

Does Fe electron transfer and atom exchange occur between Fe(II) minerals and aqueous Fe(III)?

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Fe oxides are transported as suspended sediment in rivers towards the oceans and act as a major source of iron for primary producers [1]. During this journey, the redox environment changes drastically, from dark, reducing environments in the subsurface, to light, oxidizing environments in fresh and marine surface waters and sediments. Here, we are interested in exploring whether our and others' recent findings of Fe(II)-Fe(III) electron transfer and atom exchange occur under more marine-like redox conditions, where Fe(II) can be structurally bound in a solid phase, and dissolved Fe(III) may be present as a sparingly soluble aqueous species complexed with ligands of various types [2].

In reducing environments, the reaction of Fe(II) and Fe(III) minerals is becoming widely recognized to be more complex than simply surface sorption of Fe(II). Rather, a complex process involving sorption, Fe(II)-Fe(III) electron transfer, and often extensive recrystallization both with and without secondary mineral transformation is beginning to emerge [3]. Whereas there is compelling evidence for oxidation of sorbed Fe(II) by structural Fe(III) in Fe minerals, such as goethite, magnetite, hematite, and ferrihydrite, it is unknown whether electron transfer will occur between sorbed Fe(III) and structural Fe(II) in Fe(II) minerals. It is also unclear whether significant Fe exchange will occur between aqueous Fe(III) and Fe(II) minerals.

We synthesized several Fe(II) containing minerals, such as magnetite, mackinawite, and siderite from ^{56}Fe and reacted it with aqueous ^{57}Fe (III) complexed with various Fe ligands. Mössbauer spectroscopy is specific to ^{57}Fe , and thus by synthesizing the underlying oxide from ^{56}Fe , we can turn off the signal from the solid, and isolate whether the aqueous ^{57}Fe (III) is reduced. In addition, we are using an enriched Fe isotope tracer approach, similar to our previous work [4] to determine whether significant Fe atom exchange occurs between the bulk solids and aqueous phase.

[1] Jickells et al. (2005) *Science* **308**, 67-71

[2] Rickard and Luther (2007) *Chemical Reviews* **107**, 514-562.

[3] Gorski and Scherer (2011) *Aquatic Redox Chemistry*, **1071**, 315-343

[4] Handler et al. (2009) *Env Sci Tech* **43**, 1102-1107

Graphite-bearing and graphite-depleted basement rocks in the Dufferin Lake Zone, south-central Athabasca Basin, Saskatchewan: Initial observations and future work.

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Unconformity-associated uranium deposits from the Paleo- to Mesoproterozoic Athabasca Basin in Saskatchewan, Canada, include the largest high-grade U ore deposits in the world. Most of the deposits are located at the unconformity between the sedimentary basin and the Archean to Paleoproterozoic basement. Graphite and/or carbonaceous matter (CM) are found in the basement, often concentrated along structures which can be identified as electromagnetic (EM) conductors, and potentially could act as a reductant that could trigger deposition of uranium.

The focus of this study is the Dufferin Lake Zone, an extensive "conductive" block along the trend of the Virgin River Shear Zone in the south-central Athabasca Basin. The Centennial uranium deposit occurs along this trend, although it appears to be located away from the interpreted EM conductor at depth. The significance of this observation is that typical exploration strategies of trying to identify mineralized traps along EM conductors may not always be relevant. In order to address this issue, this study aims to examine, in detail, a drill hole fence of metamorphosed basement rocks that at depth contain variable proportions of graphite, either in structures or in pelitic gneisses, but appear to have lost some or all of their graphite as the unconformity is approached.

A combination of analytical techniques will be used to characterize the textural relationships, crystallinity, and type of CM/graphite in the pelitic gneisses and shear/fault zones at various depths below the unconformity. Litho geochemistry, fluid inclusion and stable isotope analysis, and synchrotron techniques will be utilized to provide constraints on the chemical variability between graphite-bearing and graphite-depleted rocks, and the likely composition of fluids that may have removed graphite. For example, was the graphite removed by fluids moving along the unconformity or the underlying weathered rocks soon after the basin formed, or was it removed by fluids more directly involved in space and time with uranium mineralization, such as a highly corrosive basinal brine. Initial petrographic observations show much heterogeneity and complexity in the textural relationships and type of CM/graphite in the pelitic gneisses and shear/fault zones at depth. Further work will first analyze these rocks, and then the rocks within the graphite-depleted zone, prior to establishing the link between the two zones. Did the graphite or its breakdown products act as the reductant for uranium deposition?