

of recording. The resulting curves, which will be published soon, are quite different for the two types of recording apparatus. The electronic method of recording seems much more sensitive than the photographic method.

On the basis of the above observation it would seem advantageous for workers in this field to exchange samples in order to evaluate the influence of different instrumental characteristics on the thermal curves for the common clays and carbonates.

REFERENCES

1. FREDERICKSON, A. F. (1947), The mineralogy of a drill core of Arkansas bauxite: *Sc.D. Thesis*, Massachusetts Institute of Technology.
2. SPEIL, A. (1945), Applications of thermal analysis to clays and aluminous minerals: *U. S. Bureau of Mines, Tech. Paper 664*, 38-55.
3. BERKELHAMER, L. H. (1945), An apparatus for differential thermal analysis: *U. S. Bureau of Mines, Tech. Paper 664*, 38-55.
4. CUTHBERT, F. L., AND ROWLAND, R. A. (1947), Differential thermal analysis of some carbonate minerals: *Am. Mineral.*, **32**, 111-116.
5. KERR, P. F., AND KULP, J. L. (1947), Differential thermal analysis of siderite: *Am. Mineral.*, **32**, 678-680.
6. KELLEY, K. K., AND ANDERSON, C. T. (1935), Contributions to the data on thermal metallurgy, Part IV: *U. S. Bureau of Mines, Bull. 384*.
7. BECK, C. W. (1946), An improved method of differential thermal analysis and its use in the study of natural carbonates: *Ph.D. Thesis*, Harvard University.

MODE OF OCCURRENCE OF TITANIUM AND ZIRCONIUM IN LATERITES

A. F. FREDERICKSON,
Washington University, St. Louis, Missouri.

TITANIUM

Although titanium is commonly present in amounts up to three or four per cent in some bauxites and laterites, frequently no titanium mineral can be visibly identified. During an investigation (5) of a drill core of Arkansas bauxite it was found that the titanium occurs in at least four different forms:

- (1) As sphene.
- (2) As ilmenite.
- (3) As one of the polymorphous forms of TiO_2 , principally brookite.
- (4) In substitutional solid solution in the aluminum minerals.

Sphene was observed in thin sections and was collected from several horizons in the drill core. The products from concentration experiments reveal that sphene dissolves readily when exposed to circulating solu-

tions. When the sphene occurred enclosed in pisolites it was preserved from the attacking solutions and is less corroded than that collected from portions of the core that contained no pisolites.

A black mineral is found throughout the core. In places the grains are quite large but the usual appearance resembles "pepper" disseminated through a given specimen. X-ray photographs of this black mineral indicate that it is ilmenite. It alters to a yellow, earthy-appearing substance commonly occurring as pseudomorphs after ilmenite.

Several concentrates of the yellow mineral were made and checked by x-ray methods. One concentrate was prepared by rolling the altered ilmenite grains between two thin section glasses. Ilmenite rolls off the glass leaving the yellow mineral behind, if the slide is first rubbed with a finger to insure a very slight film of oil on the glass. This concentrate yielded an x-ray pattern identical with brookite.

Another concentrate of yellow grains yielded patterns indicating the presence of brookite, ilmenite, and the probable presence of a small amount of anatase. Also a small amount of sphene was present in one of the concentrates.

A spectrographic analysis of a carefully cleaned sample of the yellow material revealed the presence of the following elements:

ELEMENT	ESTIMATED PERCENTAGE
Ti	Large
Fe	0.5-1.0
Zr	small (0.3)
Al	1.0-1.5
Ca	1.0-1.5
Si	Trace

The iron and the zirconium undoubtedly replace titanium in solid solution; the calcium indicates that a small amount of sphene is present as an impurity along with the aluminum.

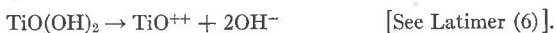
This yellow material is evidently what many authors describe as xanthitane. Some of the other names applied to this yellow mineral, and their relationship to other forms of TiO_2 , are of interest. According to Dana (4):

1. "Leucoxene, xanthotitane, xanthitane, and hydrotitanite are all identical with anatase.
2. Anatase is polymorphous with brookite and rutile.
3. Leucoxene is a name loosely applied to dull, fine grained, yellowish to brown alteration products high in titanium. It is found as an alteration product of sphene, ilmenite, perovskite, titanium magnetite, or other titanium minerals. The material consists in most instances of rutile; also, less commonly, of anatase, or sphene."

The leucoxene of Coil (3), the xanthitane of Coghill (2), and others, is, then, one of the polymorphous forms of TiO_2 . In this case, it is brookite.

The hydrates of titanium oxide, $\text{TiO}_2 \cdot \text{H}_2\text{O}$ and $\text{TiO}_2 \cdot 2\text{H}_2\text{O}$, have been described (6), but very little is known about their solubility. The unhydrated oxide does not dissolve appreciably in either acids or bases: the hydrated forms are somewhat soluble in both.

The alteration of ilmenite or sphene to brookite must obviously be a reconstructive transformation.* Because the transformation took place in an aqueous medium, the individual atoms, or atom groups involved in the transformation, must have been hydrated at one time or another. Large, recrystallized particles (they are recrystallized because they yield an x -ray diagram) have only adsorbed water; smaller particles or atom groups (in the colloidal range of sizes) may behave as gels, whereas still smaller units form true hydroxides:



If enough solution is present, the process of hydration can go to completion, that is, it may convert all of the unhydrated material into titanate ions; if only a limited amount of solution is present, it might act as a transporting medium through which the ions involved in the reconstructive transformation could travel. These ions could then order themselves and develop into one of the polymorphs of TiO_2 . When enough data are gathered on this subject, it may be possible to reconstruct the type of environment in which a particular polymorph of TiO_2 was formed in preference to some other form.

If titanium can travel in solution as a gel or as titanate ions, it is not necessary to resort to explanations such as compaction (1) to account for concentrations of titanium in clay and bauxite deposits.

ZIRCONIUM

It is interesting to note that the only places in the core where zirconium is found in the form of zircon crystals is in the pisolites. Well formed zircon crystals are found in red, unleached pisolites containing gibbsitized feldspar remnants. In the pisolites that have been leached by later solutions the remaining zircons show corroded, irregular outlines indicating that they are gradually going into solution.

The chemistry of zirconium is quite similar to that of titanium. The only oxidation state of zirconium stable in water solutions is +4. The

* A reconstructive transformation is one in which a crystal structure is destroyed and some or all of the resulting atoms recombine to form a different structure. It contrasts with displacive transformations which involve only a slight displacement of parts of the structure. If a certain critical temperature is passed, displacive transformations of the high-low type instantaneously occur (example: low-quartz to high-quartz).

dioxide of zirconium is somewhat more basic than titanium dioxide and, when hydrated, dissolves fairly readily to form the zirconyl ion, ZrO^{++} :



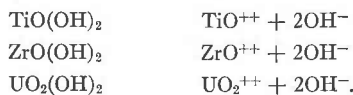
The solubility of the oxide in alkaline solution is slight and the zirconates are much less stable than the titanates (see Latimer (6)).

Zirconium, then, is removed in solution more easily than titanium and does not form secondary zirconium minerals. The large percentage of the zirconium determined in the spectrographic examination must be as zirconate ions adsorbed on the aluminum hydroxide minerals.

Because the ionic potentials† of titanium (2.43^{+4}), zirconium (2.24^{+4}) and aluminum (2.45^{+3}) are almost equal, the first two substitute for Al in the various aluminum minerals.

Zirconium was also found in a concentrate of yellow brookite, indicating that Zr^{+4} also substitutes for Ti^{+4} in some of the titanium minerals.

Because titanium, zirconium, and uranium form similar ions under certain conditions they should be closely associated:



This subject will be discussed in a separate paper now in preparation.

REFERENCES

1. ALLEN, V. T., AND NICHOLS, W. L., Weathered gravels and sands of Oregon and Washington: *Jour. Sed. Petrol.*, **16**, 52-62 (1946).
2. COGHILL, W. H., Titanium in bauxite ores and sludges: *U. S. Bur. Mines. Report of Investigation 2867* (1928).
3. COIL, F., Chemical composition of leucoxene in the Permian of Oklahoma: *Am. Mineral.*, **18**, 62-65 (1933).
4. *Dana's System of Mineralogy*, 7th Edition, Vol. 1. Elements, sulfides, sulfosalts, oxides. John Wiley and Sons, Inc., New York (1944).
5. FREDERICKSON, A. F., The mineralogy of a drill core of Arkansas bauxite: *Sc.D. Thesis*, Massachusetts Institute of Technology (1947).
6. LATIMER, W. M., The oxidation states of elements and their potentials in aqueous solutions: Prentice-Hall, Inc., New York (1938).

† Ionic potential = Z/r where Z = valence of the ion and r = the ionic radius.