Memo Report C-54-96

CHEMISTRY RESEARCH DEPARTMENT

Research Laboratory

April 28, 1954

Report on the Paper "High Pressure Minerals"

By Loring Coes, Jr., Norton Co. given at the

American Ceramic Society Meeting April 21, 1954.

H. Tracy Hall

Mechanical Investigations Section

Abstract: Coes reported equipment had been developed for attaining 45,000 atmospheres and 1000° C simultaneously. Equipment was not described. The P and T requirements as well as the chemical reactions to synthesize several silicates were given. Diamonds were not discussed.

Coes began his paper by stating that the Norton Company had been engaged in high-pressure, high-temperature work for several years and had succeeded in building equipment for simultaneously attaining temperatures of 1000° C or above at 40,000 ats. pressure. At 30,000 ats. their pressure is known to ± 1000 ats. and at 900-1000° C temperature is known to ± 30° C.

Using this equipment, Coes synthesized garnets and other silicates present in eclogite rock. Eclogite rock, a collection of silicates, is known to have formed at high pressure and temperature. Garnets have the general chemical formula $R_3''R_2'''(SiO_4)_3$ where R″ is Ca, Mg, Fe or Mn and R_2''' is Al, Fe, Ti or Cr.

Coes made the following garnets using conditions specified:

Pyrope, $Mg_3Al_2(SiO_4)_3$ about 30,000 ats. required at 900° C

(1) $2MgO + MgCl_2 * 6H_2O + 2Al(OH)_3 + 3SiO_2 \rightarrow Mg_3Al_2(SiO_4)_3$

(2) $Mg_3 * 2SiO_2 * 2H_2O + Al_2O_3 * 2SiO_2 * 2H_2O \rightarrow Mg_3Al_2(SiO4)_3 + SiO_2$

The exact thermodynamic conditions (equilibrium point) necessary for the synthesis of pyrope could not be determined. Competing reaction rates seemed to play an important role. Enstatite ($MgSiO_3$) was often formed instead of pyrope. The system was very sensitive to minor changes in conditions, for example, the presence of iron allows formation of pyrope at 25,000 atmospheres instead of 30,000 at 900° C.

I used a 35mm camera to photograph the slides as Coes showed them on the screen. Fig. 1 is a photograph of his synthetic pyrope. When queried as to the size of the crystals, Coes' only reply was that the magnification of the microscope used was 120X the usual field of view at 120 power is around 1400 µ diameter. Guessing that the picture encompasses most of the field of view gives a diameter of about 200 µ for the crystals.

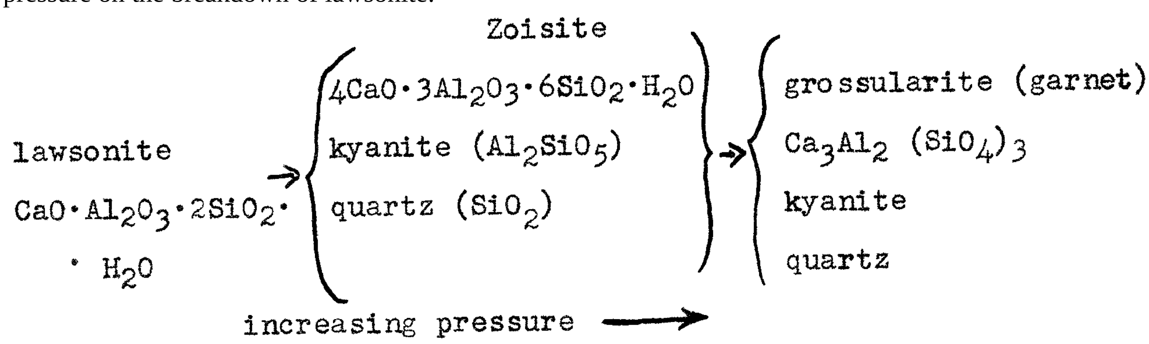
Andradite $Ca_3Fe_2\ (SiO_4)_3$ 20,000 ats., 900° C

Almandite $Fe_3Al_2\ (SiO_4)_3$ 20,000 ats., 900° C

Fig. 2 is a photograph of either Andradite or Almandite. The other members of the garnet family found in eclogite are Spessarite $Mn_3Al_2\ (SiO_4)_3$, Grossularite $Ca_3Al_2\ (SiO_3)_4$, and uvarovite $Ca_3Cr_2\ (SiO_4)_3$. Conditions for their synthesis were not given.

Two garnets not found in nature were synthesized. They were $Mg_3Fe_2\ (SiO_4)_3$ and $Fe_3Fe_2\ (SiO_4)_3$. Conditions were not given.

Garnet formation is favored by increasing pressure. The following scheme gives the effect of pressure on the breakdown of lawsonite:



Other silicate minerals were also synthesized. As examples, Coes cited a sodium, chromium pyroxene requiring 20,000 ats. at 900° C and Jadeite requiring the same conditions according to the following chemical reactions:

(1) 2NaCl + Al2O3 * 2SiO2 * 2H2O + 2SiO2→2Na Al $(SiO_3)_2$(Jadeite) + ?

or

(2) $6NaMnO_4 + 5Al_2O_3 * 2SiO_2 * 2H_2O + SiO_2 \rightarrow 6Na\ Al\ (SiO_3)_2$(Jadeite) + $2Mn_3Al_2(SiO_4)_3$ (Spessarite)

Jadeite crystals are shown in Fig. 3.

Kyanite (Al_2SiO_5) is often a by-product in the synthesis of high pressure minerals. Kyanite is found as by-products with:

Sillimanite	Al_2SiO_5
Andalusite	Al_2SiO_5

Jadeite	$NaAl\ (SiO_3)_2$
Garnet (all types)	$R_3''R_2'''(SiO_4)_3$
Dense silica	SiO_2
Enstatite	$Mg\ SiO_3$
Corundum	Al_2O_3
Zoisite	$Ca_2\ (AlOH)\ Al_2\ (SiO_4)_3$
Lawsonite	$H_4CaAl_2Si_2O_{10}$
Diaspore	$Al_2O_3 * H_2O$
Staurolite	$H_2O * 2FeO * 5Al_2O_3 * 4SiO_2$

Its synthesis is very insensitive to chemical conditions. Coes pointed to the dark aggregates such as at A in Fig. 4 as being examples of Kyanite forming in a silicate system. He didn't identify the other crystals such as at B. Most of the crystals on the slide (such as at B) are, however, readily recognized as dense silica. Coes previously reported the synthesis of dense silica in Science, July 31, 1953. They are now doing x-ray work on single crystals. Crystals of dense silica have been grown to diameters of 1mm. Coes hinted that the crystals may have useful piezoelectric properties. A mineral of compositions $Al_2\ (SiO_3)_3$ has been synthesized at 45,000 ats. and 900° C. This is the highest pressure required to form a mineral yet found. (I presume at 900° C – most of their work seems to be done at this temperature.)

Sillimanite (Al_2SiO_5), Andalusite (Al_2SiO_5), Corundum (Al_2O_3) and other minerals have also been made at high pressure and temperature.

Coes said that he didn't wish to discuss the high-pressure, high-temperature equipment because of intention to publish that information soon.

Coes avoided questioning by not appearing until time for his paper to start and by "having to catch a plane to Worcester" as soon as it was over.

Coes presentation was rapid and difficult to follow. Consequently, there may be some errors in this report.

H. Tracy Hall

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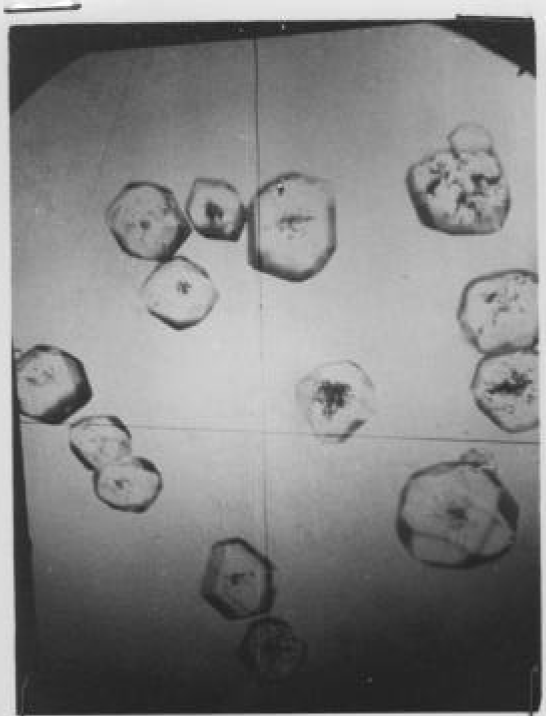

FIG. 1

FIG. 2

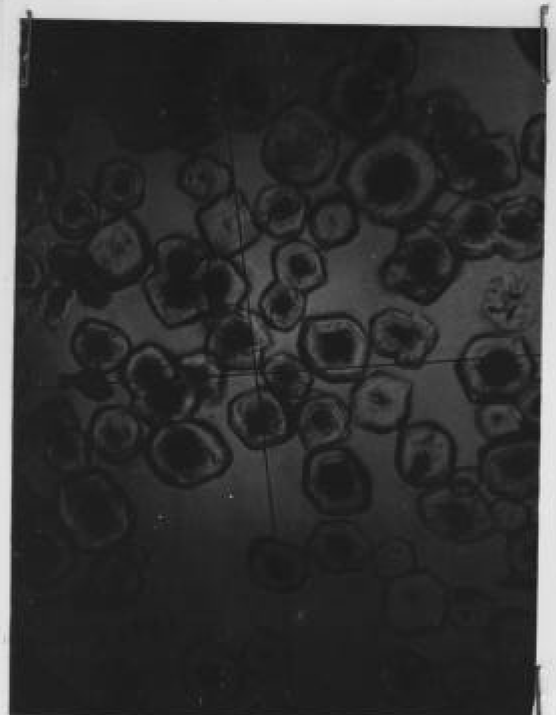

FIG. 3

FIG. 4