

A reexamination of jennite

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Abstract

Jennite is not a hydrated sodium calcium silicate as previously reported; its composition approximates to $9\text{CaO} \cdot 6\text{SiO}_2 \cdot 11\text{H}_2\text{O}$, with the possible ionic constitution $\text{Ca}_9(\text{Si}_6\text{O}_{18}\text{H}_2)(\text{OH})_8 \cdot 6\text{H}_2\text{O}$. The dehydration product called metajennite has the approximate composition $9\text{CaO} \cdot 6\text{SiO}_2 \cdot 7\text{H}_2\text{O}$ and possible constitution $\text{Ca}_9(\text{Si}_6\text{O}_{18}\text{H}_2)(\text{OH})_8 \cdot 2\text{H}_2\text{O}$. New crystal data are reported.

In the original description of this mineral, Carpenter *et al.* (1966) reported the composition as $\text{Na}_2\text{Ca}_9\text{Si}_5\text{O}_{30}\text{H}_{22}$. The analysis was made in Aberdeen, and at the time Carpenter (personal communication) expressed some doubt at the finding that sodium was present. Subsequently Maycock *et al.* (1974) reported that, using a scanning electron microscope with an analytical attachment, they had been unable to find any sodium in the mineral. We have now reexamined the original specimen from Crestmore, and also one from Israel, and confirm that both are hydrated calcium silicates containing no appreciable sodium. The specimen from Israel, of which only a few small fibers were available, was kindly provided by Professor L. Heller-Kallai. Its identity was established by X-ray fiber rotation photographs.

Both specimens were analyzed using the analytical electron microscope EMMA-4 substantially as described by Cliff and Lorimer (1975) and Cliff *et al.* (1975). In this method, a transmission electron microscope is combined with an energy-dispersive detector and, if suitably thin, electron-transparent crystals are used, absorption and fluorescence corrections are negligible, and the weight ratio C_1/C_2 of any two elements in the specimen is related to the X-ray count ratio I_1/I_2 by the expression $C_1/C_2 = m \cdot I_1/I_2$, where m is an empirical constant determined by calibration with known substances. The instrument was operated

at 100 kV with a probe current at the specimen of about 10 nA. The method allows the detection of elements with atomic number equal to or above that of Na, and gives weight ratios but not absolute percentages.

To test the method, a synthetic specimen of $\beta\text{-Ca}_2\text{SiO}_4$ and two natural specimens of pectolite ($\text{NaCa}_2\text{Si}_3\text{O}_9\text{H}$) were also examined. In all cases, thin, electron-transparent crystals were used. The only elements detected were Ca and Si in all the specimens, and Na in the pectolite specimens but not in those of jennite or $\beta\text{-Ca}_2\text{SiO}_4$. Table 1 gives count data for all the specimens. In all cases, count rates did not change with time; together with the consistency of the results for different crystals and for different parts of the same crystal, this shows that loss of Na by evaporation does not occur. Previous work (Cliff and Lorimer, 1975) showed that, for Ca: Si, $m = 1.0$; this gives atomic Ca: Si ratios of 2.02 ± 0.10 for the $\beta\text{-Ca}_2\text{SiO}_4$, 0.64 ± 0.02 for the pectolite from Scotland, 0.64 ± 0.01 for the pectolite from New Zealand, 1.46 ± 0.03 for the jennite from Crestmore, and 1.49 ± 0.04 for the jennite from Israel. The previous work gave only an approximate estimate (6.3 ± 0.8) of m for Na: Si; the present results give Na: Si ratios agreeing with the theoretical value of 0.33 if m is taken to be 4.5.

As a further test of the composition of the Crestmore specimen, Mr. J. Marr kindly made atomic absorption analyses of an 8 mg sample of the purest

Table 1. Si, Ca, and Na counts for individual particles of jennite, β - Ca_2SiO_4 , and pectolite, with individual and mean Ca:Si and Na:Si count ratios

Specimen	Counts			Count Ratios		
	Si	Ca	Na	Ca:Si	Na:Si	
Jennite (Crestmore)	6075	12921		2.127	} 2.08 \pm 0.04	
	9163	19405		2.118		
	7795	15779		2.024		
	9217	18960		2.057		
	10304	21413		2.078		
Jennite (Israel)	9109	18967		2.082	} 2.12 \pm 0.06	
	8947	19044		2.129		
	8944	18386		2.056		
	8893	19711		2.216		
	9082	19436		2.140		
β - Ca_2SiO_4 (synthetic)	9055	26699		2.949	} 2.88 \pm 0.14	
	4846	14568		3.006		
	4568	12123		2.654		
	4588	13475		2.937		
	4433	12675		2.859		
Pectolite (b)	11363	10040	676	0.884	} 0.916 \pm 0.032	} 0.0595 0.0583 0.0761 0.0649 0.0596 0.0513 0.0581 0.0682 0.0636 0.0637
	4427	4072	258	0.920		
	5214	5115	397	0.981		
	7318	6914	475	0.945		
	9231	8177	550	0.886		
	9411	8552	483	0.909		
	9349	8305	544	0.888		
	9349	8383	638	0.897		
	9566	8619	608	0.901		
	9225	8728	588	0.946		
Pectolite (c)	8748	8384	468	0.958	} 0.921 \pm 0.020	} 0.0535 0.0593 0.0528 0.0690 0.0597 0.0580 0.0698 0.0578 0.0624 0.0556
	10204	9363	606	0.918		
	12309	10969	650	0.891		
	8882	8385	613	0.944		
	9349	8659	558	0.926		
	9194	8390	533	0.913		
	9349	8479	653	0.907		
	9349	8729	538	0.934		
	9442	8560	589	0.907		
	9411	8594	523	0.913		

(a) Integrated peak minus background. (b) BM 1937, 1405 from Lendalfoot, Ballantrae, Ayrshire, Scotland.
(c) From Wairere, New Zealand.

available material, which, however, contained a little 14 Å tobermorite and possibly other impurities; this gave CaO 46.9, SiO₂ 35.9 percent (Ca:Si = 1.40). An atomic absorption analysis of a separate 6 mg sample gave Na₂O = 0.1 percent.

The original analysis reported by Carpenter *et al.* for the Crestmore specimen gave SiO₂ 28.8, CaO 46.0, Na₂O 5.0, CO₂ 1.5, H₂O 18.5, total 99.8 percent. Insufficient material was available to permit repeating the H₂O and CO₂ analyses, but a TG curve on a nearly pure 16 mg sample gave a loss of 19.2 percent at 915°C. It seems clear from the present results that the previous analysis must be rejected, either because

of analytical error or because it had been made on impure material. If one uses the Ca:Si ratio given by the EMMA analysis, together with the new value of 19.2 percent for the H₂O content, and normalizes to 100 percent, the composition comes out at SiO₂ 34.2, CaO 46.6, H₂O 19.2 percent. Taking into account also the atomic absorption results and the Ca:Si ratio of 1.49 found for the Israeli specimen, the most probable formula approximates to 9CaO·6SiO₂·11H₂O. The CO₂ found in the original analysis could well have been present in impurities, and it seems unlikely that it is an essential constituent. The dehydration product called metajennite, which is

Table 2. Unit-cell and pseudocell parameters (in Å and degrees; estimated standard deviations in parentheses)

		1	2	3
		Jennite (X-ray)	Metajennite (X-ray)	Metajennite (Electron diffraction)
True cell (Triclinic)	a	10.593	10.590	10.57
	b	7.284	7.278	7.28
	c	10.839	9.511	9.54
	α	99.67	101.03	101.0
	β	97.65	105.74	106.3
	γ	110.11	110.10	110.1
	Pseudocell (Monoclinic A-centered)	a	9.947(6)	9.945(6)
b		3.642(3)	3.639(2)	3.64
c		21.37(1)	18.67(1)	18.72
β		101.90(7)	111.44(4)	112.1
Both cells	V	757.5 Å ³	628.9 Å ³	626.3 Å ³

formed on the loss of about 7 percent of water (Carpenter *et al.*), similarly has the approximate composition $9\text{CaO} \cdot 6\text{SiO}_2 \cdot 7\text{H}_2\text{O}$.

Jennite has not been synthesized, but a semi-crystalline phase called "calcium silicate hydrate (II)" is a structurally imperfect form of it (Gard and Taylor, 1976). The composition of this phase is probably variable, and its water content depends critically on drying conditions; the preparation studied in the above work had the approximate composition $2\text{CaO} \cdot \text{SiO}_2 \cdot 3.2\text{H}_2\text{O}$. It does not contain any Na.

For both jennite and metajennite, Carpenter *et al.* reported monoclinic pseudocells obtained by ignoring the systematically weak reflections with odd values of k . We have reexamined jennite and metajennite by selected area electron diffraction, using a $\pm 60^\circ$ double tilt cartridge (Lucas, 1970) and procedures described elsewhere (*e.g.* Gard, 1971, 1976; Cliff *et al.*, 1975). The crystal data for jennite (from both Crestmore and Israel) were found to be identical with those given by Carpenter *et al.*, showing that dehydration to metajennite does *not* occur in the vacuum of the electron microscope. The pseudocell of metajennite is body-centered if referred to the axes used by Carpenter *et al.*, not primitive as stated in their paper. It is, however, more convenient to use the equivalent A-centered pseudocell given in Table 2, column 3, as this is clearly related to the A-centered pseudocell of jennite. Most crystals of both jennite and metajennite

gave sharp reflections with odd values of k , indicating closely related triclinic true cells. In both cases, a few crystals gave streaks parallel to a^* of the pseudocell, in positions indicating that b and c are doubled in the true cell if the pseudocell axes are retained.

The pseudocell parameters for both jennite and metajennite were refined using data from X-ray Guinier photographs made with monochromatized Cu radiation and quartz as internal standard ($a = 4.913$, $c = 5.405$ Å), and the parameters of the triclinic true cells calculated from them. Table 2, columns 1 and 2, gives the results. The true a , b , and γ parameters for metajennite do not differ significantly from those of jennite.

The observed density of jennite is 2.32 g cm^{-3} . If the pseudocell contents are assumed to be $9\text{CaO} \cdot 6\text{SiO}_2 \cdot 11\text{H}_2\text{O}$, the X-ray density is 2.33 g cm^{-3} and the density calculated from the mean refractive index (1.562) as described by Carpenter *et al.* is 2.36 g cm^{-3} . The X-ray, infrared, and thermal evidence reported by these workers suggests that in both jennite and metajennite there are dreierketten, ionic OH groups, water molecules, and perhaps SiOH. The ionic constitutions $\text{Ca}_9(\text{Si}_6\text{O}_{18}\text{H}_2)(\text{OH})_8 \cdot 6\text{H}_2\text{O}$ for jennite and $\text{Ca}_9(\text{Si}_6\text{O}_{18}\text{H}_2)(\text{OH})_8 \cdot 2\text{H}_2\text{O}$ for metajennite appear compatible with all the evidence. Tentative attempts to solve the structures from X-ray powder and fiber rotation data suggested that both are based on corrugated sheets of empirical composition

$[\text{Ca}_8\text{Si}_6\text{O}_{18}\text{H}_2(\text{OH})_8 \cdot 2\text{H}_2\text{O}]^{2-}$ lying parallel to (001), between which are additional Ca^{2+} ions and, in jennite, H_2O molecules.

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