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APPLICATION OF DIFFERENTIAL THERMAL ANALYSIS TO IDENTIFICATION OF THE NATURAL HYDROUS FERRIC OXIDES

William C. Kelly, *Columbia University, New York City.*

In the course of a recent study of oxidized lead-zinc ore outcrops, the writer attempted to identify the mineral species of hydrous ferric oxide by differential thermal analysis* of over 150 specimens of gossan "limonites."† These attempts proved unsuccessful, and it was found that thermal curves closely resembling standard analyses (J. L. Kulp and A. F. Trites, 1951) for (1) goethite (α-$Fe_2O_3 \cdot H_2O$), (2) lepidocrocite (γ-$Fe_2O_3 \cdot H_2O$), and (3) goethite-lepidocrocite mixtures may be produced by goethite alone—the variations depending on the degree of crystallization in the materials tested.

Kulp and Trites observed that *well-crystallized* goethite decomposes directly to α-Fe_2O_3 in the temperature range 385–405° C. (heating rate-12°/minute), producing a single strong endothermic peak in the thermal curve of that mineral (Fig. 1*A*). Lepidocrocite, having a less stable structure, decomposes at lower temperatures. Its curve (Fig. 1*B*) was described as having an endothermic reaction at about 350° C. (decomposition to γ-Fe_2O_3) followed directly by a variable exothermic peak (phase change of γ- to α-Fe_2O_3). Thermal analyses of artificial mixtures of the two minerals simply produce composite curves with double endothermic peaks (Fig. 1*E*); the lower temperature peak representing decomposition of lepidocrocite and the higher temperature peak the decomposition of the more stable goethite.

In analyzing many samples of *poorly-crystallized* goethite, the writer found that the resulting curves (Figs. 1*C*, 1*D*) were indistinguishable from standard analyses for lepidocrocite. These goethite samples were of the compact massive and light porous varieties not included by Kulp and Trites in their suite of standard samples. *X*-ray analyses of 35 of the samples yielded powder patterns with broad and frequently indistinct goethite lines. Under the electron microscope, the materials appeared as moss-like aggregates of goethite with only slight evidences of crystallization even at high magnifications. This type of material constitutes the common yellow or brown "limonite" of widespread and well-known occurrence.

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† A general term applying to any natural aggregate of unidentified hydrous ferric oxides lacking *apparent* crystallization.

Mixtures of these poorly-crystallized goethites with some of the original coarsely-crystalline goethite samples tested by Kulp and Trites produced thermal curves (Fig. 1*F*) matching the standards for goethite-lepidocrocite mixtures. Although these mixture-samples consisted entirely of goethite and were ground to a uniform particle size (200-mesh), definite differences in the degree of crystallization of the two goethite portions of each sample produced double peaks in the thermal curves. Here, the lower temperature peak represents decomposition of the poorly-crystallized goethite whereas the well-crystallized goethite decomposes at the "standard temperature" around 400° C.

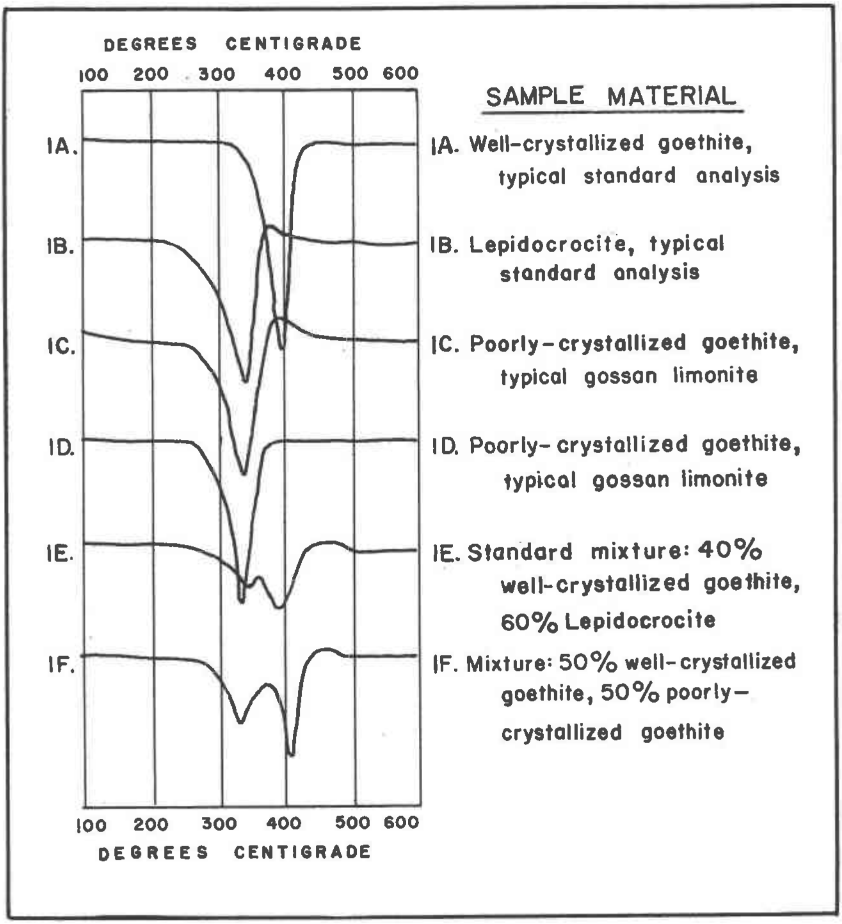

Fig. 1

Marked exothermic reactions appeared in the thermal curves of many of the poorly-crystallized goethites (Fig. 1*C*), but were absent in others (Fig. 1*D*). *X*-ray analyses of the heated products chilled at the maximum endothermic decomposition temperatures produced γ-Fe_2O_3 patterns where an exothermic reaction had appeared in the goethite curve and α-Fe_2O_3 patterns where the exothermic peak was absent. The appearance of a variable exothermic peak due to the phase change of γ- to α-Fe_2O_3 is usually associated with lepidocrocite, and, as yet, no satisfactory explanation can be offered for its erratic appearance in the thermal curves of these poorly-crystallized goethite samples.

A full report on the present thermal studies is soon to be published by the New Mexico Bureau of Mines and Mineral Resources which aided in the research, but this brief note is submitted to bring out a few of the difficulties encountered with the hydrous ferric oxides. If a curve of the type shown in Figs. 1*B*, 1*C*, or 1*D* is obtained with an unknown, there is uncertainty as to whether the oxide in question is lepidocrocite or poorly-crystallized goethite. A thermal curve with double-peaks (Figs. 1*E*, 1*F*) may represent (1) a mixture of goethite and lepidocrocite or (2) a mixture of well-crystallized and poorly-crystallized goethite.

For reliable identification of mineral species of hydrous ferric oxide present in natural aggregates, it is still necessary to resort either to *x*-ray analysis or to the use of immersion media of high refractive index (H. E. Merwin and E. S. Larsen, 1912).

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SYNTHESIS OF ALUMINUM NITRIDE MONOCRYSTALS

J. A. KOHN,* PERRY G. COTTER, AND R. A. POTTER
U. S. Bureau of Mines, Norris, Tennessee.

SYNTHESIS AND GENERAL DESCRIPTION

This note is intended to describe an interesting synthesis of aluminum nitride crystals and some of their properties. The aluminum nitride crystals were obtained incidentally during an attempt to impregnate a sintered carbide compact with alumina. Specifically, a cylindrical WC-TiC-Co compact (5/8 in. diameter × 5/8 in.) was embedded in

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* Present address: Chemical-Physics Branch, Signal Corps Engineering Laboratory, Ft. Monmouth, New Jersey.