion in a given host mineral must lie somewhere along a "control" or "fractionation line" for that mineral on a compositional plot (Text-fig. 6). If the inclusion was too small for accurate analysis, some of the surrounding host mineral may be included in the analysis, and the apparent composition will be intermediate. If the inclusion has crystallized some host mineral after being trapped, the composition point for the remaining melt will have moved along the appropriate control line in a direction away from the host-mineral point. Thus, an inclusion of composition X , in phase A, (Text-fig. 6), would evolve along control line 1 by crystallizing A on the walls; one in phase B would evolve along control line 2. These two inclusions are illustrated in the upper left of the diagram. The intersection of the two control lines provides the actual composition (X) that was trapped. The method requires the melt to have been trapped at the same stage of differentiation in crystals of the two different phases, or better still, three phases.

Fig. 6

Diagram showing use of control lines to determine the original composition of melt that was trapped in inclusions in phases A and B, crystallizing in the system A-B-C; see text for details



If we consider two melt inclusions in phase A, (Text-fig. 6), one trapped as a result of a solid inclusion of phase B, in either inclusion, the residual melt will lie along some intermediate and generally curving control line 3, depending on the ratio of A and B crystallizing. Note that for this purpose, where only the composition of the residual melt is considered, it makes no difference whether B is a daughter crystal or a solid inclusion. This difference would be very important to know, however, if the apparent gross compositions of these two inclusions were being obtained.

Watson (1976a), Clocchiatti (1977a, b) and Clocchiatti & al. (1978) used the intersecting control-line procedure to learn the composition of the original melt trapped in inclusions of crystals from basalts.

Even single analyses of melt inclusions can be informative, however, particularly if the inclusion is homogeneous. Roedder & Weiblen (1970, p. 810) analyzed a laboratory-homogenized inclusion in olivine from a lunar basalt and found that the composition was almost identical with that of the bulk rock, suggesting that this phenocryst probably formed very early and was indigenous to this magma.

In contrast, Anderson (1971) reported on an inclusion in armalcolite from another lunar sample whose composition was so different from that of the bulk rock that he suggested that the host armalcolite was an "exotic constituent" — that is, a xenocryst, rather than a phenocryst.

The existence of such inclusions having apparently anomalous compositions raises an important and still generally unanswered question as to the "boundary layer problem", *i. e.*, the degree to which the composition of the melt trapped in an inclusion corresponds to that of the bulk of the melt adjacent to the growing crystal. Obviously, there must always be compositional gradients adjacent to any growing crystal face, and diffusion, both toward and away from this zone, is continually leveling out these gradients (Anderson 1967, 1976). The width of the zone in which significant compositional differences might occur will be the speed of crystallization, the viscosity of the melt, and the amount of the host phase crystallizing from any given portion of melt, and will decrease with higher diffusion rates and with fluid flow past the crystal (*e. g.*, sinking crystals). Furthermore, different ions have different diffusion rates, so the actual composition of the fluid near the surface that might be trapped in an inclusion is difficult to calculate. Inclusions that are small relative to the width of zone at the time they are trapped will have a more nonrepresentative composition, whereas large inclusions may be nearly representative of the bulk of the fluid. I suspect, however, that as many melt-inclusion studies provide concordant results in terms of control-line plots, the real effects of boundary-layer problems on melt inclusion chemistry are generally minor. The bulk of these effects are from the crystallization of the host phase and hence are eliminated automatically by the control line procedure. In the future, when analytical procedures have been improved, the boundary-layer effects not only may be more readily detectable but also may be useful for rate studies, *e. g.* by comparing the boundary-layer differences for elements having different diffusion rates.

One of the easily obtained evidences of the composition of glassy magmatic inclusions is the index of refraction of the glass. Variations in index for a sequence of samples can sometimes be tried to differentiation processes (Clocchiatti 1975). The index of refraction is a function of all compositional parameters, of course, and hence is not free of ambiguity. It will also be subject to changes from precipitation on the walls. Kaluzhnyi (1965) was the first to show there were significant differences in the indices of refraction for glass inclusions in different minerals from the same dacite.

VOLATILE CONTENT

So far I have ignored one of the most important compositional parameters obtainable from inclusions: the volatile materials. For more than a century there have been continuous, in part heated, yet unresolved, discussions in the geologic literature on the elusive subject of the nature and actual concentrations of volatile materials in magmas. Throughout these discussions, actual samples of magma were available, in the form of melt inclusions each having at least a partial and possibly a full complement of volatile materials, just waiting for suitable analytical techniques. An example may be a grain from an Icelandic tuff (Pl. 3, Fig. 3), containing many melt inclusions. The melt must have been rich in volatile materials, because wherever a later fracture has intersected an inclusion, the opened inclusion has expelled the melt and has formed a large dark vapor bubble.

The first attempt at analysis of such volatile-rich and hence presumably hydrous melt inclusions was by Carron (1961), who obtained low totals with the new electron microprobe on glass inclusions in quartz phenocrysts, presumably because of the presence of volatile materials. Clocchiatti (1971) used infrared absorption to prove the presence of (OH)- in such glasses. Since then, Anderson (1973, 1974), Anderson & Sans (1975), Sommer (1977), and Johnston (1978) have also used the microprobe method effectively on some very water-rich magma samples (Roedder 1979b) many attempts have been made to analyze the volatile materials in melt inclusions, in the glass, in the vapor, or in the total inclusion. Several thousand analyses have been published of the gases evolved during crushing, ball milling, or heating bulk samples of rocks or minerals, many of which were of igneous origin (Roedder 1968-1979, 1972). For a variety of reasons it is seldom easy to relate these gases specifically to the inclusions present in the samples.

In addition to these bulk sample analyses, and their inherent ambiguities, various papers in the Russian literature over the past decade have presented analyses of the gases extracted from the gas bubbles in single melt inclusions in igneous minerals. Most of these analyses were performed at Novosibirsk and are generally credited to Shugurova, Dolgov, or both; these analyses involve a series of ingenious and delicate methods of releasing and transferring the tiny bubbles, under castor oil or anhydrous glycerol, from one chemical absorbent to another in sequence, and measuring the decrease in bubble diameter in each absorber. They have reported extraction and analysis, for nine different constituents, of the gases from inclusions as small as 1 μm . The exact methods used are given in a paper (Dolgov & Shugurova 1965) that has never been made available in the Western world. A later paper that is available (Dolgov & Shugurova 1966) supposedly differs only insignificantly (Dolgov *personal communication* 1967), but unfortunately it deals with the analysis of much larger bubbles, containing three to five orders of magnitude more gas. The major problems with this procedure, in addition to those of mastering the delicate micromanipulations, appear to be the lack of perfectly specific chemical absorbents, the known and finite solubility of all gases in all transfer and absorption fluids, and the logarithmic increase in internal bubble pressure (and hence solubility in any fluid) from surface tension, particularly at bubble diameters less than a few micrometers.

Other techniques are being applied to obtain direct analyses, such as the ion microprobe (Clocchiatti 1975) gas chromatography, and mass spectrometry, and particularly the combination of these last two techniques; some ingenious methods also have been devised to avoid some of the pitfalls, but these will not be discussed further here.

INCLUSIONS RESULTING FROM IMMISCIBILITY

So far, I have discussed only "normal" melt inclusions, trapped from a homogeneous melt. There are, however, many types of magmatic inclusions that form from nonhomogeneous fluids—that is, they form from mixtures of two or more immiscible fluids. I use the term "immiscibility" in a broad sense, to describe any combination of two or more fluid phases that do not mix under the specified conditions. The scientific and semantic rationale behind this seemingly odd usage has been detailed elsewhere (Roedder & Coombs 1967).

Many distinct varieties of immiscibility have been recognized, or postulated, in the process of magmatic differentiation. These varieties are

pertinent to inclusion research because the various trapped fluids have their composition determined by the immiscibility, and because, as we shall see, the immiscibility itself is frequently the cause of the trapping.

HISTORICAL BACKGROUND ON SILICATE IMMISCIBILITY

The concept that silicate liquid immiscibility in magmas is the mechanism by which certain rock types have formed was proposed by Zirkel (1866) and Rosenbusch (1887) early in the development of petrology to explain the juxtaposition of rocks having quite disparate compositions, usually without intermediate types. Rocks such as basalt and rhyolite, and various pairs of dyke rocks, were generally and conveniently assumed to have formed simply by the "splitting" of a formerly homogeneous magma into two immiscible magmas of contrasting composition.

The systems CaO-SiO_2 , MgO-SiO_2 and FeO-SiO_2 do indeed have extensive fields of immiscibility, but Greig (1927) showed, by use of a pseudoternary plot of $(\text{CaO}+\text{MgO}+\text{FeO})-(\text{SiO}_2)-(\text{Na}_2\text{O}+\text{K}_2\text{O}+\text{Al}_2\text{O}_3)$, that these fields were eliminated by the addition of just a few percent of alkalis or alumina as a third component. No igneous rock composition even approached the limits of the immiscibility field on this diagram. Furthermore, synthetic immiscibility took place only at excessively high temperatures ($\sim 1700^\circ\text{C}$). Thus, experimental verification of immiscibility was found only in geologically unlikely compositions, at geologically unreasonable temperatures. Bowen (1928) then showed that if immiscibility had indeed occurred in natural magmas, the expected lines of evidence for it had not been found in the rocks. Silicate immiscibility as a potential petrological process was thus put to rest.

Since then, however, new evidence has come to light that negates all three of the objections of Bowen and Greig. A more extensive discussion of immiscibility and the various lines of evidence for it is given elsewhere (Rodder 1978; see also Philpotts 1976 for a detailed review of immiscibility in the Monteregian alkaline province of Quebec). Here I will review only a few of the more important aspects of immiscibility in general, and present some experimental work on the low-temperature immiscibility volume in the system $\text{K}_2\text{O-FeO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$.

GENERAL BEHAVIOR OF SYSTEMS INVOLVING IMMISCIBILITY

STABLE EQUILIBRIUM IMMISCIBILITY

No difference exists thermodynamically between the process of separation, from a melt, of a crystal or a globule of a second melt. Immiscibility is usually explained on the basis of structural models of the liquid state. Unfortunately, these models involve the properties of hypothetical molecular species in solution, and no consensus has been reached concerning these species. Also, the entropy and enthalpy terms of the free energy change of the unmixing process can presumably be nearly equal and opposite, so the occurrence, extent, and temperature of immiscibility can be extremely sensitive to composition.

Bowen (1928) illustrated stable immiscibility by a simple, hypothetical, binary system that unfortunately eliminated many features of the complex systems that

more closely approach natural magmas. Perhaps the most important of these features is the very gross difference in behavior on cooling for various bulk compositions. The presented plot (Text-fig. 7) illustrates some of the possible modes of behavior for a simple ternary system A-B-C in which immiscibility in the system A-B is eliminated by the addition of C. Changes in the phase assemblage on cooling, scaled from the diagram, are shown for the six numbered compositions. Note that both the sequence of formation and relative amounts of melts L_1 (along M-O; rich in A), L_2 (along N-O; rich in B), and crystals of A, can vary widely, within a single system. Other compositions and diagrams that have other topologies can yield additional types of behavior. Thus immiscibility may decrease as temperature decreases. Fenner (1948) made a major point of this in defending the petrological significance of immiscibility, but no silicate system yet studied shows such a lower consolute point.

The essential feature of immiscibility is simply that at some temperature a given melt can no longer exist stably, and splits into two melts. The melt can arrive at this state by simple cooling (points 1, 2, 4 and 5), or by cooling and

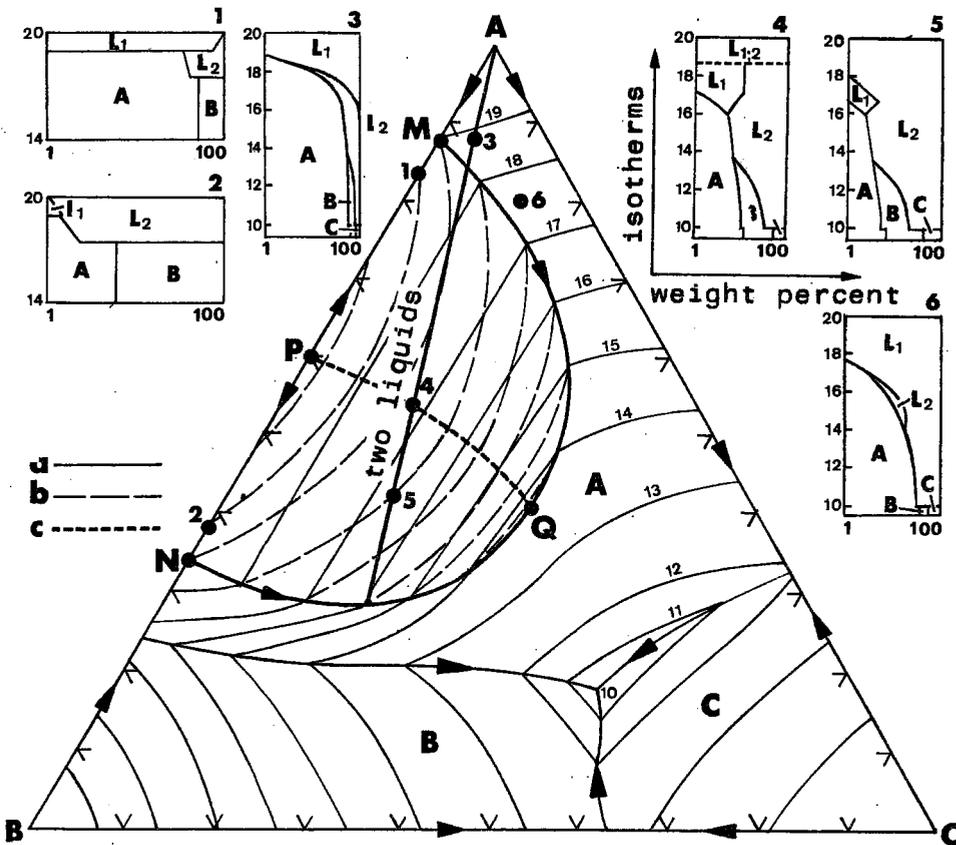


Fig. 7. Hypothetical ternary system showing immiscibility

The small diagrams show the quantitative phase relationships for six marked starting compositions from liquidus to solidus, obtained by applying the lever rule to the ternary diagram a — isotherms in liquidus, b — isotherms in liquidus, c — critical (consolute) curve; see text for details

crystallization (points 3 and 6). The splitting is independent of the presence, absence, or the amount, of crystals. Every element will have a unique partitioning between the two melts, and these partition functions can range widely.

Compositions in the area *POM* will first form a small amount of conjugate melt in the area *PON*, and *v. v.* Just as in any emulsion, the melt will then consist of globules of the new (dispersed) melt embedded in a host (continuous) melt. As they cool further, at equilibrium, each of the two melts will exchange constituents with the other. The amounts moving in the two directions across the interface (*i. e.* the meniscus) between the two melts will generally be different, so the relative amounts of the two melts will also change. These amounts can be found by applying the simple lever rule, as has been done here (Text-fig. 7) to yield the six cooling histories.

Compositions along the line *PO*, on contacting the solvus, suddenly split into approximately equal amounts of two melts. These two will have almost identical compositions at first, and on cooling will gradually diverge from *PO* along curving paths (not shown) on the solvus. These paired melts will contact the liquidus surface simultaneously, one along *MO* and the other along *NO*, at points on a tieline on that ruled surface. Thus, they must have the identical liquidus phase and liquidus temperatures, as pointed out by Bowen (1928). However, the practical application of this most important test for immiscibility is difficult at best (Roedder 1979a).

Subsequent crystallization of *A* will then result in the bulk composition of the two-melt mixture directly away from *A*, and continuous in the compositions and amounts of the two melts along *MO* and *NO*, as required by the tielines, until only one melt remains.

METASTABLE IMMISCIBILITY

Greig (1927) presented data on the system BaO-SiO_2 that revealed a novel sigmoidal curvature for the liquidus of SiO_2 — concave upward near SiO_2 , nearly flat from 5 to 25 wt. % BaO , then falling off rapidly beyond 25% BaO (*i. e.*, concave downward). He showed, on the basis of the work of Bakhuis Roozeboom (1901), that such a curvature is indicative of a field of immiscibility either above (stable) or below (metastable) the liquidus. Later work by Seward & *al.* (1968) proved that the field of immiscibility is below the liquidus in this system. As shown in the last decade or so, such metastable, subliquidus immiscibility, rather than being exceptional, is probably an inherent of many, if not most, silicate glasses, and it is now widely exploited in the glass industry. If such fields of immiscibility occur beneath other flat or sigmoidal liquidus, as in the systems albite-fayalite, leucite-forsterite- SiO_2 , and orthoclase-diopside, the depression of the liquidus by other components present in natural rocks may result in the formation of stable immiscibility. The additives may, of course, affect the immiscibility field also, so at present the results are neither implicit nor predictable.

RATE PROCESSES

After globules of a second melt have nucleated, all changes in composition of the two melts require diffusion across the interface and through both melts. As such, the processes are very similar to the growth of crystal of a solid solution from a melt, but diffusion in melts will probably be many orders of magnitude faster than in crystals (Hofmann 1975).

Because the two melts typically are different in density, they will tend to separate in a gravitational field, although the presence of a large percentage of crystals may physically prevent it. Convection will reflect the effective viscosities and the bulk densities of the mixtures of crystals and immiscible melt.

EXPECTED BEHAVIOR IN MAGMA CHAMBER

What phenomena can be expected when immiscibility occurs in a magma chamber? Field evidence from layered intrusions such as the Skaergaard (Wager & Deer 1939) provides at least a partial analogy. Although the rheological properties of the crystal-melt mixtures involved there are complex and not completely known, descent of denser masses of melt plus crystals (density currents) have apparently caused deep scouring of the crystal mush at the sides and bottom of the chamber. Immiscibility can typically yield density contrasts of ≈ 0.4 G/cm³ (McBirney 1975) or even as much as 0.87 G/cm³ (Philpotts 1972), the same as those between many crystals and melts. Hence segregation of melt masses and eventual density currents can be expected. Separation of globules of melt should be more rapid and effective than separation of crystals, however, for several reasons (Roedder 1979a).

If the dispersed phase is felsic, it should rise in a basaltic liquid. Because volatiles such as H₂O (and hence CO₂) tend to partition into the felsic phase, they will also be concentrated upward. Ambiguity arises, however, because another kind of "immiscibility" — boiling or vesiculation — also results in sweeping such volatiles upward.

SILICATE IMMISCIBILITY: THE SYSTEM K₂O-FeO-Al₂O₃-SiO₂.

THE PLANE LEUCITE-FAYALITE-SILICA

Just 30 years ago I started work on the system leucite-fayalite-silica, a plane in the quaternary system K₂O-FeO-Al₂O₃-SiO₂, since nothing was known concerning the "inside" of this tetrahedron.

The laboratory behavior of many compositions in the plane was odd and inexplicable, and an explanation was not apparent until after considerable wrestling with the problem. The peculiar behavior was eventually found (Roedder 1951a) to be a result of a field of stable silicate liquid immiscibility located well within the quaternary system, completely separate from the expected extension into the quaternary of the well-established field of immiscibility from the binary FeO-SiO₂ (Text-fig. 8), and near the liquidus surface. Because the addition of either alkalis or alumina eliminated the high-temperature field of immiscibility between CaO, MgO, or FeO and SiO₂ in all systems studied until that time, this new result was a unexpected pleasure — a good example of serendipity. The addition of alkalis and alumina (in the form of leucite) does actually eliminate the high-temperature field of immiscibility (Text-fig. 8), but further additions bring in the new field, which occurs at much lower temperatures and with much higher concentrations of alkalis plus alumina. There have been several subsequent studies of this immiscibility field (Visser & Koster van Groos 1976, 1977; Roedder 1977; Freestone & Hamilton 1977; Naslund 1976; Nakamura 1974; Watson & Naslund 1977), but various differences in experimental conditions make exact comparisons difficult.

iron contents (Text-fig. 9). Although almost primary phase field boundaries have been drawn in as solid lines, for a variety of reasons (Roedder 1978) all should be considered as tentative; the best control on these boundaries is on or near to the 1:1 $K_2O:Al_2O_3$ line, in the higher silica range, and, of course, near the limiting ternaries.

The high silica portion of the system is considerably complicated by the existence of 13 compounds, of which at least 6 show two or more crystal modifications each; and by the existence of the two separate fields or phase volumes, each representing two immiscible liquids in equilibrium with one or more crystalline phases. No quaternary compounds as such have been found, but evidence does point toward at least partial and possibly complete quaternary solid solution between several ternary compounds (Roedder 1978).

A large but still inadequate number of compositions and quench runs was concentrated around the low-temperature immiscibility volume. These runs showed that this volume displaces the tridymite/cristobalite boundary and the isothermal surfaces within the silica volume, so that they are all concave toward

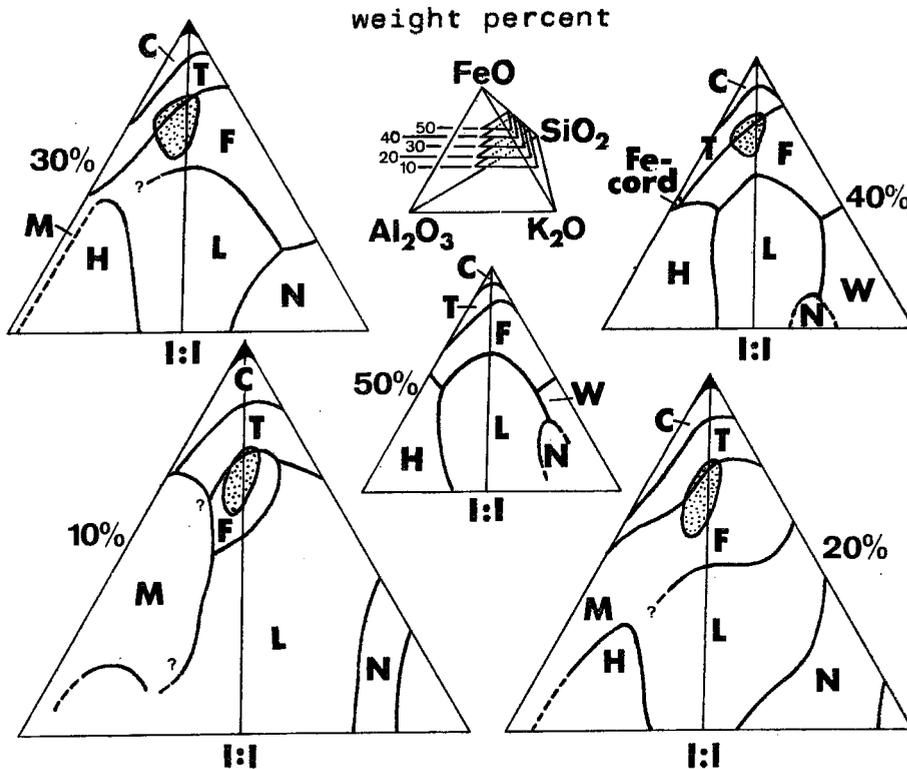


Fig. 9. The high-silica part of the system $K_2O-FeO-Al_2O_3-SiO_2$, showing primary phase volumes in the sections at the stated contents of total iron as FeO; all compositions run in metallic iron under 1 atm N_2 ; the high-temperature field of immiscibility along the $FeO-SiO_2$ sideline is in black; the phase volume (at the liquidus) of low-temperature immiscibility astride the 1:1 $K_2O:Al_2O_3$ (molar) plane is dotted; primary phase fields are shown for cristobalite (C), tridymite (T), hercynite (H), mullite (M), fayalite (F), wustite (W), "potash nepheline" (N), and leucite (L); see text for limitations on these boundaries; Text-fig. 8 is the ternary section along the 1:1 mole ratio plane

and tend to wrap around the immiscibility volume in the manner described by Irvine (1975). The isothermal surfaces in the fayalite field are also severely warped in the vicinity of this immiscibility volume, and as a consequence, compositions in this vicinity have rather unusual crystallization histories as detailed below. It is important to remember also that the extent of this volume of immiscibility (Text-fig. 9) is a minimum, because immiscibility may also occur beyond this range, but could easily have been missed by the specific compositions and temperatures investigated in this study.

In view of the many discussions of the possibilities of extrapolation from relatively simple, known systems into more complex systems, it is of interest to examine the limiting ternary systems adjacent to the low-temperature immiscibility volume. From the phase diagrams for the systems K_2O - FeO - SiO_2 (Roedder 1952), and FeO - Al_2O_3 - SiO_2 (Schairer & Yagi 1952), I doubt that many would have predicted that a few percent of K_2O or Al_2O_3 added to such ternary liquids would cause them to split. Yet the new quaternary immiscibility volume comes within ≈ 3 wt% Al_2O_3 and ≈ 2 wt% K_2O of these two ternary systems.

The geometry of this low-temperature immiscibility volume, lying across the boundary plane between the primary phase volumes of tridymite and fayalite in the quaternary system, results in some unusual isothermal surfaces and hence, some very peculiar crystallization histories, featuring drastic changes in the phase assemblage with minor changes in temperature. Not uncommonly, compositions near the immiscibility volume may form 50% crystals on 5°C drop in temperature, particularly in the vicinity of 1150°C.

One possible complication in phase relations within the immiscibility volume pertains to the K_2O/Al_2O_3 ratio of coexisting, conjugate melts, made from compositions starting with a 1:1 ratio. Do such pairs of melts lie in the 1:1 ratio plane, or do they fall on opposite sides? I have experimental evidence either way, but it is unlikely that K_2O and Al_2O_3 would partition identically. Several workers (Visser & Koster van Gross 1976, Watson & Naslund 1977, Biggar of Univ. Edinburgh & Freestone of Univ. Manchester, *personal communications*) have obtained data on this ratio in the two melts in the system leucite-fayalite-silica, but comparison and interpretation is compounded by differences in the f_{O_2} used, and particularly in the magnitude of the potassium volatilization in both the syntheses and the runs. Additional problems might well lie in the difficulties of electron microprobe analysis, for both K and Al, of minute areas of glasses of grossly differing iron content.

The immiscibility volume we see here is only the tip of the iceberg, to use an incongruous analogy. The diagram for leucite-fayalite-silica (Text-fig. 8), shows that the stable low-temperature immiscibility there is only a small part of the picture. The two inset diagrams (Text-fig. 8) are TX sections through the system along the lines indicated. Note that, along the line H-I, the two stable fields of immiscibility — at high and low temperatures — are connected with a metastable, subliquidus field of immiscibility, near the stable liquidus (Roedder 1977). This metastable extension under the liquidus is not just conjectural; it has been established experimentally. I believe that such subliquidus metastable immiscibility is probably present in most silicate systems, and may come to the liquidus surface whenever other constituents drop the liquidus faster than they drop the solvus. It is most obviously near surface in those systems having very flat or sigmoidal liquidus surfaces, but the occurrence of immiscibility upon small additions of K_2O to the FeO - Al_2O_3 - SiO_2 ternary in this system shows that such suggestive evidence need not be present.

A cursory attempt was made to determine whether the low-temperature immiscibility volume was also present in the tetrahedra representing other re-

lated systems. This was done by taking two compositions from the system $K_2O-FeO-Al_2O_3-SiO_2$ and making batches with substitutions, on a mole-for-mole basis, of Li, Na, Rb, or Cs for K. Immiscibility was verified for melts with both one-half and full substitution of Rb or Cs for K. Although no immiscibility was recognized in the limited quench runs on the other compositions, it might well be present in some restricted temperature ranges; the large amount of crystallization that took place in these compositions within a narrow range of temperatures is suggestive of possible immiscibility. Furthermore, flat or sigmoidal liquidus curves in the systems albite-fayalite, leucite-forsterite-silica, and orthoclase-dioptase suggest that such immiscibility may eventually be found in the Na- and Mg-bearing systems, when other components are added.

SILICATE IMMISCIBILITY IN NATURE

Lines of evidence for natural silicate immiscibility from general field relations, outcrops, hand specimens, and petrography have been detailed elsewhere (Roedder 1975a). The best evidence for natural immiscibility comes from microscopy and consists of the presence of a meniscus between different glasses, where the term meniscus refers to a phase boundary, and does not include gradational due to inadequate mixing, however steep the gradients. The basic problem is that if the process is truly effective and large-scale, this line of evidence by its very nature, is eliminated. This is because any large mass of magmas undergoing immiscibility will generally have abundant time for the two melts to become separated from each other, and even if not separated, it will generally have time to crystallize. Both of these processes eliminate the menisci.

Numerous recent papers have suggested that immiscibility has been involved in the origin of certain specific rocks. Such occurrences generally consist of coexisting felsic and mafic rocks, and include both over- and under-saturated types (see Roedder 1979a). Only a few of the examples will be described here but they illustrate several features common to many of the occurrences. The first is late-stage immiscibility during crystallization of the lunar and terrestrial basalts, and the second is pre-eruption immiscibility of Archean tholeiites.

LATE-STAGE IMMISCIBILITY IN THE LUNAR BASALTS

I wish I could say that I hoped to find immiscibility in the Apollo samples, but the true story is far from it, and in fact, finding it was another case of serendipity. I went to Houston to look for liquid water and CO_2 inclusions in the first Apollo-11 samples. I was completely frustrated in this attempt, however, as the mare lavas turned out to be driest rocks known to man. In looking for such inclusions, however I spent several days staring at various odd textures in these slides. Some single crystals of anorthite were packed with rounded masses of an unknown material and these, in turn, with still smaller globules. Sometimes the masses appeared in nice rows, but all embedded in a single crystal of anorthite. Some late-forming crystals, later shown to be the new mineral, pyroxferroite, contained what looked like a row of glass "teeth" or "molars" (Pl. 3, Fig. 9). Crystallization of the major part of the magma ($\sim 90-95\%$) was normal, but eventually the residual melt between the crystals became so enriched in iron and potassium that it split to form globules of a second immiscible liquid. Mi-

croprobe analyses (Roedder & Weiblen 1970—1971) showed that this liquid had the composition of a potassium granite. These immiscible liquid globules stuck to the surface of the growing, late-stage minerals, forming the bottoms of such rows of teeth and marking the onset of immiscibility. Further exsolution of this immiscible granitic melt onto these nuclei, as the host crystallized from the iron-rich melt, caused some globules to grow and coalesce, yielding the tops of the teeth.

Not until considerably later did I find samples showing much more obvious textural evidence of immiscibility, such as two coexisting glasses separated by a sharp meniscus: a colorless, low-index one and a dark brown, high-index one (Pl. 4, Fig. 1). Part of the problem was that the high index glass was never seen in large masses or in contact with pyroxene. The reason for this is now obvious, but only in retrospect: since the high index glass contains about 90 percent normative pyroxene, it crystallized readily, particularly wherever a pyroxene nucleus was available, and hence nicely eliminated the evidence for its own former existence.

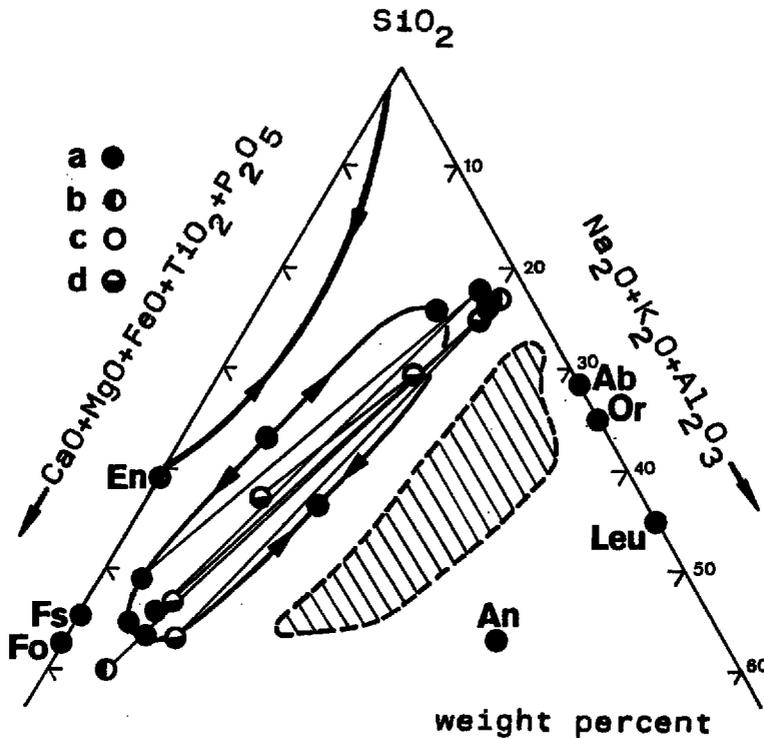


Fig. 10. Pseudoternary "Greig diagram" showing field of low-temperature immiscibility in the system leucite-fayalite-SiO₂, and tie-lines for various conjugate melt pairs (adapted from Weiblen & Roedder 1973); all compositions recalculated on the basis of plotted oxides only

a — coexisting glasses in lunar basalts from Apollo 11, 12 and 15; b — coexisting glasses in lunar basalt 14310; c — synthetic Apollo 11 sample after equilibration at 1045°C; d — Apollo 15 grain the last item is from Switzer (1975); all other data from Roedder & Weiblen (1970, 1971, 1972), and Weiblen & Roedder (1973); Most analyzed volcanic rock suites fall within the dashed field (Brooks & Gélinas 1975)

Microprobe analyses of such pairs of melts show that in composition they are essentially a titaniferous ferroproxenite and a quartz-rich potassium granite. As if the discovery of the immiscibility itself was not sufficiently serendipitous, when these analyses were plotted on a "Greig diagram" (Text-fig. 10), the two melts fall very near the plotted positions of the conjugate low-temperature immiscible melts in the system leucite-fayalite-silica. Now that the two compositions are known, this is not surprising because K_2O , FeO , Al_2O_3 and SiO_2 make up the bulk of their compositions (96.3 and 78.4% for the high-silica and high-iron melts respectively). Since then, similar analyses have been obtained from samples from all the lunar missions, including the three Soviet ones (Roedder & Weiblen 1977).

The question immediately arose — will such compositions as these show immiscibility in the laboratory? To check this, I made up a 50—50 mixture of average high-iron and average high-silica compositions, fused it at 1400°C in metallic iron, and verified that it was indeed a homogeneous green glass on quenching. Samples of this glass were then reheated to various temperatures and quenched. A run quenched at 1045°C consisted of fayalite plus two glasses (Text-fig. 10; see also Roedder & Weiblen 1971, Fig. 29).

Each and every element present, major and minor, will be partitioned between the two melts in a specific manner that will be a function of temperature, pressure, and most particularly, melt composition. It would be good to get minor and trace element distributions between the two lunar melts, to see how they agree with partition coefficients experimentally determined by Watson (1976b), but the nature of the samples generally makes this difficult. Roedder & Weiblen (1971) did establish the phosphorous distribution in the lunar samples, and found phosphorous to be much higher in the high-iron melt than in the high-silica melt, just the opposite of that expected from normal crystal fractionation (Anderson & Gottfried 1971). This partitioning of phosphorous between immiscible melts has since been experimentally verified and measured by Ryerson & Hess (1975) and by Watson (1976b). Another important "trace element" in the lunar basalt is potassium, present only in concentrations of several hundred parts per million. However, in the high-silica melts, potassium contents reach nearly 7 wt%, a 250-fold increase over those in the original bulk rocks. To achieve such an extreme enrichment in a mare basalt by crystal fractionation alone would be difficult.

LATE-STAGE IMMISCIBILITY IN TERRESTRIAL BASALTS

So silicate immiscibility had been fairly well proven in the late stages of lunar basalt crystallization. But why had such immiscibility never occurred in similar terrestrial basalts? When I looked carefully at some old slides of Hawaiian basalts (prehistoric Makaopuhi), I was pleased to find that many showed evidence of immiscibility. We simply had to go to the moon to open our eyes to what visible on Earth. We also found late-stage immiscibility in numerous other basalts, such as 1959 Kilauea Iki, 1965 Makaopuhi, North Shore Volcanic Group, Minnesota, and Disko, Greenland, and since then others have reported it in the high-Al basalts from Modoc, California (Anderson 1971), the Deccan Traps of India (De 1974), and the Jurassic basalts of Connecticut (Philpotts 1976). Philpotts has also found it in some Mid-Atlantic Ridge basalts (*personal communication*). What about modern basalt eruptions? the 1965 eruption of Kilauea on Hawaii made a lava lake. After a crust formed, Wright and Okamura (1977) set up a drill on the crust and drilled down through the crust to the liquid, taking

samples by quenching from various measured temperatures. In a sample quenched from 1020°C the melt between two plagioclase crystals has split to form two melts (Pl. 4, Fig. 5), now globules of dark high-index glass in low-index (high-silica) glass.

PRE-ERUPTION IMMISCIBILITY OF ARCHEAN THOLETTES

On of the most striking terrestrial occurrences ascribed to immiscibility is found in the series of slightly metamorphosed Abitibi tholeiitic lavas from the Canadian Archean, described by Gélinas & al. (1976).

The details of the field occurrence, in particular such features as the coalescence of flow-deformed varioles along the center of some flows and in the axial regions of lava tubes, their distribution in lava pillows, and their deformation where in contact, all seem to point to the formation of the varioles prior to extrusion. Both the varioles and the matrix now consist of a fine-grained assemblage of secondary minerals formed from the primary assemblage during the metamorphism of this belt (prehnite pumpellyite to lower greenschist facies). Both contain coarser dendritic, acicular, skeletal mafic crystals (now pseudomorphs) that may cut across the interface. These skeletal mafic minerals have swallow-tail terminations and many are hollow, ornamented chains, arranged in fan-shaped groups. Gélinas & al. (1976) identified them as quench crystals of olivine and some pyroxene, originally present in a glass that is now devitrified. The matrix also shows perlitic fractures having axiolitic acicular crystals, indicating a former glassy conditions. The contacts between the varioles and the matrix are optically and chemically sharp, to $< 10 \mu\text{m}$.

The bulk rock and the matrix for the varioles are relatively Fe enriched and have extremely low K (generally < 100 ppm). The matrix ranges from an Fe-rich rhyodacite through basalt to an ultramafic composition with SiO_2 as low as 39%. The varioles have a low-K rhyolite composition ($< 0.2\%$ K_2O). When plotted on a "Greig diagram" (Text-fig. 10), the tie-lines between variole and matrix are essentially parallel to but not coextensive with those in the system $\text{K}_2\text{O}-\text{FeO}-\text{Al}_2\text{O}_3-\text{SiO}_2$, but as these compositions contain only sodium and no potassium, the immiscibility field should be different. The distributions of Al, Ti, and P in these melts are notably different from those in other immiscible melt pairs, and immiscibility has not yet been obtained in laboratory studies on these compositions (Rutherford, *personal communication* 1978).

IMMISCIBILITY IN OTHER ROCK TYPES

The bulk compositions of most magmas on the "Greig diagram" lie to the right of the plotted position of the field of immiscibility from the system leucite-fayalite-silica (Text-fig. 10). How can such compositions develop immiscibility? Obviously, such multicomponent compositions cannot be adequately plotted in two-dimensional space, but since plagioclase would plot still further to the right (Text-fig. 10), crystallization of enough plagioclase, even though along with mafics, would drive the residual melt toward the region of immiscibility. McBirney (1975) has shown how this could have occurred at the Skaergaard, and has shown in laboratory experiments that immiscibility does indeed develop in some Skaergaard compositions at geologically reasonable temperatures.

There have been many other pertinent recent studies on a wide variety of rock types. Thus, Vogel & Wilband (1978) studied a composite dyke in South Carolina that consists of masses of basic rock embedded in granite. Such a composite dyke may be obtained in several ways, but their study of the partitioning of light rare-earth elements between these rocks seem to preclude any model involving partial melting or fractional crystallization to relate the two rock types. This leaves immiscibility as the prime candidate.

Although crystallization of the two melts tends to eliminate the textural evidence for immiscibility, I cannot visualize any process other than immiscibility that would yield distorted globules of the sort illustrated in 1971 by Phillips; in this example, globules ("ocelli") of syenite composition (Pl. 4, Fig. 6) have been squeezed against each other in a porphyritic camptonite dyke.

OTHER TYPES OF IMMISCIBILITY IN NATURE

In addition to the silicate-silicate immiscibility discussed above, many other distinct varieties of immiscibility have been recognized, or postulated, in the magmatic differentiation (Text-fig. 11). These various types of immiscibility are intimately connected with magmatic inclusion study because (1) these various fluids are trapped as inclusions, and (2) because the immiscibility itself is frequently the cause of the trapping. This is due to wetting phenomena. Gas bubbles in a vesiculating lava will normally nucleate most easily on a solid/liquid interface. If the gas phase has a contact angle of more than zero degrees (that is, if it "wets" the crystal surface to some extent), the crystal at that spot is coated with gas and cannot grow further, so the crystal grows around the gas bubble, frequently without a visible trace of melt. This process can yield a crystal full of primary gas inclusions (without a single melt inclusion) that actually grew from a silicate melt. The air inclusions in sucrose crystals ("rock candy") provide a good analogy (Roedder 1972, Plate 9-4). The record is a report by Zirkel (1873, p. 86) of a hauyne crystal with 3.6×10^{21} gas inclusions per cubic centimeter. Fenn & Luth (1973) report similar phenomena in hydrous melts of alkali feldspars in the laboratory.

The presence of such primary gas bubbles as inclusions in magmatic rocks proves that the magma was saturated with respect to that volatile phase. This information has many very important petrological consequences, for example in understanding explosive volcanism.

The "normal" magmatic inclusions discussed up to this point are those formed during magmatic differentiation by crystal fractionation from basaltic to granitic, and perhaps still further to pegmatitic melts, as shown by solid arrow 1 (Text-fig. 11). Arrow 2 represents the fractionation path taken particularly by the lunar mare basalts, and arrow 3 is thrown in to cover my ignorance as to the origin of the alkalic rocks. All other arrows represents known or suspected immiscible separations in nature. Because this paper concerns mainly melt inclusions, the top right group of five boxes (Text-fig. 11) can be dispensed with rather quickly. These boxes represent immiscible water-rich, relatively low-density fluids that may be evolved at any stage because of change in composition, decrease in confining pressure, or increase in vapor pressure. Their only real significance is that they form such mundane geological features as ore deposits. At some stage in the differentiation process, these hot immiscible water-rich fluids may become hydrosaline melts, containing as much as 50-70 weight percent chlorides (or even 84%, Kozłowski & Karwowski, 1973). Such fluids have

It is well known that globules of immiscible sulfide melt can form form basaltic liquids. Since some commercially valuable ore deposits have formed by the process of separation of an immiscible sulfide melt, it is important to know at what stage in a differentiation sequence the silicate melt became saturated with respect to sulfide (see Naldrett & al. 1979). Fortunately, the immiscible sulfide globules in melt inclusions provide this information: if the silicate liquid/sulfide globule ratio in the inclusions is uniform, the sulfide is a daughter phase, precipitated after trapping; if the ratio is highly erratic, immiscibility had occurred before trapping (Roedder 1976). If the oxygen fugacity is low, as in the lunar environments, this sulfide melt can later split out an immiscible metal phase. In some meteorites, a metal phase may precipitate directly (Text-fig. 11). Although both water and CO₂ are present in most basaltic melts, CO₂ is far more likely to constitute the immiscible "vapor" phase at high pressures, leaving the water in solution in the melt. In fact, olivine nodules from 72 localities all over the world always show evidence of the presence of an immiscible, almost pure CO₂ phase, either during the original crystallization at depth, or during ascent (Roedder 1965). An example (Pl. 3, Fig. 4), shows several 30 μ m liquid and gaseous CO₂ inclusions each having a rim of high-alumina andesitic or basaltic melt (Murck & al. 1976), in olivine from Hawaii. The presence of such CO₂, as primary inclusions requires that the silicate melt (basaltic?) from which this olivine originally crystallized was vesiculating, even at mantle depths. Another olivine nodule from Hawaii (Pl. 3, Fig. 5) contains some inclusions of basaltic silicate melt, now glass (G), some of pure CO₂ vapor and liquid (L), and some that trapped both fluids (as shown in the upper left of Fig. 5 in Pl. 3). At eruption, these CO₂ inclusions had pressures of about 5000–7000 atmospheres, but they did not decrepitate. In addition to providing evidence of deep-seated vesiculation and unambiguous data on the pressure at the time of trapping, these inclusions of CO₂ have significance to the problems of petrology such as the composition of volcanic gases and the origin of phenocrysts, carbonatites, and perhaps diammoids.

It is important to remember that these CO₂ inclusions give us no information on the relative amounts of CO₂ present in the original melt. Experimental studies at high temperature and pressure show that the amount may be small (Mysen & al. 1976) or large (Wyllie & Huang 1976), but in either case, it may be that the bulk of the vesiculation of deep-seated basalts on eruption represents the expansion of these tiny immiscible globules during pressure release. Moore & al. (1977) have shown that the vesicles in glassy quenched midocean basalts contain essentially pure CO₂, under a pressure that is a function of the depth of eruption. Some sulfur gas was also present but has since reacted with the walls to form sulfide spherules. Pineau & al. (1976) suggest, on the basis of carbon isotope studies of the CO₂ from "popping rocks" from the Mid-Atlantic Ridge, that some of this gas represents CO₂ escaping from the Earth's mantle.

An example of the direct formation of immiscible liquid iron droplets was found (Pl. 3, Fig. 6) in a grain of olivine from the Murray carbonaceous chondrite. Tiny globules of immiscible metallic iron melt precipitated on the growing olivine surface and were enclosed, along with some silicate melt. Fieni & al. (1976) have found almost pure water inclusions in whitlockite and plagioclase in another chondrite meteorite. How this would fit on the diagram (Text-fig. 11) is not apparent.

Let us consider briefly path 3 — the group of alkalic and miscellaneous rare rocks. I suspect that some of the Kiruna-type phosphate-iron oxide ores may have formed by immiscibility, but I have no inclusion evidence. Fluoride melts are immiscible with silicate melts (Kogarko & al. 1974), as are chloride melts (Roedder 1970), but the only inclusion evidence of such immiscibility in nature that I am aware of is that by Kogarko & Romanchev (1976). I strongly suspect that many carbonatite melts form as a result of immiscibility with silicates, but the only good inclusion evidence I know of is that of Rankin & LeBas (1974), who described immiscible silicate and carbonate melts during heating of inclusions in apatite from a carbonatite. Evidence for carbonate melt/H₂O-rich solution immiscibility was described by Haapala (1978) from a Finnish carbonatite, and I have found some evidence for both this immiscibility and that between carbonate melt and CO₂ in the Indian Amba Dongar carbonatite (Roedder 1973). An additional complication is provided by inclusions of hydrocarbons. A series of alkalic intrusive bodies in the U.S.S.R. and elsewhere all show an enigmatic association of hydrocarbon compound as fluid inclusions (Roedder 1972, pp. 45–47; see also Konnerup-Madsen & al. 1979).

Now let us discuss the immiscibility in lunar magmas (path 2 in Text-fig. 11). After crystallization of perhaps 95% of the melt, the lunar mare basalt magmas split to form immiscible globules of a high-silica melt of potassic granite composition in a high-iron melt of ferroproxenite composition. The lunar melts may also have had an immiscible sulfide melt present throughout much of the differentiation to the stage of silicate immiscibility (arrow to left from 2 in Text-fig. 11).

In order to understand the textures found in the lunar samples resulting from immiscibility let us look at two types of nucleation of immiscible phases, both of which have taken place in the lunar samples (Text-fig. 12). The sequence on the left represents nucleation of the new dispersed fluid out in the melt. Some globules stick to the crystal and are enclosed, with or without the host melt. Other inclusions may consist of just the host melt. The sequence on the right, however, depicts the case in which the new phase nucleates preferentially, and perhaps only, on a crystal surface. This type of nucleation may yield regular rodlike or toothlike inclusions, as more immiscible melt is added to the nuclei during growth of the host crystal. The regularity arises from the original nucleation, which can be very evenly spaced*. An example of immiscible sulfide melt (Pl. 3, Fig. 7) that nucleated on and continued to grow as rods during the growth of the enclosing fayalite host was found in the Soviet Luna 24 sample. A similar example of growth occurs as rods of potash granite glass in a pyroxferroite crystal (Pl. 3, Fig. 8) and a row of "teeth" of potash granite glass (Pl. 3, Fig. 9). Any type of immiscibility that maintains a continuing supersaturation of the exsolving phase during the growth of the host crystal can form rodlike inclusions of this type. The tubular inclusions of exsolved air seen in sugar crystals forming from water solution (Roedder 1972, Pl. 9) are another good example. In this case the immiscibility is caused by the crystallization of the host sugar. As sugar is a major component ($\sim 75\%$) of the solution, its crystallization results in significant increases in concentration of all other constituents in the solution, including dissolved air.

The most confusing feature of the two lunar immiscible silicate melts was that the major or continuous melt phase, the high-iron melt, normally crystallized completely and hence eliminated what would be the evidence for its existence, the presence of a meniscus between two different melts (Pl. 3, Figs 8 and 9); the

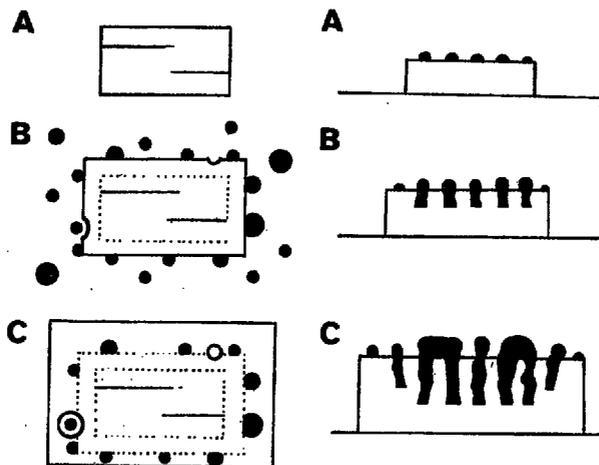


Fig. 12. Appearance of inclusions resulting from nucleation of a new dispersed immiscible fluid phase either out in the host melt (left series) or on the surface of a host crystal (right series)

* Similar regular nucleation is now exploited commercially in the manufacture of some special multiphase composite alloys, and has also been found in nature in the sulfide globules lining vesicles in the basalts (Moore & Calk 1971, Yeats & Mathez 1976).

bulk of the coexisting high-iron melt has crystallized as pyroxferroite, as the melt has a normative composition of about 85% iron-rich pyroxene. I was not absolutely certain that I really had found silicate immiscibility in the lunar samples until I found inclusions in plagioclase (e.g. Pl. 4, Fig. 1) where both melts are present as clean analyzable glasses. The petrological significance of the lunar silicate immiscibility and the evidence for similar immiscibility in many terrestrial rocks have been covered elsewhere (Roedder 1978), and Philippotts (1978) has reviewed the textural evidence for immiscibility in tholeites.

INEXPLICABLE INCLUSION TYPES

Before summarizing, I must admit that some sets of melt inclusion data are still inexplicable. I have mentioned several types of inclusions above appear anomalous, but three types from lunar mare basalts are particularly enigmatic: (1) low-K, high-Si inclusions in ilmenite; (2) inclusion in olivine (and pyroxene) with high K_D values for Fe/Mg; and (3) very high-Si inclusions in olivine. Except for these three types, most lunar melt inclusion data fairly well into a rational outline for the liquid line of descent (Roedder & Weiblen 1977a), within the rather severe limitations imposed by the necessarily spotty sampling and the nature of the available samples.

LOW-K, HIGH-SI INCLUSIONS IN ILMENITE

Many of the large ilmenite crystals in the lunar high-titanium mare basalts have 50–100 μm melt inclusions (Pl. 4, Fig. 2). Some of these are merely the normal immiscible potash granite melt (now a glass) containing ~ 76 wt. % SiO_2 and 6–7% K_2O . Other glass inclusions, even in the same ilmenite grains, also have $\sim 76\%$ SiO_2 and may look identical, but instead of 6–7% K_2O they contain an average of 0.04% K_2O , and many have no detectable K_2O by electron microprobe (most of the difference is made up by CaO). Only relatively few have intermediate compositions. When these glasses were described (Roedder & Weiblen 1975), 13 mechanisms of formation were presented, and then all were shown to be invalid. To my knowledge, no one has come forward since then with a fourteenth and workable hypothesis. Still other glassy inclusions in ilmenite are high in potassium ($\sim 2\%$ K_2O) but inexplicably low in silica (~ 35).

INCLUSIONS IN OLIVINE WITH HIGH K_D VALUES FOR Fe/Mg

The equilibrium distribution of iron and magnesium between melt and olivine crystals has been the subject of many studies. Equilibrium values of the distribution coefficient K_D ($\text{Fe}_{\text{crystal}} \times \text{Mg}_{\text{liquid}} / \text{Mg}_{\text{crystal}} \times \text{Fe}_{\text{liquid}}$), determined from laboratory data (Roedder & Emsile 1970, Longhi & al. 1978, Walker & al. 1976, Lipin 1976, Grove & Bence 1977, Takahashi 1978), are about 0.3, whereas most of the Luna 24 inclusions and many of those from the Apollo samples have analyses yielding K_D values between 0.5 and 1.5. Of several possible explanations, none are really satisfactory (Longhi & al. 1978, Roedder & Weiblen 1978).

EXTREMELY HIGH-SI INCLUSIONS IN OLIVINE

Roedder & Weiblen (1977b, 1978) reported a series of inexplicable, very high silica, clear-glass inclusions in olivine. These are isolated, moderate-sized, apparently primary inclusions in unshocked, unzoned, single-crystal fragments of intermediate olivine (Fo 51 to Fo 73) from the Luna 24 soil samples (Pl. 4, iFig. 3). When analyzed, the inclusions were found to be a relatively uniform, very high silica glass, as much as 93% SiO_2 . They were also very low in aluminium and calcium. How such extreme melts could form, how they got trapped in the olivine, and why they did not at least react with the walls to form pyroxene are still unanswered questions. The only feasible mechanism of formation suggested so far (Roedder & Weiblen 1978) invokes metastable silicate immiscibility of grossly supercooled liquids and hence is not very satisfactory.

CONCLUSIONS

There is still much to learn from melt inclusions. The new analytical tools available for their study, particularly the electron microprobe, can be expected to help. However, in the last three examples of anomalous inclusions, the data have been obtained with the electron microprobe, but the answers are not yet forthcoming. In 1802, John Playfair indicated that theory should be used to direct the observer in geology. The three enigmas I have just mentioned, and others I have not detailed, suggest that perhaps the reverse is now true. Theoretical igneous petrology has evolved considerably in recent years, but observational petrology apparently is still capable of providing some surprises and may even inspire some new theories.

Immiscibility of any type can result in the trapping of magmatic inclusions that are atypical of the bulk melt, but which provide a wealth of valuable data on magmatic processes. The present status of silicate liquid immiscibility in petrology is revived and healthy, with just enough loyal opposition to keep its proponents on their toes. In recent years experimental laboratory proof liquid immiscibility has been found with geologically reasonable compositions and temperatures in a variety of silicate systems. The typical products are a felsic, alkali-aluminosilicate melt and a mafic melt rich in Fe, Mg, Ca, and Ti.

The quaternary system $\text{K}_2\text{O}-\text{FeO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ has been studied extensively, particularly in the vicinity of the field of low-temperature silicate immiscibility. The presence of the immiscibility volume results in rapid phase changes and extensive crystallization within small temperature intervals in the vicinity of 1150°C . Similar immiscibility has been recognized in related systems with other alkali elements.

Although relatively small changes in composition can initiate or eliminate immiscibility, and vary the partition coefficients, immiscibility has been experimentally verified in such a wide range of rock composi-

tions that it might be a general feature of many systems. Only the top of the solvus is exposed generally, and hence the temperature range for stable immiscibility may be small. The possible significance of metastable immiscibility in petrology, the limits under which silicate immiscibility occurs in compositions simulating natural rocks, and the possible connection with the immiscible separation of melts of carbonate-oxide-, sulfide-, or phosphate-rich composition have yet to be investigated.

Evidence from both field and laboratory (including magmatic inclusions and experimental studies) is adequate to prove that immiscibility occurred during the formation of a relatively few natural rocks, and to suggest it in others. However, the process is such that preservation of unambiguous evidence can be expected to be relatively exceptional, even if the process was common. Therefore, one must extrapolate from the meager data base available to the assumption that immiscibility was probably much more common than just the few proven examples would indicate.

The compositional range for which there is reasonable evidence for immiscibility is striking. This range includes lavas from low-K, low-Al ultramafic and basaltic komatiites to high-K nepheline basalts, high-Al olivine tholeites, normal and high-Fe tholeites, lamprophyres, and various high-Ti lunar mare and feldspathic basalts with a 7-fold range in K/Na ratio.

Although the range of rock types is large, the most important feature, the composition of the residual melt just before splitting, is sometimes rather obscure. High or very high FeO/MgO seems to be a common but not universal feature. The composition of the felsic melt also varies widely; although most commonly it is rhyolitic, melts of trondhjemitic, syenitic or nepheline-syenitic composition are found.

Most significant, perhaps, is the great range in silica for the two melts. Because the mafic melt is generally undersaturated, and many of the conjugate felsic ones are oversaturated, immiscibility makes crossing the so-called silica-saturation barrier possible. At the time of separation the two melts must, of course, have the same activity of silica.

Most evidence for immiscibility comes from surface or near-surface rocks containing both immiscible fractions. The possibility exists, but remains to be established, that many major field occurrences involving separate rock bodies of appropriate composition, such as the associations lamprophyre-syenite, camptonite-nepheline syenite, the gabbro-granophyre association of the layered intrusions, and particularly that major source of the bimodal distribution of silica values, basalt-rhyolite, may be from subcrustal immiscibility.

The gross composition of the felsic liquid in much immiscibility is granitic, similar to granitic compositions derived by crystal fractionation. The partitioning of minor constituents in the two processes is

different, however, and future studies of trace element and isotopic distributions may well indicate that at least some terrestrial granites formed by immiscibility, although most are probably from the reworking of crustal materials or crystal fractionation. Still less easy to prove, but perhaps even more likely, is the possibility of formation of a primeval granitic crust on the Earth (or the Moon) by immiscibility; the present rocks showing evidence of immiscibility might merely represent the sweating out of the last remnants from the lithosphere.

The magmatic-inclusion study shows much promise for the future. Work is needed on several of the rate processes involved, especially diffusion processes on both sides of the crystal/glass interface, during and after inclusion trapping. Melt-inclusion data will continue to provide: (1) considerable information on the crystal, liquid, and various immiscible fluid phases present in magmas during their crystallization; (2) data on temperatures of crystallization and the sequence of phases crystallized; (3) meagre but valuable data on relative and absolute cooling rates; (4) otherwise unobtainable data on the compositions along the liquid line of descent; (5) insight into magma mixing; and (6) important data on the amount and nature of volatile materials present and their evolution during igneous emplacement. Guesses about other ways in which melt inclusions might be used in the future would be too speculative to merit space here, but I fully expect that their study will become as much an accepted part of igneous petrology as the equivalent study of aqueous inclusions has become for research in ore deposits.

I would like to close with a quotation from the father of fluid inclusion study, H.C. Sorby. It is just as appropriate now as it was 126 years ago, when Sorby was having trouble in convincing a skeptical geological fraternity that although inclusions are small, they can provide much evidence about geologic processes, if only one tries to understand what they are telling us:

„There is no necessary connexion between the size of an object and the value of a fact, and... though the objects I have described are minute, the conclusions to be derived from the facts are great” (Sorby 1858, p. 497).

Acknowledgments. I would like to thank the many people who have contributed to this paper with numerous personal discussions, through reviews of the several manuscripts at various stages, and by providing data, photographs, and references (see Roedder 1978, 1979a, b).

*U.S. Geological Survey
National Center, Mail Stop 959,
Reston, VA. 22092, USA*

REFERENCES

- ALBEE A.L., QUICK J.E. & CHODOS A.A. 1977. Source and magnitude of errors in "broad-beam analysis" (DBA) with the electron probe (Abstract). *Lunar Science*, VIII, 7-9. *The Lunar Science Institute*; Houston.
- ANDERSON A.T., Jr. 1967. Possible consequences of composition gradients in basalt glass adjacent to olivine phenocrysts (Abstract). *Amer Geoph. Union Trans.*, 48, 227.
- 1971a. Alkali-rich, SiO₂-deficient glasses in high-alumina olivine tholeiite, Hat Creek Valley, California. *Amer. Jour. Sci.*, 271, 293-303.
- 1971b. Exotic armalcolite and the origin of Apollo 11 ilmenite basalts. *Geochim. Cosmochim. Acta*, 35, 969-973.
- 1973. The before-eruption water contents of some high-alumina magmas. *Bull. Volcanol.*, 37, 530-552.
- 1974. Evidence for a picritic, volatile-rich magma beneath Mt. Shasta, California. *Jour. Petrol.*, 15 (2), 243-267.
- 1976. Magma mixing: Petrological process and volcanological tool. *Jour. Volcanol. and Geothermal Research*, 1, 3-33.
- & GOTTFRIED D. 1971. Contrasting behavior of P, Ti and Nb in a differentiated high-alumina olivine-tholeiite and a calc-alkaline andesite suite. *Geol. Soc. Amer. Bull.*, 82, 1929-1942.
- & SANS J.R. 1975. Volcanic temperature and pressure inferred from inclusions in phenocrysts. *Internat. Conf. on Geothermometry and Geobarometry*, 5-10 Oct. 1975, Penn. State Univ.
- BAKHUIS ROOZEBOOM H.W. 1901. *Die Heterogenen Gleichgewichte vom Standpunkte der Phasenlehre*.
- BARRABÉ L. & DEICHA G. 1956. Expériences de fusion et de cristallisation magmatique sur des reliquats vitreux des quartz dihexaédriques de la Guadeloupe. *Bull. Soc. Fr. Minéral. Cristallogr.*, 79, 146-155.
- & — 1957. Réanimation de magmas et interprétation de quelques particularités de leurs éléments de première consolidation. *Bull. Soc. Géol. Fr.*, 6^e série, 7, 159-169.
- BOTTINGA Y., KUDO A. & WEILL D. 1966. Some observations on oscillatory zoning and crystallization of magmatic plagioclase. *Amer. Mineralogist*, 51, 792-806.
- BOWEN N.L. 1928. *The Evolution of the Igneous Rocks*. Princeton University Press.
- BROOKS C. & GÉLINAS L. 1975. Immiscibility and ancient and modern volcanism. *Carnegie Inst. Wash. Yearb.*, 74, 240-247.
- CARRON J.-P. 1961. Premières données sur la composition chimique de certains reliquats magmatiques. *C.R. Acad. Sci.*, 253, 3016-3018.
- CLOCCHIATTI R. 1971. Composition chimique des inclusions vitreuses des phénocristaux de quartz de quelques laves acides par l'analyse à la sonde électronique. *C.R. Acad. Sci., Sér. D*, 272, 2045-2047.
- 1975. Glassy inclusions in crystals of quartz; optical, thermo-optical and chemical studies, and geological applications. *Soc. Géol. de France, Mémoires, New Series*, 54 (122), 1-96.
- 1977a. Les inclusions vitreuses des phénocristaux d'olivine et de chromite d'un "basalte picritique" de la ride médio-atlantique (d'un basalte à olivine). *C.R. Acad. Sci.*, 285, 1155-1158.
- 1977b. Les liquides silicatés piégés dans les cristaux d'olivine, de plagioclase et de pyroxène: prises d'essai du magma. Application à affinité tholéitique de la ride océanique émergée d'Asal (T. F. A. I.). *C.R. Acad. Sci.*, 284, 2203-2206.
- & HAVETTE A., WEISS J. & WILHELM S. 1978. Les bytownites du Rift d'Asal — I. Étude des verres basaltiques inclus dans les mégacristaux: nouvelle approche pour la connaissance de certains processus pétrogénétiques. *Bull. Minéral.*, 101, 66-76.
- & MERVOYER B. 1976. Contribution to the study of quartz crystals from Guadeloupe. *Bull. B.R.G.M., 2^e série, sect. IV*, 4, 311-324.
- DE A. 1974. Silicate liquid immiscibility in the Deccan traps and its petrogenetic significance. *Geol. Soc. Amer. Bull.*, 85, 471-474.
- DOLGOV Y.A. & SEFUGUROVA N.A. 1965. Ultramicrogas analysis methods: *Data on genetic and experimental mineralogy*. Novosibirsk.

- & — 1966. Research on the compositions of individual gas inclusions. *Materialy po geneticheskoi i eksperimentalnoi mineralogii*, 4. Novosibirsk, Akad. Nauk S.S.S.R. Sibirskoe Otdeleniye, Inst. Geologii i Geofizyki, 173—181.
- DONALDSON C.H. 1975. Calculated diffusion coefficients and the growth rate of olivine in a basalt magma. *Lithos*, 8, 163—174.
- FENN P. M. & LUTH W. O. 1973. Hazards in the interpretation of primary fluid inclusions in magmatic minerals. *Geol. Soc. Amer. Abstracts with Programs*, 5, 617.
- FENNER C. N. 1948. Immiscibility of igneous magmas. *Amer. Jour. Sci.*, 246, 465—502.
- FIENI C., BOURT-DENISE M., PELLAS P. & TOURET J. 1978. Aqueous fluid inclusions in feldspars and phosphates from Peetz (L6) chondrite (Abstract). Meteoritical Society Meeting, Sudbury, Ontario.
- FOUQUE F. & MICHEL-LEVY A. 1879. Minéraux reproduits artificiellement par voie ignée. *Bull. Soc. Fr. Minéral.*, 2, 105—113.
- & — 1881. Reproduction des basaltes et mélaphyres labradoriques, des diabases à structure ophitique (I). *Bull. Soc. Fr. Minéral.*, 4, 275—279.
- FREESTONE I. C. & HAMILTON D. L. 1977. Liquid immiscibility in K_2O - FeO - Al_2O_3 - SiO_2 , a discussion. *Nature*, 267, 559.
- GÉLINAS L., BROOKS C. & TRZCIENSKI W. E., Jr. 1976. Archean variolites — quenched immiscible liquids. *Can. Jour. Earth Sci.*, 13, 210—230.
- GREIG J. W. 1927. Immiscibility in silicate melts. *Amer. Jour. Sci.*, 13, 1—44, 133—154.
- GROVE T. L. & BENCE A. E. 1977. Experimental study pyroxene-liquid interaction in quartz-normative basalt 15597. *Proc. 8th Lunar Sci. Conf.*, 1549—1579.
- HAAPALA I. 1978. Fluid inclusion studies in apatite from the Sokli carbonatite, northeastern Finland. *Programs and Abstracts, IAGOD Fifth Symposium, Aug., 1978, Snowbird, Alta, Utah.*
- HOFMANN A. W. 1975. Diffusion of Ca and Sr in a basalt system. *Carnegie Inst. Wash. Yearb.*, 74, 183—189.
- IRVINE T. N. 1975. The silica immiscibility effect in magmas. *Carnegie Inst. Wash. Yearb.*, 74, 484—492.
- JOHNSTON D. A. 1978. *Volatiles, magma mixing, and the mechanism of eruption of Augustine volcano, Alaska*. Ph.D. dissertation, Univ. Washington, 177 pp.
- KALYUZHNYI V. A. 1961. Mineral-forming solutions from inclusions in minerals: *Materialy Komis. Mineralog. i Geokhim., Mezhdunar. Geol. Kong., Karpatobalkan. Assots.*, no. 1, p. 159—173.
- 1965. Optic and thermometric studies of glass inclusions in phenocrysts of hyalodacite of the Transcarpathians. *Akad. Nauk S.S.S.R. Doklady*, 160, 438—441.
- KIRKPATRICK R. J. 1976. Towards a kinetic model for the crystallization of magma bodies. *Jour. Geophys. Research*, 81, 2565—2571.
- KOGARKO L. N. & ROMANCHEV B. P. 1976. Complex studies of inclusions and genesis of alkaline rocks. *Abstracts of Fifth All-Union Conference on Thermobarogeochemistry*, Ufa, U.S.S.R., 20—23 Sept. 1976: Ufa, Bashkir Section, Acad. Sci. U.S.S.R., Inst. of Geol., p. 8—9 (in Russian; translation in *Fluid Inclusion Research — Proceedings of COFFI*, 9, 68—69).
- RYABCHIKOV I. D. & SORENSEN H. 1974. Liquid fractionation. Chapt. VI, 5 in the *Alkaline Rocks*. H. SORENSEN (Ed.). John Wiley; New York.
- KONNERUP-MADSEN J., LARSEN E. & ROSE HANSEN J. 1979. Hydrocarbon-rich fluid inclusions in minerals from the alkaline Ilimaussaq intrusion, South Greenland. *Bull. Minéral.*, 102 642—653.
- KOZŁOWSKI A. & KARWOWSKI L. 1973. Hydrated salt melt as mineral-forming medium of high-temperature mineral associations from Alam Kuh (Iran): *Abstracts of papers at Fourth Regional Conference on Thermobarogeochemistry of Mineral-Forming Processes*, 24—30 Sept. 1973: Rostov, Rostov Univ. Press. (in Russian; translation in *Fluid Inclusion Research — Proceedings of COFFI*, 7, 113—114).
- LARSON L. T., MILLER J. D., NADEAU J. E. & ROEDDER E. 1973. Two sources of error in low temperature inclusion homogenization determination, and corrections on published temperatures for the East Tennessee and Laisvall deposits. *Econ. Geol.*, 68, 113—116.

- LEMMLEIN G.G. 1930. Corrosion and regeneration of quartz phenocrysts in quartz porphyries. *Akad. Nauk S.S.S.R., Doklady, ser. A.*, 13, 341—344.
- LIPIN B.R. 1976. The origin of Fra Mauro basalts. *Lunar Sci.*, VIII, 495—497. *The Lunar Sci. Institute; Houston.*
- LONGHI J., WALKER D. & HAYS J. F. 1978. The distribution of Fe and Mg between olivine and lunar basaltic liquids. *Geochim. Cosmochim. Acta*, 42, 1545—1558.
- McBIRNEY A.R. 1975. Differentiation of the Skaergaard intrusion. *Nature*, 253, 601—604.
- MOORE J.G., BATCHELDER J.N. & CUNNINGHAM C.G. 1977. CO₂-filled vesicles in mid-ocean basalt. *Jour. Volcanol. and Geothermal Res.*, 2, 309—327.
- & CALK L. 1971. Sulfide spherules in vesicles of dredged pillow basalt. *Amer. Mineralogist*, 56 476—488.
- MURCK B.W., BURRUS R. C. & HOLLISTER L. S. 1978. Phase equilibria in fluid inclusions in ultramafic xenoliths. *Amer. Mineralogist*, 63, 40—46.
- MYSEN B.O., EGGLEER D.H., SEITZ M. & HOLLOWAY J.R. 1976. Carbon dioxide in silicate melts and crystals, Part I. Solubility measurements. *Amer. Jour Sci.*, 276, 455—479.
- NAKAMURA Y. 1974. The system Fe₂SiO₄-KAlSi₂O₆-SiO₂ at 15 kbar. *Carnegie Inst. Wash. Yearb.*, 73, 352—354.
- NALDRET A.J., HOFFMAN E.L., GREEN A.H. & NALDRETT S.R. 1979. The composition of Ni-sulfide ores: constraints on ore genesis. *Bull. Minéral.*, 102, 455—462.
- NASH J.T. 1976. Fluid-inclusion petrology — data from porphyry copper deposits and applications to exploration. *U.S. Geol. Survey Prof. Paper*, 907 D, 1—16.
- NASLUND H.R. 1976. Liquid immiscibility in the system KAlSi₃O₈-NaAlSi₃O₈-FeO-Fe₂O₃-SiO₂ and its application to natural magmas. *Carnegie Inst. Wash. Yearb.*, 75, 592—597.
- PHILPOTTS A.R. 1971. Immiscibility between feldspathic and gabbroic magmas. *Nature Phys. Sci.*, 229, 107—109.
- 1972. Density, surface tension and viscosity of the immiscible phase in a basic, alkaline magma. *Lithos*, 5, 1—18.
- 1976. Silicate liquid immiscibility: its probable extent and petrogenetic significance. *Amer. Jour Sci.*, 276, 1147—1177.
- 1977. Archean variolites — quenched immiscible liquids: a discussion. *Can. Jour Earth Sci.*, 14, 139—144.
- 1978. Textural evidence for liquid immiscibility in tholeiites. *Mineral. Mag.*, 42, 417—425.
- PINEAU F., JAVOY M. & BOTTINGA Y. 1976. ¹³C/¹²C ratios of rocks and inclusions in popping rocks of the Mid-Atlantic Ridge and their bearing on the problem of isotopic composition of deepseated carbon. *Earth Planet. Sci. Lett.*, 29 (2), 413—421.
- POTTER A.P. 1975. *Silicate liquid inclusions in olivine crystals from Kilauea, Hawaii*. M. Sc. thesis, Queen's Univ., Kingston, Ont., Canada.
- RANKIN A.H. & LeBAS M.J. 1974. Liquid immiscibility between silicate and carbonate melts in naturally occurring ijolite magma. *Nature*, 250, 206—209.
- ROEDDER E. 1951. Low temperature liquid immiscibility in the system K₂O-FeO-Al₂O₃-SiO₂. *Amer. Mineralogist*, 36, 282—286.
- 1952. A reconnaissance of liquidus relations in the system K₂O 2SiO₂-FeO-SiO₂. *Amer Jour Sci. (Bowen Vol)*, 250A, 435—456.
- 1965. Liquid CO₂ inclusions in olivine-bearing nodules and phenocrysts from basalts. *Amer. Mineralogist*, 50, 1746—1782.
- (Ed) 1968—1979. *Fluid Inclusion Research — Proceedings of COFFI*. Vol. 1 (1968) through vol. 12 (1979). *Univ. of Mich. Press; Ann Arbor, Michigan.*
- 1970. Laboratory studies of inclusions in the minerals of Ascension Island granitic blocks, and their petrologic significance. *Problems in petrology and genetic mineralogy*. Sobolev's Volume II. Moscow, "Nauka" Press, 247—258 (in Russian; translation in *Fluid Inclusion Research — Proceedings of COFFI*, v. 5, 1972, p. 129—138).
- 1971a. Metastability in fluid inclusions. *Soc. Mining Geol. Japan, Spec. Issue* 3, 327—334. (Proc. IMA-IAGOD Meeting, '70, IAGOD Vol.).

- 1971b. Natural and laboratory crystallization of lunar glasses from Apollo 11. *Mineral. Soc. Japan, Spec. Pap.*, 1, 5—12 (Proc. IMA-IAIGOD Meeting, '70, IMA Vol.).
- 1971c. Fluid inclusion studies on the porphyry-type ore deposits at Bingham, Utah, Butte, Montana, and Climax, Colorado. *Econ. Geol.*, 66, 98—120.
- 1972. The composition of fluid inclusions. *Data of Geochemistry*, Sixth Edition, M. Fleischer (Ed.), U.S. Geol. Survey Prof. Paper, 440 JJ, 1—164.
- 1973. Fluid inclusions from the fluorite deposits associated with carbonatite at Amba Dongar, India, and Okorusu, South West Africa. *Institution of Mining and Metallurgy Trans., Sect. B.*, 82, B35—B39.
- 1976. Petrologic data from experimental studies on crystallized silicate melt and other inclusions in lunar and Hawaiian olivine. *Amer. Mineralogist*, 61, 684—690.
- 1977. Liquid immiscibility in K_2O -FeO- Al_2O_3 - SiO_2 , a discussion. *Nature*, 267, 558—559.
- 1978. Silicate liquid immiscibility in magmas and in the system K_2O -FeO- Al_2O_3 - SiO_2 : an example of serendipity. *Geochim. Cosmochim. Acta*, 42, 1597—1617.
- 1979a. Silicate liquid immiscibility in magmas. *The evolution of the igneous rocks; Fiftieth anniversary perspectives*, 15—57. Princeton Univ. Press; Princeton.
- 1979b. Origin and significance of magmatic inclusions. *Bull. Mineral.*, 102, 487—510.
- & BELKIN H. E. 1979. Application of studies of fluid inclusions in Permian Salado salt, New Mexico, to problems of siting the Waste Isolation Pilot Plant. *Scientific basis for nuclear waste management*, vol. 1, G. J. McCarthy (Ed.), Plenum Pub. Corp., 313—321.
- COOMBS D. S. 1967. Immiscibility in granitic melts, indicated by fluid inclusions in ejected granitic blocks from Ascension Island. *Jour. Petrol.*, 8 (3), 417—451.
- & WEIBLEN P. W. Lunar petrology of silicate melt inclusions, Apollo 11 rocks, Proc. Apollo 11 rocks, Proc. Apollo 11 Lunar Sci. Conf., *Geochim. Acta, Suppl.*, 1, 801—837.
- & — 1971. Petrology of silicate melt inclusions, Apollo 11 and Apollo 12 and terrestrial equivalents. *Proc. Lunar Science Conf.*, 2nd, 1, Cambridge, Mass., MIT Press, 507—528.
- & — 1972. Petrographic features and petrologic significance of melt inclusions in Apollo 14 and 15 rocks. *Proc. Lunar Science Conf.*, 3rd, 1, Cambridge, Mass., MIT Press, 251—279.
- & — 1975. Anomalous low-K silicate melt inclusions in ilmenite from Apollo 17 basalts. *Proc. Lunar Science Conf.*, 6th, 147—164.
- & — 1977a. Compositional variation in late-stage differentiates in mare lavas, as indicated by silicate melt inclusions, *Proc. Lunar Science Conf.*, 8th, 1767—1783.
- & — 1977b. High-silica inclusions in olivine of Luna-24 samples. *Geophys. Research Letts.*, 4 (10), 485—488.
- & — 1978. Melt inclusions in Luna-24 soil fragments, In: MERRILL R. B. & PAPIKE J. J. (Eds), *Mare Crisium: The view from Luna-24*, New York, Pergamon Press, pp. 495—522.
- & EMSLIE R. F. 1970. Olivine-liquid equilibrium. *Contrib. Mineral. Petrol.*, 29, 275—289.
- ROSENBUSCH H. 1887. *Mikroskopische Physiographie der Mineralien und Gestein*, Band 2. Schweizerbart'sche Verlagshandlung.
- RYERSON F. J. & HESS P. C. 1975. The partitioning of trace elements between immiscible silicate melts. *EOS, Trans. Am. Geophys. Union*, 56, 470.
- SCHAIRER J. F. & YAGI K. 1952. The system FeO- Al_2O_3 - SiO_2 . *Amer. Jour. Sci.* (Bower Vol.), 250A, 471—512.
- SEWARD T. P., III, UELMANN D. R. & TURNBULL D. 1968. Phase separation in the system BaO- SiO_2 . *Jour. Amer. Ceram. Soc.*, 51, 278—285.
- SOBOLEV V. S., BAKUMENKO I. T. & KOSTYUK V. P. 1976. The possibility of using melt inclusions for petrologic conclusions. *Transactions of Akad. Nauk S.S.S.R., Siberian Branch. Geol. i Geofiz.*, 1976, no. 5, 146—149 (in Russian; translated in *Fluid Inclusion Research — Proceedings of COFFI*, 9, 178—181).
- & KOSTYUK V. P., eds. 1975. *Magmatic crystallization based on a study of melt inclusions: Novosibirsk, "Nauka" Press* (in Russian; translated in part in *Fluid Inclusion Research*, 9, 182—253).

- SOMMER M.A. 1977. Volatiles H_2O , CO_2 and CO in silicate melt inclusions in quartz phenocrysts from the rhyolitic Bandelier air-fall and ash-flow, New Mexico. *Jour Geol.*, **85**, 423—432.
- SORBY H. C. 1858. On the microscopic structure of crystals, indicating the origin of minerals and rocks. *Geol. Soc. London Quart. Jour.*, **14** (1), 453—500.
- SWITZER G.S. 1975. Composition of three glass phases present in an Apollo 15 basalt fragment. *Mineral. Sci. Invest.*, 1972—1973, *Smithsonian Contrib. Earth Sci.* **14**, 25—30.
- TAKAHASHI E. 1978. Partitioning of Ni^{2+} , Co^{2+} , Fe^{2+} , Mn^{2+} and Mg^{2+} between olivine and silicate melts; compositional dependence of partition coefficient; *Geochim. Cosmochim. Acta*, **42**, 1829—1844.
- TAKENOUCI S. 1972. Glass inclusions in quartz of volcanic rocks from mining areas. *Internat. Geol. Cong.*, 24th, Abstracts, Section 10, *Geochemistry*, p. 325.
- & IMAI H. 1975. Glass and fluid inclusions in acidic igneous rocks from some mining areas in Japan. *Econ. Geol.*, **70**, 750—769.
- & KATSURA T. 1972. Volcanic glass inclusions in rhyolite and tuff from the Chitose mine, Hokkaido. *Mining Geol.*, **22** (5), 383—391.
- TUTTLE O.F. 1952. Origin of the contrasting mineralogy of extrusive and plutonic calcic rocks. *Jour Geol.*, **60**, 107—124.
- VISSER W. & KOSTER VAN GROSS A. F. 1976. Liquid immiscibility in K_2O - FeO - Al_2O_3 - SiO_2 . *Nature* **264**, 426—427.
- & — 1977. Liquid immiscibility in K_2O - FeO - Al_2O_3 - SiO_2 , a reply. *Nature*, **267**, 560.
- VOGEL T. A. & WILBAND J. T. 1978. Coexisting acidic and basic melt: geochemistry of a composite dike. *Jour Geol.*, **86**, 353—372.
- VOGELANG H. 1867. Philosophie der Geologie und mikroskopische Gesteinsstudien. *Cohen*; Bonn.
- VOZNYAK D.K. & KALYUZHNYI V.A. 1974a. Decrepitated inclusions and their significance for reconstruction of P-T conditions of mineral formation (illustrated by quartz from pegmatites from Volhyn). *Typomorphism of Ukrainian quartz*, edited by Y.K. LAZARENKO, Acad. Sci. Ukr. S.S.R.; Kiev, Naukova Dumka Pub. House, pp. 18—24 (in Russian; translation in *Fluid Inclusion Research — Proceedings of COFFI*, **7**, 1974, p. 272—275).
- & — 1974b. Change of shape of inclusions in minerals of variable composition and its effect on the composition of the parent solution isolated in vacuoles. *Akad. Nauk S.S.S.R., Doklady*, **212** (5), 1192—1195.
- WAGER L.R. & DEER W.A. 1939. Geological investigations in East Greenland. Part III. The petrology of the Skaergard intrusion, Kangerdlugssuaq, East Part III. The petrology of the Skaergard intrusion, Kangerdlugssuaq, East
- WALKER D., KIRKPATRICK R.J., LONGHI J. & HAYS J.F. 1976. Crystallization history of lunar basalt sample 12002: Phase equilibria and cooling-rate studies. *Geol. Soc. Amer. Bull.*, **87**, 646—656.
- WATSON E.B. 1976a. Glass inclusions as samples of early magmatic liquid: determinative method and application to a South Atlantic basalt. *Jour Volcan. Geothermal Research*, **1**, 73—84.
- 1976b. Two liquid partition coefficients: experimental data and geochemical implications. *Contrib. Mineral. Petrol.*, **56**, 119—134
- & NASLUND H.R. 1977. The effect of pressure on liquid immiscibility in the system K_2O - FeO - Al_2O_3 - SiO_2 - CO_2 . *Carnegie Inst. Wash. Yearb.*, **76** 410—414. *Inst. Wash. Yearb.*, **76** 410—414.
- WEIBLEN P.W. & ROEDDER E. 1973. Petrology of melt inclusions in Apollo samples 15598 and 62295, and of clasts in 67915 and several lunar soils. *Proc. Fourth Sci. Conf., Geochim. Cosmochim. Acta, Suppl.*, **4**, Vol. 1 pp. 681—703. Pergamon Press.
- & — 1976. Compositional interrelationships of mare basalts from bulk chemical and melt inclusion studies. *Proc. Lunar. Science Conf.*, 7th, 1449—1466.
- WRIGHT T.L. & OKAMURA R.T. 1977. Cooling and crystallization of tholeiitic basalt, 1965 Makaopuhi lava lake, Hawaii, U.S. *Geol. Survey Prof. Paper*, **1004**.
- WYLLIE P.J. & HUANG W.L. 1976. High CO_2 solubilities in mantle magmas. *Geology*, **4**, 21—24.

- YEATS R. S. & MATHEZ E. A. 1976. Decorated vesicles in deep-sea basalt glass, *Eastern Pacific Jour. Geophys. Res.*, 81, 4277—4284.
- ZIRKEL F. 1866. Über die mikroskopische Zusammensetzung und Structur der diessjährigen Laven von Nea-Kammeni bei Santorin. *Neues Jb. Mineral.*, 769—787.
- 1873. Die mikroskopische Beschaffenheit der Mineralien und Gesteine. *Wilhelm Engelmann*; Leipzig.

E. ROEDDER

**WYSTĘPOWANIE I ZNACZENIE INKLUZJI MAGMOWYCH
A NIEMIESZALNOŚĆ STOPÓW MAGMOWYCH**

(Streszczenie)

Praca przedstawia wyniki badań inkluzji magmowych, zwłaszcza wypełnionych stopem krzemianowym (pl. 1—4), w próbkach minerałów ziemskich i pozaziemskich oraz ocenę ich petrologicznego znaczenia. Zwykle inkluzje, które tworzą się podczas magmowej dyferencjacji, zostały opisane z uwzględnieniem mechanizmu ich tworzenia oraz zmian w inkluzji po jej izolacji (fig. 1—6). Szczególną uwagę poświęcono niemieszalności stopów krzemianowych i interpretacji inkluzji, które powstały dzięki temu zjawisku (fig. 11—12). Włączona tu została także dyskusja o niemieszalności stopów krzemiankowych w syntetycznym systemie $K_2O-FeO-Al_2O_3-SiO_2$ (fig. 7—10) oraz w księżycowych i ziemskich bazaltach.

PLATE 1

- 1 — Scanning electron microscope photograph of a quartz phenocryst from an ignimbrite from the Valley of Ten Thousand Smokes, Katmai, Alaska, showing reentrants in the centers of the faces (from Clochiatti & Mervoyer 1976)
- 2 — Section parallel to the *c* axis through the center of a quartz phenocryst from a liparite, showing skeletal growth; the external surface of this crystal would probably have looked like that seen in Fig. 1 (from Lemmlein 1930)
- 3 — Quartz phenocryst from welded tuff in the Valles Mountains, New Mexico, showing a deep reentrant along the *c* axis that has not quite been sealed off
- 4 — Leucite phenocryst in leucite basalt from Capo di Bove, Rome, Italy (USNM rock 929), showing shell of 24 melt inclusions, one for each face of a tetrahedron; three of the six in the center and several around the outside are deep in the section and hence out of focus (see also plate 4E in Roedder & Coombs 1967)
- 5 — Olivine phenocryst from 1965 Makaopuhi basalt lava lake, Hawaii (collected at 1,135°C), containing two large primary melt inclusions, trapped by early skeletal growth (Roedder & Weiblen 1971)
- 6 — Plagioclase phenocryst from Chile, showing zone of small melt inclusions near edge (partially crossed polarizers)
- 7 — Melt inclusion in olivine trapped as a result of enclosure of a solid inclusion of spinel (black); Kilauea Iki basalt lava lake crust, from a depth of 0.7 feet (21 cm) (Roedder & Weiblen 1971)
- 8 — Olivine crystal from South Point, Hawaii (ER 63--79), showing an internal layer or "ghost" of opaque solid spinel inclusions on a former growth surface; many of these have resulted in trapping of melt inclusions (Roedder 1965)
- 9 — Group of inclusions in which only the five larger ones have nucleated vapor bubbles; the rest remain as metastable stretched fluid; although these are aqueous inclusions in salt from Mexico (Roedder & Belkin 1979), silicate melt inclusions show similar phenomena

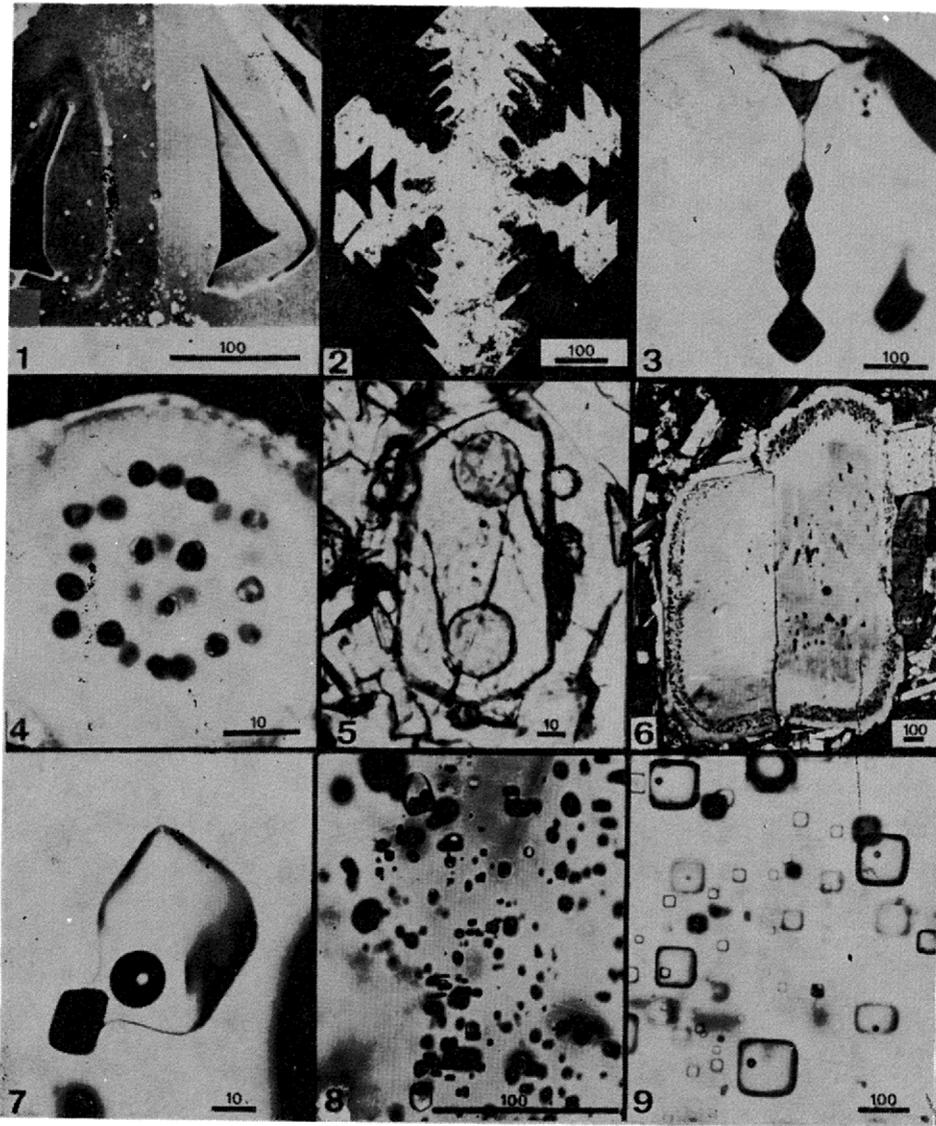


PLATE 2

- 1 — Large, clear, glassy, primary, homogeneous melt inclusions in quartz phenocryst from air-fall pumice from Sandia Canyon, New Mexico (Sommer 1977)
- 2 — Small melt inclusion in olivine from prehistoric Mākaopuhi lava lake, Hawaii, sampled at a depth of 150 feet (46 m), in which both the epitaxial ilmenite plate and the tiny globule (at top, above bubble; see *arrows*) appear to be embedded in the surrounding host (Roedder 1976)
- 3 — Small melt inclusion in olivine from lunar basalt 12018,83, containing only glass, a sulfide melt globule, and an oversize vapor bubble
- 4 — Melt inclusion in the center of a small olivine grain (lighter colored) from lunar basalt 10071,32 containing glass, ilmenite, and a sulfide globule
- 5 — Typical, large, crystallized melt inclusion in olivine from lunar basalt 12035,23, with epitaxial ilmenite plate (reflected and transmitted light (Weiblen & Roedder 1976)
- 6 — Crystallized melt inclusion in olivine from lunar basalt 12036,8 (reflected light (Roedder & Weiblen 1972)
- 7 — Basaltic glass inclusion in an olivine nodule from the 1801 flow of Kaupulehu, Hawaii, containing multiple vapor (or CO₂?) bubbles
- 8 — Glass inclusion in olivine (∞ Fo 80) from Pavlof, heated to 1,100°C for 26 h, showing dark halo that formed (Photograph by J. Sans; courtesy A. T. Anderson, Jr)
- 9 — Partly decrepitated inclusion of melt and dense CO₂ in an olivine phenocryst (xenocryst?) in olivine leucite nephelinite, Mosenberg, Westeifel, Germany (ER 64-123; Roedder 1965)

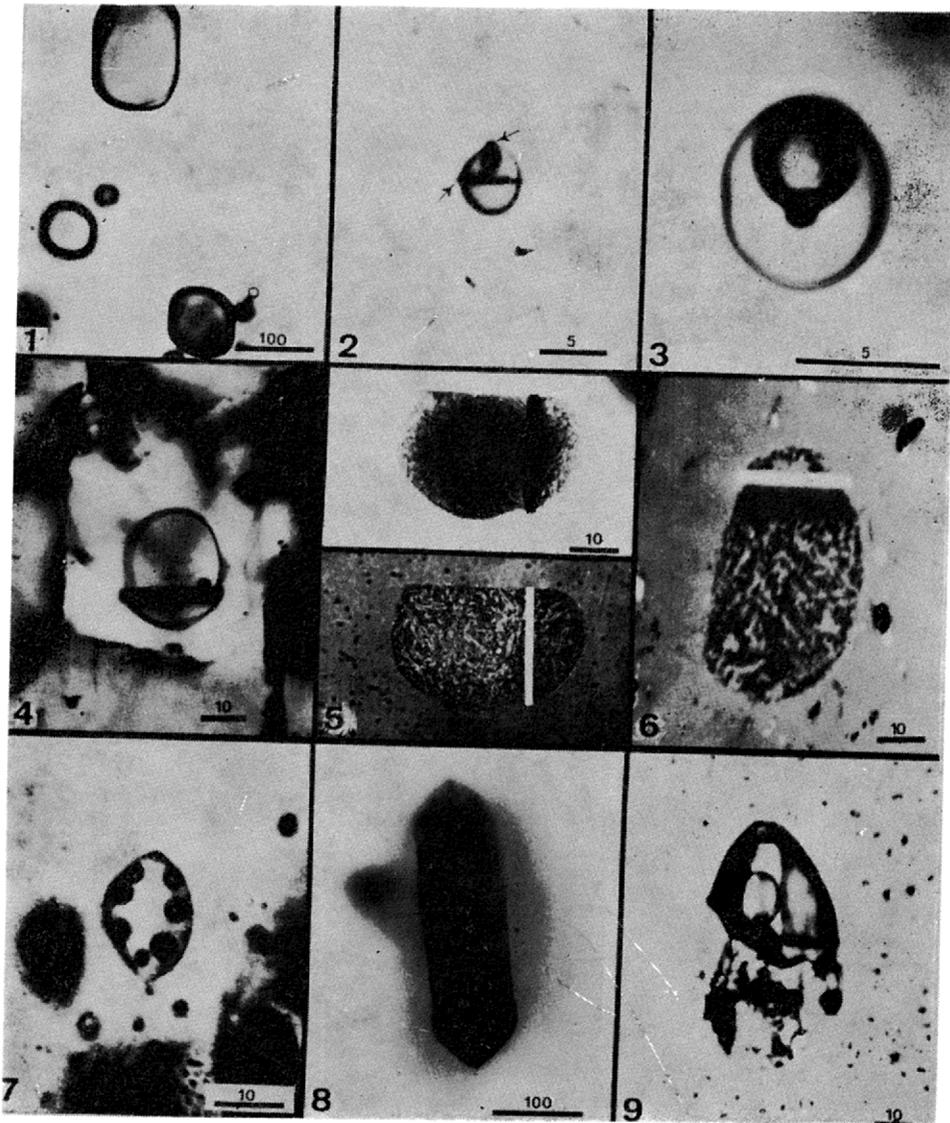


PLATE 3

- 1 — Two adjacent inclusions in the same grain of olivine from lunar sample 15555,34 in which different phase assemblages have nucleated (Roedder & Weiblen 1972)
- 2 — Melt inclusion in olivine from the prehistoric Makaopuhi lava lake in Hawaii that originally had epitaxial daughter plates of ilmenite and plagioclase; it was then homogenized in the laboratory and cooled from 1,120°C to 1,020°C over an 11-day period (Roedder 1971); this yielded a sulfide globule and several new epitaxial plates of ilmenite (*arrows*)
- 3 — Crystal fragment from an Icelandic tuff, mounted in oil, containing many silicate melt inclusions; where these have been cut by a later fracture (*arrows*; now healed), they have expelled the melt and formed a large dark vapor bubble
- 4 — Olivine from the 1801 flow of Hualalai, Kaupulehu, Hawaii (ER 63-33a) showing negative crystal cavities lined with basaltic glass (*arrows*) and a large globule of liquid CO₂ (L) and gaseous CO₂ (V); photographed at room temperature
- 5 — Isolated, presumably primary inclusions of glass (G) with a small shrinkage bubble and an opaque daughter phase, and two liquid CO₂ inclusions (L) showing characteristic dark borders and large, faint, rapidly moving central vapor bubbles; the inclusion in the upper left shows all three phases: CO₂ in it homogenizes in the gas phase at 30.91 ± 0.02°C; plane of secondary O₂ inclusions is visible along right edge; olivine from the 1801 flow of Hualalai, Kaupulehu, Hawaii (Roedder 1965)
- 6 — Immiscible globule of metallic iron (I), trapped in a growing olivine crystal from the Murray carbonaceous chondrite, that also resulted in the trapping of silicate melt (*arrows*) and a bubble (V) that probably represents shrinkage on crystallization of the iron globule as well as the shrinkage of the silicate melt
- 7 — Primary sulfide melt inclusions in a fayalite grain from Soviet Luna-24 soil sample 24077,53, in reflected light; the inclusions are actually in the form of cylindrical rods (Roedder & Weiblen 1978)
- 8 — Rodlike inclusions of glass of potash granite composition embedded in a single crystal of pyroxferroite crystal from lunar sample 1203,9
- 9 — Planar group of primary glass inclusions of potash granite composition embedded in a pyroxferroite crystal from lunar sample 12063,9; the bottoms of the "teeth" start at a plane that presumably marks the sudden onset of immiscibility in the melt; the outside of the pyroxferroite crystal is at the top of the row of "teeth" (Roedder & Weiblen 1971)

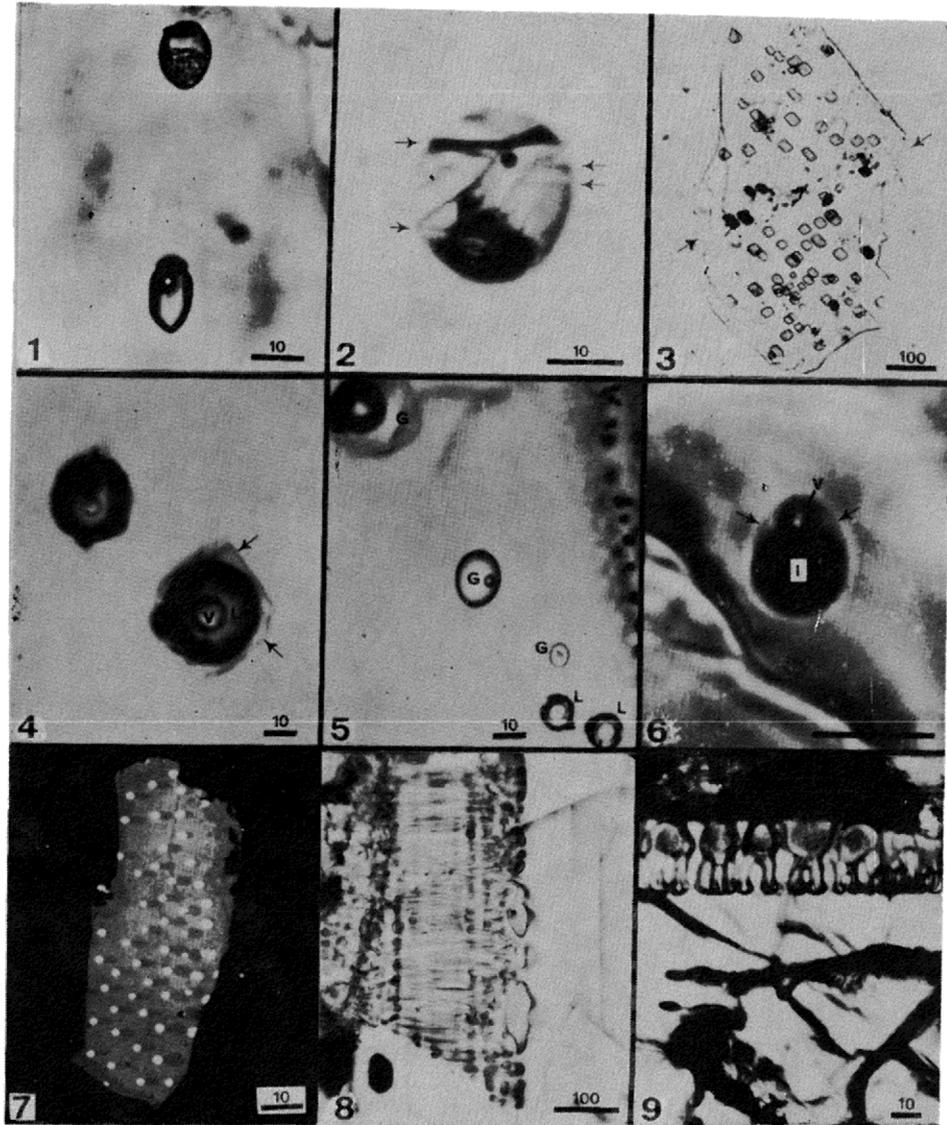


PLATE 4

- 1 — Primary inclusion of immiscible high-silica (*light*) and high-iron (*dark*) melts, now glasses, in plagioclase crystal in lunar sample 12057 (Roedder & Weiblen 1971)
- 2 — Completely isotropic, glassy high-K melt inclusion in ilmenite grain 75075,88,P8: the inclusion is viewed in transmitted plain light plus a small amount of reflected plain light to show upper surface of ilmenite; note shrinkage bubble (V) in glass
- 3 — Silicate melt inclusion, now clear, colorless, uniform glass, in an unshocked, apparently unzoned single crystal of Fe_{78} olivine from Luna-24 soil sample 2409,50-2; this inclusion does not reach the surface, but another similar glass inclusion in this grain contains 87% SiO_2 (Roedder & Weiblen 1978)
- 4 — Three of six large inclusions, all in same phenocryst of olivine, from 150 feet (46 m), deep in the prehistoric Makaopuhi lava lake, Hawaii; they contain epitaxial ilmenite (black bars) and plagioclase (light zones adjacent and parallel to the ilmenite) in feathery pyroxene (and plagioclase?); arrows mark two sulfide globules ((Roedder 1976)
- 5 — Immiscible silicate melts in basalt collected at 1020°C from the 1965 Makaopuhi lava lake, Hawaii: dark globules are high-Fe glass embedded in high-Si glass; the two glasses lie between plagioclase crystals (p)
- 6 — Globules (∞ 4 mm) of syenite composition (now crystalline) in porphyritic camptonite from a dyke in the Monteregian alkalic province, Quebec (Philpotts 1971, Text-fig. 1A)

