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Introduction (to the book Instrumental Surface Analysis of Geologic Materials)

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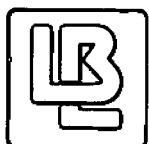https://escholarship.org/uc/item/6gs0f525

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Introduction

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I. INTRODUCTION

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1. General

1.1. Modern Advances in Instrumentation. Over the last two decades, the field of surface chemistry has enjoyed a renaissance unparalleled by any other in science. The reason for this is the advent of electronics and high vacuum technologies that have made possible the development of spectroscopic techniques that can be used to directly observe chemical and morphological conditions of a solid surface. In addition to the introduction of ultrahigh vacuum (UHV) techniques such as x-ray photoelectron and Auger spectroscopy, tremendous strides have been made in non-UHV experimental approaches. The utility of infrared spectroscopy, for example, which has been widely used to examine surface reactions since the 1950s, has been greatly enhanced by the Fourier transform approach to the technique. Similarly, Mossbauer spectroscopy, which was initially used to study surface phenomena in the transmission mode only, has demonstrated even greater utility in these studies with the development of conversion electron and emission Mossbauer spectroscopy.

1.2. Potential for Future Advances. While all of these advances in instrumentation have made it possible to make great strides in the understanding of surface chemical phenomena, they only serve as being indicative of things to

come; this is especially true with respect to applications for the study of geologic materials. Scanning tunneling microscopy (STM), for example, is just starting to be applied to mineral surfaces to give detailed information about surfaces at the atomic level. Other very new approaches, such as optical second-harmonic generation (SHG), should prove quite effective for probing at submonolayer sensitivities of interfaces that are accessible to light, including solid/liquid interfaces. Rutherford backscattering (RBS) also holds promise for studying mineral reaction systems.

1.3. Purpose of Book. The purpose of the present book is to provide a good introductory overview of a variety of techniques that can be used to study geologic surface/interface reactions. A thorough knowledge of surface reactions is extremely important in several areas of geochemistry, including mineral dissolution and precipitation (including weathering), elemental partitioning at the mineral/aqueous solution interface, and natural heterogeneous catalytic reactions. All of these fundamental geochemical processes impact heavily on the applied fields of mineral extraction, ore deposit formation, and toxic waste transport. Toxic waste transport, for example, is a process in which the sorption of heavy metal ions and organic molecules on geologic substrates plays a very important role. So, a book addressing surface chemical phenomena of geologic materials comes at a most critical time with respect to rigorously studying this social/technological issue.

2. Types of Surface Studies Involving Geologic Materials

2.1. Structure. Experimental approaches to surface studies involving geologic materials can take several forms, but all of them can be placed into four general categories: structural, analytical, electronic, and reaction chemistry studies. When one discusses structural studies of a bulk geologic material using surface-sensitive techniques, it is assumed that the clean surface of the material also represents the bulk structure. The same is true for all the types of spectroscopy described in this book; they can be used for both surface and bulk studies, depending on the experimental circumstances of how a sample is prepared (or reacted) before it is spectroscopically or microscopically examined. Under the heading of structural studies, for example, one can cite the correlation of x-ray photoelectron spectral data with the bulk structures of various aluminosilicates.

With respect to structures of species *on the surface*, the different experimental approaches are very effective. Morphological phenomena on surfaces can be studied using scanning electron microscopy, while Raman and infrared spectroscopy can provide valuable structural information on anion and organic molecule bonding modes to central heavy metal ions. Other techniques such as electron spin resonance and nuclear magnetic resonance also can provide structure-related data.

2.2. Analyses. Analytical chemical studies are focused on both the aspects of what species (qualitative) and how much of them (quantitative) are present on a geologic surface, with the most common area of interest being on

elemental analysis. With modem surface instrumentation, however, the analytical approach can be taken still further. A determination can be made as to whether the element is present as a simple elemental cation or anion or as one or more complex, polyatomic cations or anions. Quantitative information can be derived by either internal calibration (making use of relative spectral intensities) or by the use of rigorous analytical standards. In turn, these same analytical approaches can be used to monitor analytical changes on a surface as it undergoes further reactions.

2.3. Electronic States. Most surface instrumental techniques readily lend themselves to the analysis of electronic states of elements that are involved in surface reactions. This is especially true if multiple techniques are used in conjunction with one another to study a particular metal ion system. Surface techniques can be used to study diamagnetic vs. paramagnetic species of metallic ions, i.e. copper(I) vs. copper(II) by x-ray photoelectron spectroscopy. This technique can also differentiate between high- and low-spin electronic configurations of the same ion. A good example is the cobalt(III) ion, which can be either diamagnetic or paramagnetic, depending on the ligands attached to it. Electron spin resonance can give detailed information about paramagnetic chemical species such as transition metal ions and adsorbed radicals.

Additionally, the electronic state can be studied in conjunction with the elemental stoichiometry and crystallographic structure of a mineral to determine the chemical bonding; the most notable examples are the transition metal sulfide minerals.

2.4. Reaction Chemistry. The importance of surface techniques for studying interfacial chemical reactions involving geologic surfaces cannot be overstated. For that reason, a large portion of this book is directed at this application. Chemical reactions on geologic surfaces naturally encompass a wide range of reacting chemical species and geologic substrates. For this reason, such studies can impact on a large number of chemical reaction-dependent geologic areas. Perhaps the largest class of this type of reaction is that of adsorption, a surface-related process that dictates several highly important basic and applied chemical reactions involving geologic materials. Two really good examples of these are weathering of rocks and minerals (during which process surface oxidation plays an important role) and froth flotation processing of ores; still another good example of a basic area involving detailed studies of chemisorption is that of ore body formation. Many other geologic material/chemical interaction studies are highlighted in this book.

3. Geologic Surface/Interface Reactions - Overview

3.1. Surface/Gas and Surface/Liquid Interactions. Geologic surface/interface reactions are ones which typically involve reactions between a geologic surface and a gas or liquid. Schematically, simple and complex (multiple) surface/gas reactions are shown in Fig. 1. In naturally occurring interface reactions in the environment, both classes of this reaction occur. First, there are the surface/gas reactions, with the most common interaction involving air, with the process resulting in one simple product. Other gases also react with surfaces, depending on the chemical atmospheric conditions. A second

type of reaction, that of a surface/liquid reaction, is possible in theory; however, for it to be an exclusive *liquid* reaction with a geologic surface, the liquid would have to have never contained a gas or would have to be depleted of the gas prior to the reaction. Since such a scenario occurring naturally would be difficult to envision, it must be considered a process that can best be effected in the laboratory. Third, there are the surface/gas/liquid interactions. These reactions are ones involving a liquid containing a dissolved gas (or gases) reacting with a surface.

Case I represents the relatively "simple" scenario of a gas reacting with a surface under very controlled conditions, i.e., in an ultrahigh vacuum chamber where the materials are exposed to varying amounts of a gas. The gas could be oxygen, for example, reacting with a sulfide mineral in order to study the oxidation process. Under these carefully controlled conditions, the geologic material also may be annealed and ion sputtered preparatory to the reaction sequence. This approach will yield a single (hopefully, but not always) reaction product under each set of conditions and yields much useful information about stepwise reaction products during a reaction sequence and the mechanism by which a final product is achieved. This experiment is thus more controlled than a geologic surface oxidation reaction effected in the open air. In that situation, the surface oxidation process would not be a chemical process exclusively dependent on oxygen but rather on a mixture of oxygen, carbon dioxide, water vapor, and any other reactive trace gases present. If a reaction consists of a pure, degassed liquid interacting with a clean, fresh surface, and it results in one product on the surface, then Case I is also schematically

appropriate.

Case II, however, represents a more complex surface/gas interaction, that of several gases forming different product layers as they react with the previous layer formed. Regions 1, 2, and 3 represent the different products. Region 4 represents the pristine, unreacted mineral. In its contact with air, the surface is altered by atmospheric oxygen, carbon dioxide, and water vapor; this process thus creates an initial surface product, represented by Region 3. As time progresses, this same reaction proceeds or, alternatively, the new mineral surface product reacts with still yet another reactant (or, not unrealistically, several reactants) to form *another* reacted product designated by Region 2. Logical reaction candidates could be sulfur and/or nitrogen oxides. One can thus see that the "surface" of a mineral is not one simple product but more a composite of the oxidation reaction process. A very good example of this is galena, PbS; naturally oxidized galena shows a range of oxidation products on its surface, ranging from elemental sulfur to the sulfate anion. Lead oxides, carbonates, and mixed hydroxide/carbonates have also been observed, depending on the oxidation timescale and chemical conditions.

3.2. Surface/Gas/Liquid Interactions. Case II can also illustrate the underlying reasons for a potentially far more complex situation, that of a heterogeneous surface/gas/liquid reaction, in which chemical interaction of the surface products occurs. This interactions results in a "mixing", thus causing heterogeneous surface conditions. This scenario is more truly illustrative of most natural geologic surface/interface reactions, reactions in which multiple

reactants and products are involved. A very good example of Case II becoming important in a role in a surface/gas/liquid interaction with mixing is that of the natural weathering of minerals. Once the various layers of surface products are formed, rainwater can also react with them, altering the newest surface again through dissolution of the top surface product and subsequent reaction of deeper products with the newly formed solution.

Another good example of such heterogeneous reactions is that of ore processing, or froth flotation processing. Metal ions, organic compounds, and other reagents interact with ore surfaces, making the surface-dependent processing extremely complex. Again, concurrent processes such as oxidation-reduction and organic/inorganic complexation are operable, resulting in heterogeneous surface conditions. This situation also occurs when minerals undergo electrochemical surface alterations, depending on what reaction solution is used.

3.3. Caveats Concerning Surface Reaction Complexity. Both the geologic surface/gas and surface/gas/liquid scenarios discussed above serve to illustrate the inherent complexity on surface reactions involving natural geologic materials and their reactions under natural conditions. In light of this, several important warnings (or caveats) should be made concerning both the bases of such complexity and a warning that the complexity cannot be overstated. First, with respect to solid-gas interactions, the composition of the reacting gas will have a dramatic effect on both the intermediate and final reaction products; this is also true of the sequence of different gaseous reactions with a given surface. A

reaction involving a mixture of gases A, B, and C in the environment will produce different reaction products than gases A, B, and D. This is especially true if gases C and D display decidedly different reaction characteristics. In the case of C being a nitrogen oxide, for example, that reaction mixture will effect different products on an oxide mineral surface than a set containing nitrogen, water, or oxygen as gas D. Similarly, if carbon dioxide is first reacted with a hydrated metal oxide, a quite stable mixed hydroxide/carbonate mineral phase may form. If water vapor (or some other hydroxide-forming reactant) is reacted *after* the carbon dioxide, such a phase might not result. Of course, various factors, such as surface-reactant gas bond strengths, thermodynamic considerations, and lattice stability energies, come into play in deciding the final surface composition.

Another caveat concerning gas phase interactions with geologic surfaces is that--under natural conditions especially--gaseous surface products can be easily altered. Products chemisorbed on surfaces during cool, dark periods (such as at night) might be desorbed or undergo further reactions in intense, hot sunlight. This is especially true if the gas adsorbed is susceptible to photolytic effects. Depending on the components of a multiple gas layer on the surface, the gases themselves could react with one another to form new compounds.

In the case of geologic surface/liquid interactions, the complexities of the reaction system may be much more severe. This is especially true if the liquid is not a single, pure compound but rather a mixture of different liquids or a solution. Because of multiple, competing reactions at the surface/solution

interface, the final surface chemical state is a reflection of the *total, composite reaction.* In solutions involving metal ions, for example, the pH will dictate the species in solution that actually will be reacting with the surface. This can be still further complicated if the reaction system contains metal ions that can undergo oxidation/reduction or if complexing organic ligands are present. Two other experimental parameters—pressure and temperature— can make reactions at the surface even more complicated, often increasing the number of reaction products formed and thus the overall surface heterogeneity. Also, with increased temperature and pressure, the mixing of surface reaction product layers increases.

4. Philosophy and Composition of Book

When a book is first conceived, several important issues must be addressed and resolved; the present book is no exception. First, the choice of a *theme* must be one of the decisions made. In this case, *Surface Chemistry of Geologic Materials* is indeed not only the title of the book but also the theme. This is meant to encompass that concept in its entirety, i.e. the surface chemistry of geologic materials in terms of *the morphology of the surfaces, the chemical state of the original surfaces, and their chemical compositions after undergoing reactions.* This includes microscopic and spectroscopic investigations of thin films and precipitate layers by various (but complementary) techniques. The techniques include ultrahigh vacuum approaches such as x-ray photoelectron and Auger spectroscopy to study monolayer and thin film surface products as well as techniques such as infrared and electron spin resonance spectroscopy

which have been traditionally used to study thicker reaction product layers. Several can even be used for both classes of surface conditions; Mossbauer, for example, can be used in the conventional transmission mode to study thicker precipitates while also being pressed into service as emission and conversion electron Mossbauer spectroscopy to yield data more reflective of the first few surface layers. Taken as a whole, all of the techniques described in this book can give a researcher a relatively complete picture of either a virgin or reacted geologic surface.

A brief explanation should also be given concerning other criteria for selection of the techniques in the book. First, one of the operable words concerning the techniques included in this book is *complementary*. The reader can survey Table 1 and see that all types of chemical species on surfaces can be studied by one or more of the included approaches. Diamagnetic and paramagnetic species, metal ions, organic species, polyatomic cations and anions, light and heavy atoms in different chemical states--all can be studied using the various types of spectroscopy. In organizing the book and deciding what techniques to include in each chapter, one of the deciding factors was that the chapters complement one another in their coverage of both different surface chemical species and the types of geologic substrates on which the chemistry occurs.

Second, all of the techniques described herein rely on "stand alone" instrumentation; all of it is commercially available and can be placed in a research investigator's laboratory. Thus, techniques which rely on a synchrotron source, for example, have been excluded, since this would necessitate the

Table 1. A Comparison of Several Types of Surface-Applied Spectroscopy

Spectroscopy	Typical Transition Energy (eV)	Type of Transition	Surface Species Observable
Infrared	$(50 - 2.5) \times 10^{-2}$[a]	Vibrational	Most di- and poly-atomic molecules
Raman	$(50 - 0.6) \times 10^{-2}$[a,b]	Vibrational	Most di- and poly-atomic molecules
Mössbauer	$10^4 - 10^5$[a]	Nuclear	Species containing Mössbauer nuclides
Electron spin resonance	$(14 - 3.8) \times 10^{-5}$[a]	Electron spin	Paramagnetic species
Nuclear magnetic resonance	$(2.5 - 8.3) \times 10^{-7}$[a]	Nuclear spin	Diamagnetic species
X-ray photoelectron	$0.1 - 1500$[a]	Bound electron to the continuum	All elements except hydrogen and helium
Laser emission	$1.3 - 4$	Electronic	All elements that can undergo laser emission
Auger	$0.1 - 2200$	Bound electron to the continuum	All elements except hydrogen and helium

[a]Source: Delgass, W. N.; Haller, G. L.; Kellerman, R.; Lunsford, J. H., "Spectroscopy in Heterogeneous Catalysis," Academic Press: New York, 1979.

[b]The energy range of the incident and scattered radiation is ~ 2 eV.

use of a central facility. Such a facility has the normally attendant problem of a queue waiting to obtain experimental time. Also, in may cases, travel is

necessary for an investigator to make use of it.

Third, the techniques discussed in this book are ones which are, for the most part, mature enough to have been experimentally developed and generated a substantial amount of published geologic surface literature. Scanning tunneling microscopy, as mentioned above, promises to yield a wealth of information concerning mineral and other geologic surfaces. Unfortunately, only recently have researchers begun to obtain data on geological materials (principally, conducting minerals such as sulfides) using this technique. This is true also for a large number of other experimental surface approaches.

In summary, experimental approaches to studying surface phenomena have contributed greatly to the understanding of many processes and reactions involving geologic materials. Further advances in both instrumentation and their geologic applications continue to be made, being limited only by an investigator's imagination. Using these techniques, research into the understanding of both natural and laboratory-induced geologic processes has expanded rapidly, and, just like all other areas of scientific research, the future promises a continuation in its growth.

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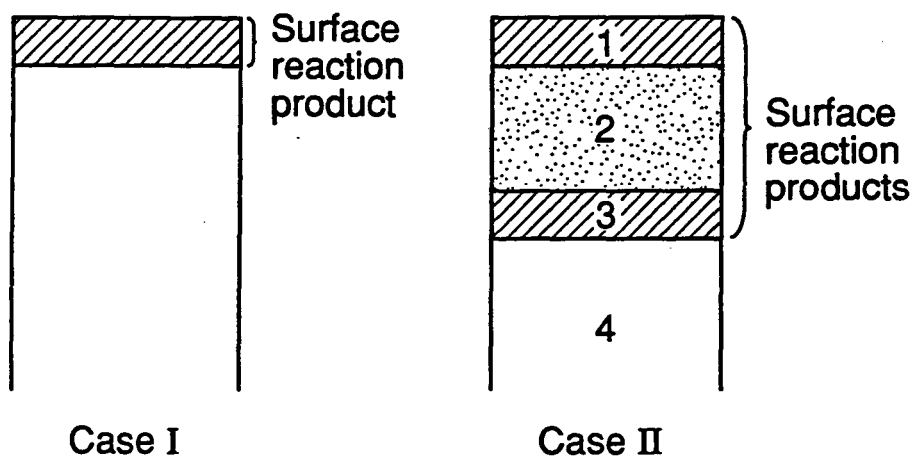
Fig. 1. Geologic surface reactions

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