Probing Sequential Chemical Extractions for Iron Speciation using Magnetic Methods

S. P. SLOTZNICK[1*], N. L. SWANSON-HYSELL[1], E. A. SPERLING[2], A. J. MILLER[2], N. A. G. M. VAN HELMOND[3], C. P. SLOMP[3]

[1] University of California, Berkeley, Berkeley, CA 94720 USA (*correspondence: sslotz@berkeley.edu)
[2] Stanford University, Stanford, CA 94305 USA
[3] Utrecht University, 3584 CD Utrecht, Netherlands

Iron speciation is one of the most mature and widely applied proxies to understand ancient oxygen levels and redox conditions in past aqueous environments. The iron speciation proxy estimates proportions of different reactive iron species in fine-grained sedimentary rocks which are mapped to redox conditions based on empirical calibrations from modern sediments. The proxy is based on a standardized extraction technique of sequentially applying acetate, hydroxlamine-HCl (in some cases), dithionite, and oxalate solutions to a powdered sample in order to dissolve iron phases and quantify the amount of iron carried by carbonates, “easily reducible” oxyhyroxides, ferric iron (oxyhyr)oxides, and magnetite, respectively. Although tested on pure minerals, fundamental technique development checks on whether this sequential extraction process accurately dissolves the targeted minerals in natural sediments and sedimentary rocks have not been performed. Our study applied rock magnetic experiments to sediment and shale samples dating from the Holocene to 1.5 Ga with diverse total iron contents, different proportions of iron from each iron speciation extraction, and distinct redox interpretations. Our approach was to characterize bulk powders as well as residues taken after each sequential extraction step in order to identify and quantify the ferromagnetic minerals that were dissolved. These data reveal distinct changes associated with the sequential extractions and the leaching of different magnetic minerals. In sedimentary rock samples, the acetate extraction at least partially dissolved siderite and paramagnetic phases, possibly other iron-bearing carbonates. The dithionite extraction appears to be the most robust in removing the targeted mineralogy as the data show it to effectively solubilize nearly all of the goethite. However, magnetic quantification of magnetite was orders of magnitude less than the iron measured in the oxalate extraction, suggesting that this step also dissolved iron-bearing silicates or remaining iron-bearing carbonates. Understanding this disparity is vital for holistic multi-proxy interpretation of past oxygen levels and communication between disciplines.