

## Stability of synthetic andradite at atmospheric pressure

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### Abstract

Compositionally pure andradite  $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$  with an average cell edge  $a = 12.059 \text{ \AA}$  was obtained by dehydration of hydroandradite at  $1100^\circ$  to  $1150^\circ\text{C}$ . At  $1160^\circ\text{C}$  it decomposed to pseudowollastonite and hematite. A 100 percent yield of andradite with a somewhat smaller cell edge  $a = 12.051 \text{ \AA}$  was obtained from devitrification of the glass at  $1150^\circ\text{C}$  and from solid state reaction between wollastonite and hematite at  $1100^\circ\text{C}$  to  $1150^\circ\text{C}$ , but only after six 22-hour cycles of repetitive grinding and heating. This andradite decomposed at  $1165^\circ\text{C}$  to pseudowollastonite and hematite. A change in cell edge  $a$  prior to decomposition was not observed for either andradite. The andradite with cell edge  $a = 12.051 \text{ \AA}$  may contain excess  $\text{Si}^{4+}$ , and consequently vacancies and ferrous iron, because of contamination by  $\text{SiO}_2$  from an agate mortar during the repetitive grinding.

### Introduction

Andradite synthesized from various starting materials under various conditions has been known to have somewhat different physical properties (Flint, McMurdie, and Wells, 1941; Coes, 1955; Christophe-Michél-Lévy, 1956; Swanson *et al.*, 1960; Ito and Frondel, 1967; Naka, Harata, and Noda, 1968; Huckenholz, 1969). Huckenholz and Yoder (1971) discussed its lattice constant and thermal behavior relative to the oxidation state of iron.

Present writers have obtained a 100 percent yield of andradite by appropriate heating of hydroandradite, of a glass of andradite composition, and of a mixture of wollastonite and hematite, all in air at one atmospheric pressure. Slight differences in the decomposition temperatures and cell edges of the resultant andradites perhaps indicate excess  $\text{Si}^{4+}$  in some of these andradites during preparation.

### Experimental

Raw materials include reagent grade  $\text{CaCO}_3$  and  $\text{Fe}_2\text{O}_3$ , and amorphous  $\text{SiO}_2$ , this latter being prepared by hydrolyzing silicon ethoxide and heating the resulting  $\text{SiO}_2$  gel at  $1200^\circ\text{C}$  for 2 hours. Glass with an andradite bulk composition was prepared by calcining the raw materials at  $1100^\circ\text{C}$  for 2 hours and melting in a platinum crucible at  $1400^\circ\text{C}$  for 1 hour. The melt was quenched into water and the lumps of the glass were ground in an agate mortar. The melt-

ing and the grinding were repeated twice. The glass's refractive index  $1.793 \pm 0.007$  suggests that it contains several percent FeO as discussed by Huckenholz and Yoder (1971).

Pseudowollastonite was prepared by heating a stoichiometric mixture of  $\text{CaCO}_3$  and  $\text{SiO}_2$  at  $1500^\circ\text{C}$  for 2 hours; wollastonite, by heating pseudowollastonite at  $1000^\circ\text{C}$  for about 1800 hours.

Hydroandradite (accompanied by amorphous  $\text{SiO}_2$ ) was prepared as follows: the glass and 30 wt percent  $\text{H}_2\text{O}$  were set in a platinum wafer and heated at  $500^\circ\text{C}$  under a pressure of 10 kbar for 20 hours by using a squeezer-type high-pressure apparatus (Dachille and Roy, 1962; Naka, Takenaka, and Noda, 1966). From its cell edge,  $12.088 \pm 0.003 \text{ \AA}$ , the hydroandradite's composition was deduced to be  $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_{2.9}(\text{OH})_{0.4}$ , which is on the join andradite-hydroandradite (Flint *et al.*, 1941). This deduction was confirmed by a thermogravimetric analysis up to  $1100^\circ\text{C}$ . Therefore the bulk composition of this hydroandradite should be accompanied by 0.1 molar fraction of amorphous silica.

The glass and later the andradite were synthesized in a SiC furnace with temperature accuracy of  $\pm 5^\circ\text{C}$ . Quenching experiments were carried out in a platinum wound furnace with temperature accuracy of  $\pm 2^\circ\text{C}$ . The products were identified by X-ray powder diffraction technique and by oil immersion microscopy. The cell edge of the garnet was determined from the 640 and the 642 reflections, referenced to an

internal standard of silicon. The amount of andradite formed was estimated from the relative intensity ratios in peak height of the 400 reflection of andradite to the 310 reflection of wollastonite in the specimens treated below 1050°C, or to the 105 and the 112 reflections of pseudowollastonite in the specimens treated above 1100°C. X-ray measurements were carried out using a Rigaku Denki diffractometer employing a filtered  $\text{CoK}\alpha$  radiation and a scintillation counter. Refractive index of andradite was measured by immersion technique.

### Results and discussion

Andradite as the only phase was obtained from hydroandradite, from the glass, and from the mixture of wollastonite and hematite.

The average cell edge  $12.059 \pm 0.003 \text{ \AA}$  of the andradite obtained by heating hydroandradite between 1100°C and 1150°C for 20 hours agrees with those of anhydrous andradite synthesized under hydrothermal conditions,  $a = 12.059 \text{ \AA}$  (Swanson *et al.*, 1960) and  $a = 12.062 \text{ \AA}$  (Naka *et al.*, 1968), and with those obtained in an oxidized and hydrous atmosphere under 1 to 30 kbar total pressure,  $a = 12.059 \text{ \AA}$  and  $12.061 \text{ \AA}$  respectively (Huckenholz and Yoder, 1971).

Between 1000°C and 1150°C the finely powdered glass of andradite composition devitrified rapidly to produce andradite plus metastable wollastonite or pseudowollastonite. Conversion of this metastable phase into andradite was very sluggish. At 1150°C, complete conversion to andradite was obtained only after six repetitions of grinding after every 22 hours of heating. Increase in amount of andradite with heating time is shown with the lattice constant of the andradite in Figure 1. The lattice constant,  $12.059 \text{ \AA}$ , of andradite from glass devitrified at 1000°C for 10 hours decreased with the repetition of heating and grinding, becoming  $12.051 \pm 0.003 \text{ \AA}$  after 130 hours of heating.

A mixture of wollastonite and hematite, ground separately for 25 hours in an agate mortar, if heated at 1100° to 1150°C for about 130 hours with interruption every 22 hours for regrinding, yielded 100 percent andradite (average  $a = 12.051 \pm 0.003 \text{ \AA}$ ;  $n = 1.889 \pm 0.007$ ). However, a mixture of pseudowollastonite and hematite, similarly treated, yielded only a trace amount of andradite.

Andradite formed from the glass and from the wollastonite-hematite mixture has a cell edge,  $12.051 \text{ \AA}$ , which is somewhat smaller than  $12.059 \text{ \AA}$ , the cell edge of andradite formed from hydroandradite. This

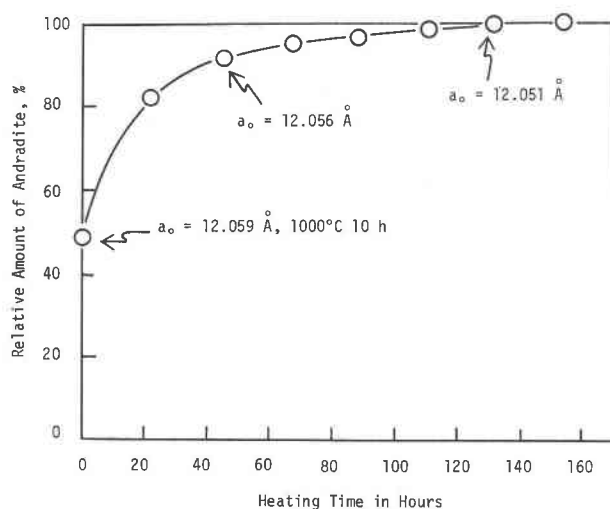


FIG. 1. Variation of relative amount for andradite devitrified from the glass at 1150°C with intermediate grinding for every 22 hours heating as a function of heating time. Starting material used was the devitrified glass at 1000°C for 10 hours. Lattice constants of andradites formed are indicated.

smaller value may indicate an excess of  $\text{Si}^{4+}$  in the andradite — and consequent reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  plus formation of structural vacancies. Such excess could result from contamination by  $\text{SiO}_2$  during the repeated grindings (in an agate mortar) required to produce a 100 percent yield of andradite from a glass or wollastonite-hematite mixture. Huckenholz and Yoder (1971), who obtained andradite with  $a = 12.056 \pm 0.003 \text{ \AA}$  by crystallization from the glass at 1050° to 1135°C, attributed the small cell edge to the presence of a small amount of ferrous iron.

The quenching experiments summarized in Table 1 show that andradite obtained from hydroandradite began to decompose at 1160°C to pseudowollastonite and hematite; however the cell edge of residual andradite remained unchanged by the heating. In addition, the andradite obtained from the mixture of wollastonite and hematite did not break down even after 7 days of heating at 1160°C, nor did its cell edge change. At 1170°C, it began to break down to pseudowollastonite and hematite. The decomposition temperature of this latter andradite is thus considered to be  $1165 \pm 5^\circ\text{C}$ . Huckenholz and Yoder (1971), on the other hand, reported that their andradite decomposed above  $1137 \pm 5^\circ\text{C}$  to pseudowollastonite, hematite, and a garnet ( $a = 12.045 \text{ \AA}$ ); that the resulting garnet contains a small amount of ferrous iron reduced from ferric iron; and that at  $1157 \pm 5^\circ\text{C}$  the garnet completely decomposed to pseudowollastonite

TABLE I. Results for the Quenching Experiments

| No   | Starting Materials | Temperature °C | Time  | Products <sup>†</sup>       |
|------|--------------------|----------------|-------|-----------------------------|
| Q-01 | Andradite*         | 1150           | 20 h  | An (a=12.059Å)              |
| Q-02 | "                  | 1160           | 20 h  | An + Pw + He<br>(a=12.059Å) |
| Q-03 | Andradite**        | 1160           | 7 day | An (a=12.051Å)              |
| Q-04 | "                  | 1170           | 5 h   | An + tr Pw + tr He          |
| Q-05 | "                  | 1175           | 5 h   | Pw + He                     |
| Q-07 | "                  | 1185           | 5 h   | Pw + He                     |
| Q-08 | "                  | 1190           | 5 h   | Pw + He + tr L              |
| Q-09 | "                  | 1200           | 5 min | Pw + He + L                 |
| Q-11 | "                  | 1200           | 2 h   | Pw + He                     |
| Q-12 | "                  | 1220           | 2 h   | Pw + He + L                 |
| Q-14 | Pw + He            | 1220           | 2 h   | Pw + He                     |
| Q-15 | Andradite**        | 1250           | 2 h   | Pw + He + L                 |
| Q-19 | "                  | 1250           | 1 day | Pw + He                     |
| Q-20 | "                  | 1285           | 1 day | Pw + L                      |
| Q-21 | Pw + He            | 1285           | 1 day | Pw + He                     |
| Q-23 | Andradite**        | 1295           | 2 h   | Pw + He + L                 |
| Q-24 | "                  | 1295           | 1 day | Pw + L                      |

\* : obtained from hydroandradite.

\*\* : obtained from wollastonite and hematite.

† Abbreviations : An, Andradite; Pw, Pseudowollastonite; He, Hematite; L, Liquid; tr, trace.

and hematite. The somewhat higher decomposition temperature of the andradite obtained from wollastonite and hematite may be explained by considering the stability of a solid solution of andradite with excess Si<sup>4+</sup>, vacancies, and ferrous iron. A number of defect garnets have been reported by van Hook (1962) and Ronninger and Mill (1973). All ionic sites in the garnet structure could conceivably have vacancies.

In the andradite from wollastonite and hematite ( $a = 12.051 \text{ \AA}$ ) quenched after holding for short period at 1190° to 1250°C, a non-equilibrium glass phase was observed, while in the mixture of pseudowollastonite and hematite quenched at the same condition no glass phase was found. Formation of the glass phase might be attributed to an assumed melting of the solid solution of the andradite. The similar non-equilibrium melting has been observed

by superheating impure quartz (Ainslie, MacKenzie, and Turnbull, 1960).

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