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Hydrogen and Oxygen Stable Isotope Compositions of Mineral Hydration and Hydroxyl Water Accessed by Thermogravimetry-Enabled Laser Spectroscopy

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The hydrogen and oxygen stable isotope composition (δ^2H and $\delta^{18}O$ values) of H_2O and OH^- molecules incorporated into the structure of hydrated and hydroxylated minerals can preserve information on the isotope composition of the mineral formation water, as well as its formation temperature. However, oxygen can exist in several bonded groups in the same mineral. In the case of kaolinite ($Al_2Si_2O_5(OH)_4$), oxygen is bound into Si-O-Si, Si-O-Al, and Al-OH groups, and the oxygen fractionation factors for each group may differ, thus representing another important source of mineral formation information. It has been an outstanding analytical problem to feasibly and accurately measure the oxygen isotope compositions of those different groups. We have developed the capability to make δ^2H and $\delta^{18}O$ measurements of the H_2O and OH^- in minerals separately from that bound in non-H_2O/OH^- groups using thermogravimetry-enabled isotope ratio infrared spectroscopy (TGA-IRIS). TGA-IRIS analysis yields H_2O/OH^- content and isotope data from detailed thermal evolution profiles, which allows differentiation between the various H_2O and OH^- reservoirs present in hydrated and hydroxylated minerals.

New $\delta^{18}O$ values produced by TGA-IRIS from several kaolinites, along with complementary conventional fluorination and IRMS measurements, allow us to add to the limited knowledge of intracrystalline oxygen isotope fractionation between that bound into Al-OH^- groups in kaolinite, and that of the bulk mineral, which we find to be 1000 ln = 18.9 ‰. Together with $\delta^2H_{Al\text{-}OH}$ measurements on kaolinite, we demonstrate the extent to which hydrogen in the Eocene-age Ione Fm (CA, USA) has isotopically exchanged with either modern or earlier water since its formation. At Mesa Alta, New Mexico (USA), kaolinite OH^- hydrogen appears to be pristine since its initial formation 147 Ma BP (early Cretaceous), and we use $\delta^2H_{Al\text{-}OH}$, $\delta^{18}O_{Al\text{-}OH}$, and $\delta^{18}O_{Total}$ measurements to determine a paleo-environmental temperature of 26.9 °C, which is significantly warmer than the modern MAT of 8.9 °C. These examples add kaolinite to the suite of hydrated minerals that have been analyzed by TGA-IRIS, including sulphides, smectites, serpentines, chlorites, micas, and iron oxides, further demonstrating the potential for TGA-IRIS techniques to open new directions and possibilities for research on hydrated minerals.