JENNITE, A NEW MINERAL

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Abstract

Jennite is a new mineral from Crestmore, California, of approximate composition $Na_2Ca_8Si_5O_{30}H_{22}$. It is triclinic, with $a=10.56$, $b=7.25$, $c=10.81$ Å, $\alpha=99°42'$, $\beta=97°40'$, $\gamma=110°04'$, $Z=1$. It forms blade-shaped crystals with length b and cleavage (001). The refractive indices are $\alpha=1.552$, $\beta=1.564$, $\gamma=1.571$; 2V (calc.)$=-74°$; $\alpha \wedge (001)=90°$, $\beta \wedge b=35$–$40°$. X-ray powder data, SED patterns, the infra-red absorption spectrum, and a thermal weight loss curve are given. When heated at 90° C. jennite loses water, giving meta-jennite, of approximate composition $Na_2Ca_8Si_5O_{26}H_{14}$; this is geometrically monoclinic, C-centered, with $a=19.87$, $b=7.24$, $c=17.70$ Å, $\beta=102°00'$. At higher temperatures poorly crystalline material, β-$CaSiO_3$, and β-Ca_2SiO_4 are successively formed. The unit cell parameters of jennite are related to those of cuspidine. The water probably occurs partly in molecular form, and partly as ionic hydroxyl groups; the ionic constitution is possibly $Na_2Ca_8(SiO_3)_3(Si_2O_7)(OH)_6 \cdot 8H_2O$. The name is proposed in honor of Colonel C. M. Jenni, discoverer of the mineral.

Introduction

The contact rocks at Crestmore, California were first described by Eakle (1917). Many subsequent investigations on them have been reported; Murdoch (1961) has given a recent survey. The object of the present paper is to describe a new mineral found at this locality by Colonel C. M. Jenni, who is now director of the geological museum at the University of Missouri. The chemical composition, x-ray powder pattern, and other data for this mineral show that it is a new species, and the name jennite is proposed in honor of its discoverer.

Occurrence

Jennite occurs as a late-stage mineral partially filling open spaces in fractured calcite-monticellite-hercynite and vesuvianite-wollastonite contact rock at Crestmore. The monticellite has been altered to serpentine plus calcite for five or more centimeters on either side of the fractures although the wollastonite in the vesuvianite-wollastonite rock has been unaffected. Jennite is always associated with 14 Å tobermorite and is occasionally found with scawtite and calcite. Scawtite and calcite are the earliest minerals in the fractures and may be encrusted by 14 Å tobermorite, jennite or both. Scawtite crystals in jennite-bearing fractures are unaltered whereas the calcite is slightly etched and corroded.

The jennite studied in the present investigation formed part of a vein

about 1 cm thick, having a central cavity. The vein consisted of several layers, some of which were composed of calcite, and others of white, fibrous material. Representative fibers from each layer were examined by x-ray rotation photographs. In some of the layers the jennite was intergrown with 14 Å tobermorite, but in others it was free from other minerals. Some 200 mg were selected for use in the investigation.
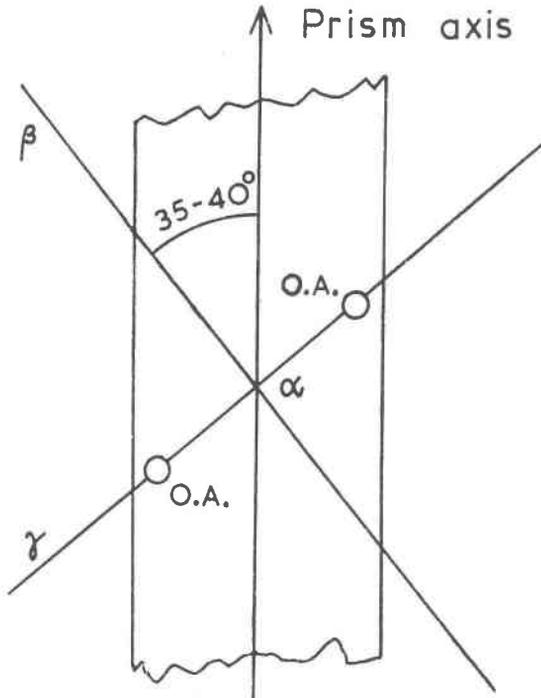
Fig. 1. Optic orientation for jennite: crystal viewed along a direction normal to the cleavage.

OPTICAL PROPERTIES

Jennite forms small blade-shaped crystals or fibrous aggregates. It is biaxial negative, with $\alpha = 1.552$, $\beta = 1.564$, $\gamma = 1.571$, all ± 0.003; 2V (calc.) $= 74°$. Fig. 1 shows the optic orientation. X is perpendicular to the cleavage, and Y makes an angle of 35–40° with the direction of elongation of the blade. Crystals lying on the cleavage show inclined extinction; when the blades are lying on edge, they show parallel extinction. These results show that the symmetry is not higher than monoclinic; the x-ray evidence, described in the next section, indicates that the mineral is triclinic.

Unit Cell and X-Ray Powder Data

The unit cell was determined from *x*-ray rotation, oscillation and Weissenberg photographs about the direction of elongation, which will be called *b*. It is triclinic. The parameters of the direct and reciprocal cells are given below:

Direct cell		Reciprocal cell	
a	10.56 Å	*a**	0.10309 Å^{-1}
b	7.25 Å	*b**	0.15095 Å^{-1}
c	10.81 Å	*c**	0.09597 Å^{-1}
α	99°42′	α^*	76°44′
β	97°40′	β^*	78°00′
γ	110°04′	γ^*	68°00′
V	748.9 Å³	V*	0.001335 Å^{-3}

The cleavage is (001). Reflections having odd values of *k* are systematically weak: the pseudo cell obtained by ignoring them is A-centered monoclinic, with *a* 9.917, *b* 3.624, *c* 21.306 Å, β 102°00′ (d$_{001}$ = 20.858 Å). The *a** and *c** reciprocal axes coincide in direction in the true and pseudo cells, and are normal to the direction of elongation. The triclinic 020 reciprocal lattice point coincides with the 111 reciprocal lattice point for the monoclinic pseudo cell. If all three axes of the pseudo cell are doubled, all reflections can be indexed on monoclinic axes; however, the reciprocal lattice has monoclinic symmetry only as regards reflections with *k* even. It the doubled monoclinic axes are used, systematic absences occur among reflections with *k* odd such that whenever *hkl* is present, *hk̄l* is absent, and vice versa. No deviations from 90° in the values of α and γ for this cell could be detected. These relationships, which are illustrated for the direct cell in Fig. 2, are similar to those found with nekoite (Gard and Taylor, 1956).

X-ray powder data (Table 1) were obtained using 6-cm and 11.46-cm diameter cameras and with a diffractometer. Filtered copper radiation (λ = 1.542 Å) was used throughout. Spacings longer than 1.8 Å were indexed, chiefly by direct comparison of 6 cm powder photographs with oscillation and rotation photographs taken on the same camera; due account was taken of intensities as well as of spacings. In the case of reflections with *k* odd, calculated spacings are listed only for d > 3.500 Å; reflections of this type and shorter spacing were extremely weak on single-crystal photographs and undetected on powder photographs.

Chemical Analysis, Density and Atomic Cell Contents

A chemical analysis gave the results shown in Table 2, column 1. The density, determined by suspension, was 2.32 g/cc. A value was also calculated from the mean refractive index using the Lorentz-Lorenz equa-

tion, assuming atomic refractions $Ca = Na = 3.25$, $O = 3.65$, $H = Si = 0$ (Howison and Taylor, 1956); this gave 2.31 g/cc. The atomic cell contents (Table 2, col. 2) were calculated from the chemical analysis assuming a density of 2.32 g/cc and the cell volume of 748.9 Å³ obtained from the x-ray investigation. On the basis of the thermal decomposition study
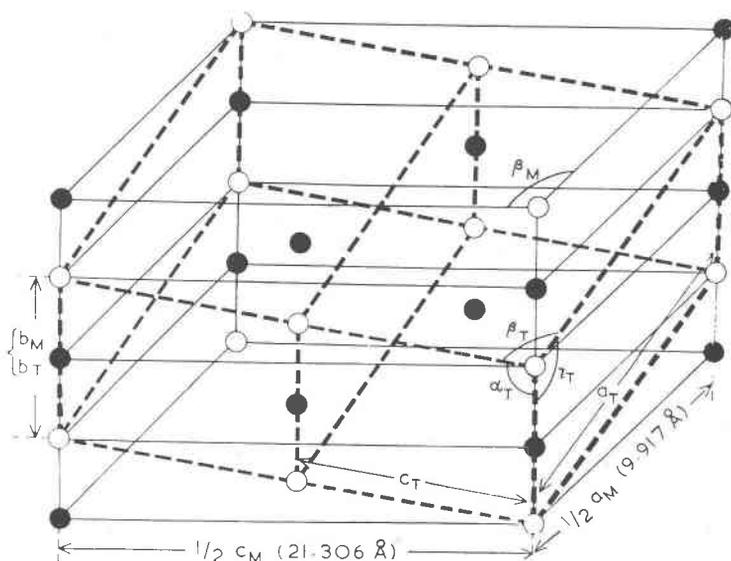
Fig. 2. Relationship between the triclinic and monoclinic cells for jennite. Thin, full lines outline four monoclinic pseudo cells (a 9.917, b 3.624, c 21.306 Å, β 102°00′). Heavy broken lines outline two triclinic cells (a_T 10.56, b_T 7.25, c_T 10.81 Å, α_T 99°42′, β_T 97°40′, γ_T 110°04′). Parameters a_M, b_M, c_M, and β_M relate to the large, monoclinic cell with a 19.834, b 7.248, c 42.612 Å, β 102°00′. Open circles denote true lattice points. Full circles denote the additional lattice points that are obtained if the weak reflections with odd values of k are ignored.

described later, it was assumed that all the water was combined. The formula approximates to $Na_2Ca_8Si_5O_{30}H_{22}$, with $Z = 1$ for the triclinic cell.

THERMAL DECOMPOSITION

A thermal weight loss curve (Fig. 3B, curve 1) was determined by heating a sample to constant weight at successively higher temperatures in nitrogen. Periods of a few days were needed at each temperature to reach constant weight, and the complete run took several weeks. The sample was heated in a platinum microboat which was placed in a silica tube furnace. The latter was filled with dry, CO_2-free N_2 before each heating period. During heating, one end of the furnace was closed and

TABLE 1. X-RAY POWDER DATA FOR JENNITE
(CuKα Radiation, 1.542 Å)

Observed		Indices hkl^2	Calculated spacing d (Å)
d (Å)	I_{rel}[1]		
10.5	vvs	001	10.420
		100	9.700
		10$\bar{1}$	7.975
		1$\bar{1}$0	6.780
		010	6.625
6.46	ms	101	6.462
		01$\bar{1}$	6.283
5.95	vvw	1$\bar{1}$1	5.932
		1$\bar{1}\bar{1}$	5.463
5.20	vvw	002	5.210
		011	5.086
		10$\bar{2}$	5.048
		2$\bar{1}$0	4.881
		200	4.850
		20$\bar{1}$	4.795
4.77	m/b	$\lbrace$ 11$\bar{1}$	4.795
		110	4.711
		01$\bar{2}$	4.648
4.48	vw	2$\bar{1}\bar{1}$	4.489
		2$\bar{1}$1	4.354
		1$\bar{1}$2	4.324
		102	4.237
4.11	w	201	4.084
		11$\bar{2}$	4.071
		20$\bar{2}$	3.987
		1$\bar{1}$2	3.963
3.93	vvw	111	3.921
3.72	vvw	012	3.703
		2$\bar{1}$2	3.635
3.55	w	$\bar{1}$20, 1$\bar{2}$1	3.570
		10$\bar{3}$	3.510
3.47	ms	003	3.473
		02$\bar{1}$, 2$\bar{2}$0	3.390
3.29	ms/b	$\lbrace$ 020, 2$\bar{2}$1	3.313
		30$\bar{1}$	3.288
		300	3.233
		202	3.231
3.19	vvw	$\bar{1}$21, 1$\bar{2}$2	3.213
		20$\bar{3}$	3.151
		02$\bar{2}$, 2$\bar{2}\bar{1}$	3.142

[1] s =strong, m =moderate(ly), w =weak, v =very, b =broad. The five strongest spacings are in bold type.
[2] Indices relate to the triclinic cell with a 10.56, b 7.25, c 10.81 Å. α 99°42′, β 97°40′, γ 110°04′. All spacings longer than 3.500 Å, and all spacings with even k-indices and longer than 1.800 Å, are listed. The matrix for transforming the indices to the large, monoclinic cell (a 19.834, b 7.248, c 42.612 Å, β 102°00′) is ‖210/010/014‖.

TABLE 1—(*continued*)

Observed		Indices	Calculated spacing
d (Å)	I$_{rel}$[1]	hkl[2]	d (Å)
3.04	s	103	3.074
		30$\bar{2}$	3.046
		021, 2$\bar{2}$2	2.966
2.92	vs	⎧12$\bar{1}$, 3$\bar{2}$0	2.926
		⎩301	2.921
2.83	s	120, 3$\bar{2}$1	2.828
2.78	m	12$\bar{2}$, 3$\bar{2}\bar{1}$	2.806
		$\bar{1}$22, 1$\bar{2}$3	2.735
		02$\bar{3}$, 2$\bar{2}\bar{2}$	2.731
2.66	s	⎧303	2.658
2.61	w	⎩10$\bar{4}$	2.658
		004	2.605
		203	2.581
		121, 3$\bar{2}$2	2.567
		022, 2$\bar{2}$3	2.543
2.52	vvw	12$\bar{3}$, 3$\bar{2}$2	2.535
		20$\bar{4}$	2.524
		302	2.522
		40$\bar{1}$	2.479
		22$\bar{1}$, 4$\bar{2}$0	2.440
2.43	vvw	400	2.425
2.40	vvw	40$\bar{2}$	2.398
		22$\bar{2}$, 4$\bar{2}\bar{1}$	2.397
		104	2.394
		220, 4$\bar{2}$1	2.355
		02$\bar{4}$, 2$\bar{2}\bar{3}$	2.324
		$\bar{1}$23, 1$\bar{2}$4	2.301
2.27	w	30$\bar{4}$	2.273
		401	2.261
		122, 3$\bar{2}$3	2.254
		22$\bar{3}$, 4$\bar{2}\bar{2}$	2.245
		12$\bar{4}$, 3$\bar{2}$3	2.221
2.21	vw	40$\bar{3}$	2.216
		221, 4$\bar{2}$2	2.177
		023, 2$\bar{2}$4	2.162
		303	2.154
		10$\bar{5}$	2.131
		204	2.119
2.08	vw	⎧005	2.084
		⎩20$\bar{5}$	2.078
		402	2.042
		32$\bar{1}$, 5$\bar{2}$0	2.040
2.04	ms	22$\bar{4}$, 4$\bar{2}$3	2.035
		32$\bar{2}$, 5$\bar{2}\bar{1}$	2.032
		40$\bar{4}$	1.994
1.984	m	⎧50$\bar{1}$	1.983
		⎨20$\bar{5}$, 2$\bar{2}\bar{4}$	1.981
		⎩320, 5$\bar{2}$1	1.974
		222, 4$\bar{2}$3	1.960
		123, 3$\bar{2}$4	1.960

TABLE 1—(*continued*)

Observed		Indices hkl[2]	Calculated spacing d (Å)
d (Å)	I_{rel}[1]		
		$50\bar{2}$	1.956
1.957	mw	105	1.956
		$32\bar{3}, 5\bar{2}\bar{2}$	1.951
1.946	mw	$\bar{1}24, 1\bar{2}5$	1.951
		500	1.940
		$12\bar{5}, 3\bar{2}\bar{4}$	1.931
1.875	vw	$50\bar{3}$	1.867
		$321, 5\bar{2}\bar{2}$	1.852
		$024, \bar{2}25$	1.851
		304	1.849
		501	1.840
1.833	vw	$32\bar{4}, 5\bar{2}\bar{3}$	1.822
		403	1.819
		$22\bar{5}, 4\bar{2}\bar{4}$	1.817
1.810	ms	$24\bar{1}$	1.812
1.735	w		
1.683	mw		
1.637	vw		
1.610	w		
1.58	vw/b		
1.521	vw		
1.486	vw		
1.455	vw		
1.413	w		
1.393	vvw		
1.365	vvw		
1.331	vw		
1.312	w		
1.266	vvw		
1.214	vvw		
1.177	vvw		
1.173	w		
1.155	vvw		
1.133	w		
1.114	vvw		
1.100	vw		

the other connected to two absorption tubes containing standard $Ba(OH)_2$ solution. After each heating period, the gas in the furnace was swept through the absorption tubes with N_2. The $Ba(OH)_2$ solutions were back-titrated with acid, the furnace opened, and the boat weighed. It was assumed that the titration gave the amount of CO_2 evolved and that the remaining loss was of water (Fig. 3B curves 2 and 3).

Samples were also heated in air at various temperatures for periods

TABLE 2. CHEMICAL ANALYSIS AND ATOMIC CELL CONTENTS FOR JENNITE

	1		2
SiO_2	28.8	Si	5.02
CaO	46.0	Ca	8.58
Na_2O	5.0	Na	1.69
H_2O (total)	18.5	H	21.50
CO_2	1.5	C	0.36
Total	99.8	O	30.93

1. Chemical analysis (by R. A. Chalmers; H_2O and CO_2 from weight and CO_2 loss curves, Fig. 3B).

2. Atomic cell contents calculated from data in column 1.

similar to those used in determining the weight loss curve, and were then examined by making x-ray rotation photographs about the direction of elongation. Figure 3A shows the phases thus detected. These phases are described below.

META-JENNITE

Jennite remains stable up to 70° C., but at 70–90° C. there is a sharp
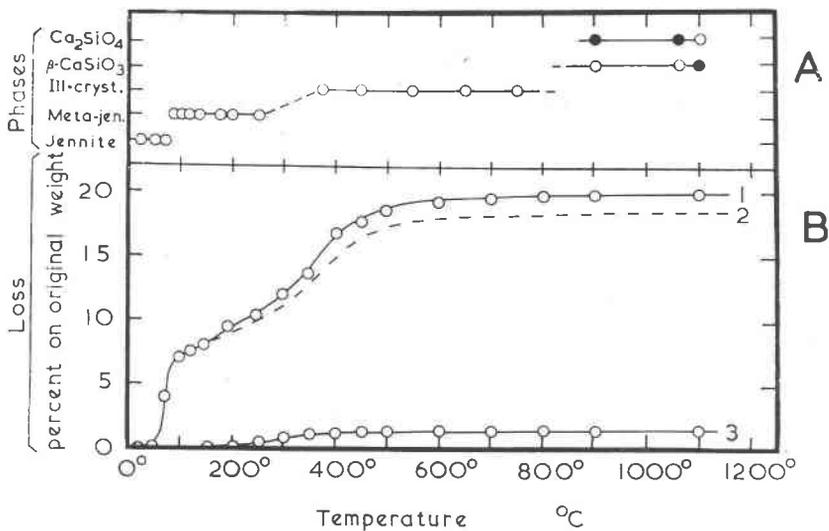
FIG. 3. Thermal decomposition results for jennite. A: Phases detected by x-rays in heated samples (meta-jen. = meta-jennite, ill cryst. = poorly crystalline material, Ca_2SiO_4 = β-Ca_2SiO_4; open circles denote major, closed circles minor constituents). B: Weight loss curves; 1, total weight loss; 2, water loss (by difference, from curves 1 and 3); 3, CO_2 loss.

loss of water, which amounts to about 7% on the initial weight (Fig. 3B). The product thus formed will be called meta-jennite; its composition is represented approximately by the formula $Na_2Ca_8Si_5O_{26}H_{14}$. Meta-jennite is the only product detectable by x-rays up to at least 250° C. but the weight continues to diminish over this temperature range. This may be due to gradual conversion to the poorly crystalline material which is the sole detectable product at higher temperatures.

Meta-jennite is crystalline and is formed topotactically; that is, a single crystal of the starting material gives a single crystal of the product in a definite crystallographic orientation. The crystallinity nevertheless deteriorates to some extent on heating, perhaps because of the gradual decomposition mentioned above, and it was not found possible to establish the unit cell of meta-jennite entirely from x-ray evidence. Selected area electron diffraction (SED) was therefore also used.

Electron Microscopy and Diffraction

Samples were taken from four parts of the hand specimen and ground with a few drops of isopropyl alcohol; specimen grids carrying carbon films were momentarily brought into contact with the resulting suspensions (Boult, 1956). After evaporation of the liquid, the specimens were examined with an A.E.I. type EM3 electron microscope. Identical SED patterns were obtained from all the crystals rexamined in two of the samples, one of which was that used for the chemical analysis, infra-red, and thermal decomposition studies. Some of the crystals were irradiated with an intense electron beam for about one minute, without any significant change in the positions of spots in the SED patterns. Similar patterns were also obtained from a sample which had been heated for 3 days at 180° C. to convert it to meta-jennite. All these patterns were in accord with the single-crystal x-ray data for meta-jennite, but not with the corresponding data for jennite. It was concluded that conversion to meta-jennite occurs in the vacuum of the electron microscope. This is not surprising, as the process is one of dehydration, and occurs at 70–90° C. in air (Fig. 3). SED patterns from one of the other samples indicated tobermorite crystals lying on their (001) faces. Out of 11 crystals examined in the fourth sample, 6 were meta-jennite, one was tobermorite lying on the (001) face, and 4 were meta-jennite of an abnormal variety which is described later.

Figure 4a shows a typical electron micrograph of meta-jennite crystals of the normal type. They are laths; as with jennite, the direction of elongation will be called b, and the cleavage (001). Figure 4b shows a typical SED pattern, obtained from such a crystal after tilting the stage so as to bring the c-axis nearly parallel to the electron beam. The pattern
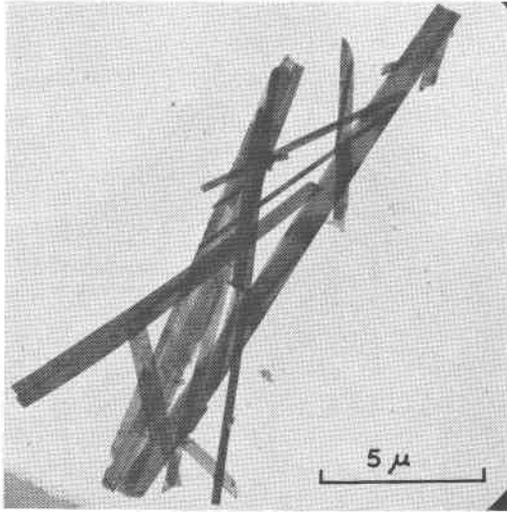
FIG. 4a. Typical electron micrograph of normal meta-jennite crystals.

shows that the reciprocal lattice is centered on the *hk0* face and that it has $d_{100} = 19.4$, $d_{010} = 7.26$ Å, $\gamma^* = 90°$. Some division of the pattern into Laue zones corresponding to different values of l is just visible in Fig. 4b; this became more marked if the stage was tilted so that the *c*-axis
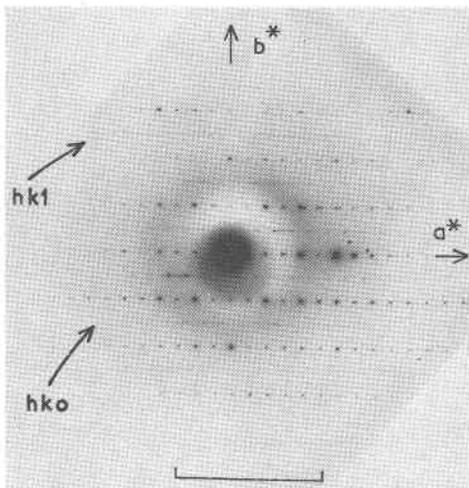
FIG. 4b. SED pattern given by a normal meta-jennite crystal lying with the *c*-axis nearly parallel to the electron beam. Most of the pattern consists of *hk0* reflections, but part of the *hk*1 Laue zone is also visible as an arc running across the top of the pattern. The scale mark represents 1Å^{-1}.

was no longer parallel to the beam. For all angles of tilt employed, all the reflections were found to lie on the centered grid shown in Fig. 4b, which extended without any displacement from each zone to the next. The lattice is therefore C-centered. From the radii of the Laue zones at various angles of tilt (Gard, 1956), c was estimated at about 16 Å. From measurements of patterns obtained from crystals lying with the (001) plane normal to the beam, values of the real cell parameters were obtained; this gave a 19.8 ± 0.1, b 7.26 ± 0.06 Å, $\gamma = 90°$ (mean for 14 crystals). By comparing these values of a and b with those of d_{100} and d_{010}, β was estimated at about 102° and α at 90°. The SED results thus indicate a C-centered, geometrically monoclinic unit cell with a 19.8 ± 0.1, b 7.26 ± 0.06, $c \approx 16$ Å, $\beta \approx 102°$. The habit of the crystals, and the available angle of tilt of the stage, did not permit the $h0l$ zone to be recorded. Its systematic absences, if any, could not therefore be deduced.

Fig. 5a shows an electron micrograph of the abnormal variety of meta-jennite mentioned previously. The crystals are less definite in outline than are those of the normal form. Fig. 5b shows the SED pattern given by one of these "abnormal" crystals, obtained with the (001) plane approximately perpendicular to the electron beam. The pattern resembles that of normal meta-jennite in the same orientation, but reflections with odd values of k take the form of continuous streaks parallel to a^*. This indicates the occurrence of stacking disorder.

X-RAY EXAMINATION OF META-JENNITE

A sample which had been heated for 3 weeks at 135° C. was studied by means of x-ray single crystal oscillation and rotation, fiber rotation, and powder photographs. The patterns could be indexed on a cell similar to that found by electron diffraction, namely, C-centered monoclinic, with a 19.87, b 7.24, c 17.70 Å, β 102°00′ ($d_{001} = 17.32$ Å). To within a few degrees in each case, the a- and b-axes were formed parallel to the corresponding monoclinic axes of the jennite. Table 3 gives x-ray powder data for meta-jennite, obtained using a 6-cm diameter camera with filtered copper radiation and with a Guinier camera. Reflections longer than 2.5 Å were indexed, mainly by direct comparison of powder, single crystal, and fiber rotation photographs taken on the same camera.

Reflections having odd values of k were systematically weak; they were visible on powder and fiber rotation photographs, but not on true single crystal photographs. It was therefore not possible to determine their h and l indices from the x-ray evidence, and the C-centering was postulated on the basis of the electron diffraction results. The x-ray results showed that $h0l$ reflections with $(h/2 + l)$ odd were absent. This indicates the presence of an n-glide plane in the pseudo structure which

Fig. 5a. Electron micrograph of "abnormal" meta-jennite crystals.

is obtained by ignoring the existence of the systematically weak reflections with k-odd.

Although both the x-ray and the electron diffraction results are compatible with the assumption of monoclinic symmetry, the possibility
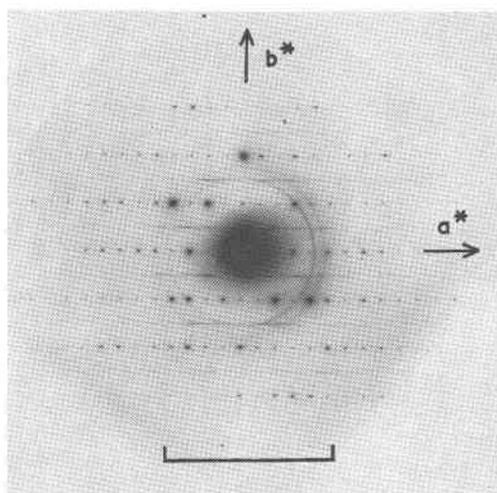
Fig. 5b. SED pattern given by an "abnormal" meta-jennite crystal lying with the (001) plane approximately perpendicular to the electron beam. The scale mark represents 1Å^{-1}.

TABLE 3. X-RAY POWER DATA FOR META-JENNITE

Observed		Calculated[2]		Observed (continued)	
d (Å)	I_{rel}[1]	hkl	d (Å)	d (Å)	I_{rel}[1]
8.6	vs	$20\bar{1}$	9.344	2.42	w
7.8	w	002	8.657	2.31	w
6.8	vvw	201	7.810	2.26	w
		110	6.785	2.13	vvw
		$20\bar{3}$	5.488	2.10	vvw
4.86	vvw	400	4.859	2.05	w
4.65	vvw	$40\bar{2}$	4.672	2.01	mw
		203	4.563	1.986	w
4.33	m	004	4.328	1.915	vvw
		402	3.905	1.887	vw
		$40\bar{4}$	3.628	1.831	w
		020	3.620	**1.817**	vs
3.55	vw	021	3.543	1.782	vvw
3.49	vvw	$20\bar{5}$	3.500	1.744	vw
3.40	vvw	220	3.392	1.698	w
		$22\bar{1}$	3.376	1.655	vvw
		022	3.340	1.623	vvw
3.31	m	$60\bar{1}$	3.311	1.603	vvw
3.25	m/b	{ 221	3.284	1.597	vvw
		{ $22\bar{2}$	3.239	1.573	vvw
		{ $60\bar{3}$	3.115	1.553	vvw
3.09	vvs/b	{ 222	3.083	1.537	vvw
		601	3.071	1.519	vvw
		205	3.066	1.504	vw
		023	3.059	1.455	w
		$22\bar{3}$	3.022	1.415	vvw
		404	2.942	1.386	w
2.93	s	$42\bar{1}$	2.923	1.337	w
		420	2.903	1.295	vw
		006	2.886	1.180	w
		223	2.836	1.166	vvw
2.78	w	{ 421	2.777	1.137	vvw
		{ 024	2.777	1.121	vvw
2.75	mw/b	{ $22\bar{4}$	2.769	1.098	vvw
		{ $40\bar{6}$	2.744	1.087	vvw
2.65	s	$60\bar{5}$	2.657	1.049	vw
2.60	vvw	603	2.603	1.011	vw
		224	2.581	0.989	vvw
2.51	w	$22\bar{5}$	2.516	0.961	vvw
		025	2.502	0.936	vvw

[1] s = strong, m = moderate(ly), w = weak, v = very, b = broad; the five strongest reflections are in bold type.
[2] Indices referred to monoclinic axes: a 19.75, b 7.24, c 17.70 Å, β 102°00′. All reflections with $k = 2n$ and $d > 2.500$ Å are listed; of reflections with $k = (2n+1)$, only the one that was detected on powder photographs is included.

cannot be excluded that the true cell is triclinic, as for jennite itself. Better data would be needed to settle this point. A possible triclinic cell, chosen to emphasize the relationship to that of jennite, would be that having a 10.57, b 7.24, c 17.70 Å, α 90°00′, β 101°10′, γ 110°01′ (d_{602} = 8.66 Å).

PRODUCTS FORMED AT 375° C. AND ABOVE

As already mentioned, meta-jennite is dehydrated gradually, over a wide temperature range, that begins as soon as the phase is formed at 70–90° C. and continues to at least 250° C. The products formed at 375–750° C. are described in Fig. 3A as "poorly crystalline material". That formed at 375° C. gave x-ray fiber rotation patterns recognizably similar to those of meta-jennite, but the reflections were broad and weak, and the preferred orientation had almost disappeared. With further rise in temperature, the products became progressively less crystalline. The 450° C. product gave diffuse powder rings with spacings of about 3.0 (moderate), 2.8 (very weak), 2.0 (very weak), and 1.8 Å (weak). The 550° C. product gave diffuse bands at 2.9–3.0 and 1.8 Å. The 650° C. and 750° C. products each gave a single, diffuse band at about 2.9 Å.

The 900° and 1060° C. products gave patterns of wollastonite (β-CaSiO$_3$). There was very slight preferred orientation, with wollastonite b (the chain direction) parallel to the direction of elongation. The patterns included a reflection at 2.75 Å which was not attributable to wollastonite, but which could have been due to β-Ca$_2$SiO$_4$. The 1100° C. product gave a powder pattern of β-Ca$_2$SiO$_4$ together with a reflection at 2.97 Å, which could have been due to wollastonite.

INFRA-RED EXAMINATION

Infra-red absorption spectra were obtained for the original mineral, for a meta-jennite sample prepared at 180° C., and for the decomposition product obtained at 500° C. A Hilger double beam instrument with a NaCl prism was used. Figures 6 and 7 give results for the 3000–3650 cm^{-1} and 650–1750 cm^{-1} regions respectively. No bands were observed between 1750 and 3000 cm^{-1}. The spectra were obtained using the KBr disk method, with 2 mg of sample in a 350 mg disk. The unheated mineral was also examined as a dry powder deposited on a NaCl plate from suspension in CCl$_4$ (for the 650–1750 cm^{-1} region), and as a mull in CCl$_4$ (for the 3000–3650 cm^{-1} region), with substantially the same results. The 180 °C. spectra are for a sample heated in the KBr disk for 18 hours at that temperature. The 500° C. spectra are for a sample heated at that temperature and then made into a KBr disk.

The unheated mineral (Figs. 6 and 7, curves A) shows bands at 3565

and 3490 cm^{-1} that can be attributed to the stretching of weakly hydrogen bonded hydroxyl groups, probably coordinated only to calcium. The broader band at about 3170 cm^{-1} could be attributed to SiOH or molecular water or both. The fact that a band also occurs at 1630 cm^{-1} indicates that molecular water is definitely present; there is no evidence for or
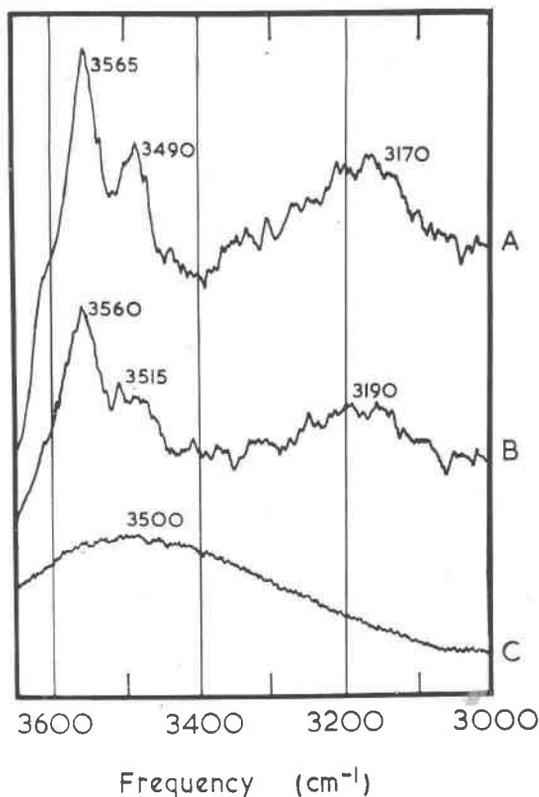
Fig. 6. Infra red absorption curves for the 3000–3650 cm^{-1} region. A. Jennite (sample in KBr disk). B. Meta-jennite (jennite sample heated at 180° C. in KBr disk). C. Poorly crystalline decomposition product (jennite sample heated at 500° C. and then examined in a KBr disk).

against the presence of SiOH. The bands at 1430–1470 cm^{-1} can be attributed to CO_3^{2-} ion. The absence of any band at 877 cm^{-1} suggests that this is not present as calcite, and is compatible with the view that it occurs in the mineral itself. The fact that the bulk of the CO_2 is lost at 200–400° C. (Fig. 3B, curve 2) also suggests that it does not occur as calcite, which would be decomposed at 500–600° C. under the conditions used. The broad group of bands with its main peaks at 905, 965,

985 and 1070 cm⁻¹ can be attributed to Si-O stretching vibrations. This part of the spectrum somewhat resembles that of cuspidine (van Valkenburg and Rynders, 1958). There are also bands at 710 and 740 cm⁻¹,
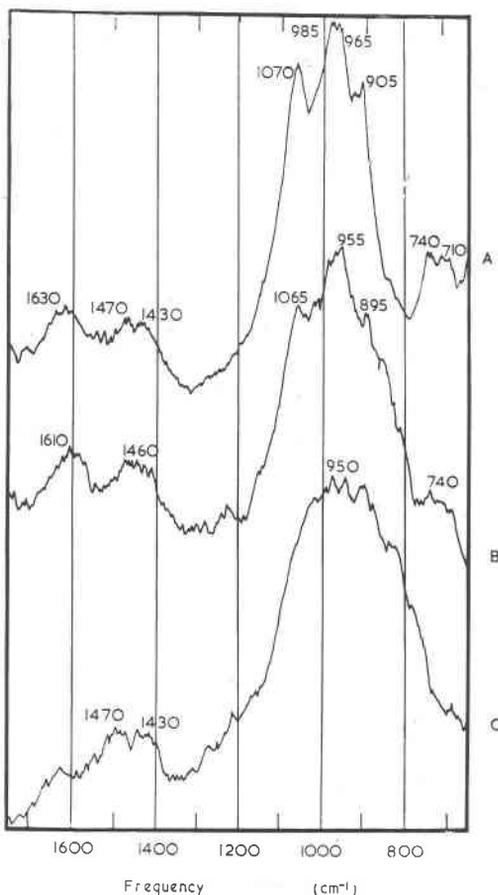
FIG. 7. Infra red absorption curves for the 650–1750 cm⁻¹ region. A. Jennite (sample in KBr disk). B. Meta-jennite (jennite sample heated at 180° C. in KBr disk). C. Poorly crystalline decomposition product (jennite sample heated at 500° C. and then examined in a KBr disk).

which can perhaps be attributed to Si-O-Si bending vibrations. If this explanation is accepted, there must be some condensation of SiO_4 tetrahedra.

The spectrum of meta-jennite (Figs. 6, 7, curves B) does not differ greatly from that of jennite. The structural changes involved in the for-

mation of mata-jennite are therefore probably small. The bands at about 1630 and 3170 cm^{-1} are still present; molecular water is therefore present in meta-jennite.

The spectrum of the 500° C. sample (Figs. 6, 7, curves C) shows marked changes. The main features are broad bands centered at about 3500 and 950 cm^{-1}; these are attributable to hydroxyl and Si-O stretching vibrations respectively. The bands characteristic of molecular water have disappeared, but carbonate absorption bands at 1430 and 1470 cm^{-1} remain. This last result appears to conflict with the analytical evidence (Fig. 3B, curve 2), and it can only be concluded that the infra-red method is more sensitive for detecting small proportions of carbonate ion. The general diffuseness of the spectrum supports the conclusion from the *x*-ray evidence that the 500° C. product is poorly crystalline.

DISCUSSION

Comparison with cuspidine. The unit cell parameters of jennite show a distinct resemblance to those of cuspidine (Smirnova *et al.* 1955):

Jennite (triclinic)	a 10.56,	d_{001} 10.43,	b 7.25 Å	γ 110°04'
Cuspidine (monoclinic)	c 10.85,	b 10.43,	a 7.55 Å	β 110°04'

The (001) face of the jennite cell is similar in parameters to the (010) face of the cuspidine cell, and the length of jennite d_{001} agrees with that of cuspidine b. The unit cell contents for cuspidine are $Ca_{16}(Si_2O_7)_4F_8$; those for jennite are approximately $Na_2Ca_8Si_5O_{30}H_{22}$.

Meta-jennite and jennite. The unit cell of meta-jennite is closely related to that of jennite. The parameters of the (001) faces of the triclinic cells agree to within experimental error   (a 10.56, b 7.25 Å. γ 110°04' for jennite, a 10.57, b 7.24 Å, γ 110°01' for meta-jennite). The thickness of the elementary layers parallel to (001) is reduced from 10.43 Å in jennite to 8.66 Å in meta-jennite. This reduction can be attributed to the loss of part of the molecular water. The stacking in the *c*-direction of the elementary layers changes when meta-jennite is formed. In jennite there is a one-layer, and in meta-jennite a two-layer arrangement. The *c*-axis is perpendicular to b in meta-jennite, but not in jennite.

The high-temperature changes. The fact that wollastonite is the first product to crystallize from the poorly crystalline decomposition product of the meta-jennite suggests a relation between the jennite structure and that of wollastonite. The lengths of the *b*-axes of the two minerals are almost identical, and the wollastonite *b*-axis tends to form parallel to the jennite *b*-axis. The replacement of wollastonite by β-Ca_2SiO_4 as the

main product at 1100° C. provides an independent check on the approximate correctness of the chemical analysis.

The ionic constitutions of jennite and meta-jennite. The present results are inadequate to establish ionic constitutions, but some points may be noted. The infra-red results indicate that both jennite and meta-jennite contain both molecular water and ionic hydroxyl groups, together possibly with Si-OH groups. The crystallographic evidence indicates a marked similarity to cuspidine, and a possible one also to wollastonite; these minerals contain $Si_2O_7^{6-}$ groups and infinite, SiO_3^{2-} chains respectively. The infra-red evidence provides some further indication of a likeness to cuspidine, and the high-temperature changes strongly support the relationship to wollastonite.

The atomic cell contents indicate five silicon atoms in the triclinic cell of jennite. This number is not compatible with either $Si_2O_7^{6-}$ groups or wollastonite-type chains as the sole type of anion; for $Si_2O_7^{6-}$ groups the number of silicon atoms per cell would be a multiple of 2, and for wollastonite-type chains it would be a multiple of 3. Possible constitutional formula, which seem to fit all the available facts, are Na_2Ca_8 $(SiO_3)_3(Si_2O_7)(OH)_6 \cdot 8H_2O$ for jennite, and $Na_2Ca_8(SiO_3)_3(Si_2O_7)$ $(OH)_6 \cdot 4H_2O$ for meta-jennite. A combination of wollastonite-type chains and $Si_2O_7^{6-}$ groups is thus postulated. It is, however, stressed that these formulae are quite speculative. Among other questions that remain to be answered are whether or not the sodium ions and calcium ions occupy distinct sites, and how the carbonate groups are accommodated in the structure.

ACKNOWLEDGMENT

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