

ACS SYMPOSIUM SERIES 415

Spectroscopic Characterization of Minerals and Their Surfaces

Lelia M. Coyne, EDITOR
San Jose State University

Stephen W. S. McKeever, EDITOR
Oklahoma State University

David F. Blake, EDITOR
NASA—Ames Research Center

Developed from a symposium sponsored
by the Division of Geochemistry
at the 196th National Meeting
of the American Chemical Society,
Los Angeles, California,
September 25–30, 1988



American Chemical Society, Washington, DC 1990



Library of Congress Cataloging-in-Publication Data

Spectroscopic Characterization of Minerals and Their Surfaces

Lelia M. Coyne, editor, Stephen W. S. McKeever, editor,
David F. Blake, editor

p. cm.—(ACS Symposium Series; 415).

Developed from a symposium sponsored by the Division of Geochemistry at the 196th National Meeting of the American Chemical Society, Los Angeles, California, September 25–30, 1988.

Includes bibliographical references.

ISBN 0-8412-1716-5

1. Mineralogy, Determinative—Congresses. 2. Spectrum analysis—Congresses.

I. Coyne, Lelia M. II. McKeever, Stephen W. S.
III. Blake, David F. IV. American Chemical Society.
Division of Geochemistry. V. American Chemical Society.
Meeting (196th: 1988: Los Angeles, Calif.) VI. Series

QE369.S65S64 1989
549'.1—dc20

89-27755

CIP

The paper used in this publication meets the minimum requirements of American National Standard for Information Sciences—Permanence of Paper for Printed Library Materials, ANSI Z39.48-1984.



Copyright © 1989

American Chemical Society

All Rights Reserved. The appearance of the code at the bottom of the first page of each chapter in this volume indicates the copyright owner's consent that reprographic copies of the chapter may be made for personal or internal use or for the personal or internal use of specific clients. This consent is given on the condition, however, that the copier pay the stated per-copy fee through the Copyright Clearance Center, Inc., 27 Congress Street, Salem, MA 01970, for copying beyond that permitted by Sections 107 or 108 of the U.S. Copyright Law. This consent does not extend to copying or transmission by any means—graphic or electronic—for any other purpose, such as for general distribution, for advertising or promotional purposes, for creating a new collective work, for resale, or for information storage and retrieval systems. The copying fee for each chapter is indicated in the code at the bottom of the first page of the chapter.

The citation of trade names and/or names of manufacturers in this publication is not to be construed as an endorsement or as approval by ACS of the commercial products or services referenced herein; nor should the mere reference herein to any drawing, specification, chemical process, or other data be regarded as a license or as a conveyance of any right or permission to the holder, reader, or any other person or corporation, to manufacture, reproduce, use, or sell any patented invention or copyrighted work that may in any way be related thereto. Registered names, trademarks, etc., used in this publication, even without specific indication thereof, are not to be considered unprotected by law.

PRINTED IN THE UNITED STATES OF AMERICA

American Chemical Society
Library
1155 16th St., N.W.

In Spectroscopic Characterization of Minerals and Their Surfaces; Coyne, L., et al.;
ACS Symposium Series; American Chemical Society: Washington, DC, 1990.

ACS Symposium Series

M. Joan Comstock, *Series Editor*

1989 ACS Books Advisory Board

Paul S. Anderson
Merck Sharp & Dohme Research
Laboratories

Alexis T. Bell
University of California—Berkeley

Harvey W. Blanch
University of California—Berkeley

Malcolm H. Chisholm
Indiana University

Alan Elzerman
Clemson University

John W. Finley
Nabisco Brands, Inc.

Natalie Foster
Lehigh University

Marye Anne Fox
The University of Texas—Austin

G. Wayne Ivie
U.S. Department of Agriculture,
Agricultural Research Service

Mary A. Kaiser
E. I. du Pont de Nemours and
Company

Michael R. Ladisch
Purdue University

John L. Massingill
Dow Chemical Company

Daniel M. Quinn
University of Iowa

James C. Randall
Exxon Chemical Company

Elsa Reichmanis
AT&T Bell Laboratories

C. M. Roland
U.S. Naval Research Laboratory

Stephen A. Szabo
Conoco Inc.

Wendy A. Warr
Imperial Chemical Industries

Robert A. Weiss
University of Connecticut

Foreword

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that, in order to save time, the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable, because symposia may embrace both types of presentation.

Preface

THE EARTH CAN BE SEEN as a 2.5-billion-square-mile heterogeneous catalytic surface. Two thirds of this surface interfaces aqueous solutions, one third a gaseous one, and a small, but disproportionately important part of it cycles irregularly between liquid and gaseous interfaces.

The earth's crust is a mineral assemblage. Mineral-based assemblages, that is, soil systems, support our natural and cultivated vegetation, both physically and nutritionally. Fossil fuels, the mainstay of our physical and economic survival, were generated via mineral-catalyzed chemical reactions. The water we drink flows over and percolates through mineral assemblages. In bathing these assemblages, the sorptive and reactive powers of minerals purify this water of and contaminate it by the chemical products of geology, biology, agriculture, and industry.

Unlike laboratory chemistry, geological chemistry occurs in thermodynamically open systems. That is to say, there is flagrant exchange of materials and energy between the system and the environment. Not only is the system as a whole not isolated from the environment, but the materials of interest are rarely isolated from each other. To further the complexity, interaction of mineral catalysts with those forms of energy most likely to affect surface-mediated reactions has barely been characterized in model systems.

The chapters in this volume have been collected in order to chart a course toward a more holistic, thus more realistic, view of mineral reactivity than can be garnered from equilibrium modeling. Spectroscopies are the tools by which structure, dynamics, and reactivity can be most directly examined. Examples include numerous means of mineral spectroscopy applied to numerous ends, such as determination of composition, purity, interaction with energy, characterization of chemically and spectroscopically special (active) centers, and adsorbate interactions. Coverage of both spectroscopy and minerals is intended to be illustrative, not exhaustive.

The initial chapters on nonoptical methods are supplied as instruction in how to describe a mineral and its surface before studying it. A distinction is made between bio- and geominerals because they are not equivalent, despite identities of their chemical formulae and crystal

structural parameters. The focus on energy storage in part two is meant as a word to the wise for those serious about consideration of the surface loci suspected of directing interfacial chemistry, lest they forget bulk influences.

In the face of all wisdom concerning choice of models, the section on active centers takes clay as a model, the mineral class that is most, rather than least, complex. Clays happen to be the mineral class most studied with respect to natural reactivity. They are among the more important classes of minerals reactive in natural systems, and they are known to include most of the generic site types thought to be influential in mineral interfacial chemistry. A special emphasis is placed on acidic and oxidizing entities because of their importance and because evidence is accumulating to indicate that they are interrelated.

It is hoped that this book will stimulate new thinking and new methodologies, and new integrations of these by physicists, chemists, geologists, and fuel, soil, agricultural, and environmental scientists who are interested in interfacial chemistry of geological surfaces. It is also hoped that it will prove useful to catalysis chemists humble enough to acknowledge that Nature may have used a few reactive tricks they've missed.

We can use our knowledge of the earth to achieve the crucial goal of stabilizing our environment, thus allowing us to develop a sensible policy for the management of energy. Realistic energy management would permit the development of a more sensibly based economy, of which one reward could be resources for further exploration. Many of us would like to see that exploration move from the terrestrial to the extraterrestrial realm, and spectroscopy can serve as a central tool in this search. We believe the approach outlined here will permit us to begin that search.

LELIA M. COYNE¹
Department of Chemistry
San Jose State University
San Jose, CA 95192

STEPHEN W. S. MCKEEVER
Department of Physics
Oklahoma State University
Stillwater, OK 74078-0444

DAVID F. BLAKE
Planetary Biology Branch
NASA-Ames Research Center
Moffett Field, CA 94035

April 18, 1989

¹Current address: Mail Stop 239-4, NASA-Ames Research Center, Moffett Field, CA 94035

Chapter 1

Spectroscopic Characterization of Minerals and Their Surfaces

An Overview

Lelia M. Coyne^{1,3} and Stephen W. S. McKeever²

¹Department of Chemistry, San Jose State University, San Jose, CA 95192

²Department of Physics, Oklahoma State University,
Stillwater, OK 74078-0444

The lithosphere is both literally and figuratively the bedrock, the solid foundation, on which understanding of geology rests. To characterize the lithosphere is to characterize not only what is, but, because of the chemical reactivity of rocks and their surface activity, it is also to characterize what was and what may become.

The first step in such a characterization process is to identify the mineral type(s), in terms of crystal structure and elemental composition. Although this information may be adequate to define what is, and to a significant degree what was, it is far from adequate to project what might become. To move toward a more predictive, rather than simply a naturalistic geology, it is essential to understand the details of chemical structure at the electronic level as well. To understand the reactions mediated by mineral surfaces it is not adequate to know the details only of the overall atomic arrangement. It is essential also to grasp the subtle, sometimes not so subtle, variations in structure and properties that can be produced by chemical alteration of a few special structural moieties, by introduction of defects (extended and point), and by interactions not only of the bulk structure, but also of these occasional centers, with energy sources. In addition, it must be constantly born in mind that the electronic structure of the surface and the bulk, while related, are far from identical, because of the termination of long-range structure at the surface. The surface of a mineral is activated relative to its bulk both chemically and electronically. To sketch the process of characterization of bulk and surface chemical and electronic structure of minerals and interrelationships between their bulk and surface properties is the purpose of this volume. The utility of such detailed characterization will become

³Current address: Mail Stop 239-4, NASA-Ames Research Center, Moffett Field, CA 94035

0097-6156/90/0415-0001\$08.25/0
© 1990 American Chemical Society

increasingly appreciated as the role of soils in environmental stability or degeneration becomes more widely recognized and better understood.

The introductory chapter and the book itself is organized around three ideas: What is the chemical structure? What is the electronic structure? What governs the surface chemical reactivity? of minerals.

The first major section of this overview will be devoted to general spectroscopic characterization with particular application to minerals. Source material on spectroscopic theory, methods and applications used in the subsequent papers will be provided in the initial paragraphs as an introduction or review. A focus will then be placed on those aspects of spectroscopy allowing investigation of the alteration of minerals by excitation, energy storage and energy transfer. These alterations occur primarily via the production of metastable excited electronic states. Such alterations may be familiar to mineralogists within the confined context of mineral spectroscopy and dating, but possibly have not been adequately appreciated with respect to their possible significance to reactivity on mineral surfaces. In connection to the degree to which excitation of minerals may alter their surface reactivity, there will be a mention of infrequently considered energy sources and the means, consequences of, and efficiency of excitation by these sources. Reference will be made to the extent to which the quantitative theory of the detailed process and degree of electronic excitation of minerals and their defect centers has not been sufficiently developed to enable useful estimations of the chemical utility of electronic excitation, particularly by non-optical energy sources.

The second major section will focus on those special centers of minerals thought to be of importance to their catalytic activity, with an emphasis on the known and possible effects of electronic excitation on the population and mode of action of these centers. Metastable states constitute a hidden variable in defective solids, a non-negligible one for non-stoichiometric ones. With regard to concepts of mineral catalysis, the only systems for which extensive spectroscopic information on mineral catalytic centers has been definitively coupled to the mechanism of a well understood surface chemical reaction is H_2/D_2 exchange on binary oxides. Existing data for the radiatively-produced catalytic center of SiO_2 will be reinterpreted and that for the thermally-produced center on MgO will be further assessed in terms of mineral structure in the second section of this overview. The MgO -promoted exchange proceeds via classical catalysis. The silica-promoted exchange proceeds only via electronic excitation of the catalyst and probably involves a one:one stoichiometric relationship between catalytic centers and exchanged product. Interestingly, in the light of this contrast is the fact that the catalytic centers of the two materials are closely chemically and electronically related.

Both these catalytic centers and the reaction mechanism on them have been better than average well-characterized by the spectroscopic methods discussed and applied in this volume. The comparison between anticipated locations of the catalytic centers for these materials also points up the importance of methodology for determining not only the number, but the accessibility of catalytic sites. Therefore, it is thought that comparisons and contrasts between thermal and "photo" chemistry, as well as many aspects of the state of present comprehension of mineral spectroscopy and mineral-mediated catalysis will be well-illustrated by a reexamination of published studies of H_2/D_2 exchange, even though this reaction is not directly relevant to applications of spectroscopy discussed in the succeeding papers.

Use of Molecular Spectroscopy to Study Bulk and Surface Electronic Structure, Energy Transfer and Storage Processes of Defined Mineral Phases

Spectroscopy is the experimental tool for the determination of chemical and electronic structure. General discussions of electronic structure can be found in (1-2), of inorganic molecular structure in (3-7) and discussions more particularly directed to that of minerals in (8-10). Discussions of spectroscopic theory and measurement techniques must, of course, be governed by the region of the electromagnetic spectrum or the particle energy distribution required to excite and/or detect the transitions of interest, given a specific material. Numerous spectroscopies were employed in the specific applications detailed in the following chapters of this book. General introductions to various spectroscopies are found in (11-12), of NMR in (13-14), of ESR in (15-16), IR in (17-18), vis/uv absorption in (19-20), luminescence and thermoluminescence in (21-23), vacuum uv in (24), electron, X and gamma-ray spectroscopies in (25-27), Mossbauer in (28). Applications of these methods specifically to minerals may be found in (29-32) and to clay minerals, in particular, in (33).

Spectroscopy is also extensively applied to determination of reaction mechanisms and transient intermediates in homogeneous systems (34-37) and at interfaces (38). Spectroscopic theory and methods are integral to the very definition of photochemical reactions, i.e. chemical reactions occurring via molecular excited states (39-42). Photochemical reactions are different in rate, product yield and distribution from thermally induced reactions, even in solution. Surface mediated photochemistry (43) represents a potential resource for the direction of reactions which is multifaceted and barely tapped. One such facet, that of solar-excited electrochemical reactions, has been extensively, but by no means, exhaustively studied under the rubric photoelectrochemistry (PEC) (44-48).

Special Considerations in Spectroscopic Studies of Mineral Structure and Energetics of Importance to Surface Chemistry

Form, Impurities and Imperfections. Minerals, being natural materials, may be selected, but not delimited by the investigator. Also, a large specific surface area is important to efficient heterogeneous catalysis. Therefore, the most notable minerals driving chemistry in geological settings frequently do not present themselves in forms readily amenable to spectroscopic examination. I.e., the minerals of surface chemical interest in geology and biology typically are not large, optically transparent, single crystals that are brilliantly colored by transition metal substituents, or artistically tinted by an occasional single type of point defect, or ionic substitution. They tend to be defective, even poorly crystallized, finely divided, high-bandgap photoconductors. They typically are not pure compounds, intrinsically, due to non-stoichiometry from inherent structural substitutions and inclusions, and extrinsically, due to mineral admixing and adsorbed organics. They are the sedimentary and soil binary oxides, hydroxides, oxy-hydroxides, silicates, aluminosilicates (the clay minerals prime among them), carbonates, sulfates, sulfides, phosphates. They support (49), may have spawned (50-51), planetary life. Characterization of their elemental composition, crystal structure and dynamics offers a difficult, but not insuperable aesthetic and intellectual challenge.

Environmental History. The complexity of their makeup might seem adequate deterrent to their systematic analysis of minerals, but, in addition to their makeup, crustal minerals bear an experience. In anthropomorphic terms, their "behavior" (properties) derives from both a "heredity" (composition and structure) and an

“environment” (geological milieu). I.e., they have been, and are continually being subjected to thermal, mixing, mechanical, chemical and radiative alterations. Spectroscopy can be applied not only to mineral structure determination, monitoring of surface-adsorbed reactants and products and reaction kinetics, but also to the production and monitoring of excited states of the mineral which may produce a different type of reactivity than the ground state substance.

The most likely of the environmental variables to be significant both to spectroscopic features of the mineral and to reactivity under geological conditions, but the one least often considered, is electronic excitation, both past and ongoing. Because of the high energies required for excitation, e.g. 8.5 e.v. for silica (52), of many of the important crustal materials, and the very high absorptivity for allowed transitions in the solid state, solar illumination is an efficient energy source for electronic excitation only for near-surface phenomena. More transmissible energy sources are required if the entire regolith is to be used as an active surface but more transmissible energy sources are available in natural systems. Their contributions to natural chemistry must also be assessed.

Whereas gamma irradiation is a low level energy source at present, gamma and particle fluxes were higher in earlier times (53). Furthermore, since the capacity of many minerals for long term electronic energy storage (23, 31) is significant in “molar” terms (54), a low level source operating over a long time period can produce significant residual excitation.

A possibly more abundant, on-going, energy source for mineral excitation is mechanical stress, producing friction or fracture. Such operations have been shown to excite very high energy transitions in organic materials and adsorbed atmospheric gases (55-56). Minerals, too, produce light when rubbed or fractured (57-58), but with them it is less apparent whether the mechanical stress is the immediate source of excitation, or whether it has triggered the release of previously-stored energy (54), or has mobilized trapped molecular fragments (59), which combine and emit light.

Another environmental factor of prime importance is weathering, i.e. cyclic exposure to water, atmospheric gases, temperature variations, abrasion. These natural processes produce alteration of the surface composition and introduce point defects which have special adsorptive and energetic properties.

Catalytically active defects of both radiation-induced and formation or “weathering-like” origins will be exemplified in the sections on H_2/D_2 exchange on simple binary oxides. This reaction will be considered in detail because it is the simplest possible chemical reaction and the mineral sites producing it have been the best characterized by spectroscopic techniques.

Mineral Sensitized Chemistry - Natural Routes to Organic Synthesis

Because minerals can be electronically excited under common geological conditions and can, to varying degrees, store energy, it is necessary at the outset to consider any mineral-mediated reaction occurring under natural conditions as possibly “photo”-catalyzed or “photo”-assisted over and beyond its activity as a classical catalytic surface or source of reactants. For minerals storing appreciable amounts of electronic excitation, a similar statement may apply to reactions studied in the laboratory. Conversely, exposure to radiation can also serve a surface deactivating or protecting role, depending on the nature of the chemical entities involved.