

Identifying processes and rates of incipient chemical weathering using Pb and U isotopes

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This study focused on the role of incipient chemical weathering on combined U and Pb isotope systematics. Understanding the effect of incipient weathering is particularly relevant for interpreting the marine Pb isotope record during glacial-interglacial transitions. Here, we investigate whether the preferential release of radiogenic Pb, displaced through alpha recoil, could explain Pb isotope variations during the recent deglaciation. Soil samples from a granitic chronosequence at the forefield of the Damma glacier were sampled for an experimental study of chemical weathering. A sequential leaching technique was employed on the <1mm grain size fraction (0.05M, 0.1M HBr; 0.05M, 0.6M HCl; leaching each fraction for 24 hours in a shaker) and the residue dissolved by pressure digestion. In order to distinguish the effects of preferential dissolution of U- and Th-rich minerals (Harlavan *et al.*, 1998) and release of alpha-recoiled Pb, we measured both the Pb isotope compositions and $\delta^{234}\text{U}$ (expressed as the permil $^{234}\text{U}/^{238}\text{U}$ variation from secular equilibrium). Most strikingly, even the moraine samples with the youngest depositional age (<10 years) are depleted in ^{234}U ($\delta^{234}\text{U} = -26\text{‰}$) and the most depleted $\delta^{234}\text{U}$ is found for moraine material that was exposed to chemical weathering for several decades ($\delta^{234}\text{U}$ as low as -43‰). The negative $\delta^{234}\text{U}$ in the leachates suggests that the soil material has already been affected by fast chemical weathering without any indication of preferential release of ^{234}U during leaching. Similarly, the various radiogenic Pb isotope compositions ($^{206}\text{Pb}/^{204}\text{Pb}$ in particular) do not show any sign for the presence of α -recoiled Pb. The Pb isotopic trends in all leached moraine samples suggest relatively congruent release of natural bulk Pb from the finest sediment fraction during the first leaching steps (although a slight offset by anthropogenic Pb contributions might be present in the first leachates). Continued leaching leads to systematic shifts towards very radiogenic $^{206,207,208}\text{Pb}/^{204}\text{Pb}$ only in the youngest samples, whereas older soil samples do not display this trend. While $^{206,207}\text{Pb}/^{204}\text{Pb}$ in the residue is lower than that of leach fraction #4 (0.6M HCl), the residual $^{208}\text{Pb}/^{204}\text{Pb}$ is systematically higher than the extracted phase. We attribute this feature to variable resistance of the U- and Th-rich minerals to weathering. Overall the U- and Pb-isotopic trends observed in this study indicate that, for the Damma glacier lithology, the depletion of U- and Th-rich labile accessory phases (such as apatite) occurs within tens- to a maximum of hundreds of years, as opposed to much longer timescales suggested in earlier studies.

Reference

Harlavan Y. *et al.*, (1998), *GCA* **62**, 33-46.

Dissolution of magnetite in hydrothermal solutions: Kinetics and speciation by *in situ* X-ray absorption spectroscopy

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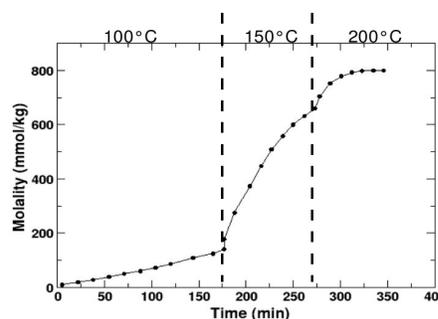
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In the research program on mineral sequestration of CO_2 , time-resolved studies dedicated to fluid-rock interactions are essential. Magnetite ($\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}_2\text{O}_4$) is an accessory host solid phase (the most reactive host candidates are basic and ultra-basic rocks), but is likely to release critical amounts of dissolved iron in the fluid, iron which is a reactant for the carbonation of carbon dioxide. Furthermore, magnetite may play a major role in the redox control of the system. For those reasons, we studied the dissolution of magnetite in hydrothermal conditions, as a function of pH, temperature and the nature of ligands in presence (the roles of sulfate and chloride ligands were quantitatively compared).

Our methodology is based on *in situ* x-ray absorption spectroscopy (XAS) on synchrotron sources. For that purpose, we use a high-pressure/high-temperature cell (Testemale *et al.*) that allows, in the same run, the determination of iron molality in the fluid in contact with a monocrystal of magnetite, the kinetics of this dissolution, and the measurement of X-ray absorption spectra at the iron K-edge (see Figure 1). The latter is a strong point of this method: the speciation and oxidation state of dissolved iron can be inferred from these x-ray absorption spectra.

We will present a kinetics model for the dissolution of magnetite, in the conditions investigated (300 bar, [30-300°C]), to be compared with literature data. In particular, the role of iron speciation and the stoichiometric nature of the dissolution will be discussed.

Figure 1: Total iron molality (Fe^{II} and Fe^{III}), as a function of time, in a 2.5M sulfuric acid solution. For each point, we acquired a XAS spectrum from which the speciation is determined.



Reference

Testemale *et al.*, (2005), *Rev. Sci. Instrum.*, **76**, 043905.