TECHNICAL PAPERS

On the Geochemistry of Columbium

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In an earlier paper the present author (*8*) has discussed the geochemistry of tantalum, in this respect, thus far, one of the more imperfectly known elements. Later an investigation of the geochemistry of columbium was carried out, based on substantially the same material. The present paper is a condensation of the results obtained.

The laboratory work was carried out in the Geochemical Laboratory, Institute of Geology, University of Helsinki, Finland. The Cb contents of the samples were determined by means of spectrochemical analysis, using a new, previously described technique (*10*).

There are some 30 to 40 species which can be classified as Cb minerals proper. Columbite and tantalite are the most common of the species in question. In minerals, Cb is found to replace Ta diadochically and to enter in a number of Ti-, Zr-, Sn-, and W-bearing, and in small amounts in Cr- and Mn-bearing, minerals. The content of Cb in certain minerals and mineral groups is presented in Table 1, which also contains information furnished by von Hevesy, Alexander, and Würstlin (*5*), Borowsky and Blochin (*1*), Panteleyev (*7*), and Sahama (*11*).

TABLE 1

	Cb_2O_5 (max. %)
Titanium minerals:	
Titanomagnetite	0.055
Ilmenite	1.3
Perovskite	4.7
Rutile	0.29
Anatase	0.067
Brookite	0.033
Sphene	3.3
Keilhauite	1.2
Zirconium minerals:	
Zircon	2
Woehlerite	>5
Astrophyllite	2.15
Eudialite	2.35
Eucolite	4.0
Catapleiite	2.2
Other minerals:	
Magnetite	0.026
Cassiterite	3.4
Wolframite	>5
Garnet group	0.001
Thorite	0.31
Tourmaline group	0.007
Thortveitite	0.95
Pyroxene group	0.013
Amphibole group	0.016
Muscovite	0.033
Biotite	0.188

As is known from work of previous investigators, the cassiterites sometimes contain high amounts of Cb. According to Goldschmidt (*4*), this fact is due to the presence of Sc and Fe columbates, $ScCbO_4$ and $FeCb_2O_6$, in the cassiterite. The electric balance is maintained by the simultaneous addition of one Sc^{3+} to every Cb^{5+} or of one Fe^{2+} to every two Cb^{5+}. Also, in wolframite $ScCbO_4$ is responsible for the presence of Cb. In Ti minerals Cb is found to replace Ti, being captured in place of this element. Some of the magnetites investigated contain traces of Cb, evidently due to the presence of small amounts of Ti in the lattice. The occurrence of Cb in Zr minerals and perhaps also in thorite is explained in a similar way.

As is shown by Sahama (*11*), Ca must be replaced by Na in sphene to maintain the electrostatic neutrality of the lattice if Ti is replaced by Cb. This rule may be extended to cover such minerals as garnet, tourmaline, the pyroxenes, and the amphiboles. The high Cb content of thortveitite is interesting and might lead to a re-examination of the chemistry of this mineral.

TABLE 2

	Cb_2O_5(%)	Cb:Ta
Monomineralic rocks	0.00004	0.4
Ultrabasic rocks	0.0023	16.4
Eclogites	0.0005	5.3
Gabbros	0.0027	17.7
Diorites	0.00052	5.5
Granites	0.003	5.0
Syenites	0.005	17.1
Nepheline syenites	0.045	384.1
Basic alkaline rocks	0.002	11.4

The micas, muscovite and biotite, contain appreciable amounts of Cb, for which there is adequate room in the capacious mica lattice. It is also evident that in biotite Cb can replace Ti. Rather high Cb_2O_5 contents are reported by Stevens (*14*) to occur in lepidolites, the maximum being 1.52 per cent in a polylithionite from Greenland.

In addition, small traces of Cb varying from some thousandths to some millionths of a per cent, are occasionally found in many sulfides, e.g. sphalerite, chalcopyrite, galena, and pyrite; the carbonates, siderite and calcite; anhydrite; scheelite; monazite and apatite; vanadinite; olivine, kyanite, topaz, beryl, nepheline, the feldspars; and still other minerals. In these cases, the adsorption of Cb compounds, such as soluble alkali metacolumbates $NaCbO_3$ and $KCbO_3$, is suggested as the cause of the contamination, in the sense extensively studied by Seifert (*12, 13*).

The third group of minerals includes: halides; corundum, hematite, quartz; barite, gypsum; cordierite, talc, antigorite, leucite; most of the feldspar minerals investigated; and many other species which were found to be free from Cb.

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The Cb contents of the different groups of igneous rocks, together with the Cb: Ta ratios, are presented in Table 2.

A remarkably high Cb content is found in ultrabasic rocks, comparing well with the average content in granites. This is evidently due to the high Ti content of these rocks, and we deal here with the replacement of CaTi by NaCb, which is, according to Niggli (*6*), responsible for the separation of Cb from the magma at a relatively early stage. Similar causes might well be responsible for the high content of this element in gabbroic rocks. In granites the concentration of Cb in the residual liquors will become evident, but the highest contents are arrived at in syenites and nepheline syenites. In this respect Cb clearly differs from Ta, which shows a maximum in granites. These results are in accordance with the observations of Goldschmidt (*2*) that both Cb and Ta are elements characteristic of granite pegmatites, while the latter element, contrary to Cb, is a less pronounced denizen of nepheline syenite pegmatites. This is clearly seen also by the Cb:Ta ratios of the two rock classes.

TABLE 3

	Cb_2O_5(%)	Cb:Ta
Minerogenic sediments	0.0018	9.0
Chemical "	0.00006	2.6
Organogenic "	0.00009	3.8
Deep sea "	0.0059	41.9

The Cb contents for sedimentary rocks are given in Table 3. As in igneous rocks, Cb in sedimentary rocks is more common than Ta. It is of interest to note the concentration of Cb in hydrolysate sediments in the beginning of the exogeneous cycle, and its even more pronounced concentration in the deep sea sediments, where the highest amounts are present in the manganese nodules.

No figures will be offered with respect to metamorphic rocks, since the geochemistry of metamorphism is, as yet, known very incompletely.

TABLE 4

	Cb_2O_5(%)	Cb:Ta
Silicate meteorites	0.000072	1.3
Meteoric irons	0.000029	3.5

The Cb contents of the meteorites are presented in Table 4 As may be seen, the amounts present are quite low.

The occurrence of Cb in mineral lattices has already been discussed. The main results are that Cb and Ta are mutually camouflaged in many minerals and that, in the mineral kingdom, Ti and Zr are the most powerful carriers of these elements. Both Cb and Ta are true satellites of Ti. As Cb is quite widely distributed in minerals, it may also be considered a quite mobile element.

By the study of the occurrence of Cb in different mineral groups and rocks the concentration of this element can be followed toward the end of magmatic crystallization. A fine example of the growing concentration of Cb with the proceeding differentiation is afforded by a series of analyses from Lapinlahti, Finland (Table 5).

During the exogeneous differentiation, a large proportion of Cb is accumulated in the hydrolysate sediments at a comparatively early stage. It may be pointed out that the average content of Cb_2O_5 in Baltic clays (0.003 per cent) is equal to the Cb average in granites. Some Cb, quite naturally, is always present in transported deposits, due to the hardness and resistance to chemical decomposition of the minerals in question. In hydrolysates the highest Cb contents are found in bauxites and laterites.

Another part of Cb is present in sea water, perhaps as a soluble alkali columbate, as is seen by its presence in marine carbonate sediments and in anhydrite. Cb is finally deposited in the deep sea sediments, the manganese nodules being especially rich in this element. This is one minor phase in the universal depoisoning of ocean water.

TABLE 5

Lapinlahti rocks	Cb_2O_5(%)
Bytownite rock	0
Hornblendite	0
Olivine gabbro	0.000008
Bytownite gabbro	0.00009
Gabbro	0.0007

The presence of Cb in certain biological substances seems to point to the possibility that this element might be able to form organometallic compounds.

All collected evidence of the general geochemical character of Cb emphasizes the purely lithophile character of this element. In addition, it belongs to the group which, on a previous occasion, has been named "granitophile" (*9*).

The average Cb content in igneous rocks is given in Table 6, together with the corresponding Ta values and the Cb:Ta ratio. The value for Cb is in close agreement with a previous average (0.002 per cent) given by Goldschmidt (*3*).

A few words may be added on the concentration of Cb in mineral deposits of economic importance. Nigeria is the most important present-day source of columbite high in Cb. This element has received considerably more attention since 1936, because of the demand of the stainless and alloy steel industries for columbite free from Ta.

TABLE 6

Cb_2O_5(%)	0.0034
Cb (%)	0.0024
Ta_2O_5(%)	0.00026
Ta(%)	0.00021
Cb:Ta	11.4

The study of the regional geochemistry of Cb reveals the concentration of this element in some local and areal centra, while other regions and geological units are known which are nearly or completely devoid of this element. In this respect the behavior of Cb is similar to that of Ta. The occurrence of Cb in the Pre-Cambrian granite groups of Finland offers results of considerable interest. There is, as in the case of Ta, a secular increase in the amount of Cb toward the geologically younger granites. However, the Post-Archean rapakivi granites form a break in this rule: they form a coherent group, independent by their geological occurrence and by their petrological, chemical, and geochemical properties.

The geochemical comparison between Cb and Ta manifests that Cb is the more common and more abundant of the two. With the use of the abundance number of Cb in igneous rocks, one can approach the question of whether or not this element follows the rule of Oddo and Harkins, according to which the elements with odd atomic number are more rare than their neighboring elements which flank them in the Periodic Table. Thus, we should expect that Cb is less abundant than Zr and Mo. The abundances of these three elements, expressed in grams per metric ton, are: Zr, 220; Cb, 24; Mo, 15. Cb most certainly does not follow the rule, but the cause of this deviation may probably be found in the too small value of Mo.

It may be stated, as a general rule, that Cb and Ta commonly occur together, and that minerals and rocks relatively high in one are also usually high in the other. Thus, these elements form a quite coherent pair, as can be expected from the similarity of their ionic radii (Cb^{5+}, 0.69A.; Ta^{5+}, 0.68A.), this being due to the lanthanide contraction, further, from the similarity of their ionic charges and of their ionic types. There is also a marked chemical similarity between these two elements. It could thus be expected that no pronounced separation between them would take place in Nature.

However, this pair is not too coherent, and it is inferior to the rare earths or to the pair Zr-Hf, as is shown by the fact that its component elements are quite often actually separated in Nature. It is even possible to find a geological unit, or area, where, in some minerals at least, the normally less abundant of these two elements predominates. Compared with the pair Zr-Hf, it is noted that geochemical camouflage is in no other case more pronounced than that of Hf by Zr. In conclusion, while easily capable of separating Cb and Ta, Nature is unable to separate Hf from Zr with her methods of analysis. This fact is reflected also in certain chemical features of these elements: no method of everyday chemical analysis is known which is suited for the determination of Hf in the presence of Zr, the separation of Hf from Zr being unexampled in difficulty. Cb and Ta, on the other hand, can be comparatively easily separated from each other by Marignac's method, and routine determinations of these elements by the ordinary methods of chemical analysis are carried out in many laboratories.

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Sensitivity of Grasses and Some Crop Plants to Isopropyl-N-Phenyl Carbamate

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It has been reported that some urethanes injure or kill grass plants when applied to soil in which the plants are growing (*1*, *2*). Greenhouse experiments were undertaken in October 1946 to study the sensitivity of various grasses to isopropyl-n-phenyl carbamate (IPC) and to compare their sensitivity to this compound with that of some dicotyledonous plants.

Seeds of grasses and dicotyledonous plants were sown in fertile potting soil to which known amounts of IPC were added.[1] In some experiments the carbamate was first mixed with a small amount of quartz sand, and this mixture was then added to soil and the seeds planted. In other experiments the carbamate-sand mixture was spread evenly on the surface of the soil after it had been potted and the seeds planted. The amount of sand used was 10 grams/pound of soil.

The IPC affected the growth of grass seedlings in varying degrees, depending on the method of application. When applied to the surface of soil at a rate equivalent to 2 pounds/acre (calculated on an area basis), IPC prevented the emergence of quack grass seedlings,[2] while 91 per cent of the seeds planted in comparable untreated soil emerged and grew vigorously. When the same amount of carbamate was worked into the upper 1 inch of soil, the treatment was less effective since 18 per cent of the quack grass seedlings emerged and grew vigorously. IPC applied at a rate equivalent to 2 pounds/acre and cultivated into soil to a depth of approximately 4 inches was even less effective in inhibiting the emergence of the seedlings.

TABLE 1

Emergence of Bluegrass and Crab Grass Seedlings*

Mg. IPC/ pound of soil	Bluegrass†		Crab grass	
	A	B	A	B
0.0	80	57	29	18
3.4	5	3	30	27
10.2	11	0	31	21
20.4	8	0	39	22
40.8	3	0	40	25

*Values represent average percentages of emergence in successive experiments, A and B. Four replications of each treatment (4 × 50 seeds) were used for each experiment.

†Although some bluegrass plants emerged in treated soil, they failed to grow more than ½ inch above the surface.

Differences in the sensitivity of grasses to IPC became apparent when crabgrass and bluegrass seeds were planted in soil containing known amounts of the chemical. Emergence of bluegrass seedlings was greatly reduced in soil that contained as little as 3.4 mg. of IPC/pound, while the emergence percentage for crab grass (*Digitaria sanguinalis*) increased with the addition of IPC to the soil (Table 1). Toole (*3*) has reported that the germination percentage for crab grass (*D. ischaemum*) was in-

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[1] Compound furnished by J. T. Baker Chemical Company, Phillipsburg, New Jersey.

[2] Quack grass seeds furnished by O. M. Scott & Sons Company, Marysville, Ohio.