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Iron Oxides

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2003

Print ISBN: 978-3-527-30274-1

Edited by Damien Faivre

Iron Oxides

From Nature to Applications

WILEY-VCH
Verlag GmbH & Co. KGaA

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14476 Potsdam
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Cover
Getty Images (No 533873287) Lkpro, Istock

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek
The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

Print ISBN: 978-3-527-33882-5
ePDF ISBN: 978-3-527-69136-4
ePub ISBN: 978-3-527-69138-8
Mobi ISBN: 978-3-527-69137-1
oBook ISBN: 978-3-527-69139-5

Typesetting SPi Global, Chennai, India
Printing and Binding

Printed on acid-free paper

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Foreword

Iron oxide and iron oxyhydroxide minerals comprise more than 5 wt% of the Earth's crust. Hematite (α-Fe_2O_3), the most abundant iron oxide in the crust, has been widely used by humans for millennia, mostly as durable pigments for artistic and personal adornment. Following the discovery, about 2000 years BCE, that it could be smelted to yield iron metal, hematite obtained economic significance as iron ore for the production of iron and, after the mid-nineteenth century, steel. Thus hematite played a significant role in the building of the modern, industrialized world. It is curious in this regard that the detritus of all corroded iron and steel exposed to molecular oxygen and water is rust, a hydrous variant of hematite. The corrosion process is catalyzed by bacterial respiration, that is, the transfer of electrons from the metal surface to molecular oxygen. An interesting example is the so-called rusticles on the hulk of the Titanic on the North Atlantic seafloor.

Hematite is antiferromagnetically ordered below 250 K; at 300 K it has a weak magnetic moment (0.02 μ_B). The second most abundant iron oxide, magnetite ($FeO{\cdot}Fe_2O_3$), is the most magnetic crustal mineral (4.1 μ_B). A naturally magnetized piece of magnetite is known as a lodestone. The attraction between lodestone and pieces of iron was first described in the sixth century BCE in China and in the fourth century BCE on the Aegean coast of Asia Minor. The earliest reports of a lodestone navigation device date to the twelfth century CE in both Asia and Europe. In subsequent centuries, marine magnetic compasses were fashioned from an iron needle that had been stroked along its length with lodestone. Columbus carried such a compass on his voyages across the Atlantic. The iron needles slowly lost their magnetization and had to be regularly treated with the lodestone in order to restore their magnetization. The importance of the magnetic compass cannot be over emphasized. It allowed navigators to keep their heading over long distances in the open ocean, even when the sun and stars were obscured. In this sense, iron oxides facilitated the great voyages of discovery that commenced in the fourteenth century.

Iron oxides have a longer connection to the biosphere. Iron is essential for all life forms because many essential proteins have active sites that contain iron. However, it is difficult for organisms to obtain iron from the environment because ferrous iron spontaneously oxidizes to ferric when exposed to molecular oxygen, and ferric iron is very insoluble. In order to protect excess accumulated iron for future use, it is deposited as a ferric oxyhydroxide, ferrihydrite, inside the protein ferritin, a quasispherical protein shell of diameter 12 nm with an 8 nm storage pocket.

Magnetite has been reported in organisms as diverse as chitons, trout, honeybees, pigeons, turtles, lobsters, and magnetotactic bacteria. The latter deposit magnetosomes, nanoscale magnetite crystals in intracellular vesicles, arranged in chains. The chain of magnetosomes comprises a permanent magnetic dipole that causes a cell to be oriented in the geomagnetic field and thus keep its heading as it swims.

Iron Oxides provides a comprehensive look at the geochemistry, biochemistry, and synthesis of iron oxides, especially at the nanoscale. It also presents recent advances in experimental methods for their study. Finally, it looks forward to applications of iron oxide minerals in chemical catalysis, environmental remediation, and medicine.

January 2015 *Richard B. Frankel*
San Luis Obispo, CA, USA

Preface

Iron oxides are ubiquitous in Nature. They can be found in geological settings as different as the surface of Mars where they mostly account for the color of the red planet or for the acidic mine drainage on Earth where their presence can help to reduce pollution. Different types of iron oxides can also be biomineralized by organisms, which in turn are used for purposes as different as iron storage, magnetic, or mechanical properties. Iron oxides are not only widely present in the environment but also have a large variety of applications that make them irreplaceable, for example, from paintings to the reconstruction of past climate and to magnetic resonance imaging. Therefore, this scientific field has evolved as a multidisciplinary field between areas as diverse as geology, biology, chemistry, and even medicine.

As a graduate student, I early on considered the book by Cornell and Schwertmann as a "must." I was studying the formation of magnetite with potential application for the search of life on Mars and as soon as I had any problem, I was able to find at least some hints for the answer in this book. I had to suffer since the book was not available in France for some time (no longer printed before reedition). Now that I have my own research group, I see my students still using this book on a nearly daily basis. Participating in conferences on the subject, I could also recognize how this book was widely used in the community. However, the last edition of the book appeared about a decade ago, and though some fields have not evolved much, some have dramatically changed. I therefore happily and positively answered the offer of Dr Reinhold Weber from Wiley-VCH to update the knowledge gained during these years in the field when we met at a conference from the German Society of Chemistry in 2014.

The book thus aims at presenting the different fields associated with iron oxides, and where those play a critical scientific role. In particular, the book starts by general overviews that cover the geological and the synthetic facets as well as the biological formation of dedicated phases in organisms such as limpets, chitons, and bacteria and also in humans. The second part of the book presents modern characterization techniques that are used to analyze iron oxides. Finally, the third part addresses some current and potential applications of iron oxides, with a particular emphasis on magnetic iron oxides, which are at the core of these applications because of their magnetic properties.

I thank the authors of the different chapters for accepting to take part in this adventure. I would like to particularly thank my past and present group members who provided several of the chapters. I also particularly appreciate R. Frankel for providing the foreword of the book. I also thank the editorial team at Wiley for their support in getting the chapters in time, formatting, and proofreading those materials. I acknowledge the support of several colleagues who reviewed the manuscripts and in particular of my close collaborator Dr. Jens Baumgartner who helped with numerous chapters. My wife Nathalie, apart from others support, provided several illustrations "from the field."

Potsdam, February 2016 *Damien Faivre*

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Iron Oxides: From Nature to Applications, First Edition. Edited by Damien Faivre.