

Iron Isotope Geochemistry of Jarosite and Implications for Iron Cycling in Sulfur-Rich Sediment

A. J. WHITWORTH^{1*}, H. E. A. BRAND², S. A. WILSON³, A. F. FRIERDICH¹

¹Department of Earth, Atmosphere and Environment, Monash University, Clayton, Victoria, Australia (*presenting author: anne.whitworth1@monash.edu)

²Australian Synchrotron, Clayton, Victoria, Australia

³Department of Earth and Atmospheric Science, University of Alberta, Edmonton, Alberta, Canada

Jarosite is a common mineral in acidic, sulfate-rich environments where it is critical in regulating the acidity of aquatic systems and the mobility of trace elements and potential contaminants. This research aims to understand jarosite formation and recrystallisation in sedimentary environments by examining the stable iron isotope geochemistry of jarosite at two coastal sites in Victoria, Australia. Jarosite occurs at high abundance as beds, veins, surface coatings and nodules within oxidized zones of sulfidic cliff sediment and as pebbles and boulders at the base of the cliffs within the intertidal zone, making these two sites ideal natural laboratories. Synchrotron powder X-ray diffraction (XRD) and ICP-MS results indicate that samples are comprised predominantly of natrojarosite, often with significant (>10 mol %) K substitution. This is unusual as K-jarosite has been found to be the predominant phase in terrestrial environments containing both K and Na. XRD results also show that the majority of the jarosite is a solid-solution of Na-K jarosite, differing from previous observations that end-member mixing predominantly occurs in nature. The iron isotope results for the jarosite samples fall between $\delta^{56}\text{Fe} = -1.91 \text{ ‰}$ and $+1.24 \text{ ‰}$, an exceptionally large range that overlaps significantly with the iron isotope results of the sulfidic sediment precursor, $\delta^{56}\text{Fe} = -0.81 \text{ ‰}$ and $+1.30 \text{ ‰}$, although the jarosite samples tend to be more depleted in ^{56}Fe . The presence of highly positive and negative $\delta^{56}\text{Fe}$ values suggests a high degree of biogeochemical Fe cycling. We propose that isotopically light Fe(II) from the sulfidic sediments is oxidised to Fe(III), where it subsequently forms jarosite, and that the jarosite slowly exchanges Fe with the environment over time. Consequently, newly precipitated jarosite is isotopically light but becomes more isotopically heavy during subsequent jarosite recrystallisation. This research confirms that iron isotope geochemistry can be used to provide insight into the geological processes involved in jarosite formation and recrystallisation.