## Helium isotopic evidence for mantle reservoirs: a matter of melting?

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The large differences in helium isotopic systematics between mid-oceanic ridge basalts (MORB) and ocean island basalts (OIB) have traditionally been used as a primary constraint on the preservation of distinct mantle reservoirs over geological time. This appears at odds with the observations for whole mantle flow. Although mantle flow can be moderately sluggish, depending on the influence of the transition zone phase changes and the role of variable rheology, model calculations show that the mantle after Earth's formation should become reasonably well mixed at present day (e.g., Van Keken and Ballentine, 104, J. Geophys. Res., 1999). Interestingly, the renewed interest in mantle mixing has led to a revival of ancient arguments for and against mantle layering, with no apparent resolution in sight. It is therefore worthwhile to explore alternatives that question whether we are reading the mantle signals correctly. For example, it has been suggested (Marc Spiegelman, pers. comm.) that the differences in MORB and OIB He isotopes could be solely due to mixing in the melt phase, where the larger percentage of melting of MORB would naturally lead to strong averaging of an OIB-like mantle signature. We have investigated this hypothesis by developing high resolution mixing models, based on our earlier work. This allows for quantitatively predictions of the differences between OIB and MORB sampling of a heterogeneous mantle using a simple proxy for mantle melting that depends on the assumed size of melting region.

## Surface chemistry of reactive mineral colloids

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The reactivity of mineral colloids in the environment is to a large extent determined by the surface chemistry of the mineral particles. The present challenge is to link the macroscopic behaviour, which determines the observations as done in the field with atomic level detail that from a fundamental perspective determines the microscopic reactivity. The combination of modern spectroscopic techniques like EXAFS, NMR, IR with quantum mechanical calculations leads to insight in the structure of species adsorbed at particular reactive surfaces. Protons, metal ions, oxyanions and natural organic matter interact at the surface of metal(hydr)oxides when present in the environment. Adsorption models are therefore needed which are based on molecular level detail and which can still handle the complexity of the environmental colloidal system. The CD-MUSIC model is a framework that can link the microscopic with the macroscopic. The (refined) MUSIC (MUlti Site Ion Complexation) model also estimates the proton affinity constants for the various reactive groups at the mineral surface, which is crucial for the basic variable charge behaviour of mineral particles. The CD stands for Charge Distribution. Inner-sphere surface complexes cannot be treated as point charges in variable charge adsorption models if one intends to use physically realistic surface species in the adsorption model. It has been shown that the charge distribution in the CD-MUSIC model determines the pH dependence of the adsorption, and that the charge distribution is linked to the structure of the adsorbed complex. The colloidal behaviour of mineral particles is also greatly affected by the charge/potential at the mineral/water interface. Adsorption of natural organic matter can have a large impact on the colloidal behaviour of the mineral particles. We have recently developed the LCD (Ligand and Charge Distribution) model that combines the NICA (Non Ideal Competitive Adsorption) model, which has been developed to describe competitive ion binding to natural organic matter, with the CD-MUSIC model to describe adsorption of natural organic matter on mineral particles. The model has so far been used to describe adsorption of some well-defined poly-carboxylic benzene molecules and FA adsorption on goethite. The model is in principal able to predict the interaction with both cat- and anions at the surface. An overview will be given of the various model concepts mentioned above in the light of the colloidal behaviour of mineral particles in the environment.