

Notes on the mineralogy and geochemistry of zinc.

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THE ionic radius of zinc (0.83 Å.) is identical with that of divalent iron (0.83 Å.) and nearly the same as that of magnesium (0.78 Å.). One would therefore expect zinc to be mineralogically closely related to iron and magnesium. It is, however, well known that this is not the case. An examination of a list of the zinc minerals which have so far been described shows that only in a few cases are the corresponding isomorphous ferromagnesian species known. As a rule zinc minerals and iron-magnesium minerals with corresponding chemical formulae are entirely different in their crystal-structure.

One might also anticipate that the zinc present in the earth's crust would be completely camouflaged in the ferromagnesian minerals, in the same way as gallium (0.62 Å.), which is about a third as common as zinc, is camouflaged in the minerals of aluminium (0.57 Å.).¹ In the case of aluminium and gallium the camouflage is a complete one, and gallium does not form minerals of its own at all. Zinc, however, is only to a small degree camouflaged in the ferromagnesian minerals in spite of the similarity of ionic radii between zinc on the one hand and iron and magnesium on the other. This is well illustrated by a recent investigation of an intergrowth of blende and Mn-Fe-garnet from a granite-pegmatite dike on the island of Kimito, Finland.² The two minerals have obviously been in equilibrium during their formation, and the garnet must be supposed to be 'saturated' in zinc. The content of ZnO in the garnet is nevertheless found to be smaller than 0.01%, giving a distribution coefficient of zinc between Mn-Fe-garnet and blende which is very low indeed.

The more easily a rare element is camouflaged in the minerals of common elements the less accessible it will be for industrial purposes. An indication of the tendency of any element to be camouflaged is

¹ V. M. Goldschmidt and C. Peters, *Nachr. Gesell. Wiss. Göttingen, Math. phys. Kl.*, 1931, p. 165.

² O. Knorring, *Compt. Rend. Soc. Géol. Finlande*, 1946, vol. 19, p. 77. [M.A. 10-420.]

therefore given by the extent to which that element must be concentrated compared with its average frequency in the lithosphere to give a deposit worth mining, and the greater the concentration factor, the smaller is the tendency to camouflage. The elements Nb, Cu, and U, which are usually regarded as being camouflaged only to a very small extent, have factors not greater than 200-300, while Sn has to be concentrated 1000 times to give a workable deposit. For Zn the factor is as high as 3000, about the same as for Au (2000) and Ag (5000).

This high figure, together with the fact that zinc deposits on the borderline of workability are very numerous and scattered all over the world, clearly demonstrate that zinc is not easily trapped in ferromagnesian minerals by incorporation in their crystal lattice.¹

To the writer's knowledge no explanation has so far been given for this unexpected behaviour of zinc. A study of the crystal chemistry of the zinc minerals, as far as this is known, seems, however, to offer a simple solution to the problem.

Blende and wurtzite, ZnS.—In these minerals Zn occurs in four-coordination, each zinc atom is surrounded tetrahedrally by four sulphur atoms, and vice versa. The distance between Zn and S is in both cases 2.35 Å., and the two minerals are structurally related in the same way as a cubic close-packing is related to a hexagonal close-packing. The corresponding Fe^{II} mineral, pyrrhotine (or troilite), has a lattice of NiAs-type with Fe^{II} in six-coordination.

Zincite, ZnO, has a structure closely related to that of wurtzite. Each Zn atom is surrounded by four tetrahedrally arranged O atoms. The distance between Zn and O is 1.96 Å. These facts are not in agreement with an ionic type of binding, for if ZnO were an ionic compound one would expect the distance between Zn and O to equal the sum of the ionic radii of these elements, 0.83 Å + 1.32 Å. = 2.15 Å. Moreover, because of the relative sizes of the two ions one would expect six-coordination instead of four-coordination as is the case with periclase

¹ According to V. M. Goldschmidt (Vid.-Akad. Skr. Oslo, I. Kl., 1938 for 1937, p. 81) the average content of zinc in the earth's crust is 40 g./ton, mainly bound in ferromagnesian minerals in igneous rocks, augites, amphiboles, and especially biotite. The vast bulk of igneous ferromagnesian minerals should make their content of zinc the one important factor for the calculation of the above figure. It is quite possible, however, that zinc, contrary to Goldschmidt's view, is present in igneous rocks as submicroscopic crystals of blende deposited on the surface of the rock-forming minerals (H. Neumann, Econ. Geol., 1948, vol. 43, p. 83) instead of being present in solid solution in augites, amphiboles, and biotite. Blende is reported as a rare mineral in igneous rocks, and is certainly not uncommon in granite-pegmatite dikes.

and artificial FeO. The quotient between the ionic radii of Zn^{2+} and O^{2-} is 0.629, and six-coordination can be shown by geometrical consideration to be the stable coordination when the quotient between the radii of the cation and the anion is between 0.414 and 0.732. The slightly too short inter-atomic distance might easily be explained by a shortening of the radius of one or both of the elements zinc and oxygen,¹ but this cannot account for the abnormal coordination number.

Even if one makes the highly improbable assumption that only the radius of Zn is shortened while that of O remains constant, which would favour four-coordination more than any other assumption, the quotient between the radii would be 0.485 and thus well within the limits of six-coordination. For geometrical reasons undirected chemical bonds in zincite are therefore impossible, and one is forced to assume that *zinc is bound to oxygen by covalent bonds directed in space towards the corner of a tetrahedron*. In accordance with such an interpretation Pauling and Huggins² have used the distance between Zn and O in zincite for the calculation of the covalent 'tetrahedral radius' of oxygen, while the inter-atomic distance in blende has been used for the calculation of the 'tetrahedral radius' of zinc.

In *Gahnite*, $ZnAl_2O_4$, zinc is again found within a group of four tetrahedrally arranged oxygen atoms. Gahnite belongs to the 'normal' type of spinels with Zn in four-coordination and Al in six-coordination.³

Whether *Franklinite*, $ZnFe^{III}_2O_4$, is a 'normal' spinel or a spinel with 'variate atom equipoints' cannot be determined by X-ray methods because of the great similarity in scattering power of Zn and Fe. It is hardly unjustified to assume that Zn occurs in four-coordination as this is the case with the great majority of zinc minerals with known coordination number.

Hetaerolite, $ZnMn_2O_4$, has a distorted spinel structure. For the same reason as for franklinite the coordination number is unknown, but may be four.

Smithsonite, $ZnCO_3$, is isomorphous with the corresponding iron and magnesium minerals, chalybite, and magnesite. Zinc is surrounded by

¹ The radii used above for the calculation of the hypothetical distance between Zn and O, if ZnO were an ionic compound, are the ionic radii for Zn and O in six-coordination. For four-coordination the hypothetical distance should be reduced by about 6%, if, indeed, elements in four-coordination are ever bound by purely ionic bonds.

² L. Pauling and M. L. Huggins, *Zeits. Krist.*, 1934, vol. 87, p. 205.

³ T. F. W. Barth and E. Posnjak, *Journ. Washington Acad. Sci.*, 1931, vol. 21, p. 255; *Zeits. Krist.*, 1932, vol. 82, p. 325. [M.A. 5-179.]

six oxygens forming a somewhat distorted octahedron. Smithsonite is the only mineral containing zinc which is with certainty six-coordinated, apart from some exceedingly rare silicates (see later).

In *Willemite*, Zn_2SiO_4 , zinc is surrounded by four tetrahedrally arranged oxygen neighbours, while the corresponding iron and magnesium minerals, fayalite and forsterite, are six-coordinated. The distance between zinc and oxygen is 1.92 Å., and similar considerations as for zincite lead to the conclusion that the chemical bonds of zinc must be covalent and directed towards the corners of a tetrahedron.

Hemimorphite, $Zn_4Si_2O_7(OH)_2 \cdot H_2O$, contains zinc tetrahedrally surrounded by four oxygens, three of which belong to Si_2O_7 groups, and one to a OH group. No ferromagnesian mineral with a corresponding formula is known.

Hardystonite, $Ca_2ZnSi_2O_7$, is isomorphous with the corresponding magnesium mineral, åkermanite, $Ca_2MgSi_2O_7$, and is an exception to the rule that zinc minerals are not isomorphous with corresponding ferromagnesian minerals. In this case, however, it is the coordination number of the magnesium, not the zinc, which is exceptional, as these elements are found in åkermanite and hardystonite surrounded tetrahedrally by four oxygens, which is normal as far as zinc is regarded, but highly exceptional for magnesium, whose normal coordination number is six.

Larsenite, $PbZnSiO_4$, a rare Franklin Furnace mineral, is a member of the olivine group, and contains zinc surrounded by six octahedrally arranged oxygen neighbours.

The structures of *Hodgkinsonite*, $MnZn_2SiO_4(OH)_2$, and *Leuco-phoenicite*, $(Mn, Mg, Zn)_8Si_3O_{12}(OH)_4$, are unknown. Both are rare and found at Franklin Furnace only. They are possibly isomorphous with the corresponding magnesium minerals, norbergite and humite, and, if so, would contain zinc in six-coordination.

The above data show that zinc is bound in four-coordination in the great majority of its minerals, and that this is the case with all the more common zinc minerals apart from smithsonite. Zinc analogues to the great number of ferromagnesian minerals are non-existent, and the reason for this is obviously that zinc has a very pronounced tendency to form covalent tetrahedrally directed bonds, while divalent iron and magnesium tend to form minerals with ionic bonds where the coordination number is six because of the size of the ions.

As a consequence of this one would expect zinc to be taken into solid solution preferably by minerals in which it can replace elements in

four-coordination. A survey of the mineral analyses where zinc is determined demonstrates that this is really the case. The writer has omitted analyses showing only a few tenths per cent. of zinc because impurities in the analysed material and analytical errors may easily account for these small figures. When a small amount of zinc is reported in only one of a long series of analyses of a certain mineral species, this mineral is also omitted from the list given below.

The following minerals are found to contain an appreciable amount of zinc: stromeyerite, CuAgS ; metacinnabar, HgS ; polybasite, $\text{Ag}_{16}\text{Sb}_2\text{S}_{11}$; pearceite, $\text{Ag}_{16}\text{As}_2\text{S}_{11}$; tetrahedrite, $(\text{Cu,Fe,Ag,Zn})_{12}(\text{Sb,As})_4\text{S}_{13}$; germanite, $(\text{Cu,Ge,Fe})(\text{S,As})$; jamesonite, $\text{Pb}_4\text{FeSb}_6\text{S}_{14}$; zinckenite, $\text{Pb}_6\text{Sb}_{14}\text{S}_{27}$; danalite, $(\text{Mn,Fe,Zn})_3\text{Be}_6\text{Si}_6\text{O}_{24}\text{S}_2$; chromite, FeCr_2O_4 ; zinc-spinel, $(\text{Mg,Zn,Fe})\text{Al}_2\text{O}_4$; hausmannite, MnMn_2O_4 ; and nigerite, $(\text{Zn,Mg,Fe}^{\text{II}})(\text{Sn,Zn})_2(\text{Al,Fe}^{\text{III}})_{12}\text{O}_{22}(\text{OH})_2$.

The structures of polybasite, pearceite, jamesonite, and zinckenite are not known in detail and nothing can be said about the coordination number.

Stromeyerite is *isomorphous* with the low-temperature modification of chalcosine. The structures of the two modifications of chalcosine are not too well known. A study of the system $\text{Cu}_2\text{S}-\text{CuS}$ has shown, however, that reversible transitions exist between chalcosine and digenite.¹ Digenite has an antiferite structure with copper in four-coordination, and the ease with which the transition $\text{chalcosine} \rightleftharpoons \text{digenite}$ takes place with change in temperature or chemical composition indicates a four-coordinated structure for chalcosine as well, and hence for stromeyerite.

The regular Zn-content of metacinnabar illustrates our point very clearly. This mineral has a lattice of the blende type with Hg in four-coordination. Cinnabar, on the other hand, has a distorted sodium chloride structure where Hg is found within an octahedral group of six sulphur atoms. In the four-coordinated metacinnabar Zn is taken into solid solution in quantities up to nearly 5%, while Zn has never been reported from the six-coordinated cinnabar at all.

Zinc is found in most tetrahedrites, occasionally in quantities up to 10% by weight. It replaces four-coordinated copper. Germanite has a lattice of the blende type where zinc replaces copper and germanium in four-coordination. The lattice of danalite is similar to that of sodalite and will, therefore, contain zinc in four-coordination.

It is not known if chromite is a spinel of 'normal' type or if it is

¹ N. W. Buerger, *Econ. Geol.*, 1941, vol. 36, p. 19. [M.A. 8-254.]

a spinel with 'variate atom equipoints'. Zinc will probably enter the four-coordinated positions of the lattice. Hausmannite has a distorted spinel structure and is isostructural with hetaerolite. Zinc probably replaces four-coordinated manganese. The positions of the atoms in nigerite (Min. Mag. 23-118, 129) are not determined, but an arrangement of O and OH is proposed giving tetrahedral and octahedral interstices. A possibility for zinc to replace a four-coordinated element is therefore indicated.

With the above list of minerals commonly containing zinc the tendency of this element to selective replacement of atoms in four-coordination is well established.

As an exception may be mentioned that at Franklin Furnace and Sterling Hill zinc is also found in a series of minerals replacing elements in six-coordination, such as brucite, pyrochroite, manganosite, zinc-amphibole, zinc-olivine (roepperite), and zinc-pyroxene (jeffersonite). An attempt to explain this phenomenon would imply a discussion of the genesis of these extraordinary deposits, and would be out of place in this paper. Excluding deposits of smithsonite, which is always of secondary origin, these two deposits are exceptional as containing six-coordinated zinc in appreciable amount, and even here nearly all the zinc present is four-coordinated in the ore-forming minerals franklinite, willemite, and zincite.

There is possibly another exception to the rule as well, which may be of far greater importance. C. S. Ross¹ has recently described zinc-bearing montmorillonite (sauconite) from Pennsylvania, and deduces from his analyses that zinc enters the octahedral positions of the lattice and not the tetrahedral ones. That clay minerals can contain zinc in solid solution may be important for the understanding of the geochemistry of Zn in the sedimentary cycle but, so far, too few data are known about the amounts of zinc in slates and clays to take this problem up for discussion.

Our present knowledge about the crystal chemistry of zinc minerals and minerals containing zinc in solid solution is limited. Many of the species mentioned above are not known in detail, and some zinc minerals have not been mentioned at all because they have never been examined by X-ray methods. In spite of this lack of information, however, the evidence summarized here seems to the writer to justify the conclusion that the one important factor which characterizes and stamps the mineralogical and geochemical behaviour of zinc is that the element

¹ C. S. Ross, Amer. Min., 1946, vol. 31, p. 411. [M.A. 10-26.]

tends to form covalent bonds directed in space towards the corners of a tetrahedron.

Most of the more common elements in the lithosphere tend to form ionic bonds with oxygen, and it is a well-established principle that the size of their ions decides their geochemical behaviour. This principle is not valid in a case like that of zinc where the element tends to form covalent bonds. The primary principle of geochemical classification of the elements must obviously be their tendency to form ionic, covalent, or metallic bonds. Secondly, elements forming ionic compounds may be classified according to ionic radii, and elements forming covalent bonds according to spatial properties of their bonds.

Apart from an important investigation by F. E. Wickman¹ on the geochemistry of the elements in sedimentary rocks, the geochemical importance of the character of chemical bonds has been hardly discussed. No doubt the reason for this is that our understanding of the nature of chemical bonds is somewhat unsatisfactory, and that we at present have no means to measure quantitatively the tendency of any element to form a certain type of chemical bond. A method of measuring such a tendency would have a wide application in geochemistry, and one of the first results would probably be the establishment of a sound theoretical basis for the classification of chemical elements as siderophile, chalcophile, lithophile, and atmophile,² which classification is at present purely empirical.

¹ F. E. Wickman, *Arkiv Kemi, Min. Geol.*, 1945, vol. 19 B, no. 2. (Preprints dated 1944.)

² V. M. Goldschmidt, *Vid.-Akad. Skr. Oslo, I. Kl.*, 1923, no. 3. [M.A. 2-159.]