

already considerably weaker than the silicon-oxygen-silicon bridge, would break down completely under the weakening influence of the boron oxygen bond. Aluminum tetrahedra thus can not be expected to share corners already shared by boron and silicon tetrahedra.

Another example of the same kind is to be found in the structure of axinite, as determined by Ito and Takéuchi (7). Though the description mentions only separate BO_3 and Si_4O_{12} groups, these groups are linked to each other by a boron oxygen bond similar to the one existing in tourmaline. The $\text{BO}_3 \cdot \text{Si}_4\text{O}_{12}$ group is shown in Fig. 2.

It is quite possible that condensation of boron and silicon tetrahedra of the types described is a common feature in the structure of boron silicate glasses, and it may be responsible for some of their properties. It may be expected to occur also in other borosilicates.

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DETERMINATION OF MAGNETITE IN CHRYSOTILE

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During work on the beneficiation of chrysotile, the need developed for a method for estimating quantitatively the magnetite content, either originally present or residual. The procedure evolved is given in detail.

A 1-gram sample of chrysotile is cut up by hand or in a Wiley mill to short lengths ($< \frac{1}{4}$ -inch), placed in a Waring blender containing 500 to 600 cc. water, and disintegrated for 3 minutes. A 0.1 molar solution of aluminum formate is added dropwise until further addition causes no marked improvement in dispersion. 1 cc. is the amount recommended in U. S. Patent 2,661,287 (1). Beating in the Waring blender is continued for 3 minutes to give a total of 6 minutes. This treatment largely disperses the chrysotile into its ultimate fibers, which are only some 200 to 300 Å units in diameter, and dislodges most of the magnetite contained therein. Transfer completely to a 1-liter beaker. (The blender used should be in

good condition and checked on iron-free chrysotile for possible contamination.)

The dislodged magnetite is removed with a strong hand magnet covered with a sheet or bag of polyethylene. The polyethylene should be large enough to act as a rope in letting the magnet into the beaker. The sheet and the magnetite are washed with distilled water, which is allowed to drain back into the beaker. It is estimated that 90 per cent or more of the magnetite present is removed at this time. The magnetite is reserved for combining with a later recovery.

Volume of the solution should now be about 750 to 800 ml. 15 grams of H_3BO_3 are added, and stirring is continued until solution is effected. Then 27 ml. (± 0.5 ml.) of 48-per cent HF is added, with vigorous stirring. The beaker is now set in a boiling hot-water bath so that water reaches the level of the liquid inside the beaker. The solution is stirred every 2 minutes, or oftener if desired. After 10 minutes the chrysotile should be largely dissolved. If dispersal has been complete, solution will probably take place in less than 10 minutes. When solution is complete, and in no case over 12 minutes, the beaker should be removed to a cold-water bath, and ice cubes added to cool immediately. As soon as the water is cool enough, immerse the hand magnet as before to collect the magnetite. Remove, wash, and combine the magnetite with the first for determination of iron. HF, HCl, and H_2SO_4 , in platinum, should suffice to dissolve the magnetite for volumetric determination.

Residual flocs of chrysotile generally indicate incomplete dispersion. A second treatment in the steam bath will usually complete the decomposition. Filtering the solution obtained from the steam-bath treatment, to recover magnetite, is not recommended because any non-dispersed material or contaminant will not dissolve, and its iron content would be estimated as magnetite.

The separation depends on three factors:

- (1) The dispersion, or deflocculation, of chrysotile by monovalent anions in combination with 3^+ or 4^+ cations (1).
- (2) The preferential formation of silicofluoride over fluoborate (2).
- (3) The low reaction rate of magnetite with the complexed fluoride solution.

With 930 milligrams of magnetite (recovered from chrysotile) present, the above procedure resulted in solution of only 16 milligrams, while similarly diluted HF alone, at room temperature, dissolved 82 milligrams of magnetite. Under actual conditions of analysis, solution of magnetite in the boric acid-hydrofluoric acid reagent was less than 0.09 per cent Fe_2O_3 (original sample basis). The amount of magnetite dissolved is a function of amount present, hence with either a small or large magnetite content the results should be accurate.

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

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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 ($\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$), (2) lepidocrocite ($\gamma\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$), 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 $\alpha\text{-Fe}_2\text{O}_3$ 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. 1A). Lepidocrocite, having a less stable structure, decomposes at lower temperatures. Its curve (Fig. 1B) was described as having an endothermic reaction at about 350° C. (decomposition to $\gamma\text{-Fe}_2\text{O}_3$) followed directly by a variable exothermic peak (phase change of γ - to $\alpha\text{-Fe}_2\text{O}_3$). Thermal analyses of artificial mixtures of the two minerals simply produce composite curves with double endothermic peaks (Fig. 1E); 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. 1C, 1D) 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.