

A CALCIUM ANALOGUE OF CHONDRODITE

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ABSTRACT

A calcium analogue of chondrodite, of composition $\text{Ca}_3(\text{SiO}_4)_2(\text{OH})_2$, has been prepared hydrothermally from tricalcium silicate at 600–700° C. The unit-cell is monoclinic with a 11.42, b 5.05, c 8.94 Å, β 109.3°, space-group $\text{P}2_1/a$, $Z=2$. The crystals are prisms with length b , very low birefringence, positive elongation, and mean refractive index 1.630. Dehydration occurs at 650–700° C. The name calcio-chondrodite is suggested.

INTRODUCTION

In an earlier paper on tricalcium silicate hydrate (Buckle, Gard, and Taylor, 1958), mention was made of a synthetic silicate mineral or mixture of minerals loosely termed "gamma-hydrate(s)." The name was chosen because the x-ray powder pattern closely resembled that of dicalcium silicate γ -hydrate or dicalcium silicate hydrate (C) (Heller and Taylor, 1956). The substance was found as an impurity in tricalcium silicate hydrate preparations made hydrothermally at 350–500° C. It has now been prepared in a purer state and its composition and crystallographic properties determined. These show that it is a calcium analogue of chondrodite $((\text{Mg}, \text{Fe})_5(\text{SiO}_4)_2(\text{OH}, \text{F})_2)$, and the name calcio-chondrodite will be used.

PREPARATION AND OPTICAL EXAMINATION

Pastes of anhydrous tricalcium silicate ($\text{Ca}_3\text{O}(\text{SiO}_4)$; 0.5 gm.) and water (0.3–0.5 ml.) were autoclaved in closed bombs of 7 ml. capacity at 600–700° C.; the pressures developed were not known accurately but were estimated from the degree of filling of the bombs to be between 3000 and 5000 p.s.i. The technique was similar to that already described (Buckle, Gard, and Taylor, 1958). Below 600° C., tricalcium silicate hydrate was also formed, and above 700° C. other, as yet unidentified phases, appeared. Times of autoclaving varied from one to three days, the longer times giving better crystallized products.

A typical photomicrograph of one of the preparations (Fig. 1) shows, chiefly, prismatic crystals up to 70 μ long. These appear pseudo-hexagonal in the most commonly observed orientation and somewhat resemble olivine crystals. They had positive elongation, very low birefringence, and mean refractive index 1.630 ± 0.003 . Many showed either simple or multiple twinning across a plane parallel to the prism axis. A little calcite was also observed.

X-RAY INVESTIGATION

Rotation and $h0l$, $h1l$, and $h2l$ Weissenberg photographs were taken

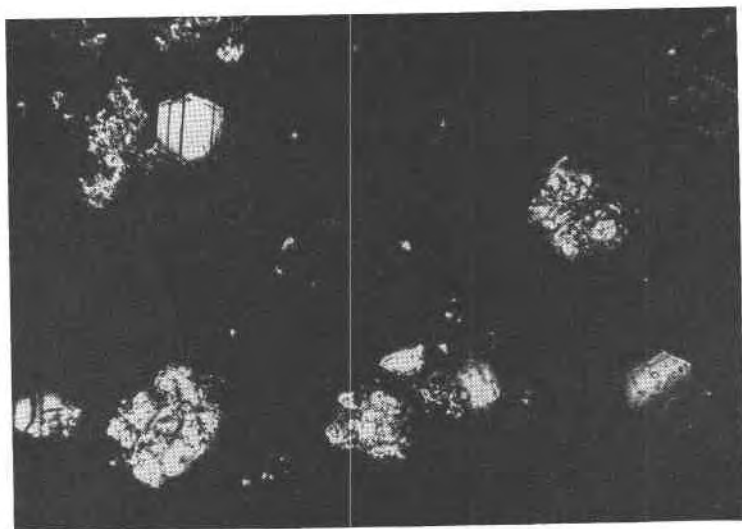


FIG. 1. Photomicrograph of a typical preparation, showing simple and twinned prismatic crystals of calcio-chondrodite. Crossed nicols, $\times 300$.

about the prism axis (b), and rotation and equatorial Weissenberg photographs were taken about the axis normal to (001). Filtered copper radiation was used for all exposures. The unit-cell was found to be monoclinic with a 11.4, b 5.05, c 9.0 Å, β 108.4°. $0k0$ reflections were absent for k odd, and $h0l$ for h odd; the space-group is thus $P2_1/a$. The parameters a , c , and β are related by the equation $a = -4c \cos \beta$, and all reflections are therefore indexable in terms of an orthorhombic cell with a 11.4, b 5.05, c 34.2 Å. The crystal used was twinned across (001), which enhanced the pseudo-orthorhombic character.

X -ray powder data for a typical preparation are given in Table 1. Spacings larger than 1.8 Å were indexed, chiefly by superposition of powder and rotation photographs. A few weak lines (marked *) could not be indexed and are probably due to impurities; some can be attributed to calcite. From the indexing of the powder data, the monoclinic cell parameters were refined to a 11.42, b 5.05, c 8.94 Å, all ± 0.05 Å, β $109.3^\circ \pm 0.5^\circ$.

THERMAL DECOMPOSITION, ANALYSIS, AND CELL CONTENTS

A dehydration isobar (Fig. 2) was obtained at $p_{H_2O} = 6$ mm., using the procedure already described (Buckle, Gard, and Taylor, 1958). Loss of weight occurred in three stages. Comparison with reference data showed that the first, at 380° C., could be attributed to calcium hydrox-

TABLE 1. X-RAY POWDER DATA FOR CALCIO-CHONDRODITE
 Obtained using 6 cm. and 11.46 cm. diameter cameras with CuK_α radiation.

Observed (spacings (Å), intensities, and indices)			Calculated spacings (Å)	Observed (spacing (Å), intensities, and indices)			Calculated spacings (Å)
8.45	vw	001	8.45	2.54	ms	11 $\bar{3}$	2.55
5.42	s	200, 20 $\bar{1}$	5.40	2.51	m	212, 21 $\bar{3}$	2.52
4.24	w	002	4.23	2.48	m†	41 $\bar{1}$	2.49
3.98	mw	201, 20 $\bar{2}$	3.99	2.46	vw	120, 12 $\bar{1}$	2.46
3.79	ms	111	3.81	2.41	vvw*		
3.67	w	210, 21 $\bar{1}$	3.69	2.36	vw	401, 40 $\bar{3}$	2.37
3.31	s	11 $\bar{2}$	3.33	2.27	w*		
3.23	vvw*			2.02	w	402, 40 $\bar{4}$	2.00
3.11	vvw*			1.914	vvw*		
3.02	vs†	31 $\bar{1}$	3.03	1.903	vs	222, 22 $\bar{3}$	1.905
2.92	s	310	2.94	1.898	mw	42 $\bar{1}$	1.897
2.89	s	202, 20 $\bar{3}$	2.91	1.870	vvw*		
2.84	vvw	40 $\bar{1}$	2.85	1.846	mw	420, 42 $\bar{2}$	1.845
2.76	s	31 $\bar{2}$	2.78	1.820	mw	511	1.818
2.69	m	400, 40 $\bar{2}$	2.70	1.801	ms	600, 60 $\bar{3}$	1.805
2.57	ms	311	2.58				

Observed spacings (Å) and intensities (continued)

1.775	w	1.504	vvw	1.292	vvw	1.145	w
1.724	m	1.494	vvw	1.277	w	1.12	w
1.695	w	1.469	vw	1.266	vw	1.105	vw
1.682	ms	1.459	w	1.261	w	1.09	w
1.657	s	1.433	vw	1.242	vw	1.075	mw
1.619	vw	1.418	vw	1.232	w	1.065	vw
1.599	vvw	1.405	vw	1.218	vvw	1.04	vw
1.575	vvw	1.388	vvw	1.207	vw	1.02	m
1.552	m	1.376	vvw	1.196	vw	0.981	mw
1.540	vvw	1.352	vw	1.173	m	0.862	w
1.523	vvw	1.331	vvw	1.160	m	0.813	ms

* Lines probably due to impurity.

† Lines probably partly due to calcite.

ide, and the second, at 530–600° C., to calcite. The final stage, at 650–750° C., therefore represents decomposition of the silicate mineral. From the heights of the steps attributed to calcium hydroxide and calcite, the phase composition was estimated to be calcium hydroxide, 3%; calcite, 11%; silicate (by difference), 86%. X-ray powder photographs of the residue after heating at 750° C. gave a slightly modified pattern of γ -dicalcium silicate.

Chemical analysis of the specimen used for the dehydration work gave

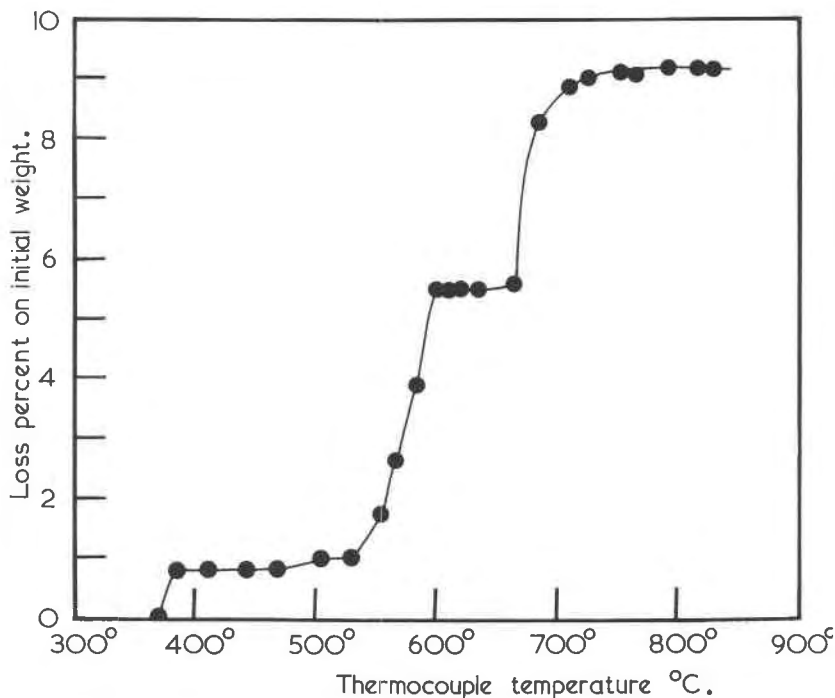


FIG. 2. Dehydration isobar of a typical preparation. The steps at 380°, 530–600°, and 650–750° C. represent decomposition of calcium hydroxide, calcite, and calcio-chondrodite respectively.

Ca: Si = 2.88. In conjunction with the evidence from the dehydration isobar, this leads to the composition $5\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ for the silicate mineral. The density of this specimen, determined by suspension of compressed pellets in bromoform-benzene mixtures after degassing under reduced pressure, was 2.80 gm.cm.^{-3} . Correction for calcium hydroxide and calcite gives the value 2.84 gm.cm.^{-3} . This agrees well with the theoretical value of 2.85 gm.cm.^{-3} calculated for the cell contents $2[5\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}]$.

DISCUSSION

The present results show that the substance previously called "gamma-hydrate(s)" is in fact a single phase of composition $5\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$. In Table 2, some properties of olivine, γ -dicalcium silicate, chondrodite, and the new compound are compared. γ -dicalcium silicate is known to have a structure resembling that of olivine (O'Daniel and Tscheischwili, 1942), and the relation of the new compound to γ -dicalcium silicate is analogous to that of chondrodite to olivine. It seems reasonable to con-

TABLE 2. COMPARISON OF PROPERTIES OF OLIVINE, CHONDRODITE, γ -DICALCIUM SILICATE, AND CALCIO-CHONDRODITE

Composition	Olivine (Mg,Fe) ₂ SiO ₄	Chondrodite (Mg, c) ₂ (SiO ₄) ₂ (F,GF) ₂	γ -dicalcium silicate Ca ₂ SiO ₄	Calcio-chondrodite Ca ₃ (SiO ₄) ₂ (OH) ₂
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Monoclinic
Unit cell	<i>b</i> 10.21 Å <i>a</i> 4.755 Å <i>c</i> 5.985 Å —	<i>a</i> 10.27 Å <i>b</i> 4.733 Å <i>c</i> 7.87 Å β 109°2'	<i>b</i> 11.28 Å <i>a</i> 5.06 Å <i>c</i> 6.78 Å —	<i>a</i> 11.42 Å <i>b</i> 5.05 Å <i>c</i> 8.94 Å β 109°18'
$-a/c \cos \beta$	—	1.06	—	1.00
Space group	<i>Pbnm</i>	<i>P</i> 2 ₁ / <i>a</i>	<i>Pbnm</i>	<i>P</i> 2 ₁ / <i>a</i>
Z	4	2	4	2
Habit	Prisms often elongated $\parallel c$	Often (010) tablets	Prisms	Prisms elongated $\parallel b$
Twinning	Rare	Multiple on (001)	?	Single or multiple across a plane $\parallel b$
Principal source of data	Bragg and Brown (1926)	Taylor and West (1928)	O'Daniel and Tscheischwili (1942)	This investigation

clude that it is a calcium analogue of chondrodite, with the ionic constitution $(Ca_3(SiO_4)_2(OH)_2)$.

Chondrodite belongs to a series of minerals structurally derived from olivine, which also includes clinohumite, humite, and norbergite. Taylor and West (1928, 1929), who determined the crystal structures of the minerals in this series, showed that their cell parameters could be calculated from those of olivine. Analogous calculations for the calcium series give the results:

Calcium analogue of:	Formula	Cell parameters	Z		
			<i>c</i> (Å)	β	
Clinohumite	Ca ₉ (SiO ₄) ₄ (OH) ₂	<i>a</i> = 5.05 Å	15.52	100.5°	2
Humite	Ca ₇ (SiO ₄) ₃ (OH) ₂				
Chondrodite	Ca ₅ (SiO ₄) ₂ (OH) ₂	<i>b</i> = 11.28 Å	8.94	108.4°	2
Norbergite	Ca ₃ (SiO ₄) ₂ (OH) ₂				
			10.17	90°	4

The predicted values for calcio-chondrodite agree well with those actually found. Calcium analogues of the other three minerals are so far unknown; the resemblance between the *x*-ray powder patterns of calcio-chondrodite and dicalcium silicate hydrate (C) suggests a near relationship, which is being further investigated.

Calcio-chondrodite apparently differs from the magnesian or iron-containing minerals in that no isomorphous replacement of hydroxyl by fluorine is essential to its composition. All natural specimens of chondrodite appear to contain fluorine, and attempts to synthesize it have been successful only when fluorine was present (Van Valkenburg, 1957).

The *x*-ray powder data given by Keevil and Thorvaldson (1936) for tricalcium silicate hydrate suggest that their product contained calcio-chondrodite as an unsuspected impurity. More recently, Roy (1958) has mentioned a "Phase X" formed under conditions comparable with those used to prepare calcio-chondrodite in the present investigation. Comparison of her optical and *x*-ray powder data for this phase with those of our calcio-chondrodite¹ suggest that the two are probably identical.

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¹ Private discussion, September 1957.