

## Review of

I.A.M. Ahmed and K.A. Hudson-Edwards (eds.) (2017): **Redox-reactive minerals: Properties, reactions and applications in natural systems and clean technologies**. EMU Notes in Mineralogy, 17, European Mineralogical Union and Mineralogical Society of Great Britain and Ireland: London. ISBN 978-0-90305657-1, XII, 447 p., £ 50 (institutions), £ 40 (individuals)

DAVID RICKARD, School of Earth and Ocean Sciences, Cardiff University, Cardiff CF10 3AT, Wales – [rickard@cardiff.ac.uk](mailto:rickard@cardiff.ac.uk)

Redox-reactive minerals are naturally occurring solid materials that are *partly or fully-composed of redox-reactive elements* (Gilbert & Waychunas, this volume p. 55). In chemistry, a redox reaction is the sum of two reactions which involve electron exchange: a reduction reaction and an oxidation reaction. So redox-reactive minerals are naturally occurring solid chemical compounds which are involved in electron exchange reactions. This might include most minerals since although many cations do not display variable oxidation states in the natural environment, most anions found in minerals, such as oxygen and sulfur, do. However, in the context of this volume, redox-reactive minerals are essentially those that can serve as electron donors or acceptors for abiotic reagents or microbial metabolic processes at ambient temperatures. This includes minerals which have redox-reactive surfaces as well as mineral nanoparticles. Even so, as noted by the Editors in the introduction, the volume is mainly concerned with iron and manganese minerals. The volume complements the excellent volume 16 in the series on *Mineral Reaction Kinetics*, edited by Heinrich & Abart (2017).

This 447-page volume consists of 14 chapters, including a short introductory chapter by Ahmed & Hudson-Edwards. The editors group the papers around two themes with the first six chapters focusing on redox-reactive minerals in natural systems and the final seven chapters dealing with clean technologies and engineered systems. The chapters represent an eclectic mix of reviews mostly up to 2012, of theoretical, environmental and industrial aspects of redox-reactive minerals and redox-reactive materials.

## Theoretical aspects

Chaneac & Jolivet review the influence of iron oxide structure and size on redox reactivity. Actually the review includes iron oxyhydroxides as well as iron oxides and also a substantial section on Mn redox chemistry (p. 22–24) in discussing redox catalysis. Gilbert & Waychunas consider the timescales of mineral redox reactions, specifically electron transfer between a molecule and a hydrated iron oxide or iron hydroxide surface. This quite succinct review (38 p.) provides a good introduction to the theory of surface reaction rate processes and describes some experimental techniques. It updates earlier contributions of, for example, Stumm & Morgan (1981), Rosso & Vaughan (2006) and Brantley *et al.* (2008) to 2012 and complements the volume edited by Heinrich & Abart noted above. It should be widely read. At the other end of the spectrum, Ahmed, Acero and Auqué consider biogeochemical modeling of redox processes in low-temperature natural systems through the prism of pe–Eh equilibrium diagrams.

Vaughan & Coker discuss biogeochemical redox processes of sulfide minerals. It appears to have been written mainly about 2007 for, although there are occasional references to 2013 (and even a book in press by Karen-Hudson & Vaughan for 2017) they refer on p. 102 to a *most recent review* in 2005 and present a summary diagram from Posfai & Dunin-Borkowski from 2006 – although this citation is missing from the reference list. Lee, Jones, Romano and Tebo discuss the formation of manganese oxide minerals by bacteria. This is a useful update until 2013 of the biogeochemistry of Mn oxidation by microorganisms since the breakthrough insight by Luther (2005) proposing that Mn(II) oxidation and Mn(IV) reduction is facilitated by two one-electron transfer steps.

## Environmental aspects

In the environmental area Klingelhöfer, Rull, Venegas, Gasquez and Medina present a chapter entitled *Mössbauer and Raman spectroscopic in situ characterization of iron-bearing minerals in Mars: their exploration and cultural heritage*. This is an entertaining and thought-provoking contribution. Obviously it is unlikely that Martian iron-bearing minerals have any cultural heritage at present, since actual samples are limited to the rare Martian meteorites. The authors link the Martian studies with field studies in the Rio Tinto and Jaroso Ravine sites in Spain and archeological artefacts since they used the miniaturized Mössbauer and Raman techniques developed for the 2018 rover vehicle of ESA's ExoMars mission. The point being that esoteric blue skies research has demonstrable and, in this case, rapid applications in diverse field of engineering and technology.

Peacock, Lalonde and Konhauser present a 52-page review of the iron minerals as *archives of Earth's redox and biogeochemical evolution*. I like the concept of minerals as archives of Earth evolution as it succinctly encapsulates this burgeoning field of frontier international research. The review is quite comprehensive up until around 2012 with about 250 references. This is a rapidly developing field of research and there have been substantial developments since that time, especially in geochemical and isotopic proxies as well as complementary advances in the application of molecular genetics to biological evolution (*e.g.* Lyons *et al.*, 2015; Rickard *et al.*, 2017). The authors did not have the opportunity to refer to recent extensive reviews including, for example, the 801-page monograph by Rickard (2012) which listed over 3000 references and the 250-page update on sulfate-reducing prokaryotes by Rabus *et al.* (2015) with over 1000 citations. However, the review by Peacock *et al.* is a fine contribution which presents a solid introduction to a number of basic concepts in the field.

## Clean technologies

Some authors enter into the spirit of the multidisciplinary aims of the volume. Thus Vaughan & Coker, for example, add a final 2-page note to their 25-page review on the application of biogeochemical redox processes of sulfide minerals to clean technologies. Lee, Jones, Romano and Tebo include a one-page discussion on the environmental applications of Mn-oxidizing enzymes and bacteriogenic Mn oxides in their 23-page review of Mn oxide mineral formation by Mn-oxidising bacteria.

The remaining chapters are focused more specifically on clean technologies. Coker, Watts and Lloyd show how magnetite-based nanomaterial can be tailored by dissimilatory Fe(III)-reducing and Fe(II)-oxidizing bacteria and the consequent potential use in environmental mediation strategies and biomedical applications. Pearce, Rosso, Patrick and Felmy follow this with an account of the impact of iron redox chemistry on nuclear waste disposal. This is a fine review by international leaders in the field and constitutes essential reading for anyone working in this field or starting on a project involving the disposal of nuclear waste. It should also be essential reading for the politicians making decisions about nuclear waste disposal, but this is, I fear, too much to ask. Johnson, McCann and Clarke consider the breakdown of organic contaminants in soil by manganese oxides. They present a fairly comprehensive review of Mn oxide biogeochemistry in this chapter. They state (p. 321) that the significance of Mn oxides tend to be overlooked in biogeochemistry because of their relative lack of abundance compared to iron oxides. However, I doubt if any current biogeochemist in this field underestimates the significance of these phases in redox processes in the natural environment. The more recent application discussed by the authors is in the potential application of Mn oxides for the recovery of soils contaminated by organic pollutants. These organic contaminants are pernicious and probably more environmentally threatening than the more familiar inorganic ones. By contrast with inorganic chemistry, I find that the organic biogeochemistry of natural environments is still not fully appreciated and tends to be treated as a specialized niche subject. Johnson *et al.*'s introduction to organic geochemistry in this context is therefore a welcome contribution. Hudson-Edwards & Kossoff revisit the reuse and remediation of mine wastes. Bogush, Kim and Campos review the use of redox-reactive minerals in arsenic, nitrate, persistent organic pollutants and pathogenic microbes from water. Decic & Serre consider the application of redox-active porous metal-organic framework structures. Although this is a new field in materials science and has exceptional potential, it is divorced from mineralogy and the chapter sits uneasily with its colleagues in this volume.

## General information

The volume is the 17th to be produced by the European Mineralogical Society in its Notes in Mineralogy series which was initiated by EMU President Giovanni Ferraris of the University of Turin and the first volume was published in 1997. The volume is attractively presented and with abundant color images. It is available as a softbound print copy, from the Mineralogical Society of Great Britain and Ireland. It is priced at 55 GBP for Institutions or 40 GBP to individuals. Full e-text content, in the form of individual papers, is available by institutional subscription and/or via Athens affiliation from Geoscience World E-books.

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