DFT+U study of the iron sulphide mineral greigite (Fe_3S_4)

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Natural biological systems are capable of fixing environmental CO_2 under moderate conditions, suggesting the great potential of bio-inspired catalysts in future carbon-activation technologies. Investigations into the iron sulphide mineral greigite (Fe_3S_4) and its pre-cursor mackinawite (FeS) [1] have shown them to be structurally similar to (Ni, Fe)S cubane cluster molecules implicated in the development of proto-metabolism, the pre-cursor to life [2]. Modern-day bio-catalysts with the (Fe,Ni)S cubane-cluster structure metabolise such volatile molecules as H_2, CO and CO_2. Greigite is the thio-spinel analogue of the well-known ferrimagnetic oxide magnetite (Fe_3O_4). Whilst Fe_3O_4 is a very well studied material, the absence of a reliable theoretical treatment of greigite has held back the understanding of this important mineral.

In this work, density functional theory simulations of the spinel structure of greigite highlight the importance of electron correlation in this material, in the form of the Hubbard U correction term. In the absence of a U value the simulations predict a normal spinel arrangement for the magnetic sturcture, but on the introduction of a finite U parameter the calculations correctly reproduce the inverse magnetic arrangement, with a mixture of ferric and ferrous Fe on octahedral Fe sites. The cubic unit cell structure is correctly reproduced for all U values tested. For higher values of U (≥4ev) the electronic structure calculations indicate that the S atoms reduce the ferric Fe, leaving only ferrous iron in octahedral sites. The density of states for the spinel structure of greigite is shown to correspond to that of a semi-metal. In analogy with the Verwey transition in magnetite, a monoclinic form of greigite is postulated. This hypothetical structure is examined and found to be energetically unfavourable for all U values simulated, indicating that greigite takes the spinel form down to low temperatures. We finally present preliminary calculations of the greigite surface and cubane clusters.

[1] Devey, Grau-Crespo & de Leeuw (2008) *J. Phys. Chem. C* **112**, 10960-10967. [2] Russell & Hall (1997) *J. Geolog. Soc.* **154**, 377-402.

Linking the continental growth record of igneous and sedimentary Rocks

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Continental growth models are largely based on radiogenic isotopes in mantle-derived igneous rocks or in fine-grained continental sediments. Making the link between both igneous and sedimentary records is therefore the keystone of crustal growth studies. At issue is to understand how the compositions of a range of source rocks are then recorded in the sediments, especially because it is difficult to assess the relative contributions of sources of different ages in any sample of bulk sediment.

The Frankland River in SW Australia offers an opportunity to link sediments to their source rocks, because it drains just two crustal blocks with specific age distributions [1]. The distribution of Hf model ages in detrital zircons sampled along the river offers insight into the proportions of different source terranes that have contributed to the bulk sediment. This allows determining the erosion factor 'K', which relates the model age of the bulk sediments to the average model age of the continental blocks from which they derived.

Significantly the Hf data in zircon is consistent with the Nd data in bulk sediments, at the scale of both the Frankland River [this study] and the Australian continent [2]. However previous studies on bulk sediments were limited by the assumption of the K factor's value [2]. Now this can be calculated in sediments from modern river systems, by using Hf isotopes in zircon. This allows more quantitative models to be developed, linking the continental growth record of igneous and sedimentary rocks.

[1] Cawood *et al.* (2003) *Earth Planet. Sci. Lett.* **210**, 259-268. [2] Allègre & Rousseau (1984) *Earth and Planet. Sci. Lett.* **67**, 19-34.