TRANSITION FROM MAGMATIC TO HYDROTHERMAL CONDITIONS IN MAGMA CHAMBERS: EVIDENCE FROM MINERALOGY, CHEMISTRY AND FLUID INCLUSIONS IN ALKALI-SYENITE NODULES OF THE "BRECCIA MUSEO" PYROCLASTIC FLOW (CAMPI FLEGREI, NAPLES, ITALY)

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Object of the present study are feldspathoid-bearing syenite nodules which belong to the lithic horizon (Breccia Unit) of the Breccia Museo formation. The Breccia Museo, is a volcanic breccia which crops out in the SW sector of the Phlegrean Fields, an active volcanic field located immediately west of Naples, Italy. The Breccia Museo has been interpreted by several authors as result of the explosive activities of different monogenetic vents (Perrotta, Scarpati, 1994) or the proximal facies of the Campanian Ignimbrite, a widespread pyroclastic flow deposit which occurred about 35.000 ybp (Rosi et al., 1983). Perrotta and Scarpati (1994), on the basis of the distinctive textural, structural and lithological characteristic, divide the deposit in four stratigraphic units grouped in two overlapped depositional units named, respectively, Lower Depositional Unit (LDU) and Upper Depositional Unit (UDU); the two depositional units are divided by a co-ignimbrite ash-fall deposit. Both the LDU and the UDU show facies variations interpreted by authors as resulting from the interaction between the flow and the paleomorphology.

The nodules are composed primarily of potassium feldspars (up to 80% of the constituents), subordinate plagioclase, scapolite (a S and Cl-rich member of the cancrinite-group) amphibole, pyroxene, biotite, magnetite, titanite and apatite. The homogeneous composition of feldspars from core to rim suggests a substantial equilibrium with the host liquid. Most of the observed fluid inclusions were hosted by potassium feldspar and, to a lesser extent, by scapolite.

A preliminary fluid inclusion study was carried out in thin sections and on small fragments of xenoliths, which were examined and analyzed by SEM-EDS. EDS analysis was carried out on daughter minerals, whose identification was based on EDS spectra and, where possible, on crystal habit. Room-temperature observations allowed to identify various types of fluid inclusion: (1) one-phase liquid-rich; (2) two-phase aqueous, liquid + vapor, liquid-rich inclusions (most of these inclusions were found in healed fractures or cleavages of the host minerals); (3) three-phase and multiphase aqueous inclusions containing one or more daughter minerals. The study of daughter minerals in fluid inclusions revealed the presence of many different phases: *Chlorides*: Na (halite) and K (sylvite) chlorides were found in many opened inclusions. They were often associated and occupied more than half of the volume of inclusion. Fe- and Mn-chlorides often occurred as irregular masses or coated the wall of the inclusions; *Sulfides*: minerals showing Fe, Cu and S peaks were identified as pyrite, pyrrhotite and chalcopyrite, based on peaks ratio and morphology. Noteworthy is the occurrence of sphalerite and argentite/acanthite; *Sulfates*: although SEM-EDS analysis does not reveal the degree of hydration, a Ca and S phase was identified as anhydrite ($CaSO_4$) from morphology; *Carbonates*: in some inclusions a mineral showing exclusively a Ca peak was observed. We consider this mineral to be calcite in agreement with crystal morphology. Other phases, identified as carbonates, were dolomite, cerussite and a Zn daughter mineral tentatively identified as smithsonite ($ZnCO_3$).

SEM-EDS and electron microprobe analysis of the nodules showed a high abundance of U, Zr Nb, Th and REE elements in late stage minerals such as apatite, Zr bearing minerals (i.e. zircon baddeleyite and zirkelite), pyrochlore-group minerals, thorite and phosphate (monazite group); zircon and baddeleyite have UO_2 concentrations of up to 9 and 4.5 wt.%, respectively and Th enriched zircons (ThO_2 up to 50 wt.%) were also observed. Baddeleyite shows also enrichment in Nb_2O_5 (up to 7 wt.%, among the highest concentrations reported from terrestrial baddeleyite). Zirconolite is relatively enriched in Nb and Th (up to 14 and 15 wt.%, respectively) and, to a lesser extent, in REE and Y (up to 4 wt.% and 3 wt.%, respectively). Pyrochlore, which shows a large compositional variation, is the main mineral concentrating Nb in the nodules (up to 37 wt.%) and has a relative abundance of ZrO_2 (up to 16 wt.%), ThO_2 (up to 8 wt.%) and UO_2 (9 to 31 wt.%). Phosphates are enriched in ThO_2 (up to 21 wt.%) and REE (mainly Ce_2O_3 and La_2O_3 up to 13 wt.% and 12 wt.%, respectively) and often show zonation. Other minerals observed were sulfides, carbonates and tungstates.

Many of the accessory phases occur with typically hydrothermal textures (i.e. replacement, vugs, in-filling). Furthermore, the nodules show high abundance of small miarolitic cavities. On the basis of mineralogy and fluid inclusion evidences, these cavities have been interpreted by the authors to be magmatic in origin and to represent the probable site of vapor bubbles exsolving from late-stage magmatic fluid separation. Complex daughter crystal assemblages found in multiphase fluid inclusions of the nodules of the Breccia Museo give evidence of high solute entrapment. The high salinity of the trapped fluids is testified by high abundance of chlorides, sulfides and, to a lesser extent sulfates and carbonates. Such evidences suggest that fluids trapped represent a hypersaline/sulfur rich with minor CO_2 content fluids exsolved by a crystallizing magma.

Microprobe data and fluid inclusion observations of the nodules show the partition of fluorine, chlorine and sulfur in the syenite. Fluorine is incorporated in biotite (about 5 wt. %) and, subordinately amphibole; chlorine and sulfur are incorporated in scapolite, cancrinite-group minerals and trapped in the form of magmatic brine. The high abundance of halite and sylvite found in the fluid inclusions suggest a temperature of formation in the range of 400° - 600° C. Such a range of temperature can be considered as a lower limit temperature for an early stage hydrothermal condition. We are currently carrying on microthermometric experiments to confirm this hypothesis.

Texture, mineralogy and chemistry of the alkali-syenite of the Breccia Museo strongly suggest that these nodules recorded the transition from magmatic to hydrothermal conditions in the local magma chamber. This transition was sited in an upper part of the magma chamber. According to Melluso et al., (1995), the composition of the erupted products of the Breccia Museo Deposit is compatible with the progressive downward tapping of a shallow magma chamber thermally and chemically zoned. After an early eruptive phase during which the upper, most differentiated level of the magma chamber was tapped, the sudden collapse of the roof of the magma chamber triggered the subsequent eruption of the remaining magma (ranging in composition from trachyte to trachiphonolite), which formed the Breccia Unit and the Upper Pumice Flow Unit (Perrotta, Scarpati, 1994; Scandone, 1990).

High temperature and hypersaline immiscible fluids play a key-role in ore-metal transport processes. Many studies on magmatic systems (Roedder, 1984) report the presence of high-salinity fluid inclusions (i.e. the presence of a Cl-rich, high-density aqueous phase) related to a major ore deposit (i.e. Cu and Mo porphyry deposits). These inclusions have equivalent homogenization temperatures Th > 500° C and salinity > 40% NaCl equivalent. Similar occurrences are also reported from Italian subvolcanic systems (De Vivo et al., 1995; Lowenstern, 1994).

Various experimental works have pointed out that many ore metals tend to partition into a hypersaline chloride-bearing brine exsolved from a silicate melt (Candela, Piccoli, 1995). Trace and RE elements can also be efficiently extracted from magma from Cl-rich fluids (Haas, Shock, 1994; Kravchuk, Keppler, 1994). On the other hand, the role of S in transport mechanisms is often underestimated, even if sulfate-rich fluids are reported in peralkaline, silicic magmatic intrusions and in orthomagmatic fluids related to porphyry-copper deposits (Hansteen, Burke, 1990). The occurrence of sulfides (pyrite, pyrrhotite, calchopyrite) along with chlorides and sulfates and Fe- Mn oxides suggests that the redox state of the magmatic solutions shifted towards relatively oxidized conditions. Concerning the partition of REE into S-rich fluid, Wood (1990) states that sulfate-REE complexes can predominate over aqueous species in absence of other ligands. Furthermore, the temperature strongly affects the REE-complex stability constant: increasing temperatures produce an increase in constant values for fluoride, sulfate and chloride (in this order). Therefore chloride and sulfates, which were present in the magmatic system of the Breccia Museo Deposit, could have played an important role in the REE selective enrichment in the accessory minerals of the nodules.

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