The influence of melt structure on the partitioning of trace elements

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Partitioning of trace elements between melt and crystal is a versatile tool to reconstruct the origin of igneous rocks, thus it is essential to understand the controlling parameters. It is generally accepted that the partitioning of trace elements (TE) is controlled by T, p, fO_2 and crystal chemistry (e.g. [1]). Several studies have also proposed a significant influence of the melt composition and thus melt structure on TE partitioning [2 – 4]. Particularly, Prowatke & Klemme's results [4] on TE partitioning between melt and titanite, which varied over several orders of magnitude, suggest a strong control of the melt composition and thus melt structure. To date there is no clear understanding of the relationship between melt structure and element partitioning. Ponader & Brown [5] report already that coordination of some rare earth elements (REE) in quenched melts changes with the degree of polymerization of the melts, this was used to explain differences in chemical partitioning. However they did not provide a direct correlation between the analysis of the element coordination and partitioning data.

In this study, different melt compositions were taken from Prowatke & Klemme [4], doped with selected REE (0.5 wt%, 2 wt%) and synthesized as glasses. EXAFS was used to get information about coordination and radial distances to the neighboring atoms of the REE in the glasses. Resonant Inelastic X-ray Scattering (RIXS) provides information about the electronic structure and was used to derive further constraints on the coordination. The measured EXAFS spectra show small variation in the distance to the first oxygen neighbours to the different glasses. The RIXS and high resolution XANES indicate only slight differences in site symmetries. Although only preliminary, our results show that the strong difference in element partitioning correlates only with rather small changes in the TE coordination.

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Formation of carbonate minerals during magmatic/hydrothermal alteration of volcanic rocks at Unzen volcano, Japan

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The alteration processes of dacitic and andesitic rocks of Unzen volcano are characterized by almost complete substitution of amphibole phenocrysts with two types of carbonates (up to 20 wt.%), quartz, muscovite and chlorite. In this study we investigate the main factors responsible for the alteration of porous volcanic rocks at Unzen.

It is determined that unaltered dacite has pores in the range from 100 nm to 10 μm, whereas the most frequent pore sizes for coherent altered dacites are observed in the range between 30 and 400 nm. All samples are characterized by interconnected porosity.

The unaltered amphiboles exhibit a homogeneous oxygen isotopic composition, with $\delta^{18}O$ vs VSMOW varying between 6.6 and 7.0‰, pointing to their primary magmatic origin. The oxygen isotopic composition of carbonates substituted amphiboles ranges from 6.0 to 9.1‰ vs VSMOW and their carbon isotopic composition varies between –4.7 and –6.4‰ vs VPDB. It implies that magmatic CO_2 and primary silicates provide the main sources for the carbonate carbon and carbonate oxygen, respectively. Hydrogen isotope composition of unaltered amphiboles shows typical magmatic signatures (δD=-48‰) without any evidence for late- or post-magmatic contamination by meteoric waters.

A series of hydrothermal fluid/rock interaction experiments in different systems, i.e. dacite or pure amphibole + H_2O, $H_2C_2O_4 \cdot 2H_2O$, $Ag_2C_2O_4$, Pl, $CaCO_3$ in different proportions were conducted at temperatures from 300 to 700°C and at pressures from 100 to 300 MPa, respectively. The first analyses of the experimental products show that amphiboles participate in exchange reactions with fluid with the formation of new mineral phases, e.g. $CaSiO_3$, however the size of produced phases was too small for proper identification. Raman spectra confirm that carbonates are indeed present as secondary phases in altered amphiboles (<5μm), providing constraints on the carbonation reactions.

Further experiments are required to reproduce natural mineral assemblages and to determine typical conditions for carbonate formation in Unzen conduit.