

Ferric iron control on the stable hydrogen isotope composition of interstratified clay minerals from seafloor hydrothermal sites

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The crystal chemistry of interstratified clay minerals reflects their origin and transformations under evolving conditions. Stable isotope data can improve our understanding of these conditions if the controls on mineral-water isotopic fractionation are fully understood. Here we describe the stable hydrogen and oxygen isotope compositions of interstratified glauconite-nontronite, talc-nontronite, and talc-saponite from submarine hydrothermal sites, with an emphasis on the Red Sea Atlantis II Deep. Across the localities investigated, these clay minerals have very low $\delta^2\text{H}$, ranging from -145 to -127‰ for talc-nontronite, -135‰ for nontronite, -129 to -85‰ for glauconite-nontronite, and -95 to -59‰ for talc-saponite. Their $\delta^{18}\text{O}$ becomes less positive in the order nontronite ($+22.2\text{‰}$), glauconite-nontronite ($+15.4$ to $+20.5\text{‰}$), talc-nontronite ($+12.7$ to $+16.1\text{‰}$), and talc-saponite ($+3.4$ to $+11.9\text{‰}$). Oxygen isotope temperatures range from $\sim 40^\circ\text{C}$ for nontronite to $\sim 135\text{--}300^\circ\text{C}$ for talc-saponite. A positive covariation exists between the $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of talc-nontronite and glauconite-nontronite from the Atlantis II Deep site. Fe^{3+} substitution in octahedral and tetrahedral sites has strongly affected the clay mineral-water hydrogen isotope fractionation. We propose that increasing Fe^{3+} substitution into tetrahedral and octahedral sites causes progressive weakening of clay mineral O–H bonds. We posit that hydroxyl hydrogen is more poorly shielded from Fe^{3+} by surrounding oxide (oxygen) than is the case for most other octahedral or tetrahedral cations. The poorer shielding is a consequence of ferric iron's larger ionic radius and higher charge, which results in a lengthening of O–H bonds that favours ^1H over ^2H in hydroxyl groups. Our results also show that Fe-rich, interstratified clay minerals, such as glauconite-nontronite, are produced at the lowest temperatures whereas more Mg-rich phases, such as talc-saponite, are formed at the highest temperatures. Evolving fluid chemistry and fluid pathways are important factors affecting the phases that crystallize. Glauconite layers likely replace precursor nontronite during diagenesis, with redox changes causing Fe-reduction and an increase in layer charge that facilitates interlayer K-fixation. Similarly, talc-saponite isotopic and chemical compositions change with temperature, fluid chemistry and Fe^{3+} content, while crystallizing at variable depths from the sediment-water interface, depending on preferred access to the hottest hydrothermal fluids.