

Insights into magmatic processes from combined crystal age and compositional data

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Many, if not most, crystals in volcanic rocks preserve chemical records of subvolcanic processes (such as growth in multiple magmas and storage in a mush or plutonic body) that extend well beyond the life time of the liquids that brought them to the surface. Uranium-series disequilibria represent one of few methods of measuring absolute crystal ages in young volcanic systems, thereby placing chemical, textural, and/or isotopic data in a temporal framework. We present here a synthesis of our recent work [1-5] combining U-series crystal ages with other types of information, which provides new insights into magmatic processes.

Intermediate magmas erupted at Volcán Quizapu, Chile, and Mt. Hood, USA, are the result of mixing of silicic and mafic magmas. We used U-series ages of plagioclase in combination with crystal size distributions, trace-element zoning, and diffusion modeling to constrain both the pre-mixing and post-mixing storage times of crystals [3-5]. Plagioclase in both systems have U-series ages of ka to tens of ka, representing the total average storage time of the crystals. In contrast, diffusion modeling permits a maximum of days to weeks of crystal storage in the host magmas post-mixing. These data suggest that crystals remain in the 'active' (i.e., eruptible) part of the reservoir for thousands of years yet eruption follows quickly on mixing.

Studies of crystals in rhyolitic systems of different volumes may provide insights into processes that are common in silicic melt generation yet may be obscured in larger systems. We have analyzed zircon and plagioclase in three rhyolitic systems ranging from small (South Sister, USA [2]) to intermediate (Okataina Caldera Complex, New Zealand [1]) to large (Yellowstone, USA). Combinations of age data with trace-element and Hf isotopic compositions show the coeval presence of chemically-distinct magma or mush bodies in all three systems; only Yellowstone shows evidence for effective homogenization of the liquid fraction of the magma prior to eruption. If these results generally hold for other systems, it would imply that (only) the largest silicic eruptions are preceded by accumulation of a significant body of liquid that remains in the subsurface long enough to homogenize. Such bodies would likely be detectable by seismic imaging prior to eruption.

[1] Klemetti et al. (2011) *EPSL* **305**, 185-194. [2] Stelten and Cooper (2012) *EPSL* **313-314**, 1-11. [3] Eppich et al. (2012) *EPSL* **317-318**, 319-330. [4] Ruprecht and Cooper (in press) *J. Petrology*. [5] Ruprecht et al. (in press) *J. Petrology*.

Discrimination between biotic and abiotic rates of stabilization of Se(VI) in soil

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Selenium (Se) is an essential micronutrient for organisms, with a narrow range of concentrations lying between deficiency and toxicity. ⁷⁹Se is a long-lived fission product generated by the nuclear industry and in the context of risks assessment studies from nuclear waste repository, it is one of the main potential contributor to the dose to population [1]. Selenium is present in the soil under different oxidation states (+VI; +IV; 0 and -II), that controlled its behaviour. Selenate (Se(VI)) which may preferentially form highly mobile complexes on the surface of numerous solids, is considered to be potentially the most mobile form in the environment [2]. However, biotic or abiotic reduction processes could transform selenate into lower Se oxidation state promoting its stabilization in soil [3, 4].

To discriminate between the impacts of biotic and abiotic processes on Se(VI) stabilization in soils, stirred flow through reactor (SFTR) experiments were realised. A regenerated cellulose dialysis tubing containing a sterilised (abiotic modality) or a raw (biotic modality) silty clay loam soil suspension was placed in SFTR containing a 3×10^{-3} mol.L⁻¹ NaCl solution. A 10^{-8} mol.L⁻¹ radiolabelled ⁷⁵Se(VI) solution was injected in SFTR during 3 to 20 days (flow rate between 2 to 30 ml.h⁻¹) and then flushed by a NaCl solution (6 days). Se interactions with soil were followed by analyses on the outlet solution.

The results obtained showed that a simple equilibrium model based on reversible exchange reactions can not be applied to fit the experimental data as, for both biotic and abiotic conditions a fraction of Se(VI) was stabilised in soil. The use of a simple kinetic model that involves a fraction of selenate sorbed on the solid surface sites accessible for water lixiviation, and another fraction stabilized resulting in biotic or abiotic reduction was shown to better describe experimental results. (Figure 1).

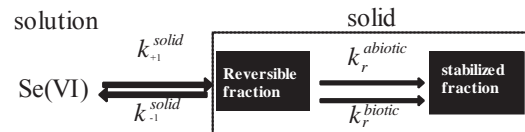


Figure 1 : Kinetic model describing Se(VI) stabilisation in soil under biotic or abiotic conditions

The kinetic parameters of the model were adjusted in two steps : (1) on abiotic experiments for k_{s1}^{solid} , k_{-1}^{solid} , $k_r^{abiotic}$ (with $k_r^{biotic} = 0$) and (2) on the biotic conditions, for k_r^{biotic} , by considering that abiotic parameters remain constant.

[1] Aguerre & Frechou (2006) *Talanta* **69**, 565-571. [2] Séby et al. (1998) *Analisis* **26**, 193-198. [3] Siddique et al. (2006) *Bioresource. Technol.* **97**, 1041-1049. [4] Olegario et al. (2010) *J. Nanopart. Res.* **12**, 2057-2068.