THE OCCURRENCE OF THE NATIVE ELEMENTS

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Native elements are defined as those existing in nature in the free state, not chemically combined with other elements, altho in many cases more or less admixed with others. A list of them was published in the initial number of this magazine.[1] Some elements are almost always found native, others only exceptionally so, while about half of the elements known to chemists have been observed only in compounds with one another. What are the reasons for these relations?

Just as in biology, certain features of organisms are connected with heredity and others with environment, so here we find both inherent properties and external circumstances concerned in the determination of whether an element can exist in the native state or not. Of the inherent properties the chief one is chemical affinity, the influence which leads elements to enter into chemical compounds. The principal external circumstance is the fact that the element oxygen is present in the earth in great abundance, amounting, it is calculated, to 50% of the whole. Let us consider the manner in which these causes cooperate to produce the relations observed.

It will be most convenient to take up the elements in the groups represented by the vertical columns of the Periodic System[2], since the elements in these groups show similarities which enable the occurrence of several to be discussed at the same time. For the sake of completeness gaseous elements will be included, altho they are not usually regarded as minerals.

The first column contains but one element, hydrogen. Hydrogen is a gas which possesses considerable affinity for oxygen and other non-metallic elements. It therefore occurs in the earth mostly in compounds, but as its compounds are decomposed at temperatures such as exist in igneous magmas, it is given off by volcanoes. If it escapes in a heated condition it burns in the oxygen of the air to form steam, but if cooled before coming into contact with the air it may remain in the free state, for it does not unite with oxygen when cold. A minute amount appears to be normally present in the atmosphere.

The six gases of the second column, helium, neon, argon, krypton, xenon and niton, are peculiar in that they show practically no chemical affinity, no definite compounds of them with other elements having been prepared. They therefore exist normally in the free state, and they make up about one per cent by volume of the earth's atmosphere. Helium is also found in certain radioactive minerals, such as uraninite, being one of the end-products

[1] *Am. Min.* **1**, (1), 8, 1916.
[2] *Am. Min.* **1**, (1), 7, 1916.

of the disintegration of the radioactive elements; while niton, also known as radium-emanation, is given off as an intermediate stage in this disintegration.

The elements of the third column, known as the alkali metals, possess great affinity for oxygen and other elements, and are incapable of existing in the air or in the rocks for any length of time without turning into oxides. Two of them, sodium and potassium (Na and K) have, nevertheless, been shown to occur free in nature in the peculiar condition known as the dispersoid state. When the radiations given out by radium or other radioactive elements act upon certain compounds slight decomposition occurs, and the component elements are set free, becoming disseminated thru the unchanged substance as submicroscopic particles. In the case of the mineral halite, which is chemically sodium chloride, the particles of sodium thus liberated cause the mineral to assume a blue color. Specimens of such blue halite, as well as of the corresponding potassium compound sylvite, have long been known to mineral collectors, but the explanation of the color has been shown to lie in the presence of minute amounts of the respective metals in this "dispersoid" condition only in the most recent years.[3]

Copper, silver and gold (Cu, Ag and Au), the metals constituting the fourth column, exhibit comparatively slight chemical affinity, especially toward oxygen, this decreasing in the order named. They are readily set free from their compounds, and once in this condition, are likely to remain so. They accordingly are frequently found in the native state, gold being, indeed, almost unknown in any other form.

In the next column, that of alkaline earths, chemical affinity is again marked, and only one member, calcium, has been reported to occur native, in the dispersoid state, as the coloring matter of certain specimens of the mineral fluorite[4]; its existence can not as yet be regarded as proved.

Two members of the sixth column, zinc and mercury, have been observed native, altho the chemical activity of the former is so great that its occurrence is rather unexpected, and has indeed been questioned. Mercury, however, is comparatively inactive, not uniting with oxygen in the cold, and is often found free in cavities in its ores.

No members of the seventh or eighth columns appear to occur in the native state, for their chemical activity is extreme, but in the ninth column the first, (and possibly the second), element has been so found. Carbon is an element which possesses strong affinity for oxygen, but requires heating to high temperatures for direct union to take place; once liberated from its compounds therefore, it is fairly stable. Its liberation is believed to have

[3] Professor E. Goldstein, *Nature*, **94**, 494, 1914.
[4] Professor C. Doelter, *Sitzb. Akad. Wiss. Wien*, **1908**, 1312.

been accomplished in most cases by the action of heat and pressure on its compounds with hydrogen. Silicon is, on the other hand, liberated from its compounds only with great difficulty, and would not be exepcted to occur native under ordinary circumstances. It has merely been suggested to be the cause of color of smoky quartz, in which it may exist in dispersoid condition.[5]

In the ninth column germanium is extremely rare, but tin and lead (Sn and Pb) are well known metals, oxidized somewhat readily in the air, yet reduced from their compounds without difficulty. Tin has been reported as occurring native in many deposits of its oxide, and altho some of these reports are no doubt erroneous, it seems probable that native tin does at times occur. Lead is found in fissures in connection with ores in which sulfur is deficient.

All of the five members of the tenth column have been reported to occur native. Nitrogen, a gas, is abundant in the atmosphere in the free state, since it unites with oxygen only under such exceptional conditions as the presence of an intense electrical discharge. Phosphorus, on the other hand, is highly active chemically and unites with oxygen with such violence that its occurence in minerals in the free state is decidedly unexpected. It has been reported to exist in a stony meteorite[6], (containing 8% of metallic iron) but this seems highly improbable, as it unites with iron directly, to form the iron phosphide schreibersite. Perhaps the phosphorus observed was temporarily set free either by the actual drilling operation or by local decomposition of iron phosphide in the presence of a limited amount of air. Its occurrence in the dispersoid form in phosphate rocks has been reported also. Arsenic, antimony and bismuth, the remaining members, are less active than phosphorus, and altho they unite with oxygen, can be readily reduced again. All three are well known to occur native in connection with deposits of other minerals containing them.

Coming to the eleventh column, vanadium is an element with strong affinity for oxygen, which accordingly does not occur free in ordinary rocks; but it is found to a slight extent in meteorites, which have formed in the presence of limited amounts of oxygen; even here it is not in the pure state, but is alloyed with a large excess of iron, and can only be detected by analysis. Columbium and tantalum are rare elements which also unite readily with oxygen and are reduced from compounds with difficulty. Nevertheless an alloy of the two has been discovered in certain gold-washings in Asia, and is sold by mineral dealers under the name of native tantalum.

The elements of the twelfth column are again all found native. Oxygen, altho it unites with most other elements, is present in the air in large amount. Sulfur, selenium, and tellurium have con-

[5] Koenigsberger and Müller, *Centr. Min. Geol.* **1906**, 73, note.
[6] Dr. O. C. Farrington, *Am. J. Sci.*, **15**, 71, 1903.

siderable affinity for oxygen, but where reducing action can take place in the presence of an insufficient amount of air they may be set free, and once in this form do not unite with oxygen unless heated. They are also given off in the gaseous form from volcanoes.

The metals of the thirteenth column form oxides which are decomposed only with difficulty, and none of them have been observed native in terrestrial rocks. Chromium is shown by analysis to occur alloyed with the iron of some meteorites.

The halogen elements, which appear in the fifteenth column, have little affinity for oxygen, but unite readily with metallic substances. It is therefore surprising that any of them should be found free in nature, yet they all have been reported. Certain varieties of the mineral fluorite, a compound of calcium with fluorine, contain in minute cracks traces of free fluorine gas, which has probably been liberated by radioactive processes. Chlorine, another gaseous element, is liberated from its compounds by radioactivity also, but is better known in volcanic emanations, where it is formed by complex reactions in the magma. Bromine, which may be either a liquid or a gas at ordinary temperatures, has been reported to occur free by Professor Vernadsky[7]; while iodine, in solid colloidal form, according to the same authority was reported as early as 1877. The last two are, however, of doubtful authenticity.

The single element of the sixteenth column, manganese, is a metal possessing such strong affinity for oxygen and other elements that it could not exist in the free state in the earth for any length of time; alloyed with iron, however, it is protected from attack, and it has been observed to be present in both terrestrial and meteoric irons, tho in relatively small amount.

The metals of the last column show a gradual decrease in chemical activity downward, iron uniting readily with oxygen, while platinum does not unite directly with it, except at high temperature. Iron is, however, readily reduced from its compounds by carbon, and occurs native where opportunity for such reduction has been offered, and where the resulting metal has not been exposed to the action of moist air for any length of time; it is also present in practically all meteorites, which have evidently formed under conditions where oxygen was limited in amount. Cobalt and nickel are found alloyed with iron, and the nickel sometimes exceeds the iron in amount. The remaining six metals occur more or less alloyed together, or alloyed with iron and nickel. They are comparatively resistant to oxidation and are rarely found in other than the metallic state.

Over half of the known chemical elements have thus been reported to occur in the native state.[8]

[7] *Opuit Opisatel'noi Mineralogii* (*Descriptive Mineralogy*, Russian) **1**, 1908.

[8] A discussion of the nomenclature and classification of the native element minerals will appear in a forthcoming number of the Journal of the Washington Academy of Sciences.