

Fe(II)-Catalyzed Recrystallization of Iron Oxides in Natural Systems

ANDREW J FRIERDICH^{1,*}, SCARLETT C SOUTHALL¹,
STEVEN MICKLETHWAITE¹, AND SIOBHAN A WILSON²

¹ School of Earth, Atmosphere & Environment, Monash
University, Clayton, VIC 3800, Australia

² Department of Earth and Atmospheric Sciences, University
of Alberta, Edmonton, AB T6G 2E3, Canada

*Presenting author: andrew.frierdich@monash.edu

Laboratory-based geochemical experiments enable us to gain insights into more complicated natural systems by using carefully controlled conditions. Such experiments have shown that aqueous Fe(II) catalyzes the recrystallization of synthetic iron oxide minerals (e.g., goethite and hematite) and yet the driving mechanisms for this process, even within 'simple' laboratory systems, remain poorly understood. Here we present experimental evidence that the initial crystallite size of goethite is the primary control on the susceptibility of goethite to undergo recrystallization in Fe(II)-bearing solutions, that the crystallite size increases proportionately with the extent of recrystallization, and that recrystallization ceases once crystallite size reaches a stability threshold. These results thus suggest that Fe(II)-catalyzed recrystallization of goethite is favorable due to crystallite coarsening. Consequently, crystallite size may be a predictive feature of the potential reactivity of iron oxides in soils and engineered systems, and hence the mobility of associated metal ions.

These results are crucial for extending experimental studies of iron oxide reactivity to natural systems where iron oxides often contain several weight percent quantities of aluminum and nickel. Although nickel and aluminum substitution has been shown to inhibit goethite recrystallization, it is still unclear whether this inhibition is due to the presence of this metal within the crystal structure or whether the synthesis of such materials generates goethite particles of large grain size and high degrees of crystallinity. To conclude, we explore the extent of Fe(II)-catalysed recrystallisation of a variety of synthetic goethite materials having variable amounts of Ni substitutions and compare these results to naturally occurring goethite having similar characteristics. Resolution of this problem is central to extending laboratory-based results to natural iron oxides and their susceptibility to recrystallization during Fe redox cycling in sedimentary and aquatic environments on the modern and early Earth.