

Negative verification of micas as hydrogen isotope reference materials. What next?

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The dioctahedral (muscovite, phengite, eg. USGS 58) and trioctahedral (biotite, eg. USGS 57) micas, which belong to the 2:1 layer type phyllosilicates group, are the currently available reference materials for hydrogen (H) stable isotope composition and H content in silicate minerals and natural glasses. Those micas have been the only reference minerals used in diverse methods of H isotope analysis employing either slow (continuous) heating removal of hydrogen from a mineral by dehydroxylation and dehydrogenation, or instantaneous (flash-type) thermal conversion, and also H analysis using Secondary Ion Mass Spectrometry. Some of these methods have been suffering from the lack of appropriate H isotope standards that will not change their δD value in the course of heating. Also, the H content in these micas has not been verified using external methodology and crystallochemical constraints.

In this study, we verify the published H contents and question micas' applicability as H isotope reference materials, using thermogravimetry, X-ray diffractometry, and thermal conversion elemental analysis of the H isotope ratios. Both muscovite and biotite standards have been found to undergo progressive H isotope fractionation during their sequential dehydroxylation and dehydrogenation, making them potentially unreliable for any H isotope ratio determination method. Because of the interlayer space available for proton-hopping and H₂O formation, micas allow H fractionation proportional to the degree of dehydroxylation, however, dehydrogenation linked to Fe(II) oxidation and electron transfer in biotites allows even more extensive H isotope fractionation during H removal.

After testing various groups of phyllosilicates, we found negligible H isotope fractionation during sequential H removal in kaolinite, the 1:1 layer type dioctahedral phyllosilicate mineral. The kaolinite interlayer space filled with OH-bonds does not permit easy proton hopping, whereas its dehydroxylation results in immediate structural collapse. No dehydrogenation of kaolinite has been observed. Commonly available in large quantities as a pure mineral, easy to synthesize, and having a stable chemical formula and H content, kaolinite is suggested as a new class of reference materials for H isotope ratio and H content determination in silicates.

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