

In situ measurements vs. lattice strain model calculations: Distribution of REE between Grt and Cpx in garnet peridotites from Vitim (Siberia)

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We present newly determined REE-distribution coefficients between clinopyroxene (cpx) and garnet (grt), which can be used to model and understand geochemical processes such as crystallisation, differentiation and melting.

From the literature it is known that discrepancies exist between calculated REE-distribution coefficients from natural samples (whole-grain separates) and those collected from experimental run products. To address these discrepancies we measured cpx and grt of grt-peridotites xenoliths from the Vitim volcanic field in Siberia. The samples were selected because they are well studied, formed over a restricted P-T range (1050-1200°C, 2.1-2.5 GPa) and do not show evidence of metasomatism and other secondary processes. The minerals were analysed in-situ, within thin sections, by electron microprobe and secondary ion mass spectrometer (SIMS). Only samples with unzoned minerals were used for the determination of REE-distribution coefficients, which were calculated from mineral core compositions.

The cpx-grt distribution coefficients vary between 240 and 360 for La and between 0.03 and 0.07 for Yb, which is consistent with experimental data from Burgess and Harte (2004) at temperatures between 900° and 1000°C. Compared to mineral separate data for REE from Vitim xenoliths (Ionov *et al.* 1993) the newly determined Kds are in good agreement, but show less scatter for the HREE between different samples. This may be explained by the ability to avoid micro-inclusions by in situ SIMS analyses.

In the original lattice strain model the physical characteristics of the cation site in grt and cpx are used to predict distribution coefficients for various trace elements in equilibrium with a melt. In our case there is no melt, and our calculations are therefore based on one measured distribution coefficient to predict the others (Yb is used here). The predicted Kd pattern agrees well for the HREE (Er to Tm) with the measured, but is less steep (hinges on Yb). The maximum differences are a factor of about 2 (La to Er). We will explore the model parameters that may contribute to this remaining discrepancy.

Age and variability of dissolved organic carbon in the St. Lawrence River

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Riverine export of dissolved organic carbon (DOC) to the global ocean represents about 0.25×10^{15} gC/yr. Various studies have shown that this DOC mainly derives from terrestrial organic matter (OM). It is generally considered to be refractory and transported conservatively to the ocean. However, recent work has shown that many rivers transport a high-¹⁴C content DOC. Knowledge of the age (residence time) of both labile/refractory components of DOC and of its variability is essential for a robust assessment of the role of riverine DOC in the global carbon cycle. Here we report chemical and isotopic composition of DOC from the St. Lawrence River, with a focus on ¹⁴C ages of labile vs. total DOC fractions, and on the spatial, seasonal to interannual variability of DOC export. Alkaline CuO oxidation was used to study a refractory DOC component and to identify sources and degradation stages of terrestrial organic matter. Our results indicate some variability in total DOC from year to year, but more notably, temporal and spatial variability in ¹⁴C-activities of the refractory DOC component, which represent approximately 6 to 30% of total DOC and yielded ¹⁴C-activities ranging between 75 and 96% of modern carbon (pMC). From these values, ¹⁴C-activities of labile compound were estimated and ranged between 100 and 111pMC. Labile DOC compounds are thus very young or have a short residence time in this system. This residence time is much shorter than the one estimated for water flowing through the Great Lakes/St. Lawrence River system, thus suggesting prominent terrestrial sources for this reactive organic carbon. Although accounting for lower overall DOC fluxes, refractory material display ages that suggest aging for a significant time in soils of the watershed.