Subsolidus relations between CaAl₂Si₂O₈ and Ca₂P₂O₇

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Abstract

A compound containing equal molar proportions of anorthite and calcium pyrophosphate was synthesized under anhydrous conditions in the range of 1130 to 1260°C. Above this range it melts incongruently to anorthite, β Ca₃P₂O₈, and liquid. This intermediate compound has a repeat distance of 11.5A, representing a layer of α Ca₂P₂O₇ and a half cell of anorthite stacked normal to the *a–b* plane. Parameters are: $a = 9.559(3)$, $b = 10.231(4)$, $c = 12.083(5)$A, $\alpha = 93.17(2)$, $\beta = 108.12(2)$, and $\gamma = 89.10(2)$. Cell parameters of anorthite synthesized in equilibrium with this intermediate compound indicate little solid solution of phosphorus in anorthite.

Introduction

Anorthite is an end member of feldspar, the most abundant mineral group in the lithosphere, and apatite is an ubiquitous accessory mineral in igneous rocks. In feldspar the aluminum and silicon are in tetrahedral coordination, as is phosphorus in apatite. The close association of the minerals and the presence of oriented apatite in host feldspars suggest that there may be some solid solution between the minerals, or an intermediate phase at elevated temperatures. This paper reports the relations along joins representing compositions intermediate between anorthite and calcium phosphates.

Relations among dicalcium silicate and tricalcium phosphate were reported by Nurse *et al.* (1959) and Gutt (1963). They show continuous solid solution between α dicalcium silicate (C₂S) and tricalcium phosphate (C₃P) at temperatures above 1450°C. Nagelschmidtite (C₇PS₂) is isostructural with α C₂S and is part of this solid solution. Two intermediate phases at lower temperatures have limited solid solution. One composition can be represented ideally as (C₂S)₂(C₃P) and the other, called silicocarnotite, as (C₂S)(C₃P). Revised limits of solid solution for these phases have been reported by Fix *et al.* (1969).

Calcium pyrophosphate (C₂P) has a β–α inversion at 1140°C (Hill *et al.*, 1944); the parameters of the alpha polymorph are given by Calvo (1968). The relation between C₂S and C₂P and subsolidus relation among calcium aluminates and C₃P or C₂P are essen-

tially unknown; however, at liquidus and solidus temperatures there are no intermediate compounds.

The coupled substitution of aluminum and phosphorus for two silicons in alkali feldspars was reported by Simpson (1977). It was unknown whether a similar coupled substitution could be found for the calcium aluminum silicates or whether such substitutions would be negated by the stability of several of the calcium phosphates.

Experiments

Approach

Experiments were designed to provide a reconnaissance of the relations in part of the system CaO–SiO₂–Al₂O₃–P₂O₅, principally at 1200°C. Most compositions fall close to the join between CaAl₂Si₂O₈ (CAS₂) and Ca₂P₂O₇ (C₂P). Samples were prepared from reagent-grade CaCO₃, CaHPO₄, and Al₂O₃, laboratory-grade kaolin, and finely divided quartz. The reagents were mixed in alcohol, dried, and lightly compacted before sintering. All experiments were conducted in air, and temperatures were controlled to ±10°C. Experiments ranged from several days to several months.

Results

Mixtures along the CAS₂–C₂P join at 1000°C yielded anorthite with apatite [Ca₅(PO₄)₃OH] or β Ca₃P₂O₈ after two months. Reactions were in-

complete, and some reactants recrystallized. The crystallization of apatite in this system is consistent with early reports showing that the partial pressure of water vapor in air is sufficient for the formation of apatite, even at temperatures above 1000°C.

At 1200°C, mixtures between CAS_2 and C_2P reacted to yield a new compound. Based on the mixtures and yields, the composition is about $(CAS_2)(C_2P)$, and the phase will hereafter be called C_3APS_2. The phase is easily recognized by a strong (001) (11.5A) X-ray diffraction peak. Initially the phase was recovered from a rapidly cooled charge, but some charges have also been cooled slowly. The phase shows no evidence of decomposition as a result of the slow cooling or of holding at 805°C for 5 days. Liquidus relations were not determined; however, one sample raised to 1430° melted, at 1360° a quenched sample contained glass and euhedral crystals of β $Ca_3P_2O_8$, and at 1290°C the assemblage was anorthite, β $Ca_3P_2O_8$, and glass. Experiments at 1262°C yielded C_3APS_2. Thus, C_3APS_2 melts incongruently in the range of 1262–1290°C. It appears to be stable to temperatures at least as low as 805°, but its synthesis required temperatures above 1130°C.

Anorthite was synthesized at 1200°C, and its cell parameters were compared to anorthite synthesized in equilibrium with β $Ca_2P_2O_8$, calcium pyrophosphate, or orthorhombic $AlPO_4$. No significant differences in cell parameters were found between the feldspars synthesized. This lack of difference indicates either that little phosphorus enters anorthite or that phosphorus has little effect on cell parameters. Furthermore, the extensive substitution of aluminum and phosphorus for two silicons, as found for the alkali feldspars by Simpson (1977), is absent in anorthite.

Nature of C_3APS_2

Composition

C_3APS_2 was analyzed by electron microprobe with the Bence and Albee (1968) corrections. Ramona albite and fluorapatite were used as standards. Both slowly cooled and quenched samples were analyzed; no significant differences were found. The analyses, cast into atomic ratios based on 15 oxygen, and the standard deviations, are given in Table 1. The stoichiometry is nearly $Ca_3Al_2P_2Si_2O_{15}$; i.e., the compound contains essentially equal molar proportions of anorthite and calcium pyrophosphate molecules.

Table 1. Structural formula of C_3APS analyzed by electron microprobe

	Atomic Ratio	Ideal
Ca	2.90 (4)*	3
Al	1.99 (4)	2
P	1.95 (7)	2
Si	2.09 (6)	2

*parenthesized figures represent the estimated standard deviation (esd) in terms of least units cited for the value to their immediate left, thus 2.90(4) indicates an esd of 0.04.

The analyses show a slight calcium deficiency and silicon excess.

Crystallography

C_3APS_2 was crystallized by sintering and solid reaction; therefore the crystals are anhedral, small, and include crystals of corundum. Most C_3APS_2 crystals are equant with a diameter of 0.02 mm. The mean refractive index is 1.57, and the birefringence is low. Generally crystals have undulatory extinction.

X-ray diffractograms of C_3APS_2 show a strong reflection representing a d spacing of about 11.5A, giving the pattern the appearance of a layer silicate. Similarity between the $a–b$ parameters of anorthite and α $Ca_2P_2O_7$ suggests that C_3APS_2 may be a layered compound stacked normal to the $a–b$ plane. The sum of half of the polar axis for anorthite plus c for α $Ca_2P_2O_7$ is 11.5A, the value found for C_3APS_2.

Table 2. X-ray powder diffraction data for $Ca_3Al_2P_2Si_2O_{15}$

hkl	d(calc.) A	d(obs.) A	I	hkl	d(calc.) A	d(obs.) A	I
001	11.46	11.44	100	$\bar{2}$30	2.729	2.728	9
010	10.21	10.14	5	$\bar{2}\bar{2}$2	2.700	2.703	4
100	9.08	9.02	7	123	2.646	2.655	3
0$\bar{1}$1	7.84	8.01	6	040	2.554	2.544	46
$\bar{1}$11	6.67	6.70	4	2$\bar{1}$3	2.503	2.503	14
101	6.23	6.19	3	1$\bar{1}$4	2.472	2.476	3
002	5.73	5.77	14	302	2.386	2.387	15
0$\bar{1}$2	5.12	5.14	13	1$\bar{2}$4	2.303	2.303	5
$\bar{1}$12	5.11	5.09	8	$\bar{2}$15	2.276	2.277	5
021	4.57	4.66	3	1$\bar{4}$2	2.236	2.239	4
200	4.54	4.55	64	124	2.214	2.213	4
$\bar{1}$20	4.46	4.46	37	$\bar{4}$22	2.174	2.171	3
$\bar{2}$02	4.27	4.21	10	2$\bar{3}$3	2.084	2.084	9
003	3.82	3.82	20	143	2.040	2.039	10
$\bar{1}$13	3.79	3.76	3	plus 12 other peaks to 1.700			
$\bar{1}$13	3.65	3.66	4				
2$\bar{1}$1	3.61	3.60	15	a =	9.559 (3)* A		
220	3.39	3.39	3	b =	10.231 (4) A		
1$\bar{2}$2	3.35	3.35	16	c =	12.083 (5) A		
$\bar{3}$01	3.18	3.17	32	α =	93.17 (2)		
202	3.12	3.12	2	β =	108.12 (2)		
$\bar{1}$23	3.06	3.06	52	γ =	89.10 (2)		
$\bar{1}$04	3.02	3.02	12				
212	2.954	2.952	45				
$\bar{3}$10	2.905	2.901	17				
004	2.865	2.878	43				
$\bar{2}$23	2.831	2.825	55				
0$\bar{1}$4	2.799	2.780	20				

*parenthesized figures represent the estimated standard deviation (esd) in terms of least units cited for the value to their immediate left, thus 9.559(3) indicates an esd of 0.04.

Assuming a layered anorthite–α $Ca_2P_2O_7$ model, the diffraction pattern was indexed and the cell parameters calculated with the program of Appleman and Evans (1973). The observed and calculated values are shown in Table 2. The compound is triclinic.

Conclusions

The substitution of phosphorus in anorthite is very limited, in contrast to substitutions possible in alkali feldspar. An intermediate compound forms at high temperature on the anorthite–calcium pyrophosphate join. This compound, C_3APS_2, contains alternate layers of anorthite and α calcium pyrophosphate, and the 11.5A d spacing gives a strong X-ray diffraction peak. Synthesis of C_3APS_2 requires temperature above 1130°C. This temperature requirement and the α calcium pyrophosphate layers of the structure suggest that the β–α inversion of calcium pyrophosphate, reported to be at 1040°C, is a prerequisite for its formation. The phase shows no decomposition with slow cooling or with the cooling arrested for five days at 805°C.

Natural occurrence of C_3APS_2 has not been reported. The phase would require a high-temperature origin in a nearly anhydrous environment. The phase is most likely in high-alumina systems having a calcium-to-phosphorus ratio lower than common magmas. One such environment might be lunar anorthosites.

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