Magma dynamics at Mount Etna (Italy) inferred from geochemistry of gas emissions

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Since 2007 we have performed a geochemical monitoring of some fumaroles located in the rim of Voragine crater at Mount Etna. The acquired data have been integrated with those from peripheral gas emissions, monitored since 1996. As a first step, the gas mixtures have been quantitatively corrected for post-magmatic processes such as interaction with shallow aquifers. Then, the systematics of He-Ar-CO_2 allowed us to assess the degassing path of the emitted gases and the absolute pressures at which are released. As a result, peripheral gases are fed by volatiles exsolved from magma batches residing in a range of pressure comprised between 200 and 400 MPa, while summit fumaroles get also gases from lower pressures (~130 MPa). These pressures well agree with geophysical and petrological investigations that recognize ponding zone of magma at 5-12 km b.s.l. and at 2-3 km b.s.l.

In addition to pure magma degassing processes, also mixing of the volatiles exsolved at different pressures occurs and influences the chemical and isotope variations, especially of crater fumaroles. Indeed, temporal monitoring of $\delta^{13}C_{CO2}$ and He/Ar ratio showed that variable proportions of mixing as well as variable degassing pressure strongly depend on magma dynamics at depth. In particular, a progressively deep component seems to prevale during pre-eruptive phases reflecting magma recharge at depth, while the pure degassing component pertains to shallow volatile component prevaling during post-eruption periods.

Finally, long-term monitoring of $^3He/^4He$ ratios from both peripheral and crater gases has allowed us to sistematically recognize phases of increase of the isotope ratios, occurred months before the onset of eruptive activity at all the sampled emissions. Considering what above stated, these phases would be related to refill of the plumbing system by ^{3}He-rich magmas, being thus very primitive and rising directly from the mantle. Recently, this behavior has been also recorded before 2011-2012 and 2013 volcanic activities, which have been characterized by frequent episodes of fire fountains and lava flows from the New South East Crater (NSEC). We point out that the last phase of magma recharge at depth is still ongoing suggesting that the new eruptive period, started in early 2013, could be further fed in the following months.

μ-XRD, μ-XRF, and μ-XANES synchrotron analyses of heterogeneous mine-waste materials related to AMD processes

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In this work, we studied the mineralogical and chemical variations of some representative mine-waste samples from the Fe-Cu sulphide Libiola Mine, by means of combined synchrotron-based μ-XRD, μ-XRF, and μ-XANES analyses performed at ESRF beamlines (Grenoble). Mine waste is acid generating (Marescotti *et al.*, 2010) and is characterized by a high amount of completely to partially altered sulphide-rich mineralizations. Other than acid generation, the major environmental problem is the mobilization of potential toxic elements (PTEs) that can be concentrated in waters and soils. We studied three different Fe-oxides and -oxyhydroxides rich samples representative of a) stratified crust formed by the ageing of soft precipitates formed from acid mine waters discharged at mine adits, b) partially altered massive pyrite-rich mineralizations which contain the transition from unaltered to completely alteres sulphide-mineralizations (Carbone *et al.*, 2012), and c) partially altered stockwork pyrite-rich mineralizations.

In this study, we demonstrated that the combined use of micro-synchrotron-based techniques (performed at ID18f and ID21 beamlines) can be succesfully applied to monitor the alteration processes that occur betwwen sulphides and their oxidation products. In particular, the combined use of μ-XRD and μ-XRF highlighted a different behaviour of some ecotoxic elements, such as Zn and As, during the evolution of the alteration process. A quantitative analysis of the sulphide/sulphate ratio was performed using the μ-XANES S k-edge spectra, while the Fe k-edge spectra were used in order to obtain the distribution of Fe^{3+} between primary and secondary phases.

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