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SOME PROBLEMS OF CHEMICAL MINERALOGY*†

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INTRODUCTION

The retiring president of the Mineralogical Society is customarily called upon to deliver an address, and although no restrictions are laid upon him, it is generally expected that from the depths of his experience he will deliver words of wisdom to the assembled multitude on some phase of mineralogy in which he is well qualified. Having heard quite a few such addresses and now having gone through the experience of preparing one, I am in favor of the practice, mostly because I think it is extremely valuable to the retiring president to be forced in this way to reflect on what he has done and the relation of his accomplishment to the broad field of mineralogy.

It must admit that when I began to think of what to say here today I was rather perplexed. My work for the past eight years has been largely administrative, so that if this talk were to reflect my recent work, it would have to deal with subjects such as whether papers can be moved more efficiently from right to left or vice versa, and whether when planning a budget one should allow 5% or 10% as a safe contingency fund. This might have been instructive, but probably not interesting. It occurred to me that as an alternative, I might read to you some choice excerpts from letters received from persons whose descriptions of new minerals I have abstracted in the *American Mineralogist*. This would have been interesting, but probably not instructive.

Fortunately it has also been necessary for me as a member of Earl Ingerson's staff in the Geochemistry and Petrology Branch of the U. S. Geological Survey to do a good deal of thinking about the functions of a laboratory whose purpose is the application of chemical, spectrographic, mineralogical, x-ray, and petrographic techniques to the solution of geological problems. As one result of such thinking, I have accumulated over a period of years notes on research problems that seemed to me to be worthy of attention, and I propose to discuss some of these problems today. This talk might thus have been entitled "Some Problems I

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Hope I Have Time to Tackle Some Day." The point of view is primarily that of a chemist. Perhaps I should apologize for restricting myself to problems of chemical mineralogy—my excuse is not lack of appreciation of other phases of mineralogy, but merely my ignorance of them. I am afraid that I have the distinction of being the only President of this Society whose training was so concentrated in the field of chemistry that according to the requirements set forth by the U. S. Civil Service Commission, I am not eligible for appointment to the position even of junior mineralogist in the government service. So I shall speak as a chemist—perhaps we can say as a geochemist—about several problems that are not too closely related to one another except that all of them need attention by chemists.

STABILITY RELATIONS OF POLYMORPHS

The first such problem to be discussed is the problem of the stability relations and the conditions of formation of polymorphous substances. These substances are familiar to all mineralogists; a few of the best-

TABLE 1. SOME POLYMORPHOUS NATURALLY OCCURRING SUBSTANCES

ZnS	Sphalerite—Wurtzite
HgS	Cinnabar—Metacinnabar
FeS ₂	Pyrite—Marcasite
Fe ₂ O ₃	Hematite—Maghemite
As ₂ O ₃	Arsenolite—Claudetite
Sb ₂ O ₃	Senarmontite—Valentinite
TiO ₂	Rutile—Anatase—Brookite
SiO ₂	Quartz—Tridymite—Cristobalite
CaCO ₃	Calcite—Aragonite
Al ₂ SiO ₅	Kyanite—Andalusite—Sillimanite
MgSiO ₃	Enstatite—Clinoenstatite

known examples are listed in Table 1. These compounds have been the subject of researches for many decades—crystallographic, chemical, physical, and, more recently, x -ray studies. They have been and are of special interest to the economic geologist in that they offer the possibility of furnishing clues as to the conditions of formation of mineral deposits. What do we really know of the stability relations and conditions of formation of the polymorphs listed in Table 1? Not nearly as much as most of us would like.

Nearly 40 years ago, the Geophysical Laboratory published a series of papers on the stability relations and conditions of formation of the silica minerals (Fenner, 1913), the sulfides of iron, zinc, and mercury (Allen *et al.*, 1912, 1914), and calcium carbonate (Johnston, Merwin, and

Williamson, 1916). In these papers, the effects of temperature, acidity, and composition were carefully considered. Unfortunately the results have been misinterpreted by some later workers; in an understandable attempt at simplification, too much stress has been laid on the effects of temperature and acidity, and not enough on the effects of variation in composition. Loose statements like the following have been made all too frequently:

The presence of wurtzite indicates that the ore-forming solution was acid,

or

Cinnabar is precipitated only from alkaline solutions.

Such statements *may* be correct, but in the words of the modern psalmist, "It ain't necessarily so." Such statements neglect the effect of composition.

The researchers at the Geophysical Laboratory clearly recognized the importance of the effect of foreign ions on the stability of polymorphous forms. This is shown by the graph on page 348 of the 1912 paper of Allen, Crenshaw, and Merwin for the pair sphalerite-wurtzite. Even more striking effects might be expected when one of the polymorphs is the unstable form at all temperatures when pure. Johnston, Merwin, and Williamson (1916) discussed this in some detail, and after citing experimental work going back 100 years remarked (p. 500), "It is possible that aragonite containing other material in solid solution may not be unstable with respect to calcite," and (p. 509) "Now the solubility of pure aragonite is not much greater than that of calcite, and this difference would be diminished by the presence of other materials in solid solution in the aragonite; it is conceivable, therefore, that such impure aragonite should be really stable in contact with the natural waters in which it formed. On this basis, then, it is plausible (though not yet established) that natural aragonite containing other substances in solid solution should be practically stable under certain conditions." Today, 36 years later, it is still plausible, and still not yet established for CaCO_3 .

Allen and his coworkers showed that metacinnabar was metastable with respect to cinnabar at all temperatures. Recently Rittner and Schulman (1943) studied the effects of cadmium on the transition metacinnabar-cinnabar in synthetic solid solutions. The data summarized in Table 2 show that even a very small amount of cadmium has a very marked effect on the transition, and it is possible that metacinnabar might be stable if enough cadmium were present in solid solution. Naturally occurring metacinnabar commonly contains appreciable amounts of zinc and iron, and spectrographic analyses made in the laboratory of the Geological Survey by Cyrus Feldman have shown that

germanium is present in most cinnabar and metacinnabar. On this basis, it is plausible (though not yet established) that natural metacinnabar containing other substances in solid solution should be practically stable under certain conditions.

TABLE 2. HgS-CdS SOLID SOLUTIONS TREATED WITH $(\text{NH}_4)_2\text{S}$ SOLUTION

Wt. % Cd	Time of Treatment	Result
0	2 days	100% cinnabar
0.006	3 days	100% cinnabar
0.13	14 days	100% cinnabar
0.32	10 weeks	Cinnabar, little metacinnabar
0.64	10 weeks	Metacinnabar, cinnabar
1.3	10 weeks	Metacinnabar

Data of Rittner and Schulman, 1943.

Recent analyses in our laboratory show that rutile from the alkalic rocks at Magnet Cove, Arkansas, contains 1.2% niobium, whereas brookite from the same locality contains 2.4% niobium. Is this accidental, or cause and effect or, as W. T. Pecora suggests, shrewd sampling on the part of the field geologist? Unfortunately, comparatively little experimental work has been done in the past 25 years. Some years ago, a series of papers by M. J. Buerger and M. C. Bloom of the Massachusetts Institute of Technology was devoted to consideration of polymorphism (Buerger, 1934, 1935, 1936); Buerger and Bloom (1937); Bloom and Buerger (1937); Bloom (1939). These papers discussed the effect of variation in composition; it was shown experimentally for Sb_2O_3 that the metastable form persisted if certain impurities were present in the compounds.* A similar explanation was offered for the persistence of tridymite and cristobalite at low temperatures (Buerger, 1935, Fig. 2, p. 190). The explanation seems reasonable for such open framework structures; it is strengthened by the discovery of a variety of tridymite, named christensenite, that contains about 5% of NaAlSiO_4 in solid solution (Barth and Kvalheim, 1944). Recent *x*-ray studies strongly indicate that the presence of impurities has considerable effect in determining which polymorph formed in syntheses of Bi_2O_3 (Sillén, 1938) and of silicon carbide (Lundqvist, 1948).

Thus we have good evidence that both direct atom-for-atom substitution, as in wurtzite or metacinnabar, and the interstitial type of foreign

* A different explanation was recently advanced by Frueh (1952), who believes that a hydrogen bond is present in valentinite.

ions in open structures, as in Sb_2O_3 , may have profound influence on the stability relations of polymorphous substances. I should like to cite just one more pair of minerals that deserves study—the dimorphs of Fe_2O_3 , hematite and maghemite. Unpublished studies made over a period of years by my colleague Charles Milton have shown that maghemite, gamma- Fe_2O_3 , occurs far more commonly than is generally supposed. It is known to be unstable with respect to hematite. Why then is it formed in Nature, and why does it persist? We do not know. If I may be permitted to speculate, is it possible that the presence of non-oxidizable ions such as magnesium or nickel, perhaps filling some of the vacant iron positions in the gamma- Fe_2O_3 structure, causes the formation of maghemite rather than of hematite? Plausibility is lent to this speculation by the observation that maghemite is abundant in the oxidized zones of a nickel-iron sulfide deposit. We hope that it may be possible to isolate and analyze pure samples of maghemite and to study the course of oxidation of synthetic magnetites containing known amounts of magnesium and nickel.

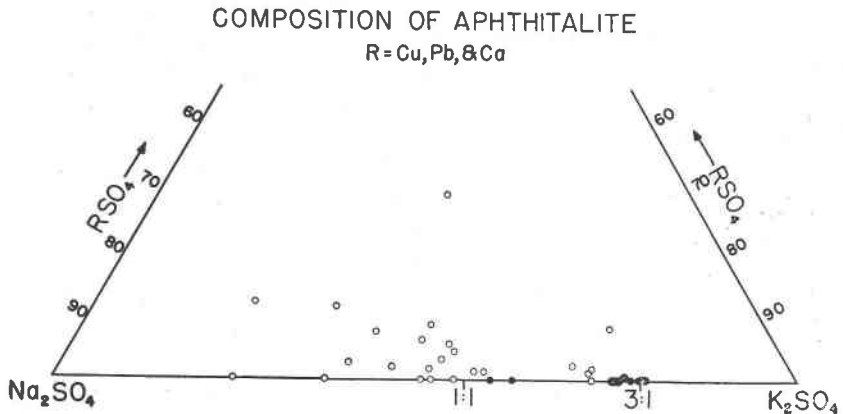
In view of the very great interest in trying to use polymorphous forms as guides to learning the conditions of formation of ore deposits, it is discouraging to note how little experimental work has been done in this field for the past 20 or 30 years. We need new analyses, chemical and spectrographic, for major and minor elements on samples of known environment; we need new studies on mineral synthesis, dry and hydrothermal. Here is plenty of work for the chemist.

RELATION OF COMPOSITION TO PARAGENESIS

So much then for the effect of the environment on which form of a polymorphous compound may be precipitated. Let us turn to another familiar theme—the variation of composition of minerals as related to the environment in which they were formed. It is gratifying that this theme has become so familiar. I should like to recall to you two studies of this sort, and then to consider other work that might profitably be undertaken.

The first mineral I shall discuss is the uncommon mineral apthitalite, a rhombohedral solid solution of potassium and sodium sulfates (note that K_2SO_4 and Na_2SO_4 are orthorhombic). The mineral is of unusual interest because it has two very different modes of origin: crystallization from saline solutions at temperatures below 100°C ., and formation as a product of volcanic and fumarolic activity at relatively high temperatures. Figure 1 shows analyses of 10 samples from potassium salt deposits (Germany, Poland, California, and New Mexico); the range of concentration is small, with most samples having K:Na about 3:1. The

25 analyses shown of apthitalite of volcanic origin (from Vesuvius, Etna, and Kilauea) show a much wider range of composition, the K:Na ratio ranging from 3:1 to 1:2; they also show the presence of appreciable amounts of Pb, Cu, and Ca in solid solution. The system K_2SO_4 - Na_2SO_4 - H_2O has been studied (Hamid, 1926; Druzhinin, 1938) and it has been found that the range in composition of the rhombohedral solid solutions that are stable is very small. The system K_2SO_4 - Na_2SO_4 and K_2SO_4 - Na_2SO_4 - $PbSO_4$ (Perrier and Bellanca, 1940), K_2SO_4 - Na_2SO_4 - $CuSO_4$ (Bellanca and Carapezza, 1951), and K_2SO_4 - Na_2SO_4 - $CaSO_4$ (Bellanca,



1942) have all been studied. The results are in good agreement with the observations on natural material; the range of solid solutions in the anhydrous systems at melting temperatures is much more extensive than in the system with water.

I have discussed this uncommon mineral because the relations are so simple that they should be better known, especially to teachers. Let us turn now to more common minerals. It is surprising how little information is readily available even for the commonest minerals as to how their composition varies with their geological environment. There are some minerals, including some of the most common ones, for which we know that we have very little information. For example, this was true of the mineral chromite until about 10 years ago—partly because its analysis is extremely difficult. We now have two fine sets of analyses of chromite, one set of chromites from the Bushveld complex (van der Walt, 1941), the other of chromites studied by the U. S. Geological Survey from many

ore deposits in the Western Hemisphere (Stevens, 1944). The latter shows that the composition of chromite varies much more than has generally been supposed. His results were interpreted by Thayer (1946) from the standpoint of the geological environment. Thayer showed that when Stevens' analyses are grouped on a regional basis, considerable order appears in what seemed to be random variation in composition and that this order reflects the effect of the geological environment. Thus the alumina-rich chromites of Cuba are closely associated with troctolites and gabbros. Petrographic evidence shows that the chromite has reacted with the gabbroic magma with the formation of anorthite at the expense of part of the alumina content of the chromite, and this explains why these chromites show a rather wide range in Al_2O_3 content. In contrast, the chromites from the feldspar-free peridotites of the Pacific coast are low in Al_2O_3 . We have here just the beginnings of deciphering a complex problem; the U. S. Geological Survey has under way a detailed study of the chromites of the Stillwater complex in Montana, which we hope will help to fill some of the gaps in our knowledge.

These are examples of what has been done; we need further work on many other minerals. There are some regional studies, as for example, those by Professor Larsen and his coworkers on the variation in composition of such minerals as biotite and amphibole in the San Juan district, Colorado (Larsen et al., 1936, 1937, 1938) and in the southern California batholith (Larsen and Draisin, 1950). For some minerals, it is hard to say whether the data are adequate. Summaries have been published for a few, as for example for the garnet group (Wright, 1938). Similar compilations for other minerals are badly needed. For example, the existing analyses of the amphiboles and the micas need to be assembled and studied critically, and every relationship of composition to physical and optical properties and to geological environment ought to be squeezed out. Not only would this help greatly in systematizing what we know, but it would certainly show us where the gaps are that need to be filled. Probably no one will disagree as to the need; just as probably, few if any will be willing to undertake such a task of compiling. We are all prone to take compilations for granted, to be extremely critical of the way they are done, and to consider them somewhat unworthy of our own great talents. This is really too bad, because there is little doubt that a good critical review saves much more time than it takes and points out valuable researches that ought to be done. As an example, a critical study of the 50 most recent analyses of biotite made in 1941 by J. J. Fahey, R. E. Stevens, and me showed that there were glaring deficiencies in the published determinations of Li_2O , F, and H_2O , and alerted our

laboratory to the need for better methods of analysis for these constituents of micas.

One other mineral ought to be mentioned. We hope soon to begin work on the mineral magnetite. Examination of the literature shows relatively few analyses of pure magnetite, yet even these few are very suggestive. For example, there are just a few analyses of magnetite from diabases and Tertiary lavas and every one of these is very high in MgO content—in fact two of them are actually magnesioferrite rather than magnetite. There are also a few analyses of magnetites from nepheline syenites and phonolites; each shows a high content of MgO and Al_2O_3 and an appreciable content of MnO as well. We have been collecting and purifying samples of magnetite of various origins and we hope to have something to report in the future.

By this time, each of you has probably thought of a dozen other minerals that ought to be studied in this way; there ought to be no shortage of work for the chemists!

DISTRIBUTION OF MINOR ELEMENTS AMONG MINERALS OF A ROCK

I shall go on now to another, closely related problem—that of the minor elements in rocks and their distribution among the constituent minerals of the rocks. Twenty-five years ago, Professor Papish of Cornell University lectured to the Geological Society of America on the possibilities of the spectrographic method of analysis, and V. M. Goldschmidt and the Noddacks used the method in the early 1930's to increase our knowledge of the abundance and distribution of many of the rarer elements. But it has taken 20 years of patient work to develop the method and to standardize the results, and even now only a handful of laboratories in North America are applying the spectrophotograph to the solution of geological and mineralogical problems. The developments in this field during the past few years, plus the rapid advances in the use of colorimetric methods for trace amounts that have been led by Professor Sandell at Minnesota, promise to bury us under a mass of data.

Again I should like to give a few examples of research that have been done and to mention some additional problems that ought to be studied. To date there have been very few studies in which the distribution of the elements among the minerals of the rocks has been determined. One such study, of exceptional interest, is that by C. S. Ross, M. D. Foster, and A. T. Myers (1953) on the minerals of dunites and of olivine-rich inclusions in basalt. They determined the major and minor elements present in a series of olivines, orthopyroxenes, clinopyroxenes, and spinels separated from rocks from many localities. The distribution of elements such as Ni, Co, Cr, and Mn among these minerals is of particular importance. Two other reports should be mentioned: the study of

Caledonian rocks of Scotland by Nockolds and Mitchell (1948), and that of the igneous rocks of the Skaergaard intrusive of eastern Greenland (Wager and Mitchell, 1943, 1951). The mineralogical and geochemical implications of their data can scarcely even be touched upon here; only a few points can be mentioned. For example, it is interesting to compare the data of Nockolds and Mitchell on granites, granodiorites, and similar rocks with those of Ross and coworkers on ultramafic rocks. Nockolds and Mitchell found chromium to be highly concentrated in monoclinic pyroxene, with much lower concentrations in hornblende and biotite; they found lithium to appear almost exclusively in biotite, and vanadium to appear in highest concentrations in the micas, with appreciable but lesser amounts in pyroxenes and hornblende.

The Skaergaard intrusive is the only highly differentiated igneous rock mass for which we have detailed work on major and minor constituents. One must be cautious in drawing generalizations, since the Skaergaard magma was somewhat unusual in composition, particularly in its high content of iron and low content of potassium. The data of Wager and Mitchell show that chromium and nickel are largely precipitated, like magnesium, in the first fractions to crystallize, whereas cobalt and vanadium come out over a much wider range of concentration. If we now consider further the distribution of these elements in the individual minerals, we begin to get a picture of what happens during differentiation and we can compare the data for these gabbroic rocks with those for granodiorites and ultramafics. The nickel, which is largely in the first fractions, is almost entirely in the olivine; cobalt precipitates over a wider range of composition and is distributed between the olivine and pyroxene; and copper precipitates still later and is present in both ilmenite and magnetite as well as in pyroxene. Vanadium behaves very much like copper. In the earlier stages, vanadium is present almost entirely in the pyroxene; as crystallization proceeds, more and more vanadium is present in the magnetite, up to 0.5% in magnetite of some of the gabbros.

Several applications to problems of economic geology are apparent. The data show that most of the copper content of these rocks is present in silicate minerals, and it is only at a late stage of differentiation that copper-bearing sulfides appear. Another point is this—can the results explain the fact that deposits of titaniferous magnetite the world over that occur in close association with gabbros and anorthosites invariably contain high concentrations of vanadium? Wager and Mitchell have pointed out that crystallization differentiation accounts for concentrations of 0.5% or thereabouts in the magnetites of the Skaergaard intrusive, but that many titaniferous magnetites from other localities contain much higher concentrations of vanadium. We badly need similar

studies of other intrusive masses before we can assume that the mechanism of differentiation offers an adequate explanation.

These few examples are perhaps enough to indicate that the possible applications of further research along these lines to mineralogy, economic geology, and petrology are almost unlimited. I shall cite just two other major problems.

The first is the problem of the composition, mineralogy, and mode of origin of the marine black shales. Comparatively little work was done on these until recent years, but unpublished work by the U. S. Geological Survey plus several published papers (Westergård, 1944; Goldschmidt *et al.*, 1948; Schneiderhöhn *et al.*, 1949; McKelvey and Nelson, 1950; Leutwein, 1951) give just enough information to show how complex and difficult the problem is. These rocks contain, on the average, more vanadium, more chromium, more copper, and more molybdenum—not to mention more uranium—than most igneous rocks. Sad to say, we know very little of the form in which these elements are present in the black shales. We need to separate the minerals and to find out where these elements are concealed before we can hope to solve the problem of the mode of formation of these rocks.

The second problem [to which this type of research needs to be applied is that hardy perennial—the origin of alkalic rocks such as the nepheline syenites. Forty years ago, C. H. Smyth (1913) pointed out that any explanation of the origin of these rocks had to account for the unusual concentration in them of elements such as the rare earths, titanium, zirconium, and thorium. In spite of that, few of the multitude of papers on the subject have even mentioned this aspect. We do not have enough determinations of the minor elements in alkalic rocks, and still fewer of their distribution among the minerals of such rocks. Our laboratory has begun such studies, under the direction of W. T. Pecora, not only because of the petrological problems, but also because it seems likely that these rocks may become important sources of such elements as titanium, the rare earths, and niobium.

APPLICATION OF MINERALOGICAL THINKING TO PROBLEMS OF EXTRACTIVE METALLURGY

Finally, I should like to consider briefly a fourth type of problem—the use of the mineralogical approach to problems of extractive metallurgy. This, of course, is not new. It is not a very profound idea that when one attempts to separate two elements occurring together in an ore, it helps to know in what minerals the elements are present. Unfortunately there are still too many metallurgists and chemists to whom this idea has not yet penetrated. I should like to quote to you three statements made in 1944 and 1945 about three different manganese oxide ores:

1. "Gravity concentration and flotation failed to reduce the BaO content, indicating that the BaO is very intimately associated with the manganese." This statement led us to investigate the ore, which was found in the U. S. Geological Survey laboratory to consist chiefly of the barium manganese oxide mineral psilomelane.

2. "Jigging, high-intensity magnetic separation, and flotation failed to remove the contamination by zinc." Since zinc-bearing manganese oxides are not very common, this ore was also investigated. It contains as a major constituent the mineral hetaerolite, $ZnMn_2O_4$.

3. "Your suggestion that the mineral is a lead-bearing hollandite is of great interest, since a study of practical means of reducing the lead content of the concentrates has led us to the conclusion that most of the lead was not amenable to separation by customary mechanical or chemical means."

It is saddening to think of the wasted effort in each of these instances in the attempt to separate elements that were combined in a single mineral. The point is not that mineralogists should feel smug and superior; on the contrary, the moral I should like to draw is that these are illustrations of *our* failure to educate metallurgists and chemists to recognize the proper role of the mineralogist and the need for his services instead of tackling such problems by empirical methods. If mineralogists did not hold themselves aloof from these practical problems, they would perhaps create more widespread recognition of what they can do.

Let us look at the more positive side of the mineralogical aspects of problems of extractive metallurgy. Industrial developments of the past few years have made it imperative to find new sources of some of the rarer elements. One such is niobium (columbium), and I should like to mention briefly work in our laboratory aimed at finding new sources of this element. Details are being published elsewhere (Fleischer *et al.*, 1952).

From general geochemical considerations and from the data in the literature, it appeared that the highest concentrations of niobium are in granitic pegmatites and in alkalic rocks; further that niobium should be closely associated with the elements titanium, zirconium, and tungsten. With these generalizations as guides, we have determined the niobium content of many titanium minerals, and we have found that titanium minerals associated with gabbros and anorthosites have very low niobium contents, whereas rutile, perovskite, and ilmenite from alkalic rocks are high in niobium and constitute potential sources of that element.

Another point of attack started from data that showed (Murata and Gordon, 1952) that nepheline syenites from Arkansas contained appreciable amounts of niobium, and further that Arkansas bauxites formed by the weathering of these alkalic rocks contained even more niobium,

about 0.05% Nb on the average—about a pound per ton. This is perhaps not very impressive, but calculation shows that the Arkansas bauxite processed annually contains about nine-tenths as much niobium as the total annual world production.

Figure 2 gives a simplified flow sheet of the treatment of bauxite with the niobium contents of the various products. The niobium is concen-

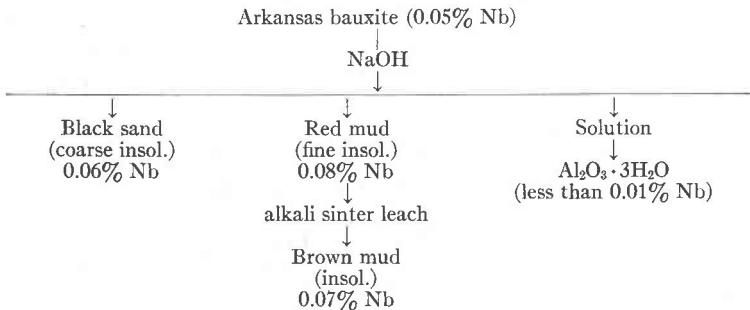


FIG. 2. Nb IN BAUXITE TREATMENT.

trated in the insoluble fractions, of which the brown mud forms the major part. We have not yet attempted mineralogical fractionation of this extremely fine grained material. Fractionation of the black sand by means of heavy liquids and magnetic separations gave the data of Table 3. It will be noted that a fraction was obtained that contained 0.66% Nb and 46% TiO₂, one that may therefore be of commercial interest.

This is a simple illustration of why it is not enough to know the concentration of an element in an ore and why we also need to know the element's concentration in the different minerals of the ore. The general trend in extractive metallurgy in recent years has been toward the utilization of ever lower grades of ore and also toward the recovery of

TABLE 3. FRACTIONATION OF BLACK SAND FROM ARKANSAS BAUXITE

Material	Percent of Total	Percent Nb	Percent TiO ₂
Black sand	100	0.064	not detd.
Float at 2.9 (calcite, quartz, etc.)	14.5	not detd.	not detd.
Magnetite	51.5	0.025	5.2
Mainly limonite	14.8	0.04	not detd.
Ilmenite+limonite	15.9	0.14	not detd.
Ilmenite	2.8	0.66	46
Zircon+sphene+rutile	0.5	0.45	not detd.

Mineralogical separations by Marie L. Lindberg; spectrographic analyses by Janet D. Fletcher.

more and more of the minor elements. I believe that mineralogists can and should play a very important role in the future development of this field.

CONCLUSION

I have discussed some of the chemical problems of mineralogy that deserve more attention. They require more than routine analyses by chemists; they demand the best thinking of chemists of research caliber. It is the duty of mineralogists and geologists to arouse the interest of chemists in such problems and to enroll them in full partnership in these researches.

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