

## Magma mixing as a petrological clock to measure the timescale of volcanic eruptions: Experiments and numerical models

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Magma mixing processes generate different fluid dynamic domains in which chemical exchanges between magmas can be strongly modulated, depending on the ability of the two melts to spread across the magmatic system. These structural domains, tightly linked to the chaotic nature of the mixing, are preserved in volcanic glasses as fractal structures.

Detailed petrological studies of lava microstructures generated by magma mixing reveal the presence, in the same system, of highly heterogeneous volumes of melts in which both depletion and enrichment of trace elements occurs, depending on the values of their diffusivity, triggering a 'diffusive fractionation' process.

Numerical simulations in which the mixing process is induced by applying a chaotic advection numerical scheme and a chemical diffusion model, reveal that the 'diffusive fractionation' of trace elements, analogous to that observed in lava flows, can be readily achieved and that the extent of this process depends upon the mixing time.

Chaotic magma mixing experiments were performed by mixing natural magmatic compositions from Phlegrean Fields. Experiments were carried out at different mixing times. Micro-analysis of experimental runs confirms a very variable mobility for the different trace elements, depending on their diffusivity. Equations relating the degree of 'diffusive fractionation' of trace elements to the time-scales of mixing are derived from experimental data.

Application of the 'diffusive fractionation' conceptual model to several pyroclastic sequences from Phlegrean Fields (Italy) allows us to apply the relationships derived from numerical models and experiments to estimate mixing time-scales. Results indicate that mixing processes lasted for a few days prior to eruption. These short time-scales for the mixing process argue in favor of the hypothesis that refilling of magma chambers and magma mixing processes likely was the key processes triggering eruptions.

We show that the combination of chaos theory, classic petrology, microtextural evidence, numerical simulations and experimental petrology is a highly effective and much needed approach to increase our knowledge on the behavior of volcanic systems, especially for the key issue of constraining time-scales of volcanic eruptions and hazard assessment at active volcanic centres.

## Competitive ligand exchange between Cu-humate complexes and methanobactin

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Methane oxidation by methanotrophs depends on the availability of copper and the efficiency of copper acquisition by methanotrophic bacteria. In natural environments such as soils, peat bogs, and surface waters, the presence of natural organic matter, having a high affinity for copper, can potentially control the bioavailability of copper. To mobilize copper, methanotrophs have developed a unique copper uptake system, similar to the siderophore-based iron uptake systems, involving the synthesis of a copper-binding ligand (so-called methanobactin). The aim of the current study is to investigate the competition between methanobactin and natural organic matter for copper binding.

Methanobactin used in the experiments has been isolated and purified from *Methylosinus trichosporium* OB3b cultures [1]. A well characterized humic acid extracted from a humified organic horizon of a Humic Gleysol was used as a model for natural organic matter. Kinetics of ligand exchange between Cu-humate complexes and methanobactin have been studied by means of UV-vis absorption spectroscopy. Concurrent competition of humic substances and methanobactin for copper binding were investigated in batch experiments and analyzed by size exclusion chromatography (SEC) coupled to an ICP-MS. Online monitoring of SEC eluates allowed the direct determination of the amount of copper bound to methanobactin and humic acid, respectively.

UV-vis absorption spectra indicated a fast uptake of Cu from humic acid. A substantial partitioning of methanobactin into humic acid was not observed. The observed equilibrium Cu speciation was quantitatively compared to model calculations using the previously derived conditional stability constants for proton and copper binding by methanobactin and the NICA-Donnan parameters determined for the humic acid used in this study [2].

[1] Pesch, M.-L. *et al.* (2011) *Geochemical Transactions* **12**: 2. [2] Christl, I. *et al.* (2001) *Environ. Sci. Technol.* **35**, 2512-2517.