

Intracrystalline oxygen isotope thermometry of goethite

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Paleoclimate records derived from lake deposits, stalagmites, soil carbonates, and marine sediments provide valuable archives of climatic variability in the geologic past. However, deposits of these types limit our spatial and temporal sampling to depositional environments. Weathering reactions triggered by meteoric water-rock interactions commonly produce Fe-oxyhydroxides, mainly goethite (FeOOH), at the Earth's surface, driven by dissolution of ferrous-iron bearing phases such as carbonates, silicates and oxides. The stable isotopic composition of these Fe-oxyhydroxides largely reflect that of meteoric water, thus providing a valuable target for producing paleo-hydrologic and climatic records in previously unsampled regions and/or times in Earth's history. A strength of Fe-oxyhydroxides as a paleoclimate archive is that one can simultaneously determine formation age by the (U-Th)/He-⁴He/³He method.

Studies of the stable isotope geochemistry of hydroxyl-bearing silicate minerals, such as kaolinite, muscovite and chlorite, have demonstrated differences in oxygen isotopic composition between structurally-non-equivalent crystal sites within a single mineral (Hamza and Epstein, 1980). This intracrystalline fractionation has been proposed as a single-mineral thermometer for the mineral smectite (Delgado and Reyes, 1996). Because goethite also has structurally non-equivalent oxygen sites, we set out to extract two fractions of oxygen that differ from one another in $\delta^{18}\text{O}$, in a way that depends on mineral growth temperature and thus is suitable for single-phase geothermometry. We selected two naturally occurring samples, a surface weathering product from the Hamersley Range of Western Australia and a pegmatitic goethite from the Pikes Peak region of Colorado. We attempted to preferentially sample $\delta^{18}\text{O}$ of the hydroxyl group oxygen by cryogenically capturing water released by heating to 400° C. We define the difference between the bulk $\delta^{18}\text{O}$ and hydroxyl group $\delta^{18}\text{O}$ as $\Delta^{18}\text{O}$; we find our Hamersley goethite has a $\Delta^{18}\text{O}$ of 17.9‰ and the Pikes Peak goethite a $\Delta^{18}\text{O}$ 13.9‰. This 4‰ difference between our two samples is of the correct direction and appropriate order of magnitude to reflect a thermodynamic control on intracrystalline partitioning, and suggests the possibility of using this method for intracrystalline thermometry of goethite.

Delgado, A., & Reyes, E. (1996) *GCA*, 60(21), 4285-4289.

Hamza, M. S., & Epstein, S. (1980). *GCA*, 44(2), 173-182.