

Dissolution rates of plagioclase feldspars at 22 °C as a function of pH and plagioclase composition

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Feldspars are the most abundant mineral in the Earth's crust and thus play an integral role in the plethora of natural geochemical processes including global element cycling. Moreover, as a major reservoir of silicate mineral bound Ca, plagioclase dissolution may serve as an important source of the divalent cations required for mineral carbonation [1]. Our ability, however, to model such processes is currently confounded by inconsistencies among plagioclase rate data measured in distinct laboratories; corresponding rates reported in the literature vary by as much as 3 orders of magnitude. In addition there is a nearly complete lack of measured dissolution rates for the Ca-rich feldspars at alkali conditions. This laboratory study has been designed to overcome some of these ambiguities.

The steady state, far-from-equilibrium dissolution rates of 5 distinct plagioclases ranging in composition from albite (An_{8.9}) to anorthite (An_{88.8}) were measured in mixed flow reactors at 22±2° C and pH from 2 to 11. The dissolution rates of all plagioclases based on silica release rates show a common U-shaped behaviour as a function of pH where rates decrease with increasing pH at acid condition but increase with increasing pH at alkaline conditions. As previously observed, constant pH plagioclase dissolution rates increase with increasing anorthite content at acid conditions; measured anorthite dissolution rates are ~2.5 orders of magnitude faster than those of albite at pH~2. Perhaps more significantly plagioclase dissolution rates are independent of plagioclase composition at alkaline conditions. Preliminary interpretation and data fitting suggests that plagioclase dissolution rates are consistent with their control by the detachment of Si-rich activated complexes formed by the removal of Al from the mineral framework. Taking account of this mechanism and transition state theory yields a robust equation that describes plagioclase dissolution rates as a function of the composition of both the mineral and fluid phase over the full range of pH found in natural systems.

[1] Gudbrandsson *et al.* (2011) *Geochim. Cosmochim. Acta* **75**, 5496-5509.

Ferromanganese crusts as proxies for deep water Ni, Cu, Zn and Fe isotope variations

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While ferromanganese (Fe-Mn) crusts have long been characterized by elevated concentrations of Ni, Co, and Cu arising from their very slow growth rates (1-6 mm/Ma), the sources of metals in hydrogenous seafloor deposits and their record of evolving deep sea metal fluxes remain strikingly unresolved. Temporal geochemical variations in Fe-Mn crusts were mostly investigated for paleoceanographic studies of oceanic circulation and climate variations with radiogenic isotope (Pb, Nd, Os). Since transition metals are actively involved in key biogeochemical processes, it is crucial to understand how metal oceanic sources and internal cycling responded to major oceanic perturbations in the past. As a result, unlocking the history of trace metals using transition metal isotopes is now receiving growing interest.

Here, we report high resolution Ni-Cu-Zn-Fe isotope profiles in two Fe-Mn crusts collected in the North Pacific Ocean (Apuupuu seamount, south of Hawaii). This record provide a comprehensive view of the last 6 Ma. Results show that Ni, Cu and Zn isotope variabilities are restricted with $\delta^{60/58}\text{Ni}_{\text{SRM986}} = +1.73 \pm 0.03\%$, $\delta^{65/63}\text{Cu}_{\text{SRM976}} = +0.64 \pm 0.04\%$ and $\delta^{66/64}\text{Zn}_{\text{SRM3168a}} = +2.12 \pm 0.06\%$. In contrast, $\delta^{56/54}\text{Fe}$ values range from -0.04 to -0.68‰ and differ between both crusts, albeit showing concomitant kink of Fe isotopes at ~2-2.5 Ma correlating with Pb isotope ratios. Overall, Ni, Cu, and Zn isotope records in Fe-Mn crusts are consistent with their modern oceanic values, after consideration of potential isotope fractionation during incorporation in Fe-Mn oxides, while Fe isotope record is strongly affected by local effects due to short residence time and local halmyrolitic and/or hydrothermal sources.