6 / Crystal Chemistry and Geochemistry in Oslo: 1922–1929

GOLDSCHMIDT DESCRIBED HIS plans for the Raw Materials Laboratory in the post–World War I period as follows:[1]

> "After the end of the first world war, when a new economic situation had developed, I recommended the continuance of research work along more general lines on raw minerals materials and the study of general scientific problems closely connected with the utilization of mineral raw materials. Among the problems proposed here there was one of outstanding importance, i.e. to find the general laws and principles which underlie the frequency and distribution of the various chemical elements in nature—the basic problem of geochemistry. I proposed to attack the problem from the view point of atomic physics and atomic chemistry, and to find out the relationships between the geochemical distribution of the various elements and the measurable properties of their atoms and ions"(original English).

Concurrently with their search for element 72, Goldschmidt and Thomassen began an extensive research on the abundance and distribution of the rare earth elements: yttrium (AN 39) and the sequence from lanthanum (AN 57) to lutetium (AN 71); Goldschmidt introduced the term *lanthanides* for the latter sequence. Information in this field was almost totally lacking, because of the extreme difficulty in separating the individual elements by the classical methods of chemical analysis. Their X–ray spectra, however, showed the relatively simple pattern of lines in a regular progression from one element to the next. An enormous advantage was that it was unnecessary to separate out the individual elements—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 and his research assistants separated the rare earths from a large number of different minerals, and Thomassen analyzed these separates with his

X-ray spectrograph. On the basis of these results they were able to estimate the relative abundances of these elements, as shown in Fig. 5, where they are normalized to the homologous element yttrium having an arbitrary abundance of 100. The figure confirms that cerium is the most abundant lanthanide, followed by neodymium, the remaining elements being relatively rare. The most remarkable feature is the sawtooth pattern of the abundances. This had been foreshadowed by Oddo in 1914 and independently by Harkins in 1917, in what is now known as the Oddo–Harkins rule. They stated it in the form that odd-numbered elements tended to be less abundant than even-numbered elements. On the basis of their results, Goldschmidt and Thomassen refined the rule, as follows: "Elements of odd atomic number are less abundant than their immediate neighbors of even atomic number."

They found no evidence for the presence of element 61 in any mineral. Nevertheless, Goldschmidt continued to search for it, as evidenced by his correspondence with Assar Hadding. Hadding to Goldschmidt (March 10, 1926): "How goes your search for 61?"

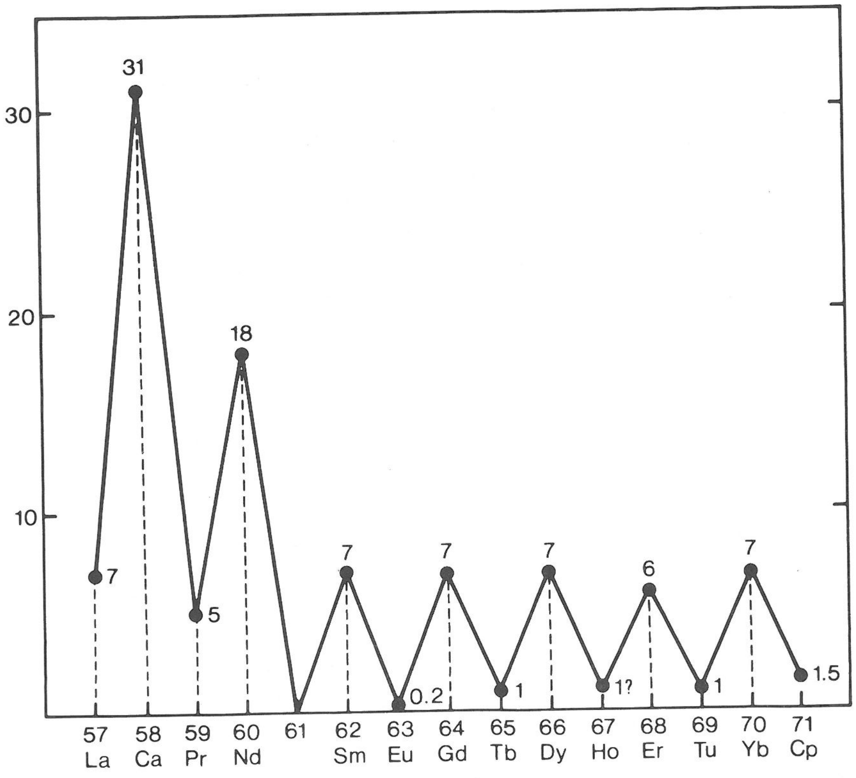


FIG. 5. The relative abundances of the lanthanides, referred to yttrium = 100 (Goldschmidt and Thomassen, *Geochemische Verteilungsgesetze der Elemente III*, p. 49, 1924). Note: Element 71 Cp (cassiopeium) is now Lu (lutetium).

Goldschmidt to Hadding (March 11, 1926): "I am still trying to find 61." He eventually decided that 61 did not exist in nature as a stable element. Goldschmidt and Thomassen also commented on the exceptionally low abundance of europium, even compared to the other odd–numbered elements. In 1926 Goldschmidt showed that this was due to the fact that under reducing conditions europium behaved differently from other rare earth elements in that it was present in the bivalent state; the bivalent europium ion has a considerably larger radius (1.17Å) than the trivalent ion (0.96Å) and is therefore excluded from the common rare earth minerals but accepted in calcium minerals. This phenomenon is now widely recognized and termed the *europium anomaly;* it is much used in the interpretation of the evolution of igneous rocks, especially those from the Moon, which crystallized under strongly reducing conditions.

During 1924 Goldschmidt's research tempo was greatly increased by the addition of three young scientific assistants paid from Raw Materials Laboratory funds: Tom. Barth, Gulbrand Lunde, and William Zachariasen,[2] all of whom had notable careers. The first fruits were the determination of the crystal structures of the oxides of the rare earth elements, published in 1925 as *Geochemische Verteilungsgesetze der Elemente IV*, with co–authors Ulrich[3] (research fellow from Prague) and Barth. In the introduction Goldschmidt acknowledges the work of Lunde in the preparation of the oxides, and Zachariasen in the interpretation of the X–ray data. Goldschmidt had a unique collection of purified rare earth compounds, the gift of his friends George de Hevesy and Auer von Welsbach.[4]

One of the remarkable results of this research was the discovery that the unit cell dimensions of the lanthanide oxides decrease regularly with increasing atomic number of the element (Fig. 6). This is contrary to the normal increase in unit cell dimensions with increase in atomic number—for example the cell dimensions of Sc_2O_3 (AN 21) and Y_2O_3 (AN 39) are 9.79Å and 10.60Å, respectively. These results demonstrated that the sizes of the lanthanide ions must decrease with increasing atomic number, the reason being that the orbital electrons needed to balance the increasing number of protons in the atomic nucleus are added not to the outer shell, but to an inner shell, and the effective radius of the ion is thereby diminished. As a result, the radius of yttrium falls near those of dysprosium and holmium, which explains the previously observed division of the lanthanides into the cerium group (those occurring naturally in cerium minerals, essentially La—Sm) and the yttrium group (those occurring in yttrium minerals, essentially Eu—Lu). It also explains why hafnium (AN 72) has essentially the same radius as zirconium (AN 40), and tantalum (AN 73) as niobium (AN 41).

Goldschmidt discussed this phenomenon at length in *Geochemische Verteilungsgesetze der Elemente V* (1925) and termed it the *lanthanide contraction.*

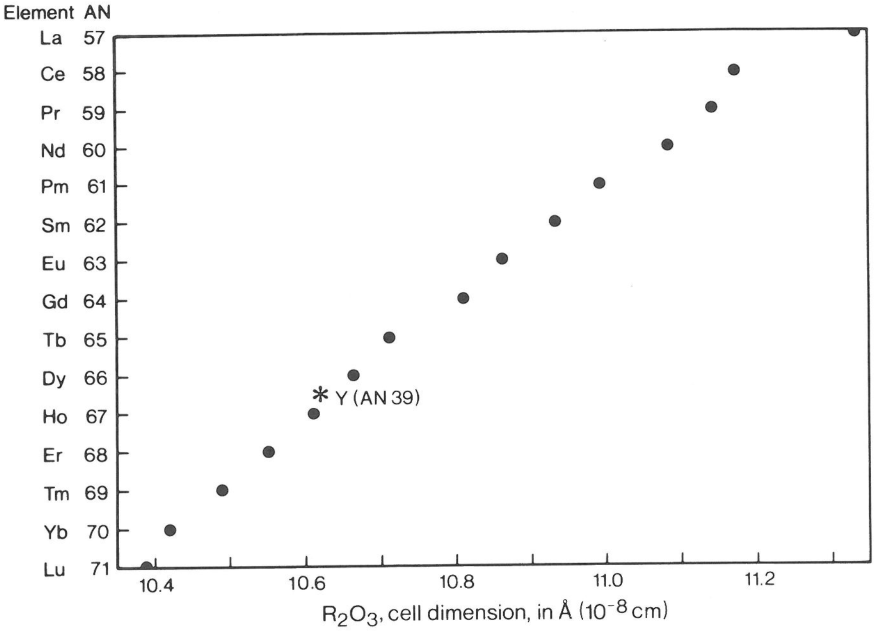


FIG. 6. Unit cell dimensions of cubic lanthanide oxides, illustrating the lanthanide contraction (from Goldschmidt, Ulrich, and Barth, *Geochemische Verteilungsgesetze der Elemente IV,* 1925, with additional data on Ce and Pm).

For Goldschmidt, the time was now ripe for a systematic attack on the problems of crystal structure. Following the discovery of the diffraction of X-rays by crystals by von Laue in 1912, the structure of some simple compounds such as halite ($NaCl$) and sphalerite (ZnS) had been worked out. These investigations showed that in most inorganic compounds the concept of individual molecules was not valid—a crystal consisted of positively and negatively charged atoms (cations and anions) held together by electrostatic attraction, whose centers were placed at defined points on a geometric lattice. The smallest unit from which this lattice was derived by repetition is known as the unit cell (for example, the unit cell of NaF is a cube with fluorine anions at each corner and the center of each face, and sodium cations at the center of each edge). By 1920 the structure of the atom as postulated by Rutherford and Bohr was generally accepted—a positively charged nucleus surrounded by electrons in orbital shells. It was clear that in crystals the atoms or ions behaved essentially as spheres with a defined radius of the order of 1Å (10^{-8} cm). The size of a unit cell was controlled by the number and sizes of the constituent atoms or ions; however, until the size of a specific ion was known, it was not possible to determine ion sizes from unit cell determinations.

This impasse was broken in 1923 when the Finnish scientist J. A. Wasastjerna determined from optical considerations the ionic radii of fluorine, F^{1-} and oxygen, O^{2-} as 1.33Å and 1.32Å, respectively. Goldschmidt seized upon these data as the key to a complete revolution in the science of crystal chemistry. By determining the unit cell dimensions of oxide and fluoride compounds of the type AX and AX_2 (A being a metal, X oxygen or fluorine) he could determine the ionic radii of the metallic elements;[5] by replacing oxygen or fluorine with other anions, he could then determine anionic radii.

Then followed a period of hectic activity in his Mineralogical Institute and the Raw Materials Laboratory. Between 1924 and 1926 Lunde prepared most of the compounds; Barth made more than 1300 X–ray photographs;[6] and Zachariasen, whose mathematical prowess Goldschmidt greatly admired, determined many of the crystal structures. In May 1926 Goldschmidt was ready with the first table of ionic radii (Table 2). Shortly thereafter, Linus Pauling at the California Institute of Technology, using a different approach through wave mechanics, produced a similar table. The correspondence between the two tables was a brilliant confirmation of the theoretical background.

Goldschmidt summarized the development of his crystal chemistry in the foreword to *Geochemische Verteilungsgesetze der Elemente VII* (1926):

> "This monograph, the seventh in the series *Geochemische Verteilungsgesetze der Elemente,* comprises the theoretical results of crystal chemical studies. The experimental work, which is the basis for the theoretical considerations, was originally undertaken for purely practical purposes, in order to establish the laws of isomorphism, since isomorphic relationships determine in large part the geochemical and technical behavior of the chemical elements. The experimental work in the field of crystal chemistry, which has been carried out during the past few years in the Mineralogical Institute of the university, thus had the purpose of elucidating the geochemical distribution and technical properties of economically important raw materials. These researches, carried out largely for the Norwegian Government's Raw Materials Commission, yielded a series of crystal–chemical generalizations which expanded the work beyond the original considerations. Again and again the experimental work invoked general considerations of crystal chemistry and, I believe, thereby contributed greatly to the original purely practical purposes of our work.
>
> For the geologist and for the chemist, crystallography was previously a purely descriptive science, useful in the recognition and differentiation of crystalline material—either minerals or technical products. Our results have united crystallography and technology on the basis of new principles; crystal chemistry has provided a series of important laws of geochemical association, has enabled predictions of the geochemical distribution of the elements, and

Table 2. Empirical ionic radii (Goldschmidt, 1926) and theoretical ionic radii (Pauling, *J. Amer. Chem. Soc.*, vol. 49, p. 763, 1927), in Ångstrom units.

Atomic number	Element name	Ionic charge	Goldschmidt	Pauling
3	Lithium	1+	0.78	0.60
4	Beryllium	2+	0.34	0.31
5	Boron	3+	—	0.20
6	Carbon	4+	0.2	0.15
7	Nitrogen	5+	0.1–0.2	0.11
8	Oxygen	2−	1.32	1.40
9	Fluorine	1−	1.33	1.36
11	Sodium	1+	0.98	0.95
12	Magnesium	2+	0.78	0.65
13	Aluminum	3+	0.57	0.50
14	Silicon	4+	0.39	0.41
15	Phosphorus	5+	0.3–0.4	0.34
16	Sulfur	2−	1.74	1.84
17	Chlorine	1−	1.81	1.81
19	Potassium	1+	1.33	1.33
20	Calcium	2+	1.06	0.99
21	Scandium	3+	0.39	0.41
22	Titanium	4+	0.64	0.68
23	Vanadium	5+	0.65	0.59
24	Chromium	6+	0.64	0.52
25	Manganese	2+	0.91	0.80
26	Iron	2+	0.83	0.75
27	Cobalt	2+	0.82	0.72
28	Nickel	2+	0.78	0.69
29	Copper	1+	—	0.96
30	Zinc	2+	0.83	0.74
31	Gallium	3+	0.62	0.62
32	Germanium	4+	0.44	0.53
34	Selenium	2−	1.91	1.98
35	Bromine	1−	1.96	1.95
37	Rubidium	1+	1.49	1.48
38	Strontium	2+	1.27	1.13
39	Yttrium	3+	1.06	0.93
40	Zirconium	4+	0.87	0.80
41	Niobium	5+	0.69	0.70
42	Molybdenum	4+	0.68	0.66
44	Ruthenium	4+	0.65	0.63
45	Rhodium	3+	0.68	—
47	Silver	1+	1.13	1.26
48	Cadmium	2+	1.03	0.97
49	Indium	3+	0.92	0.81
50	Tin	4+	0.74	0.71
52	Tellurium	2−	2.11	2.21
53	Iodine	1−	2.20	2.16
55	Cesium	1+	1.65	1.69
56	Barium	2+	1.43	1.35

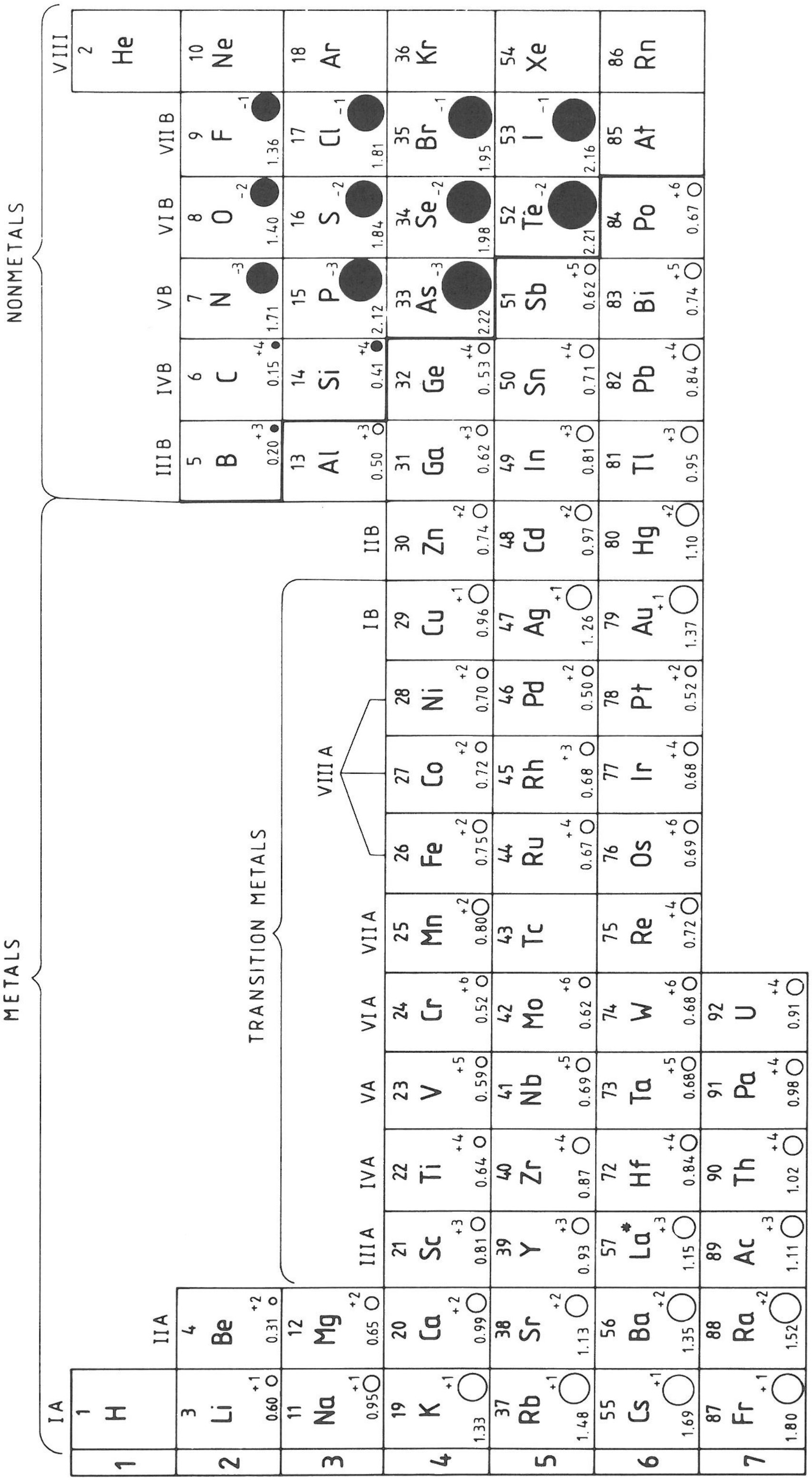
Table 2. Continued.

Atomic number	Element name	Ionic charge	Goldschmidt	Pauling
57	Lanthanum	3+	1.22	1.15
58	Cerium	3+	1.18	—
59	Praseodymium	3+	1.16	—
60	Neodymium	3+	1.15	—
62	Samarium	3+	1.13	—
63	Europium	3+	1.13	—
64	Gadolinium	3+	1.11	—
65	Terbium	3+	1.09	—
66	Dysprosium	3+	1.07	—
67	Holmium	3+	1.05	—
68	Erbium	3+	1.04	—
69	Thulium	3+	1.04	—
70	Ytterbium	3+	1.00	—
71	Lutetium	3+	0.99	—
74	Tungsten	4+	0.68	0.66
76	Osmium	4+	0.67	0.65
77	Iridium	4+	0.66	0.64
79	Gold	1+	—	1.37
80	Mercury	2+	1.12	1.10
81	Thallium	3+	1.05	0.95
82	Lead	4+	0.84	0.84
90	Thorium	4+	1.10	1.02
92	Uranium	4+	1.05	0.97

> above all the new crystal chemistry provides chemists and metallurgists theoretical principles and techniques to supplement the previous empirical procedures" (translated from German).

Goldschmidt established the following rules relating ionic size to atomic structure (Fig. 7):

1. For elements in the same group (vertical column) of the Periodic Table, the ionic radii increase as the atomic numbers of the elements increase. This is, of course, to be expected, since for elements in the same group of the Periodic Table the number of electron orbits around the nucleus, and hence the effective radius, increases in going down the column.
2. For positive ions of the same electronic structure the radii decrease with increasing charge. For an example, we may take the elements in the second horizontal row of the Periodic Table, all of which have two electrons in the inner orbit and eight in the outer orbit: the ionic radii decrease from Na^{1+} = 0.98Å to S^{6+} = 0.34Å. As electrons are lost the nucleus exerts a greater pull on those remaining, thus decreasing the effective radius.


METALS
NONMETALS
TRANSITION METALS
IA
IIA
IIIA
IVA
VA
VIA
VIIA
VIII A
IB
IIB
IIIB
IVB
VB
VIB
VIIB
VIII
1
2
3
4
5
6
7
1 H
2 He
3 Li +1 0.60
4 Be +2 0.31
5 B +3 0.20
6 C +4 0.15
7 N -3 1.71
8 O -2 1.40
9 F -1 1.36
10 Ne
11 Na +1 0.95
12 Mg +2 0.65
13 Al +3 0.50
14 Si +4 0.41
15 P -3 2.12
16 S -2 1.84
17 Cl -1 1.81
18 Ar
19 K +1 1.33
20 Ca +2 0.99
21 Sc +3 0.81
22 Ti +4 0.64
23 V +5 0.59
24 Cr +6 0.52
25 Mn +2 0.80
26 Fe +2 0.75
27 Co +2 0.72
28 Ni +2 0.70
29 Cu +1 0.96
30 Zn +2 0.74
31 Ga +3 0.62
32 Ge +4 0.53
33 As -3 2.22
34 Se -2 1.98
35 Br -1 1.95
36 Kr
37 Rb +1 1.48
38 Sr +2 1.13
39 Y +3 0.93
40 Zr +4 0.87
41 Nb +5 0.69
42 Mo +6 0.62
43 Tc
44 Ru +4 0.67
45 Rh +3 0.68
46 Pd +2 0.50
47 Ag +1 1.26
48 Cd +2 0.97
49 In +3 0.81
50 Sn +4 0.71
51 Sb +5 0.62
52 Te -2 2.21
53 I -1 2.16
54 Xe
55 Cs +1 1.69
56 Ba +2 1.35
57 La* +3 1.15
72 Hf +4 0.84
73 Ta +5 0.68
74 W +6 0.68
75 Re +4 0.72
76 Os +6 0.69
77 Ir +4 0.68
78 Pt +2 0.52
79 Au +1 1.37
80 Hg +2 1.10
81 Tl +3 0.95
82 Pb +4 0.84
83 Bi +5 0.74
84 Po +6 0.67
85 At
86 Rn
87 Fr +1 1.80
88 Ra +2 1.52
89 Ac +3 1.11
90 Th +4 1.02
91 Pa +4 0.98
92 U +4 0.91

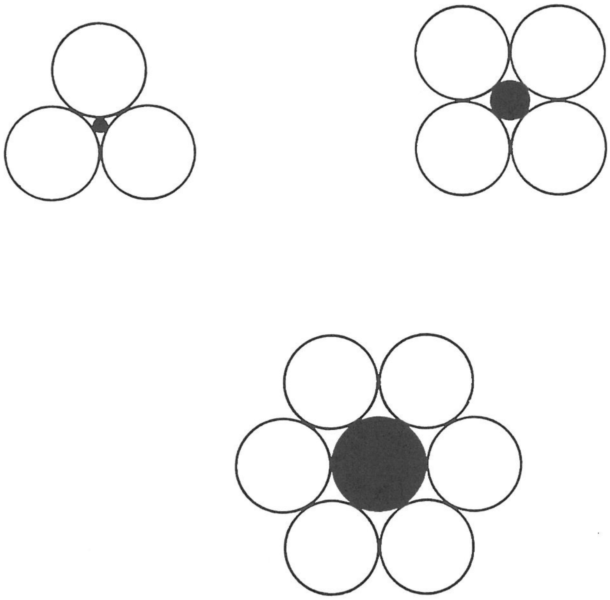


FIG. 8. Planar representation of the relationship between radius ratio and coordination number (after Goldschmidt, *Geochemische Verteilungsgesetze der Elemente VII*, p. 113, 1926).

3. For an element that can exist in several valence states, i.e., form ions of different charge, the higher the positive charge on the ion, the smaller the radius, for example: $Mn^{2+} = 0.91Å$, $Mn^{3+} = 0.70Å$, $Mn^{4+} = 0.52Å$. This is a corollary of the preceding rule.

In an ionic structure (and most inorganic compounds can be considered as ionic structures) each ion tends to surround itself with ions of opposite charge. Goldschmidt demonstrated that the number that can be grouped around the central ion depends upon the radius ratio between the two (Fig. 8). By assuming that ions act as rigid spheres of fixed radii, he calculated the stable arrangements of cations and anions for particular radius ratios from geometric considerations (Table 3). Goldschmidt realized his assumption was not entirely valid; he wrote: "We must regard the edifices of crystal structure not as constructions made from rigid spheres, but as dynamic equilibria, the dimensions (of the atoms and atomic groupings) yielding to some degree to interatomic binding and repulsive forces".[7] Nevertheless, the concept of the radius ratio has proved extremely fruitful in elu-

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FIG. 7. The Periodic Table of the elements, illustrating ionic sizes; La* occupies the space for the lanthanides, La (57) to Lu (71), their ionic size ranging from $La^{3+} = 1.15Å$ to $Lu^{3+} = 0.85Å$. Open circles are cations, solid circles anions.

Table 3. Relationship between radius ratio and coordination number for ions as rigid spheres (after Goldschmidt, *Geochemische Verteilungsgesetze der Elemente VIII,* p. 15, 1927).

Radius ratio ($R_{\text{cation}}/R_{\text{anion}}$)	Arrangement of anions around cation	Coordination number of cation
0.15–0.22	Corners of an equilateral triangle	3
0.22–0.41	Corners of a tetrahedron	4
0.41–0.73	Corners of an octahedron	6
0.73–1	Corners of a cube	8
>1	Closest packing	12

cidating crystal structures. For example, in the many AX compounds with the sodium chloride structure, each cation is surrounded by six anions, i.e., the cation is six–coordinated. With a larger cation–anion ratio, as with the large cesium ion, a different structure becomes stable, the cesium chloride structure, in which the coordination number is eight.

Many cations occur exclusively in a specific coordination; others, which have a radius ratio lying near the theoretical boundary between two types of coordination, may occur in both. Thus calcium can be accommodated in either six– or eight–coordination with oxygen, and aluminum in either six– or four–coordination; sometimes both types of coordination can be present in the same compound.

In his considerations of crystal chemistry Goldschmidt greatly expanded the concepts of *isomorphism* and *polymorphism,* and elucidated many puzzling features of these phenomena. The term *isomorphism* was introduced by the German chemist Mitscherlich in 1819, who prepared crystals of KH_2PO_4, KH_2AsO_4, $(NH_4)H_2PO_4$, and $(NH_4)H_2AsO_4$ and found that their crystal forms were essentially identical. By Mitscherlich's original definition, substances with analogous formulas and similar crystallography were said to be isomorphous. Goldschmidt widened this concept by showing that substances with analogous formulas and with ions of the same coordination usually had the same structure, as demonstrated by the large number of compounds with the sodium chloride structure. Sometimes the chemical analogy was not obvious; Goldschmidt showed that boron nitride, BN, had the same structure as graphite (hexagonal carbon);[8] he speculated that there might be a high–pressure form of boron nitride with the structure and properties of diamond. This cubic form of boron nitride was subsequently synthesized by the General Electric Company in 1957, and is marketed under the trade name of Borazon.

Polymorphism refers to the phenomenon whereby an element or compound crystallizes in more than one structure; for example, diamond and graphite are polymorphic forms of carbon. Goldschmidt showed that many instances of polymorphism are associated with changes in coordination number—in graphite each carbon is linked to three other carbon atoms to form a sheet structure, whereas in diamond each atom is linked to four other atoms in a three-dimensional structure. This explanation for polymorphism and isomorphism was illustrated by Fig. 9. For cations with a radius less than 1.0Å, the borates, nitrates, and carbonates all have the same trigonal crystal structure, that of calcite, $CaCO_3$; for cations with a radius greater than 1.0Å, a different structure (orthorhombic), that of the $CaCO_3$ polymorph aragonite, is the stable form. For divalent calcium, with an ionic radius of 0.98Å, both structures are possible.

Goldschmidt also considered the relationship between crystal structure and other physical properties. He pointed out that, for compounds with the same structure, the hardness was related to the ionic charge. On a scale of 1 to 10 the hardness of compounds with the sodium chloride structure is directly related to the charges on the ions, thus:

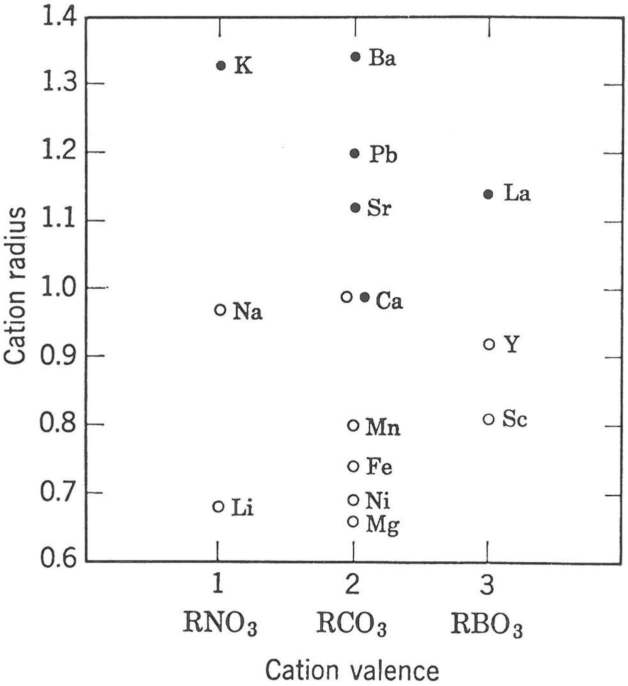

FIG. 9. Effect of cation radius in determining crystal structure: ○ = trigonal; ● = orthorhombic (after Goldschmidt and Hauptmann, *Nachr. Ges. Wiss. Göttingen, Math.-phys. Klasse*, p. 53, 1932).

Compound	NaF	MgO	ScN	TiC
Ionic charge	1	2	3	4
Hardness	3.2	6.5	7 to 8	8 to 9

He developed a *model principle* to construct crystals with a prescribed atomic arrangement and pre–determined physical properties. As an example, he cited Zn_2SiO_4 and Li_2BeF_4, which have the same crystal structure but very different physical properties:

	Zn_2SiO_4	Li_2BeF_4
Hardness	5.5	3.8
Melting Point	1510°C	470°C
Solubility in H_2O	Insoluble	Rather soluble

In subsequent years this principle has been widely applied to synthesize compounds with desirable physical properties.

A great contribution of the new crystal chemistry to the advancement of geochemistry was the prediction of the occurrence and distribution of minor and trace elements, through a knowledge of their atomic and ionic radii. The development of reliable methods for the analysis of minerals showed that many of them are variable in composition; substitution of one element by another is the rule rather than the exception. When this phenomenon was first observed in the mid-nineteenth century it was described in terms of the concept of solid solution or mixed crystals, which implied the presence, in a homogeneous crystal, of molecules of two or more substances. For example, the common mineral olivine, an iron–magnesium silicate whose formula is $(Fe,Mg)_2SiO_4$, was described as a solid solution of Mg_2SiO_4 and Fe_2SiO_4. Since Mg_2SiO_4 and Fe_2SiO_4 are isomorphous, solid solution was often equated with isomorphism, despite the fact that many isomorphous compounds show little or no solid solution, and extensive solid solution may occur between components that are not isomorphous. The new crystal chemistry provided a radically improved interpretation. In an ionic structure there are no molecules, the structure being an infinitely extended network of regularly spaced ions. Any ion in the structure may be replaced by a different ion of similar radius without causing serious distortion of the structure, just as a bricklayer, running short of red bricks, may incorporate yellow bricks of the same size here and there in his wall. Since minerals crystallize from naturally occurring solutions containing many elements other than those essential to the mineral, they often incorporate some foreign ions in the structure. Goldschmidt showed that provided the radii of substituting and substituted ions do not differ by more than 15%, a wide range of substitution may be expected. It is not essential that the substituting ions have the same charge or valency, provided that electrical neutrality is maintained by concomitant substitution elsewhere in the structure. For example, potash feldspar commonly contains some barium: Ba^{2+} substitutes for K^{1+} and electrical neutrality is maintained by the coupled substitution of Al^{3+} for Si^{4+}. These concepts provided the clues that Goldschmidt was to exploit during the next decade in the elucidation of the geochemistry of many rare elements.

In addition to the concept of camouflage, mentioned in the case of zirconium–hafnium, where a rare element is camouflaged in the minerals of a more common element with the same ionic charge and essentially the same size (other examples are Al^{3+}—Ga^{3+}, Si^{4+}—Ge^{4+}); Goldschmidt introduced the concepts of *capture* and *admission.* When a minor element has a similar ionic radius but a higher charge than that of a major element (or the same charge or a lesser radius) it will be preferentially incorporated in a crystallizing mineral, and hence is "captured" by it. Thus Ba^{2+} (1.34Å) is captured by potassium minerals (K^{1+} = 1.33Å). On the other hand, when a minor element has a similar ionic radius but a lower charge than those of a major element, it is less readily incorporated, and is said to be "admitted" into those minerals containing the major element. Thus Li^{1+} (0.78Å) is admitted into magnesium (Mg^{2+} = 0.78Å) minerals. In capture and admission of ions of different charge the charge balance is maintained by concomitant substitution elsewhere in the crystal lattice.

After 1926 the tempo of research at the Mineralogical Institute slowed somewhat. Ulrich had returned to Prague. Thomassen had left for the California Institute of Technology in December 1924; he returned in October 1927 but resigned in July 1929 to accept a professorship in chemical engineering at the University of Michigan. Barth took his doctoral examination in September 1927 and accepted a position at the Technical University of Berlin; in this connection, Goldschmidt wrote the following recommendation: "Since autumn 1924 he has been scientific assistant at the Mineralogical Institute. I praise his personal qualities, as an extremely reliable, dutiful, and diligent co–worker." Zachariasen produced a 165-page monograph on the structure of ABO_3 compounds for his doctoral examination in October 1928 and went to do research with Sir Lawrence Bragg in Manchester, and from there to a professorship in the University of Chicago in 1930. In 1929 Lunde became director of the Norwegian Cannery Association laboratory in Stavanger. After 1927 Goldschmidt was preoccupied with the proposed move to Göttingen.

In 1927, however, Goldschmidt acquired an outstanding coworker, Felix Machatschki,[9] from Graz in Austria, who came to the Mineralogical Institute with a Rockefeller Scholarship. He worked with Goldschmidt for some years, first in Oslo and then as guest lecturer in Göttingen in 1929–30, except for a period with Sir Lawrence Bragg in Manchester in 1928–29. He absorbed Goldschmidt's ideas on crystal chemistry and isomorphism and immediately applied them to significant mineralogical problems. He attacked the problem of silicate structures, which Goldschmidt had largely avoided because of their complexity. In a short paper published early in 1928 on the structure of the feldspars he demolished current theories of silicate structure based on hypothetical silicic acids, and established the concepts on which a new theory was built. As the fundamental unit of silicate structures he proposed a tetrahedral group of four O^{2-} ions around a central Si^{4+} ion. This Si^{4+} ion could be replaced by an Al^{3+} ion, also in four–coordination with oxygen, but aluminum could also occur in six–coordination with oxygen, a dual role which was to explain many otherwise puzzling mineral compositions. The tetrahedra could be linked through oxygen atoms to form a variety of structures. In the feldspars every oxygen ion is shared by two adjacent tetrahedra and the ratio $Si + Al:O = 1:2$, giving the formulae $KAlSi_3O_8$ (orthoclase), $NaAlSi_3O_8$ (albite), and $CaAl_2Si_2O_8$ (anorthite) and explaining the complete solid solution between albite and anorthite (the plagioclase feldspars), despite the difference in their formulas.

In 1929 Machatschki secured another triumph when he derived a satisfactory formula for tourmaline, whose chemistry John Ruskin described in 1891 as "more like a medieval doctor's prescription than the making of a respectable mineral." By a careful evaluation of many chemical analyses, and the application of the new concepts of crystal chemistry, he derived the formula $XY_9B_3Si_6H_xO_{31}$; in X and Y he grouped cations of similar size, as follows: $X = Na^{1+}, Ca^{2+}$; $Y = Li^{1+}, Mg^{2+}, Mn^{2+}, Fe^{2+}, Al^{3+}$. He showed that the unit cell of tourmaline contained three of these formula units.

Other visiting scientists from abroad were Dorothy Wyckoff,[10] a petrologist from Bryn Mawr College in Philadelphia, and Adolf Pabst, a mineralogist from the University of California, who spent the academic year 1928–29 at the Mineralogical Institute. Goldschmidt wrote of Pabst (letter, March 14, 1929): "He must be classed among the very best scientists who have visited my laboratory, certainly among the best five". Pabst went on to a distinguished career as Professor of Mineralogy at the University of California at Berkeley, and received the premier award of the Mineralogical Society of America, the Roebling Medal, in 1965.

In 1927 Goldschmidt's mother suffered a stroke with paralysis on one side, and the Goldschmidt household employed a housekeeper, Miss Marie Brendingen, who remained a devoted servant until Goldschmidt's death in 1947. During 1928 he was frequently absent, giving invited lectures in northern Europe and supervising the construction of a new Mineralogical Institute in the University of Göttingen. During that summer he developed a serious lung condition as a result of the incautious use of hydrofluoric acid in his experiments; he lost his voice completely for some time, and spent the month of July at the spa at Bad Ems recuperating. While there he wrote to Zachariasen (July 24, 1928) " . . . Yesterday and the day before I was visited by Dr. Bernal from Cambridge. We talked crystal chemistry for up to 12 hours, without me becoming hoarse. . . . " Bernal had a distinguished career, both in science and politics; he gave the memorial address to the Chemical Society of London after Goldschmidt's death.

Goldschmidt was nominated for the Nobel Prize in chemistry for 1929.[11] However, the prize for that year went to Arthur Harden and Hans von Euler, for their researches on fermentation processes. It took some years for the significance of the new crystal chemistry to be recognized in wider scientific circles; I can recall no mention of it in my graduate studies in chemistry in the University of New Zealand in the late 1930's.

In March 1929 Goldschmidt gave two invited lectures in London. One, to the Faraday Society, entitled *Crystal Structure and Chemical Composition,* was a comprehensive exposition of the new crystal chemistry, as developed by him and his associates in Oslo. The other, to the Royal Institution, was entitled *The Distribution of the Chemical Elements,* and outlined the development of his ideas on geochemistry since the publication of his *Der Stoffwechsel der Erde* in 1922. An example in this paper illustrates his genius in obtaining a simple solution to a complex problem, in this case the average composition of the Earth's crust. He noted that if it were possible to obtain an average sample of a large part of the Earth's crust consisting mainly of crystalline rocks, its chemical analysis would give a reliable picture of the composition of the crust as a whole. Such an average sample was provided, he pointed out, by the glacial clay widely distributed in southern Norway, which represents the finest rock flour deposited by melt water from the Fennoscandian ice sheet. During previous years the Raw Materials Laboratory had made numerous analyses of these clays for technological purposes. From 81 analyses of different samples of this material he calculated the following average:

SiO_2	Al_2O_3	$FeO+Fe_2O_3$	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	H_2O
59.19	15.68	6.96	3.38	3.20	2.10	3.74	0.80	0.21	3.06

In 1924 F. W. Clarke and H. S. Washington in the U.S. had derived an average composition of the igneous rocks of the Earth's crust, based on Washington's collection of 5159 superior analyses selected from the literature. Their results, calculated to 100 percent with the elimination of H_2O, are as follows:

SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5
60.18	15.61	3.14	3.88	3.56	5.17	3.91	3.19	0.16	0.30

As Goldschmidt commented, the correspondence between the two sets of figures is remarkable, especially when the effects of hydration and solution, which result in the leaching of sodium and calcium from the clays, are taken into account.

Goldschmidt also applied his data on ionic radii to an intriguing consideration of the composition of the Earth's crust or lithosphere. The Earth's crust consists almost entirely of oxygen compounds, mainly silicates of aluminum, calcium, magnesium, sodium, potassium, and iron. Nine elements—O, Si, Al, Fe, Ca, Na, K, Mg, and Ti—make up over 99% of the total. Of these, oxygen is absolutely predominant. As he pointed out, this predominance is even more marked when the figures are recalculated to atom percent and volume percent (Table 4). In terms of number of atoms, oxygen exceeds 60%. If the volume of the different atoms, or rather ions, is calculated, oxygen makes up more than 90% of the total volume occupied by the elements. Thus the Earth's crust is essentially a packing of oxygen anions, bonded by silicon and the ions of the common metals. As Goldschmidt remarked, the lithosphere may well be called the oxysphere.

Table 4. The composition of the Earth's crust, in terms of weight percent, atom percent, and volume percent of the elements (Goldschmidt, *Neues Jahrb. Mineral. Beilage, Abt. A*, vol. 57, p. 1119, 1928).

Element	Weight %	Atom %	Radius (Å)	Volume %
O	46.59	62.46	1.32	91.77
Si	27.72	21.01	0.39	0.80
Al	8.13	6.44	0.57	0.76
Fe	5.01	1.93	0.82	0.68
Mg	2.09	1.84	0.78	0.56
Ca	3.68	1.93	1.06	1.48
Na	2.85	2.66	0.98	1.60
K	2.60	1.43	1.33	2.14
Ti	0.63	0.28	0.64	0.22

On Goldschmidt's departure from Norway in 1929, King Haakon honored him by making him a Knight (First Class) of the Royal St. Olav's Order, for services to Norwegian science.

On September 26, 1929, Goldschmidt gave an invited lecture at the University of Helsinki. After the lecture his long–time colleague and friend, Pentti Eskola, spoke as follows:[12]

> "Honored guest, Professor Goldschmidt, it is for me a pleasant duty to thank you for your visit and for sharing with us the results of your researches. I recall a conversation with you a long time ago as to the value of lectures, now that scientific results are so readily communicated by publication. You replied that personal communication could transmit ideas and inspiration to the listeners far better than the printed word. Your lecture today has demonstrated the truth of that reply, and is a stimulus to our scientific work.
>
> Since I had the good fortune some years ago to work closely with you on a daily basis, and thus know you better, perhaps, than most of your audience, I would like to speak about Professor Goldschmidt rather than to him. I want to express my great admiration for him, both for his impressive personality and for his enormous

scientific achievements. There is something titanic about him, including his discovery of titanium dioxide as a pigment, of which your audience may be unaware. I can truly say that he has fought a titanic fight against many difficulties, not least health problems, which many times have threatened his scientific career. It is only his remarkable energy and his ability to work both day and night that has enabled him to achieve his unique scientific results. As he himself has told me, genius is nothing more than extreme perseverance. I think that is an exaggeration, inspiration is also needed, but perseverance is certainly an important factor.

When, at the age of twenty–three, he published his great work *Die Kontaktmetamorphose im Kristianiagebeit* petrographers throughout the world at first had difficulty in appreciating his concepts. Even if it was realized that petrology is essentially physical chemistry applied to rocks, this was considered of purely theoretical significance. Many scientists were astounded by this demonstration of the practical applications. Younger researchers, not too indoctrinated in current petrographic theory, were able to apply his new principles. I was one of them, and ever since have endeavored to apply chemical theory to the study of rocks. This led to collaboration between Goldschmidt and myself, which ten years ago took me to Oslo, where I stayed for almost a year.

This was a year of intensive work for me. I often discovered how my ideas developed through conversations and discussions with Professor Goldschmidt. I will give one example. One morning, when I was on my way up to my room on the fourth floor of the Mineralogical Institute, I met Professor Goldschmidt on the stairs between the second and third floors. At that time I was studying the nature and origin of eclogites. We began to talk about eclogites and the interior of the Earth. We stood there several hours, until we noticed other staff members leaving for lunch! We had talked the morning away, but that morning was most stimulating for me.

Ever since 1906, when the 18–year Goldschmidt developed a method for measuring the radioactivity of minerals, hardly a year has gone by without his making some significant scientific discovery. It would take too long to enumerate them. During my time in Oslo petrology was his primary concern, although he had already begun his researches into crystal chemistry. In his lectures he often expressed completely original ideas, and when I listened to this youthful professor I frequently had the impression that this was a wise old man deciphering nature's secrets. There was often a certain personification of atoms and crystals, that their secrets could only be unlocked through some sort of cunning. I think I discerned something of this approach in the lecture we have just heard. In his lectures during my Oslo visit he discussed the ideas which were not published until some years later in the classic papers *Stammestypen der Eruptivesteine* and *Der Stoffwechsel der Erde*. Some of his ideas were published in a preliminary form in his monographs on the Stavanger region, which were especially significant for us in Finland, because he expounded on the role of metasomatism in the formation of migmatites. When Professor Goldschmidt lectured on silicate metasomatism in Stockholm, a Swedish geologist, Harald Johansson, commented that the lecturer was accusing the chemical elements, previously known for stable occurrence, for a type of loose living. Goldschmidt replied that this was not unknown even in the best families! It is now realized, thanks largely to Professor Goldschmidt's researches, that metasomatism is a very important process in the formation and alteration of rocks.

It should be mentioned that Professor Goldschmidt completed the Stavanger manuscript in an afternoon and evening [1919] while he was suffering from peritonitis. He wanted to complete the manuscript because he was doubtful of surviving his illness. When late in the evening the manuscript was finished he went directly to the hospital and was immediately operated on.

Thereafter he began the researches which are his greatest achievement till now, whose results have been published in a series of eight monographs entitled *Geochemische Verteilungsgesetze der Elemente*. Professor Wasastjerna is more competent than I to comment on the crystal chemistry. However, in these monographs Professor Goldschmidt has founded a new scientific field more closely linking geology with physics and chemistry than ever before. We must wish him all success in his continued work in this field, but as a petrologist I hope that he will continue to consider himself as a petrologist and mineralogist and not only as a chemist" (translated from Swedish).