RARE METALS HANDBOOK

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In Appreciation of

COLIN GARFIELD FINK

1881–1953

Pioneer in the field of rare metals, distinguished contributor to knowledge of electrometallurgical techniques, and ingenious experimenter, his loss by the electrochemical profession is compensated only by the rich heritage he leaves as a teacher whose infectious curiosity and energetic enthusiasms inspired all who were his students, as a devoted servant and builder of The Electrochemical Society for which he was Secretary from 1921 to 1947, as a prolific producer of original research which made common many rare metals, and as an amiable, devoted friend. Truly his works and life will be perpetuated by the stimulus he gave to so many others by personal and scientific contacts; they will detail and expand the fields whose vistas he outlined.

PREFACE

This book has been designed to accomplish the following purposes:

1. To bring together for the first time the available reference data on over 34 rare or uncommon metals—the latest methods of production from ores or other raw materials, the chemical and physical properties, fabrication techniques, and present and potential uses.

2. To offer an authoritative, concise and readily available background to the man who desires information about a specific metal or metals, and at the same time to give him selected bibliographical references to enable him to conduct a more detailed search if he so desires.

3. To provide a convenient source of data for the man who has a general question, such as "What metals have melting points over 1000°C and densities below that of steel?"

The treatment has been limited to emphasis upon the metallic or elemental form with only a minor presentation of material about compounds, interesting though these are in many instances. This has been dictated by space considerations as well as the desire to concentrate attention on the metals themselves, which often receive scanty treatment in most inorganic chemistry treatises.

The list of metals selected for inclusion is admittedly arbitrary, but it covers most of the less common metals about which there is an expanding interest. While there may be debate of an academic nature as to whether elements like boron and silicon are metals, they do exhibit some of the properties commonly regarded as characteristic of metals, and the growing interest in them in several fields of metallurgy warrants their inclusion in this book.

As pointed out in the final chapter, it so happens that cost alone is a worthy basis for regarding a given metal as rare or common. A classification of metals in order of increasing price per pound reveals that of the first 13 only one of the metals included in this book, manganese, appears among them. Also, of the metals not covered in this book, only mercury, silver, and gold appear further down the list. This is not surprising since cost is a good measure of the availability and scope of usage of a metal regardless of the relative rarity of raw materials, complexity of processing, etc., for the production of a metal in commercially attractive form.

The designation, "Rare Metals," was chosen as being simple and not misleading as compared with other names considered, i.e., "Less Common

Metals" or "Unusual Metals" or even "Extraordinary Metals." It suffers from a certain amount of inaccuracy, of course, but the term is such that most people in the field will know exactly what group is meant to be covered by the phrase "Rare Metals." The long use of the term by such pioneers as Drs. John W. Marden and Colin G. Fink in the symposia of the Electrochemical Society, where many of the original reports of the isolation and properties of these metals have been presented, was a major factor in choosing the name for the "Rare Metals Handbook."

This book would not have been possible, of course, without the cordial cooperation of the contributors to it. To each of these busy men who generously gave the time required to prepare the individual chapters the Editor is deeply indebted, and to all of them his heartfelt thanks are given. He wishes especially to express his appreciation to those who, having completed their work at an early date, patiently awaited the slower submission of the chapters by others who were delayed for one reason or another in the completion of their contributions.

Deep appreciation is due to Dr. John R. Musgrave of The Eagle-Picher Company for his early assistance in selecting the elements included in the book and his enthusiasm for its purpose, to the late Francis M. Turner of Reinhold Publishing Corporation, to the late Dr. Colin G. Fink of Columbia University, to Dr. John W. Marden of Westinghouse Electric Corporation, and to A. A. Smith, Jr., of American Smelting and Refining Company. All supported the initiation of the work and generously drew upon their wide circles of friends to suggest contributors for the various chapters.

Special thanks are expressed for the continued stimulation and personal assistance given by Fred P. Peters, Vice President of the Reinhold Publishing Corporation, whose friendships in and knowledge of the metals field are only equalled by his stature in these respects in the field of technical literature. In a similar manner the cooperation of G. G. Hawley, Executive Editor of the Reinhold Book Division, has been most helpful in the completion of this work. To him and to Miss Jeanne Bergquist go sincere appreciation for their handling of the manuscript and their coordination of almost as many styles of usage as there are chapters in the book.

Acknowledgment is made of the valued assistance of Dr. Charles L. Mantell in supplying data and reviewing the chapter on "Manganese" by the Editor.

Without the help of these friends and many others who gave support and advice the completion of the work would have been much more difficult.

Finally, sincere thanks are given my wife, Merrylyn, for undergoing many lonely evenings so that the multitude of details associated with an activity of this sort could be handled, and for her candid advice and criticism.

CLIFFORD A. HAMPEL

Homewood, Ill.
February, 1954.

CONTENTS

1: THE RARE METALS

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The last war not only affected profoundly major fields of science and technology, but it also stimulated the rate at which new developments were applied and widened the scope of their applications. These trends have continued since that time and no evidence of any slackening of steady progress has appeared.

New and widespread interest has been aroused with respect to materials by which the changing but ever-expanding demands of technology can be satisfied. Materials hitherto unknown, or if known, regarded as little more than scientific curiosities, have been demanded for the new techniques and developments.

In a prime position among such materials are the rare or uncommon metals. The accelerated rate of consolidation of the gains of science has placed new significance upon more than laboratory quantities of the rare metals. Whereas before the war only a few workers devoted their scientific activities to them, hundreds are now working with and expanding the knowledge about their procurement and utilization, as evidenced, for example, by the large number of research and development programs directed to the production and application of these metals.

The well-known story of uranium, and to a lesser extent of thorium, for atomic energy purposes hardly needs repeating, but it serves to illustrate the sudden and increasing demand for a metal so scarce that in 1940 only a few grams of good uranium were in existence. Information about it was so scanty that even the melting point was not known accurately. (For example, the "Handbook of Chemistry and Physics" in 1943 lists the melting point as less than 1850°C (3362°F), while it is now known to be 1130°C (2071°F)). At the same time a supply of high-purity beryllium had to be provided to serve as a source of neutrons for the uranium pile.

The nuclear energy program has since created an interest in other metals of specific properties, notably gallium, indium, and bismuth, to serve as possible heat transfer media, and hafnium-free zirconium as a material of construction of high corrosion resistance and low neutron absorption cross section.

The rapidly growing electronics industry has demanded a host of rare metals for a variety of purposes—germanium and silicon for transistors and other devices where semiconductors are needed, selenium for photoelectric cells and rectifiers, tungsten and beryllium for x-ray tubes, tantalum for transmitting tubes and capacitors, molybdenum for receiving tubes, and platinum and tungsten for contacts, to cite a few examples.

The requirement for cobalt alloys to be used for high-temperature service and permanent magnets has created an acute demand for cobalt, whose production rate formerly was about equal to that of silver. Titanium, whose high strength and low weight are so interesting to the aircraft and marine industries, has received a phenomenal amount of attention and will soon take its place among the major metals of the mechanical world.

Many other fields likewise require one or more of the rare metals to satisfy the peculiar properties needed for practical application of new developments, but the above serve to indicate the varied and growing demand for these metals.

Why are these metals rare or uncommon? One or more of several reasons can be advanced to explain the situation. (1) The natural supply or abundance in the earth's crust may be small. (2) Even if a metal is fairly prevalent, the concentration in accessible deposits may be so low as to require the handling and processing of huge amounts of worthless material in order to extract even small quantities of the desired element in either compound or elemental form. Or, to put it another way, deposits of ore in economically desirable concentrations are few. (3) The chemical and physical properties of the element may be such that conversion to the elemental form is very difficult. (4) Even though available, the element may not have enough attractive properties or uses to create a demand for it in competition with other available materials on a cost basis.

The common denominator of all these reasons is, of course, economics. The ingenuity of chemists, engineers, and metallurgists is sufficient to find ways of providing the element in the desired form if cost is no barrier. However, the present or potential cost of the metal must be low enough to make its production and application worthwhile before the metal will take its place in the economy. The outstanding exceptions to the last statement are those metals vital to the national defense, notably uranium, where of course cost is no barrier.

The economic factor has another influence which has retarded the greater production and use of many of the rare metals. Markets are often not certain until the metal is available in assured supply; and vice versa, the metal often is not produced in appreciable quantity until the market is certain—a vicious cycle that can be broken by the courageous producer who deliberately sets out to find markets and uses for a metal he knows he can produce. This, of course, is a common practice in the chemical industry, which develops many new products each year and then finds uses and outlets for them. This practice is being followed to an increasing degree by the producers of metals and is one reason for the widespread interest in the rare metals.

Natural Occurrence

While many other factors may also affect the availability of a metal an as item of commerce and use, the prevalence of it in the earth's crust is a most important factor, and a knowledge of the relative abundance of the metals in the crust of the earth points up the other reasons for the relative commonness or rareness of any one metal in our civilization.

One of the most recent compilations of the average amounts of the elements in the earth's crust is given by Mason;[6] it is based largely upon data developed by the late V. M. Goldschmidt of Norway and the late F. W. Clarke, for 41 years Chief Chemist of the U. S. Geological Survey until his retirement in 1925. Table 1 gives the order of occurrence of the elements in grams per ton or parts per million.

This assembly of the order of prevalence of the elements reveals a host of interesting relationships. The first eight elements—oxygen, silicon, aluminum, iron, calcium, sodium, potassium, and magnesium—comprise about 99 per cent of the crust, but only one, oxygen, is present extensively as an element, and only one, iron, is used chiefly in elemental form. However, aluminum also has become one of the more common commercial metals, and magnesium is also used to a considerable extent. It is of interest to note that the production rates of steel, aluminum, and magnesium in the United States at the present time are roughly in the ratio of 1000:10:1. Sodium is produced in much greater quantity than magnesium, and is used more as a chemical reducing agent than as a metal. One other of the eight, calcium, is made commercially, but in relatively small amounts.

Two of the most commonly used elements that are naturally present and used in elemental form, sulfur and carbon, are 13th and 14th, respectively, in the list, and the next, chlorine, ranks second to iron in the tonnage converted to and used in the form of the element.

Thus, of the first 15 elements in order of abundance (through chlorine),

TABLE 1. THE AVERAGE AMOUNTS OF THE ELEMENTS IN THE EARTH'S CRUST IN GRAMS PER TON OR PARTS PER MILLION*

(Omitting those present in less than 0.001 g/ton: Ne, Kr, Xe, Ra, and the short-lived radioactive elements)

O	466,000	Ge	7
Si	277,200	Be	6
Al	81,300	Sm	6.5
Fe	50,000	Gd	6.4
Ca	36,300	Pr	5.5
Na	28,300	Sc	5
K	25,900	As	5
Mg	20,900	Hf	4.5
Ti	4,400	Dy	4.5
H	1,400	U	4
P	1,180	B	3
Mn	1,000	Yb	2.7
S	520	Er	2.5
C	320	Ta	2.1
Cl	314	Br	1.6
Rb	310	Ho	1.2
F	300	Eu	1.1
Sr	300	Sb	1?
Ba	250	Tb	0.9
Zr	220	Lu	0.8
Cr	200	Tl	0.6
V	150	Hg	0.5
Zn	132	I	0.3
Ni	80	Bi	0.2
Cu	70	Tm	0.2
W	69	Cd	0.15
Li	65	Ag	0.1
N	46	In	0.1
Ce	46	Se	0.09
Sn	40	A	0.04
Y	28	Pd	0.01
Nd	24	Pt	0.005
Cb(Nb)	24	Au	0.005
Co	23	He	0.003
La	18	Te	0.002?
Pb	16	Rh	0.001
Ga	15	Re	0.001
Mo	15	Ir	0.001
Th	12	Os	0.001?
Cs	7	Ru	0.001?

* From Brian Mason, "Principles of Geochemistry" (copyright 1952 by John Wiley & Sons, Inc., New York), p. 41. Reprinted by permission of the publisher.

only oxygen, sulfur, and carbon occur and are used widely in the native uncombined form. Also, iron, chlorine, aluminum, sodium, and magnesium are the leading elements, in that order, which are reduced to the elemental state for application. In our industrial civilization oxygen is the major element in tonnage use as an element, even if the biological consumption is disregarded; carbon is next; and iron is third.

Noteworthy is the relative abundance in the earth's crust of many elements which are not commonly used in large quantities, such as titanium, rubidium, zirconium, and vanadium. Conversely, elements that have long played important roles in our civilization really are quite scarce. Copper is about as abundant as tungsten and much less so than manganese, zirconium, and vanadium. Nitrogen is no more abundant than cerium, tin is less abundant than lithium, and lead and molybdenum are about equal to gallium. Thorium and uranium are both more abundant than boron, and vanadium is somewhat more prevalent than zinc. Mercury is much less abundant than the rare earths, beryllium, and tantalum.

It is rather startling to find that rubidium ranks 16th in order of prevalence, almost as abundant as chlorine, when it and its compounds are so little known in chemistry and are such uncommon articles of commerce.

The Oceans as Source of Metals

The oceans, which cover over 70 per cent of the earth's surface, contain an average of 3.5 per cent of dissolved solids—an insignificant quantity as compared with the weight of the earth's crust, but one of utmost importance in that the oceans are so accessible. Of more consequence, the constituents are in solution. As is well known, much effort and cost are often involved in dissolving solids prior to further processing and ultimate recovery of desired products, so the fact that sea water is a solution, admittedly dilute, has definite technological importance.

Some 50 elements are known to be present in sea water, and undoubtedly others found in marine organisms were derived from sea water. Table 2 presents the concentrations of the elements in sea water as developed by Sverdrup, Johnson, and Fleming.[9] The concentration ratios are remarkably constant over the globe because of the homogeneity of the oceans. Ranges are given for many of the elements and represent variations in concentrations due to localized conditions and to biological activity which changes with depth.

The order of prevalence of elements in sea water differs markedly from that given in Table 1 for the earth's crust (which includes the oceans and other bodies of water making up the hydrosphere), for several

TABLE 2. ELEMENTS PRESENT IN SOLUTION IN SEA WATER*
(excluding dissolved gases)

Element	Concentration (g/ton)
Cl	18,980
Na	10,561
Mg	1,272
S	884
Ca	400
K	380
Br	65
C (inorganic)	28
Sr	13
(SiO_2)	0.01–7.0
B	4.6
Si	0.02–4.0
C (organic)	1.2–3.0
Al	0.16–1.9
F	1.4
N (as nitrate)	0.001–0.7
N (as organic nitrogen)	0.03–0.2
Rb	0.2
Li	0.1
P (as phosphate)	>0.001–0.10
Ba	0.05
I	0.05
N (as nitrite)	0.0001–0.05
N (as ammonia)	>0.005–0.05
As (as arsenite)	0.003–0.024
Fe	0.002–0.02
P (as organic phosphorus)	0–0.016
Zn	0.005–0.014
Cu	0.001–0.09
Mn	0.001–0.01
Pb	0.004–0.005
Se	0.004
Sn	0.003
Cs	approx. 0.002
U	0.00015–0.0016
Mo	0.0003–0.002
Ga	0.0005
Ni	0.0001–0.0005
Th	<0.0005
Ce	0.0004
V	0.0003
La	0.0003
Y	0.0003
Hg	0.0003
Ag	0.00015–0.0003
Bi	0.0002
Co	0.0001
Sc	0.00004