

## MINERALOGICAL NOTES

### OXYGEN-RICH APATITE

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#### ABSTRACT

Apatite containing over 2 percent excess oxygen has been synthesized at 100°C. This apatite is hexagonal; although it has an abnormally large  $a$  relative to hydroxylapatite. Heating experiments indicate that the excess oxygen is retained to more than 580° C.

#### INTRODUCTION

Apatite has attracted attention in regard to catalytic, ion exchange, and solid state properties. Generally a chemical variant or a nonstoichiometric compound of apatite yields such properties. This note reports the conditions of synthesis and some properties of a variant of apatite containing several percent oxygen that is liberated by heating or solution of the crystals.

#### SYNTHESIS

Reagent grade tricalcium phosphate was heated to 1100°C for 12 hours in an open platinum crucible, ground, and then reheated for another 12 hours. After such treatment the material gave an X-ray pattern of whitlockite [ $\beta$ -Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>]. This whitlockite was then boiled in 30 percent hydrogen peroxide for 12 hours. The product was needles of apatite about 1.5 by 0.2  $\mu$ m. The only components in this synthesis were calcium, phosphate, water, and hydrogen peroxide. Hereafter the product of this synthesis will be referred to as peroxide apatite.

A second method synthesis employed the same procedure except that tricalcium phosphate was unheated prior to boiling in hydrogen peroxide. Such unheated material gave a diffuse X-ray pattern of apatite, which improved markedly after boiling in hydrogen peroxide.

The advantages to the described methods of synthesis are that the apatites are free of other phases and the systems are simple chemically.

#### PROPERTIES

Apatite formed by the reaction of whitlockite plus hydrogen peroxide solution has  $a = 9.500 \pm 0.002$ ,  $c = 6.875 \pm 0.002$  Å. These values are for material X rayed immediately after formation. For reference McConnell (1965) gives the unit cell for synthetic hydroxylapatite as:  $a = 9.416 \pm 0.002$  and  $c = 6.883 \pm 0.002$  Å. Thus the peroxide apatite has an abnormally large  $a$  and a slightly decreased  $c$  relative to hydroxylapatite. With drying peroxide apatite at 110°C, the  $a$  and  $c$  parameter remain constant within the limit of measurement.

The oxygen-rich apatite was chemically analyzed (Table 1). Calcium was determined by EDTA titration, phosphate as the quinolinium salt of

molybdophosphoric acid, and one water analysis was by a modified Penfield method. Oxygen was determined by measurement of the quantity of evolved gas upon treatment of the sample with acid. A collection tube similar to the carbonate tube described by Shapiro and Brannock (1956) was used. Oxygen was also measured, with a standard oxygen electrode, by solution of the sample with HCl in previously degassed water of a known volume. The electrode is specific for oxygen; however, the nature of the evolved gas was further confirmed by its ability to oxidize hot copper.

TABLE 1. CHEMICAL ANALYSES OF OXYGEN-RICH APATITE  
(DRIED AT 110°C)

| CaO   | P <sub>2</sub> O <sub>5</sub> | O <sub>2</sub> |                | H <sub>2</sub> O |          |
|-------|-------------------------------|----------------|----------------|------------------|----------|
|       |                               | Electrode      | Volumetrically | By diff.         | Measured |
| 52.71 | 42.37                         |                | 2.12           |                  |          |
| 52.53 | 42.15                         | 2.20           | 2.14           |                  | 2.64     |
| 52.72 | 42.30                         |                |                |                  |          |
| Mean  | 52.65                         | 42.27          | 2.15           | 2.93             | 2.64     |

The analyses show that the material has a calcium to phosphate ratio of 1.58 compared to 1.67 for normal apatite. The material is deficient in calcium, a finding consistent with its formation from whitlockite in an acid media.

Apatite formed by reaction of unheated tricalcium phosphate with boiling hydrogen peroxide also contains excess oxygen, 0.56 percent. However, the quantity is significantly less than that of the apatite previously described. Lattice parameters of this material dried at 110°C are  $a = 9.435 \pm 0.003 \text{ \AA}$  and  $c = 6.870 \pm 0.003 \text{ \AA}$ . Thus this material has a slightly enlarged  $a$  and decreased  $c$  relative to normal hydroxylapatite.

#### HEATING EXPERIMENTS

The apatite containing 2.1 percent excess oxygen was heated, in steps, to 775°C. After drying at 110°C and heating to 320°C weight loss is less than 0.2 percent. Heating from 320°C to 450°C results in roughly 1.5 percent weight loss. After heat treatment to 580°C, all of the excess oxygen, about 2.1 percent, is retained. Thus the first weight loss of the sample corresponds to the loss of water and not oxygen. The retention of excess oxygen to 580°C indicates that the excess oxygen is not simply part of a loosely sorbed surface, but rather incorporated in these crystals

and in some manner in combination with water causes the marked enlargement in *a*.

With heating to 775°C, total weight loss was 4 percent, and the sample decomposed to apatite plus whitlockite with the mixture containing 0.2 percent excess oxygen.

#### ACKNOWLEDGMENTS

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#### ORIENTATION OF ETHYLENE GLYCOL MONOETHYL ETHER MOLECULES ON MONTMORILLONITE

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#### ABSTRACT

A study of the intensities of basal reflections from ethylene glycol monoethyl ether-montmorillonite indicates that the plane of symmetry of the aliphatic chain lies perpendicular to the clay oxygen surface. The complex appears to contain two layers, each of which has one-half the molecular density of ethylene glycol layers on montmorillonite. The value of  $d(001) = 16.0 \text{ \AA}$  makes this complex potentially useful for identification of expandable and mixed-layered expandable clays in cases where line interference is encountered on diffractograms from glycol or glycerine treated samples.

An X-ray diffraction study has been made of the ethylene glycol monoethyl ether<sup>1</sup>-montmorillonite complex ( $d(001) = 16.0 \text{ \AA}$ ). The complex should prove useful in the identification of montmorillonite and mixed-layer illite-montmorillonite in cases where ethylene glycol or glycerol complexes produce diffraction maxima that are interfered with by contributions from other minerals in a mixed sample. An additional reason for interest in this reagent lies in its suggested use for the determination of surface areas of clays (Carter, Heilman, and Gonzalez, 1965).

<sup>1</sup> Available from Fisher Scientific Co.