Melt-rock reaction in oceanic troctolites (Ligurian ophiolites, Italy) as revealed by trace element chemistry of olivine

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Several recent studies have documented that reactions between melt and crystal mush in primitive gabbroic rocks (via reactive porous flow) has an important control in the formation of the lower oceanic crust and the evolution of MORBs. In this context, an open issue concerns the origin of olivine-rich rocks, whether they formed by fractional crystallization of primitive melts or by open system reactive percolation of pre-existing (possibly mantle-derived) olivine matrix. To address this topic, we performed high-quality in-situ trace element analyses (by LA-ICP-MS) of olivine in the ideal study case of the Erro-Tobbio ophiolite Unit (Ligurian Alps), where mantle peridotites show gradational contacts with an hectometer-scale body of troctolites and plagioclase wehrlites, and both are cut by later decameter-wide lenses and dykes of olivine gabbros. Previous studies [1] inferred that they represent variably differentiated crystallization products from primitive MORB-type melts. Olivines in the three rock types (mantle peridotites, troctolites, ol-gabbros) exhibit distinct geochemical signature and well-defined elemental correlations. As expected, compatible elements (e.g. Ni) show the highest contents in peridotites (2580-2730 ppm), intermediate in troctolites (2050-2230 ppm) and lowest in gabbros (1355-1420 ppm), whereas moderate incompatible elements (e.g. Mn, Zn) show the opposite behaviour. By contrast, highly incompatible elements like Zr, Hf, Ti, HREE are variably enriched in olivines of troctolites and the enrichment in absolute concentrations is coupled to development of significant HFSE/REE fractionation (Zr_N/Nd_N up to 80). Preliminary AFC modeling show that such large Zr_N/Nd_N ratios in olivines are consistent with a process of olivine assimilation and plagioclase crystallization at decreasing melt mass, in agreement with textural observations. In-situ trace element geochemistry of olivine, possibly combined with CPO measurements, thus appears a powerful tool to investigate reactive percolation and the origin of olivine-rich rocks in the lower oceanic crust.

Quantification of the *in situ* heterogeneity of RMs for microanalytical methods

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A range of laboratory techniques is available for the geochemist wishing to characterize the chemical and/or isotopic compositions of solid materials at the nanogram or smaller sampling mass range. Examples of widely available techniques are based on the electron probe, laser ablation ICP-MS and secondary ion mass spectrometry (SIMS).

When operating at such small test portion masses there are three fundamental requirements that a reference material (RM) should enable: (1) method calibration, which is typically based on one or a few discrete fragments of the RM, (2) evaluation of method repeatability, which is commonly based on multiple analyses on a single RM fragment, and (3) method development and validation. An additional consideration is that most such materials must necessarily be characterized using laboratory methods operating at the milli-gram or larger sampling scale.

In order to meet all of these requirements it is evident that a microanalytical RM must be assessed for heterogeneity *in-situ* at a variety of scales, and that the corresponding heterogeneity component must be considered for each application being undertaken. When calibrating an instrument it is essential to know the likely variation between the mean content of individual sample aliquots (chips or fragments). This information can commonly be obtained from "bulk sample" analyses conducted on mm-sized units, be it via wet chemical, gas source mass spectrometer or other methods. For evaluating the repeatability of a microanalytical method it is necessary that the *in situ* heterogeneity of the material be quantified at the equivalent sampling scale. For method development and validation a detailed knowledge of a RM's major element composition, as well a knowledge of its heterogeneity at the given sampling scale, are both necessary.

Our work focuses on developing experimental and mathematical tools that will quantify *in situ* heterogeneity at the various sampling scales while taking into account the analytical uncertainties intrinsic to the laboratory method being used to characterize such variations. The ultimate goal of our work is to enable SIMS to assess in detail the isotopic characteristics of candidate RMs at sampling masses well below 1 ng and with overall heterogeneity being evaluated at the < 0.1 ‰ level.

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