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GEOCHEMISTRY OF BISMUTH

Edited by

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and

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SERIES EDITOR'S FOREWORD

The philosophy behind the "Benchmark Papers in Geology" is one of collection, sifting, and rediffusion. Scientific literature today is so vast, so dispersed, and, in the case of old papers, so inaccessible for readers not in the immediate neighborhood of major libraries that much valuable information has been ignored by default. It has become just so difficult, or so time consuming, to search out the key papers in any basic area of research that one can hardly blame a busy person for skimping on some of his or her "homework."

This series of volumes has been devised, therefore, to make a practical contribution to this critical problem. The geologist, perhaps even more than any other scientist, often suffers from twin difficulties—isolation from central library resources and immensely diffused sources of material. New colleges and industrial libraries simply cannot afford to purchase complete runs of all the world's earth science literature. Specialists simply cannot locate reprints or copies of all their principal reference materials. So it is that we are now making a concerted effort to gather into single volumes the critical materials needed to reconstruct the background of any and every major topic of our discipline.

We are interpreting "geology" in its broadest sense: the fundamental science of the planet Earth, its materials, its history, and its dynamics. Because of training in "earthy" materials, we also take in astrogeology, the corresponding aspect of the planetary sciences. Besides the classical core disciplines such as mineralogy, petrology, strucuture, geomorphology, paleontology, and stratigraphy, we embrace the newer fields of geophysics and geochemistry, applied also to oceanography, geochronology, and paleoecology. We recognize the work of the mining geologists, the petroleum geologists, the hydrologists, and the engineering and environmental geologists. Each specialist needs a working library. We are endeavoring to make the task of compiling such a library a little easier.

Each volume in the series contains an introduction prepared by a specialist (the volume editor)—a "state of the art" opening or a summary of the object and content of the volume. The articles, usually some twenty to fifty reproduced either in their entirety or in significant extracts, are selected in an attempt to cover the field, from the key papers of the last century to fairly recent work. Where the original works are in foreign languages, we have endeavored to locate or commission translations. Geologists, because of their global subject, are often acutely aware of the oneness of our world. The selections cannot, therefore, be restricted to any one country, and whenever possible an attempt is made to scan the world literature.

To each article, or group of kindred articles, some sort of "highlight commentary" is usually supplied by the volume editor. This commentary should serve to bring that article into historical perspective and to emphasize its particular role in the growth of the field. References, or citations, wherever possible, will be reproduced in their entirety—for by this means the observant reader can assess the background material available to that particular author, or, if desired, he or she, too, can double check the earlier sources.

A "benchmark," in surveyor's terminology, is an established point on the ground, recorded on our maps. It is usually anything that is a vantage point, from a modest hill to a mountain peak. From the historical viewpoint, these benchmarks are the bricks of our scientific edifice.

RHODES W. FAIRBRIDGE

PREFACE

Bismuth has received little study by the geochemical community. Data, therefore, are scanty. Goldschmidt reviewed the early literature on this subject and presented a masterful summary of that information. Bismuth has both chalcophilic and lithophilic properties in the upper lithosphere. However, those bismuth minerals of economic importance are all chalcophilic in nature.

Our interest in compiling a review of bismuth geochemistry was triggered primarily by the striking absence of data on the element in Turekian and Wedepohl's review of elemental abundances in different units of the earth's crust.

Of all the elements, bismuth appeared to be the one for which little reliable data was available. Subsequently, we reviewed much of the literature on bismuth reported in chemical abstracts since 1960. From this review came the decision that a compilation of selected articles on the geochemistry of bismuth would be helpful in our work and perhaps to others. The present volume is a natural outgrowth of that assessment.

We expect there will be criticism and second guessing on the articles included in this collection. That is only natural. We do feel, however, that each paper included herein has contributed significantly to advancing our knowledge of the geochemistry of bismuth.

To the best of our knowledge, the Russian articles presented here appear in English translation for the first time. We encountered several problems with the Russian papers. Among them were the difficulty in obtaining clean copy for reproduction of figures and photographs. All of the figures have been redrafted. No easy solution to the photographic problem presented itself. In addition, even after securing copies of the original Russian articles, we found no affiliation for some of the authors was indicated.

The articles included in this collection have been grouped into five topics: Part I, General Geochemistry; Part II, Bismuth in Meteorities; Part III, Rock-Forming Processes; Part IV, Phase Equilibrium; and Part V, Economic Geology—Ore Deposits.

The element deserves far more attention and study than it has received to date. It is our hope that this situation will be changed by the publication of this volume. We feel that the articles selected herein will serve as a practical and useful introduction to the geochemistry of bismuth and possibly induce further studies of the natural distribution and occurrence of this element.

ERNEST E. ANGINO
DAVID T. LONG

CONTENTS

INTRODUCTION

Bismuth is an element that has been little studied over the years by the geochemical profession. Several reasons exist for this situation, but two in particular seem clearly to be responsible for this state of affairs. Until about 1965, the analysis of bismuth in rocks and minerals was a rather difficult, time-consuming, and involved task. With the introduction of neutron activation and atomic absorption spectrometry, a major restriction on studies of bismuth distribution in geologic materials was removed. The second reason can be summarized by a statement sometimes heard among geochemists: "It is not an interesting element."

An awareness of these two facts helps to explain the dearth of material in the literature treating most facets of the geochemistry of bismuth. This literature gap has made the task of selecting articles for inclusion in this volume both easy and difficult at the same time—that is, the task was difficult because clearly the largest number of papers dealing exclusively with bismuth appears in the Russian literature with all the attendant problems of translation and obtaining copy.

If one considers the topics and papers covered in this compendium, it should become clear to anyone that considerable expansion of our knowledge of the geochemistry of bismuth is still to come. In brief, information on bismuth geochemistry is not extensive.

Bismuth has the properties (e.g., low melting point) that make it likely that it will become better known and more widely used in the future. It is not an element of great abundance, nor are any of its minerals very common. Bismuth as an element is frequently found in the native state, but it and its minerals are also quite dispersed in the matrix of many rocks and minerals.

The metal is commonly obtained commercially as a by-product of lead and copper smelting. Uses of bismuth and its componds are widespread but no one use requires great volume. Even in alloys, the metal is consumed in small quantities, but its unusual properties create important uses for it. It possesses curative medicinal properties, has a low melting point (271°C), forms alloys quite easily, and expands on solidifying. For example, Wood's metal (Bi-Sn-Cd) melts at 60°C, and other alloys melt at even lower temperatures, thus making bismuth a key metal in the use of automatic water sprinklers for fire control.

Its principal uses, however, are for medicinal and cosmetic preparations and in electrical and electronic apparatus. Other uses are in enameling, printing of fabrics, forming of special optical glass, making of fuses, locker safety plugs, and innumerable other minor applications. The potential of bismuth as a guide element in the geochemical exploration for other metals is beginning to be realized.

In spite of these uses and unusual properties, knowledge of the geochemistry of bismuth is still poorly disseminated or known. Thus, we felt the need to compile informative and key articles from the widely scattered literature on bismuth. These data will serve to make the geochemistry of bismuth better known and make information more available to new investigators.

As was noted in the Preface, extensive data on the geochemistry of bismuth is scarce. A review of the several parts of the Data of Geochemistry series (U.S. Geological Survey Prof. Paper 440) and of the now standard references of Taylor (1964) and Turekian and Wedepohl (1961) confirms this observation. Of the ten rock categories in Turekian and Wedepohl for which concentration values are normally given, entries for bismuth are listed under only two.

Accounting for this situation is difficult, for knowledge of the geochemistry of bismuth must be one of the keys to an understanding of the origin of our planet. Given the low melting point (271°C) of bismuth and its volatility, that any bismuth is present on the earth at all is surprising—if we accept the "hot" earth theory of our planet's origin. Why didn't all the bismuth boil off? As we know, "bismuth is lost progressively with temperature increase during the heating of geologic material, including primitive meteorites and basalt (BCR-1) for one (1) week at temperatures ranging from 500°-1000°C or more in a low-pressure (initially $\sim 10^{-5}$ atm H_2) system" (M. Lipschutz, pers. comm.).

The general geochemistry of bismuth is determined primarily from general principles and from mineralogical analyses. For upper lithospheric rocks and minerals, bismuth clearly has chalcophilic characteristics. In most deposits and occurrences known to contain bismuth, the element accompanies sulphide minerals or occurs in secondary alteration products of sulphides and their related compounds. Under certain conditions, the element also possesses lithophilic characteristics in the upper lithosphere.

Due to the lack of data, obtaining a well-authenticated value for the concentration of bismuth in the earth's crust is difficult. Taylor (1964) gives a crustal average for bismuth of 0.17 ppm. The correct value probably lies between 0.1 and 0.2 ppm. Bismuth is, however, likely to be concentrated in granitic magmas, and residual liquids formed therefrom.

Because of the recent studies of meteoritic data and recognition of the fact that bismuth may be a key element in tracing some of the cosmic reactions to which meteorites have been subjected, we now have a fair understanding of the geochemistry of bismuth in meteorites.

Knowledge of the behavior of bismuth in weathering processes is scarce. It is limited primarily to data on reactions in the oxidation zone of ore deposits. Except for its concentration in ferrugenous bauxites, little is known of the pathway of bismuth in soil formation or in the soils themselves. Bismuth is commonly present in most ranks of coal. Little reliable data exists on the concentration of bismuth in sedimentary rocks (Turekian and Wedepohl 1961).

Sulphide minerals of bismuth and sulphide minerals containing bismuth are commonly found associated with hydrothermal mineral deposits. As noted by Goldschmidt (1954, p. 482), bismuth minerals are also known as products of pneumatolysis associated with recent volcanic action. Bismuth is commonly associated with gold, selenium, and tellurium in high-temperature hydrothermal deposits. A common occurrence of bismuth is with (in) the mineral galena (PbS). From the literature, there appears to be a direct correlation between bismuth and temperature. The bismuth concentration of galenas increases with increasing temperature of mineral formation. Bismuth will very likely play a major role in the search for new mineral deposits in the United States and elsewhere. Knowledge of its role as a "pathfinder element" in geochemical exploration is still imperfectly understood, but clearly its use is in the development stage.

One area of the study of bismuth where we have a reasonable understanding of the relations involved is that of phase equilibria. Several published articles, including those in this compilation, summarize the phase relationships in bismuth systems. Levin, Robins, and McMurdie (1964) present data for Bi_2O_3–MoO_2–PbO; Bi_2O_3–PbO; and Bi_2O_3–PbO–WO_3. Van Hook (1960), Salanci (1965), and Craig (1967) have done extensive work on the Bi_2S_3–PbS system. Van Hook (1960) and Craig (1967) also carried out considerable work on the $AgBiS_2$–PbS system.

In sum, we hope that this volume on the geochemistry of bismuth will serve two purposes: first, to make information on the geochemistry of a rare and widely dispersed, but needed element more available and second, by collecting key articles on an interesting element into one volume, to stimulate further research on bismuth as another step in the endeavor to expand our knowledge of the geochemistry of the elements.

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Part I

GENERAL GEOCHEMISTRY

Editors' Comments on Papers 1, 2, and 3

1 **ANGINO**
Bismuth: Element and Geochemistry

2 **KUPČÍK**
Bismuth: Crystal Chemistry

3 **AHRENS and ERLANK**
Bismuth: Isotopes, Abundances, and Interelement Relationships

Since little is known of the detailed geochemistry of bismuth and what is known is widely scattered in the literature, we decided to include three papers to serve as an introduction to the general geochemistry of bismuth.

Several brief summaries of the geochemistry of bismuth are available, including the two classic treatises on geochemistry by Rankama and Sahama (1950) and Goldschmidt (1954). The three papers in this section were selected because they provide a broad overview of our present knowledge of the geochemistry of the element bismuth. They include much of the pertinent material contained in the earlier reviews, in particular that from Goldschmidt and Rankama and Sahama.

In Paper 1, Angino gives a brief summary of the chemical physical properties of bismuth. This paper is provided as background material to introduce the articles that follow on the chemistry of bismuth in natural materials. Brief comments on some of the more common bismuth minerals are provided, followed by a more extensive discussion of the chemistry of bismuth in aqueous solution. From this information, it is obvious why the +3 valent state of bismuth is that seen in natural minerals. Although bismuth has many properties similar to those of antimony and arsenic, the common occurrence in nature of a +5 valent state is not one of them.

A review of the geochemistry and mineralogy of the element suggest that the crustal abundance of bismuth is around 0.2 ppm, although a considerable degree of uncertainty accompanies this figure. As is demonstrated, bismuth is a widely distributed element, but tends to become enriched in late magmatic differentiations. Mineralogically, bismuth is most commonly present in galenas. Paper 1 also presents some data on the marine geochemistry of bismuth.

Ernest E. Angino, the author of Paper 1, received his doctorate from the University of Kansas in 1961. After three years at the Department of Oceanography of Texas at A & M University, he joined the faculty of the University of Kansas in 1965 where he currently is professor of geology and civil engineering.

Papers 2 and 3 are from the section on bismuth in the *Handbook of Geochemistry* edited by K. H. Wedepohl. They provide valuable information on abundances, distribution, occurrences of bismuth in minerals, isotopes, and other physical data.

Knowledge of the crystal chemistry of bismuth is of considerable help in understanding the distribution of bismuth in minerals. In Paper 2, V. Kupčík presents an excellent summary of the geochemical occurrence of bismuth as controlled by crystallo-chemical relations. The main bismuth mineral groups are discussed. These groups include: (1) metallic bismuth and alloys; (2) sulfides, selenides, tellurides, and sulfosalts; and (3) oxides, oxosalts, and halogen-oxosalts. For many of the rarer bismuth minerals, formulae, Bi-O interatomic distances, structural data, interatomic distances, coordination shape, and references are tabulated.

Extensive data on bismuth are collected in the several tables presented in Paper 3 by Ahrens and Erlank. The long list of bismuth minerals presented in this paper will be of considerable help to anyone unfamiliar with the element, as many minerals containing bismuth are relatively rare. One should be cautioned, however, that the list is not complete. Some data on the phase equilibrium of bismuth is presented, and a brief summary and discussion of bismuth occurrences is given. An interesting observation in Paper 3 is the lack of qualitative data for bismuth in tektites.

From their review of bismuth geochemistry in igneous rocks, Ahrens and Erlank conclude that "the present data allow no firm conclusions to be drawn as to the variation of Bi in the various igneous rock types and with magmatic differentiation." They further conclude that "detailed knowledge regarding the mechanism of substitution of bismuth in sulfide minerals is lacking." These reviews show that many more data are required before we can state with confidence what the crustal abundance of bismuth is, how it moves through the magmatic processes, and what are its pathways to specific minerals.

L. H. Ahrens has contributed greatly over the years to expand-