



Weathering processes revealed by seasonal variations in stable isotope ratios in rivers: The example of Mg

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River water major element chemistry and isotopic ratios are generally controlled by mixtures of waters with differing end-member compositions such as surface runoff, groundwater and rain water. The compositions of such end-members are either inherited from heterogeneity in the original lithological sources (e.g. carbonate, silicate) or from process-related fractionation of elemental or isotopic ratios during weathering. Distinguishing process-related variations from lithological mixing trends is a problem fundamental to partitioning weathering fluxes between different sources, and understanding the underlying mechanisms that control chemical weathering. In many studies, distinguishing chemical signatures in river waters related to lithology from those related to weathering processes is complex because of heterogeneous lithology in most catchments.

In this study the $^{26}\text{Mg}/^{24}\text{Mg}$ ratio (expressed as $\delta^{26}\text{Mg}$) was analysed by MC-ICP-MS from a mono-lithological granitic, weathering-limited, first order catchment from the Swiss Alps. The Damma glacial forefield (part of the BigLink project), is one of the largest multi-disciplinary experimental catchments of its kind with complementary multi-tracer research on soil chrono-sequence development and water chemistry. Water samples were collected every two weeks during the 2008 melt season, from three localities. The advantage of having a continuous sequence of samples from the same sites, is that lithology remains constant over the sampling season, providing the opportunity to deconvolve the in-situ weathering processes. At this site, the solute Mg in the rivers is thought to be dominated by contributions from biotite weathering, with much lower contributions of Mg from chlorite, amphibole and cyclic inputs.

As in most rivers, Mg is one of the major components in the dissolved load of these rivers. Mg concentrations show variations of up to a factor of eight over the seasonal cycle, which although closely related to discharge, are more complex than dilution with varying runoff [1]. More likely, they relate to mixtures of water bodies with distinct chemical compositions. $\delta^{26}\text{Mg}$ in the dissolved load of the rivers has a significantly lower isotopic composition than the bulk granite and biotite (greater than ‰ in some cases). This is caused by fractionation of the $^{26}\text{Mg}/^{24}\text{Mg}$ ratio during weathering, consistent with previous data on Mg isotopes in rivers [2]. Sub-epsilon level analytical precision reveals that the data show a continuous trend in their isotope ratios across a seasonal cycle but show no simple relationship to concentration. It is unlikely that the trends are directly related to simple uptake of Mg by vegetation because of the extremely sparse plant cover at the site. Rather, at least three other physicochemical processes might impact on the isotope ratios of Mg in these river waters. Firstly, ^{24}Mg might be preferentially leached into solution during mineral weathering. Secondly, ^{26}Mg could be preferentially retained during the formation of secondary phases, such as clays, amorphous phases or oxides. Thirdly, the river waters could be strongly impacted upon by changes in the exchangeable reservoir which could fractionate the isotope ratios of Mg. These three processes are not mutually exclusive and the relative importance of each will be discussed.

[1] Anderson S. P., et al (2003) *Chemical Geology* 202, 293-312.

[2] Tipper E.T., et al (2006) *EPSL* 250, 241-253.