



Chemical and redox variations affected by differentiation in Mt. Etna (Italy) magmatic system

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During its activity, Mt. Etna underwent repeated changes of eruptive style and rock composition. Some of these variations are ascribed to the particular geodynamic setting in which Mt. Etna appears, namely that of the African subduction under the European plates. Presently, its volcanic activity consists of effusive and explosive eruptions marked by high gas fluxes. The increase in volatile and alkali contents of Etnean magmas that occurred in the last decades are mainly ascribed to variations in the mantle source(s).

Olivine hosted melt inclusions were analysed in products of the last 15 ky for their chemical composition, volatile content and Fe speciation, in order to interpret the chemical variability and the oxidation state of Etnean magmas as well as and their possible evolution. Samples were selected from the most primitive products of picritic composition (Mg#= 67–70, Fo89–91) of the Fall Stratified (FS) eruption, the Mt. Spagnolo eccentric lavas (Mg#= 52–64, Fo82–88) and from more recent 2002–2013 eruptive products (Mg#=33–53, Fo68–83).

Crystal fractionation and degassing processes were modelled at temperatures of 1050–1300 °C, pressures <500 MPa, and oxygen fugacity between 1 and 2 log units above the nickel-nickel oxide buffer, in order to interpret melt inclusions data.

The variability of the major elements contents in the MIs, characterized by the decrease of MgO (1-12 wt%) and CaO/Al₂O₃ ratio (up to 1.5) and the increase of alkalis (1–6 wt% K₂O; 1-8 wt% Na₂O), suggests a continuous differentiation trend, which is mostly reproduced by the fractional crystallization of olivine + spinel + clinopyroxene ± plagioclase, in order of appearance. Similarly, the volatiles contents are extremely variable, with the highest H₂O (up to 6 wt%) and CO₂ (~0.6 wt%) contents found in FS magma, suggesting minimum entrapment depths up to 12-16 km below sea level. The variability of the S content (up to 0.43 wt% in the older Mt. Spagnolo inclusions) does not show a strong correlation with other volatiles content nor with the decrease of pressure, suggesting other influencing parameters, such as the variation of redox conditions.

Fe³⁺/ΣFe ratios (0.15-0.36) by X-ray Absorption Near Edge Spectroscopy (XANES), obtained for some of these melt inclusions, embayments and matrix glasses, are weakly correlated with their volatile content, but strongly correlated with some major elements, particularly with respect to MgO and K₂O (markers of melt differentiation). We argue that the differentiation process plays a major role in determining the observed Fe³⁺/ΣFe ratios, and therefore in constraining the oxidation state of Etnean magmas (NNO-1 < fO₂ < NNO+2).

The modelling of fractional crystallization and degassing processes concurs to suggest that the chemical variability of Etnean magmas, during the last 15 ky, can be mostly ascribed to melt differentiation due to fractional crystallization (and degassing) of a highly oxidized, primitive and hydrous FS magma-type. Such a process occurs along highly variable P-T-fO₂ paths, accompanied by reduction of the oxidation state, and occasionally by mixing processes, crustal assimilation and volatile flushing.