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HIGH-PRESSURE MINERALS

By Loring Coes, Jr.

Norton Company
Worcester, Massachusetts

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During the past several years, a study of high-pressure minerals has been in progress in this laboratory. At the outset this work consisted of a systematic survey of the naturally occurring high-pressure minerals, especially those found in the eclogite rocks.

New techniques, to be described in a later communication, were devised for working in closed systems at pressures up to 45,000 atmospheres and temperatures up to 1000°C.

Using these techniques, it was found possible to synthesize most of the well-known high-pressure minerals and to determine approximately their fields of stability. The exact determination of the fields of stability was not possible in many cases because the products produced reactions which seemed to be controlled by rates influenced by minor changes in the composition of the reaction mixture.

Table I shows the species synthesized, together with the reaction mixture found to be the most favorable and the temperature and pressure under which the mineral crystallized as the major reaction product. The conditions listed are by no means necessary for the formation of the species. Many can be formed under lower pressure, but they are accompanied by larger amounts of less densely packed by-products.

All the minerals listed in Table I were obtained in well-crystallized form. They were identified by optical and X-ray methods. No discrepancies from accepted values were observed in any case.

Table I. Minerals Synthesized

Species	General formula	Best reaction mixture	Best conditions: Pressure (atm.)	Best conditions: Temp. (°C.)
Garnet group				
Andradite	$Ca_3Fe_2(SiO_4)_3$	Wollastonite, Fe_2O_3, $FeCl_3$	20,000	900
Uvarovite	$Ca_3Cr_2(SiO_4)_3$	Wollastonite, $Cr(OH)_3$, $CrCl_3$	20,000	900
Grossularite	$Ca_3Al_2(SiO_4)_3$	Kaolin, SiO_2, CaO, $CaCl_2$	20,000	900
Pyrope	$Mg_3Al_2(SiO_4)_3$	Kaolin, SiO_2, MgO, $MgCl_2$	30,000	900
Spessartite	$Mn_3Al_2(SiO_4)_3$	SiO_2, $Al(OH)_3$, $Al(NO_3)_3 \cdot 6H_2O$, MnO_2	10,000	900
Almandite	$Fe_3Al_2(SiO_4)_3$	Kaolin, Fe_2O_3, SiO_2, $FeCl_2 \cdot 4H_2O$	10,000	900
Aluminum silicates				
Andalusite	Al_2SiO_5	Kaolin + various sodium salts	10,000	700
Sillimanite	Al_2SiO_5	Kaolin + various fluorides	10,000	700
Kyanite	Al_2SiO_5	Kaolin + $Al(OH)_3$	20,000	900
Topaz	$Al_2SiO_4(F,OH)_2$	AlF_3, $Al(OH)_3$, SiO_2	20,000	900
Pyroxenes				
Jadeite	$[Na_2Al_2(SiO_3)_4]$	Kaolin + Na_2CO_3	20,000	900
$NaCr(SiO_3)_2$		$Na_2Cr_2O_7$ + SiO_2	20,000	900
Epidote group				
Epidote	$Ca_2(FeOH)Fe_2(SiO_4)_3$	Kaolin, SiO_2, CaO, $FeCl_2 \cdot H_2O$	10,000	800
Zoisite	$Ca_2(AlOH)Al_2(SiO_4)_3$	Same as grossularite	10,000	800
Miscellaneous				
Vesuvianite	$Ca_{10}Al_4(Mg,Fe)_2Si_9O_{34}(OH)_4$	Kaolin, $Ca(OH)_2$, $MgCl_2 \cdot 6H_2O$	10,000	700
Lawsonite	$H_4CaAl_2Si_2O_{10}$	Kaolin, $Ca(OH)_2$, $Ca(NO_3)_2 \cdot 6H_2O$	10,000	700
Staurolite	$HFeAl_5Si_2O_{13}$	Na_2SiO_3, $Al(OH)_3$, SiO_2, MgO, $FeCl_2 \cdot 6H_2O$	10,000	800
Bertrandite	$H_2Be_4Si_2O_9$	BeO, SiO_2, H_2O, NH_4Cl	20,000	900

In the garnet group, spessartite, uvarovite, and grossularite are low-pressure species. Almandite and andradite are in the intermediate-pressure range, whereas pyrope requires the highest pressure of all known garnets.

Pyrope, the garnet of eclogite, has not been synthesized at pressures below 30,000 atmospheres at any temperature. The presence of a small amount of iron greatly reduces the formation pressure and pyrope containing 5% almandite can be synthesized at 25,000 atmospheres. Since all natural pyrope contains at least this much almandite, no evidence was found to show that any natural garnet was crystallized at a pressure in excess of 25,000 atmospheres.

In the aluminum silicate series, kyanite is formed easily under pressure and is often formed as a by-product in reactions carried out at high pressure. Its formation is very insensitive to the chemical composition of the reaction mixture. It has been found as a by-product in the synthesis of all the aluminum-containing silicates listed with the exception of topaz. The simultaneous crystallization of kyanite and topaz has never been observed. The formation of one seems to exclude the formation of the other.

What controls the formation of andalusite and sillimanite is not completely clear. Both can be crystallized in the pressure and temperature range in which kyanite can also crystallize, but their formation is controlled by chemical factors. Andalusite has not been formed in the absence of sodium. Sillimanite has not been formed in the absence of fluorine. The evidence indicates a complete solid solution series from sillimanite to topaz. This helps to explain the observed fact that kyanite and topaz are never formed in the same reaction.

The pyroxene group minerals, jadeite and the corresponding sodium chromium silicate, also can be synthesized under pressure. The latter is unknown as such in nature, but it is a component of the chrome diopside of eclogites. These pyroxenes can be formed at a pressure less than 20,000 atmospheres at a temperature of 900°C. and therefore represent lower pressure phases than the eclogite garnets.

The epidote and zoisite occasionally found in eclogites can be synthesized at even lower pressures, as can the minerals vesuvianite, lawsonite, and staurolite.

Overall, the minimum pressure at which the eclogite rocks could have formed is fixed by the pyrope garnet which requires a pressure of 30,000 atmospheres at 900°C.

During the course of this work, some new high-pressure silicates were discovered. These include the garnets $Mg_3Fe_2(SiO_4)_3$, $Mn_3Fe_2(SiO_4)_3$, and $Mg_3Cr_2(SiO_4)_3$ and an aluminum silicate, $Al_2O_3 \cdot 3SiO_2$. The aluminum silicate requires a pressure of 40,000 atmospheres at 900°C. for its formation and is the highest pressure phase discovered thus far. It separates from a variety of systems containing alumina and silica at this pressure or above. Even some garnets, particularly spessartite, are decomposed by pressures over 40,000 atmospheres with the formation of this silicate.

Its properties are as follows: $N\alpha = 1.67$; $N\gamma = 1.675$; biaxial positive; $2V = 90°$; triclinic.

Work is continuing to determine the fields of stability of the minerals synthesized.