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PIXE mapping on multiphase fluid inclusions in endoskarn xenoliths of AD 472 eruption of Vesuvius (Italy)

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Abstract

In this work we report a microthermometric and proton-induced X-ray emission (PIXE) mapping investigation on multiphase fluid inclusions hosted within nepheline and clinopyroxene of endoskarn xenoliths present in the deposits of the AD 472 eruption of Vesuvius. PIXE mapping on magmatic fluid inclusions repesents a useful tool for the characterization of the composition of magma derived fluids, exsolved from active magma chambers. In fluid inclusions we observed the occurrence of widespread solid phases formed by Fe, Pb, Zn, As ± Cu ± Mn, suggesting the good metal transport capability of Vesuvius magmatic fluids, which interacted with carbonate country rocks leading to the formation of endoskarn.

Key words: fluid inclusions; PIXE; Vesuvius magma chamber; exsolved fluids.

Introduction

Magma-derived fluids are important in geologic processes (metal sequestration and ore deposition) but are intrinsecally transient. Fluid inclusions trapped and sealed in crystals are by far the most representative of fluid compositions that existed during and after crystal growth (Roedder, 1979). As a consequence fluid inclusion investigation in many cases represents the unique opportunity to obtain data on these fluids.

In the last years, fundamental informations about the major and trace element composition of magmatic hydrothermal fluids have been provided by in situ analysis of individual fluid inclusions by several tecniques (PIXE, LA-ICP-MS, Synchrotron X-Ray fluorescence, Heinrich et al., 1992, 2003; Audetat et al., 1998; Ulrich et al., 1999, 2002; Philippot et al., 2001; Vanko et al., 2001; Kamenetsky et al., 2002; Kurosawa et al., 2003). Here we apply PIXE tecnique to fluid inclusions present in endoskarn xenoliths from AD 472 subplinian eruption of Vesuvius (Fulignati et al., 2001).

The aim of this paper is to provide further insights into the physical nature and composition of magma-derived fluids represented by multiphase fluid inclusions, present in endoskarn xenoliths.

The AD 472 magma chamber of Vesuvius

Somma-Vesuvius is a K-alkaline Quaternary stratovolcano of southern Italy, with a somma caldera (Mount Somma) and an inner cone (Vesuvius). During the past 18 ky several explosive eruptions of different magnitude, including at least four Plinian and six sub-Plinian outburst, have occurred. All the main eruptions have both Plinian phases and important phases dominated by magma-water interaction, which always involves fluids hosted in the deep Mesozoic carbonate formations or in the shallow volcanic sequences. The involvment of hydrothermal fluids from a thermometamorphic halo is sometimes suggested by the presence of altered lithics and their fluid inclusions. The deposits of each explosive eruption show both fall and flow deposits. Fall deposits are variably stratified pyroclastics surges and phreatomagmatic, lithic rich pyroclastic flows occur frequently during major events. The phreatomagmatic phases of subplinian eruptions generally occur during the final stages of the sustained column.

The AD 472 eruption products vary in composition from early stage leucititic phonolite to late stage K-phonotephrite (Rosi and Santacroce, 1983). The compositional zoning of products is interpreted to reflect regular withdrawal from a compositionally and thermally stratified shallow (< 5 km) magma chamber (Cioni et al., 1998). The solidification front of the magma chamber (in the sense of Marsh, 1995) consists of foid-bearing syenites and clinopyroxenites and grades continously into carbonate country rocks through a skarn shell (Fulignati et al., 2001, 2004). The estimated temperatures for the solidification front range from < 850 °C (upper part of the magma chamber, foid-bearing syenites) to ~ 1150 °C (lower part of the magma chamber, cumulate from clinopyroxenites to olivin clinopyroxenites).

Analyses of melt and fluid inclusions from juveniles and foid-bearing syenitic xenoliths reveal that a hydrosaline fluid phase was exsolved from the upper parts of the magma chamber (Fulignati et al., 2001; Fulignati and Marianelli, 2007) and was involved in skarn genesis in the carbonate-bearing peripheral portions of the magmatic reservoir (Fulignati et al., 2001, 2004; Gilg et al., 2001). In particular, the occurrence of fluid inclusions in skarn xenoliths, from AD 472 eruption, indicates circulation of a magmatic hypersaline fluid phase in the peripheral upper parts of magma chamber. The multiphase (carbonate-bearing) melt inclusions are thought to result from a magmatic-derived hypersaline fluid that reacts with carbonate wall rocks (Fulignati et al., 2001), inducing carbonate melting through sintectic reactions (Lentz, 1999). This complex fluid (Na-K-Ca-carbonate-chloride-rich hydrosaline melt) metasomatizes the rigid crust generating a typical endoskarn. The paucity of fluid inclusion-bearing xenoliths suggests that the exsolution of a hypersaline fluid phase is probably not extensive in the peripheral parts of the AD 472 chamber. As a consequence the exsolved fluids are mainly confined at the solidification front-carbonate wall rock interface of the magma chamber.

Analytical methods

Microthermometric experiments on fluid inclusions were carried out in the fluid inclusion laboratory of the Earth Sciences Department of the University of Pisa with a Linkam TS 1500 heating stage and an optical heating stage, designed in the Vernadsky Institute of Geochemistry, Moscow (described by Sobolev et al., 1980). The accuracy of measurements was around ± 10 °C for both stages, controlled by the melting point of pure silver, gold and $K_2Cr_2O_7$. SEM-EDS analyses were performed using a Philips XL30 apparatus equipped with EDAX Genesis (Earth Sciences Department, University of Pisa) at 20 kV accelerating energy and about 0.1 nA beam current. The inclusions were opened by fracturing the host crystals in air. The samples were carbon coated and analyzed immediately after, with the aim to prevent as much as possible the lost of the daughter minerals.

Proton-induced X-ray emission (PIXE) methodology have been used for the characterization of the composition of our fluid inclusions. PIXE is a non destructive tecnique consisting of bombarding the sample with a high energy beam of protons. Protons eject inner shell electrons wich produces an X-ray emission characteristic for each element. The focussed beam penetrates the mineral (around ten micrometers depth) and interacts with species contained in the fluid inclusions without destroing them. Due to the absorption of soft X-rays by the host crystal PIXE can be used for analysis of elements with atomic number higher than 30. In this work qualitative PIXE maps of fluid inclusions were obtained by using a 0.3-0.7 nA beam of 3 MeV protons focussed into ≈ 2μm beam with new nuclear microprobe CSIRO-GEMOC, Australia (Ryan et al., 2001a, b).

Results

Fluid inclusions were found in rare skarn xenoliths present in the lithic rich layers from proximal outcrops of the deposits of the AD 472 eruption of Vesuvius. These xenoliths are holocrystalline rocks and consist of fassaitic clinopyroxene, phlogopite, nepheline, calcite and apatite. On the basis of previous studies of the magma chamber wall rock interface, we interpreted these rocks as endoskarn. These rocks are in fact produced by the interaction of the rigid crust of the magma chamber with magmatic-derived hypersaline fluids, which have reacted with carbonate wall rock, giving rise to Na-Ca-K-carbonate-chloride rich hydrosaline melt (Fulignati et al., 2001, 2004).

Based on petrographic observation, the shape and orientation of inclusions is consistent with entrapment during crystal growth, and thus the studied inclusions are identified as primary, following criteria provided by Roedder (1984) and Goldstein (2003). The studied inclusions are hosted within nepheline and clinopyroxene. They are multiphase fluid inclusions characterized by a vapor bubble, deformed by the occurrence of several daughter minerals, and a very small amount of interstitial liquid that is rarely visible under microscope (Figure 1). Chlorides, silicates, sulfates, carbonates, sulfides and oxides are always present among the daughter minerals (Figure 2), in some cases fluorides also occur (Fulignati et al., 2001).

Microthermometric experiments on these inclusions were carried out showing that daughter minerals totally melt at 800-830 °C (Figure 3). Vapor bubble homogenization occurs only in a few fluid inclusions between 860-885 °C. These homogenization temperatures are

Figure 1. Microphotographs of multiphase fluid inclusion in endoskarn xenoliths. Plane polarized light. Scale bar 40 μm.

comparable with the conditions of skarn genesis, as reported in Fulignati et al. (2004), or slightly higher, as some homogenization values are probably overestimated due to the deformation of the cavity of the inclusions during heating experiments. Some solids (possibly heterogeneously trapped silicates) often persist to higher temperature (840-980 °C, Figure 3).

Nuclear microscopy by PIXE was used to image element distribution of several fluid inclusions within the root zone of the nepheline and clinopyroxene crystals. PIXE maps were carried out on single multiphase fluid inclusions. PIXE element images of typical inclusions (Figure 4) always show the occurrence of metals and that individual solid phases were variable in terms of metal content. For example, we recognized solids enriched in Fe, Pb, Zn ± As ± Cu ± Mn (Figure 4A, B, C, D); Fe, Mn (Figure 4 B); Mn, Zn (Figure 4D); and Mn (Figure 4D). The composition of the liquid phase is undefined owing to its scarcity at room temperature.

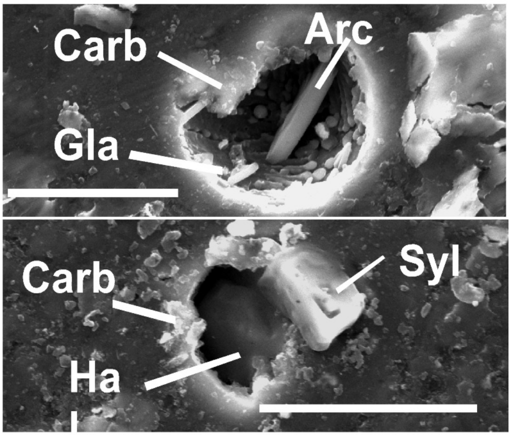

Figure 2. Scanning electron microscope images of exposed multiphase fluid inclusions, found in endoskarn xenolith, containing chlorides [halite (Hal) and sylvite (Syl)], sulfates [glaserite (Gla) and arcanite (Arc)], and Na-Ca carbonate (Carb). Scale bar is 20 μm.

Discussion and Conclusions

Processes of exsolution of an aqueous fluid phase during late magmatic differentiation play an important role either in volcanology and in the generation of magmatic-hydrothermal ore deposits (Hedenquist and Lowenstern, 1994). Magma-derived fluids are however intrinsically transient as regard their chemical composition (Kamenetsky et al., 2002). The rare opportunity to describe their original composition is offered by fluids exsolved from active magma chambers, which are entrapped during crystal growth as fluid inclusions. These entrapped magmatic-derived hypersaline fluids are thought to be the

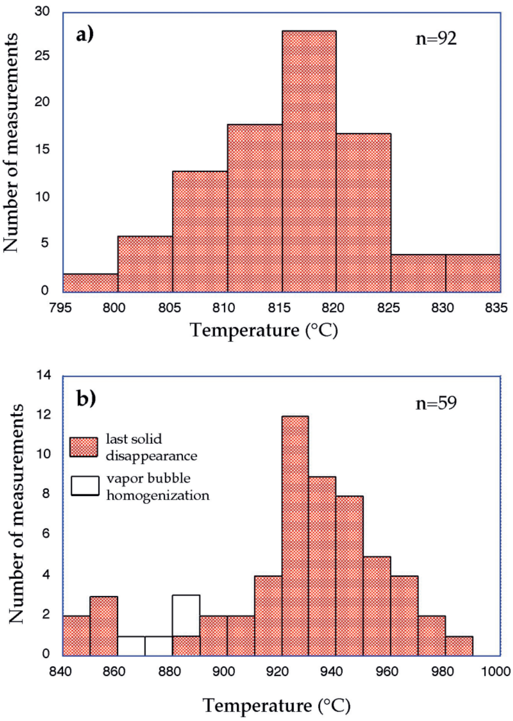

Figure 3. Hystograms of: a) temperature of halite homogenization; b) temperature of vapor bubble homogenization and last solid disappearance. n = number of measurements.

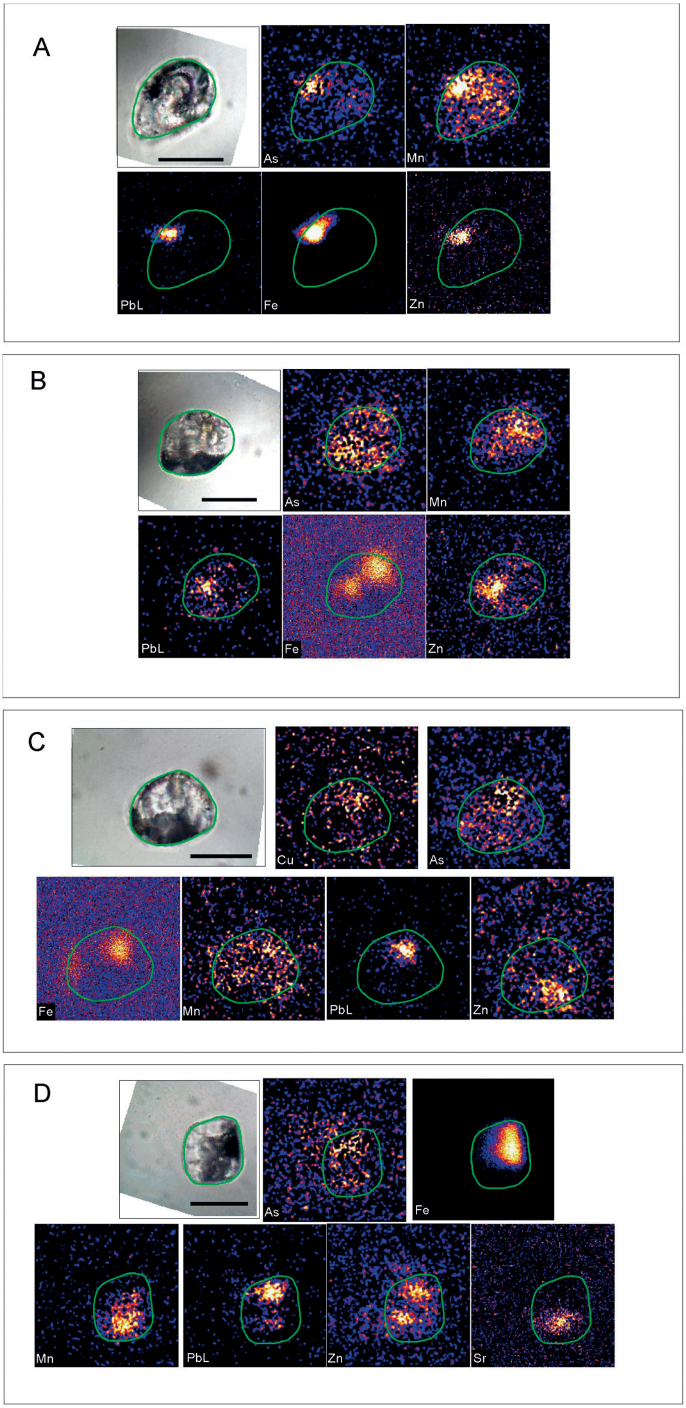

Figure 4. Optical images and proton-induced X-ray emission (PIXE) element maps of individual multiphase fluid inclusions. Color scale (from dark to white) in each element image is normalized to its own maximum. Increasing intensity is proportional to element concentration. Optical images show inclusions before PIXE analysis. Green outlines on element maps mark boundaries of fluid inclusions. Solids enriched in Fe, Pb, Zn ± As ± Cu ± Mn (Figure 4A, B, C, D); Fe, Mn (Figure 4B); Mn, Zn (Figure 4D); and Mn (Figure 4D).
Scale bar represents 20 µm.

result of the interaction between hydrosaline fluids and carbonate wall rock, giving rise to Na-Ca-K-carbonate-chloride rich hydrosaline melt.

Coupled microthermometry and trace element analysis of single fluid inclusions are a useful tool to trace the processes that affect magma derived fluids exsolved from active magma chambers. The high temperature of homogenization of investigated fluid inclusions (860-885 °C) supports a magmatic origin for the fluids involved in skarn reaction at the peripheral portions of AD 472 magma chamber of Vesuvius. PIXE analysis allow mapping trace element distribution of single fluid inclusions present in endoskarn xenoliths. The occurrence of solid phases formed by Fe, Pb, Zn, As ± Cu ± Mn suggests that these elements were abundant in the fluids exsolved from the AD 472 magma chamber. This testifies the metal transport capability of Vesuvius magmatic fluids, which interacted with carbonate country rocks leading to the formation of endoskarn, confirming the preliminary data reported in Fulignati et al. (2001). These results, coupled with recently published data on composition of multiphase magmatic fluid inclusions, representative of the fluid exsolved from peripheral parts of the magma chamber of AD 79 eruption (Fulignati et al., 2011), indicate that hypersaline fluid phases released by the crystallizing phonolitic upper parts of the sub-Plinian and Plinian Vesuvius magma chambers have the capabilty to carry ore-forming elements. The exsolution of metal enriched fluids from Vesuvius magma chambers well agree with the occurrence of scheelite, stibnite and galena mineralization frequently found in skarn xenoliths from the deposits of Plinian eruptions (Fulignati et al., 2005). These results represent clear evidence on the involvment of this metal-enriched magmatic fluids during skarn forming processes at Vesuvius, although there are no evidence of metal ore deposits around the volcano.

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