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# Silicate-melt inclusions in magmatic rocks: applications to petrology

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## Abstract

Silicate-melt inclusions in igneous rocks provide important information on the composition and evolution of magmatic systems. Such inclusions represent accidentally trapped silicate melt ( $\pm$  immiscible  $H_2O$  and/or  $CO_2$  fluids) that allow one to follow the evolution of magmas through snapshots, corresponding to specific evolution steps. This information is available on condition that they remained isolated from the enclosing magma after their entrapment. The following steps of investigation are discussed: (a) detailed petrographic studies to characterise silicate-melt inclusion primary characters and posttrapping evolution, including melt crystallisation; (b) high temperature studies to rehomogenise the inclusion content and select chemically representative inclusions: chemical compositions should be compared to relevant phase diagrams.

Silicate-melt inclusion studies allow us to concentrate on specific topics; inclusion studies in early crystallising phases allow the characterisation of primary magmas, while in more differentiated rocks, they unravel the subsequent chemical evolution. The distribution of volatile species (i.e.,  $H_2O$ ,  $CO_2$ , S, Cl) in inclusion glass can provide information on the degassing processes and on recycling of subducted material. In intrusive rocks, silicate melt inclusions may preserve direct evidence of magmatic stage evolution (e.g., immiscibility phenomena). Melt inclusions in mantle xenoliths indicate that high-silica melts can coexist with mantle peridotites and give information on the presence of carbonate melt within the upper mantle. Thus, combining silicate-melt inclusion data with conventional petrological and geochemical information and experimental petrology can increase our ability to model magmatic processes. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Igneous petrology; Silicate-melt inclusions; Fluid phase; Immiscibility processes; Primary magma

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## 1. Introduction

Silicate-melt inclusions are small droplets of silicate melt entrapped in different minerals during their growth (Fig. 1) (Sorby, 1858; Vogelsang, 1867; De-

icha, 1955). For this reason, they provide a unique possibility of reconstructing the chemical composition of a magma (silicate melt + volatiles) at a specific stage of its evolution, from its formation at mantle depth through its ascent and release at the surface. This depends on the assumption that inclusions behave as closed (= isolated) systems after their formation; i.e., after trapping of silicate melt in the microcavity, these microsystems closed and

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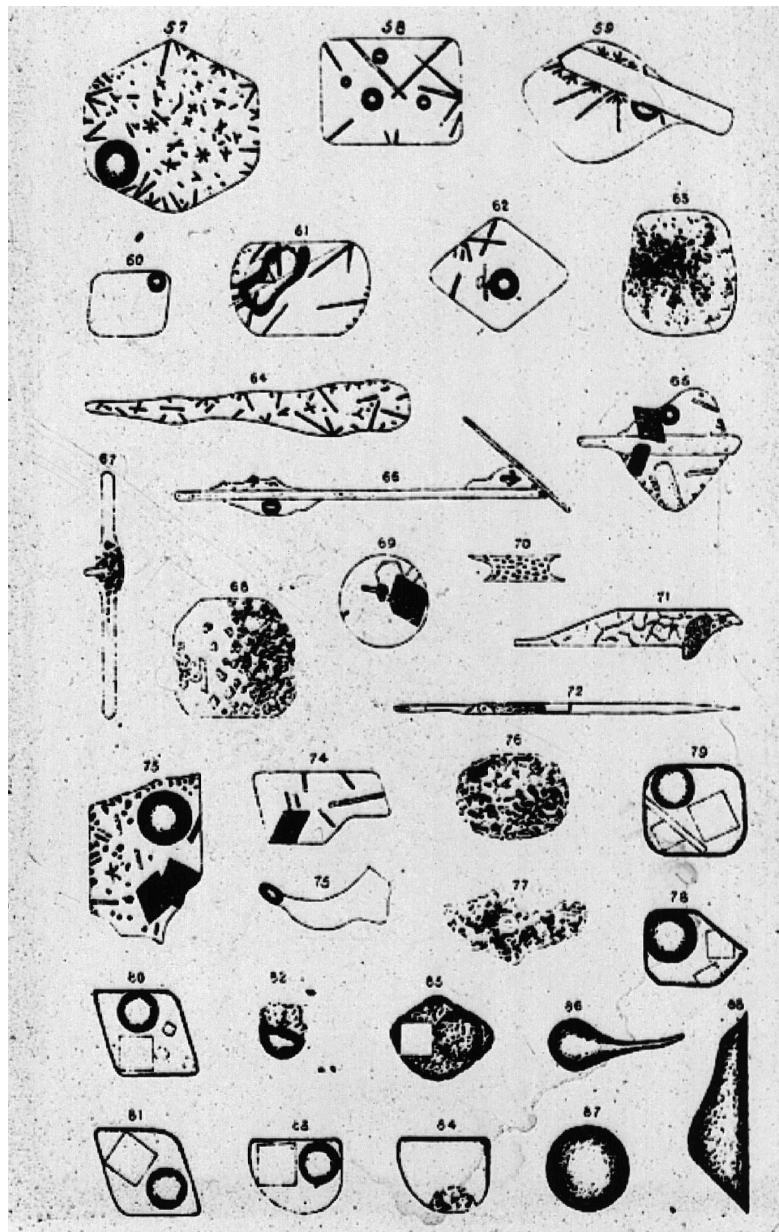


Fig. 1. Photograph showing the original drawings of silicate-melt inclusions in effusive and intrusive rocks by Sorby (1858). Silicate-melt inclusions were mainly studied in phenocrysts from lavas of the Vesuvius and in quartz grains in granites from Cornwall (e.g. St. Austell).

evolved independently from the host minerals and the enclosing lava.

A number of previous reviews on silicate-melt inclusions concentrate on their general characteristics. In particular, the reader is referred to the work of Clochiatti (1975), Sobolev and Kostyuk (1975),

and Roedder (1984) on silicate-melt inclusions, their formation mechanisms, and the study techniques. More recently, Roedder (1992) discussed the information, which melt inclusions provide on magmatic immiscibility processes. Touret and Frezzotti (1993) gave a summary of study techniques of silicate-melt

inclusions in granitic rocks and the information they can provide in plutonic environments. The most recent reviews by Lowenstern (1995) and Sobolev (1996), which focus on the applications of silicate-melt inclusions for the study of magmatic volatiles and on the formation mechanisms of silicate-melt inclusions, give exhaustive reviews of updated study techniques.

The purpose of this paper is to introduce igneous petrologists to the study of silicate-melt inclusions in volcanic and plutonic environments, and to illustrate how melt inclusions can be used in igneous petrology studies. The first part focuses on the significance of melt inclusions and on the information that can be obtained by petrographic and microthermometric analyses. The second part concentrates on the most recent literature devoted to the application of silicate-melt inclusion studies in igneous petrology, including (a) the evolution of the magma, especially the identification of primary liquids; (b) the characterisation of volatile evolution in igneous systems; and (c) the understanding of chemical transfer in the lithosphere (e.g., metasomatism).

## 2. Silicate-melt inclusions: some basic principles

### 2.1. General characteristics of silicate-melt inclusions

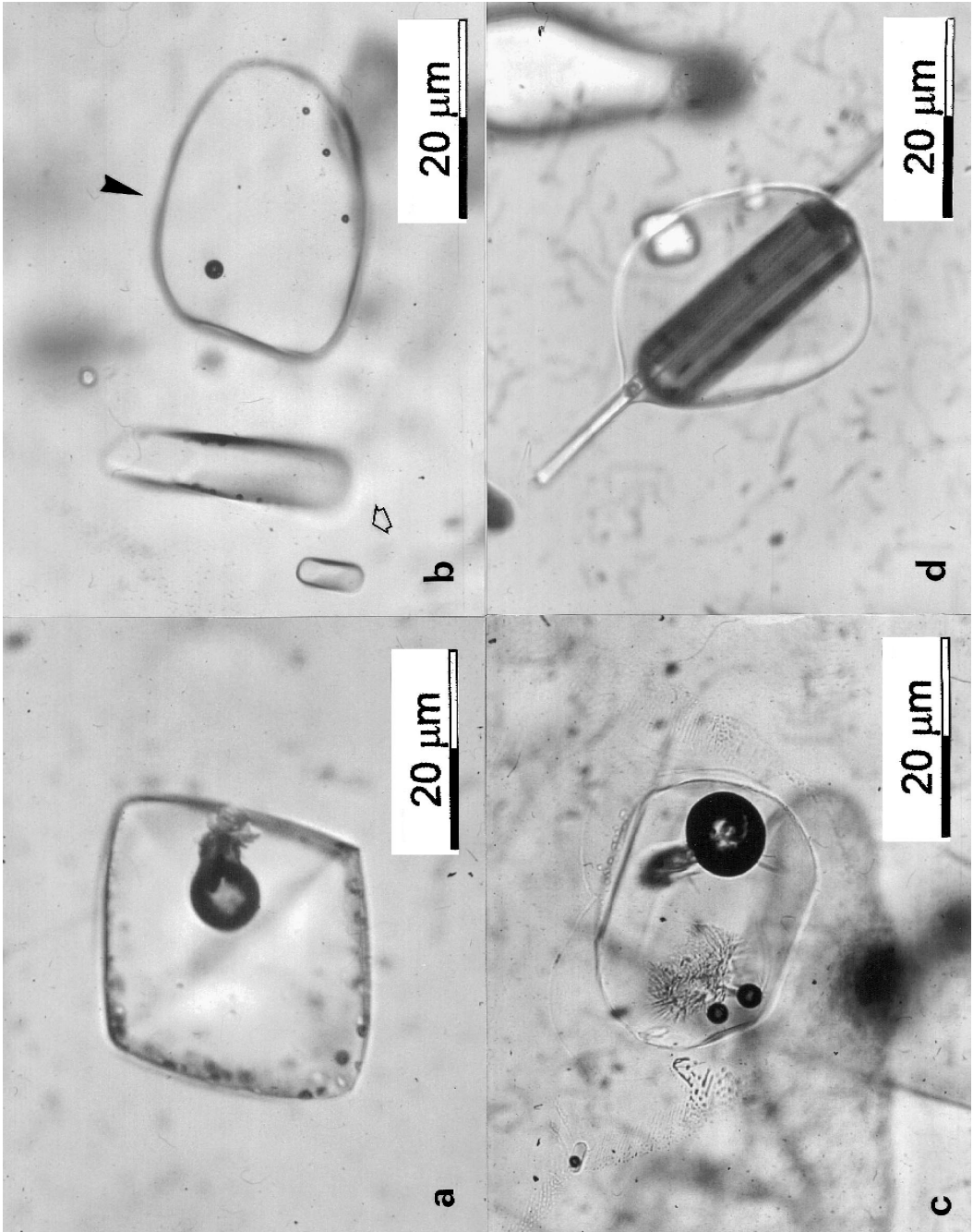
In volcanic rocks, silicate-melt inclusions consist of glass  $\pm$  one or more gas bubbles  $\pm$  daughter mineral phases (Fig. 2a). The size of the bubble is a first important observation since its relative size will depend mainly on cooling behaviour, melt composition and volatile content of the inclusion. In volatile-poor melts, a single shrinkage bubble (near vacuum, < 0.5 vol.%; Fig. 2a) is observed, although some inclusions contain only glass (Fig. 2b, open arrow). In volatile-rich melts, fluids under pressure may be present within the bubble. These, however, may be hard to discover; the density of a fluid phase depends on the pressure at time of trapping and low-density fluids are difficult to detect. As temperatures of trapped melts are high (800–1200°C), fluid densities will be significant only at elevated pressures > 0.1 kbar ( $V = nRT/P$ ). An alternative way to identify the presence of volatiles in the bubble in a silicate-

melt inclusion is to estimate the percentage by volume of the gas bubble in the glass. A volatile-rich magma will yield to larger bubbles at room temperature (vacuum + gas; compare Fig. 2b and c).

Most silicate-melt inclusions are primary since they are trapped during the growth of the surrounding host crystals; secondary melt inclusions forming trails within single crystals are only occasionally observed (i.e., in mantle xenoliths). Primary silicate-melt inclusions form under a number of conditions related to irregularities in crystal growth, including defects of growth due to different processes (i.e., stagnation, undercooling, kinking), wetting by an immiscible fluid phase, or trapping of solid inclusions (Fig. 2d) (see Sobolev and Kostyuk, 1975; Roedder, 1984).

In quartz crystals, irregularities of growth (i.e., skeletal growth and corrosion gulfs) may control the distribution of inclusions within a single crystal (Fig. 3a and b). Fig. 3b shows the preferential distribution of melt inclusions in the {1120} faces of a  $\beta$ -quartz crystal. Olivine and pyroxene crystals show a tendency to trap inclusions in a more random way (Fig. 3c); whereas in plagioclase, silicate-melt inclusions line the growth zones of the crystal (Fig. 3d). Nakamura and Shimakita (1984) and Bacon et al. (1992) have shown how silicate-melt inclusions are trapped along resorbed nuclei (patchy zoning) or at sharp compositional boundaries in zoned crystals. Thus, a variation in  $T$  and/or  $X_{\text{H}_2\text{O}}$  or mixing processes are to be taken in account for the formation of melt inclusions in plagioclase.

The resulting inclusion shapes vary, but very often inclusions have smooth morphologies, following the symmetry of host-mineral phases (Fig. 3c, d). Similar to that observed in fluid inclusions, regularly shaped inclusions (i.e., negative crystals; Fig. 2a) result from reequilibration processes between host mineral and the inclusions (i.e., lowest surface energy, see also TEM investigations, Viti and Frezzotti, 2001). A rounded melt inclusion may reequilibrate to a negative-crystal shape if held at 800°C for 50 days (Clocchiatti, 1975). Manley (1996) illustrated how the shapes of silicate-melt inclusions in quartz crystals from the Badlands lava flows of Idaho change progressively from irregular in crystals formed just before eruption, to mature negative-crystal shapes in quartz phenocrysts that nucleated



earlier. Solution and reprecipitation of the host mineral on the inclusion walls leading to negative-crystal morphology is not considered to modify the melt composition, which, therefore, can be considered representative of the trapped magma.

Any successful silicate-melt inclusion study must be preceded by careful petrographic investigations. An optical microscope is sufficient to locate silicate-melt inclusions. As these are often very small ( $< 30 \mu\text{m}$ ), high magnification objectives should be used (25 and/or  $50\times$ ) on crystal separates or on double-polished thick sections (100–300  $\mu\text{m}$ ) identical to those used for fluid inclusion studies (see Shepherd et al., 1985 for preparation). Investigations on conventional petrographic thin sections are not recommended, since these do not allow observation in the third dimension, precluding the recognition of important characteristics, such as size, shape, distribution, presence of cracks, etc. Sorby (1858) proposed two investigation steps: (1) identification of the petrographic character of the inclusions, and (2) characterisation of their evolution after trapping. These points are still relevant today since what we know about the formation of melt inclusions has been obtained mainly through microscopic studies.

## 2.2. Evolution of silicate-melt inclusions after trapping, during and after magma solidification

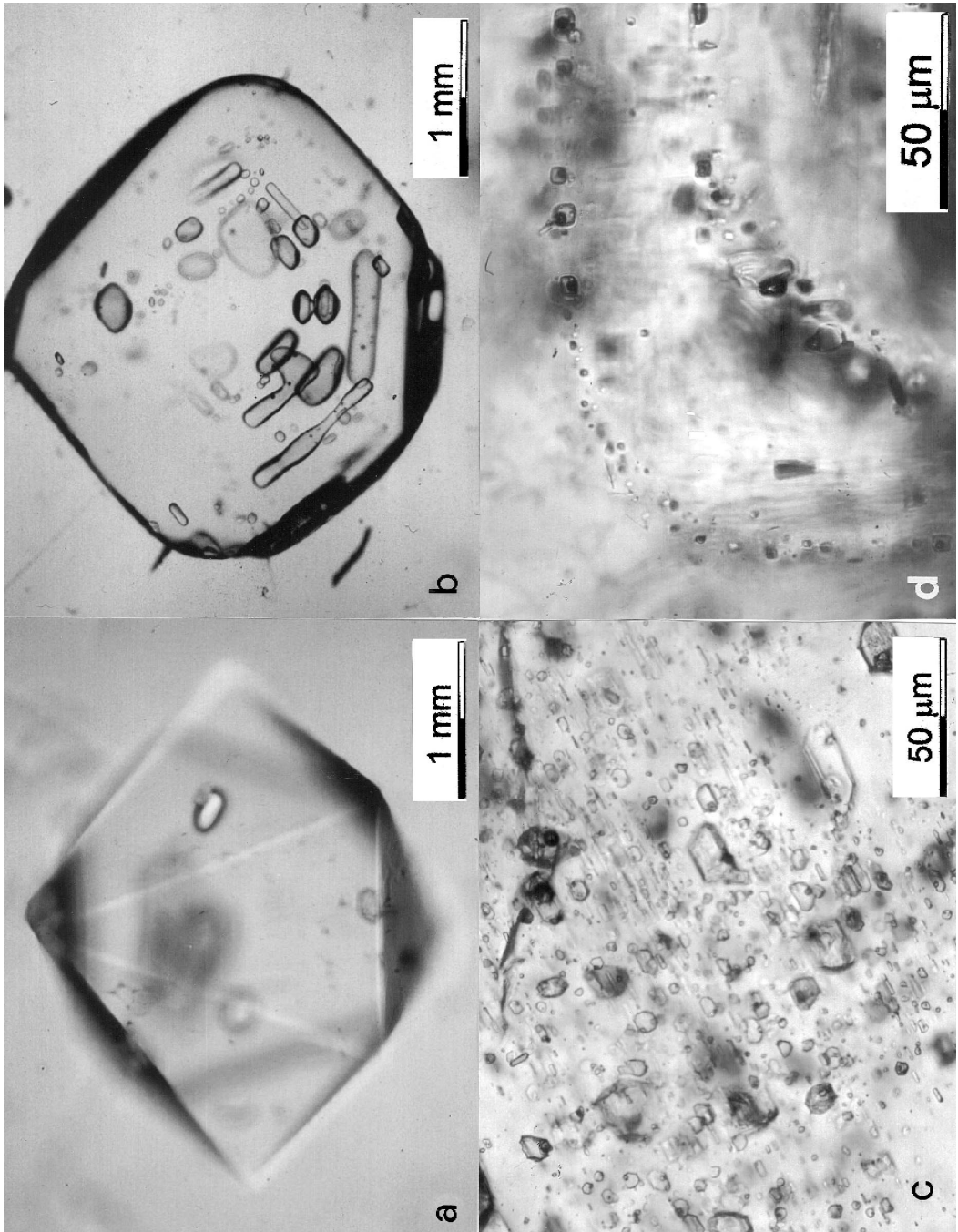
On cooling from magmatic temperatures, the most common processes affecting the silicate-melt inclusions are *crystallisation* and *devitrification*. The first process occurs when the crystalline phase grows from a molten silicate liquid, whereas the latter results from partial reorganisation of the glass to form microlites. In slow-cooling effusive rocks, most silicate-melt inclusions lose host-mineral components to growth on the inclusion walls (often improperly called “epitaxial” growth) and other components

to crystallisation of daughter-mineral phases within the inclusion. Fig. 4 shows an example of a silicate-melt inclusions, which underwent to crystallisation processes. From an original alkali-basalt trapped within the inclusions, Mg, Ca, Fe and Si are lost on crystallisation of clinopyroxene on the walls. Daughter clinopyroxene composition is progressively Ca- and Fe-enriched, and Mg-depleted (compare analyses D and E in Fig. 4). Crystallisation processes drive the residual glass to a trachytic composition (analysis A in Fig. 4).

Crystallisation of the host mineral on the inclusion walls is a nonequilibrium process, which does not simulate the differentiation of the crystallising magma; silicate-melt inclusions may crystallise, in fact, only the host phase — even if the trapped melt is saturated with other mineral phases — because of heterogeneous nucleation on the inclusion walls. One such example is illustrated by clinopyroxene-hosted silicate-melt inclusions in alkali-basalt lavas from Mt. Etna (Frezzotti et al., 1991; Fig. 5). After trapping, silicate-melt inclusions crystallised more than 30% clinopyroxene on the inclusion wall, before becoming saturated in the host-mineral phase. Such a massive crystallisation increased the  $\text{H}_2\text{O}$  content in the residual melt, and amphibole began to grow within the cavity (Fig. 5c). When volatile saturation was reached, new fluid phases and daughter minerals nucleated at the interface with the gas bubble. The resulting volatile enrichment after the crystallisation is extreme; chlorine contents as high as 1 wt.% were measured in the residual glass; these high values lead also to growth of Cl-rich apatite grains in the gas bubble (Fig. 5e).

The degree of evolution of silicate-melt inclusions is dependent on the inclusion size and on the cooling times. In fast-cooling lavas, silicate-melt inclusions do not devitrify or become finely crystalline. Cooling rates following entrapment of silicate-melt inclusions

Fig. 2. Photomicrographs of quartz phenocrysts showing general characteristics of silicate-melt inclusions in lavas. (a) Silicate-melt inclusion with negative crystal shape (bipyramidal habitus). The inclusion consists of glass, a bubble and a small daughter mineral present beside the gas bubble; from the Mt. Doré (J.L.R. Touret, private collection). (b) Silicate-melt inclusions in quartz from the Mt. Doré (J.L.R. Touret, private collection). One inclusion consists of glass and various bubbles (indicated with a black arrow). Others are bubble-free (indicated with an empty arrow). (c) Fluid-rich silicate-melt inclusion, which contains three large gas bubbles. This feature may be interpreted as trapping of a fluid saturated magma; from Mt. Amiata (Italy). (d) Glassy bubble-free silicate-melt inclusion; the inclusion formed during trapping of a solid inclusion; from the Mt. Doré (J.L.R. Touret, private collection).



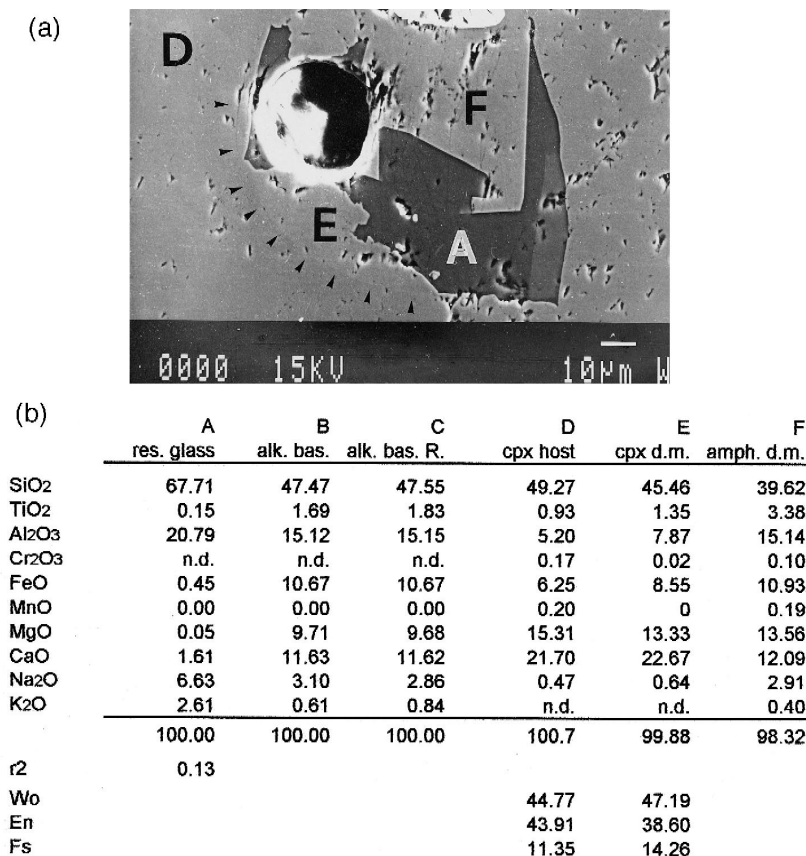


Fig. 4. Chemical modifications in silicate-melt inclusions, which occur after trapping. (a) Secondary-electron image of a clinopyroxene phenocryst containing a silicate-melt inclusion, which is open to the surface; alkali-basaltic lava from Mt. Etna. The inclusion contains residual glass, various daughter minerals and a bubble; note that this last one appears as an empty hemisphere. Clinopyroxene crystallisation on the cavity walls may be recognised because of a slight change in colour (lined by arrows). The different letters indicate points selected for analyses. (b) Fractionation process calculation for the originally trapped melt, assuming a primary basaltic composition. (A) Residual glass composition after crystallisation of daughter mineral phases: mean of three analyses. (B) Initial melt composition. (C) Recalculated initial melt composition. (D) Host clinopyroxene composition. (E) Composition of clinopyroxene crystallising on the cavity walls. (F) Composition of amphibole crystallising within the inclusion. Res. = residual; alk. = alkali; bas. = basalt; R. = recalculated; d.m. = daughter minerals. Analyses from Frezzotti et al. (1991).

are indeed much more important than absolute age of host rocks (Fig. 5). Very old silicate-melt inclusions

might remain *glassy on conditions that they cooled very quickly*.

Fig. 3. Photomicrographs indicating typical distribution of silicate-melt inclusions in the different mineral species. (a) Bipyramidal  $\beta$ -quartz phenocryst from the Mt. Doré (J.L.R. Touret, private collection). Melt inclusions are visible out of focus. (b) Bipyramidal quartz phenocryst cut perpendicular to the  $c$ -axis (001). Distribution of primary silicate-melt inclusions follows the host-quartz symmetry. This arrangement indicates that silicate-melt inclusions formed filling gaps within the (11 $\bar{2}$ 1) faces, because of skeletal growth of quartz (i.e. edges growing faster than faces); from Mt. Doré (J.Touret, private collection). (c) Distribution of silicate-melt inclusion in orthopyroxene filling the whole crystal; From Tenerife, Canary Islands. (d) Zonal-array distribution of silicate-melt inclusions in a plagioclase phenocryst from Panarea, Aeolian Islands. The presence of inclusions at compositional boundaries indicates that they may be formed because of changing of crystallisation conditions.



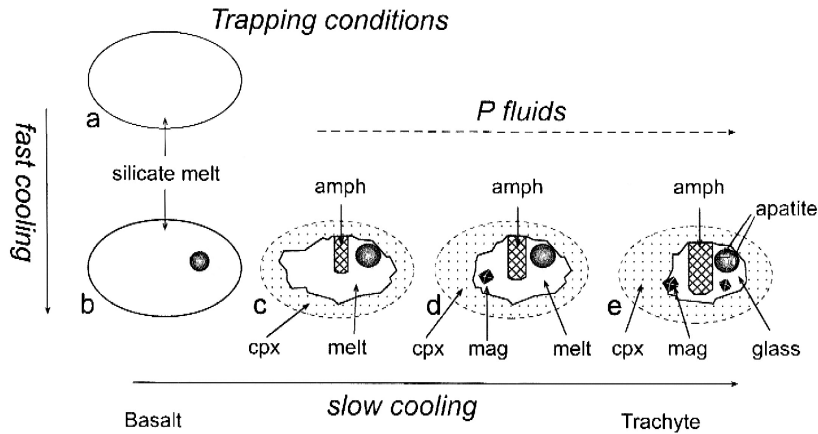


Fig. 5. Schematic drawing illustrating the after-trapping evolution of a silicate-melt inclusion hosted in clinopyroxene, depending on the cooling rates of the host rock. (a) Filling of the cavity with silicate melt of basaltic composition, at trapping conditions. (b) A fast cooling of the host rocks bring to supercooled silicate-melt (glass) and a shrinkage bubble; no daughter minerals form. (c) In slow-cooling conditions, host clinopyroxene grows on the inclusion walls, followed by amphibole crystallisation. (d) In the residual glass, clinopyroxene, amphibole and opaque crystallisation drives the concentration of some volatiles over the solubility limit, forming daughter minerals within the glass bubble. (e) General view of the silicate-melt inclusion after cooling to room temperature. The residual glass has a trachytic composition. Modified after Frezzotti et al. (1991).

After formation of the rocks, circulating fluids may interact with preexisting silicate-melt inclusions. In this way, the original chemical signature of an inclusion will be lost. Interaction with aqueous fluids changes the chemical composition of the glass: in extreme cases inclusion cavities become filled with argillic minerals. Such postmagmatic phenomena, rather rare in lavas, are frequently observed in sub-volcanic and intrusive rocks. Nevertheless, silicate-melt inclusions may be preserved in subvolcanic systems, even if they experienced a long-lasting hydrothermal fluid circulation. A systematic study of quartz and plagioclase phenocrysts from drill hole samples (maximum depth 500 m) of Calabona microtonalite porphyry-copper deposit (Sardinia, Italy) revealed the presence of preserved silicate-melt inclusions (i.e., transparent and isotropic glass, no daughter mineral phases or devitrification processes) in quartz crystals at all depths (Fig. 6a) (Frezzotti et al., 1992).

Since a slow-cooling history enhances all crystal-melt interaction processes, it can be expected that silicate-melt inclusions in plutonic rocks will be extremely complex. In addition, effects, such as the reequilibration of the host minerals during the post-

magmatic cooling (especially recrystallisation of quartz, perthitisation of K-feldspar), may lead to a change of shape or to the complete destruction of inclusions. As a result, silicate-melt inclusions in intrusive rocks are very different from those in lavas (“stone inclusions”, Sorby, 1858; “magmatic remnants”, Touret and Frezzotti, 1993). The preservation of the original chemical character is rare. The identification of silicate-melt inclusions in most plutonic rocks requires specific investigations since their after-trapping evolution result in partial to complete crystallisation. They appear dark or opaque, and with a typical granular aspect (Fig. 6b, c, d). There are two features, however, that allow the identification of silicate-melt inclusions in plutonic rocks: (i) the presence of coloured glass, that typically shows a spotted anisotropy due to devitrification (Fig. 6b, c); (ii) the presence of one or more gas bubbles, although completely deformed (Fig. 6c, arrow).

### 2.3. Identification of magmatic immiscibility

Silicate-melt inclusions illustrate a remarkable variety of melt-related immiscibility phenomena (Roedder, 1992): silicate-silicate, silicate-sulphides

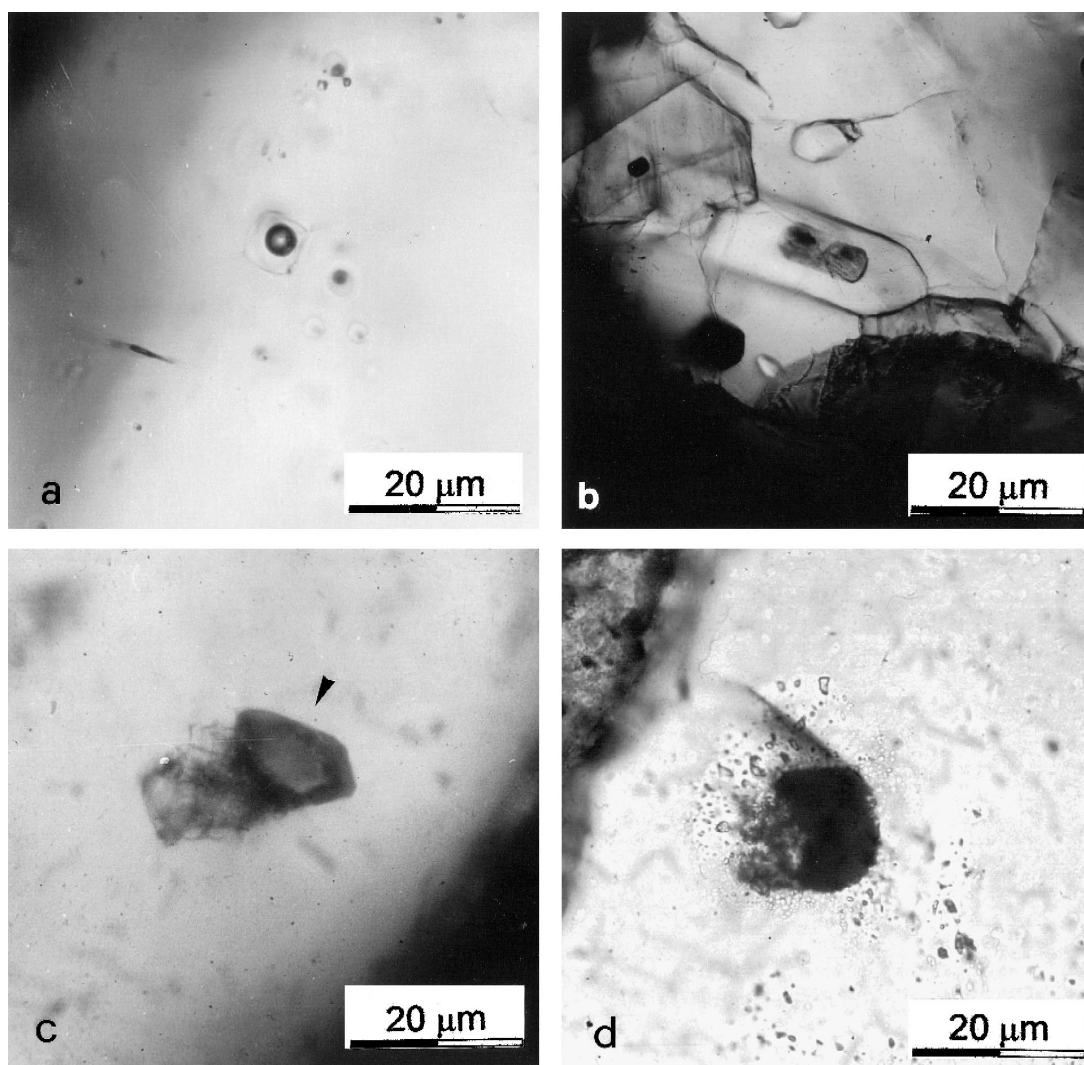


Fig. 6. Photomicrographs showing general characteristics of silicate-melt inclusions in porphyries and intrusive rocks. (a) Silicate-melt inclusion in a quartz phenocryst from a microtonalite porphyry copper, Calabona, Sardinia, Italy. The inclusion is well preserved and consists of glass and a very large bubble, showing no devitrification processes. (b) Silicate-melt inclusion in a zircon, from the Laramie anorthosite complex, USA (Frost and Touret, 1989). The inclusion has a brownish aspect, due to devitrification of the glass. (c) Preserved silicate-melt inclusion in a quartz crystal from the Mt. Genis granite, Sardinia, Italy. The inclusion is completely recrystallised (brownish spotted appearance); however, a large gas bubble is present (indicated with an arrow). (d) Rests of a silicate-melt inclusion from granite of the Arburese complex, Sardinia Italy. The inclusion appears almost black and it is clearly altered. Fluid inclusions are present inclusions around the cavity.

(or other ores), silicate–carbonate, silicate/carbonate fluids. The morphological evidence of immiscibility is always the same: a droplet (globule) of one phase within another of contrasting composition. Such direct evidence, however, might be blurred by further evolution of the unmixed melts, notably “epitaxial” crystallisation of mineral phases (e.g., Roedder and

Weiblein, 1979, or other references in Roedder, 1984, Chap. 18).

### 2.3.1. *Heterogeneous trapping of immiscible phases*

When two or more fluid phases coexist around growing crystals (magmatic immiscibility), a hetero-

geneous mixture may be trapped with very different ratios of the coexisting phases in different inclusions. If the magma was oversaturated with fluid phases at the time of trapping, inclusions will contain variable proportions of silicate melt and fluid. This specific case of heterogeneous trapping corresponds to the magma “first- and second-boiling” of magma processes, as described by Burnham (1979).

Evidence that basaltic magmas are saturated in CO<sub>2</sub> prior to eruption is commonly observed in phenocrysts (Roedder, 1965) and in mantle xenoliths, where mixed CO<sub>2</sub> + basaltic glass inclusions are ubiquitous (see Andersen and Neumann, 2001). In high-silica rocks, many examples of fluid saturation during crystallisation have been described, with the identification of mixed silicate glass + brines ± CO<sub>2</sub> in quartz and feldspar grains (cf. Roedder and Coombs, 1967; Reyf and Bazheev, 1977; Lowenstern 1993; De Vivo and Frezzotti, 1994). Fig. 7a illustrates the typical characteristics of heterogeneous trapping of silicate melt and brines at high temperatures. These mixed inclusions yield direct evidence of fluid chemistry at the magmatic stage. The petrographic identification of heterogeneous trapping of fluid and melt within single inclusions is, thus, a reliable way to prove the coexistence of the fluid phase (mainly brines and/or CO<sub>2</sub>) with the silicate melt. When magma undergoing incipient boiling is trapped as inclusions, then these inclusions will contain multiple gas bubbles (Fig. 7b). Vesiculation characteristics might also provide important information.

Similarly, if two distinctly different silicate melts were present during crystallisation, then an inclusion may contain melts of contrasting compositions. The evidence for this, however, is so far very rare. Roedder and Weiblein (1970, 1979) described one of the best-documented examples in lunar basalts. They reported silicate-melt immiscibility, where two contrasting glasses (high-silica and high-iron, respectively) were present in the inclusions, separated by a sharp meniscus.

### 2.3.2. Homogeneous trapping of a single fluid phase, followed by *in situ* immiscibility

Unmixing processes in silicate-melt inclusions may occur also after the formation of the inclusions: the melt was trapped as a single homogeneous phase

and immiscibility occurred within the inclusion (in situ immiscibility; Clocchiatti, 1975). Common to most silicate-melt inclusions in effusive rocks is the in situ volatile oversaturation. After trapping of the magma within the inclusion cavity, fluid saturation may be induced by cooling and/or by daughter-mineral crystallisation (like boiling processes in most magmatic rocks). In a similar way, silicate-melt inclusions will experience a drop of external pressure, as the host magma rises. This may lead to degassing of fluids (i.e., CO<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub>S) and crystallisation of daughter minerals (i.e., carbonates, apatite, sulphides) within the already formed microcavity. If the trapped silicate-melt phase was water-rich, and decompression very fast, the pressure of newly formed aqueous fluids may become high enough to cause decrepitation of the inclusion. Since these are high-temperature processes, they may result in the expulsion of water from the original inclusion, reorganised as tiny fluid inclusions arranged along the cavity apices as depicted in Fig. 7c.

Immiscibility after-trapping will *always* result in constant proportions of the various phases present in the inclusions. Frezzotti et al. (1994) described in situ carbonate melt–silicate melt immiscibility in olivine crystals in peridotite xenoliths from La Gomera (Canary Islands). Fig. 7d shows that Mg-rich silicate glass + primary carbonate droplets occur with constant phase proportions within single silicate-melt inclusions. The sharp meniscus separating the carbonate and the silicate phases indicate that immiscibility occurred at high temperatures. The carbonate droplet, therefore, appears to represent a quenched liquid, resulting from unmixing within the inclusion from an original homogeneous carbonate-rich melt.

Crystallisation processes within single melt inclusions might also bring the residual melt into unstable compositions, with consequent unmixing into two chemically distinct melts, as observed in some silicate-melt inclusions in plagioclase phenocrysts from andesitic lavas (Karimsky Volcano, Kamchakta; Clocchiatti and Krasov, 1979). Massive crystallisation of the host phase brought the residual melt to unmix into two immiscible liquids, occurring at room temperatures as globules of dark pyroxenitic glass enclosed in transparent high-alkali and silica glass.

In situ immiscibility processes may, thus, modify the original composition of the trapped melt. In

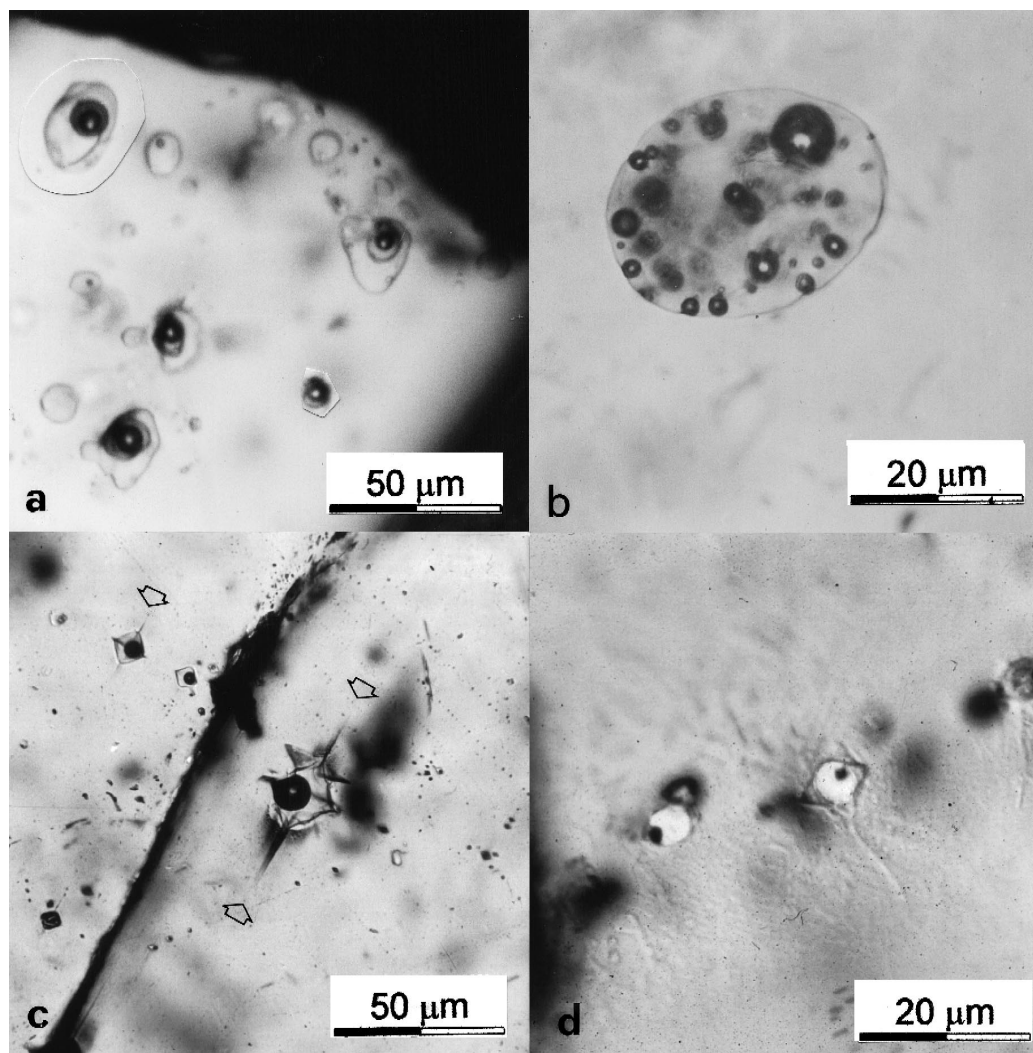


Fig. 7. Photomicrographs illustrating immiscibility processes in silicate-melt inclusions. (a) Photomicrograph taken at 900°C in a quartz crystal from Mt. Genis granite, Sardinia, Italy. At high temperatures, some inclusions consist of silicate-melt and an hypersaline liquid in presence of a gas bubble. Note the different fluid-melt ratios in the different inclusions. Many inclusions consist only of silicate-melt. These features are interpreted as resulting from heterogeneous trapping, at magmatic temperatures of immiscible silicate melt and high-salinity fluids (magmatic immiscibility). Inclusions are at different focus depths. (b) Large glassy silicate-melt inclusion in a quartz grain in quartz-rich xenoliths hosted in lavas from Salina (Aeolian Islands, Italy). The inclusion contains numerous gas bubbles; this results from heterogeneous trapping of magma and volatiles at early stages of immiscibility. (c) Glassy silicate-melt inclusions in a quartz phenocryst from a microtonalite porphyry, Calabona, Sardinia, Italy. All inclusions contain large gas bubbles, and microfractures stretch out from the inclusion apices. Swarms of tiny fluid inclusions mantle the microfractures and form greyish halos around the inclusion cavity (arrows). The fluid inclusions are interpreted as resulting from decrepitation of the silicate-melt inclusions due to volatile oversaturation, which occurred after the inclusion formation. (d) Two coplanar mixed carbonate + silicate-melt inclusions in a secondary trail in an olivine porphyroblast in a dunite xenoliths from La Gomera, Canary Islands (crossed polarisers). The inclusions consist of a strongly birefringent rounded carbonate crystal rimmed by silicate glass and an opaque. The curved carbonate-glass boundary indicates that at some time two immiscible liquids coexisted in the inclusions: one carbonate-rich, and the other silicate-rich. Constant proportions of these two phases in different inclusions are interpreted as resulting from in-situ immiscibility, after trapping of a homogeneous melt.

addition, since these processes depend only on the after-trapping evolution of the inclusions in a closed system, they might be totally unrelated to the evolution of the enclosing magma. Therefore, only heterogeneous trapping of distinct coexisting phases characterise immiscibility processes at magmatic stages. The following criteria are proposed to distinguish the two processes, based on petrographic observations (Fig. 8):

(i) homogeneous melt entrapment — immiscibility occurs after inclusion formation. The inclusions are characterised by high and constant phase 1/phase 2 ratios (i.e.,  $> 0.2$ ; black dots in Fig. 8);

(ii) heterogeneous melt entrapment — two or more fluid phases coexisted prior to inclusion formation (magmatic immiscibility). The inclusions have extremely variable phase 1/phase 2 ratios (squares in Fig. 8). The presence of inclusions containing only one of the two phases should be expected. If the melt was entrapped when immiscibility processes were at an early stage, a single silicate-melt inclusion may contain several (up to tens) droplets of one phase within the other.

Note that this is a statistical method and it *must* be based on a great number of observations. Very high vapour–glass ratios observed in a few individual inclusions may, in fact, correspond to inclusions

leaked at high temperatures, because of fracturing of the host phenocrysts.

### 3. Selection of representative inclusions: homogenisation studies

Petrographic studies are fundamental for the characterisation of silicate-melt inclusions. Complete studies, however, require high temperature microthermometry (entrapment temperature of melt inclusions; Sobolev and Kostyuk, 1975; Sobolev et al., 1991; Roedder, 1984), electron microprobe analyses (major-element and trace-element analysis; Nielsen and Sigurdsson, 1981; Lowenstern and Mahood, 1991), Ion microprobe (trace-element and isotope analyses, H<sub>2</sub>O quantitative analyses; Kovalenko et al., 1988; Ihinger et al., 1994; Deloule et al., 1995), Fourier-transformed infrared spectroscopy (H<sub>2</sub>O and CO<sub>2</sub> quantitative analyses; Ihinger et al., 1994; Lowenstern, 1994a) and, more recently, laser-ablation microprobe inductively coupled plasma-mass spectrometry (trace elements; Taylor et al., 1997). Basic principles of these techniques have been reviewed in a number of papers and will not be discussed here. A summary of data obtainable by the different techniques is given in Table 1, as a general guide for “typical analyses”.

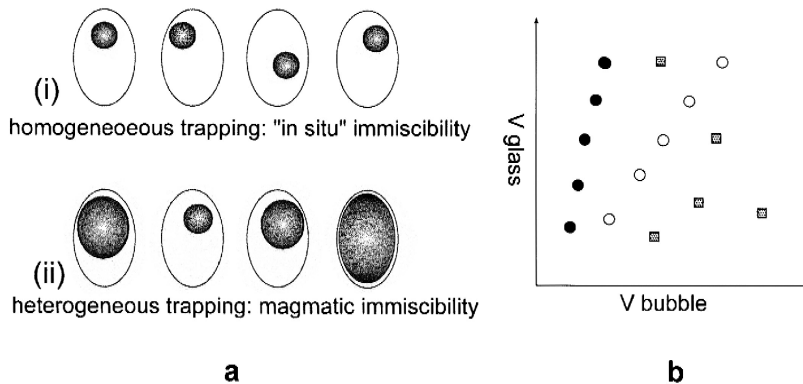


Fig. 8. Schematic drawing representing magmatic immiscibility as recorded by silicate-melt inclusions according to the timing between inclusion formation and immiscibility processes. (i) and (ii) Saturated magmas: homogeneous vs. heterogeneous trapping. (b) Plot of the glass volume ( $V$ )/vapour bubble volume ( $V$ ) in different inclusions. White and black dots correspond to volumetric vapour/glass ratios in single inclusions, which trapped a homogeneous magma. Grey squares indicate volumetric vapour/glass ratios in single inclusions that trapped immiscible phases. Homogeneous trapping is always characterised by constant glass/vapour bubble volumes. Redrawn after Touret and Frezzotti (1993).

Table 1  
Schematic report of major investigation techniques applied to the study of silicate-melt inclusions

Methodology	Sample preparation	Obtainable data	Problems
High- <i>T</i> microthermometry	Minimal: double polished thick sections, free of glue or resin	Melting temperatures of daughter phases; Total homogenisation temperatures; Revitrification of inclusions; Identification of immiscibility processes	Overestimation of measured temperatures; Nonvalid for oversaturated magmas; Quenching techniques
Microprobe	Standard microprobe sections or as for high- <i>T</i> microthermometry	Chemical composition of the glass; Volatile phases: Cl, S, P, F; Indirect calculation of H <sub>2</sub> O concentration	Migration of small low-charge elements during analysis; Indirect H <sub>2</sub> O calculation; Heterogeneity of the glass
Secondary-ions mass spectroscopy	Standard gold-coated sections or as for high- <i>T</i> microthermometry	Chemical composition of the glass; Detection limit of ppm for some elements; Little spots (20 μm); Easy sample preparation	Standards
Micro-infrared spectroscopy	Complicated: the precise thickness of the inclusion should be known	Quantification of H <sub>2</sub> O and OH <sup>-</sup> in glass; Quantification of CO <sub>2</sub> and (CO <sub>3</sub> ) <sup>2-</sup> in glass	Standards; Difficult sample preparation
Micro-Raman spectroscopy	Minimal: double polished thick sections	Quantification of gases in gas bubble; Characterisation of daughter minerals; Very little spots (1–2 μm)	Quantitative analyses in glasses

However, before temperature and chemical data are collected, it is of major importance to determine if these data might be useful for the goal of the specific research: i.e., are the silicate-melt inclusions still chemically representative? A major concern, when selecting, which inclusions to investigate is the identification of silicate-melt inclusions in which the glass composition has changed due to post-trapment crystallisation and/or alteration. Some of these processes, in particular those related to interaction with the external system, may be recognised during petrographic observations (e.g., cracks radiating from the inclusions, dark appearance, unusually large gas bubbles, etc.). We still need to develop criteria, however, to recognise the extent of chemical changes that occurs within single inclusions even *without* exchange with the external system.

Silicate-melt inclusions, which undergo post-trapment crystallisation, do not follow the same differentiation as the host magma. A common way to check if the silicate-melt inclusions have retained their original composition is the revitrification (i.e., remelting) in the laboratory by bringing the inclusions to homogenisation temperatures followed by quenching. Rehomogenisation does not necessarily imply disappearance of the gas bubble; the tempera-

ture at which the daughter phases have been remelted approximates the minimum trapping temperature of the inclusion (Sobolev and Shimizu, 1993). To revitrify a silicate-melt inclusion, there are two main techniques: (1) heating and quenching under visual control, using a high-temperature heating stage (Sobolev et al., 1980), and (2) heating of single crystals in a platinum quench-furnace, followed by drop-quenching (Zapunnny et al., 1988). Each of these techniques has its benefits and inconveniences, which are summarised in Table 2.

Reheating of inclusions involves some problems: homogenisation kinetic is, in fact, highly dependent on the viscosity of the silicate melt, melting rate of

Table 2  
Major characteristics of remelting techniques applied to silicate-melt inclusions

	Heating stage	Furnace heating
Sample preparation	Yes	No
Large amount of sample	No	Yes
Observation of phase transition	Yes	No
Direct temperature control	Yes	No
Quenching time	1–2 s	< 1 s

daughter minerals, and the diffusion rates of volatiles (e.g., hydrogen) within the inclusions. If inclusions are properly homogenised, their composition should match the major element trends followed by the host magma. Underheating or overheating the inclusions may have major consequences: over-heating may promote loss of trace elements that are compatible with the host minerals (i.e., Ni in olivine; Sr in plagioclase), and of volatiles, such as H<sub>2</sub>O and CO<sub>2</sub> dissolved in the glass. Underheating will not dissolve all daughter minerals and/or growth along the inclusion walls. As a result, glass composition will be very different from those expected.

The reliability of silicate-melt inclusions should be evaluated using a number of independent criteria. Nielsen et al. (1998) recommends the following: (a) a careful petrographic observation with high-magnification objectives of single inclusions to identify possible fractures and/or trapping of solid phases that are not true daughter minerals (this first observation is useful to select inclusions for rehomogenisation). After reheating: (b) an examination of the glass homogeneity by performing two or more chemical analyses within the same inclusion, (c) a comparison of the chemical analyses to the host lavas using relevant phase diagrams, and d) a correlation of the S and Fe contents of rehomogenised melt inclusions relative to lavas (altered inclusion glass has often very low S contents).

#### 4. Applications of silicate-melt inclusion studies to the petrology of magmatic systems

##### 4.1. High-temperature evolution of trapped melts

In the last 20 years, most studies published on silicate-melt inclusions report high-temperature experiments (i.e., microthermometry, see Roedder, 1984, 1992; Touret and Frezzotti, 1993; Li, 1994 for a review), since these may give direct information on trapping temperatures. In addition, such experiments represent the only possible way to trace the evolution of magmatic fluids at magmatic temperatures, and are a necessary tool to rehomogenise the inclusion glass (see above). During heating, a silicate-melt inclusion will, in theory, follow the reverse of the cooling path after entrapment (Fig. 9). At room

temperature ( $T_0$ ; Fig. 9), the inclusion consists of glass (G), bubble (V), crystalline aggregates (S; i.e., devitrification products)  $\pm$  one or more daughter minerals. On heating, the disappearance of crystalline aggregates is observed at  $T_1$  (Fig. 9), and the inclusion becomes more transparent ( $G + S + V \rightarrow G + V$ ). A sort of reorganisation is observed, but without clear melting. Beginning of melting occurs when the glass passes into a silicate melt ( $T_2$ ;  $G + V \rightarrow G + V + L$ ). This temperature, at difference with what observed in fluid inclusions, is difficult to record, because of progressive slow melting. Daughter minerals, if present, begin to melt at these temperatures. At  $T_3$  the inclusion homogenises ( $L + V \rightarrow L$ ) to a single phase. Theoretically this temperature represents the minimum temperature of crystallisation of the host-mineral phase ( $T_1$ ; Fig. 9). This is valid only for magmas that were undersaturated with volatiles at the time of trapping.

If the magma was saturated in volatiles at the time of trapping, total homogenisation has *no* direct petrological significance: it will occur at very high temperatures and will be variable, according to different fluid/glass ratios within single inclusions (cf. Fig. 8). The evolution of a mixed fluid and silicate-melt inclusion (heterogeneous trapping) from a granitic rock is sketched in Fig. 10. At room temperature, the inclusion is crystallised (Fig. 10a). Immiscible volatiles show up as H<sub>2</sub>O-rich fluids (liquid + vapour; Fig. 10a) and salt cubes (S in Fig. 10a). On heating, the inclusion becomes progressively more transparent and salt cubes within the bubble begins to melt at 500°C (Fig. 10b). Glass passes to a silicate melt at 700°C (Fig. 10c); the last daughter mineral disappears at 850°C (Fig. 10c). Nevertheless, the bubble is present up to unrealistic high temperatures (> 1250°C) (Fig. 10d). On cooling from magmatic temperatures, two different types of behaviour are recorded depending on starting temperatures. Cooling from the temperature of disappearance of the last crystal (Th), the inclusion follows a reverse path, resulting in a totally glassy inclusions at room temperature + immiscible brines (revitrification) (compare Fig. 10a and d). Cooling after the total homogenisation at very high temperatures gave a different evolution: (a) the nucleation of brines at high temperatures, approximately 100°C lower than total homogenisation; (b) at about 700°C, a shrinkage

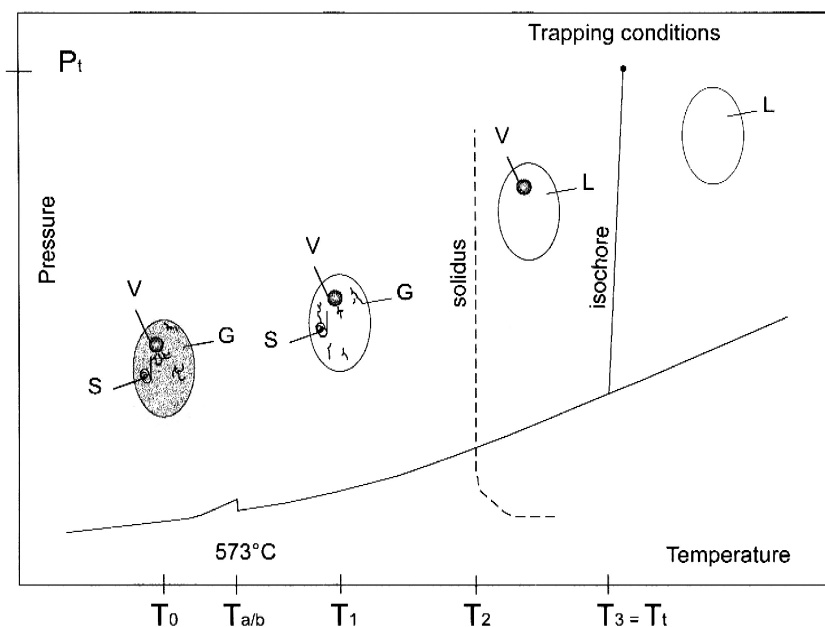


Fig. 9. Schematic pressure and temperature diagram of a silicate-melt inclusion behaviour in quartz, during high-temperature experiments. At  $T_0$ , the inclusion consists of glass and a shrinkage bubble and daughter minerals. On heating, the inclusion becomes progressively more transparent until at  $T_2$ , glass begins to melt. Homogenisation is reached at  $T_3$ ; this temperature corresponds to trapping temperature ( $T_t$ ), due to the very steep isochore path, see text. Note that at the  $\alpha$ - $\beta$  quartz transition ( $573^\circ\text{C}$ ), the inclusion undergoes to a slight volume increase, resulting in a drop of the internal pressure. G = glass; V = vapour; L = liquid; S = solids (i.e. daughter minerals);  $P_t$  = pressure at trapping conditions. Redrawn after Touret and Frezzotti (1993).

bubble forms, caused by contraction of the melt during undercooling. The resulting revitrified inclusion contains two distinct bubbles, a volatile-rich one, and a shrinkage one (Fig. 10f). It is evident that, in this case, inclusions do not give any indication on the trapping conditions; nevertheless, they record evidence for entrapment of immiscible silicate melt and hypersaline liquids at magmatic stages.

Roedder (1984) and Belkin (1994) report many of the difficulties related to heating-stage experiments. Various authors, find unreasonably high magmatic temperatures (i.e., due to high heating rates and/or volatile oversaturated magmas). Additional complications may arise from experimental problems, in particular interaction between silicate melt and host and/or homogenisation kinetic; and from melting of originally altered inclusions. In a general way, the fastest the heating experiment is attained, the highest is the apparent homogenisation, because of melting rates of daughter minerals and diffusion of volatiles.

The maximum heating rate during experiments should equal the dissolution rate of daughter minerals.

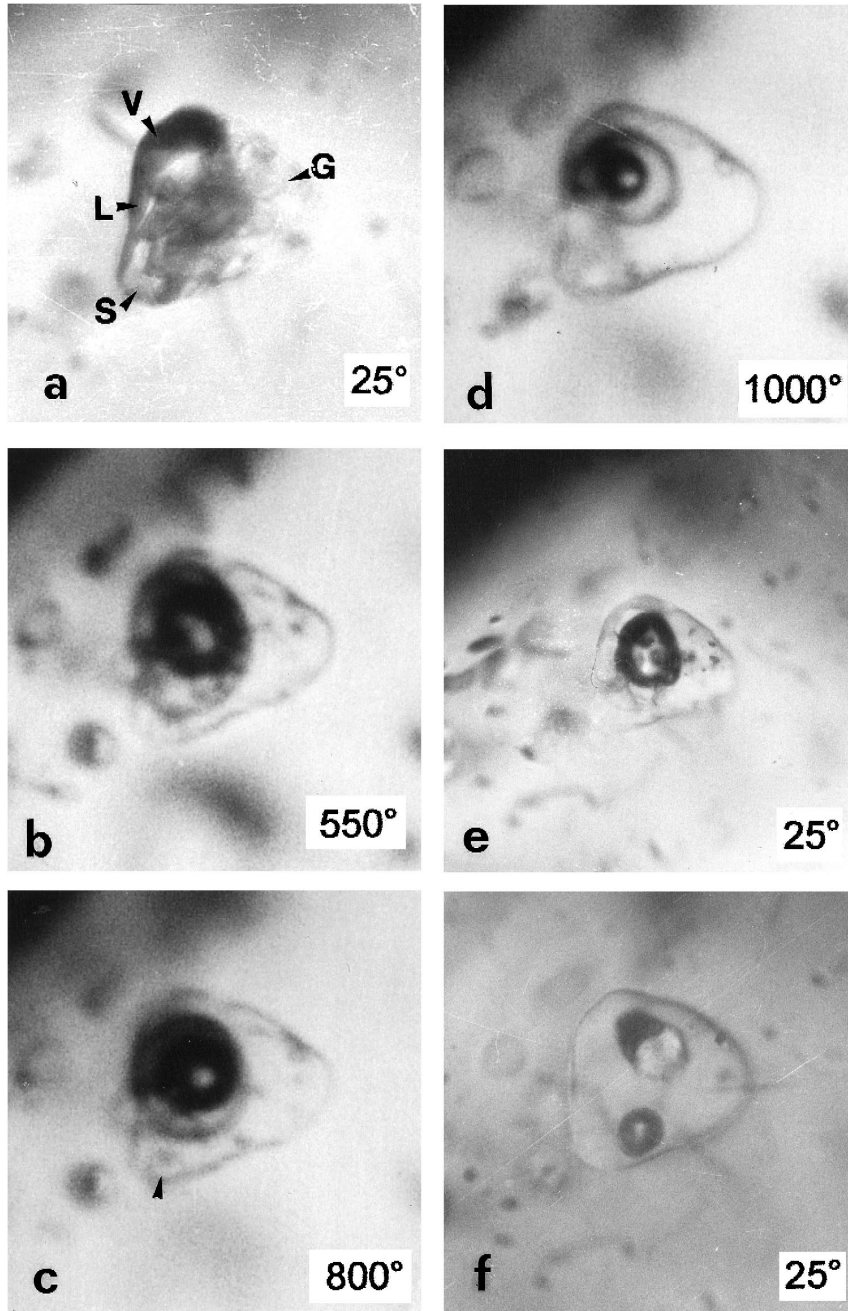
#### 4.2. Chemical composition

Data on major and trace elements may contribute to the understanding of major issues in igneous petrology: (a) they allow reconstruction of the primary melt composition and formation conditions of basaltic and alkali-basaltic melts in the mantle (Clocchiatti and Massare, 1985; Gurenko et al., 1991; Sobolev and Shimizu 1993; Sobolev and Danyushevsky, 1994); (b) they can characterise fractional crystallisation processes (Métrich et al., 1991; Lu et al., 1992; Vaggelli et al., 1993); (c) they can demonstrate the importance of assimilation and or mixing processes (Anderson, 1976; Anderson and Wright, 1972; Hervig and Dunbar, 1992). Mixing, assimilation and contamination processes in magmas obscure this information in whole rocks.



Most studies are concentrated on silicate-melt inclusions in magnesian olivine, as they are generally pristine. Since diffusion of a single element depends mainly on its diffusion coefficient and concentration in the single minerals, olivine is, by no doubt, a most

favourable host, as it contains the minimum concentration of most elements that characterise the silicate melt. Silicate-melt inclusion in olivine can be considered representative for the composition of primary melts for most major and trace elements, with excep-



tion for Mg, Fe, Si, (Sobolev, 1996). Sometimes, the Mg/(Mg + Fe) ratios of the glass may have been modified (i.e., the inclusions may result enriched in Mg contents). First, because the  $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$  in the glass may be significant; secondly, because Fe-oxide or sulphide may form within the inclusions and Fe may diffuse during cooling. Petrological calculations and rehomogenisation techniques should be applied in order to correct these effects.

Kamenetsky and Clocchiatti (1994, 1996) used major and trace element variations in the different melt inclusions in olivine phenocrysts from Mg-rich tholeiitic, transitional and alkaline basalts from primitive, ancient and prehistoric magmas at Mt. Etna, to delineate an origin from distinct parental magma sources. The range of composition of the glasses could not be explained by fractional crystallisation processes but was probably generated during partial melting in the mantle. In addition, the comparison of the petrologic characters of Mt. Etna magmas with adjacent areas (i.e., Aeolian arc) pointed to a progressive depletion of the mantle source by continuous magma extraction and subsequent evolution.

Sobolev (1996) gave a milestone indication that the analyses of trace and light element in silicate-melt inclusions might be a very powerful tool to follow the different stages of melting and extraction of melts formed at mantle conditions. This author found that the silicate-melt inclusions in olivine phenocrysts in basalts from the Mid-Atlantic ridge at 9°N contained primary melts of contrasting composition (LREE ultra-depleted vs. enriched melts), compared to the basaltic host lavas. The author interpreted this as the result of melting in the presence of garnet and evolution in an open system. Mixing of the primary melts occurred at depth in the mantle during crystallisation and transport. More recently, a very important insight into the generation of magmas

in back arc basin tectonic setting was given by Kamenetsky et al. (1997) in the seamounts of Valu Fa ridge, Lau basin. These authors identified two distinct primary melt compositions on the basis of coupled melt inclusions and host-phenocryst chemistry.  $\text{H}_2\text{O}$ -rich, high-CaO, low- $\text{Al}_2\text{O}_3$  magnesian basalts represented one magma series, while the other one was low-CaO boninite magma. In addition, all silicate-melt inclusions contained variable concentrations of incompatible trace elements, which the authors explained with a systematic addition of a LILE-, Pb- and Cl-rich component to the mantle wedge source. This exotic component was believed to be an aqueous fluid phase released by the subducting oceanic slab, as invoked in most models for arc-magma genesis. The overall model proposed by these the authors is partial melting of a refractory hydrated subarc lithosphere, probably lined by pyroxene-rich veins (i.e., high-Ca magma series).

Isotopic analyses on individual silicate-melt inclusions are also very powerful tools to investigate magma-source problems. Saal et al. (1998) confirmed the presence of two-component mixing for oceanic island basalts from Mangaia (Cook Islands) and Tahaa (Society Islands). The silicate-melt inclusions in olivine ( $\text{Fo}_{84-89}$ ) preserved a far greater difference in Pb isotopes than in the whole rocks, amounting 50% of the worldwide range of ocean island basalts, and defining a linear trend (Fig. 11). These authors concluded that the entire Austral chain and the Society Islands array can be explained by mixing of magmas with different isotopic composition (HIMU and EMII components), which were present in the volcanic plumbing system before or during melt aggregation.

Among other important isotopic research is the systematic study of boron concentration and isotopic composition in silicate-melt inclusions in olivine

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Fig. 10. Behaviour of fluid oversaturated silicate-melt inclusions during high-temperature experiments, and cooling. (a) At room temperature, the inclusion consists of partly devitrified glass (G), vapour (V), water (L) and salt (S). (b) On progressive heating, the glass appears more transparent (revitrification?) and the salt progressively melts in the aqueous fluid. Melting of the silicate glass begins at 700°C. (c) At 800°C, the inclusion consists of silicate melt, high-salinity liquid and vapour bubble. A single daughter mineral is still present in the inclusion (indicated with an arrow). (d) At 1000°C the inclusion has not yet reached the homogenisation: the high-salinity fluids and the silicate glass will not homogenise, since they were trapped simultaneously as immiscible fluid phases. Total homogenisation is reached only by forcing the system up to 1250°C. (e) During cooling from 800°C, the salt nucleates again at temperature below 500°C. At room temperature, the inclusion consists of transparent glass, high-salinity fluids and a bubble. (f) At cooling from total homogenisation, first, a bubble nucleates and then a second bubble containing the high-salinity fluid forms.

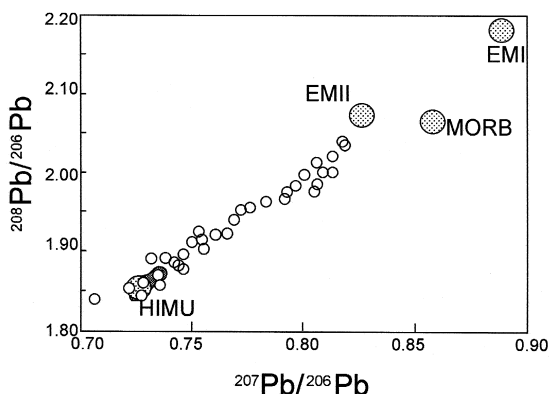


Fig. 11. Variation of the Pb isotopic composition (white dots) for single silicate-melt inclusions hosted in olivine and clinopyroxene of the Mangaia Basalt; the isotopic composition for Mangaia whole-rock lavas is also reported (dark grey area). Analyses  $2\sigma$  errors are not indicated. Large dotted circles represent the four end members of the mantle tetrahedron projected on the  $^{208}\text{Pb}/^{206}\text{Pb}$  vs.  $^{207}\text{Pb}/^{206}\text{Pb}$  plane. The silicate-melt inclusion data span a much wider isotopic range (almost 50% of oceanic island basalts) than the whole-rock lavas. This feature is explained in terms of a two component mixing, see text. Redrawn after Saal et al. (1998).

crystals ( $\text{Fo}_{87-91}$ ) and quenched glasses from primitive tholeiitic lava flows and pillow lavas from the neovolcanic rift zone (the Reykjanes and Hengill fissure swarms) in Iceland, which were supposed to represent primary mantle melts (Gurenko and Chaudisson, 1997). The inclusions contained variable amounts of B, whereas  $\delta^{11}\text{B}$  values were nearly constant and  $= -11.3$  ( $\sigma \pm 1.9$ )‰. In the Icelandic mantle, the B contents recalculated on the basis of melt-inclusion compositions were, thus, different (Reykjanes  $= 0.21 \pm 0.05$  ppm; Hengill  $= 0.13 \pm 0.03$  ppm) and reflect zones with variable B concentration but similar  $\delta^{11}\text{B}$ .

Trace-elements analyses of the silicate glass may illustrate mixing and differentiation processes. Métrich et al. (1991) used rare earth element distribution in melt inclusions in olivine and lavas to identify mixing processes in the magma chamber of Lakagigar in Iceland. Enriched LREE patterns defined quartz–tholeiite compositions, while the second component had flat REE pattern. Hervig and Dunbar (1992) used linear trends of trace elements in melt inclusions to show how mixing processes were responsible for the chemical zonation observed in the Bishop tuff. In a similar way Lu et al. (1992)

outlined the amount of crystal fractionation in the same rocks. At Mt. Vesuvius, Vaggelli et al. (1993) calculated the amount of fractional crystallisation, using the variation in composition of silicate-melt inclusions within single phenocrysts, from the core to the rim of the host grains.

#### 4.3. The volatile contents of silicate-melt inclusions

Silicate-melt inclusion studies are a viable way to assess magmatic volatile contents prior to, and during crystallisation processes. There is considerable evidence that silicate-melt inclusions may have retained their original volatile content: very high water and  $\text{CO}_2$  contents have been measured in silicate-melt inclusions (e.g.,  $\text{H}_2\text{O}$  up to 7–8 wt.%;  $\text{CO}_2$  10–15,000 ppm, in silicic magmas) with corresponding very high saturation pressures.

The measurement of the  $\text{H}_2\text{O}$  and  $\text{CO}_2$  content of the inclusion glass allows the estimation of the preruptive volatile evolution of the magma. Anderson et al. (1989) measured  $\text{H}_2\text{O}$  and  $\text{CO}_2$  contents in melt inclusions from the Bishop Tuff and revealed a progressive  $\text{H}_2\text{O}$  decrease and  $\text{CO}_2$  increase in glass, from the early to the late ash-flows. At Mt. Vesuvius, Raia et al. (2000) reported variable amount of aqueous volatile phases in silicate-melt inclusions from lavas and scoriae of medieval (AD 472 to 1139) and modern (AD 1631–1944) interplinian activity. In the silicate glass, the water content variation coupled with incompatible element trends indicated crystallisation of magmatic fluid-saturated silicate melt for the medieval magmas, while the modern magmas resulted from crystallisation under fluid-undersaturated conditions. The authors further presented clear relationships between the volatile evolution and the eruptive behaviour of Vesuvius in medieval and modern times.

In another study, Barclay et al. (1996) analysed the volatile ( $\text{H}_2\text{O}$  and  $\text{CO}_2$ ) contents of silicate-melt inclusions in phenocrysts of quartz and feldspar in peralkaline rhyolites from volcanoclastic deposits of different eruptive styles in Major Island, New Zealand. These authors found a similar water content in all melt inclusions (4.5 wt.%) and concluded that the differences in eruptive style were not related to the  $\text{H}_2\text{O}$  content of the magma, but reflected different rates of magma ascent and supply. Similar results

were obtained on Plinian and Pelean ejecta of Mount Pelée in Martinique (Martel et al., 1998), where the preeruptive content of water in the magma was similar and the efficiency of explosive degassing was controlled by the mode of magma ascent.

Care must be taken when interpreting H<sub>2</sub>O and CO<sub>2</sub> data from silicate-melt inclusions, as diffusion processes may have occurred. Dissociation of water in the inclusion glass might result in diffusion of H<sup>+</sup> to the host mineral with resulting oxidation and consequent precipitation of magnetite or hematite within the inclusions (i.e., oxidation of Fe<sup>2+</sup>), lowering the original water content of the melt substantially (Sobolev et al., 1991). CO<sub>2</sub> may be partitioned into the shrinkage bubble. The presence of dislocations around the inclusion cavity may also promote

CO<sub>2</sub> diffusion, especially in olivine crystals (Viti and Frezzotti, 2001).

Revitrication of the inclusions may result in considerable water loss during reheating (Sobolev and Danyushevsky, 1994). Raia et al. (2000) constrained the extent of H<sub>2</sub>O loss during high-temperature experiments, in silicate-melt inclusions from lavas and scoriae from the Vesuvius. The water contents of silicate-melt inclusions heated at 1200°C for 24 h resulted lower by one order of magnitude than those in unheated silicate-melt inclusions. Ihinger et al. (1994) used experimental heating runs in hydrous rhyolitic glass to outline a two-step release process: the first at ~500°C corresponding to molecular water and the latter at ~900°C corresponding to hydroxyl species.

Table 3  
Sulphur concentrations in homogenised glass of silicate-melt inclusions from rocks of different localities

Location	Host mineral	S (wt.%)	FeO <sub>tot</sub> (wt.%)	SiO <sub>2</sub> (wt.%)	References
<i>Batan Islands, Philippines</i>					
<i>Mantle xenoliths#</i>	Ol	0.04–0.25#	1.3–2.8	58–62	Métrich et al., 1999
<i>Basalts#</i>	Ol	0.08–0.15#	7.3–9.1	44–49	Métrich et al., 1999
<i>Tahaa Island, Polynesia</i>					
<i>Mantle xenoliths and basalts</i>	Ol, Px	0.01–0.15	3.8–9.0	50–63	Schiano et al., 1992
Various locations, <i>mantle xenoliths</i>	Ol, Opx, Cpx	0.02–0.05	0.8–5.1	54–63	Schiano and Clocchiatti, 1994
Kilauea, Hawaii, <i>basalts</i>	Ol	0.00–0.18	7.8–13.4	48–53	Anderson and Brown, 1993
Lakagigar, Iceland, <i>basalts</i>	Ol, Px, Pl	0.09–0.18	9.0–12.8	49–50	Métrich et al., 1991
<i>M. Ema</i>					
M. Rossi, <i>basalts</i>	Ol, Cpx, Pl	0.07–0.28	10.2–11.9	44–51	Clocchiatti and Métrich, 1984
M. Silvestri, <i>basalts</i>	Ol, Pl	0.11–0.36	9.2–11.1	44–51	Clocchiatti and Métrich, 1984
<i>Historic alkali basalts</i>	Ol, Cpx, Pl	0.01–0.22	8.1–10.4	44–52	Métrich and Clocchiatti, 1989
<i>Vesuvius</i>					
<i>Historic lavas</i>	Ol, Cpx	0.07–0.34	2.2–9.2	45–55	Vaggelli et al., 1993
1944 <i>K-tefrites</i>	Ol, Cpx, Lc	0.02–0.24	6.2–9.37	46–49	Marianelli et al., 1999
Vulsini, Roman province	Ol	0.11–0.25	5.8–7.4	47–51	Kamenetsky et al., 1995
Stromboli, <i>basalts</i>	Ol, Px	0.09–0.11	9.1–10.2	52–53	Allard et al., 1994
<i>Various locations</i>					
<i>Basalts and andesites</i>	Ol, Pl	0.05–0.33	4.8–11.8	51–59	Anderson, 1982
Mt. St. Helens, 1980, <i>dacites</i>	Pl	0.01	1.9	69.9	Rutheford et al., 1985
Eikeren-Skrim <i>granite</i>	Qtz	0.00–0.02	2.5–2.7	68–70	Hansteen and Lustenhouwer, 1990
Pinatubo, 1991 <i>rhyolites</i>	Ol, Pl	0.01–0.07	0.6–1.3	75–77	Westrich and Gerlach, 1992
Nevado de Ruiz, 1985 <i>dacites</i>	Anh, Opx, Pl	0.01–0.02	1.3–2.5	72–77	Fournelle, 1985
Mt. Genis, <i>granite</i>	Qtz	0.00–0.07	0.1–4.7	67–78	Frezzotti, et al., 1992
Bishop tuff, <i>rhyolites</i>	Qtz	0.01	0.5–0.6	77	Anderson et al., 1989

Ol = olivine, Px = pyroxene, Opx = orthopyroxene, Cpx = clinopyroxene, Pl = Plagioclase, Lc = leucite, Anh = anhydrite, # = concentrations in glasses that are oversaturated with sulphur.

Other volatile phases than  $H_2O$  and  $CO_2$  are very useful to delineate the preruptive degassing behaviour in magmas, since they are little affected by posttrapping evolution of inclusions. Lowenstern (1995) has recently summarised Cl, S and F data from high-silica magmas from more than 20 localities, concluding that felsic magmas may contain substantial amounts of Cl (up to 3000 ppm) and F (up to 1500 ppm) and low S (< 200 ppm). Very high Cl contents (1 wt.%) are reported in silicate-melt inclusions in alkaline rhyolites, showing a strong positive correlation between melt Na content and Cl solubility (Lowenstern, 1993).

#### 4.4. Behaviour of sulphur species

Although  $H_2O$  and  $CO_2$  constitute the most common volatile species in most magmas, understanding, the preruptive abundance and distribution of sulphur in melts is of paramount importance for its major role in assessing volcanic eruptions, and in modelling the geochemical cycle of elements in subduction zones. Some analyses of concentrations of sulphur in silicate-melt inclusions in basaltic and silicic magmas from different localities are reported in Table 3. Sulphur concentrations are higher in basaltic melts (up to 0.36 wt.%) and decrease considerably in high-silica melts (0.07 wt.%).

In relatively oxidised magmas dissolved sulphur will occur dominantly as sulphate, while in more reduced conditions, the magma contains substantial amounts of sulphur as sulphide. Further complications result from the fact that reduced sulphur-bearing melts can be saturated with a FeS-rich Fe–S–O liquid, commonly indicated as “sulphide melt”. Studies of silicate-melt inclusions have shown that sulphide is the dominating sulphur species in basic and ultrabasic MORB and OIB magmas. Immiscible sulphide globules are commonly observed in silicate-melt inclusions in alkali-basalt and in oceanic island mantle xenoliths (cf. Andersen and Neumann, 2001), indicating a direct relationship between sulphur solubility and FeO content of the melt (Fig. 12). It is worth noting, however, that the presence of immiscible droplets of sulphide melts within silicate-melt inclusions *does not always represent a primary feature* (e.g., sulphur saturation of the trapped magma), but might be induced by other processes (e.g., inter-

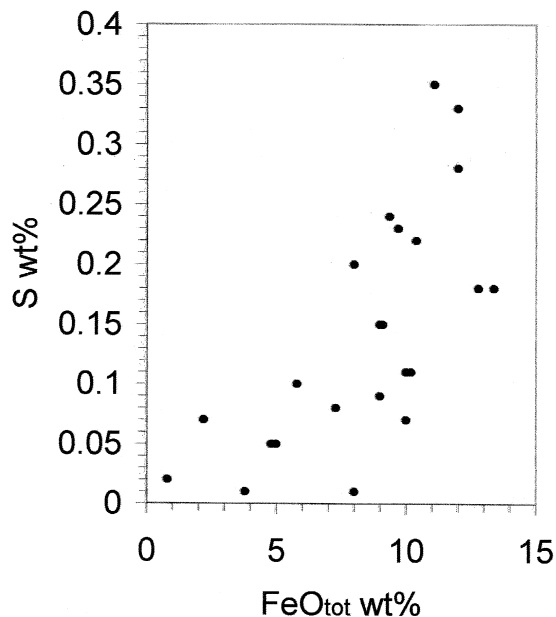


Fig. 12. The relation between S and  $FeO_{tot}$  in glasses of inclusions in lavas and intrusive rocks from different localities worldwide. Sources of analyses are given in Table 3.

*nal* crystallisation processes during the after-trapping evolution of melt inclusions, or even reheating of inclusions in the lab).

Analyses of sulphur concentrations in silicate-melt inclusions may potentially give important indications on its preruptive degassing behaviour. Sulphur concentrations in glass of inclusions from basaltic lavas at Etna (Clocchiatti and Métrich, 1984; Métrich and Clocchiatti, 1989) allowed us to delineate a two-step degassing process: a first degassing episode occurring in the magma chamber, and a second stage, taking place at the surface. One of the best indications, so far, of a S-rich fluid phase present at depth in subduction zone magmas was very recently reported by Métrich et al. (1999). These authors described magmatic immiscibility between S-rich silicate melt, sulphide melt and  $H_2O$ –S-rich vapour in mantle xenoliths from the Batan Philippine Island. Sulphur-rich aqueous fluids are present as  $H_2O$  fluid inclusions containing sulphide globules. The authors concluded that the sulphur was inherited and derived from a subducting slab, through aqueous fluids or hydrous melts. Furthermore, the heterogeneous distribution of sulphur among fluid and melt phases

may in part explain the highly variable S-content present in arc-magma.

Speciation of sulphur in the gaseous phase is also dependent on  $f_{O_2}$  conditions. Experimental studies (Katsura and Nagashima, 1974) have shown that  $H_2S$  is the dominant gaseous phase under reduced conditions ( $f_{O_2} = QFM - QFM + 1$ ), while higher  $f_{O_2}$  conditions, would stabilise  $SO_x$ -dominated fluids. Despite the large S-bearing gaseous emissions associated with eruptions, especially in oxidised subduction-related environments (cf. Pinatubo, El Chichon, etc.), S-bearing fluid species (mainly  $SO_2$  and  $H_2S$ ) are almost absent in fluid and melt inclusions in erupted lavas and associated rocks. Presence of  $SO_2$  fluids have been identified only in a few cases: by microthermometry in the  $CO_2$ -rich bubbles of silicate-melt inclusions in clinopyroxene phenocrysts from calc-alkaline lavas of Panarea (Aeolian Islands; Nazzareni et al., 1997), and 1–2 mole% of  $SO_2$  were detected by Raman analyses in  $CO_2$ -rich melt-free inclusions from metasomatised mantle xenoliths from Tenerife (Canary Islands; Frezzotti, unpublished data).

### 5. Significance of silicate-melt inclusions in plutonic rocks

Although first recognised about 150 years ago by Sorby, silicate-melt inclusions in plutonic rocks were not considered an issue during the classic years of study of silicate-melt inclusions in volcanic rocks. This was mainly for the idea that in plutonic rocks, all magmatic stages are cancelled by the very long cooling history of the host rocks (i.e., Weisbrod, 1981). Additional uncertainties were given by the fact that most petrologists have been unaware of what a silicate-melt inclusion in a plutonic rock should “look like”.

In shallow intrusions, recent studies have documented that silicate-melt inclusions, although devitrified to different extents, might preserve primary characters. Frezzotti (1992) identified crystallised silicate-melt inclusions with large gas bubbles in quartz crystals from M. Genis Hercynian leucogranite in Sardinia. Upon heating, the inclusions revitrify and melt at variable temperatures (750–900°C). At these high temperatures, two liquids are present in the

inclusions: a silicate melt and brines, corresponding to the simultaneous trapping of magmatic fluids and silicate melt (Fig. 7a). The saline brines represent magmatic fluids exsolved from the granite magma at the final stages of crystallisation; these are the direct result of liquid immiscibility and not concentrated by boiling of aqueous fluids. Chemical analyses of the glass show that only a few inclusions might be considered representative for high-silica granite composition (Fig. 13). Most analyses, in fact, clearly show two distinct evolution trends: (a) remelting of host quartz during analyses, characterised by a progressive increase in the  $SiO_2$  content of the glass; and (b) change of the primary composition via alteration, with progressively more feldspar-like composition of the glass.

Silicate-melt inclusions, thus, yield direct evidence of fluid composition at magmatic stage in study intrusions. Further evidence of hypersaline (i.e., salt melts) magmatic fluid composition have been reported by other authors at the Eikeren-Skrim granite in Norway (Hansteen and Lustenhouwer, 1990) and in intrusive rocks present as xenoliths in lavas,

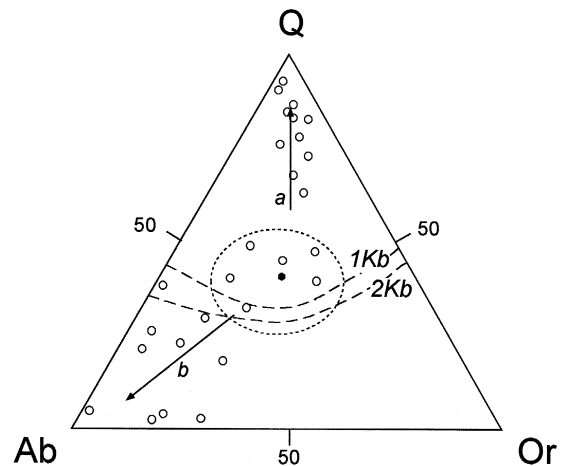


Fig. 13. Quartz (Q)–Albite (Ab)–Orthoclase (Or) in a percent-by-weight ternary phase diagram, showing the major element composition of silicate glasses from reomogenised silicate-melt inclusions (white dots) and whole rock (black dot) from Monte Genis granite. The figure shows that very few analyses might be representative of whole-rock composition. Two opposite evolution trends are recorded by the silicate-melt inclusions: (a) overheating and remelting of host quartz; (b) alteration of the inclusions by fluids with enrichment in Na (redrawn after Frezzotti, 1992).

notably at Ascencion Island, (Roedder and Coombs, 1967), at Pantelleria (De Vivo et al., 1992, 1993; Lowenstern, 1994a,b), and at Ventotene (De Vivo et al., 1994), and suggested that hypersaline fluids may be a common feature of felsic magmas. At Ventotene, De Vivo et al. (1994) reported magmatic immiscibility between silicate melt and brines in presence of CO<sub>2</sub> fluids.

Only if intrusion cooled very fast silicate-melt inclusions may preserve pristine chemical characters. Webster et al. (1997) examined totally recrystallised inclusions in quartz from a pegmatite occurring in Variscan granites associated to mineralised greisen veins at the Ehrenfriedersdorf Sn–W deposit in central Erzgebirge (Germany). The inclusions were composed by extremely differentiated peraluminous glass, strongly enriched in Sn (1000–2000 ppm), F, P, Li, Rb, Cs, Nb, Ta, Be.

Large amounts of data on the homogenisation temperatures of silicate-melt inclusions in plutonic rocks have been collected. Li (1994) reported thousands of measurements of homogenisation temperatures of silicate-melt inclusions in plutonic rocks, both in accessory phases (i.e., zircon) and in primary phases (i.e., quartz, pyroxene, and olivine). He concluded that measured temperatures are representative of the crystallising condition of host rocks. The extensive compilation of Th data by Thomas (1991) and Thomas et al. (1996) indicated that there is a remarkable correlation between Th and composition in plutonic rocks, higher Th being associate to lower-silica rocks.

With all the difficulties and limitations that the study of silicate-melt inclusions in plutonic rocks certainly has, it is clear that their study may have important consequences for magmatic studies. The potential of silicate-melt inclusion studies was investigated in a recent paper by Touret and Frezzotti (1993) that described how rests of melt inclusions (magmatic remnants) might be identified in quartz crystals from plutonic rocks. These authors concluded that in plutonic environments the primary goal of silicate-melt inclusion analyses is the identification of the magmatic stage evolution of crystallising rocks. In some cases, the characterisation of magmatic fluids is still possible, even in those inclusions that experienced an irreversible loss of primary chemical characters of the glass.

## 6. Melt inclusions in mantle xenoliths

The study of melt inclusions in mantle xenolith has recently drawn much attention by many petrologists since it may give important information for the interpretation of metasomatic processes, causing the introduction of incompatible elements into depleted regions of otherwise fertile mantle. One of important conclusions from several studies of melt inclusions in xenoliths minerals has been that they may preserve the composition of high-pressure melts, because the large elastic modulus of their host phase prevents them from decompression during ascent and from chemical reequilibration at low pressure. By contrast, interstitial glasses in xenoliths continuously reequilibrate and their chemistry largely reflects low-pressure conditions (Schiano and Bourdon, 1999; Schiano et al., 2000).

Almost all studies of melt inclusions in mantle xenolith have revealed the presence of alkali-rich high-silica melt ± carbonates or CO<sub>2</sub> fluids. These high-silica melts differ substantially from the inclusions generally found in alkali-basalts, since they are very rich in Cl, CO<sub>2</sub>, water, and LREE and might, thus, be responsible for the patent and cryptic metasomatic processes observed in the host rocks. About the role and formation of these high-silica melts in mantle conditions, there is at present quite a lively discussion, involving about ten possible genetic hypotheses, summarised by Andersen and Neumann (2001). Nevertheless, since trace-element analyses of the silicate glass in the inclusions might explain the increase in incompatible elements observed in the mantle rocks, most authors (cf., Schiano and Clocchiatti, 1994; Neumann et al., 1995; Wulff-Pedersen et al., 1996, 1997) have agreed upon the possible role of fluid-rich silicic melts as metasomatic agents.

Melt inclusions in xenoliths are a potential powerful tool to investigate carbonate melts in the mantle. Primary carbonates in peridotite xenoliths have been reported only in rare cases, e.g., Spitzbergen (Ionov et al., 1996) and mantle metasomatism by carbonate melts has been invoked on indirect evidence only (Yaxley et al., 1991; Ionov et al., 1993). Two aspects are significant to explain the absence of carbonates in mantle rocks. Firstly, carbonate melts are ephemeral as they will be consumed during reactions

with the mantle wall rocks (Green and Wallace, 1988); secondly, carbonates coexisting with silicates could not survive transport, even in the fastest ascending magma, because of rapid decarbonation upon decompression (Canil, 1990). Conversely, primary carbonates deriving from carbonate melts could be occasionally preserved in melt inclusions, and in interstitial glasses in mantle xenoliths. These are found as immiscible phases occurring along with a silicate melt (Fig. 7d). In all occurrences, overall agreement exist in the composition of the carbonates (mainly dolomite), but there is strong discrepancy on the nature of the other glass component associated with carbonate: (1) association of carbonate with high-silica and alkali melt as found in Tahaa archipelago (Schiano et al., 1992) and the Kerguelen Islands (Schiano et al., 1994); (2) association of carbonates with ultrabasic melts as reported in Spitzbergen (Amundsen, 1987) and La Gomera, Canary Islands (Frezzotti et al., 1994). Carbonates and associated silicate glasses of variable composition result from separation of immiscible silicate melt and a carbonate melt.

Melt inclusion investigations suggest that primary carbonate-rich melts in the mantle are far more widespread than derived from literature study. Migration of hot carbonate melt has extremely important consequences for the degassing of the mantle. Fluid release may, in fact, promote cracking and facilitate ascent of basaltic melts. In addition, upwardly migrating carbonate melts may unmix and degas large amounts of CO<sub>2</sub>-rich supercritical fluids that might in part being trapped as fluid inclusions. In this hypothesis, a large part of the CO<sub>2</sub> inclusions present in mantle xenoliths (cf. Andersen and Neumann, 2001) might originate through degassing of ephemeral carbonate melts or carbonates.

## 7. Concluding remarks

In this brief overview, I have attempted to summarise possible information that can be achieved by silicate-melt inclusion studies, illustrating some basic principles of this technique, and reporting some major temperature and chemical data, so far obtained,

that may be useful to understand magmatic processes.

A successful silicate-melt inclusion investigation is based on the assumption that inclusions have remained closed, and selection of right inclusions should be based on careful petrographic and high-temperature observations. With this in mind, a simple petrographic microscope is sufficient to characterise magmatic processes, such as immiscibility phenomena. Chemical data might be obtained through various analytical methods. Although they represent “second-hand” figures (silicate-melt inclusions must be revitrified through laboratory experiments), they are better indicators of the geochemical evolution of major trace and incompatible elements in the magmas, than host crystals and/or lavas. For these reasons, I expect a great increase of interest in the forthcoming years by most igneous petrologists. This tendency has already started as shown by the exponentially increasing number of papers published on this subject in the last 5 years, which also indirectly indicates that this kind of studies is not anymore confined to inclusion specialists.

General suggestions for the future will go along with the developments of analytical techniques and in particular with the fast-expanding new laser techniques. Future studies should concentrate on isotope analyses. Laser analytical techniques might bring to “in situ” possibility of dating silicate-melt inclusions by Ar–Ar methods expanding our knowledge on the crystallisation processes. Major expectations concern the newly developing techniques, which combine UV laser optics and mass spectrometry to analyse stable isotopes in individual silicate-melt inclusions. Knowledge of stable isotope fractionation between dissolved and gaseous volatiles, together with solubility measurements, may be used to reconstruct the isotopic composition of the undegassed magma. This will also help to characterise source regions of volatile phases present in the magma.

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## References

- Allard, P., Carbonelle, J., Métrich, N., Loyer, H., Zettwoog, P., 1994. Sulphur output and magma degassing budget of Stromboli Volcano. *Nature* 368, 326–330.
- Amundsen, H.E.F., 1987. Evidence for liquid immiscibility in the upper mantle. *Nature* 327, 692–695.
- Andersen, T., Neumann, E.R., 2001. Fluid inclusions in mantle xenoliths. *Lithos* 55, 299–318 (this volume).
- Anderson, A.T. Jr., 1976. Magma mixing: petrological processes and volcanological tools. *J. Volcanol. Geotherm. Res.* 1, 3–33.
- Anderson, A.T. Jr., 1982. Parental basalts in subduction zones: implication for continental evolution. *J. Geophys. Res.* 87, 7047–7060.
- Anderson, A.T. Jr., Brown, G.G., 1993. CO<sub>2</sub> contents and formation pressures of some Kilauean melt inclusions. *Am. Mineral.* 78, 794–803.
- Anderson, A.T. Jr., Wright, T.L., 1972. Phenocrysts and glass inclusions and their bearing on oxidation and mixing of basaltic magmas, Kilauea Volcano, Hawaii. *Am. Mineral.* 57, 188–216.
- Anderson, A.T., Newman, S., Williams, S.N., Druitt, T.H., Skirius, C., Stopler, E., 1989. H<sub>2</sub>O, CO<sub>2</sub>, Cl and gas in plinian and ash-flow rhyolite. *Geology* 17, 221–225.
- Bacon, C.R., Newman, S., Stopler, E., 1992. CO<sub>2</sub> in some Kilauean melt inclusions and the volcanology of Kilauea. *Am. Mineral.* 78, 794–803.
- Barclay, M.R., Carroll, M.R., Houghton, B.F., Wilson, C.J.N., 1996. Pre-eruptive volatile content and degassing history of an evolving peralkaline volcano. *J. Volcanol. Geotherm. Res.* 74, 75–87.
- Belkin, H.E., 1994. Microthermometric investigation: Th and Tm. Practical and theoretical aspects. In: De Vivo, B., Frezzotti, M.L. (Eds.), *Fluid Inclusions in Minerals: Methods and Applications*. Pontignano (Siena): Short Course of the IMA Working Group “Inclusions in Minerals”. Virginia Polytechnic Institute and State Univ. Press, Blacksburg, VA, pp. 7–25.
- Burnham, C.W., 1979. Magmas and hydrothermal fluids. In: Barnes, H.L. (Ed.), *Geochemistry of Hydrothermal Ore Deposits*. 2nd edn. Wiley, New York, pp. 71–136.
- Canil, D., 1990. Experimental study bearing on the absence of carbonate in mantle derived xenoliths. *Geology* 18, 1011–1013.
- Clocchiatti, R., 1975. Les inclusions vitreuses des cristaux de quartz. Etude optique, termo-optique et chimique. Application géologiques. *Mem. Soc. Geol. Fr.*, 54.
- Clocchiatti, R., Krasov, N., 1979. Cristallisation fractionnée et immiscibilités dans les liquides silicate calco-alcalins piégés dans les phénocristaux des plagioclases des laves du volcan Karimsky (Kamchatka, USSR). *C. R. Acad. Sci. Paris, Sér. D* 289, 1–4.
- Clocchiatti, R., Massare, D., 1985. Experimental crystallisation growth in melt inclusions: the possibility and limitation of the method. *Contrib. Mineral. Petrol.* 89, 193–204.
- Clocchiatti, R., Métrich, N., 1984. Témoignages de la contamination dans les produits des éruptions explosives des M. Silvestri (1892) et M. Rossi (1669) (Mt. Etna). *Bull. Volcanol.* 47, 909–928.
- Deicha, G., 1955. Les lacunes des cristaux et leurs inclusions fluides. Massons, Paris.
- Deloule, E., Paillat, O., Pichavant, M., Scaillet, R., 1995. Ion microprobe determination of water in silicate glasses: methods and applications. *Chem. Geol.* 125, 19–28.
- De Vivo, B., Frezzotti, M.-L., 1994. Evidence for magmatic immiscibility in Italian subvolcanic systems. In: De Vivo, B., Frezzotti, M.-L. (Eds.), *Fluid Inclusions in Minerals: Methods and Applications*. Pontignano (Siena): Short Course of the IMA Working Group “Inclusions in Minerals”. Virginia Polytechnic Institute and State Univ. Press, Blacksburg, VA, pp. 209–215.
- De Vivo, B., Frezzotti, M.-L., Mahood, G., 1992. Fluid inclusions in xenoliths yield evidence for fluid evolution in peralkaline granitic bodies at Pantelleria (Italy). *J. Volcanol. Geotherm. Res.* 51, 78–90.
- De Vivo, B., Frezzotti, M.-L., Lima, A., 1993. Immiscibility in magmatic differentiation and fluid evolution in granitoids xenoliths at Pantelleria: fluid inclusion evidence. *Acta Vulcanol.* 3, 195–202.
- De Vivo, B., Torok, K., Ayuso, R.A., Lima, A., Lirer, L., 1994. Fluid inclusion evidence for magmatic silicate–saline immiscibility and geochemistry of alkaline xenoliths from Ventotene Island (Italy). *Geochim. Cosmochim. Acta* 62, 55–78.
- Fournelle, J., 1985. Anhydrite in Nevado de Ruiz November 1985: relevance to the sulfur problem. *J. Volcanol. Geotherm. Res.* 39, 189–201.
- Frezzotti, M.-L., 1992. Magmatic immiscibility and fluid phase evolution in the M. Genis granite (SE Sardinia). *Geochim. Cosmochim. Acta* 56, 21–33.
- Frezzotti, M.-L., De Vivo, B., Clocchiatti, R., 1991. Melt–mineral–fluid interactions in ultramafic nodules on alkaline lavas from M. Etna (Sicily, Italy) as recorded by melt and fluid inclusions. *J. Volcanol. Geotherm. Res.* 47, 209–219.
- Frezzotti, M.-L., Ghezzi, C., Stefanini, B., 1992. The Calabona intrusive complex (Sardinia Italy): evidence for a porphyry copper system. *Econ. Geol.* 87, 201–212.
- Frezzotti, M.-L., Touret, J.L.R., Lustenhouwer, W., Neumann, E.-R., 1994. Melt and fluid inclusions in dunite xenoliths from

- La Gomera, Canary Islands: tracking the mantle metasomatic fluids. *Eur. J. Mineral.* 6, 805–817.
- Frost, B.R., Touret, J.L.R., 1989. Magmatic CO<sub>2</sub> and saline melts from the Sybille monzosyenite, Laramie anorthosite complex. *J. Petrol.* 29, 669–729.
- Green, D.H., Wallace, M.E., 1988. Mantle metasomatism by ephemeral carbonate melts. *Nature* 336, 459–462.
- Gurenko, A.A., Chaudisson, M., 1997. Boron concentration and isotopic composition of the Icelandic mantle; evidence from glass inclusions in olivine. *Chem. Geol.* 135, 21–34.
- Gurenko, A.A., Sobolev, V.A., Kononkova, N.N., 1991. Petrology of the primary magma of the Reykjanes Peninsula rift tholeiites. *Geochem. Int.* 28, 58–71.
- Hansteen, T., Lustenhouwer, W.J., 1990. Silicate-melt inclusions from a mildly peralkaline granite in the Oslo Paleorift, Norway. *Mineral. Mag.* 54, 195–206.
- Hervig, R.L., Dunbar, N.W., 1992. Cause of chemical zoning in the Bishop (California) and Bandelier (New Mexico) magma chambers. *Earth Planet. Sci. Lett.* 111, 97–108.
- Ihinger, P.D., Hervig, R.L., McMillian, P.F., 1994. Analytical methods for volatiles in magmas. *Volatiles in Magmas*. In: Carroll, M.R., Holloway, J.R. (Eds.), *Rev. Mineral.*, vol. 30, pp. 67–129.
- Ionov, D.A., Dupuy, C., O'Reilly, S.Y., Kopytova, M.G., Genshaft, Y.S., 1993. Carbonated peridotite xenoliths from Spitzbergen: implications for trace element signature of mantle carbonate metasomatism. *Earth Planet. Sci. Lett.* 119, 283–297.
- Ionov, D.A., O'Reilly, S.Y., Kopytova, M.G., Genshaft, Y.S., 1996. Carbonate-bearing mantle peridotite xenoliths from Spitzbergen: phase relationships, mineral compositions and trace element residence. *Contrib. Mineral. Petrol.* 125, 375–392.
- Kamenetsky, V., Clocchiatti, R., 1994. Melt inclusions as a potential guide into Mt. Etna magma chemistry. In: De Vivo, B., Frezzotti, M.-L. (Eds.), *Fluid Inclusions in Minerals: Methods and Applications*. Pontignano (Siena): Short Course of the IMA Working Group "Inclusions in Minerals". Virginia Polytechnic Institute and State Univ. Press, Blacksburg, VA, pp. 363–376.
- Kamenetsky, V., Clocchiatti, R., 1996. Primitive magmatism of Mt. Etna: insights from mineralogy and melt inclusions. *Earth Planet. Sci. Lett.* 142, 553–572.
- Kamenetsky, V., Metrich, N., Cioni, R., 1995. Potassic primary melts of vulsini (Roman province): evidence from mineralogy and melt inclusions. *Contrib. Mineral. Petrol.* 120, 186–196.
- Kamenetsky, V., Crawford, A.J., Eggins, S., Muehe, R., 1997. Phenocrysts and melt inclusion chemistry of near axis seamounts, Vula Fa Ridge, Lau Basin; insight into mantle wedge melting and the addition of subduction components.
- Katsura, T., Nagashima, S., 1974. Solubility of sulfur in some magmas at 1atm. *Geochim. Cosmochim. Acta* 28, 517–531.
- Kovalenko, V.I., Hervig, R.I., Sheridan, M.F., 1988. Ion microprobe analyses of trace elements in anorthoclase, hedenbergite, aenigmatites, quartz, apatite, and glass in pantellerite: evidence for high H<sub>2</sub>O contents in pantellerite melt. *Am. Mineral.* 73, 1038–1045.
- Li, Z., 1994. The silicate-melt inclusions in igneous rocks. In: De Vivo, B., Frezzotti, M.L. (Eds.), *Fluid Inclusions in Minerals: Methods and Applications*. Pontignano (Siena): Short Course of the IMA Working Group "Inclusions in Minerals". Virginia Polytechnic Institute and State Univ. Press, Blacksburg, VA, pp. 73–94.
- Lowenstern, J.B., 1993. Evidence for a copper-bearing fluid in magma erupted at the Valley of Ten Thousand Smokes, Alaska. *Contrib. Mineral. Petrol.* 114, 409–421.
- Lowenstern, J.B., 1994a. Dissolved volatiles concentrations in ore-forming magma. *Geology* 22, 893–896.
- Lowenstern, J.B., 1994b. Chlorine, fluid immiscibility, and degassing in peralkaline magmas from Pantelleria, Italy. *Am. Mineral.* 79, 353–369.
- Lowenstern, J.B., 1995. Applications of silicate-melt inclusions to the study of magmatic volatiles. *Magmas, Fluids, and Ore Deposits*. In: Thompson, J.F.H. (Ed.), *MAC Short Course*, vol. 23, pp. 71–100, Victoria, British Columbia.
- Lowenstern, J.B., Mahood, G.A., 1991. New data on magmatic H<sub>2</sub>O contents of pantellerites with implication for petrogenesis and eruptive dynamics at Pantelleria. *Bull. Volcanol.* 54, 78–83.
- Lu, F.Q., Anderson, A.T., Davies, A.M., 1992. Melt inclusions and crystal-liquid separation in rhyolitic magmas of the Bishop tuff. *Contrib. Mineral. Petrol.* 110, 113–120.
- Manley, C.R., 1996. Morphology and maturation of melt inclusions in quartz phenocrysts from the Badlands rhyolite flow, southwestern Idaho. *Am. Mineral.* 81, 158–168.
- Marianelli, P., Sbrana, A., Metrich, N., 1999. Shallow and deep reservoirs involved in magma supplies of the 1944 eruption of Vesuvius. *Bull. Volcanol.* 61, 48–63.
- Martel, O., Pichavant, M., Bourdier, V., Traineau, J., Holz, F., Scaillet, B., 1998. Magma storage conditions and control of eruption regime in silicic volcanoes: experimental evidence from Mt. Pelée. *Earth Planet. Sci. Lett.* 156, 89–99.
- Métrich, N., Clocchiatti, R., 1989. Melt inclusion investigation on the volatile behavior in historic Alkali-Basaltic magmas of Etna. *Bull. Volcanol.* 51, 185–198.
- Métrich, N., Sigurdson, H., Meyer, P.S., Devine, J.D., 1991. The 1783 Lakagigar eruption in Iceland: geochemistry, CO<sub>2</sub> and sulfur degassing. *Contrib. Mineral. Petrol.* 107, 435–447.
- Métrich, N., Schiano, P., Clocchiatti, R., Maury, R.C., 1999. Transfer of sulfur in subduction settings: an example from Batan Islands (Luzon volcanic arc, Philippines). *Earth Planet. Sci. Lett.* 167, 1–14.
- Nakamura, M., Shimakita, S., 1984. Dissolution and syneutrimpositional change of melt inclusion in plagioclase. *Earth Planet. Sci. Lett.* 161, 119–133.
- Nazzareni, S., Frezzotti, M.-L., Peccerillo, A., Zanazzi, P.F., 1997. Fluid inclusions and crystalchemical studies in calcalkaline lavas from Panarea (Aeolian Islands): preliminary data. *Plinius* 18, 153–154.
- Neumann, E.-R., Wulff-Pedersen, E., Johnsen, K., Andersen, T., Krogh, E., 1995. Petrogenesis of spinel harzburgite and dunite suite xenoliths from Lanzarote, eastern Canary Islands: implication for upper mantle. *Lithos* 35, 83–107.
- Nielsen, H.C., Sigurdson, H., 1981. Quantitative methods of electron microprobe analyses of sodium in natural and synthetic glasses. *Am. Mineral.* 66, 547–552.
- Nielsen, R.L., Michael, P.J., Sours-Page, R., 1998. Chemical and

- physical indicators of compromised melt inclusions. *Geochim. Cosmochim. Acta* 65, 831–839.
- Raia, F., Webster, J.D., De Vivo, B., 2000. Pre-eruptive volatile contents of Vesuvius magmas: constraints on eruptive history and behavior: I. The medieval and modern interplinian activities. *Eur. J. Mineral.* 12, 179–194.
- Reyf, F.G., Bazheev, Y.D., 1977. Magmatic chloride solutions and tungsten mineralisations. *Geochem. Int.* 14, 45–51.
- Roedder, E., 1965. Liquid CO<sub>2</sub> inclusions in olivine-bearing nodules and phenocrysts from basalts. *Am. Mineral.* 50, 1746–1782.
- Roedder, E., 1984. Fluid inclusions. *Rev. Mineral.* 12.
- Roedder, E., 1992. Fluid inclusion evidence for immiscibility in magmatic differentiation. *Geochim. Cosmochim. Acta* 56, 5–20.
- Roedder, E., Coombs, V.D., 1967. Immiscibility in granitic melts, indicated by fluid inclusions in ejected granitic blocks of Ascension Islands. *J. Petrol.* 8, 417–451.
- Roedder, E., Weiblein, P.W., 1970. Lunar petrology of silicate-melt inclusions, Apollo 11 rocks. *Apollo 11 Lunar Sci. Conf. Proceedings. Geochim. Cosmochim. Acta, Suppl.* (1), 801–837.
- Roedder, E., Weiblein, P.W., 1979. Melt Inclusions in Lunar Soil Fragments. *Proc. 9th Lunar Sci. Conf.*, Pergamon, New York, NY, pp. 495–522.
- Rutherford, M.J., Sigurdson, H., Carey, S., Davies, A., 1985. 1980 Eruption of Mt. S. Helens: 1. Melt composition and experimental phase equilibria. *J. Geophys. Res.* 90, 2929–2947.
- Saal, A.E., Hart, S.R., Shimizu, N., Hauri, E.H., Layne, G.D., 1998. Pb isotopic variability in melt inclusions from oceanic Island basalts, Polynesia. *Science* 283, 1481–1484.
- Schiano, P., Bourdon, R., 1999. On the preservation of mantle information in ultramafic nodules: glass inclusions within minerals versus interstitial glasses. *Earth Planet. Sci. Lett.* 169, 173–188.
- Schiano, P., Clocchiatti, R., 1994. World-wide occurrence of silica-rich melts in subcontinental and suboceanic mantle minerals. *Nature* 368, 621–624.
- Schiano, P., Clocchiatti, R., Joron, J.L., 1992. Melt and fluid inclusions in basalts and xenoliths from Tahaa Islands, Society archipelago: evidence for a metasomatized upper mantle. *Earth Planet. Sci. Lett.* 111, 69–82.
- Schiano, P., Clocchiatti, R., Shimizu, N., Weis, D., Mattielli, N., 1994. Cogenetic silica-rich and carbonate-rich melts trapped in mantle minerals in Kerguelen ultramafic xenoliths: implications for metasomatism in the oceanic upper mantle. *Earth Planet. Sci. Lett.* 123, 167–178.
- Schiano, P., Clocchiatti, R., Bourdon, B., Burton, K.W., Thellier, B., 2000. The composition of melt inclusions in minerals at the garnet spinel transition zone. *Earth Planet. Sci. Lett.* 174, 375–383.
- Shepherd, T.J., Rankin, A.H., Alderton, D.H., 1985. *A Practical Guide to Fluid Inclusion Studies*. Blackie & Sons, Glasgow.
- Sobolev, A.V., 1996. Melt inclusions in minerals as a source of principal petrological information. *Petrologiya* 4, 228–239.
- Sobolev, A.V., Kostyuk, V.P., 1975. Magmatic crystallisation based on a study of melt inclusions. *Proc. Coffi* 9, 182–235.
- Sobolev, A.V., Shimizu, N., 1993. Ultra-depleted primary melt included in olivine from the Mid-Atlantic ridge. *Nature* 363, 151–153.
- Sobolev, A.V., Danyushevsky, L.V., 1994. Petrology and geochemistry of boninites from the north termination of the Tonga Trench: constraints on the generation conditions of primary high Ca-boninite magmas. *J. Petrol.* 27, 865–897.
- Sobolev, A.V., Dmitriev, L.V., Barsukov, V.L., Nevzorov, V.N., Slutsky, A.V., 1980. The formation conditions of high-magnesium olivines from the monomineral fraction of luna-24 regolith. *Proc. 11th Lunar Planet. Sci. Conf.*, 105–116.
- Sobolev, A.V., Portnyagin, M.V., Dmitriev, L.V., Tsamerian, O., Danyushevsky, L.V., Kononkova, N.N., Shimizu, N., Robinson, P.T., 1991. Petrology of ultramafic lavas and associated rocks of the Troodos Massif, Cyprus. *Petrology* 14, 379–412.
- Sorby, H.C., 1858. On the microscopic structure of crystals, indicating the origin of minerals and rocks. *Geol. Soc. London Q. J.* 14, 453–500.
- Taylor, R.P., Jackson, S.E., Longrich, H.P., Webster, J.D., 1997. In situ trace element analyses of individual silicate melt inclusions by laser microprobe inductively coupled plasma mass spectrometry (LAM-ICP-MS). *Geochim. Cosmochim. Acta* 61, 2559–2567.
- Thomas, R., 1991. Melt and fluid inclusion studies in the variscan post-kinematic granites of the Erzgebirge Mts. *Abstr. ECROFI XI, Firenze, Plinius* 5, 216–217.
- Thomas, R., Rhede, D., Trumbull, R.B., 1996. Microthermometry of volatile-rich silicate melt inclusions in granites. *Abstr. PACROFI VI*, 139.
- Touret, J.L.R., Frezzotti, M.-L., 1993. Magmatic remnants in plutonic rocks. *Bull. Soc. Geol. Fr.* 164 (II), 229–242.
- Vaggelli, G., De Vivo, B., Trigila, R., 1993. Silicate-melt inclusions in recent Vesuvius lavas (1631–1944): analytical chemistry. *J. Volcanol. Geotherm. Res.* 58, 367–376.
- Viti, C., Frezzotti, M.-L., 2001. Transmission electron microscopy applied to fluid inclusion investigations. *Lithos* 55, 125–138 (this volume).
- Vogelsang, E., 1867. *Philosophie der Geologie und Mikroskopische Gesteinsstudien* vol. 1 Choen und Sohn, Bonn.
- Webster, J.D., Thomas, R., Rhede, D., Förster, H.-J., Seltmann, R., 1997. Melt inclusions in quartz from an evolved peraluminous pegmatite: geochemical evidence for strong tin enrichment in fluorine-rich and phosphorus-rich residual liquids. *Geochim. Cosmochim. Acta* 61, 2589–2604.
- Weisbrod, A., 1981. Fluid inclusions in shallow intrusives. *Short Course in Fluid Inclusions: Application to Petrology*. In: Hollister, L.S., Crawford, M.L. (Eds.), *MAC Short Course*, vol. 6, pp. 241–277.
- Westrich, H.R., Gerlach, T.M., 1992. Magmatic gas source for the stratospheric SO<sub>2</sub> cloud from the June 15, 1991, eruption of Mt. Pinatubo. *Geology* 20, 867–870.
- Wulff-Pedersen, E., Neumann, E.-R., Jensen, B.B., 1996. The upper mantle under La Palma, Canary Islands: formation of silicic melt and its importance as a metasomatic agent. *Contrib. Mineral. Petrol.* 125, 113–139.
- Wulff-Pedersen, E., Neumann, E.-R., Vannucci, R., Bottazzi, P., Ottolini, L., 1997. K-rich melts in the mantle produced by reaction between peridotite and infiltrating basaltic melts: ion

- probe data on glasses and minerals in veined xenoliths from La Palma, Canary Islands. *Contrib. Mineral. Petrol.* 61, 345–356.
- Yaxley, G.M., Crawford, A.J., Green, D.H., 1991. Evidence for carbonatite metasomatism in spinel peridotite xenoliths from western Victoria, Australia. *Earth Planet. Sci. Lett.* 107, 305–317.
- Zapunyy, S.A., Sobolev, V.S., Bogdanov, A.A., Slutskiy, L.V., Dmitriyev, L.V., Kunin, L.L., 1988. An apparatus for high-temperature optical research with controlled fugacity. *Geokhimiya* 7, 1044–1052.