

Uncovering the structural basis behind the reactivity of white rust: An X-ray and neutron total scattering study

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Fe(II)-hydroxide, or white rust (WR), is a highly reactive but enigmatic solid phase that acts as a critical reduced starting point in many Fe-based systems. Although assumed to be rare in natural systems exposed to today's oxidising atmosphere, WR could have played a key role in mediating redox transformations and surface-catalysed reactions on early Mars and the early Earth [1].

As an inherently unstable material, WR oxidises in air within seconds to form a mixture of Fe-phases, and it is an anomalously strong reductant capable of reducing protons in water to form H₂(g) [2]. An early study demonstrated that this reductive capacity is further catalysed by UV light and by the presence of structural impurities (i.e., Ni, Fe(III) and Pt) [3], but in the absence of detailed structural characterisation, the basis for this reactivity remains unknown.

Due to its reactivity, studies of WR are rare and hence a number of basic questions regarding its structure and reactivity remain unanswered.. Parise *et al* (2000) [4] refined the structure of partially deuterated WR Fe(OH_{0.86},OD_{0.14})₂, prepared hydrothermally and heated to 90°C. Here, we investigate a fully deuterated WR (Fe(OD)₂) synthesised at lower temperatures and through techniques designed to mimic precipitation in surface systems (e.g., 25 -50 °C). We used neutron total scattering to obtain a complete view of the WR and its magnetic properties. X-ray absorption spectroscopy was also used to refine the local structure and oxidation states of white rusts prepared at variable conditions.

Results suggest a layered CdI₂-type structure of white rust with magnetic ordering at 10K. The new structural compares well with XAS constraints and provides structural basis to its anomalous reactivity and its relationship to other well-known Fe-phases.

[1] Schoonen, M., *et al.* (2004) *Ambio*, 33, 539-551. [2] Wander, M. & Schoonen, M. (2008) *Orig Life Evol Biosph* 38, 127-137. [3] Schrauzer, G. & Guth, T. (1976) *JACS*, 98, 3508-3513. [4] Parise *et al.* (2000). *Am. Mineral.*, 85(1), 189-193.