Pyrophosphate groups in the structure of canaphite, $CaNa_2P_2O_7 \cdot 4H_2O$: The first occurrence of a condensed phosphate as a mineral

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Abstract

Canaphite, previously described as an orthophosphate, $CaNa_2H_2(PO_4)_2 \cdot 3H_2O$, is shown by crystal-structure analysis to be a natural pyrophosphate identical to synthetic α-Ca-$Na_2P_2O_7 \cdot 4H_2O$. The structure, which has been refined to a residual of 5.7%, is monoclinic, Pc, with $a = 5.673(4)$, $b = 8.48(1)$, $c = 10.529(5)$ Å, $\beta = 106.13(6)°$, and $Z = 2$. Canaphite is the first example of a condensed phosphate occurring as a mineral. Such natural polymerization of phosphate tetrahedra is implied to be possible under conditions of low temperature and crystallization in the sole presence of alkali and alkaline-earth ions.

Introduction

Although numerous phosphates crystallize as minerals, the number of phosphate species being exceeded only by those of the silicates, oxides-hydroxides, and sulfides-sulfosalts, it has long been believed that they are made up entirely of orthophosphates and that the polymeric phosphate anions familiar to the inorganic chemist do not occur in mineral structures. Thus Liebau (1970) stated categorically that "All naturally occurring phosphates are monophosphates because the P–O–P bond of the condensed phosphates is readily hydrolyzed by water." Similarly, Byrappa (1983) concluded from a study of condensed phosphates synthesized under hydrothermal conditions that these compounds cannot occur in nature.

Although widely accepted, the above generalization is not strictly valid, as reference to any comprehensive textbook of physiology will show. In fact, the dipolyphosphate (pyrophosphate) ion, $(P_2O_7)^{4-}$, is produced in large quantities in the human body during the synthesis of proteins and other macromolecular substances (Russell, 1976) and is found in low concentrations in blood, saliva, and other body fluids, all of which are natural, aqueous chemical systems. Moreover, certain crystalline pyrophosphates, namely the monoclinic and triclinic polymorphs of calcium pyrophosphate dihydrate, $Ca_2P_2O_7 \cdot 2H_2O$, occur naturally in the cartilage of the joints, and under pathological conditions these crystals may be released into the synovial fluid, causing the disease pseudogout or "calcium pyrophosphate crystal deposition disease" (Howell, 1985, and references therein). Pyrophosphate ion is also adsorbed onto the surfaces of calcified tissues in the body

and may make up as much as 1% of the total inorganic phosphate in bone and dentin (Russell, 1976).

The fact that no condensed phosphates have hitherto been reported as minerals suggests that the "no natural polyphosphates rule" may apply in geologic environments, if not in nature generally. We now present evidence that even this limited form of the rule does not hold, that evidence being the existence of the mineral canaphite, which was originally described as an orthophosphate, $CaNa_2H_2(PO_4)_2 \cdot 3H_2O$, by Peacor et al. (1985). A determination of the crystal structure of canaphite in this laboratory proves that it is, in fact, identical to synthetic α-calcium disodium pyrophosphate tetrahydrate, $CaNa_2P_2O_7 \cdot 4H_2O$, whose structure was described by

Table 1. Atomic coordinates of canaphite

Atom	x	y	z
Ca	0.0000	0.0124(2)	0.0000
Na(1)	0.2252(8)	0.3982(5)	0.9621(4)
Na(2)	0.7417(9)	0.3669(5)	0.4665(4)
P(1)	0.1791(6)	0.2411(3)	0.2924(3)
P(2)	0.3891(5)	0.0739(3)	0.8096(3)
O(1)	0.3308(11)	0.9027(8)	0.1626(6)
O(2)*	0.7769(12)	0.8527(8)	0.1165(6)
O(3)	0.0736(13)	0.2224(8)	0.1462(6)
O(4)*	0.1501(12)	0.5852(9)	0.1156(6)
O(5)	0.9956(12)	0.2055(8)	0.3688(7)
O(6)	0.3209(12)	0.3900(7)	0.3306(7)
O(7)*	0.8044(12)	0.5858(9)	0.3460(7)
O(8)*	0.6257(12)	0.3879(10)	0.1130(7)
O(9)	0.6434(11)	0.8721(8)	0.3819(6)
O(10)	0.1933(12)	0.8578(8)	0.3636(6)
O(11)	0.3969(12)	0.1115(7)	0.3392(6)

Note: The x and z coordinates of Ca were set to zero to fix the origin. Esd's are in parentheses.
* Water oxygens.

TABLE 2. Anisotropic temperature factors (Å²) for canaphite

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca	0.0136(9)	0.0163(11)	0.0099(8)	0.0000(9)	0.0038(7)	0.0001(9)
Na(1)	0.0250(23)	0.0231(24)	0.0273(21)	−0.0006(19)	0.0032(17)	−0.0019(21)
Na(2)	0.0259(23)	0.0227(25)	0.0257(20)	0.0081(19)	0.0062(17)	0.0005(20)
P(1)	0.0156(12)	0.0098(12)	0.0107(10)	0.0012(11)	0.0037(8)	0.0012(12)
P(2)	0.0131(12)	0.0081(11)	0.0101(10)	−0.0012(10)	0.0054(9)	−0.0027(11)
O(1)	0.0193(38)	0.0163(39)	0.0150(32)	−0.0039(28)	0.0069(28)	−0.0035(31)
O(2)*	0.0166(38)	0.0223(41)	0.0177(34)	−0.0016(30)	0.0049(26)	−0.0027(33)
O(3)	0.0225(38)	0.0161(37)	0.0182(34)	−0.0024(28)	0.0048(28)	−0.0024(32)
O(4)*	0.0204(42)	0.0226(44)	0.0244(38)	0.0040(33)	0.0004(31)	0.0041(34)
O(5)	0.0172(37)	0.0132(37)	0.0224(33)	0.0006(27)	0.0082(28)	0.0021(30)
O(6)	0.0172(38)	0.0108(37)	0.0174(33)	−0.0079(26)	−0.0058(26)	−0.0104(29)
O(7)*	0.0232(42)	0.0179(39)	0.0298(38)	0.0054(32)	0.0033(31)	−0.0019(33)
O(8)*	0.0195(43)	0.0409(55)	0.0350(44)	−0.0134(38)	0.0000(32)	0.0009(38)
O(9)	0.0107(38)	0.0186(41)	0.0147(34)	−0.0010(28)	−0.0032(26)	0.0013(30)
O(10)	0.0161(35)	0.0164(38)	0.0158(32)	−0.0034(28)	0.0097(26)	−0.0045(31)
O(11)	0.0195(38)	0.0078(36)	0.0267(41)	−0.0010(28)	0.0076(32)	0.0011(31)

Note: Temperature factors are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \cdots 2hka^*b^*U_{12})]$. Esd's are in parentheses.
* Water oxygens.

Cheng et al. (1980). Canaphite is therefore the first example among minerals of a condensed phosphate.

CRYSTAL STRUCTURE

The crystal structure of canaphite was determined in a straightforward manner. When examination of the structure showed that it contains pyrophosphate groups, we carried out a search of the literature for similar compounds and discovered that the structure is identical to that of α-CaNa$_2$P$_2$O$_7\cdot4$H$_2$O (Cheng et al., 1980). We shall therefore only briefly describe the structure analysis here, and then only because such corroboration is essential in light of the seeming improbability of the occurrence of this compound as a mineral.

Canaphite is monoclinic, space group Pc, with $a = 5.673(4)$, $b = 8.48(1)$, $c = 10.529(5)$ Å, $\beta = 106.13(6)°$, and $Z = 2$ (Peacor et al., 1985). The **a** and **c** axes are reversed relative to the setting of Peacor et al. Intensity data were obtained utilizing a crystal of dimensions $0.49 \times 0.04 \times 0.08$ mm from the type specimen, graphite-monochromated Mo$K\alpha$ radiation, a Supper automated diffractometer system, scanning rates of 2° or 4° per minute, and background counting times of 25 s on both sides of peaks. Data were corrected for Lorentz-polarization and absorption effects, giving rise to a final data set of 1326 reflections, of which 121 were unobserved.

The crystal structure was solved using the direct-methods program MITHRIL (Gilmore, 1983), supplemented by electron-density and difference electron-density syntheses. The refinement with SHELX-76 (Sheldrick, 1976) converged to final residuals of 5.7% (unweighted) and 4.2% (weighted) utilizing neutral-atom scattering factors (Doyle and Turner, 1968), anomalous scattering corrections (Cromer and Liberman, 1970), reciprocal variances of the $|F|$ (obs) as weights, and anisotropic temperature factors. Attempts to locate the H atoms were unsuccessful. The final atomic coordinates are listed in Table 1, anisotropic temperature factors in Table 2, structure factors in Table

3,[1] and selected interatomic distances and angles in Table 4.

The structure is essentially identical to that found by Cheng et al. (1980) and therefore will not be described in detail here. It consists of chains of alternating Ca ions and pyrophosphate groups linked through Na atoms and water molecules. We have, however, included a table of interatomic distances and angles for canaphite, as the paper by Cheng et al. contains only an abbreviated compilation of these parameters for the synthetic phase. In addition to monoclinic α-CaNa$_2$P$_2$O$_7\cdot4$H$_2$O, there also exists a C-centered monoclinic β polymorph having a structure similar to the α form (Cheng et al., 1979) and a triclinic γ form of unknown structure.

DISCUSSION

The data reported above appear to provide proof that pyrophosphate units do indeed occur in a mineral structure. However, when canaphite was originally described (Peacor et al., 1985) there was some residual uncertainty about its authenticity as a mineral because (1) it existed only on a single specimen in the collection of L. Neal Yedlin, who, being deceased, could provide no information about the specimen's provenance; (2) the specimen label only vaguely identified the locality where it was collected as "Haledon, N. J. 8–19–66"; (3) the occurrence of a phosphate on zeolite crystals (stilbite) from Triassic traprock is unusual; and (4) canaphite crystals are overgrown on stilbite, but no minerals or other materials coat the canaphite. In short, canaphite had the appearance of a "bathtub mineral," i.e., one which is produced synthetically by placing a host rock in a solution containing dissolved salts and allowing the solution to evaporate. As

[1] A copy of Table 3 may be ordered as Document AM-88-363 from the Business Office, Mineralogical Society of America, 1625 I Street, N.W., Suite 414, Washington, D.C. 20006, U.S.A. Please remit $5.00 in advance for the microfiche.

TABLE 4. Selected interatomic distances (Å) and angles (°) in canaphite

	Na(O,H₂O)₆ and Ca(O,H₂O)₆ octahedra		
Na(1)–O(7)*	2.365(7)	Na(2)–O(7)*	2.331(8)
–O(8)*	2.385(7)	–O(2)*	2.414(8)
–O(4)*	2.386(8)	–O(5)	2.414(8)
–O(10)	2.391(8)	–O(6)	2.426(7)
–O(6)	2.420(8)	–O(4)*	2.445(7)
–O(3)	2.765(8)	–O(8)*	2.775(9)
Mean	2.452	Mean	2.468
		–O(11)	2.976(8)
Ca–O(9)	2.280(6)		
–O(5)	2.303(7)	Na(1)–Na(2)	3.401(6)
–O(10)	2.314(6)	Na(2)–Ca	3.511(5)
–O(3)	2.315(7)	Na(1)–Ca	3.574(5)
–O(1)	2.352(6)		
–O(2)*	2.409(7)		
Mean	2.329		
	Pyrophosphate group		
P(1)–O(6)	1.492(6)	P(2)–O(10)	1.497(6)
–O(3)	1.497(6)	–O(9)	1.503(6)
–O(5)	1.512(6)	–O(1)	1.504(6)
–O(11)	1.625(6)	–O(11)	1.601(6)
Mean	1.532	Mean	1.526
O(6)–P(1)–O(11)	100.5(3)	O(9)–P(2)–O(11)	103.3(4)
O(5)–P(1)–O(11)	106.3(3)	O(10)–P(2)–O(11)	106.8(4)
O(3)–P(1)–O(11)	107.1(4)	O(1)–P(2)–O(11)	108.4(4)
O(3)–P(1)–O(5)	112.9(4)	O(1)–P(2)–O(10)	111.4(4)
O(3)–P(1)–O(6)	113.5(4)	O(1)–P(2)–O(9)	112.7(3)
O(5)–P(1)–O(6)	115.2(4)	O(9)–P(2)–O(10)	113.5(4)
Mean	109.3	Mean	109.4
O(6)–O(11)	2.398(9)	O(9)–O(11)	2.435(9)
O(3)–O(6)	2.499(8)	O(1)–O(10)	2.480(8)
O(3)–O(5)	2.507(8)	O(10)–O(11)	2.488(9)
O(3)–O(11)	2.512(9)	O(1)–O(9)	2.504(8)
O(5)–O(11)	2.512(9)	O(9)–O(10)	2.509(8)
O(5)–O(6)	2.536(9)	O(1)–O(11)	2.519(9)
Mean	2.494	Mean	2.489
P(1)–P(2)	2.910(3)	P(1)–O(11)–P(2)	97.4(2)
P(2)–Ca	3.409(3)	P(1)–Na(1)	3.516(5)
P(1)–Ca	3.415(3)	P(1)–Ca	3.540(3)
P(2)–Na(1)	3.439(5)	P(1)–Na(2)	3.630(5)
P(2)–Ca	3.470(3)	P(1)–Na(1)	3.800(5)
	(H₂O–O) and (H₂O–H₂O) ≤ 3.2 Å		
O(7)*–O(9)	2.658(10)	O(2)*–O(4)*	3.104(10)
O(1)–O(2)*	2.739(9)	O(2)*–O(11)	3.125(9)
O(4)*–O(6)	2.754(9)	O(3)–O(4)*	3.136(10)
O(3)–O(8)*	2.838(10)	O(7)*–O(10)	3.162(9)
O(1)–O(4)*	2.875(10)	O(6)–O(7)*	3.171(9)
O(7)*–O(8)*	2.911(10)	O(4)*–O(8)*	3.181(10)
O(2)*–O(10)	2.989(8)	O(2)*–O(5)	3.222(8)
O(4)*–O(5)	3.067(9)	O(6)–O(8)*	3.231(9)
O(2)*–O(9)	3.096(8)		

Note: Esd's are in parentheses.
* Water oxygens.

a result of these relations, a determined search for additional data regarding the source of canaphite was made at the time of its original description, but that search was unsuccessful.

When canaphite was found to possess a structure that violates the "no natural polyphosphates rule," thus raising additional doubt as to its authenticity as a mineral, another effort was made to ascertain the type locality of canaphite, the circumstances of its discovery, and how it came into the possession of L. Neal Yedlin. Thanks to information provided by two mineral collectors, Sidney Sterris and Curt Segeler of New York, we have established that canaphite was first discovered and collected by Mr. Sterris at the Great Notch Quarry near Little Falls, New Jersey, in 1966 (Sterris et al., 1987). Several specimens were taken from a cavity near the top of the back wall of the quarry and one of them was eventually obtained by Mr. Yedlin. Comparison of a canaphite specimen made available to us by Mr. Segeler with the type specimen that originally came from the Yedlin collection shows that the two are identical in appearance. Regarding the immediate environment of the canaphite occurrence, Mr. Sterris has stated (pers. comm.) that the crystals occurred in a pocket exposed to the surface by only a narrow crack, that the pocket occurred in the highest part of the quarry wall and that there was no evidence of human activity in the vicinity, aside from normal quarrying operations. That is, there was no evidence of contamination of the site by garbage, human or animal waste, or industrial waste water, all of which might conceivably serve as a source of pyrosphosphate and thus reduce canaphite to the status of an artifact. Moreover, as the cavity was located near the top of the quarry wall, one cannot invoke contaminated circulating groundwater as a source for the chemical components of the mineral. The pedigree of canaphite as a natural phase rather than a manmade artifact would thus seem to be adequately validated.

Synthetic phosphates with highly condensed units such as chains and sheets are well-known in chemistry (Corbridge, 1985). As the stability of such units decreases with increasing degree of polymerization, it is not surprising that canaphite has a structure with the minimum of vertex sharing in the form of $(P_2O_7)^{4-}$ groups. Indeed, the pyrophosphate ion is only a little less stable with respect to hydrolysis than the analogous pyrosilicate ion, $(Si_2O_7)^{6-}$, the calculated ΔE values for the hydrolysis reactions being -23 and -20 kJ/mol, respectively (O'Keeffe et al., 1985). In addition, the degree of polymerization should generally decrease with increasing temperature. The occurrence of canaphite as crystals growing on stilbite implies that it formed from solutions below the temperature of formation of stilbite and therefore at very low temperatures, which is consistent with optimization of conditions for polymerization. Lastly, polymerization is more likely given the presence only of nontetrahedrally coordinated cations of low charge and large radius, giving rise to a minimum contribution of charge of such cations to bridging anions. The presence of Na^+ and Ca^{2+}, which reflect a zeolite-rich environment, are compatible with this requirement. Other occurrences of pyrophosphates should therefore be rare and restricted to very low temperature environments in which solutions are rich only in alkali and alkaline-earth ions.

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