

Piemontite schists from Haast River, New Zealand

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SUMMARY. Piemontite-bearing metachert horizons are recorded from regionally metamorphosed eugeosynclinal rocks at Haast River, in the Southern Alps of New Zealand. Piemontite schist mineralogical assemblages produced by epidote-amphibole facies metamorphism are described petrographically, and are compared with lower grade occurrences in the Haast Schist Group.

A chemical analysis yields a composition of $(\text{Ca}_{1.75}\text{Mg}_{0.02}\text{Mn}_{0.25}\text{Na}_{0.03}\text{K}_{0.01})(\text{Al}_{2.23}\text{Fe}_{0.53}\text{Mn}_{0.24}\text{Ti}_{0.01})\text{Si}_{3.06}\text{O}_{12}(\text{OH})_{0.9}$, which is compared graphically with other metamorphic, hydrothermal, and metasomatic piemontites.

Single-crystal Weissenberg and powder camera X-ray data are given, and an attempt made to relate these X-ray parameters to chemical variation within the piemontite composition range.

PIEMONTITE was first recorded in New Zealand by Turner (1933) who described quartz-muscovite-piemontite schist boulders from the Shotover River, Central Otago. Since then, similar rocks have been found elsewhere in the Haast Schist Group (Hutton, 1940, 1942; Turner, 1946; Mason, 1955).

Further localities, from higher metamorphic grades than previously recorded, are here described from the Haast River area, South Westland. As with the Central Otago occurrences the piemontite schist is found interbedded with greenschist, spessartine metacherts, and rare ultrabasic schists in a dominantly quartzofeldspathic schist sequence; a typical eugeosynclinal association.

Piemontite as a metamorphic mineral has been recorded from Japan (Koto, 1887; Tsuboi, 1936; Hashimoto, 1957, 1959, 1960; Hirowateri, 1954; Suzuki, 1924; Ernst, 1964; Banno, 1964; Seki *et al.*, 1969; Ishibashi, 1969), California (Mayo, 1932; Smith and Albee, 1968), Timor and Celebes (De Roever, 1940, 1947), Russia (Voznesenskii, 1961), France (Lacroix, 1888), India (Nayak, 1961; Sadashivaiah, 1958; Bilgrami, 1956), Norway (Morton and Carter, 1963), and New Zealand.

Many of the localities cited above show characteristically a metamorphism of high pressure or high-pressure intermediate type (Miyashiro, 1961). However, the metamorphic facies series under study at Haast River, while lacking staurolite, kyanite, and sillimanite zones (as defined for pelites), is otherwise more akin to Barrovian type metamorphism. Piemontite also occurs in a low-pressure intermediate metamorphic terrain at the Tanzawa Mountains, Japan (Seki *et al.*, 1969). This would suggest that it is bulk chemistry (especially oxidation state) that controls the occurrence of metamorphic piemontite, and that its appearance is not confined to any single facies series (cf. experimental data, Strens, 1964).

Field occurrence

The new localities of piemontite schist are from the garnet zone of the Haast Schist Group (fig. 1).

In the field the piemontite schist typically occurs as a massive or semischistose unit, composed often of intimately interlaminated piemontite- and spessartine-bearing

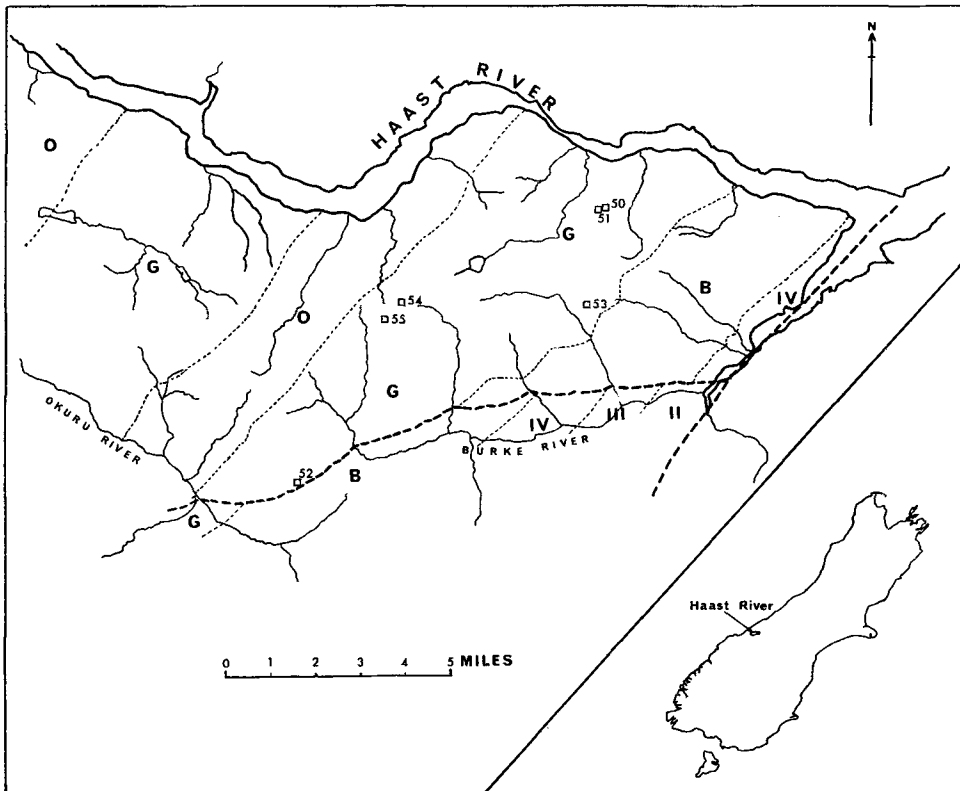


FIG. 1. Locality map. Haast River, South Island, New Zealand (II, III, IV—Chlorite subzones, B—Biotite zone, G—Garnet zone, O—Oligoclase zone. First three numerals of O.U. catalogue number omitted, i.e. 50 = 27650).

(rarely epidote-bearing) metacherts. Mineralogical assemblages recorded from the Haast River area are:

- O.U.27650 Qtz-alb-mus-phlog-piem-spess-hemat-apat-tourm
- O.U.27651 Qtz-alb-mus-phlog-piem-hemat-apat-tourm
- O.U.27652 } Qtz-alb-mus-phlog-piem-spess-chlor-hemat-tourm-sph
- O.U.27653 }
- O.U.27654 Qtz-alb-mus-phlog-piem-trem-spess-apat-tourm-sph.

These garnet-zone schists differ mineralogically from the Central Otago piemontite schists described by Hutton (1940, 1942) in the development of a very pale brown

phlogopitic mica. A phlogopite isograd here defined for piemontite schist would correspond to, or be upgrade of, the biotite isograd defined for the dominant lithology of the area, a quartzofeldspathic schist.

The highest grade piemontite schist (O.U.27654) from the uppermost part of the garnet zone was selected for detailed petrographic, geochemical, and X-ray work. Its mineralogy and chemistry are now discussed in detail.

Mineralogy

Quartz. The predominance of quartz, typically forming xenoblastic interlocking grains up to 0.2 mm in diameter, is a reflection of the bulk rock composition (partial whole rock analysis SiO_2 89.46%).

Albite. Interbedded quartzofeldspathic schists and greenschists from the garnet zone in the Haast area are characterized by the coexistence of albite and oligoclase feldspars (Crawford, 1966). In the associated metacherts, however, only albite has been identified, where it occurs as elongate grains up to 1 mm in length, and often with a length: breadth ratio of 20:1.

Micas. In certain piemontite schists muscovite, magnesium-rich chlorite, and phlogopite can coexist, although in the specimen studied only muscovite and phlogopite are present. Mica flakes show perfect parallel orientation, defining a schistosity surface accentuated by crude segregation of quartz- and piemontite-rich laminae. The phlogopite is characteristically pale in colour, but with distinctive pleochroism: $\gamma = \beta$ yellow brown, α pale yellow brown, $\beta = \gamma = 1.604 \pm 0.001$. A partial chemical analysis gave TiO_2 1.04%, FeO 2.11%, and MgO 19.4%, which data, together with R.I., suggests an approximate composition (Heinrich, 1946) of: $\text{K}_2(\text{Fe}^{3+}_{0.63}\text{Fe}^{2+}_{0.25}\text{Ti}_{0.12}\text{Mg}_{4.10}(\text{Al}^{3+} + \text{Mn}^{2+})_{0.9})\text{Si}_6\text{Al}_2\text{O}_{20}(\text{OH})_4$.

Garnet. Although generally idioblastic, the habit of some garnets suggests a formation at a late metamorphic stage, since it poikiloblastically encloses piemontite and hematite. Skeletal aggregates and elongate grains are common features. Furthermore, within thin piemontite-rich bands sandwiched between thicker quartz laminae there is often 'end to end' or en-echelon growth of elongate garnet, albite, and phlogopite grains. Garnets from piemontite schists often show anomalous optical properties, often with a pronounced birefringence, and with a few grains of rounded outline showing complex internal structures resembling twinning.

Physical and chemical properties determined, n 1.816 ± 0.002 , a 11.730 \AA , MnO 21.17%, would suggest an approximate composition (Winchell, 1958) of $\text{Spess}_{60}\text{Pyr}_{10}\text{And}_{30}$. This dominantly Mn^{2+} , Fe^{3+} garnet is similar in composition to those described from Californian piemontite schists by Smith and Albee (1968).

Amphibole. A colourless to very pale green amphibole is occasionally present, often occurring as radiating clusters around garnet crystals. Properties γ 1.639 ± 0.002 , γ : [001] 18° , $2V_a$ $80^\circ \pm 2^\circ$ would indicate a composition within the actinolite-tremolite series of $\text{Ca}_2\text{Mg}_{4.4}\text{Fe}_{0.6}\text{Si}_8\text{O}_{22}(\text{OH})_2$.

Piemontite occurs as minute prismatic crystals generally less than 100 μm in length, but which nevertheless impart a pink colouration to the schist. Crystallographic forms present in the prisms are $\{10\bar{1}\}$, $\{001\}$, and $\{100\}$, with twinning $\{100\}$ fairly common. Although generally homogeneous, crystals in some schists are zoned, with a characteristically coloured piemontite core, rimmed by a colourless, manganese-poor epidote. Optical and X-ray properties are listed in Table I.

TABLE I. *O.U.27654—Piemontite*

		No. of ions on basis of 13(O,OH)		
SiO ₂	38.15	Si	3.062	α 1.740 \pm 0.0005 [†] , yellow
TiO ₂	0.12			β 1.766 \pm 0.002, pale pink
Al ₂ O ₃	23.56	Al	2.229	γ 1.800 \pm 0.002, crimson
Fe ₂ O ₃	8.70	Ti	0.007	$\gamma > \alpha > \beta$ $\delta = 0.060$
FeO	n.d.	Fe	0.526	
MnO	7.24*	Mn	0.238	α : $[001]$ 6° \pm 1°; 2V _{γ} calc 84° [‡]
MgO	0.14			
CaO	20.33	Mn	0.254	D _{meas} 3.488 \pm 0.005 g/cm ³
Na ₂ O	0.20	Mg	0.017	D _{calc} 3.484 g/cm ³
K ₂ O	0.13	Ca	1.748	a 8.843 \pm 0.001 Å
H ₂ O ⁺	1.68	Na	0.031	b 5.665 \pm 0.001 Å
H ₂ O ⁻	0.00	K	0.014	c 10.150 \pm 0.001 Å
Sum	100.25	OH	0.900	V 459.88 \pm 0.01 Å ³
				β 115° 15'

* All manganese present expressed as Mn²⁺.

[†] All refractive index measurements made with Na_D light (α refractive index measured by single variation methods).

[‡] Due to the extremely fine grain size of the mineral, the optic axial angle could not be measured. n.d. Not detected (cf. Smith and Albee).

Tourmaline. As previously recorded by Hutton, 1940, piemontite schists typically contain minor amounts of fine-grained elbaite tourmaline. In these higher-grade schists the tourmaline occurs again as small (<100 μm) colourless elongate prisms, concentrated in piemontite- and spessartine-rich bands. ω 1.659 \pm 0.001, very pale pinkish brown, ϵ 1.629 \pm 0.001, colourless, absorption $\omega > \epsilon$.

Opaque. Although manganese oxide stains are occasionally noticed on schistosity and joint surfaces, X-ray work indicated only hematite as a primary phase in the piemontite schists. Sphene and rounded apatite occur in accessory amounts.

Analytical results

Piemontite was separated by heavy liquid and electromagnetic techniques. Due to the fine-grained nature of the separate (<45 μm) there were very minor amounts of quartz and hematite in the sample, probably not exceeding 1% of the total.

The separate was analysed by a combination of atomic absorption, flame photometer, spectrophotometer, and wet chemical standard techniques (table I).

Although trivalent manganese was not determined, it is clear from the atomic

formula that Mn, presumably in different oxidation states, must occupy both octahedral and large cation (Ca) sites. The equal partition of manganese between the two structural sites is unusual, although other analyses taken from the literature often contain appreciable amounts of eight-fold co-ordinated manganese.

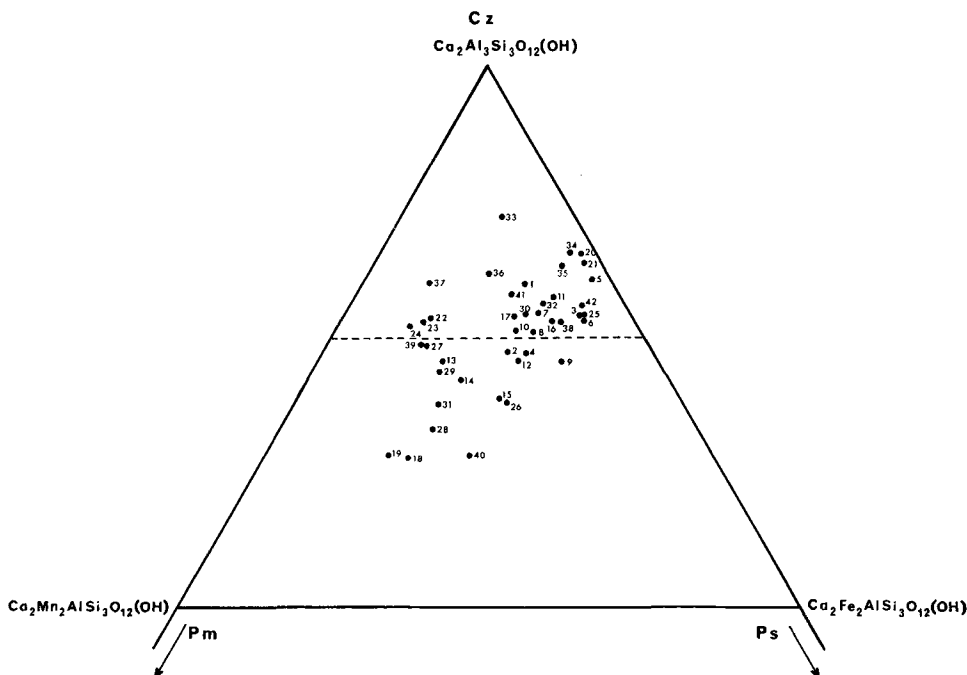


FIG. 2. Cz-Pm-PS diagram showing range of piemontite composition. 1. This paper. 2. Hutton (1940). 3-8. Smith and Albee (1968). 9. Hashimoto (1959). 10. Suzuki (1924). 11. Tsuboi (1936). 12-14. Marmo, Neuvonen, and Ojanpera (1959). 15. Hirowateri (1954). 16. Tono (in Hashimoto, 1957). 17. Koto (1887). 18-19. Bilgrami (1956). 20-1. Hutton (1938). 22. Williams (1893). 23. Short (1933). 24. Guild (1935). 25, 27, 28. Malmquist (1929). 26. Oedman (1950). 29. Långban piemontite—new analyses Strens (1966). 30. Ernst (1964). 31. Seki *et al.* (1969). 32. Banno (1964). 33. Lyashkevich (1958). 34-40. Strens (1966). 41-2. Ishibashi (1969).

The composition, together with piemontites taken from the literature, is plotted on the cz-ps-pm diagram of Deer, Howie, and Zussman (fig. 2). There is quite a wide range in composition, with low-grade metamorphic and hydrothermal piemontites (including withamite) being manganese-poor, and grouped about a composition $\text{Ca}_2\text{FeAl}_2\text{Si}_3\text{O}_{12}\text{OH}$. Increasing substitution of Mn into the structure is evident with metasomatic and Mn-ore occurrences, a trend in general agreement with the prediction of Miyashiro and Seki (1958).

X-ray data

A powder photograph of piemontite was taken using a 114.83-mm diameter Debye-Scherrer camera with a 70-hour exposure to Mn-filtered Fe- $K\alpha$ radiation. In addition, oscillation and equi-inclination Weissenberg photographs were prepared from a

piemontite prism 90 μm long and 30 μm wide, mounted with b axis parallel to the axis of the camera. Photographs of the $h0l$, $h1l$, and $h2l$ layer-lines of piemontite each involved 48-hour exposure to Ni-filtered $\text{Cu-K}\alpha$ radiation.

TABLE II. *O.U.27654—Piemontite*

<i>hkl</i>	d_{calc}	d_{obs}	<i>I</i>	<i>hkl</i>	d_{calc}	d_{obs}	<i>I</i>	<i>hkl</i>	d_{calc}	d_{obs}	<i>Ik</i>
001	9.180	9.226	0.3	114	1.879	1.880	4	430	1.373	1.372	1
*100	7.998	8.003	2	124	1.878			*502	1.343	1.344	1.344
*†102	5.009	5.019	4	*312	1.860	1.859	0.6	240	1.335	1.355	0.4
*110	4.623	4.620	1	130	1.838	1.839	0.6	142	1.308	1.309	0.7
111	4.611			131	1.837			342	1.297	1.297	1.5
*†200	3.999	3.996	5	132	1.767	1.767	1	*017	1.278	1.278	0.6
†111	3.772	3.770	1	*422	1.743	1.744	0.8	*†308	1.269	1.269	0.8
†211	3.485	3.495	4	230	1.708	1.707	1	423	1.269		
*†102	3.403	3.405	2	232	1.705			136	1.237	1.237	1.238
*†201	3.200	3.203	3	*†206	1.690	1.689	1	432	1.221	1.221	0.8
*003	3.060	3.060	0.7	*†306	1.670	1.669	1	530	1.220		
†302	2.906	2.903	10	132	1.651	1.651	1	706	1.191	1.191	0.7
†113	2.902			†106	1.637	1.639	441	1.183	1.185	0.7	
*020	2.832	2.831	4	†420	1.633	to	4	008	1.148	1.147	0.7
*†211	2.786	2.788	1	†511	1.631			150	1.122	1.122	1
*†013	2.692	2.690	4	214	1.630	151	1.122				
*†120	2.670	2.670	4	†124	1.630	1.628	207	1.113	1.113	1.113	1
121	2.668			*†322	1.617	1.617		0.5			
†311	2.592	2.598	5	033	1.607	1.607	0.5	441	1.113	1.103	1
*†202	2.528	2.528	4	505	1.587	1.587	2	543	1.103		
*†122	2.466	2.468	1	†115	1.578	1.577	1	537	1.087	1.087	0.5
†022	2.410	2.407	5	†412	1.540	1.540	2	544	1.087		
*†113	2.304	2.302	3	*†510	1.539			346	1.080	1.081	0.6
†222	2.305			333	1.537	1.537	0.4	108	1.073	1.073	1.5
†401	2.154	2.159	3	232	1.513	1.514	0.5	145	1.073	1.063	1
221	2.121	2.121	3	†224	1.459	1.458	3	028	1.064		
*†023	2.079	2.079	2	304	1.459			812	1.058	1.058	1.5
*†203	2.045	2.045	2	034	1.458	1.441	1	153	1.033	1.034	1
*413	2.005	2.005	1.5	*207	1.442			735	1.033		
404	1.984	1.983	0.5	040	1.416	1.417	3	637	1.033		
105	1.984			433	1.417			546	1.016	1.016	0.8
305	1.950	1.951	0.5	*†215	1.405	1.404	1.5	019	1.004	1.004	0.3
213	1.924	1.922	1	†422	1.393	1.394	3	6.0.10	0.975	0.974	0.6
				†520	1.393						

* Reflection used for unit cell refinement. † Strong reflection on Weissenberg photographs.

Preliminary unit cell parameters were measured from the Weissenberg photographs and these values used to generate d spacings of all allowed hkl reflections for a mineral of space group $P21/m$ (programme devised by R. A. Eggleton, Department of Geology, Canberra, modified by P. B. Read, Otago). The powder camera reflections were then compared with the generated d spacings and corresponding reflections indexed. Repeated cycles of reflection indexing and unit cell dimension refinement by least squares analysis (Evans, Appleman, and Handwerker, 1963) continued until the vast majority of reflections were indexed.

In all 28 unambiguously indexed reflections were used for the final unit cell refinement, giving values as listed in table I.

Discussion

Strens (1966, fig. 2, 5, 6, and 7) summarized the optical and X-ray properties of the Mn epidotes, and found that with the substitution of manganese into the epidote structure there is an increase in the b cell dimension, with associated decrease of a and c . There is, however, a fairly wide scatter when unit cell dimensions are related to (Fe Mn) content of the piemontite.

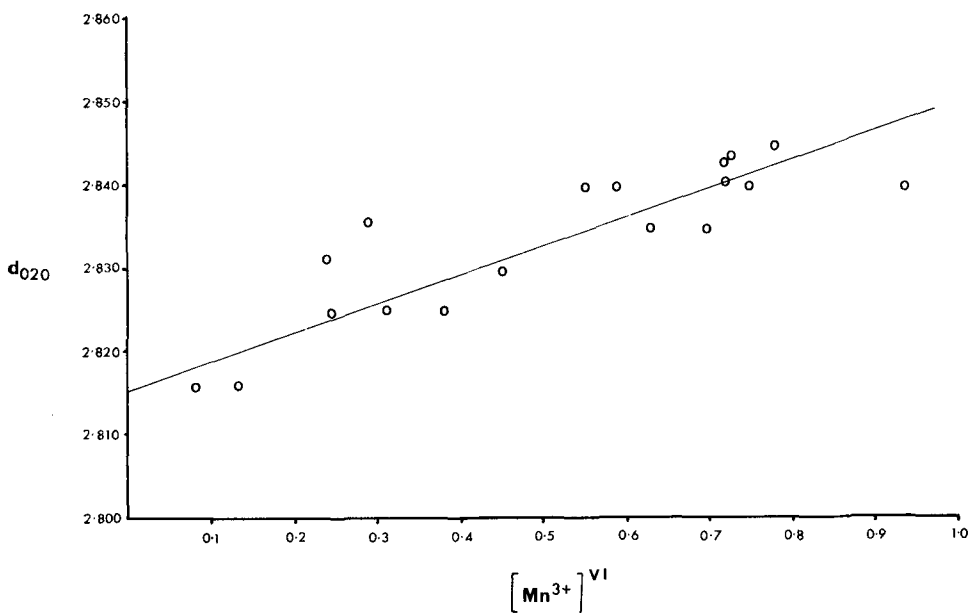


FIG. 3. Plot of d_{020} against Mn^{3+} for piemontite.

Using the indexed pattern above as a standard and reviewing the literature it was found possible to broadly relate the d spacing of only one reflection, 020, to the piemontite chemical composition. As shown in fig. 3 there appears a linear relationship between d_{020} and $[\text{Mn}^{3+}]^{\text{VI}}$, although with a wide scatter. The divergence seen could be ascribed to two factors, the experimental error in measurement of unit cell dimensions, and the effect of the Fe^{3+} content of the piemontite. In the former, an error in the measurement of b of only ± 0.01 Å would result in a shift in d_{020} of ± 0.005 Å, a very significant error considering the total variation observed. Strens (1966) has already shown for the Al-Fe epidotes that there is a linear increase of b with increasing Fe^{3+} and this component would consequently be expected to affect the $[\text{Mn}^{3+}]^{\text{VI}}$ versus d_{020} plot.

However, despite the paucity of accurate X-ray data, it would seem that an estimate of the Mn^{3+} content of a piemontite can be obtained from such a graph.

Acknowledgements. I wish to extend my thanks to Dr. P. B. Read for invaluable assistance in the X-ray and associated computer work of this study, and to Professor D. S. Coombs who critically read the manuscript. A grant from the New Zealand Universities Research Grant Committee is gratefully acknowledged.

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[Manuscript received 22 December 1969]