

# SUBSTITUTIONS IN THE OLIVINE LAYER OF NORBERGITE

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**Abstract.** The cation site of the olivine layers of norbergite may be occupied by several different ions ranging in size from Al to Ca. Silicates which in their pure state are structurally different from olivine may form olivine structure slabs in norbergite.

## Introduction

The first successful synthesis of humite minerals seems to have been done more than one hundred years ago by DAUBRÉE (1851). Later JANDER and FETT (1939), VAN VALKENBURG (1955 and 1961), RANKAMA (1947), BUCKLE and TAYLOR (1958) and HINZ and KUNTH (1960) produced artificial humite minerals, and SAHAMA (1953) discussed the general and physical chemistry of humites.

The atomic structure of the humite minerals, of which norbergite is one, is formed by alternating slabs of olivine and sellaite arranged parallel to (100) (TAYLOR and WEST 1929). The general humite formula may be written  $(A_2BC_4)_n \cdot Mg(F,OH)_2$  where  $n$  is a whole number between 1 and 4. Because of the change of symmetry when  $n$  is successively changed, there is no mixed crystal formation among the humite minerals (e.g. HINZ and KUNTH 1960).

Natural chondrodite and clinohumite are monoclinic and have oblique extinction. The synthetic analogues have parallel extinction and are therefore difficult to distinguish optically from the orthorhombic minerals norbergite and humite. The different humite group minerals, however, are easily distinguished by their X-ray powder patterns, and the diagnosis used for the present study is based upon powder technique. The results presented below are confined to synthetic norbergite, the properties of which may be somewhat different from its natural analogue.

Natural olivines may be considered as mixed crystals of the three end members forsterite, fayalite, and tephroite. Monticellite has an atomic structure similar to that of olivine, but the atomic sites occupied by Mg in forsterite are split into two different sets of sites which are occupied by either Ca or Mg (BROWN and WEST 1927). Because of this structural difference between forsterite and monticellite, the mixed crystal formation between them is limited.

It was shown by O'DANIEL and TSCHUISCHWILI (1942) that the low temperature modification of  $\text{Ca}_2\text{SiO}_4$  has an atomic structure similar to that of forsterite. BREDIG (1949), therefore, suggested the presence of an extensive solid solution in the system  $\text{Ca}_2\text{SiO}_4\text{-Mg}_2\text{SiO}_4$ . The experimental data of FERGUSON and MERWIN (1919), RICKER and OSBORN (1953), and ROY (1956) demonstrate that mixed crystals are found only within very limited compositional ranges of this system, thus making Bredig's suggestion untenable.

The present experiments were undertaken to see if this limited mixed crystal formation occurred in the system  $\text{Mg}_2\text{SiO}_4\cdot\text{MgF}_2\text{-Ca}_2\text{SiO}_4\cdot\text{MgF}_2$  also, or if the slabs of sellaite exerted a stabilizing effect upon the olivine structure components in norbergite.

### Experiments

At  $1000^\circ\text{C}$  the decomposition of  $\text{MgF}_2$  under formation of  $\text{MgO}$  is comparatively slow and may be disregarded for the 30-minute runs of most of the present syntheses. At higher temperatures the decomposition of  $\text{MgF}_2$  is rapid and may interfere significantly with the experimental results (see e.g. RANKAMA 1947). Syntheses giving diffraction lines originating from periclase were considered as failed and are not included in the present study.

Mixtures of  $\text{CaCO}_3$ ,  $\text{MgO}$ , and  $\text{SiO}_2$  corresponding to 10% intervals between  $\text{Mg}_2\text{SiO}_4$  and  $\text{Ca}_2\text{SiO}_4$  were sintered at  $1300^\circ\text{C}$  and mixed with  $\text{MgF}_2$  to give norbergite proportions. These mixtures were heated for 30 minutes at  $1000^\circ\text{C}$ , and they all appeared to yield one phase only. Their X-ray powder pattern corresponds to that of norbergite, and, consequently, the norbergite type minerals corresponding to the system  $\text{Mg}_2\text{SiO}_4\cdot\text{MgF}_2\text{-Ca}_2\text{SiO}_4\cdot\text{MgF}_2$  appear to form a complete mixed crystal series in contradistinction to the system  $\text{Mg}_2\text{SiO}_4\text{-Ca}_2\text{SiO}_4$  where the mixed crystal formation is very restricted.

Table 1. Various  $A_2BC_4$  compounds and corresponding humite group minerals. Data from Buckle and Taylor (1958), Strunz (1957) and this work

$A_2BC_4$ minerals		Corresponding $(A_2BC_4)_n \cdot DE_2$ minerals
Olivines orthorhombic	$Mg_2SiO_4$	Natural and synthetic humites
	$Fe_2SiO_4$	Unknown
	$Mn_2SiO_4$	Alleghanyite
Monticellite orthorhombic	$CaMgSiO_4$	$CaMgSiO_4 \cdot MgF_2$
Calcio-olivine orthorhombic	$Ca_2SiO_4$	$Ca_2SiO_4 \cdot MgF_2$ $(Ca_2SiO_4)_2 \cdot Ca(OH)_2$
Merwinite monoclinic	$Ca_3Mg(SiO_4)_2$	$Ca_3Mg(SiO_4)_2 \cdot MgF_2$
Willemite trigonal	$Zn_2SiO_4$	$Zn_2SiO_4 \cdot MgF_2$ with Mn possibly Hodgkinsonite

In the system  $Mg_2SiO_4$ – $Ca_2SiO_4$  there is one phase which is structurally different from olivine: monoclinic merwinite,  $Ca_3Mg(SiO_4)_2$ , while the composition corresponding to merwinite in the norbergite series has norbergite structure. This indicates that the sellaite layers of norbergite favour the existence of olivine structure slabs even for compositions which do not exist as olivine structure minerals in their pure state.

This point is further exemplified by the existence of the yellow zinc silicate 'norbergite' which formed in small amounts by solid state reaction of trigonal willemite ( $Zn_2SiO_4$ ) and  $MgF_2$  at 1000° C.

It appears that even larger variations in the ionic radii in the olivine slabs of the synthetic norbergite type minerals are tolerated. The norbergite analogue of chrysoberyl seems to have formed in smaller quantities in a mixture of  $Al_2BeO_4$  and  $MgF_2$  heated at 1150° C for 30 minutes. Attempts to replace Al by the larger Y, thus producing a  $Y_2BeO_4 \cdot MgF_2$  'norbergite' were unsuccessful.

Table 2. Length of unit cell edges in  $A$  units of some norbergite type minerals

		$a_0$	$b_0$	$c_0$
Fluoro-norbergite .....	$Mg_2SiO_4 \cdot MgF_2$	8.73	4.67	10.32
Fluoro-calcio-norbergite .....	$Ca_2SiO_4 \cdot MgF_2$	8.73	4.69	10.36
Zinc-silicate norbergite .....	$Zn_2SiO_4 \cdot MgF_2$	8.72	4.67	10.3

### Conclusions

The small changes in unit cell edge lengths of the  $Mg_2SiO_4 \cdot MgF_2$ - $Ca_2SiO_4 \cdot MgF_2$  norbergite series support the idea that norbergite is constructed of a rigid oxygen-sellaite framework (Table 2). The presence of sellaites layers in humite type minerals stabilizes the olivine structure of the interlayered slabs so that compounds like  $Ca_3Mg(SiO_4)_2$  and  $Zn_2SiO_4$ , whose structures differ from that of olivine, reconstruct their atomic arrangement to form olivine slabs in norbergite type minerals.

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