

## Compositional evolution of melts during ascent through the ocean crust based on olivine-hosted melt inclusions

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Here we present volatile (CO<sub>2</sub>, H<sub>2</sub>O, F, S, Cl), major, and trace element data from >150 olivine-hosted, glassy, melt inclusions and glasses erupted on the fast-spreading East Pacific Rise (EPR) and intermediate-spreading Juan de Fuca Ridge (JdFR). We provide geochemical constraints on both compositional variations and depths of crystallization beneath the respective ridge axes using vapor-saturation pressures derived from volatile concentrations. Vapor-saturation pressures calculated from equilibrium CO<sub>2</sub>-H<sub>2</sub>O concentrations suggest crystallization occurs over a range of depths from below the crust-mantle transition to the seafloor for both the fast-spreading EPR and the intermediate-spreading JdFR. Combining these depths of crystallization with major and trace element concentrations of the melt inclusions, results in a detailed picture of how melt compositions evolve as they ascend through the ocean crust.

Major and trace element concentrations of the melt inclusions show no consistent fractional crystallization or melt-rock reaction trends with depth. For example, the most primitive melt inclusion compositions (MgO >9.5 wt%) are found at all depths within the crust, while the more evolved compositions are restricted to the shallow crust. This suggests that some melts ascend through the ocean crust with little to no differentiation, while other melts crystallize during ascent. Melt-rock reaction processes should result in a decrease in Al<sub>2</sub>O<sub>3</sub> and CaO/Al<sub>2</sub>O<sub>3</sub> concentrations with decreasing depth due to olivine and plagioclase assimilation and precipitation of clinopyroxene, however, this is not observed in our melt inclusions. Finally, major element and volatile concentrations from the EPR are more variable in the upper crust compared to the lower crust. For instance, Cl concentrations in EPR melt inclusions formed in the upper crust range from 10 to 66 ppm, compared to only 42 to 51 ppm in melt inclusions formed deeper in the crust. This may result from higher degrees of fractional crystallization and/or increased fluid-rock interaction in the shallow crust.

## Evaluating the control on the kinetic Cr isotope fractionation factor: a reactive transport modeling approach

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Fractionation of the four stable Cr isotopes (<sup>50</sup>Cr, <sup>52</sup>Cr, <sup>53</sup>Cr and <sup>54</sup>Cr) is a well-accepted proxy for demonstrating Cr(VI) reduction occurring in geological systems [1]. Regarding Cr(VI) contaminated sites, tracking of Cr(VI) reduction is especially powerful when assessing the natural Cr(VI) reduction capacity or when performing an efficiency control of in-situ remediation measures. For typical near neutral pH-values, field scale Cr(VI) reduction efficiency has been quantified using a Rayleigh-type model assuming that the effective kinetic Cr isotope fractionation factor  $\alpha_{kin}$  is known [2]. This requirement, however, is often very difficult to achieve. Even at the laboratory scale, published values for  $\alpha_{kin}$  vary over a large range (0.9950-0.9985) [1, 3-4]. Most of these studies propose different Cr(VI) reduction mechanisms as being responsible for the wide range of  $\alpha_{kin}$ . Alternatively, varying reaction rates and/or transport limitations have been suggested as the cause for the large range of  $\alpha_{kin}$ .

To quantitatively assess the different possible contributions on  $\alpha_{kin}$  two series of reactive transport model simulations were performed using the code Toughreact [5]. The proposed reaction network is based on a novel multi-continuum approach and the specification of a <sup>53</sup>Cr(OH)<sub>3(s)</sub> – <sup>52</sup>Cr(OH)<sub>3(s)</sub> solid solution forming the product of Cr(VI) reduction. In doing so, Cr(VI) reduction was considered to occur at solid surfaces and Cr isotope fractionation was modeled by defining an equilibrium fractionation factor only.

Simulating Cr(VI) reduction occurring along a 1D flow path suggested that for a given reaction mechanism  $\alpha_{kin}$  can vary over a large range. According to our simulations, the lower range of  $\alpha_{kin}$  (=larger fractionation) is defined by a reaction mechanism's theoretical equilibrium fractionation factor. In contrast, high reduction rates and/or transport limitations induced by Cr(VI) transport to reactive surfaces can shift  $\alpha_{kin}$  to values close to 1 (=no fractionation). In the second series of model simulations our modeling approach was used to propose an alternative kinetic interpretation for the low  $\alpha_{kin}$  observed in the Cr(VI) reduction experiment performed by Dossing et al. [4].

Our generic model simulations suggest that the individual contributions of reaction rates, transport limitations and reaction mechanisms should be addressed more carefully when interpreting experimentally determined kinetic Cr isotope fractionation factors and Cr isotope data derived from field sites. Reactive transport models that can treat isotopic fractionation caused by homogeneous and heterogeneous reactions coupled to transport form a unique tool for quantitative assessment of these individual contributions and for providing constraints on the field scale Cr(VI) reduction efficiency.

[1] Ellis et al. (2002) *Science* **295**, 2060-2062. [2] Wanner et al. (2011) *Appl. Geochem.* in press, doi: 10.1016/j.apgeochem.2011.11.009. [3] Zink et al. (2010) *Geochim. Cosmochim. Acta* **66**, 1095-1104. [4] Dossing et al. (2011) *Chem. Geol.* **285**, 157-166. [5] Xu et al. (2011) *Comp. & Geoscience*. **37**, 763-774.