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GEOCHEMICAL ASSOCIATION OF
NIOBIUM (COLUMBIUM) AND TITANIUM
AND ITS GEOLOGICAL AND
ECONOMIC SIGNIFICANCE

By Michael Fleischer, K. J. Murata, Janet D. Fletcher, and Perry F. Narten

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ABSTRACT

Niobium in rocks occurs in highest concentrations in granitic pegmatites and in alkalic rocks such as the nepheline syenites. It occurs commonly as a substituent in titanium minerals. Weathering of alkalic rocks produces bauxite enriched in niobium. Analyses show bauxite from Arkansas to contain an average of 0.05 percent Nb. The niobium present in the Arkansas bauxite processed annually is equal in amount to about 80 percent of that imported annually by the United States. Fractionation of black sand from Arkansas bauxite shows the niobium to be concentrated chiefly in an ilmenite fraction containing more than 40 percent TiO_2 and as much as 0.86 percent Nb.

Analyses of titanium minerals from many sources show the presence of niobium, the amount present varying with the type of rock in which the minerals occur. Minerals from alkalic rocks and from granitic pegmatites are highest in niobium content.

Metallurgical research is needed, especially on the possibility of recovering niobium and titanium from chlorination processes.

INTRODUCTION

Niobium (columbium) has recently become important in the manufacture of certain high-temperature and non-creep steels. The United States imported

more than 1-1/2 million pounds of niobium ore (concentrates) in 1949 (Clark, 1951);¹ domestic production was very small. The world production has come from granitic pegmatites and as a byproduct of the recovery of cassiterite from placers derived from granitic rocks.

Early in 1951 the Geological Survey undertook a search for new sources of niobium. Fortunately the general pattern of the geochemical behavior of niobium was fairly well known from an earlier summary of the literature (Fleischer and Harder, 1945) and from the comprehensive researches of Rankama (1948). From these it was possible to select for further study several types of material in which niobium might be present in concentrations sufficient to make them of interest as source materials.

Those selected as the most promising types of material were (1) alkalic rocks, especially nepheline syenites; (2) bauxites derived from alkalic rocks; (3) titanium minerals and ores; (4) zirconium minerals and ores; (5) tungsten minerals and ores; and (6) tin minerals and ores. The present report is a preliminary account of work on the first three. Niobium has been found in concentrations sufficiently high to justify research on the metallurgical processes for its separation and recovery. The search for new sources of niobium will be continued, and it is hoped that this report will stimulate others to begin the required metallurgical research.

¹See Literature cited

ACKNOWLEDGMENTS

We are indebted to our colleagues M. K. Carron, J. I. Dinnin, and Leonard Shapiro, who made chemical analyses; Elizabeth L. Hufschmidt, J. C. Rabbitt, and H. J. Rose, Jr., who made spectrographic analyses; and Jewell J. Glass and Marie L. Lindberg, who made mineralogical separations. R. P. Bryson, E. P. Kaiser, J. J. Norton, and W. T. Pecora, of the Geological Survey, contributed advice as to the selection of samples for analysis.

Samples for analysis were contributed by the following companies, who kindly granted permission to publish the results obtained. Alcoa Mining Co., American Cyanamid Co., Dulin Bauxite Co., Consolidated Chemical Industries, Dulin Bauxite Co., E. I. du Pont de Nemours Co., The Glidden Co., National Lead Co., New Jersey Zinc Co., and Ventures, Ltd.

CENERAL GEOCHEMICAL CONSIDERATIONS

Niobium is a chemical element with atomic number 41 and atomic weight 92.91. It belongs to the fifth group of the periodic table and is quinquevalent in most of its compounds. Niobium is a rare element; Rankama (1948, pp. 48-52) estimates its abundance in igneous rocks to be 0.0024 percent, which would make it about thirty-first in abundance of the elements.

The empirical ionic radius of niobium is given as 0.69A. (Ahrens, 1952), not very different from those of magnesium (0.66A.) and ferrous iron (0.74A.). The valence of niobium, however, is so much higher that one would expect that magnesium and iron minerals formed in the early stages of magmatic crystallization would not contain much niobium. This expectation has been verified experimentally. As crystallization of igneous rocks proceeds, niobium is preferentially concentrated in the residual magma as shown by Goldschmidt (1937) and by Rankama (1948). According to Rankama, the igneous rocks of highest niobium content are the granites (0.0021 percent), the syenites (0.0035 percent), and the nepheline syenites (0.031 percent). Of all igneous rocks, therefore, the nepheline syenites and similar alkalic rocks contain more than 10 times the concentration of other rocks and appear to be the most promising for further study.

Goldschmidt (1937, p. 667) points out that niobium would be expected, considering its ionic potential, to be concentrated during weathering processes; he states that for bauxite the factor of concentration is 4 to 5 as compared with the parent rock. Because the nepheline syenites are rocks high in niobium, bauxites derived from them should be particularly rich in niobium. This has now been tested and verified in the laboratory of the Geological Survey and a summary of the results on Arkansas bauxites has been published in a recent paper (Gordon and Murata, 1952). The study is being pursued further, particularly to learn the mode of occurrence of the niobium and its distribution in the bauxite district and among the minerals of the bauxite.

One would expect that niobium would occur as a substituent for elements of high valence having ionic radii close to 0.60A. These include quinquevalent

Ta (0.68A.), quadrivalent Ti (0.68A.), Zr (0.79A.), Sn (0.71A.), and Mo (0.62A.), and hexavalent W (0.62A.). This is confirmed by experimental data except for molybdenum. The very close association of niobium and tantalum is well known. Rankama (1948, pp. 48-52) points out that these elements are separable in nature and that the Nb:Ta ratio, which averages 11.4, is very much higher (384) in nepheline syenites. The association of niobium with titanium has been shown by the work of Hevesy, Alexander, and Würlstin (1929), Kunitz (1936), Borowsky and Blochin (1937), Panteleleev (1938), and Rankama (1948). The niobium content of titanium minerals, with particular attention to their geological environment, is also under investigation in the Geological Survey laboratories. A summary of the results up to now, including data from the literature, is given below. Studies of the association of niobium with tungsten, tin, zirconium, and molybdenum will be reported later.

METHOD OF SPECTROGRAPHIC ANALYSIS

The spectrographic analyses were made under the following conditions:

Excitation: 220-volt ballasted d-c arc, run at 15.5 a. Arc gap maintained at 3.5 mm throughout the burning period. Arc image focussed on the slit at 5.5 magnification, and light from the central 2 mm part allowed to enter the spectrograph.

Spectrograph: Wadsworth-mounting type of grating spectrograph with dispersion of 5A/mm in the first order.

Wavelength range covered: 2,230 - 4,730A in the first order. Such a wide range is unnecessary for analyses solely for Nb, but was recorded so that the spectrograms would be available for future study of other elements.

Electrodes: High-purity graphite rods, 1/4 in. diameter, with thin-walled cavity as described by Myers (1951); used as the anode.

Plate: Eastman III-O, developed at 20°C for 5 min in DK-50 developer.

Plate calibration: Method of Dieke and Crosswhite (1943). Iron lines present in spectra of a quartz-microcline mixture containing 1 percent Fe₂O₃ (matrix of comparison standards) were used.

Microphotometer: Projection comparator-microphotometer employing a scanning slit at the plate.

Nb lines used: 3163.40 and 3194.98A. Limit of detection, 0.01 percent in the samples as analyzed.

Analytical curves were established by means of a set of standards containing known concentrations of Nb₂O₅ and Ta₂O₅ (high-purity oxides) in a matrix consisting of 60 parts of quartz, 40 parts of microcline, and 1 part of Fe₂O₃, 25-mg portions being arced to

completion. The standards were made by successive dilutions to contain 1.00, 0.464, 0.215, 0.100, 0.0464, 0.0215 0.00100 percent Nb and Ta. No internal standard was used. The quartz-feldspar-iron oxide matrix will hereafter be referred to as the pegmatite base.

All rocks and minerals were first crushed, quartered, and ground in agate mortars to pass 150-mesh silk bolting cloth. Bauxites and clays were then ignited at 900°C and the loss in weight noted so that the final percentage of Nb could be calculated to the original, unignited state.

In order to analyze materials of greatly different chemical composition by means of the pegmatite-base standards, the samples were further treated in such a way as to make their composition more nearly that of the standards. Igneous rocks were mixed with one-half their weight of pure quartz. All other materials were mixed with an equal weight of a powder composed of 95 percent quartz and 5 percent Na₂CO₃.

The prepared samples were then analyzed by arcing to completion duplicate 25-mg portions. All samples showing 0.05 percent or more of Nb were next diluted with sufficient pegmatite base so that their reanalysis would be done at a concentration level of about 0.015 percent Nb. This practice resulted in greater accuracy for samples high in Nb because these (in the diluted state) closely approached the comparison standards in composition. As a test of the reproducibility of the method, a number of samples were analyzed in duplicate on several plates on different days. Considering the mean of the duplicate on each plate as a determination, the results were within \pm 10 percent of the average of all determinations.

To date, only a few samples have been analyzed chemically, and we are indebted to J. I. Dinnin and M. K. Carron, of the Geological Survey, for the chemical results tabulated below.

	Percent Nb	
	Spectrographic	Chemical
Bauxite-----	0.053	0.05
Bauxite-----	.050	.03
Brookite-----	2.4	2.7
Wolframite-----	1.3	1.2
Lepidolite-----	1.1	1.2

EXPERIMENTAL RESULTS

Niobium in igneous rocks

The average content of niobium in various types of igneous rocks was determined by Rankama (1948) by the analysis of 78 samples with the following results:

	Percent Nb (average)
Anorthosites and dunites-----	0.00003
Diorites-----	.0004
Eclogites-----	.0004
Basic alkaline rocks-----	.0014
Ultrabasic rocks-----	.0016
Gabbros-----	.0019
Granites-----	.0021
Syenites-----	.0035
Nepheline syenites-----	.031

Our studies have confirmed the relatively high niobium content of nepheline syenites and related rocks and have shown that high niobium content is particularly characteristic of those alkaline rocks with which are associated the remarkable masses of crystalline CaCO₃ generally referred to as "carbonatites." As further study of these rocks, particularly of the mode of occurrence of the niobium in them, is under way, we shall reserve detailed discussion and merely present the data available on all rocks that have been reported to contain as much as 0.01 percent Nb. These data are assembled in table 1. Nearly all the 52 rocks listed are nepheline syenites or related rocks, with only a few rocks of granitic composition and a few mafic rocks that are associated with alkaline rocks. No quantitative data are yet available on the distribution of niobium among the minerals of these rocks, although it is known that the niobium is largely concentrated in such titanium minerals as rutile, ilmenite, perovskite, and sphene. Analyses of these minerals separated from the above-mentioned or from similar rocks are listed in table 8 and are discussed below under the heading "Niobium content of titanium minerals." Part of the niobium in some of these rocks is present in zirconium minerals such as zircon, eudialyte, and catapleilite, and part is in some rocks as the niobium minerals pyrochlore (alkaline rocks) and columbite or microlite (granitic rocks).

Niobium in bauxites

We have extended the work of Gordon and Murata (1952), whose analyses of 14 bauxites and bauxitic clays from Arkansas showed a minimum content of 0.02 percent Nb, a maximum content of 0.1 percent Nb, and an average content of 0.05 percent Nb. Table 2 lists these analyses and those of 32 additional samples which confirm the earlier results. Further work is in progress to determine how the niobium content varies in different parts and types of bauxite deposits in Arkansas and to determine the distribution of niobium among the minerals of the bauxite.

Analyses have also been made by the Geological Survey of many samples of bauxite derived from rocks other than alkaline rocks, including material derived from basaltic rocks, gneisses, and limestones. These samples have much lower contents of niobium; none was found that contained as much as 0.01 percent Nb. The samples include 5 lateritic bauxites from Oregon, collected by J. W. Hosterman; 28 high-alumina clays from Idaho and Washington, collected by I. G. Sohn and J. W. Hosterman; 3 bauxites from Surinam, Dutch Guiana, kindly furnished by Aluminum Co. of America and American Cyanamid Co.; and 1 bauxite from Berbice, British Guiana, kindly furnished by American Cyanamid Co. Rankama (1948) reports 0.004 percent Nb in bauxites from Melegessbanya, near Gant, Hungary, and from Rock Run, Ala. It is of interest to note (table 3) that samples of red mud from treatment of Surinam and Jamaica bauxites both contained 0.02 percent Nb, which suggests that these bauxites contain some thousandths of a percent of Nb.

We hope to analyze bauxites which are from localities, other than Arkansas, where the bauxite

Table 1.--Niobium content of rocks reported to contain 0.01 percent or more Nb

	Locality	Number of samples	Percent Nb	Type of rock	Collector	Analyst
1	Arkansas: Pulaski and Saline Counties.	9	0.016-0.035	Nepheline syenite----	M. Gordon, R. P. Bryson.	K. J. Murata, H. J. Rose, Jr.
2	Arkansas, Saline County-----	1	.04	Tinguaite dike-----	W. T. Holser----	K. J. Murata.
3	Arkansas, Magnet Cove-----	5	.02-.06	Alkalic rocks-----	W. T. Pecora----	K. J. Murata, H. J. Rose, Jr.
4	Arkansas, Potash Sulfur Springs.	6	{ .05, .15, .27 1.6, 2.7, 3.0	----do-----	{ W. T. Pecora, E. Ingerson.	J. D. Fletcher, K. J. Murata.
5	Colorado, Iron Hill-----	11		Altered alkalic rocks--		J. D. Fletcher.
6	Idaho, Lemhi County-----	2	.01, .03	Alkalic rocks-----	V. R. Wilmarth---	H. J. Rose, Jr.
7	New Hampshire, Bartlett-----	1	.02	Granite pegmatite-----	W. A. Roberts---	K. J. Murata.
8	New Jersey, Beemerville-----	1	.01	Granite-----	W. T. Holser----	Do.
9	New Mexico, Wind Mountains---	1	.02	Nepheline syenite-----	----do-----	Do.
10	----do-----	1	.34	----do-----	----do-----	Do.
11	New Mexico, Black Mountains---	1	.03	Eudialyte syenite-----	----do-----	Do.
12	New Mexico, Jemez Mountains---	2	.01	Nepheline syenite-----	----do-----	Do.
13	Texas, Sierra Diablo-----	4	.05-.2	Rhyolites-----	C. S. Ross-----	Do.
14	Greenland, Julienahaab dist.--	2	a.32, .21	Alkalic rocks-----	A. Slaughter----	J. C. Rabbitt.
15	Sweden, Gellaberg, Skåne-----	1	.017	Nepheline syenite-----	-----	Ussing (1912).
16	Germany, Hammer-----	1	.02	Feldspar basalt-----	-----	Rankama (1948).
17	Portugal, Serrade Monchique---	1	.04	Phonolite-----	-----	Do.
18	U.S.S.R., Mariupol dist.-----	7	.02-.08	Nepheline syenite-----	-----	Rankama (1948).
19	U.S.S.R., Kola Peninsula-----	1	.11	----do-----	-----	Morozewicz (1930).
				Titanomagnetite olivinite.	-----	Rankama (1948).

^aThe accuracy of these old chemical analyses is questionable.

Table 2.--Niobium content of Arkansas bauxite

Sample no.	Percent Nb	Collector	Analyst
1	0.02	M. Gordon-----	K. J. Murata.
2	.04	-----do-----	Do.
3	.050	-----do-----	Do.
4	.06	-----do-----	Do.
5	.03	-----do-----	Do.
6	.02	-----do-----	Do.
7	.04	-----do-----	Do.
8	.053	-----do-----	Do.
9	.07	-----do-----	Do.
10	.04	-----do-----	Do.
11	.1	-----do-----	Do.
12	.02	W. R. Griffiths-----	Do.
13	.02	R. P. Bryson ---	Do.
14	.08	J. I. Tracey, Jr.-----	Do.
15	.085	M. Gordon---	Do.
16	.028	-----do-----	Do.
17	.048	-----do-----	Do.
18	.033	-----do-----	Do.
19	.04	Alcoa, Hurricane Creek-----	Do.
20	.051	} Reynolds Metal Co., Hurricane Creek.	J. D. Fletcher.
21	.047		Do.
22	.045		Do.
23	.051		Do.
24	.051		Do.
25	.049		Do.
26	.05	R. P. Bryson-----	K. J. Murata.
27	.055		H. J. Rose and E. H Hufschmidt.
28	.036	-----do-----	Do.
29	.03	-----do-----	Do.
30	.03	-----do-----	Do.
31	.04	-----do-----	Do.
32	.082	-----do-----	Do.
33	.050	-----do-----	Do.
34	.03	-----do-----	Do.
35	.04	-----do-----	Do.
36	.02	-----do-----	Do.
37	.02	-----do-----	Do.
38	.02	-----do-----	Do.
39	.034	-----do-----	Do.
40	.043	-----do-----	Do.
41	.054	-----do-----	Do.
42	.057	-----do-----	H. J. Rose and E. H Hufschmidt.
43	.057	-----do-----	Do.
44	.034	-----do-----	Do.
45	.067	-----do-----	Do.
46	.050	-----do-----	Do.
Average, 46 samples-----			0.045
Average, 39 individual samples-----			.044
Average, 7 composite samples (nos. 20-25, 46)-----			.049

Descriptions of samples:

1. Dark reddish-brown to black bauxite pebbles filling channels in the lower bauxite bed in the Fletcher mine of Reynolds Mining Corp. in the $W\frac{1}{2}SE\frac{1}{4}SW\frac{1}{4}$ sec. 11, T. 2 S., R. 14 W., Saline County.
2. Oxidized ferruginous granitic-textured bauxite from a weathered outcrop in the Pruden mine, Alcoa Mining Co., $NE\frac{1}{4}SW\frac{1}{4}$ sec. 16, T. 2 S., R. 14 W., Saline County.
3. Red bauxite with black pisolites ("birds-eye ore") from mining face in the west part of the Section 16 mine, Alcoa Mining Co., $SE\frac{1}{4}SW\frac{1}{4}$ sec. 16, T. 2 S., R. 14 W., Saline County.
4. Granitic-textured bauxite ("sponge ore") block from along company road in Middle Maud mine, Alcoa Mining Co., in $SW\frac{1}{4}SE\frac{1}{4}$ sec. 22, T. 2 S., R. 14 W., Saline County.
5. Poorly pisolitic bauxite containing fine siderite, from U. S. Bur. Mines drill hole 3-019, depth 267 feet, South Ironton deposit, W.A. Dreher property, in the $NW\frac{1}{4}SE\frac{1}{4}$ sec. 14, T. 1 S., R. 12 W., near Ironton, Pulaski County.

Descriptions of samples, table 2--Continued

6. Pisolitic bauxite hardcap with fluid pisolites from U. S. Bur. Mines drill hole 6-127B, depth 278 feet, Bates deposit, in the NW $\frac{1}{4}$ NE $\frac{1}{4}$ sec. 21, T. 1 S., R. 12 W., Pulaski County.
7. Pisolitic bauxite cut by a vein of crystalline siderite in U. S. Bur. Mines drill hole 16-048, depth 455.2 feet, in the East Bauxite deposit, International Paper Co. property, in the SE $\frac{1}{4}$ sec. 31, T. 2 S., R. 13 W., Saline County.
8. Poorly pisolitic bauxite containing siderite and chlorite, from U. S. Bur. Mines drill hole 16-052, depth 473.0 to 473.1 feet, East Bauxite deposit, International Paper Co. property, SE $\frac{1}{4}$ sec. 31, T. 2 S., R. 14 W., Saline County.
9. Poorly pisolitic siliceous bauxite from U. S. Bur. Mines drill hole 16-052, depth 451.9 to 452.2 feet.
10. Tannish-gray bauxitic underclay from U. S. Bur. Mines drill hole 16-052, depth 480.5 to 480.6 feet.
11. Fragmental kaolinitic underclay from U. S. Bur. Mines drill hole 16-052, depth 488 feet.
12. Type III bauxite deposit. Transported pebbly bauxite with gibbsitic to kaolinitic matrix, from east face of the Harley pit mine of Dulin Bauxite Co., SE $\frac{1}{4}$ SE $\frac{1}{4}$ sec. 24, T. 1 N., R. 12 W., Pulaski County.
13. Type III bauxite deposit. Cross-bedded bauxite from ore body in Reichart shaft mine, NW $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 2, T. 1 S., R. 12 W., Pulaski County.
14. Type IV bauxite deposit. Transported light-tan bauxite rubble, at or near top of upper bauxite bed, near middle of west wall of the Midwest Pit mine of Midwest Mines Co. in the E $\frac{1}{2}$ NE $\frac{1}{4}$ NE $\frac{1}{4}$ sec. 24, T. 2 S., R. 14 W., Saline County.
15. Harris deposits near Bryant.
16. Ratcliffe mine, Pulaski County.
17. Stuckey pit at Bauxite.
18. Section 26 mine near Bauxite.
19. Hurricane Creek plant.
20. Reynolds. Month-end composite, July, August, September 1947.
21. Reynolds. Month-end composite, June, July, August 1948.
22. Reynolds. Month-end October 1949.
23. Reynolds. Month-end April 1950.
24. Reynolds. Month-end April 1951.
25. Reynolds. Month-end November 1951.
26. Reynolds. Bauxite from Hurricane Creek plant.
27. Bauxitic clay (from Consolidated Chemical Industries plant stockpile), Bierman mine, Pulaski County.
28. Bauxite (from plant stockpile), Bierman mine.
29. Bauxite. Monthly composite, Berry-Mayhan mine; SW $\frac{1}{4}$ NE $\frac{1}{4}$ sec. 2, T. 1 S., R. 12 W., Pulaski County. American Cyanamid Co., Berger Plant.
30. Bauxite, low-iron type (raw composite) Dan Rauch mine, SE $\frac{1}{4}$ NE $\frac{1}{4}$ sec. 9, T. 1 S., R. 12 W., Pulaski County. American Cyanamid Co.
31. Bauxite, calcined product from blend of bauxite, Dixie mine, SW $\frac{1}{4}$ SW $\frac{1}{4}$ sec. 36, T. 1 N., R. 12 W., Pulaski County, and BC-400 mine, SE $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 31, T. 2 S., R. 13 W., Saline County. Dulin Bauxite Co.
32. Bauxite, high organic content typical; part granitic and part pisolitic. Bertha Extn. mine, SE $\frac{1}{4}$ sec. 27, T. 2 S., R. 14 W., Saline County. Alcoa Mining Co.
33. Bauxite, granitic, grab sample from conveyor belt. Nielson Underground mine, NW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 26, T. 2 S., R. 14 W., Saline County. Alcoa Mining Co.
34. Bauxite, grab sample by shaft, BC-400 mine, SE $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 31, T. 2 S., R. 13 W., Saline County. Dulin Bauxite Co.
35. Bauxite(?) from thin bed in Wilcox formation (core sample), middle of sec. 28, T. 2 S., R. 14 W., Saline County. Alcoa Mining Co.
36. Bauxite, auger drill sample, upper 6 feet; Lewis mine, NW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 9, T. 1 S., R. 12 W., Pulaski County. American Cyanamid Co.
37. Bauxite, auger drill sample, 6 to 12 feet; Lewis mine, NW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 9, T. 1 S., R. 12 W., Pulaski County. American Cyanamid Co.
38. Bauxite, auger drill sample, 12 to 18 feet; Lewis mine, NW $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 9, T. 1 S., R. 12 W., Pulaski County. American Cyanamid Co.
39. Bauxite, daily mine production. Harris mine, NE $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 36, T. 1 S., R. 14 W., Saline County. Reynolds Mining Co. 12-13-51.
40. Bauxite, daily mine production. Harris mine, NE $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 36, T. 1 S., R. 14 W., Saline County. Reynolds Mining Co. 12-14-51.
41. Bauxite, daily mine production. Harris mine, NE $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 36, T. 1 S., R. 14 W., Saline County. Reynolds Mining Co. 12-19-51.
42. Bauxite, daily mine production. Harris mine, NE $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 36, T. 1 S., R. 14 W., Saline County. Reynolds Mining Co. 12-30-51.
43. Bauxite, daily mine production. Harris mine, NE $\frac{1}{4}$ NW $\frac{1}{4}$ sec. 36, T. 1 S., R. 14 W., Saline County. Reynolds Mining Co. 12-31-51.
44. Bauxite, daily mine production (12-31-51), Bray mine, sec. 35, T. 1 S., R. 14 W., Saline County. Reynolds Mining Co.
45. Bauxitic clay, one-day withdrawal (12-19-51). Elrod-Harris low-grade pile, sec. 35, T. 1 S., R. 14 W., Saline County, Reynolds Mining Co.
46. Bauxite. Monthly composite for January, 1952, metal-grade shipments by Alcoa from Arkansas.

has been derived from alkalic rocks and which may therefore be expected to be high in niobium content. Among such localities are the following:

Poços da Caldas, Minas Gerais, Brazil.
Ile de Los, French Guinea, French West Africa.
Gold Coast, western Africa.

Niobium in byproducts of bauxite plants

As stated previously, no data are yet available as to the distribution of niobium among the minerals present in bauxite. However, it is highly improbable from geochemical considerations that it is present in high concentrations as a substituent in the aluminum oxide hydrates or ferric oxide hydrates that constitute the bulk of bauxite ore. Rather, niobium would be expected to be present in solid solution in the titanium and zirconium minerals. If this is correct, it might reasonably be expected that niobium could be concentrated in some stage of the chemical processing of bauxite ore.

In brief, the treatment of bauxite, as carried out at the Hurricane Creek, Ark. plant of the Reynolds Metal Co., is as follows: The bauxite is digested in hot sodium hydroxide solution. The insoluble material is separated from it as coarse material ("black sand") and fine material ("red mud"). From the solution, $Al_2O_3 \cdot 3H_2O$ is crystallized, leaving "spent liquor." The black sand is discharged into a special tailings pond. The red mud is mixed with $CaCO_3$ plus Na_2CO_3 and sintered, after which it is leached to recover more alumina. The leached residue ("brown mud") is discharged into a tailings pond.

By analyzing samples obtained through the courtesy of Mr. W. W. Binford, superintendent of the Hurricane Creek plant of the Reynolds Metal Co., we have been able to follow the course of the niobium during the process. The analytical data are given

in table 3; they show that niobium is concentrated in the material that is insoluble in NaOH solution.

The brown mud, although its niobium content is slightly higher than that of the black sand, is not a very attractive material on which to attempt further concentration because the material is so fine-grained. Work so far has therefore been confined to the black sand. A study by the U. S. Bureau of Mines (Calhoun, 1950) showed that titanium-rich and iron-rich concentrates could be prepared by tabling and by magnetic separation. The data on these concentrates are given in table 4. Through the courtesy of Mr. Binford, samples of these concentrates were obtained by the Geological Survey and analyses for niobium are given in table 4.

The titanium-rich concentrate was further purified in our laboratory by Miss Jewell J. Glass by means of magnetic and heavy-mineral separations. Data on the fractions obtained, given in table 5, show that the niobium content can be raised to over 0.8 percent. It is hoped that further work will permit the analysis of the individual pure minerals.

As a check, a black sand (No. 12 of table 3) was subjected to heavy-mineral and magnetic separations. The procedure was as follows: Approximately 300 grams was crushed to pass 80-mesh. The material passing 270-mesh was not investigated further. The portion passing 80-mesh and retained on 270-mesh was separated twice in methylene iodide (spgr 3.2). The heavy fraction was then divided into the following magnetic fractions: Magnetic to the hand magnet, magnetic at 0.1, 0.2, 0.3, and 0.5 amperes and nonmagnetic at 0.5 amperes at a slope of 20° towards the nonmagnetic side of a Franz Isodynamic Separator. The results, given in table 6, agree in general with those of tables 4 and 5.

Comparable products from the East St. Louis, Ill., plant of the Aluminum Company of America have not been studied. However, we have fractionated

Table 3.--Niobium content of products of treatment of Arkansas bauxite^a at the Hurricane Creek plant, Reynolds Metal Co.

No.	Product	Percent Nb	Analyst
1	$Al_2O_3 \cdot 3H_2O$ -----	<0.01	K. J. Murata
2	Calcined alumina-----	< .01	Do.
3	Spent liquor-----	< .01	Do.
4	Sinter filtrate-----	< .01	Do.
5	Red mud-----	.08	Do.
6	Brown mud-----	.07	Do.
7	-----do-----	.076	Do.
8	-----do-----	.069	Do.
9	-----do-----	.073	Do.
10	Sinter residue-----	.09	Do.
11	Black sand-----	.06	Do.
12	-----do-----	.064	H.J. Rose, Jr.
13	-----do-----	.062	Do.
14	-----do-----	.052	Do.
15	-----do-----	.048	Do.
16	-----do-----	.048	Do.
17	-----do-----	.052	Do.

^aSamples of red mud from treatment of Surinam and Jamaica bauxite each contained 0.02 percent Nb.

Table 4.--Analyses of titanium- and iron-rich concentrates from black sands from the Hurricane Creek plant, Reynolds Metal Co.

	Ti Concentrate ¹		Fe Concentrate ²		Ti Concentrate ¹		Fe Concentrate ²
	(a)	(b)			(a)	(b)	
TiO ₂ -----	41.2	39.9	8.0	CaO-----	0.6	---	0.5
Fe-----	20.1	19.9	46.5	Ignition loss--	2.2	---	12.2
Mn-----	8.9	---	---	Percent Nb----	³ 0.67	---	³ 0.032
Al ₂ O ₃ -----	9.4	---	8.9				
SiO ₂ -----	2.6	---	1.4				

a. After Calhoun (1950). Analysis by U. S. Bureau of Mines.

b. Leonard Shapiro, U. S. Geol. Survey, analyst.

¹This concentrate was 3.4 percent by weight of the black sand.

²This concentrate was 4.5 percent by weight of the black sand.

³H. J. Rose, Jr. and Janet D. Fletcher, U. S. Geol. Survey, analysts.

a black sand kindly furnished by Mr. Laurence Litchfield of Alcoa Mining Co. This was produced from an experimental Wilfley-table installation later discontinued (letter from Laurence Litchfield to M. Fleischer, January 21, 1952). Analyses on the fractions, given in table 7, show that the material is similar to the titanium-rich concentrate from the Hurricane Creek plant (table 5) except that it contains much siderite and little magnetite.

Niobium in titanium minerals

Although the geochemical association of niobium with titanium has long been recognized and many analyses of titanium minerals in the literature show appreciable niobium contents, little attention has been paid to the variation of niobium content with the type of rock in which the titanium minerals occur. Determinations of the niobium content of the common titanium minerals are assembled in table 8, omitting only the rarer silicates. Data on the latter are given by Fleischer and Harder (1945) and by Rankama (1948).

Many more analyses are needed on material of known paragenesis, but a few generalizations can be made from the data in table 8. It seems clear that minerals from alkaline rocks and from granitic pegmatites are highest in niobium and that those associated with anorthositic and gabbroic are lowest. This is shown best by the data for ilmenite. The largest masses of titanium-rich rocks, such as the huge ilmenite-magnetite deposits associated with the

anorthositic-gabbro of the Adirondacks and Quebec, are very low in niobium content; the ilmenite from the beach sands of Florida and India, presumably derived from crystalline rocks, have Nb contents ranging from 0.04 to 0.40 percent; and ilmenite from alkaline rocks is highest (up to 0.9 percent).

The few data available in table 8 indicate that when rutile and ilmenite occur together, rutile generally has the higher niobium content. Of the 35 rutile samples listed in table 8, 12 have Nb contents more than 1 percent. Most rutile, however, will probably be found to contain 0.05 to 0.3 percent Nb, with samples of higher Nb content found in granitic pegmatites and alkaline rocks.

The 20 perovskite analyses listed in table 8 include 13 or 14 from alkaline rocks. Those highest in niobium occur in carbonatites associated with alkaline rocks.

POSSIBILITY OF RECOVERY OF NIOBIUM FROM ARKANSAS BAUXITE AND FROM TITANIUM MINERALS

The data reported as the result of this work suggest the possibility that niobium may be obtained from three sources not now utilized:

1. As a byproduct from Arkansas bauxite.
2. From titanium minerals used in the manufacture of titanium metal.
3. From titanium minerals from alkaline rocks such as the carbonatites.

Table 5.--Analyses of fractions of titanium-rich concentrate referred to in table 4

[Separations by Jewell J. Glass]

	Percent of total	Percent Nb ^a	Percent TiO ₂ ^b
Original titanium-rich concentrate--	100	0.67	39.9
Fractions:			
Magnetite-----	12.4	.026	1.3
Calcite and quartz-----	10.5	(^c)	---
Ilmenite plus limonite-----	73.3	.79-.86	46-50
Mainly zircon, with some rutile, sphene, ilmenite.	3.8	.87	36
	100.0	---	---

^aSpectrographic analyses by Janet D. Fletcher.

^bChemical analyses by Leonard Shapiro.

^cNot determined.

Table 6.--Analyses of fractions of a black sand from bauxite

[Separations by Marie L. Lindberg; analyses by Janet D. Fletcher]

Material	Percent of total	Percent of -80, +270	Percent Nb
Original black sand-----	100	---	0.064
Minus 270-mesh-----	24.7	---	(1)
Float in methylene iodide-----	10.9	14.5	(1)
Sink in methylene iodide:			
Magnetic to hand magnetate-----	38.8	51.5	.025
0.1 amp.-----	6.7	8.9	.035
.2 amp.-----	4.4	5.8	.064
.3 amp.-----	12.0	15.9	.14
.5 amp.-----	2.1	2.8	.66
Nonmagnetic at 0.5 amp.-----	.4	.5	.45
	100.0	99.9	

¹Not determined.

Production of bauxite from Arkansas in 1949 was 1,094,924 long tons of dried bauxite equivalent (Mote and Kurtz, 1951). Assuming that the average

Table 7.--Analyses of fractions of black sand from Wilfley table (Alcoa)

[Separations by Marie L. Lindberg; analyses by K. J. Murata]

Material	Percent of sample	Percent Nb
Original black sand-----	100	---
Mainly siderite-----	55	0.06
About 90 percent ilmenite--	32	.57
Ilmenite with much limonite	3	.16
Zircon with some anatase and rutile.	10	.08

content of Nb is 0.05 percent, this corresponds to 547.5 long tons or 1.2 million pounds of niobium--80 percent of the amount imported by the United States in the same year.

The data in table 3 show that niobium is concentrated in the red and brown muds and in the black sands. The data of table 4 to 7 show the niobium to be concentrated in the titanium-rich fraction of the black sands; it is probable that this is also true of the red and brown muds. These might, however, contain more rutile and sphene and less ilmenite than the black sands, but quantitative data are lacking. The problem of obtaining niobium from Arkansas bauxite thus appears to be one of treating a concentrate containing approximately 40 to 50 percent TiO_2 and 0.5 to 0.9 percent Nb.

Most of the ilmenite processed in the United States is used in the manufacture of TiO_2 pigment. This involves solution of the ore in acid, followed by hydrolysis to precipitate titanium dioxide. It is probable that niobium accompanies the titanium in this precipitation and that its recovery would be very difficult. On the other hand, the production of titanium metal is increasing very rapidly. This process involves the chlorination of titanium-rich ore to form TiCl_4 . Since TiCl_4 boils at 136°C and NbCl_5 at 243°C , conditions are favorable for obtaining good separations, as recently demonstrated

on a laboratory scale by Atkinson, Steigman, and Hiskey (1952). Further research on the process is obviously needed, as well as a study of the economic factors.

Research is also needed on the possibility of using rutile, brookite, or perovskite, such as that obtained from alkaline rocks. As readily seen from the data in table 8, these minerals contain much higher Nb contents than the ilmenite concentrates from Arkansas bauxite, but they lack the advantage of known availability in large tonnages. The possibility of recovering niobium from perovskite-pyroxene in alkaline rocks has been discussed for the deposits of the Kola Peninsula, U. S. S. R. (Eliseev and Nefedov (1940), Gerasimovsky (1939, 1940); for the deposits of the Kaiserstuhl, Baden, Germany (Leibbrandt, 1948); and for the deposits of Tororol, Uganda (Hudson and Dunkin, 1951).

The Geological Survey is continuing its investigations of rutile, brookite, and perovskite at Magnet Cove, Ark., and of similar deposits elsewhere. It is to be hoped that metallurgical researches on the recovery of niobium from these titanium minerals will be carried out by other laboratories.

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Table 8.--Niobium content of titanium minerals

No.	Percent Nb	Locality	Type of occurrence	Analyst
Rutile (including the variety ilmenorutile) (TiO ₂)				
1	0.004	Italy, Trentino, Pfitschthal-----	-----	Rankama (1948).
2	.01	Norway, Søndeled-----	-----	Hevesy and others (1929).
3	.013	Arkansas, Magnet Cove-----	Nepheline syenite-----	Do.
4	.015	Finland, Tipasjarri-----	-----	Rankama (1948).
5	.02	Norway, Kragerø-----	Gabbro-----	Hevesy and others (1929).
6	.04	Virginia, Roseland-----	Anorthosite-----	H. J. Rose, Jr.
7	.04	U. S. S. R., Sugamak-----	-----	Rankama (1948).
8	.043	Norway, Bamle-----	Gabbro-----	Do.
9	.05	Vermont, Hartford-----	-----	Hevesy and others (1929).
10	.068	Australia, Blumberg-----	-----	Rankama (1948).
11	.07	Norway, Bamle-----	Gabbro-----	Do.
12	.084	U. S. S. R., Kasoi Brod-----	-----	Do.
13	.13	Finland, Liperinsalo-----	-----	Do.
14	.15	Switzerland, Kriegalp-----	-----	Hevesy and others (1929).
15	.18	Norway, Risør-----	Gabbro-----	Rankama (1948).
16	.18	Florida-----	Beach sand-----	J. D. Fletcher.
17	.19	Norway, Kragerø-----	Gabbro-----	Rankama (1948).
18	.20	Italy, Pfitschthal-----	-----	Hevesy and others (1929).
19	.20	Florida-----	Beach sand-----	J. D. Fletcher.
20	.21	Australia-----	-----do-----	Do.
21	.23	Brazil-----	Alluvial-----	Do.
22	.26	Florida-----	Beach sand-----	Do.
23	.28	Idaho, Clearwater-----	Placer-----	Do.
24	1.3	Arkansas, Magnet Cove-----	Carbonate veins in nepheline syenite---	Do.
25	2.0	Texas, Marfa-----	Tertiary silicified tuffs-----	Do.
26	4.3	South Dakota, Keystone-----	Granite pegmatite-----	Hess and Wells (1911).
27	4.8	Malaya, Kuala Kangsur dist.-----	Placer-----	Crook and Johnstone (1912).
28	6.0	W. Australia, Globe Hill-----	Granite pegmatite-----	Edwards (1940).
29	12.5	U. S. S. R., Ilmen Mountains-----	Alkalic rock-----	Chernik (1921).
30	15.2	-----do-----	-----do-----	Prior and Zambonini (1908).
31	16.3	Italy, Craveggia-----	Granite pegmatite-----	Do.
32	19.5	Brazil, Espírito Santo, Colatina-----	-----	Tavora and Scorza (1948).
33	20.9	British Guiana-----	Placer-----	Smith (1946).
34	22.5	Norway, Ireland-----	Granite pegmatite-----	Prior and Zambonini (1908).
35	23.3	W. Australia, Melville-----	-----do-----	Edwards (1940).
Brookite (TiO ₂)				
36	0.01	Switzerland, Riederstobel-----	Alpine cleft-----	Hevesy and others (1929).
37	.023	U. S. S. R., Urals-----	Placer-----	Rankama (1948).
38	.38	Arkansas, Magnet Cove-----	Nepheline syenite-----	Do.
39	2.4	-----do-----	Altered novaculite-----	K.J.Murata and E.L. Hufschmidt.

Table 8.--Niobium content of titanium minerals--Continued

No.	Percent Nb	Locality	Type of occurrence	Analyst
Anatase (TiO ₂)				
40	0.032	Switzerland, Binnenthal-----	Alpine cleft-----	Rankama (1948).
41	.047	-----do-----	-----do-----	Do.
42	1.8	California, Cady Mountain-----	Granite pegmatite-----	K. J. Murata.
Perovskite (CaTiO ₃) (including the niobian variety dysanallyte and the cerian variety loparite)				
43	0.006	U. S. S. R., Urals, Achmatovsk-----	-----	Rankama (1948).
44	<.01	-----do-----	-----	Hevesy and others (1929).
45	.47	U. S. S. R., Kola Peninsula-----	Nepheline syenite-----	Rankama (1948).
46	3.1	Arkansas, Magnet Cove-----	-----do-----	Mar (1890).
47	3.3	-----do-----	-----do-----	Rankama (1948).
48	3.4	Germany, Kaiserstuhl-----	Carbonatite-----	Houser (1908).
49	5.1	Arkansas, Magnet Cove-----	-----do-----	H. J. Rose, Jr.
50	5.6	-----do-----	-----do-----	K. J. Murata.
51	5.6-6.8	U. S. S. R., Kola Peninsula (5 samples)---	Nepheline syenite-----	Bykova (1941).
52	11.3	Germany, Kaiserstuhl-----	Carbonatite-----	Meigen and Hugel (1913).
53	15.6	Ceylon, Prov. Uva-----	Limestone in placer-----	Chernik (1914).
54	18.2	Germany, Kaiserstuhl-----	Carbonatite-----	Meigen and Hugel (1913).
Ilmenite-magnetite ores				
55	0.0002	Finland, Attu Parainen-----	-----	Rankama (1948).
56	.006	Finland, Otanmaki-----	Amphibolite-----	Do.
57	<.01	New York, Lake Sanford (9 samples)-----	Anorthosite-gabbro-----	E. L. Hufschmidt.
58	<.01	Quebec, Allark Lake (2 samples) -----	-----do-----	Do.
59	<.01	Costa Rica-----	-----	Do.
60	.018	Norway, Hitterø-----	Granite pegmatite-----	Rankama (1948).
61	.039	U. S. S. R., Ilmen Mountains-----	Alkalic rocks-----	Do.
62	.18	U. S. S. R., Vuorikylä-----	-----	Do.
Ilmenite (FeTiO ₃)				
63	0.00002	Norway, Egersund-----	Anorthosite-----	Hevesy and others (1929).
64	.0002	South Africa-----	Gabbro?-----	Do.
65	.0003	U. S. S. R., Urals, Miask-----	Granite pegmatite?-----	Do.
66	.001	India-----	Placer-----	Do.
67	.005	Norway, Blaa fjeld-----	Anorthosite-----	Rankama (1948).
68	<.01	New York, Adirondacks (4 samples) -----	Anorthosite-gabbro-----	J. D. Fletcher.
69	<.01	Quebec, Baie St. Paul (5 samples) -----	-----do-----	Do.
70	<.01	North Carolina, Lenoir-----	Metamorphosed basic rocks-----	Do.
71	<.01	Virginia, Piney River-----	Anorthosite-----	Do.
72	<.01	Virginia, Roseland-----	-----	Do.
73	<.01	Norway (3 samples)-----	Anorthosite?-----	Do.

74	.01	Norway-----	Placer-----	Hevesy and others (1929).
75	.039	Florida-----	Beach sands-----	J. D. Fletcher.
76	.040	-----do-----	-----do-----	Do.
77	.05	Australia-----	-----do-----	Do.
78	.065	Florida-----	-----do-----	Do.
79	.07	-----do-----	-----do-----	Do.
80	.085	-----do-----	-----do-----	Do.
81	.09	Florida-----	-----do-----	Do.
82	.090	India, Quilon-----	-----do-----	Do.
83	.095	-----do-----	-----do-----	Do.
84	.10	Florida-----	-----do-----	Do.
85	.12	-----do-----	-----do-----	Do.
86	.14	India, Quilon-----	-----do-----	Do.
87	.18	U. S. S. R., Azov region-----	-Beach sands, derived from granite pegmatite.	Yurk and Bresser (1940).
88	.20	Florida-----	Beach sand-----	J. D. Fletcher.
89	.28	California, Tulare Co.-----	Granite pegmatite-----	Do.
90	.35	-----do-----	-----do-----	Borowsky and Blochin (1937).
91	.4	U. S. S. R., Mariupol-----	Nepheline syenite-----	Yurk and Bresser (1940).
92	.5	Uganda, Tororol-----	-----do-----	H. J. Rose, Jr.
93	.4-.9	U. S. S. R., Ilmen Mountains-----	-----do-----	Panteleev (1938).
94	.57-.86	Arkansas bauxite (4 samples)-----	Bauxite-----	J. D. Fletcher.

Sphene (CaTiSiO₅) (including keilhauite variety)

95	0.0001	Norway, Kragerø-----	-----do-----	Hevesy and others (1929).
96	.001	Switzerland, St. Gotthard-----	-----do-----	Do.
97	.001	Italy, Zillerthal-----	-----do-----	Do.
98	.002	Switzerland, Binnenthal-----	-----do-----	Do.
99	.002	Norway, Arendal-----	-----do-----	Do.
100	.011	Norway, Kragerø-----	-----do-----	Do.
101	.02	Norway, Søndeled-----	-----do-----	Do.
102	.02	U. S. S. R., Urals, Miask-----	Granite pegmatite-----	Sahama (1946).
103	.023	Norway, Arendal-----	-----do-----	Hevesy and others (1929).
104	.03	Switzerland, Binnenthal-----	-----do-----	Rankama (1948).
105	.03	Finland, Ylojarvi-----	-Gabbro-----	Sahama (1946).
106	.09	Canada, Eganville-----	-----do-----	Hevesy and others (1929).
107	.10	Canada, Pontiac Co.-----	-----do-----	Rankama (1948).
108	.13	Norway, Risør-----	Gabbro-----	Do.
109	.15	Finland, Iivaara-----	Nepheline syenite-----	Do.
110	.20	Sweden, Hajstorp-----	-----do-----	Do.
111	.20	Germany, Aschaffenburg-----	Nepheline syenite-----	Do.
112	.21	U. S. S. R., Transbaikalia, Sviatoy Noss--	-----do-----	Do.
113	.24	U. S. S. R., Kola Peninsula-----	Nepheline syenite-----	Sahama (1946).
114	.25	-----do-----	-----do-----	Rankama (1948).
115	.48	Finland, Parainen-----	Limestone-----	Sahama (1946).
116	.77	U. S. S. R., Kola Peninsula-----	Nepheline syenite-----	Do.
117	.84	Norway, Kragerø-----	-----do-----	Rankama (1948).
118	1.06	U. S. S. R., Kola Peninsula-----	Nepheline syenite-----	Sahama (1946).
119	1.12	U. S. S. R., Nuolainniemi, Core-----	Granite pegmatite-----	Do.
120	2.3	U. S. S. R., Nuolainniemi, Shell-----	-----do-----	Do.

