R. M. Cornell, U. Schwertmann

The Iron Oxides

Structure, Properties, Reactions, Occurences and Uses

Second, Completely Revised and Extended Edition

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Cover Illustration
Prehistoric cave painting of a red horse from Lascaux. The colours used in the painting were obtained from the local deposits of red and yellow ochres, i. e. iron oxides. Similar ochre deposits in Southern France are still mined for pigment production today. As colouring agents, iron oxides have served man more or less continuously for over 30,000 years. A major, modern technological application of these compounds (mainly in synthetic form) is as pigment.
(Courtesy of Musée National de Préhistorie Les Eyzies).

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Contents

Preface to the Second Edition

Since this book first appeared, there have been hundreds of new publications on the subject of iron oxides. These have covered a wide range of disciplines including surface chemistry, the geosciences, mineralogy, environmental science and various branches of technology. In view of the amount of new material that is available, we decided, that once the copies of the first edition were exhausted, we would prepare a second edition that would incorporate the new developments.

As before, our aim has been to bring all aspects of the information concerning iron oxides into a single, compact volume. All the chapters have been revised and updated and new figures and tables added. The book is structured according to topic with the same arrangement as in the first edition being followed. In view of the recent recognition of the impact iron oxides have on environmental processes, a chapter dealing with the environmental aspects of these compounds has been added. The book concludes with a considerably expanded bibliography.

We hope that this new edition will continue to be of interest to all those researchers who, in one way or another, are involved with iron oxides.

Numerous persons and institutions from around the world again supplied data, figures, colour pictures and electron micrographs and technical help. These include Dr. H. Chr. Bartscherer (München), Mr M. Burlot (Apt), Dr. R. Båumler and Dr. Becher (Freising), Mr H. Breuning (Stuttgart), Dr. J. M. Bigham (Columbus, USA), Dr. G. Buxbaum (Bayer), Dr. L. Carlson (Helsinki), Dr. R. A. Eggleton (Canberra), Dr. F. G. Ferris (Toronto), Dr. R. W. Fitzpatrick (Adelaide), Dr. D. Fortin (Ottawa), Dr. M. R. Fontes (Guatemala), Professor R. Giovanoli (Bern), Dr. G. Glasauer (Guelph), Dr. M. Hanslick (München), Dr. P. Jaesche (Freising), Dr. A. A. Jones (Reading), Dr. R. C. Jones (Honolulu), Dr. D. E. Janney (Tempe), Dr. R. Loeppert (College Station), Professor S. Mann (Bristol), Dr. E. Murad (Marktredwitz), Dr. H. Maeda (Tsukuba), Professor A. Manceau (Grenoble), Professor E. Matijevic (Potsdam, USA), Mrs U. Maul (Freising), Dr. J. P. Muller (Paris), Musée National de Préhistoire (Les Eyzies, France), Mr R. Miehler (München), Dr. T. Nagano (Naka), Dr. H. Naono (Uegahara), NASA (Houston), Professor A. Posner † (Perth), Mrs M. Sauveté (Apt), Dr. N. Sabil (München), Dr. P. Schad (Freising), Dr. A. Scheidegger (Zürich), Dr. T. Schwarz (Berlin), Dr. A. Scheinost (Zürich), Dr. D. Schüler (Bremen), D. Schwertmann (Freising), Professor H. Stanjek (Aachen), Dr. P. Self (Adelaide), Professor T. Sugimoto (Sendai), Dr. K. Tazaki (Ishikawa), Dr. T. Tessier

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One of us (U. S.) thanks Professor Kogel-Kuabner for permission to use the facilities of The Soils Department in Weihenstephan and Dr. H. Becker and other colleaques in this institute for advice and assistance in the use of the computer.

Finally, we should like to thank the staff of Wiley-VCH for their patience and cooperation in the production of this book.

May 2003

R. M. Cornell
U. Schwertmann

Preface to the First Edition

Iron oxides have served man for centuries. Since the red and yellow ochres were first used to help produce prehistoric paintings in caves such as those at Lascaux, the role of iron oxides has expanded enormously. Their application as pigments and their ability to catalyse various chemical reactions, their role as the precursors of iron and steel and their activity as adsorbants in the ecosphere are just a few examples of the contribution of these compounds to the well-being of man.

As long ago as 1937, Fricke and Hüttig reviewed the state of the art regarding metal oxides in "Hydroxyde und Oxydhydrate", a book in which 50 pages were devoted to those of iron. To the best of our knowledge, no review of this topic has appeared since. This is surprising in view of the immense amount of research activity and information concerning iron oxides which has accumulated in recent decades. As shown in Chapter 1, workers from a range of different disciplines are interested in these compounds. Recently developed techniques such as EXAFS, AFM and STM are being applied to elucidate details of the interior and surfaces of iron oxides. Owing to the small size (nm range) and degree of disorder in many iron oxide crystals, only these modern techniques have the capacity to provide the information necessary for understanding of the behaviour of these compounds. The data from all these investigations are distributed over publications in diverse journals with the result that workers in one field are often unaware of development in other areas.

This book is aimed at collecting all aspects of the information about iron oxides into one compact volume. It provides a coherent text with a maximum of homogeneity and minimum overlap between chapters. It is structured according to topics, i. e. surface chemistry, dissolution behaviour, adsorption etc. For each topic a general introduction is followed by a section which reviews current knowledge concerning the different iron oxides. The latter section includes much detailed information and recent data from the authors' own laboratories. As this is intended to be a handbook, an extensive list of references to help the reader expand various details is provided. We have also indicated some of the numerous opportunities for further research in this field.

The book is intended for those researchers who, whatever their discipline, are working with iron oxides. We hope it will be of use to these representatives of extremely diverse fields who are linked by their common interest in this fascinating group of compound.

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In compiling this book we received substantial help from a large number of people.

Professor R. Giovanoli (Universität Bern) was invaluable in reading and commenting on various chapters, supplying electron micrographs and other data and in discussing various matters. Our warmest thanks to Dr. H. Stanjek (Technische Universität, München) for reviewing different chapters, for discussion and for contributions. He also produced new computer drawings of the structure models of the Fe oxides. We are indebted to various other colleagues for reading certain chapters, for helpful comments and for valuable additions. These include Dr. G. Buxbaum (Bayer AG, Krefeld), Dr. J. W. E. Faßbinder (Bayer. Landesamt für Denkmalpflege, München), Dr. S. Glasauer (University of California, Berkeley), Dr. A. Hugot-LeGoff (Université P. and M. Curie, Paris), Dr. S. G. McMillan (University of Otago, Dunedin, N.Z.), Dr. E. Murad (Bayer. Geol. Landesamt, Bamberg), Professor P. W. Schindler (Universität Bern), Professor W. Schneider (ETH, Zürich) and Dr. P. Weidler (ETH, Zürich).

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The wonderful cooperation of all these people has been invaluable. Our sincere thanks goes to all of them. Finally we thank VCH for their support and outstanding patience during this period.

Perth and Freising, July 1996

R. M. Cornell
U. Schwertmann

Abbreviations

AES	Auger electron spectroscopy
AFM	atomic force microscopy
Ak	akaganéite
ASTM	American Society for Testing and Materials
ATP	adenosine triphosphate
ATR	attenuated total reflectance
bcc	body-centred cubic
BCF	*B*urton-*C*abrera-*F*rank mechanism
bcp	body centered (close) packing
BET	*B*runauer, *E*mmett and *T*eller
BIF	banded iron formation
BM	Bohr magneton
CCC	critical coagulation concentration
ccp	cubic close packing
CDTA	cyclohexylene dinitrilo tetraacetic acid
CFSE	crystal field stabilization energy
CIE	Commission Internationale de l'Eclairage
CIR	cylindrical internal reflectance
CSIRO	Commonwealth Scientific Industrial Research Organization
DCB	dithionite-citrate-bicarbonate
DDL	diffuse double layer
DLVO	Derjaguin, Landay,Verwey and Overbeek
DRS	diffuse reflectance spectroscopy
DSC	differential scanning calorimetry
DTA	differential thermal analysis
DTPA	diethylene triamine pentaacetic acid
ED	electron diffraction
edl	electrical double layer
EDTA	ethylene diamine tetra acetic acid
EGME	ethylene glycol monoethylether
EPR	electron paramagnetic resonance spectroscopy
ESR	electron spin resonance
EXAFS	extended X-ray absorption fine structure
FAO	Food and Agriculture Organization
Fh	ferrihydrite
FTIR	Fourier-transform-infrared (spectroscopy)
GR	green rust
Gt	goethite
hep	hexagonal close packing
HFO	hydrous ferric oxide

Hm	haematite
HRTEM	high resolution transmission electron microscopy
HS	high spin
IAP	ion activity product
iep	isoelectric point
IR	infrared
IUPAC	International Union of Pure and Applied Chemistry
LEED	low energy electron diffraction
LOI	loss on ignition
Lp	lepidocrocite
LS	low spin
M	metal
MCL	mean coherence length
MD	multidomain
Mh	maghemite
MIO	micaceous iron oxide
Mt	magnetite
MW	molecular weight
NMR	nuclear magnetic resonance
NTA	nitrilotriacetic acid
ppzc	pristine point of zero charge
PS	photoelectron spectroscopy
PSD	pseudo single domain
pzc	point of zero charge
pznpc	point of zero net proton charge
pzse	point of zero salt effect
RR	redness rating
RT	room temperature
RTP	room temperature and pressure
SAD	selected area diffraction
SAXS	small-angle-X-ray-scattering
SD	single domain
SEM	scanning electron microscopy
SHE	standard hydrogen electrode
SIMS	secondary ion imaging mass spectroscopy
SIRM	saturation isothermal remanent magnetization
SP	superparamagnetic
STM	scanning tunnelling microscopy
STP	standard temperature and pressure
TEA	triethanolamine
TEM	transmission electron microscopy
TGA	thermal gravimetric analysis
UV-Vis	ultraviolet-visible
WHH	width at half height
XAFS	X-ray absorption fine structure
XANES	X-ray absorption near edge structure
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Colour Plates

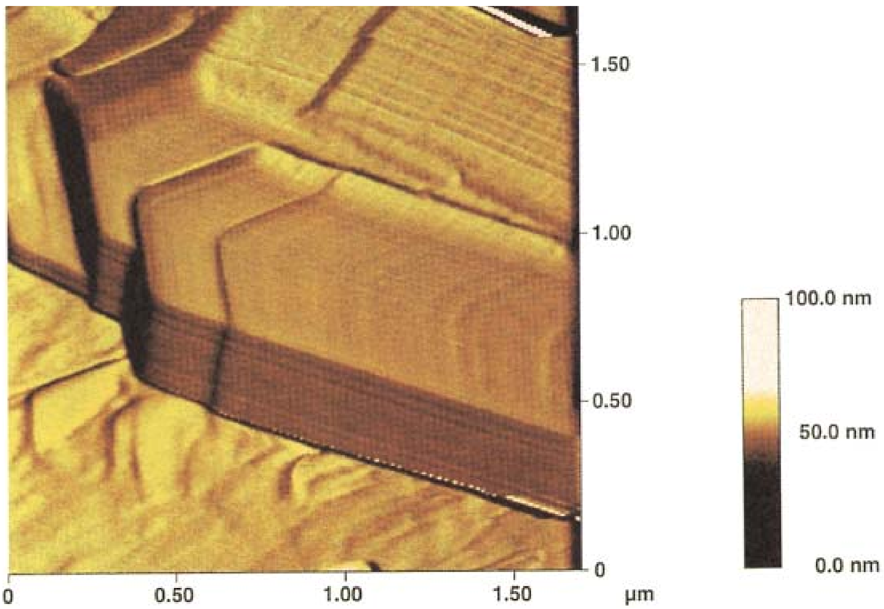

Plate 4.1 Atomic force microscope image of a synthetic goethite crystal scanned in deflection mode (see Weidler et al., 1996 , with permission, courtesy P. Weidler).

Plate 6.1 Colours of Fe^{III} oxides

Plate 6.II Effect of particle size and cation substitution on the colour of Fe^{III} oxides

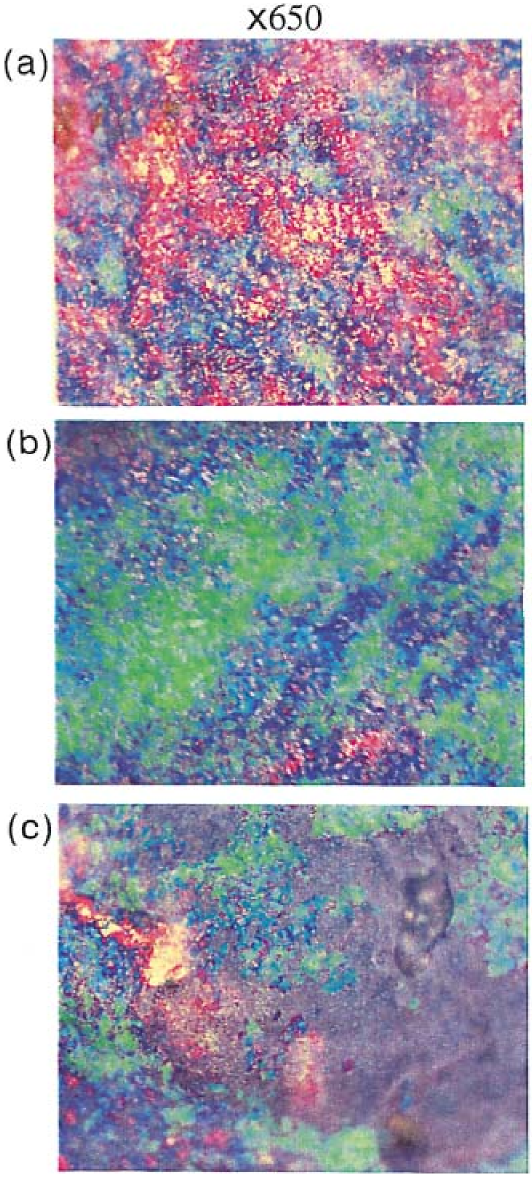

Plate 10.I Optical microscope images of the irridescent regions on the surface of the dry β-FeOOH sol (x650) (Reprinted from Maeda & Maeda, copyright 1996. With permission and Courtesy, H. Maeda).

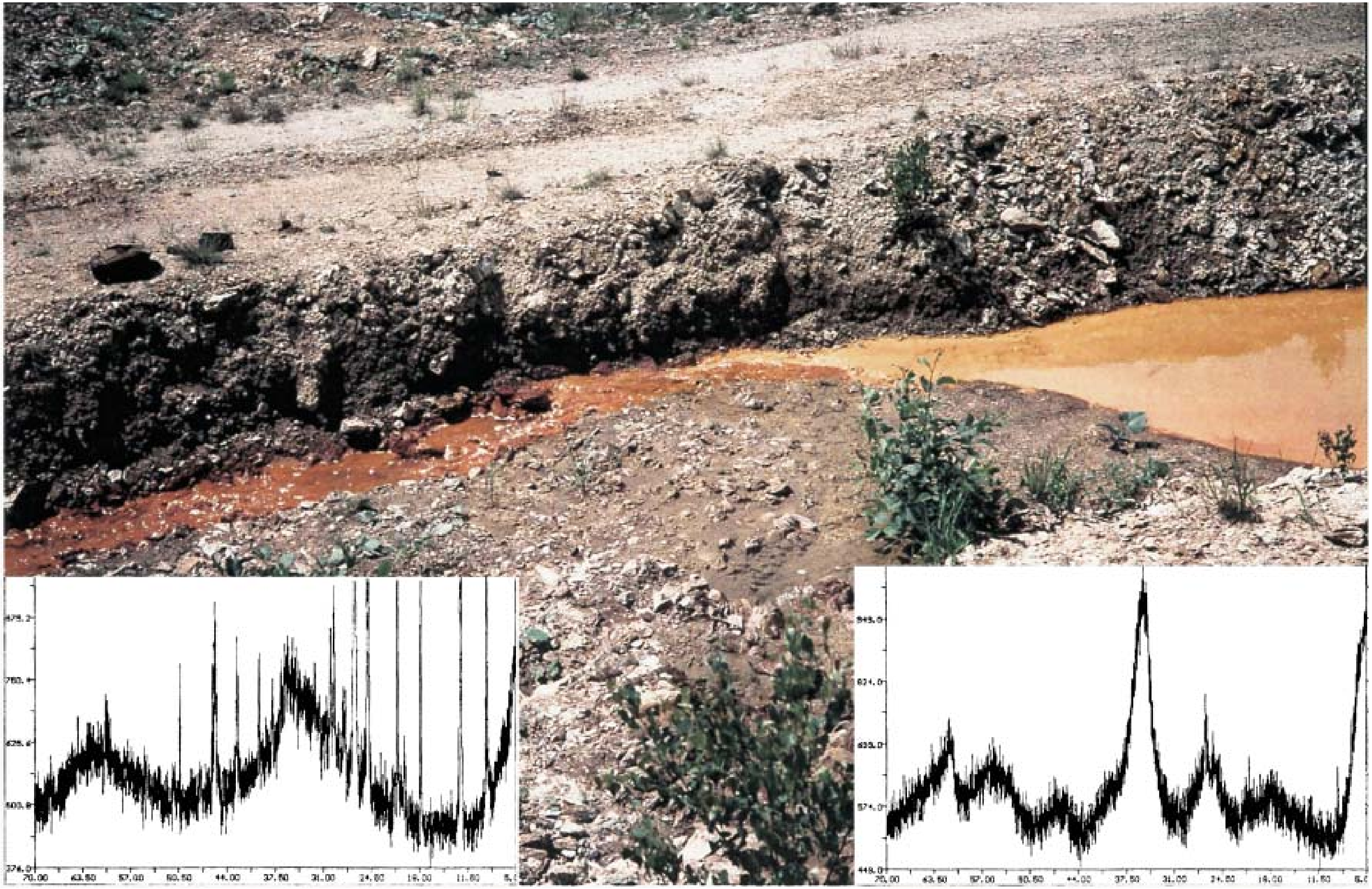

Plate 13.1 The colour changes of the ochreous precipitates formed from ferriferous acid mine water from a lignite mine near Sokolov, Czech Republic, and their X-ray patterns clearly indicate the abrupt transition from schwertmannite at a water-pH of 3.7 on the right to 2-line ferrihydrite after neutralization by a pH 8.2-water on the left side (arrows) (Courtesy E. Murad; Murad & Rojik, 2003, with permission).

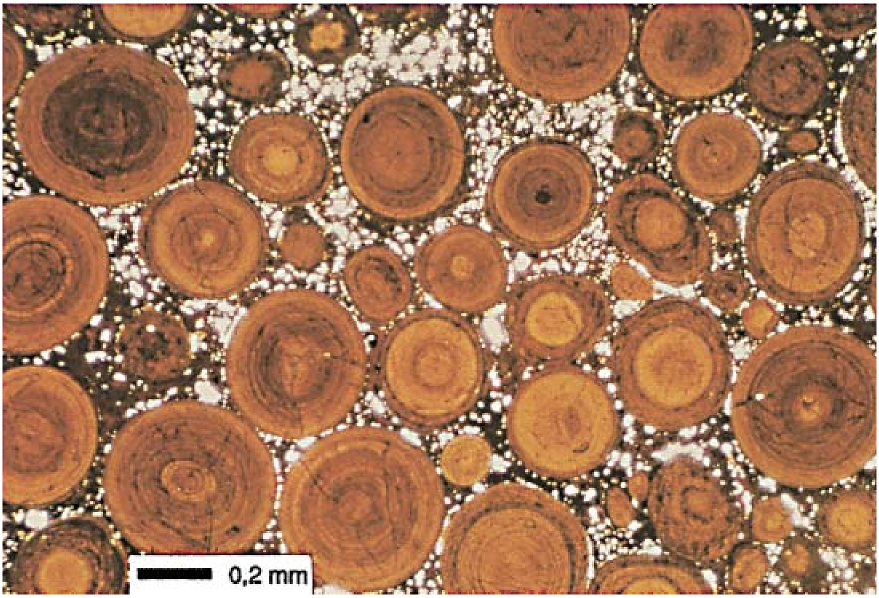

Plate 15.I Iron oxide ooids in a silty matrix from an iron oolite – a thin section. Fula, Sudan (Schwarz, 1992; Courtesy T. Schwarz).

Plate 15.II Iron oxide formation by atmospheric weathering of a pyrite vein in a limestone (photo courtesy, Ph. Jaesche).

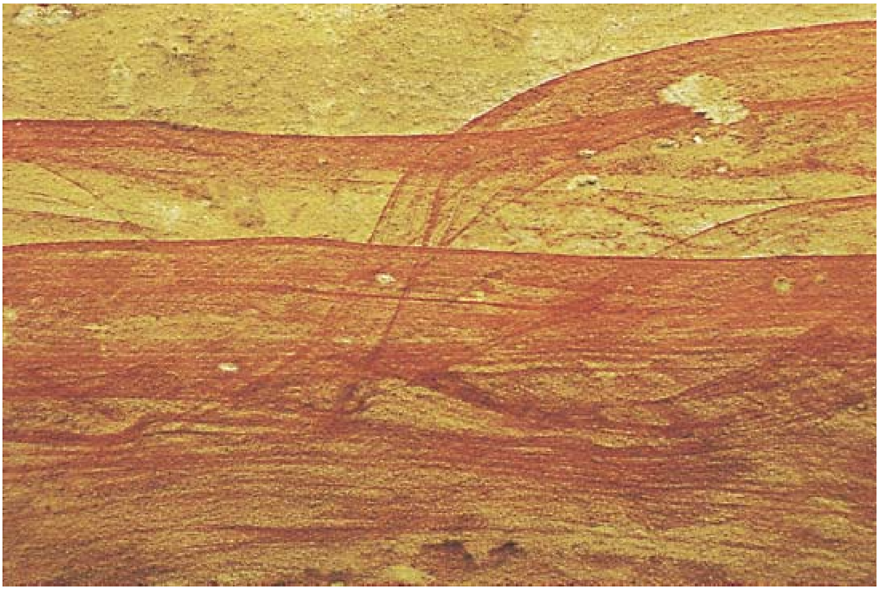

Plate 15.III Iron oxide bands in sandy-gravelly Pleistocene sediments, South Australia (Art object by Nicolaus Lang, courtesy H. Stanjek).

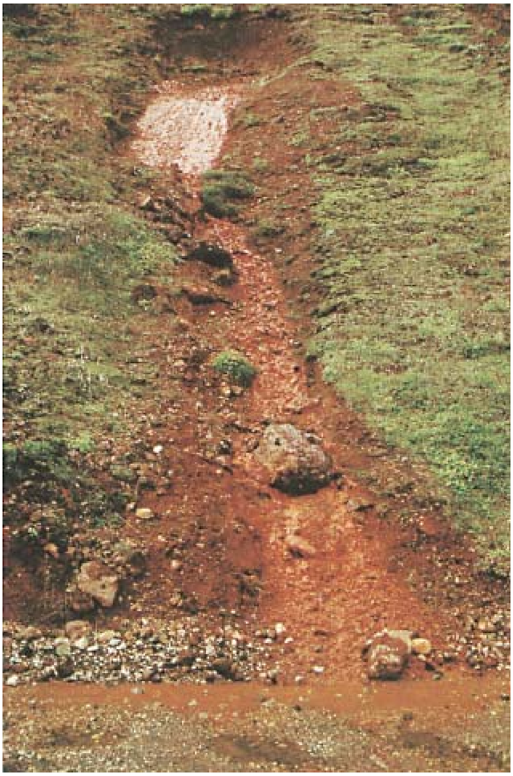

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Plate 15.V Drain pipe clogged with ferrihydrite (courtesy H. Kuntze).

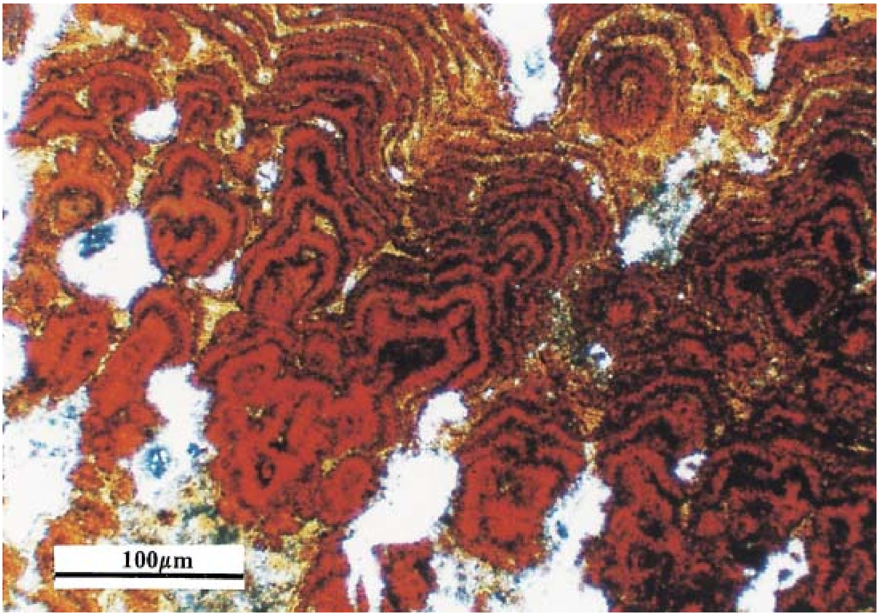

Plate 15.VI Rhythmic Fe oxide bioformation from a volcanic spring near Kyoto (Tazaki, 2000; with permission).