4 / The Raw Materials Laboratory

WORLD WAR I WAS to produce a profound change in Goldschmidt's scientific development. As the war progressed, Norway was largely cut off from overseas, and sources of raw materials, previously imported, were badly needed. In 1916 he was investigating the possibility of replacing imported bauxite with Norwegian clay or feldspar as raw material for aluminum production. In November 1917 the Norwegian government decided to finance research into the mineral resources of the country, and established a Commission for Raw Materials, with Goldschmidt as Chairman. On his initiative the commission approved the founding of Statens Råstofflaboratorium (the State Raw Materials Laboratory), which was set up in the newly built Geological Museum in the Oslo suburb of Tøyen. This gave the opportunity to obtain staffing and equipment for the new laboratory, financed by the Department of Industry and Commerce, thereby providing Goldschmidt with an institute independent of the university.[1]

One of the first fruits of this new organization was of much greater scientific than economic importance. In May 1918 Goldschmidt visited the Fen region in southern Norway to investigate the possible exploitation of the limestone known to occur there. He noted the presence in this limestone of a rare niobium mineral, pyrochlore, $(Na,Ca)_2Nb_2O_6(OH,F)$, and drew the conclusion that this was due to the local intrusion of sodium-rich igneous rocks. In August he spent a week in the area together with Professor Brøgger, during which they discovered and mapped a remarkable variety of unusual rocks. They completed the mapping during a further visit in May 1919, and Brøgger undertook the mineralogical and petrographical investigations. This resulted in Brøgger's classic 408-page monograph[2] *Das Fengebiet in Telemark, Norwegen,* a principal result being that the "limestone" was not a sedimentary rock, as had been thought, but had been intruded as a carbonate–rich melt. Carbonate–rich melts had been invoked by a few earlier petrologists, but never with the wealth of descriptive detail given by Brøgger. The Fen region is generally recognized as the type locality for carbonatites (the term introduced by Brøgger), as similar rocks in many parts of the world are now known.

Some of the Fen carbonatites contain considerable amounts of the phosphate mineral apatite. During World War II (until he left Norway in 1942) Goldschmidt had a research project, financed by the Agricultural Department, for the manufacture of phosphate fertilizer from this material. The importance of this research for Norwegian agriculture saved him, at least temporarily, from deportation to Poland in 1942. After World War II the carbonatites were mined for pyrochlore as a source of niobium, a metal needed in applications of atomic energy, and as a component of special steels.

The early work of the Raw Materials Laboratory concentrated on finding Norwegian sources of previously imported materials, and developing substitutes where possible. These included the possible production of aluminum from clays or anorthosite (a rock present in large deposits in Norway and containing 30% or more Al_2O_3); the use of potassium minerals, especially biotite, as a substitute for imported potassium fertilizers; the search for phosphate deposits; and the utilization of Norwegian ilmenite ($FeTiO_3$) in the preparation of titanium dioxide for use in paints. This led Goldschmidt to investigate more closely the chemical nature of economic minerals, and thus to the study of crystal chemistry. Fortuitously, this coincided with the development of new and powerful techniques for elucidating crystal structure. X–ray diffraction by solids had been discovered by Max von Laue[3] in 1912 and applied to the determination of crystal structures, especially by W. H.[4] and W. L. Bragg[5] in England. However, their procedures required the use of large well–formed crystals, sample preparation and data gathering were tedious and time–consuming, and World War I effectively suspended most research in this field. P. Debye and P. Scherrer in 1916 and A. W. Hull in 1917 independently developed the powder diffraction technique, which eliminated the need for good crystals and made data gathering relatively simple and rapid. Goldschmidt was to exploit this new technique brilliantly, and he used it to develop a new science of crystal chemistry.

J. D. Bernal,[6] a British physicist who specialized in crystal chemistry, recounts the following story of how Goldschmidt adopted X–ray diffraction as a research tool:[7]

> "The actual story as he told it to me—I don't know whether it is true or not, but it is a good Goldschmidt story—was that it all came about through a lawsuit. At the end of the first World War the then government of this country, feeling that it had to protect the British chemical industry which had been left so undeveloped before the war, produced a tariff on the import of organic chemicals. Among those referred to was calcium carbide. The chemical interests in this country claimed it was an organic chemical; the Norwegian government maintained it was not. A test case was to be fought in

> London. Goldschmidt was briefed by the Norwegian government to be the expert witness on the subject. He certainly was not an organic chemist, but he read a textbook on the boat going across and set forth bravely for the law court. When he learned on arrival that the British government expert was Sir William Pope, he decided after all it would not do and he would have to fight him on another ground. Luckily he knew Sir William Bragg, so he took a crystal of calcium carbide and asked him to work out the structure (incidentally he got it completely wrong, but no one could know that at the time), and Goldschmidt fought the case on the basis that this was the structure of an inorganic crystal. There could be no argument against this on chemical grounds, and calcium carbide was finally exempted. The Norwegian government was naturally pleased and asked how it was done. He put it all down to X-rays and on the strength of this obtained an X-ray tube and a powder camera."

At this time Goldschmidt began recruiting a remarkable group of young research associates, all of whom were to have distinguished careers. In 1918 Ivar Oftedal[8] joined the museum staff as a student assistant and began an association with Goldschmidt which lasted throughout the latter's life; on his death Oftedal succeeded him as Professor of Mineralogy. Lars Thomassen[9] graduated as a chemical engineer in 1919, and from then until 1929 (except for two years at the California Institute of Technology, 1925–27) was Goldschmidt's principal research associate. He was responsible for the construction and operation of the X-ray equipment. In June 1921 Kristoffer Stenvik[10] joined the Raw Materials Laboratory as a technical assistant. He studied mineralogy, petrology, and chemistry at the university, and became Goldschmidt's right-hand man, especially in the development and utilization of olivine as a refractory. They complemented each other in a remarkable manner—Goldschmidt with his theoretical knowledge and fertile ideas, and Stenvik with his technical expertise.

The utilization of olivine is one of the great success stories of the Raw Materials Laboratory. Norway has large deposits of olivine, which are easily exploitable and readily accessible for shipping. Originally, Goldschmidt visualized olivine as a source of magnesium and magnesium compounds, since Norwegian olivine contains up to 50% MgO. However, for this purpose the extraction techniques were uneconomic, compared with the availability of magnesium from salt deposits and sea water. He then turned to the utilization of olivine as a refractory material, inspired, so he said, by observing the resistance of olivine xenoliths in basalt to melting and chemical attack, despite their immersion in molten lava. In 1925 he found that magnesium-rich olivine has a much higher melting point than previously thought, and began investigating its technical use as a refractory. During the 1930's he continued the early investigations, largely at his own expense, and obtained numerous patents in Europe, North America, and other countries, from which he eventually received considerable income. The great expansion in the commercial use of olivine came, however, after his death in 1947.

The year 1922 appears to have been a critical one in the development of Goldschmidt's concept of geochemistry and his plans for research thereon. He wrote two short but seminal papers, *Der Stoffwechsel der Erde* (The differentiation of the Earth), 25 pages, and *Geochemische Verteilungsgesetze der Elemente* (The laws of distribution of the chemical elements), 17 pages, the first of a series of nine monographs published from 1923 to 1938. In "Stoffwechsel" he outlined his ideas as follows:

> "It is conceivable that the original state of the Earth was a homogeneous or nearly homogeneous mixture of the chemical elements and their compounds. Today, however, the Earth is far removed from a homogeneous state. The material distribution within the Earth has by no means reached a final equilibrium state; we observe instead an active redistribution of matter and energy. The processes which have resulted in the inhomogenity of our planet and still contribute to the migration of material I would summarize in the expression "Der Stoffwechsel der Erde" " (p. 3, translated from German).

By analogy with the composition of meteorites (at that time generally believed to be fragments from a disrupted planet), which contain a nickel–iron alloy, iron sulfide (FeS), and silicate minerals, Goldschmidt postulated that the initial condition of the Earth was a molten ball surrounded by a gaseous atmosphere. The molten ball would have three immiscible liquids—nickel–iron, iron sulfide, and silicate. As a result of gravitational forces, the densest liquid, nickel–iron, would sink to form a core; the core would be surrounded by the sulfide liquid, possibly including some metallic oxides; and the silicate liquid, being the least dense, would form the mantle. This he termed the primary geochemical differentiation; the chemical elements would distribute themselves between the three liquid phases according to their affinity for metal, sulfide, or silicate; gases such as nitrogen and oxides of carbon would form the primitive atmosphere. The next step, the secondary geochemical differentiation as he called it, was the cooling and crystallization of the silicate liquid. The denser minerals, mainly iron–magnesium silicates, would tend to sink; the less dense minerals, mainly quartz and feldspars, would tend to float and eventually aggregate to form the continental crust. The crystalline minerals acted as sorting mechanisms for individual elements by accepting those that could be accommodated within the rigid structures and rejecting those either too large or too small.

On the basis of these considerations, Goldschmidt devised the geochemical classification of the elements into four groups: *siderophile* (those with an affinity to nickel–iron), *chalcophile* (those with sulfide affinity), *lithophile* (those with silicate affinity), and *atmophile* (those normally present as gases). The geochemical character of an element is clearly related to its position in the Periodic Table,[11] as is seen in Table 1.

Table 1. Geochemical classification of the elements in relation to the Periodic System (after Goldschmidt, *Vidensk. Skrifter. I. Math.–naturv. klasse*, No. 3, p. 5, 1923).

Atmophile: $\underline{\text{N}}$
Lithophile: Na
Chalcophile: $\underline{\underline{\text{Zn}}}$
Siderophile: $\underline{\underline{\underline{\text{Fe}}}}$

H																	$\underline{\text{He}}$
Li	Be											B	C	$\underline{\text{N}}$	O	F	$\underline{\text{Ne}}$
Na	Mg											Al	Si	P	$\underline{\underline{\text{S}}}$	Cl	$\underline{\text{Ar}}$
K	Ca	Sc	Ti	V	Cr	Mn	$\underline{\underline{\underline{\text{Fe}}}}$	$\underline{\underline{\underline{\text{Co}}}}$	$\underline{\underline{\underline{\text{Ni}}}}$	$\underline{\underline{\text{Cu}}}$	$\underline{\underline{\text{Zn}}}$	$\underline{\underline{\text{Ga}}}$	$\underline{\underline{\underline{\text{Ge}}}}$	$\underline{\underline{\text{As}}}$	$\underline{\underline{\text{Se}}}$	Br	$\underline{\text{Kr}}$
Rb	Sr	Y	Zr	Nb	$\underline{\underline{\underline{\text{Mo}}}}$		$\underline{\underline{\underline{\text{Ru}}}}$	$\underline{\underline{\underline{\text{Rh}}}}$	$\underline{\underline{\underline{\text{Pd}}}}$	$\underline{\underline{\text{Ag}}}$	$\underline{\underline{\text{Cd}}}$	$\underline{\underline{\text{In}}}$	$\underline{\underline{\underline{\text{Sn}}}}$	$\underline{\underline{\text{Sb}}}$	$\underline{\underline{\text{Te}}}$	I	$\underline{\text{Xe}}$
Cs	Ba	La-Lu	Hf	Ta	$\underline{\underline{\underline{\text{W}}}}$	$\underline{\underline{\underline{\text{Re}}}}$	$\underline{\underline{\underline{\text{Os}}}}$	$\underline{\underline{\text{Ir}}}$	$\underline{\underline{\underline{\text{Pt}}}}$	$\underline{\underline{\underline{\text{Au}}}}$	$\underline{\underline{\text{Hg}}}$	$\underline{\underline{\text{Tl}}}$	$\underline{\underline{\text{Pb}}}$	$\underline{\underline{\text{Bi}}}$			
			Th		U												

When Goldschmidt proposed his geochemical classification of the elements in 1923, few quantitative data were available on which to base his ideas. The geochemical nature of an element could, of course, be established by measuring its distribution between three liquid phases of iron, iron sulfide, and silicate. He recognized the difficulty in carrying out these measurements in the laboratory, but remarked that meteorites provide us with such an experiment in a fossilized condition. Many meteorites consist of nickel–iron, troilite (FeS), and silicate, all of which probably solidified from a melt. The distribution of a specific element between these three phases would be established when the system was liquid and can be determined by mechanically separating these phases and analyzing them individually. From such analyses the partition of the elements between metal, silicate, and sulfide can easily be calculated. In the following years Goldschmidt and his co-workers made many measurements of the content of various elements in nickel–iron, troilite, and silicate of meteorites. He realized that these measurements also provided the data to establish the cosmic or absolute abundances of the elements, since meteorites provided an unaltered sample of the material which coalesced to form our Solar System. He used these data to compile the first table of the absolute abundances of the elements, which he published in 1938, and which provided the basis for theories of the origin of the elements. At a time when the study of meteorites was a scientific backwater largely confined to description and classification, Goldschmidt's perception of the fundamental significance of meteorite compositions for geochemistry is another example of his scientific genius.

In 1922 Goldschmidt established the conceptual basis for his new geochemistry. It now remained to flesh out this skeleton with experimental data on the distribution of the chemical element in minerals and rocks. This required two sorts of information: a knowledge of the crystal structures of the minerals, which controlled the distribution of the elements, and the analysis of these minerals for their elemental composition, both major and minor. The time was ripe, because of the availability of newly developed analytical techniques. X–ray powder diffraction provided a rapid method for the determination and comparison of crystal structures. For the elemental analysis of minerals a new technique had just become available. In 1921 Assar Hadding,[12] a Swedish scientist and friend of Goldschmidt, had designed an X–ray spectrograph specifically for the analysis of minerals. X–ray spectra show a relatively simple pattern of lines in a regular progression from one element to the next. An enormous advantage over classical chemical analysis was that it was unnecessary to separate out the individual elements—the mineral grains were mounted directly on the X–ray target, and a single spectrum showed the lines for each of the elements present, and the intensities of the lines were approximately proportional to the amount present.

Goldschmidt's appreciation of the value of Hadding's X–ray spectrograph for his geochemical researches is expressed in a letter dated January 19, 1924:

> "Dear friend. . . . Every day I am more and more convinced of the excellence of the X–ray spectral analysis technique for our work on the laws of distribution of the chemical elements. No other method is capable of producing so rapidly and exactly the analyses needed for my work on this problem. My institute has never acquired a more useful piece of equipment. . . . You can be justifiably proud to have developed this method, which opens a whole new field in mineralogical research" (translated from Norwegian).

In March 1922 Thomassen built an X–ray spectrograph to Hadding's design. It was destined to be used for many investigations in Goldschmidt's institute during the next few years, but its first application was the search for element 72.