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Coombsite, Mn analogue of zussmanite, and associated Mn-silicates, parsettensite and caryopilite, from southeast Otago, New Zealand

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Abstract A new Mn-silicate mineral, coombsite, isostructural with zussmanite, has been found in a 50 cm thick rhodonite-quartz lens at Watsons Beach, southeast Otago. The Mn-rich lens is cut by thin carbonate veinlets consisting of rhodochrosite and rare kutnohorite. Stilpnomelane-related Mn-silicate, parsettensite, occurs in the lens as dark-coloured aggregates and as dispersed crystals in the quartz often associated with coombsite. Rarely, the brown Mn-silicate, caryopilite, occurs associated with concentrations of carbonate.

Occurring in rhodonite and quartz is a new brown-coloured fibro-lamellar mineral, **coombsite**, the Mn analogue of zussmanite. The name is given in honour of Professor D. S. Coombs of the University of Otago. Coombsite is hexagonal (rhombohedral) with a 11.828, c 29.146 Å, D_{calc} 3.063, D_{meas} 3.0, ε 1.600, ω 1.619. TheX-ray powder pattern of coombsite closely resembles that of zussmanite, and the axial constants accord well with the expected values of Mn-substituted zussmanite. An average of five WDS EPMA analyses gives SiO_2 45.18, TiO_2 0.01, Al_2O_3 3.59, FeO* 3.28, MnO 38.19, MgO 1.08, CaO 0.03, Na_2O 0.08, K_2O 2.19, and total 93.63 (wt%). The chemical formula of the coombsite is approximately $K_{1.0}Na_{0.1}(Mn_{11.8}Fe_{1.0}Mg_{0.6})(Al_{1.5}Si_{16.4})O_{42}(OH)_{14}$ or $K(Mn,Fe,Mg)_{13}(Si,Al)_{18}O_{42}(OH)_{14}$.

The parsettensite is monoclinic with a 39.047, b 22.701, c 12.332 Å, ∠β 95.62°, D_{calc} 2.628, D_{meas} 2.69, α 1.560, β ≒ γ 1.595, $2V_x$ 0°, pleochroic in X colourless, Y and Z reddish brown. Average of three EPMA analyses gives SiO_2 45.64, Al_2O_3 4.26, FeO* 6.64, MnO 31.96, MgO 1.24, CaO 0.02, Na_2O 0.06, K_2O 1.61, and total 91.43 (wt%). The caryopilite is monoclinic with a 5.686, b 9.848, c 7.487 Å, ∠β 104.61°, D_{calc} 2.910, D_{meas} 3.0, α 1.610, β ≒ γ 1.635, $2V_x$ 0°, pleochroic with X pale brown, Y and Z brown. Average of four EPMA analyses is SiO_2 35.28, TiO_2 0.01, Al_2O_3 1.48, FeO* 9.88, MnO 42.04, MgO 1.27, CaO 0.13, Na_2O 0.04, K_2O 0.09 and total 90.22 (wt%).

Keywords coombsite; zussmanite Mn analogue; new Mn-silicate mineral; parsettensite; caryopilite; Otago; New Zealand

INTRODUCTION

A lenticular body of Mn-rich siliceous rock, about 0.5 × 1 m, has been found among beach exposures in the transitional pumpellyite-actinolite to pumpellyite-prehnite facies metagreywacke-argillite sequence in the Chrystalls Beach accretionary melange complex (Nelson 1982) of the Tuapeka Group, Caples Terrane, at Watsons Beach (170°10′E, 46°15′S; NZMS 260 grid reference: H45/900456), southeastern Otago, South Island, New Zealand. Probable Triassic tube fossils from sandstone (Campbell & Campbell 1970), and Triassic–Jurassic radiolarians from phosphatic nodules in sandstone (Hada et al. 1989) have been reported from rocks nearby. The locality is 3.5 km southwest of the site of a Mn-silicate lens rich in pyroxmangite, rhodonite, rhodochrosite, spessartine, and quartz, from which the rare Mn mineral akatoreite has been described (Read & Reay 1971); this occurrence is in rocks of the slightly higher grade in the pumpellyite-actinolite facies.

The Watsons Beach Mn-silicate lens consists mainly of rhodonite and quartz, with a subordinate amount of rhodochrosite and trace amounts of kutnohorite, manganoan calcite, spessartine garnet, apatite, parsettensite, caryopilite, and a new mineral, **coombsite**†. Fine rhodonite and quartz crystals of 50–100 µm in diameter, often associated with a small amount of rhodochrosite, make up the compact matrix of the lens. Quartz also occurs in the lens as anastomosing veins composed of a mosaic of grains about 0.5 mm in size. There are large sphenoid crystals of rhodonite, up to 0.5 mm in diameter, grown in the fine-grained quartz matrix. Pyroxmangite does not exist in the lens, though the lens containing akatoreite, 3.5 km north, contains this phase. Spessartine crystals 3–50 µm in diameter are occasionally found dispersed in the rhodonite-quartz matrix along the edge of rhodonite concentrations. Numerous carbonate veins up to 1 mm in width, consisting of rhodochrosite and subordinate manganoan calcite and rare kutnohorite, are present.

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*Total iron as FeO.

†The name was approved by the Commission on New Mineral and Mineral Names, IMA.

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There are also thin crosscutting quartz veins of a later generation transecting all pre-existing textures including parsettensite aggregates.

Chemical compositions of the rhodonite, spessartine, rhodochrosite and kutnohorite analysed by EPMA* are shown in Table 1. The rhodonite and spessartine are a low-Fe variety similar to the minerals reported from a small rhodonite-spessartine lens in chlorite zone schist at Crown Range, western Otago (Hutton 1957). The Watsons Beach minerals are somewhat more lime rich, though as a whole the chemistry of the minerals from the two localities is similar.

Parsettensite occurs as 100–300 μm diameter flaky crystals aggregated in dark-coloured patches up to 5 cm in size, replacing rhodonite-quartz. Parsettensite also occurs in isolated laths or fan-shaped crystal aggregates in quartz and it is often associated with the new mineral coombsite.

Coombsite is found as brown patchy aggregates a few millimetres in diameter among rhodonite and quartz, sometimes associated with parsettensite and spessartine. Caryopilite occurs rarely as brown aggregates of a few millimetres in size in rhodochrosite concentrations.

Coombsite is named in honour of Professor Douglas Saxon Coombs, University of Otago. The type material (OU34460) is deposited in the Museum of the Geology Department, University of Otago, and Smithsonian Institution, Washington, D.C., U.S.A.

MINERALOGY OF COOMBSITE, PARSETTENSITE, AND CARYOPILITE

Coombsite, its properties and the relation to zussmanite

Coombsite consists of aggregates of fibro-lamellar crystals up to 20 μm in length, and often shows semispherulitic texture. The crystals are pale brownish yellow with very weak pleochroism ω > ε. The mineral has straight extinction, length slow, and first-order red to purple interference colour in standard thin sections.

The powder pattern of coombsite, obtained with an X-ray diffractometer equipped with a graphite monochrometer, from a sample packed in an aluminium holder using Ni-filtered CuKα radiation, closely resembles that of zussmanite (Table 2). Coombsite diffraction line spacings are consistently larger than those of the corresponding zussmanite lines. Relative intensities of the corresponding lines of the two minerals agree well, except that recorded intensities for zussmanite (hkl)

Table 1 Chemical compositions of rhodonite, spessartine, rhodochrosite, and kutnohorite.

	Rhodonite		Spessartine		Rhodochrosite		Kutnohorite
	Otago†	Crown Range‡	Otago†	Crown Range‡	Otago†		Otago†
					Matrix	Vein	
SiO_2	45.90	46.42	35.40	35.87			
TiO_2	0.01		0.42				
Al_2O_3	0.04	0.07	20.38	20.84			
Fe_2O_3		0.11		0.06			
FeO	0.54*	1.49	0.10*	1.78	0.45	2.00	4.79
MnO	46.94	47.62	36.95	38.24	60.19	57.23	15.64
MgO	0.09	0.92	0.00	0.22	0.02	0.08	3.29
CaO	6.65	3.26	6.31	2.72	0.92	2.12	34.02
Na_2O	0.02		0.01				
K_2O	0.01		0.01				
H_2O^-		0.18		0.15			
Total	100.20	100.07	99.58	99.88	61.58	61.43	57.74
O =	3	3	12	12			
Si	0.99	1.00	2.92	2.95			
Ti	0.00		0.03	0.00			
Al	0.00	0.00	1.98	2.02			
Fe^{+3}		0.00		0.02			
Fe^{+2}	0.01	0.03	0.01	0.12			
Mn	0.86	0.86	2.58	2.67			
Mg	0.00	0.03	0.00	0.03			
Ca	0.15	0.08	0.56	0.24			
Na	0.00		0.00				
K	0.00		0.00				
Total	2.01	2.00	8.08	8.05			
$FeCO_3$					0.73	3.23	7.72
$MnCO_3$					97.53	92.74	25.34
$MgCO_3$					0.04	0.17	6.88
$CaCO_3$					1.64	3.78	60.72
Total					99.94	99.92	100.66

*Total iron as FeO.
†Watsons Beach, SE Otago. This paper.
‡Hutton (1957).

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*An automated 3 spectrometer wavelength dispersive probe JXA-5A operated at 15 kV using Bence-Albee correction.

lines, (306, 312), (315, 401), and (410, 324), are weaker than these measured here for coombsite.

The similarities indicate that coombsite has virtually the same crystal structure as zussmanite. Coombsite diffraction lines are indexed by analogy with the known zussmanite data, and axial parameters have been calculated using 9 preferred diffraction lines for 17 indexed atomic planes. The resulting axial parameters are compared with the values for zussmanite that have been newly calculated on the same combination of lines from JCPDS 19-1500* (Table 2).

The densities of coombsite and zussmanite are calculated on the cell volume and the molecular contents. The values (Table 2) are in keeping with the measured values

The unit cell volume of the Watsons Beach coombsite is 4.8% larger than that of the zussmanite. This corresponds to a 5.7% difference for the ideal Fe and Mn end-members of the assumed zussmanite-coombsite series, and agrees well with the difference for other Fe-Mn oxysalts series (e.g., fayalite-tephroite 5.7%, and siderite-rhodochrosite 5.8%).

The chemical composition of coombsite is shown in Table 3 along with that of zussmanite averaged from Muir Wood (1980). Cations allocated to 49 oxygens along with the chemical formula of zussmanite, $KFe_{13}(Al,Si)_{18}O_{42}(OH)_{14}$, are also shown. The formula requires 18 cations in the tetrahedral sites, 13 in the octahedral sites, and 1 in the 12 co-ordination sites, and this is almost fulfilled in both mineral analyses. The Watsons Beach coombsite chemical formula is approx. $K_{1.0}Na_{0.1}(Mn_{11.8}Fe_{1.0}Mg_{0.6})(Al_{1.5}Si_{10.4})O_{42}$ $(OH)_{14}$, whereas the idealised coombsite formula is $KMn_{13}(Al,Si)_{18}O_{42}$ $(OH)_{14}$. The coombsite is too fine grained and too intimately mixed with other phases to allow adequate separation for a direct water determination. The (OH) content is assumed to be as in zussmanite.

Zussmanite was first described from Franciscan metasediments at Laytonville, California, by Agrell et al. (1965). This is still the sole locality at which the mineral has been found. Lopes-Vieira & Zussman (1969) showed the rhombohedral crystal structure with stacked layers of edge-shared Fe-(O,OH) octahedra, and six-membered ring (Si,Al)-O tetrahedra, and the layers are linked by rings of three (Si,Al)-O tetrahedra and K ions. The idealised formula of zussmanite based on this structure is $KFe_{13}(Al,Si)_{18}O_{42}$ $(OH)_{14}$. The hexagonal true cell contains 3 formula units including 13 Fe(O,OH) octahedra in each layer. Various stacking disorders found in the zussmanite were studied by Jefferson (1976).

Muir Wood (1980) described a zussmanite-related mineral "ZU2" phase associated with zussmanite and also occurring at one other locality (Coos County, Oregon) which contains up

Table 2 X-ray powder pattern and physical properties of coombsite and zussmanite (estimated standard deviations are in parentheses).

Coombsite†		Zussmanite‡		
d (Å)	I	d (Å)	I	hkl
9.68	100	9.60	100	003
		5.82	2	104, 110
		4.98	4	105, 113
4.835	30	4.78	45	006
3.844	5	3.78	10	107, 205
3.737	15	3.69	8	116, 212
		3.38	4	108, 214
3.241	25	3.19	25	009, 207
		2.92	2	208, 220
2.845	*	2.79	4	119, 217
2.793	70	2.74	10	306, 312
		2.61	2	314, 218
2.556	90	2.51	16	315, 401
2.426	5	2.39	6	$00\underline{12}$
2.349	10	2.31	4	309, 317
2.241	50	2.20	10	410, 324
		2.14	2	413
2.034	10	2.00	6	$31\underline{10}$, 416
1.940	10	1.908	8	$31\underline{11}$, $21\underline{13}$
		1.806	4	$21\underline{14}$
		1.731	4	$31\underline{13}$, $32\underline{11}$
1.6796	12	1.653	8	3114
1.6385	20	1.616	10	434, 520
1.6187	15	1.594	10	$00\underline{18}$, 345
		1.531	2	526, 612
1.5334	10	1.510	6	$13\underline{16}$

	Coombsite†	Zussmanite‡
Hexagonal cell		
$\underline{a}$ (Å)	11.828(2)	11.647(2)
$\underline{c}$ (Å)	29.146(9)	28.682(6)
V (Å^3)	3531(1)	3370(1)
Rhombohedral cell		
$\underline{a}$ (Å)	11.875(4)	11.689(3)
∠ (°)	59.74 (4)	59.76 (3)
V (Å^3)	1177(1)	1123(1)
Density		
D_{calc}	3.063	3.149
D_{meas}	3.0(1)	3.146**
Refractive indices		
ε	1.600(1) pale brownish yellow	1.623** colourless
ω	1.619(1) pale brownish yellow	1.643** green

* Peak overlapped with rhodochrosite peak.

** Agrell et al. (1965).

†This paper.

‡JCPDS 19-1500. The original data of the University Museum, Department of Geology and Mineralogy, Oxford University gave a_{hex} 11.65, c_{hex} 28.668 Å, whereas Agrell et al. (1965) gave $\underline{a}$ 11.66, $\underline{c}$ 28.69 Å.

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*Joint Committee on Powder Diffraction Standards, International Centre for Diffraction Data. Mineral Powder File No. 19-1500.

to 16.6% MnO. Despite the overall similarity of the powder patterns of this phase and zussmanite, there are some differences which led him to conclude that "ZU2" may have a different structure from zussmanite.

The powder pattern of coombsite differs from those of the "ZU2" phase and of minnesotaite. A manganiferous variety of the latter has been described in association with zussmanite by Muir Wood (1980).

Guggenheim & Eggleton (1987, 1988) categorised modulated 2:1 layer silicates into "island" and "strip" structure types. Zussmanite, stilpnomelane, and bannisterite are examples of the "island" structures which have a somewhat isolated tetrahedral group "island" in the tetrahedral layer, whereas minnesotaite and ganophyllite have a "strip" structure in the tetrahedral layer. Single crystal diffraction study of coombsite has not been possible due to its fine grain size.

Parsettensite and caryopilite—their mineralogical properties

Parsettensite occurs in the Mn-silicate lens as aggregates of flaky dark-coloured mineral as well as occasional dispersed crystals in the rhodonite-quartz matrix. The mineral is reddish brown in transmitted light. Its high-order interference colour in sections cut perpendicular to the flakes resembles that of biotite, but the flaky crystals always show narrow sectors and exhibit wavy extinctions. The optical axial angle appears almost zero on the elastic axis X, and the mineral is strongly pleochroic in X colourless, Y and Z reddish brown.The X-ray pattern accords well with the pattern of original parsettensite reported by Geiger (1948, also JCPDS 25-8). In Table 4 are shown data from Watsons Beach and original data from Parsettens along with those reported by Guggenheim & Eggleton (1988).

Table 3 Chemical compositions of coombsite and zussmanite.

	Coombsite†	Zussmanite‡
SiO_2	45.18	47.40
TiO_2	0.01	0.02
Al_2O_3	3.59	3.76
FeO*	3.28	36.23
MnO	38.19	1.96
MgO	1.08	1.89
CaO	0.03	0.07
Na_2O	0.08	0.22
K_2O	2.19	1.78
Total	93.63	93.33
O = 49		
Si	16.41	16.87
Ti	0.00	0.01
Al	1.54	1.58
Fe	1.00	10.78
Mn	11.75	0.59
Mg	0.58	1.00
Ca	0.01	0.03
Na	0.06	0.15
K	1.01	0.81
Total	32.36	31.82
Si+Al	17.95	18.45
M**	13.34	12.40

* Total iron as FeO.

**M = Fe + Mn + Mg + Ca.

†This paper. Average of 5 EPMA analyses.

‡Average of 13 EPMA analyses from Muir Wood's (1980) 15 data in appendix 3. Numbers of analyses averaged are: 3, 4, 12, 21, 22, 27, 59, 60, 65, 68, 76, 85, and 86. Numbers 50 and 66 are not included in the average as they are abnormally high in MnO contents.

Parsettensite has been regarded as the Mn equivalent of stilpnomelane (Geiger 1948), but Ozawa et al. (1986) showed by single crystal electron diffraction of parsettensite from the original locality and of a similar mineral from Kumahata, Kumamoto, Japan, that the unit cell contains 7 × 7 Mn(O,OH) octahedra, arranged in a different manner from stilpnomelane. They gave $\underline{a}$ 39.1 Å, $\underline{b} = \underline{a}\sqrt{3}$ 22.6 Å and d_{001} 12.6 Å monoclinic unit cell. Two possible unit cells may be deduced from their data, one is with approximately ∠β 95.6°, $\underline{a}$ 39.0, $\underline{b}$ 22.7, and $\underline{c}$ 12.4 Å, and another approximately ∠β 120.7°, $\underline{a}$ 39.3, $\underline{b}$ 22.8, and $\underline{c}$ 14.5 Å. Guggenheim & Eggleton (1988) used the latter axial setting. As their data contain questionable line indexing, re-indexing of their data was carried out. According to our calculations, reasonable indices can not be given for several of their diffraction lines, and those lines have no equivalents in Geiger's (1948) data from Parsettens as well as in our Watsons Beach material. The axial parameters calculated for the parsettensite using ∠β 120.7° setting led to larger cell volumes which did not give plausible calculated densities. Therefore the three parsettensite data were indexed using ∠β 95.6°. The results are shown in Table 4. Many of the additional lines of Guggenheim & Eggleton's (1988) data do not fit to any reasonable indices. The axial parameters in Table 4 are calculated using selected data.

The chemical composition of the Watsons Beach parsettensite (average of three results) is shown in Table 5, along with the analytical data of the minerals from the original locality, Parsettens, Switzerland (Jakob 1923), and Kumahata, Japan (Ozawa et al. 1986). The chemical formula of parsettensite deduced from the chemical analyses and the half cell content shown by Ozawa et al. (1986) is $K_2(Mg,Fe,Mn)_{49}(Al,Si)_{72}O_{168}(OH)_{42}\ 28H_2O$.

Densities calculated on the basis of $O_{336}(OH)_{84}\ 56H_2O$ per unit cell gave reasonable values as compared to the measured values. The K_2O content of Watsons Beach parsettensite is widely variable between 1 and 10%, according to EDS done at Australian National University using TPD probe, as well as WDS at Otago University. To minimise K migration, the analyses were carried out under various analytical conditions including different beam current, beam size, peak and background measurement times, and sample movement at various speeds during analyses. While other elemental concentrations vary slightly, SiO_2 concentrations change in reciprocal relation to those of K_2O. Unusually high concentration of K_2O in EPMA analyses was observed by Plimer (1977) in a structurally similar mineral, bannisterite, from Broken Hill, Australia. Craw (1981) observed an increase of K concentration in stilpnomelane if the beam was trained on the same spot for an extended period. High concentration of K in the Watsons Beach parsettensite is not likely to be an artefact as in the case of Craw (1981) but the reason for the phenomenon is not clear. The most likely three analyses are chosen to get the listed average in Table 5.

The Watsons Beach parsettensite contains a considerable amount of Fe and would better be called an Fe-rich or ferroan parsettensite. The cell volume of this mineral is smaller than the parsettensite from the original locality, and the density and refractive indices are higher.

Caryopilite occurs as brown patchy aggregates a few millimetres in size in rhodochrosite-rich portions of the Mn-silicate lens. Under the microscope, the mineral is seen as pale-brown pleochroic scaly crystals <50 µm in length. A small amount of parsettensite co-exists with it.

X-ray powder pattern, physical properties, and chemistry of the caryopilite are in good accordance with those of the caryopilite from the original locality, Pajsberg, Sweden (Hamberg 1889; Larsen 1925; Kato 1963), a mineral from Ichinomata mine, Kumamoto, Japan (Yoshimura et al. 1958; also JCPDS 31-831), and the one from Hurricane Claim, Olympic Peninsula, Washington, U.S.A. (Guggenheim et al. 1982). The data for the four caryopilites are shown in Table 6. Yoshimura et al. (1958) gave a one-layer monoclinic cell for the Ichinomata caryopilite, with $\underline{a} = \underline{b}\sqrt{3}$, $\underline{b}$ 9.8, $\underline{c}$ 7.5 Å, and ∠β 104.6°. Guggenheim et al. (1982) found in their caryopilite X-ray powder patterns a small amount of trigonal phase in addition to monoclinic host. The trigonal phase gave only weak characteristic diffraction lines, however, and is not found in other records including Watsons Beach material. In Table 6, only monoclinic (1M) phase lines are shown, although the data from Washington show additional trigonal phase lines. Axial parameters of the four caryopilites have been newly calculated based on the indexing given by Guggenheim et al. (1982).

The Washington mineral has a larger cell volume than the other three minerals. This is in accord with the chemical compositions and calculated cell contents of the mineral (Table 7) as it has more large-sized Mn ions and less small-sized Fe and Mg ions than the minerals from other localities. The densities calculated using formulae of the type $(Mn,Mg,Fe)_6Si_4O_{10}(OH)_8$ with one formula unit per unit cell are in keeping with the measured values, D_{meas} (Table 6).

Table 4 X-ray powder pattern, cell dimensions, and properties of parsettensite (estimated standard deviations are in parentheses).

	Otago*		Parsettens†		Parsettens‡		
	d (Å)	I	d (Å)	I	d (Å)	I	hkl
	12.55	100	12.1	100	12.62	200	001
					11.37	40	020
					9.62	25	
					8.62	15	
					7.34	10	
	6.23	7	6.2	20	6.27	30	$10\bar{2}$, 002
	4.545	4	4.5	40	4.51	50	721
					4.28	30	$71\bar{2}$
	4.167	9	4.2	60	4.195	50	$10\bar{3}$
	3.794	4	3.84	50	3.78	24b	123
	3.676	14	3.70	50	3.70	50b	722
	3.243	7	3.26	20			070
	3.118	7	3.14	50	3.145	40	713
					3.006	15	
					2.923	20	
	2.784	7	2.79	80	2.791	70	$71\bar{4}$
					2.708	20	
	2.635	21	2.65	100	2.639	100	$\underline{14}11$
					2.512	20	772
					2.464	15	015
	2.408	14	2.42	50	2.417	60	$\underline{14}0\bar{3}$
			2.36	40			773
	2.167	7	2.18	40	2.174	40	$\underline{14}0\bar{4}$
			2.04	20			$\underline{14}72$, 106
	1.935	6	1.943	10			$\underline{14}0\bar{5}$
					1.628	70	$\underline{21}03$
					1.615	45	$0\underline{14}0$
					1.575	35	$\underline{14}16$
					1.570	1	
					1.516	20	$72\bar{8}$
$\underline{a}$ (Å)	39.047(7)		39.28(2)		39.04(1)		
$\underline{b}$ (Å)	22.701(7)		22.59(2)		22.610(5)		
$\underline{c}$ (Å)	12.332(3)		12.38(2)		12.427(6)		
∠β(°)	95.62(1)		95.7(1)		95.67(3)		
V ($Å^3$)	10879(5)		10928(24)		10916(7)		
D_{calc}	2.628		2.581				
D_{meas}	2.69		2.59				
α	1.560(1)		1.546				
β	1.595(1)						
γ	1.595(1)		1.576				
$2V_x$ (°)	0						
X	colourless		clear yellow to colourless				
Y, Z	reddish brown		light greenish yellow				

*Watsons Beach, SE Otago. This paper.

†JCPDS 25-8: X-ray data from Geiger (1948); other physical properties from Jakob (1923).

‡Guggenheim & Eggleton (1988). hkls are re-indexed.

Table 5 Chemical compositions of parsettensite.

	Otago†	Kumahata‡	Parsettens§
SiO_2	45.64	45.80	42.90
TiO_2	0.00	0.02	
Al_2O_3	4.26	4.43	4.35
V_2O_5			0.32
Fe_2O_3			0.35
FeO*	6.64	0.68	
MnO	31.96	36.20	34.43
MgO	1.24	2.58	2.70
CaO	0.02	0.22	tr.
Na_2O	0.06		0.20
K_2O	1.61	0.77	0.94
H_2O^+			9.66
H_2O^-			3.15
Total	91.43	90.70	99.27**
O = 189			
Si	64.19	63.99	63.41
Al	7.06	7.29	7.58
Fe^{+3}			0.39
Fe^{+2}	7.81	0.79	
Mn	38.07	42.84	43.04
Mg	2.60	5.37	5.93
Ca	0.03	0.33	
Na	0.16		0.57
K	2.89	1.37	1.77
Total	122.81	121.98	122.69

* Total iron as FeO.

**Includes CO_2 0.25 and HCl 0.02.

†Watsons Beach, SE Otago. This paper. Average of 3 EPMA analyses.

‡Ozawa et al. (1986).

§Jakob (1923).

Table 7 Chemical compositions of caryopilite.

	Otago†	Pajsberg††	Ichinomata‡	Washington§
SiO_2	35.28	36.16	35.54	35.4
TiO_2	0.01			
Al_2O_3	1.48	0.35	1.74	0.78
Fe_2O_3		1.33		
FeO*	9.88		1.06	0.72
MnO	42.04	46.46	47.00	52.1
MgO	1.27	4.80	3.76	0.58
CaO	0.13	0.28	1.25	0.00
Na_2O	0.04			0.15
K_2O	0.09	0.20**		0.02
H_2O^+		9.81	8.68	
H_2O^-			1.41	
Total	90.22	99.85***	100.44	89.75
O = 14				
Si	4.11	4.17	4.07	4.22
Ti	0.00			
Al	0.20	0.05	0.24	0.11
Fe	0.96	0.12	0.10	0.07
Mn	4.25	4.54	4.58	5.26
Mg	0.22	0.83	0.64	0.10
Ca	0.02	0.03	0.15	0.00
Na	0.01			0.03
K	0.01			0.00
Total	9.78	9.74	9.78	9.79

* Total iron as FeO.

** Total alkalis as oxides.

***Includes PbO 0.37 and Cl 0.09.

†Watsons Beach, SE Otago. This paper.

††Hamberg (1889) and Larsen (1925).

‡Yoshimura et al. (1958), also JCPDS 31-831.

§Guggenheim et al. (1982). The atomic allotment is recalculated.

Table 6 X-ray powder pattern, cell dimensions, and physical properties of caryopilite (estimated standard deviations are in parentheses).

	Otago*		Pajsberg†		Ichinomata‡		Washington§		1M
	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	hkl
	7.22	100	7.31	100	7.28	100	7.30	80	001
	3.62	50	3.63	80	3.63	60	3.639	50	002
	2.814	30	2.797	40	2.81	70	2.825	60	$20\bar{1}$, 130
	2.520	75	2.508	70	2.51	90	2.521	100	$20\bar{2}$, 131
							2.427	7	003
	2.346	30	2.308	20	2.37	10	2.382	20	201, $13\bar{2}$
	2.100	15	2.103	20b	2.10	40	2.101	35	$20\bar{3}$, 132
	1.966	7	1.973	10b	1.97	10	1.968	20	202, $13\bar{3}$
			1.800	10b	1.80	5	1.820	2	004
	1.725	12	1.728	10b	1.73	10	1.731	25	$20\bar{4}$, 133
	1.641	17	1.634	20	1.634	50	1.643	35	060, $33\bar{1}$
							1.626	20	203, $13\bar{4}$
	1.601	12			1.595	30	1.603	25	061, 330, $33\bar{2}$
$\underline{a}$ (Å)	5.686(2)		5.654(6)		5.662(2)		5.6927(5)		
$\underline{b}$ (Å)	9.848(2)		9.80(2)		9.805(3)		9.8595(8)		
$\underline{c}$ (Å)	7.487(3)		7.542(9)		7.533(3)		7.5095(7)		
∠β(°)	104.61(3)		104.15(9)		104.46(3)		104.646(8)		
V (Å³)	405.6(2)		405.3(9)		405.0(3)		407.79(6)		
D_{calc}	2.910		2.835		2.852		2.904		
D_{meas}	3.0(1)		2.83–2.91		2.87				
α	1.610		1.603		1.6055				
β	1.635		1.632		1.6325				
γ	1.635		1.632		1.6325				

*Watsons Beach, SE Otago. This paper.

†Kato (1963).

‡Yoshimura et al. (1958), also JCPDS 31-831.

§Guggenheim et al. (1982), partial data. Weak lines due to the trigonal phase and 13 additional lines down to 1.087 Å are given in the original table.

Note: Axial parameters and densities are newly calculated for all listed caryopilites using the hkl of Guggenheim et al. (1982).

The Watsons Beach mineral contains 9.88% FeO* and it is one of the most Fe-rich varieties of caryopilite known. The Fe-rich character of the Watsons Beach parsettensite and caryopilite may be a reflection of a relatively high pressure crystallisation.

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