The behaviour of Mg isotopes during the formation of clay minerals

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If we consider that silicate minerals are the dominant source of Mg to rivers [1], and therefore seawater, it is important for us to understand how Mg isotopes behave during the alteration of primary silicates and formation of secondary phases such as clay before we can successfully interpret past changes in the Mg isotopic composition (δ^{26}Mg) of the oceans

To address this we present Mg isotope data from natural, synthetic and experimentally synthesised clay minerals, and characterize the isotopic fractionation associated with the incorporation of Mg into structural and exchangeable sites [2]. The three natural clay minerals (illite, montmorillonite and kaolinite) have bulk δ^{26}Mg values that span a 2‰ range. Their isotopic composition depends on the balance between structural and exchangeable Mg. The exchangeable Mg in each clay is relatively enriched in isotopically light Mg compared to bulk or acid leached residual clay. This exchangeable Mg (-1.49 to -2.03‰) is within the range of δ^{26}Mg values found in many natural waters [e.g. 3]. Further experiments involving adsorption of Mg with an isotopically characterised δ^{26}Mg value suggest that the clay minerals adsorb Mg with little or no isotopic fractionation. To characterize the behaviour of Mg isotopes during clay mineral formation we synthesized brucite ($Mg(OH)_2$), which we consider to be a good analogue for the octahedral sheet of Mg-rich clay minerals. We show that brucite becomes enriched in the heavy isotopes of Mg with the corresponding solution becoming relatively isotopically light. The system reaches a steady state after 10 days with a final fractionation factor ($\alpha_{\text{solid-solution}}$) of 1.0005 at near-neutral pH.

Our results show that clay minerals contain two pools of Mg that can be isotopically distinct. The final bulk δ^{26}Mg value of a clay must be dependent on the relative proportion of Mg present in structural and exchangeable sites, and the isotopic composition of each Mg pool. Because of differences in structure between different clay minerals we conclude that their bulk δ^{26}Mg values can also be highly heterogeneous.

[1] Wilkinson & Algeo 1989, *Am. J. Sci.* **289**, 1158-1194. [2] Wimpenny *et al* 2014, *GCA*, **128**, 178-194. [3] Tipper *et al* 2006, *EPSL*, **250**, 241-253.