Chromian epidote and zoisite in kyanite amphibolite, Southern Alps, New Zealand

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Abstract

Chromian zoisite (up to 0.40% Cr_2O_3) and epidote (up to 7.12% Cr_2O_3) occur as inclusions in calcic plagioclase in kyanite amphibolite, Southern Alps, New Zealand. Electron microprobe analyses indicate solid solution towards a $Ca_2Cr_2Si_3O_{12}(OH)$ end-member of the epidote series from $Al_{97.4}Fe_{5.4}Cr_{8.0}$ to $Al_{79.6}Fe_{4.8}Cr_{15.6}$ with increasing $Cr^{3+} \rightleftharpoons Al^{3+}$ substitution in the octahedral M(3) site.

Chromium-bearing epidote and zoisite are rare minerals and reported occurrences are scarce. Eskola (1933) analyzed an epidote (tawmawite) in a quartzite from Outukumpu, Finland, which contains 6.79% Cr_2O_3. Zoisite with 0.33% Cr_2O_3 is found in corundum-bearing zoisite amphibolite, Matabatu Mountains, Tanganyika (Game, 1954). Chromian epidote and zoisite occur as tiny (30–90 μm) grains together with chromite and hornblende enclosed within calcic plagioclase (An_{82-85}) in kyanite amphibolite that is found as float within oligoclase-zone schists near the Alpine Fault, Southern Alps of New Zealand (Findlay, 1979). The epidote and zoisite contain up to 7.12% and 0.40% Cr_2O_3, respectively (Table 1) and individual grains are chemically homogeneous. The zoisite and epidote are presumably in equilibrium coexistence within plagioclase although they were not observed in contact with one another. The amphibolite in which they are found consists of a high-pressure assemblage of kyanite (1.0–3.0% Cr_2O_3), green hornblende (0.6–2.3% Cr_2O_3), heterogeneous plagioclase (An_{82-85} and An_{40-48}), $\pm$ paragonite, rutile and chromite. The amphibolite has undergone partial retrograde metamorphism during later shearing producing an S-surface defined by margarite (0.5–0.9% Cr_2O_3) and Mg-chlorite (0.8–1.5% Cr_3O_3).

The general formula of the epidote minerals can be expressed as $A_2M_3Si_3O_{12}(OH)$ where M represents octahedrally-coordinated cations and A represents larger cations, principally Ca. Compositional variation within the epidote group is restricted to the octahedral sites mainly with respect to $Al \rightleftharpoons Fe^{3+} \rightleftharpoons Mn^{3+}$ substitutions thus leading to incomplete solid solution between $Ca_2Al_2Si_3O_{12}(OH)$, Ca_2Fe_2

Table 1. Representative EPMA[+] analyses of Cr-zoisite and epidote, from a kyanite amphibolite, Kini Creek, Southern Alps

	Zoisite		Epidote	
	a[+]	b[+]	a[+]	b[+]
SiO_2	40.21	40.01	38.66	38.19
TiO_2	0.02	0.07	0.09	0.13
Al_2O_3	33.12	32.14	26.95	24.73
Fe_2O_3*	0.67	0.91	2.60	2.27
Cr_2O_3	0.23	0.40	3.72	7.12
MnO	0.07	0.07	0.19	0.14
MgO	0.02	0.02	0.19	0.21
CaO	24.17	25.02	24.18	23.98
Na_2O	0.01	0.01	0.00	0.09
Total	98.52	98.63	96.58	97.86
Formulae on basis of 12.5(O)				
Si	3.027	3.025	3.063	3.071
Al	2.939	2.865	2.518	2.284
Fe^{3+}	0.038	0.052	0.155	0.134
Cr^{3+}	0.014	0.024	0.233	0.441
Ti^{4+}	0.001	0.004	0.005	0.007
Mn^{2+}	0.004	0.004	0.013	0.009
Mg	0.002	–	0.022	0.024
Ca	1.950	2.027	1.968	2.013
Na	0.001	0.001	–	0.014
M-sites	3.00	2.95	2.95	2.90
A-site	1.95	2.03	1.97	2.03
Mol% Al	98.3	97.4	86.6	79.9
Fe	1.2	1.8	5.4	4.7
Cr	0.5	0.8	8.0	15.4

a, b, grains with minimum and maximum Cr_2O_3 contents respectively.

* All Fe as Fe_2O_3.   0.00 indicates <0.01 wt%.

[+] Analyses made with JEOL Superprobe 733 microanalyser at Analytical Facility, Victoria University of Wellington, with an operating voltage of 15 kV and beam current of 0.3μA.
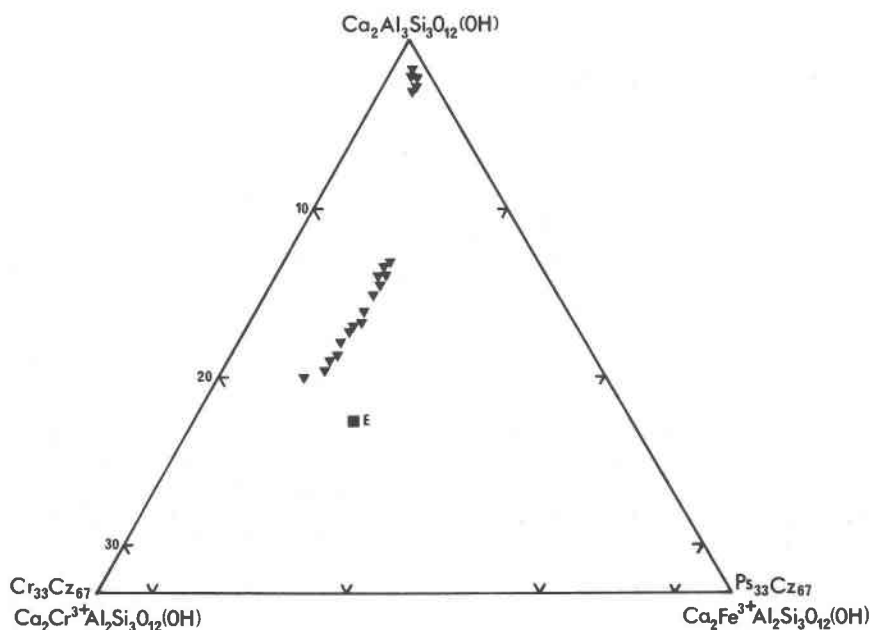
Fig. 1. Extent of solid solution for Cr-zoisite and epidote analyses (in terms of Al–Cr–Fe variation in octahedral sites), kyanite amphibolite. Theoretical end-member compositions are also indicated. E represents the tawmawite analyzed by Eskola (1933).

$Si_3O_{12}(OH)$ and $Ca_2Mn_2Si_3O_{12}(OH)$ end-members. The substitution of Cr^{3+}, presumably into the M(3) octahedral sites as with Fe^{3+} (Dollase, 1971), also indicates solid solution towards a $Ca_2Cr_2Si_3O_{12}$ (OH) end-member. Compositional variation of coexisting zoisite and epidote analyzed from one of the kyanite amphibolite samples is plotted in terms of ternary Al–Fe–Cr end members in Figure 1 and demonstrates limited solid solution between $Al_{86.6}Fe_{5.4}Cr_{8.0}$ and $Al_{79.6}Fe_{4.8}Cr_{15.6}$. In the zoisites Cr^{3+} solubility is confined between $Al_{98.3}Fe_{1.1}Cr_{0.5}$ and $Al_{97.4}Fe_{1.8}Cr_{0.8}$. The tawmawite analysis given by Eskola (1933) is notably more Fe-rich than the chromian epidotes analyzed here (Fig. 1). This may reflect bulk compositional control and/or analytical error as the recalculated analysis does not conform closely to the ideal epidote formula.

The composition of the epidote and zoisite is therefore highly dependent on the types of ions available, *i.e.*, bulk composition, and, in turn, the intercrystalline cation partitioning of Cr^{3+} among other coexisting phases. In this case the kyanite amphibolite contains 0.34 wt.% Cr_2O_3, and the presence of chromite indicates that the coexisting zoisite–epidote, together with the other silicate phases, are saturated in Cr^{3+}. A 'maximum' substitution of about 33 percent $(Fe + Mn)^{3+}$ for Al in epidote–piemontite (*e.g.*, Miyashiro and Seki, 1958) suggests that chromian

epidote with a similar 'optimum' amount of Cr^{3+} = Al substitution may yet be found.

By analogy with the increasing amounts of Cr-substitution in kyanite at high pressures (24 mole% "Cr_2SiO_5," at 20 kbar and 31 mole% at 30 kbar (Seifert and Langer, 1970), it is possible that Cr epidote, approaching $Cr_{33}Cz_{67}$ in composition would only be stable at very high pressures in chromium-rich metabasic rocks.

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