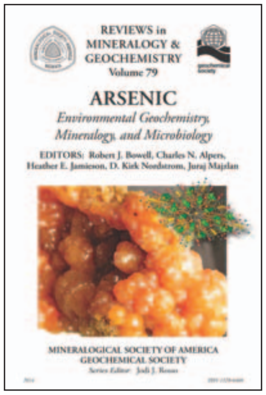
ARSENIC ENVIRONMENTAL GEOCHEMISTRY, MINERALOGY, AND MICROBIOLOGY[1]

Arsenic is an element with a fascinating and, in many ways, frightening history. Long before its isolation as an element in 1250, it was known (probably in the form of the naturally occurring oxide) to ancient civilisations, such as the Romans, for its poisonous properties. Indeed, it was almost certainly a favourite 'weapon' of assassins in those distant times. Interest in arsenic in the modern era still centres on its poisonous character, but now it is the inadvertent release of arsenic into sediments, soils and waters that is the focus. In particular, anthropogenic arsenic associated with the mining and processing of arsenical ores, or associated with the industrial uses of arsenic, have been of major concern. Of even more concern has been the natural contamination of aquifers in countries such as Bangladesh and Bengal. The impact of aquifer contamination on the health of millions of people has led to this being described by epidemiologists as 'the greatest poisoning of a population in history'.



Given these concerns, it is not surprising that the literature on arsenic, including its mineralogy and geochemistry, has grown very rapidly in recent years. Contributions have ranged from popular texts, such as the excellent book *Venomous Earth* by Andrew A. Meharg (2006, Macmillan Publishers Ltd.), to articles in all of the leading specialist journals in the field. *Elements* magazine devoted one of its early issues, which I had the privilege of editing, to arsenic (*Elements* 2006, v2n2; see also the update by Vaughan and Polya in *Elements* 2013, v9n4, p315-316). In rapidly developing areas of science, it is essential to have good review papers and books which provide pathways into the subject matter for teachers and researchers. The *Reviews in Mineralogy and Geochemistry* (RiMG) series published by the Mineralogical Society of America and the Geochemical Society fulfil precisely this role, and many in this series have become 'classics'. Volume 79 of the RiMG Series, entitled *Arsenic: Environmental Geochemistry, Mineralogy and Microbiology*, is a timely and welcome addition to this list of publications. As with the majority of RiMG books, its publication has been linked to a short course that brought together the authors of the fourteen chapters with attendees, who ranged from beginning students to established researchers.

The book begins with a sixteen-page introductory overview of the environmental geochemistry of arsenic written by the editors of this volume (Bowell, Alpers, Jamieson, Nordstrom and Majzlan). The second chapter, entitled 'Parageneses and Crystal Chemistry of Arsenic Minerals', is a comprehensive review of what the authors (Majzlan, Drahota and Filippi) rightly call the 'labyrinthine world of arsenic minerals' – there are more than 560 minerals containing arsenic as an essential constituent. This chapter makes up more than a quarter of the book, is very well illustrated with 68 figures, and lists almost 700 references to the original sources. The majority of the illustrations are beautifully clear representations of the crystal structures of the important arsenic-containing minerals and mineral families. The 'parageneses' referred to in the title of Chapter 2 are the subject matter of the first third of this chapter. Here the term 'paragenesis' is used in the sense of characteristic assemblages (such as magmatic–hydrothermal arsenic minerals, arsenic minerals in coal, in mine wastes, or in soil and fluvial systems). As is appropriate, this part of the book is illustrated photomicrographs, field photographs and hand-specimen photographs. It is a pity that these could only be reproduced in black and white. Cost is generally a concern when using full-colour images, although an insert with 22 colour plates tied to a number of the other chapters is a welcome addition mid-way through this volume.

The information provided in Chapter 2 comes mainly from data obtained using the long-established techniques of mineralogy, ranging from field observations to optical and electron microscopy to X-ray crystallography. Another fundamental area essential to understanding the structure and stability of arsenic minerals, and also of arsenic species in aqueous solution, is concerned with their thermodynamic properties, which are reviewed in Chapter 4 by Nordstrom, Majzlan and Konigsberger. As these authors point out, quantitative geochemical calculations that enable one to predict the behaviour of arsenic in the environment are not possible without reliable thermodynamic databases. The authors review existing thermodynamic data 'with a focus on internal consistency, and the quality of the original measurements' and where possible 'update with new data' and point out discrepancies. This chapter, like others in this volume, is packed with detailed data, much of it in the form of tables.

The dramatic increase in the amount of published data on arsenic mineralogy and geochemistry in recent years has been partly due to technique development. In particular, synchrotron radiation has provided (and is providing) new insights into the occurrence and speciation of arsenic, including at low concentrations in solids or fluids and at surfaces. Chapter 5 by Foster and Kim on X-ray absorption spectroscopy as applied to arsenic speciation in solids provides an excellent review of one aspect of such studies. In understanding the behaviour of arsenic in the environment, speciation is a crucial factor. Speciation is a topic directly addressed in two other chapters. Leybourne, Johannesson and Asfaw (Chapter 6) offer practical guidance for measuring arsenic speciation in environmental media, ranging from the problems of sampling and preservation of samples to discussions on the wide variety of measurement techniques. Campbell and Nordstrom (Chapter 3) focus on aqueous speciation and the processes of adsorption of arsenic on mineral surfaces. They also review redox reactions of arsenic and provide speciation calculations for sets of reported water compositions (i.e. acid mine, geothermal and ground waters) to show the behaviour of arsenic speciation over a wide range of natural conditions.

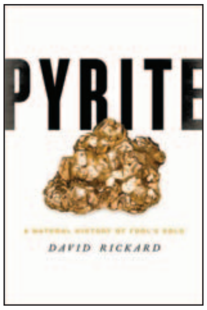
Another area of research on arsenic which has been growing very rapidly is the area I would describe as the 'geo–bio interface'. The recognition that interactions between microbes and minerals occur in environments at or near the Earth's surface is now well established, and related to this are the subjects discussed by Amend, Saltikov, Lu and Hernandez (Chapter 7) under the title 'Microbial Arsenic Metabolism and Reaction Energetics'. As these authors point out, there are over 240 strains of bacteria and archaea that can oxidize As(III) or reduce As(V) for energy gain or detoxification. The geo–bio interface of most significance, and which takes us to the heart of our concerns regarding the toxicity of arsenic, is, of course, the interface with humans. A brief, but useful, summary of the health risks of exposure to arsenic is given in Chapter 8 (Mitchell), which covers the various environmental sources, the nature of arsenic toxicity, the regions of the world affected by high arsenic levels, and the regulations governing maximum permissible levels with the example of the standards set in the USA. Chapter 9 is an interesting, but more specialised, contribution from Basta and Juhasz, who discuss the methods that can be used to test for the bioavailability of arsenic derived from soil ingestion by humans.

The remaining five chapters, a quarter of this book, return to material that will be much more familiar to most readers of RiMG volumes. Craw and Bowell (Chapter 10) provide an overview of arsenic minerals in mine waste, and these authors follow this up by an account of methods for the management of arsenic by the mining industry (Chapter 11).

1 Bowell RJ, Alpers CN, Jamieson HE, Nordstrom DK, Majzlan J (eds) *Arsenic: Environmental Geochemistry, Mineralogy, and Microbiology*. Reviews in Mineralogy and Geochemistry 79, Mineralogical Society of America, i-xv + 635 pages, ISBN 978-0-939950-94-2, US$40

PYRITE: A NATURAL HISTORY OF FOOLS GOLD[2]

David Rickard has pulled off a remarkable trick by writing a book on mineralogy and geochemistry that will entertain and interest an unusually wide range of readers. The Preface indicates that the target audience is a popular readership. Indeed, the book is accessible to beginners of science and to amateur mineral enthusiasts. Yet it also provides a wealth of new knowledge for most professionals. Even though I thought I was fairly well informed about sulfides, I found the book full of surprises and very enlightening.



The title is simply *Pyrite*, the word stretching across the front cover in large capital letters, presumably stressing the importance of the mineral even before the book is opened. When reading the Prologue, I felt slightly skeptical by the phrase, repeated several times, that "pyrite is the mineral that made the modern world." Is pyrite so very special? Does this mineral deserve a book to itself? The answer is an emphatic "Yes!" The first few chapters remove any doubts that a reader may have about the great importance and special role that pyrite has played in the history of our civilization.

Pyrite is one of the few minerals with which the general public is familiar, probably because of its fame as "fool's gold." It is appropriate, then, that the first chapter takes us on a dizzying journey through time and cultures, from ancient Greece via the medieval realms of England, Germany, and China, to modern Europe and North America, in search of the origins and uses of the concept of "fool's gold," and the association of this term with pyrite. It will probably astonish many readers to learn that pyrite played a major role in the colonization of both Canada and the United States by Europeans. The motivation was finding real gold, which usually turned out to be either inadvertently or fraudulently misidentified pyrite. An analysis of what "pyrite" meant during Classical, Arab, and Medieval times reveals that it was often called "marcasite", whereas at other times the term "pyrite" referred to several different sulfide minerals. I was delighted to receive an explanation for how and why the widespread, and to me annoying, term "iron pyrites" got into the literature.

We also learn that the origins of our civilization are closely connected to pyrite. The use of fire was vital to the evolution of humans, and pyrite was key to making fire portable: the mineral was used in fire-lighting kits up to the Iron Age. In addition, because it was a source of sulfur and sulfuric acid, pyrite was the foundation for the development of the earliest chemical industry, pharmaceutical industry, the modern arms industry, and the production of fertilizers. I, like many mineralogists, had been vaguely familiar with the technological uses of pyrite. Yet, the text is rich in historical details and facts that I had never come across before. The insights of Rickard ensure a compelling read for all.

The first half of the book provides a fascinating account of the cultural history and practical importance of pyrite; the second half emphasizes more contemporary science. A chapter on the structure of pyrite introduces the reader to the history of crystallography and explains how pyrite played a pivotal role in science by being one of the first structures to be determined by W. H. Bragg and W. L. Bragg. The eye-catching pyrite cubes, dodecahedra, and framboids are a delight, and the formation pathways of distinct crystal morphologies are described in detail, again providing many surprising new facts. We are then drawn into the depth of the ocean: hydrothermal vents and the origins of massive sulfide deposits, then on to bacterial sulfate reduction and the formation of sedimentary pyrite, which is described in an engaging style and with great insight. We are then introduced to inorganic and bacterial oxidation of pyrite and their resulting acid environments, as well as the roles of sulfur compounds in atmospheric pollution. In places, the author uses pyrite as an excuse to wade into his favorite topics and educate his readership about important environmental issues.

All pieces of the pyrite geochemical puzzle fall into place in the chapter entitled "Pyrite and the Global Environment," in which we receive the big picture of the role of pyrite in the global cycles of sulfur, oxygen, and carbon dioxide, and how sulfur isotopes in pyrite hold the key to understanding the history of our planet. Pyrite has been implicated in several origin-of-life hypotheses, which are summarized and made digestible for the nonexpert reader. The book concludes with a chapter that discusses current industrial uses of pyrite as a source of various metals (including gold), and we even get a glimpse into the possible future in which pyrite could be used as a material for solar cells.

This book convinces the reader that pyrite deserves its special distinction among minerals, both because of its historical and cultural importance and because of the major roles it has played in important areas of science and technology. In fact, halfway through the book I started wondering what other minerals could belong to the same exclusive club. It is hard to find more than a handful: quartz, calcite, magnetite, apatite, and halite are the ones that are on my list.

A strength of the book is its historical perspective in which every facet of science that is related to pyrite is viewed and narrated. The depth and breadth of the author's knowledge, as well as his humor, makes the book a delightful read. My only critical comment concerns the figures: there are a number that are in greyscale that really should have been printed in color.

David Rickard's several decades' worth of original research experience and the associated knowledge he has accumulated are condensed in this highly entertaining and very informative book. I recommend it to anyone interested in geochemistry, in mineralogy, and in science generally.

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2 David Rickard (2015) *Pyrite: A Natural History of Fool's Gold*. Oxford University Press, Oxford, UK, 320 pp, ISBN 978-0-19-020367-2, £20.49

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The last three chapters are essentially case studies of particular deposits: Chapter 12 on the Giant Mine (Yellowknife, Canada; by Jamieson), Chapter 13 on the Empire Mine (California, USA; by Alpers, Myers, Millsap and Regnier) and Chapter 14 on the Tsumeb Deposit (Namibia; by Bowell). These three chapters emphasise the importance of hydrogeochemistry and its influence on arsenate mineral stability. Unusually, the chapter on the Empire Mine also served as a field-trip guide for a visit by the short course participants. Another unusual feature coming at the end of this volume is a mineral-name index that lists the pages where particular minerals are mentioned. This index complements the appendices of Chapter 2, which list most of the arsenate, arsenite and common arsenic sulphide and arsenide minerals. Such editorial touches further enhance the usefulness of these tabulations.

Overall, this is a very welcome addition to the prestigious RiMG series and maintains the high standards that have been set in terms of authoritative content and excellent presentation. It is almost certain to become a 'best seller'.

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