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Introduction

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1.1

Iron Oxides: From Nature to Applications

As the name of the book “Iron oxides: from nature to applications” suggests, iron oxides are not only widespread in the environment, but also widely used by mankind in a variety of applications (Figure 1.1). Both this ubiquitous presence in nature and the utilization as tools have been established for centuries and are still valid today. The first illustrative examples of iron oxides certainly are compass needle or rust (Figure 1.2). Iron oxides are present in solid, liquid, and gaseous environments, with respective examples such as rocks, as mineral inclusion in swimming bacteria or in aerosols. Depending on the type of use, several sources of iron oxides exist. Applications range from the heavy steel production to medicine and art. The different aspects of mineral formation and their use as well as modern characterization techniques are reviewed in this book.

As a consequence of this omnipresence and significance in scientific and technological fields, a multidisciplinary interest has emerged with iron oxides at the center of its focus (Figure 1.3). The books in the collection by Cornell and Schwertmann were the most recent examples of efforts to summarize the knowledge on the subject [1–3]. Here, we focus on scientific aspects that have developed in the meantime and are therefore mostly not present in the book series published more than a decade ago. We also present some topics that were simply not addressed previously. This is particularly true for biological iron oxide formation, the role of which has only recently been recognized, as well as for the application aspects related to the iron oxides, which were not in the focus of the previous books.

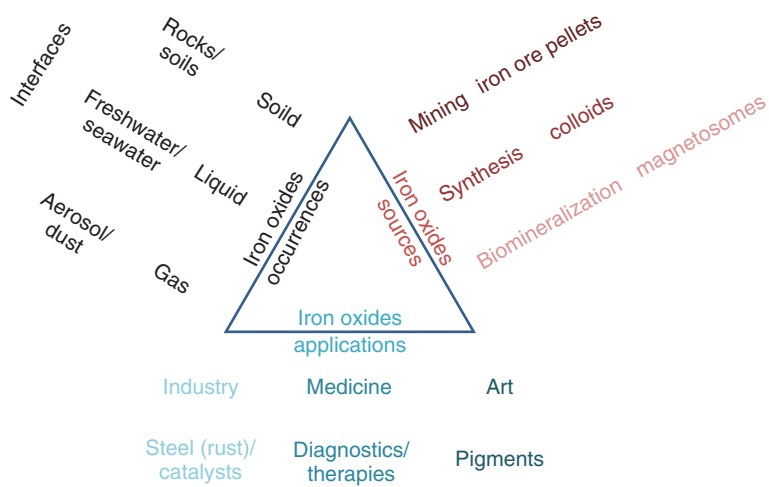


Figure 1.1 Scheme of the iron oxide occurrences, sources, and applications.



Figure 1.2 Images of agricultural machine left in a field for decades (a). A closer view clearly shows the presence of rust (b).

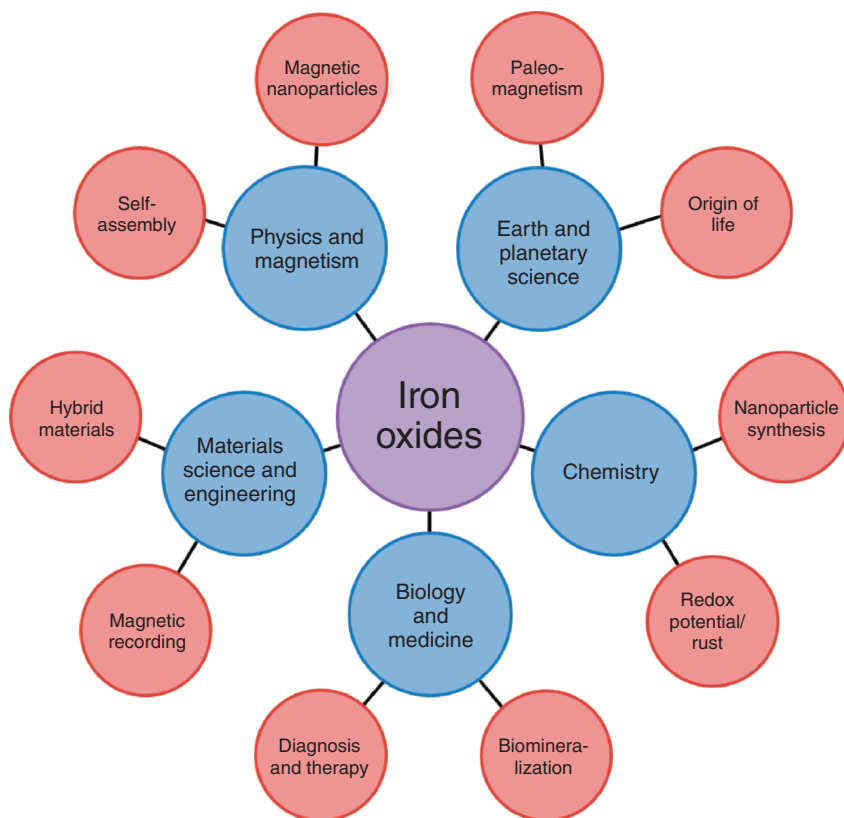


Figure 1.3 The iron oxides at the core of a multidisciplinary interest.

1.2

A Very Brief Overview of the Iron Oxides and How They Found Names

There are 16 iron oxides, hydroxides, or oxyhydroxides recognized so far, all called in short iron oxides (Table 1.1). Most of them were discovered and described at the beginning of the nineteenth century. In the table below, the compounds are simply classified based on their composition, that is, they are made from ferric, ferrous, or ferric and ferrous iron; and contain oxides (“O”), hydroxides (“OH”), or oxides and hydroxides.

With the advancement of the characterization and synthesis techniques, some of them were only named or fully characterized after lively debates. For example, the first mineral listed below (wüstite) was initially called *lozite* [4], before the name “Wüstit” (in German) was given by Schenck *et al.* [5] in recognition of Fritz Wüst, the founding director of the Kaiser Wilhelm Institute of Iron Research in Düsseldorf (Germany) (which later became the Max Planck Institute of Iron Research). The case of maghemite is even more striking: if magnetite was long

Table 1.1 Summary of the different known iron oxides.

	Iron oxides	Iron oxyhydroxides	Iron hydroxides
Fe(II) compounds	Wüstite FeO [4, 5]		“White rust” – Fe(OH) ₂ [6, 7]
Fe(II)-Fe(III) compounds	Magnetite Fe ₃ O ₄ [8]	“Green rusts” – Fougèrite [Fe ²⁺ ₄ Fe ³⁺ ₂ (OH) ₁₂] [CO ₃] ₁ ·3H ₂ O [9]	
Fe(III) compounds	Hematite α-Fe ₂ O ₃ [8] β-Fe ₂ O ₃ [11] Maghemite γ-Fe ₂ O ₃ [13] δ-Fe ₂ O ₃ [15] ε-Fe ₂ O ₃ [19]	Goethite α-FeOOH [8] Akaganéite β-FeOOH [12] Lepidocrocite γ-FeOOH [14] Feroxyhyte δ-FeOOH [16–18] Ferrihydrite 5Fe ₂ O ₃ ·9H ₂ O [20, 21] Schwertmannite Fe ₈ O ₈ (OH) ₆ (SO ₄)·nH ₂ O [8, 22]	Bernalite Fe(OH) ₃ [10]

The references to the minerals are discussed in the text since some mineral names have varied over time.

known, martite was presented as having an intermediate composition between Fe₂O₃ and Fe₃O₄, closer to hematite in composition but with an octahedral form similar to magnetite [23]. However, after the compound was obtained in the lab by oxidation of magnetite [24], it was called *ferro-magnetic ferric oxide* and its natural existence was questioned [25]. Wagner confirmed its natural occurrence and discussed that the name “ferro-magnetic ferric oxide” was too long, the name “oxidized magnetite” misleading as the mineral in question did not contain any ferrous iron and therefore he proposed “maghemite,” probably as a condensed form of “magnetite” and “hematite” [13]. This in turn was problematic to Winchell [26], who disliked the fact that the name “maghemite” suggested a magnetic hematite. This author argued that maghemite should be used in the case of hematite being deoxidized to the composition of magnetite while retaining its own space-lattice and becoming magnetic. Finally, Winchell proposed “oxymagnetite” [26], a name that did not become established in the community, where maghemite is now the name recognized by the International Mineralogy Association (IMA).

Another dispute, which is certainly more contemporary, concerns ferrihydrite. It is not related to the name, rather to the structure of the mineral, which was first reported by Towe and Bradley in 1967 [27] and named 4 years later by Chukhrov [20]. Despite its ubiquitous presence in environmental environments, its sole existence as nanometer-scaled materials had made its characterization difficult by traditional X-ray diffraction techniques based on long-range order analysis. About 10 years ago, Michel *et al.* proposed a structure based on 20% tetrahedrally and 80% octahedrally-coordinated iron and a *P6₃mc* space group [28] but structural

research is ongoing [29]. This short introductory chapter hopefully illustrates the fact that iron oxide related research has been and remains a lively field of broad interest.

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