Barian mica and distribution of barium in metacherts and quartzofeldspathic schists, Southern Alps, New Zealand

RODNEY H. GRAPES

Research School of Earth Sciences, Victoria University of Wellington, New Zealand

Abstract

Zoned barian muscovite (2.52–5.66% BaO) and unzoned biotite (0.99–1.77% BaO) occur in two amphibolite grade metacherts of the Alpine schists, Southern Alps, New Zealand. The Ba-micas are associated with quartz–chlorite–Mn-garnet–tourmaline–apatite–sulphide $\pm$ oligoclase $\pm$ rutile $\pm$ magnetite $\pm$ ankerite. Increasing Ba (core to rim) in the muscovite is accompanied by a decrease in Si, Ti, Fe + Mg, and K and an increase in $^{[4]}$Al, $^{[6]}$Al, and Na. The main substitution that accounts for entry of Ba into both micas is $^{[A]}Ba^{2+} + {}^{[4]}Al^{3+} \rightleftharpoons {}^{[A]}K^+ + {}^{[4]}Si^{4+}$ and possibly $^{[A]}Ba^{2+} \rightleftharpoons {}^{[A]}K^+ + \square$. Compositional variation of the muscovite is also governed by the substitutions, $^{[6]}Al^{3+} + {}^{[4]}Al^{3+} \rightleftharpoons {}^{[6]}(Mg,Fe)^{2+} + {}^{[4]}Si^{4+}$, and $^{[A]}Na^+ \rightleftharpoons {}^{[A]}K^+$. The presence or absence of oligoclase, rutile, magnetite and Mg/(Mg + Fe) ratio of coexisting biotite control the Na, Ti, Fe and Mg contents of muscovite in the respective metacherts. Important variables controlling the occurrence of Ba-mica is the Ba-rich composition of the metacherts (1387 and 2741 ppm Ba) and metamorphic grade. In metacherts, siliceous and quartzofeldspathic schists with <1000 ppm Ba barium increases with increasing K_2O content indicating that in K-feldspar-absent rocks barium is mainly contained in micas (<0.70% BaO). In greenschist facies metacherts and siliceous schists with high Ba (>1000 ppm) and low K_2O, barian micas are not present and most of the Ba occurs in baryte $\pm$ barian carbonate with implication of a significant original hydrothermal-hydrogenous input. Although low grade illite/sericite/smectites containing Ba are the most likely precursor of the barian micas in the metacherts, strong marginal Ba enrichment in the muscovite indicates a later Ba-metasomatism resulting from the breakdown of baryte under reducing conditions during amphibolite facies metamorphism.

KEYWORDS: mica, barium, metachert, schist, Southern Alps, New Zealand.

Introduction

IN comparison to reported occurrences of barium-rich trioctahedral micas with up to 25% BaO, in alkaline volcanic rocks (e.g. Wendlandt, 1977; Thompson, 1977; Mansker *et al.*, 1989), marbles and calc-silicate rocks (e.g. Solie and Su, 1987; Bol *et al.*, 1989), analyses of dioctahedral micas with substantial amounts of barium ('oellacherite') are scarce. An early analysis of barian muscovite with 9.89 wt.% BaO from Franklin, New Jersey, by Bauer and Berman (1933) has since been re-analysed by electron microprobe which gave values between 4.8 and 6.3% BaO (Dunn, 1984). Schreyer *et al.* (1981) have analysed a strongly zoned barian fuschite with BaO ranging from 0.73% (core) to as much as 10.32% (rim) from a corundum–fuschite rock, Mashishi-

mala, Transvaal. Biotite coexisting with the barian fuschite is unzoned and contains 4.41% BaO. Barian muscovite with 3.9–8.3% BaO in association with Ba-feldspar (celsian/hyalophane) occurs in stratabound Ba–Zn mineralised rocks of the Scottish Dalradian (Fortey and Beddoe-Stephens, 1982) and Dymek *et al.* (1983) report a metamorphic Cr–Ba muscovite with 7.76% BaO. All these occurrences are from unusual bulk rock compositions because in the vast majority of low-medium grade pelitic/psammitic rocks white micas contain less than 0.6% BaO and rarely up to 1.8% BaO (see Guidotti, 1984, and references contained therein) with the BaO content of biotite typically ranging between 0.02 to 0.50% (e.g. Kwak, 1968; Ramsey, 1973; Guidotti and Guggenheim, 1977; Tracy, 1978).

Within the Alpine schists, Southern Alps of

New Zealand, Ba-micas occur in rare metachert layers associated with metabasite and quartzofeldspathic schist. In this paper the chemistry and origin of Ba-mica, and in particular barian muscovite, is discussed with respect to the distribution and source of barium in metacherts and associated quartzofeldspathic schist lithologies of the Southern Alps and Otago areas.

Sample location and description

Barium micas occur in two metachert horizons about 0.5–1.0 m thick that are interlayered with amphibole facies (oligoclase zone) metabasite and intercalated quartzofeldspathic schist in the Fox River Valley (No. 28666) and from the Copland River Valley (No. 29170), Southern Alps. Localities are shown in Fig. 1. The metacherts are strongly laminated (mm scale) between pale pink garnet/mica-rich and quartz-rich lamellae. Mineral assemblages of the metacherts are:

No. 28666. Quartz–muscovite–biotite–chlorite–Mn-garnet–tourmaline–apatite–ankerite–sulphide.
No. 29170. Quartz–oligoclase–muscovite–biotite–Mn-garnet–tourmaline–apatite–rutile–magnetite–sulphide.
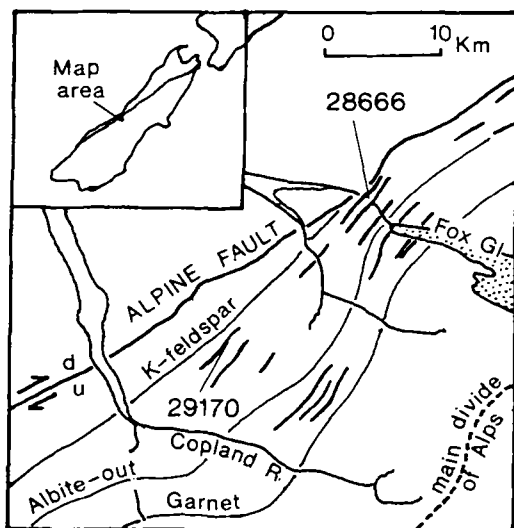

FIG. 1. Map showing location of the barium-rich metacherts Nos. 28666; 29170) that contain barian micas, Southern Alps, New Zealand. Thick solid lines are metabasites intercalated with quartzofeldspathic schist. Lines labelled garnet, albite-out and K feldspar are isograds.

Mica compositions and substitutions

Representative analyses of barian muscovite and biotite from the metacherts are given in Table 1. Backscattered electron imaging (BEI), such as that shown in Fig. 2A and B, indicates that the muscovite is invariably zoned with discontinuous rims enriched in barium, whereas biotite is essentially chemically homogeneous with respect to Ba distribution. Because of the highly variable Ba content in the muscovite, all analyses are plotted in Fig. 3, where oxide atomic proportions are plotted against Ba. Increasing amounts of Ba in the white mica is accompanied by a decrease in Si, Ti, Mg + Fe, and K and an increase in $^{[6]}Al$, $^{[4]}Al$ and Na. This variation can be described in terms of both coupled and independent substitutions involving all three structural sites. The main substitution that probably accounts for the incorporation of Ba into muscovite and biotite is,

$$^{[A]}Ba^{2+} + {}^{[4]}Al^{3+} \rightleftharpoons {}^{[A]}K^+ + {}^{[4]}Si^{4+}, \quad (1)$$
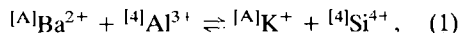
(e.g. Wendlandt, 1977). A further substitution in the interlayer sites of both micas could involve a 1:1 replacement of K by Ba accompanied by the formation of a vacancy such as,

$$^{[A]}Ba^{2+} \rightleftharpoons {}^{[A]}K^+ + \square \text{ (e.g. Guidotti, 1984).} \quad (2)$$
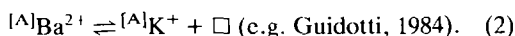
This substitution might in part account for the atom deficiency of between 0.05–0.095 and 0.089–0.092 from the theoretical 1.000 interlayer site occupancy (on the basis of (O)), of muscovite and biotite respectively (Table 1). Another possible Ba substitution in the muscovite,

$$^{[A]}Ba^{2+} + {}^{[6]}(Mg,Fe)^{2+} \rightleftharpoons {}^{[A]}K^+ + {}^{[6]}Al^{3+}, \quad (3)$$
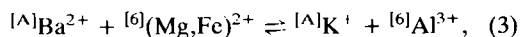
does not seem to have occurred, as Fe and Mg both decrease with increasing Ba. As substitution (3) is a combination of (1) and the phengite substitution, $^{[6]}(Mg,Fe)^{2+} + {}^{[4]}Si^{4+} \rightleftharpoons {}^{[6]}Al^{3+} + {}^{[4]}Al^{3+}$, it would appear that both are independent of one another. This is supported by the fact that the amount of phengite substitution in the barian muscovite is comparable to that in Ba-poor white mica in other metachert horizons of the same metamorphic grade (Grapes, unpublished data). Increasing $^{[6]}Al$ and $^{[4]}Al$ indicates that besides (1) the other main substitution in the barian muscovite is the Tschermak substitution

$$^{[4]}Al^{3+} + {}^{[6]}Al^{3+} \rightleftharpoons {}^{[4]}Si^{4+} + {}^{[6]}(Fe,Mg)^{2+}. \quad (4)$$
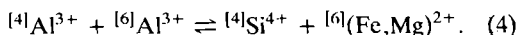
Increasing Na with decreasing K in the muscovite is indicative of a further interlayer substitution of $^{[A]}Na^+ \rightleftharpoons {}^{[A]}K^+$ leading to a significant paragonite component of up to 17.7 atomic %.

Table 1. Representative electron microprobe analyses (means and standard deviations) of barian white mica and biotite (O = 11) from metacherts (28666; 29170), Southern Alps, New Zealand.

	28666			29170		
	white mica		biotite	white mica		biotite
	cores	rims		cores	rims	
	n=12	n=15	n=10	n=9	n=10	n=15
SiO_2	46.95±0.09	44.56±0.07	39.77±0.22	46.14±0.15	45.48±0.04	37.44±0.25
TiO_2	0.86±0.01	0.51±0.02	1.01±0.04	0.95±0.01	0.88±0.01	1.94±0.04
Al_2O_3	31.87±0.29	34.15±0.34	18.06±0.43	30.82±0.19	32.56±0.09	18.09±0.34
FeO*	0.90±0.02	0.92±0.02	9.12±0.43	1.78±0.04	1.52±0.11	14.00±0.18
MnO	-	-	0.30±0.06	-	-	0.33±0.06
MgO	2.08±0.02	1.36±0.03	16.69±0.47	2.06±0.02	1.92±0.08	13.59±0.08
Na_2O	0.62±0.03	1.24±0.02	0.24±0.01	0.50±0.04	0.76±0.03	0.20±0.01
K_2O	9.02±0.16	6.95±0.18	9.01±0.12	8.49±0.20	8.30±0.06	8.94±0.09
BaO	2.60±0.17	5.42±0.24	1.59±0.15	3.50±0.20	4.93±0.15	1.17±0.20
Total	94.90	95.11	95.74	94.24	96.35	95.70
Si	3.173	3.048	2.871	3.171	3.089	2.775
Al	0.827	0.952	1.129	0.829	0.911	1.225
Σ [4]	4.000	4.000	4.000	4.000	4.000	4.000
Al	1.712	1.801	0.408	1.668	1.696	0.356
Fe^{2+}	0.051	0.053	0.551	0.102	0.086	0.868
Mn	-	-	0.018	-	-	0.021
Mg	0.209	0.139	1.796	0.211	0.194	1.501
Ti^{4+}	0.044	0.026	0.055	0.049	0.045	0.108
Σ [6]	2.016	2.019	2.828	2.030	2.021	2.854
Na	0.081	0.164	0.034	0.067	0.180	0.029
K	0.778	0.606	0.830	0.744	0.719	0.846
Ba	0.069	0.145	0.045	0.094	0.131	0.034
Σ [A]	0.929	0.915	0.909	0.905	0.950	0.909

*All iron as FeO.

Bulk rock composition and mica chemistry

The two amphibolite grade metacherts that contain Ba-micas have barium contents of 2741 ppm (No. 28666) and 1387 ppm (No. 29170), (Table 2). In amphibolite facies metacherts with comparatively low bulk Ba contents (<300 ppm Ba) muscovite is typically homogeneous with respect to BaO content (0.35–0.44%) although some larger grains have relatively BaO-enriched overgrowths with 1.49–1.58% BaO. Associated biotite is unzoned and contains 0.18–0.31% BaO. Although the amount of Ba in No. 28666 is only about half that in No. 29170 (Table 2) the range of Ba-substitution in muscovite in the two metacherts is similar. This reflects the presence of biotite (with a greater modal amount in No. 29170) and the partitioning of Ba between the two micas $[K_D = (Ba/K)_{musc (cores)}/(Ba/K)_{biot} = 1.43–1.60$ (28666) and 3.4–4.0 (29170)]. Separation of the barian muscovite Fe, Ti, and Mg trend lines in Fig. 3 is also controlled by the respective bulk compositions of the two metacherts and the presence of other phases such as magnetite and rutile in No. 29170, their absence in No. 28666 and the more Mg-rich composition of coexisting biotite in No. 29170 [Mg/(Mg + Fe) = 0.78] with respect to that in No. 28666 [Mg/(Mg + Fe) =

0.63]. Na variation also deserves comment as it appears evident that the amount of Na substitution in barian muscovite is related to the partitioning of Na into plagioclase, e.g. sodic oligoclase in No. 29170 (bulk rock $Na_2O = 0.44\%$), while No. 28666 does not contain plagioclase (bulk rock $Na_2O = 0.03\%$) although the muscovite contains more Na.

Distribution of barium

Barium is one of the most abundant trace elements in quartzofeldspathic schists of the Southern Alps and Otago areas with concentrations ranging from 10 to 1000 ppm Ba (Grapes et al., 1982; Coombs et al., 1985; Roser and Cooper, 1990). With the exception of rocks that contain K-feldspar, i.e. chlorite zone semischists with detrital K-feldspar (0.28–0.69% BaO) and high-grade oligoclase zone rocks with neometamorphic K-feldspar (0.56–1.32% BaO) in the Southern Alps, most of the barium is present in white mica and biotite (0.07–0.69 and 0.08–0.54% BaO respectively) as shown in Fig. 4 where bulk rock Ba increases with increasing K_2O. In contrast, associated metachert lithologies have widely varing Ba contents of between <20 and
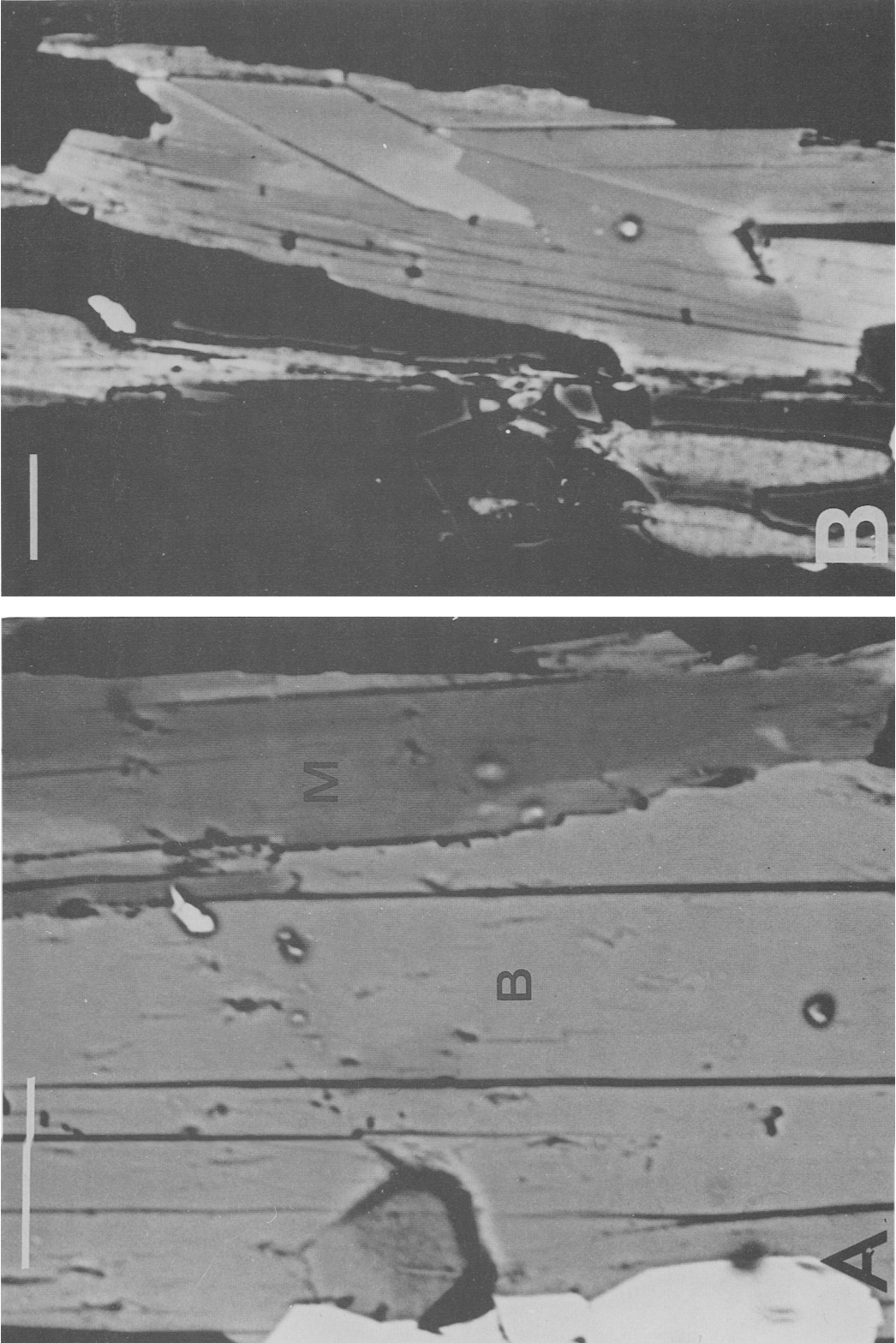
FIG. 2. Backscattered electron image photos of barian micas in metacherts, Southern Alps, New Zealand. A. Coexisting muscovite (M) and biotite (B). Muscovite shows marginal enrichment in Ba (lighter grey tone). In contrast the biotite is homogeneous with respect to Ba content. No. 29170. B. Muscovite grains showing marginal enrichment in Ba (light grey tone). The greater the Ba content the lighter the grey tone. No. 28666. Bar scales = 10 μm.
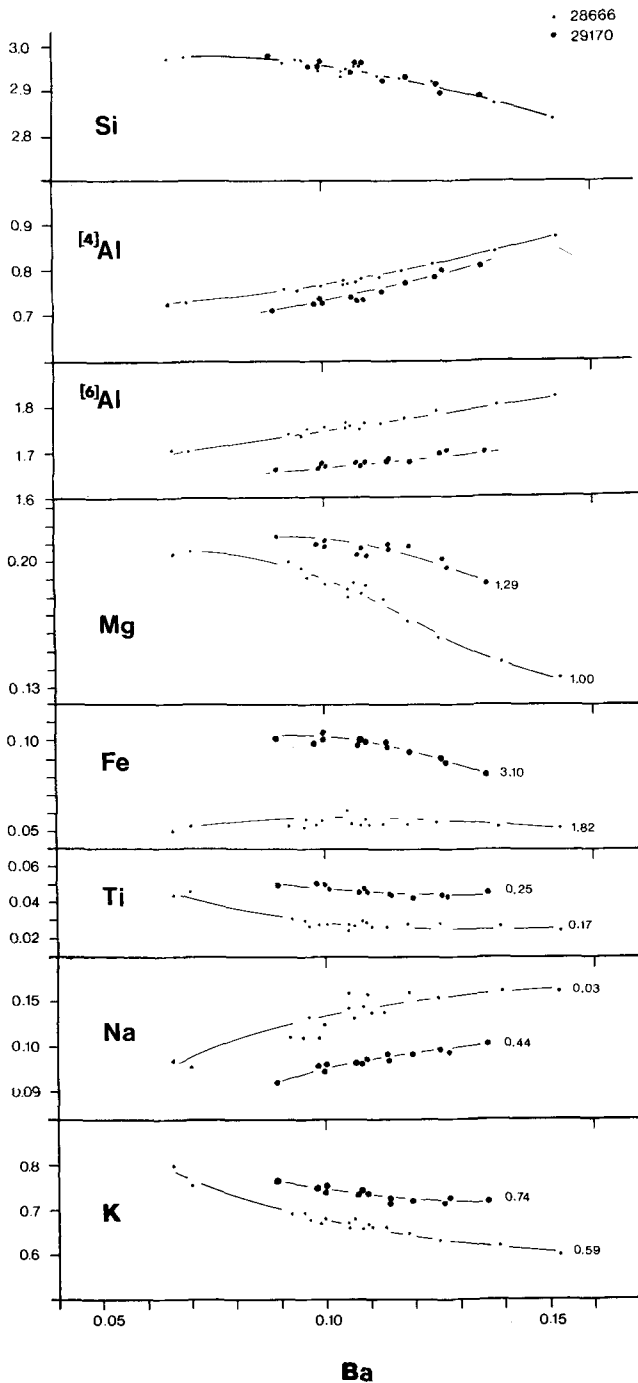
FIG. 3. Plot of Si, [4]Al, [6]Al, Mg, Fe, Ti, Na, and K versus Ba (atomic proportions on the basis of O = 11) in barian muscovite from metacherts (28666 and 29170), Southern Alps, New Zealand. Values to the right of the trend lines are wt.% oxide amounts in host metacherts (Fe values = FeO + Fe$_2$O$_3$). (Table 2.)

Table 2. XRF analyses of metacherts (Nos. 28666; 29170), Southern Alps, New Zealand.

	28666	29170		28666	29170
wt.%					
SiO2	89.81	85.54	Ba	2741	1387
TiO2	0.17	0.25	Cr	10	13
Al2O3	3.44	5.21	Ce	11	5
Fe2O3	0.18	0.13	Ga	3	5
FeO	1.64	2.97	Nb	2	5
MnO	0.88	1.22	Ni	81	35
MgO	1.00	1.29	Pb	5	16
CaO	0.62	1.05	Rb	20	23
Na2O	0.03	0.44	Sr	60	77
K2O	0.59	0.74	V	14	40
P2O5	0.05	0.19	Y	13	39
LOI	0.64	0.13	Zn	56	54
Total	99.65	99.16	Zr	41	66

3000 ppm at K_2O contents of <1.5% (Fig. 4). This reflects the presence of minor amounts of either barium-poor mica in samples with low Ba concentrations of <300 ppm or of variable amounts of baryte, barian carbonate or barian mica in samples with Ba concentrations >300 ppm. In comparison with quartzofeldspathic schist lithologies, mildly manganiferous (piemontite-bearing) quartz-rich schists (Coombs et al., 1985) typically have higher Ba contents (250–1700 ppm) over a similar range of K_2O (i.e. <2.5%), (Fig. 4). In these rocks the white micas contain 0.11–0.41% BaO and in Ba-rich samples (Ba > 1000 ppm) small amounts of barite occur within the matrix and/or along schistosity planes and joints (Kawachi et al., 1983).

Source of barium

Barium is especially enriched in metalliferous pelagic sediments (e.g. 0.07–2.35 wt.% Ba; Dymond et al., 976) in the vicinity of oceanic ridges. Particulate baryte is deposited together with amorphous silica from white smoker chimney edifices developed on seafloor basalt (Haymon and Kastner, 1981). High concentrations of barium can also occur in present day deep sea sediments composed mainly of calcareous and siliceous tests (Church, 1979) and Adachi et al. (1986) report carbonate-free porcellanites with 1300–3600 ppm Ba from the North Pacific containing baryte that partly replaces chalcedony. Therefore, in areas of pelagic sedimentation, the primary source of barium is hydrothermal, and concentration of barium may result by direct precipitation as baryte, substitution of barium into clays (e.g. smectites) and zeolites (e.g. harmotome), adsorption into Fe–Mn oxide particles and through extraction from the water column by marine organisms with later fixation of

barium in sediments by dissolution of biological debris (e.g. Goldberg and Arrhenius, 1958; Bostrom et al., 1976; Heath and Dymond, 1977; Church, 1979; Gurvich et al., 1979; Dehairs et al., 1980). Additional terriginous barium is added by detrital feldspars and micas (e.g. Gurvich et al., 1979). The inset diagram of Fig. 4 indicates that the shift towards higher barium for a given K_2O content from quartzofeldspathic schist through manganiferous quartz-rich schist to Ba-enriched metachert (effectively a biogenic silica dilution trend, e.g. Coombs et al., 1985) reflects an increasing degree of hydrothermal–hydrogenous Ba content and therefore deposition sites increasingly distal from a continental margin but also remote from an active spreading ridge (Grapes, in prep.). Therefore, it may be significant that the Ba-rich metacherts are closely associated with ?allochthonous intraplate oceanic metabasalts in the Southern Alps (Grapes and Palmer, 1982). During diagenesis and low-grade metamorphic recrystallisation of quartzofeldspathic, i.e. greywacke-type, sediments (up to prehnite:pumpellyite facies grade) when detrital feldspars and micas become unstable, barium is mobilised and tends to be incorporated into newly formed sericitic mica (Grapes, in prep.). In more siliceous lithologies with high initial concentrations of hydrothermal–hydrogenous barium and low clay content barium remains in baryte or possibly forms barium carbonate both within the rock matrix or in veins.

Barium metasomatism

Although low-grade smectites/illite/sericite are the most likely precursors of barium containing micas in the Alpine metacherts and quartzofeldspathic schists, the strong marginal Ba-enrichment of muscovite in the metacherts studied here implies a later Ba-metasomatism. This is considered to have resulted from the breakdown of a Ba-rich source such as baryte. The former presence of baryte in the metacherts containing barian micas is inferred from the occurrence of baryte in some greenschist facies metacherts (e.g. Hutton, 1940; Kawachi et al., 1983) and the fact that baryte does not occur in higher grade metacherts (e.g. Cooper, 1971; Grapes et al., 1982). Therefore, in addition to bulk composition, metamorphic grade is also an important factor controlling the formation of barian mica. Under favourable $f_{O_2}-f_{S_2}$ conditions baryte can have a high thermal stability (e.g. Segnit and Gelb, 1970) and may survive up to amphibolite grade conditions of metamorphism (e.g. Fortey and Beddoe-Stephens, 1982). The presence of
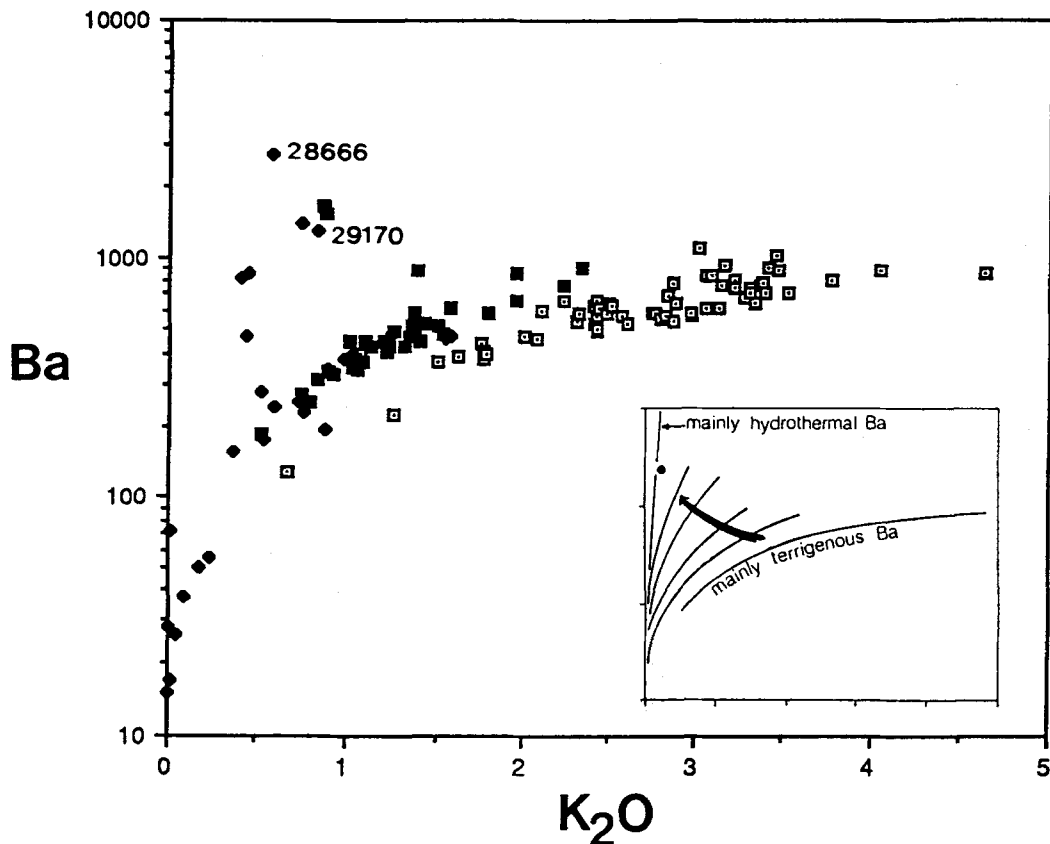
FIG. 4. Plot of ppm Ba versus wt.% K_2O for quartzofeldspathic schists from the Southern Alps and Otago area (open squares; 80 analyses; Grapes *et al.*, 1982; Roser, 1983; Coombs *et al.*, 1985; Roser and Cooper, 1990); mildly manganiferous quartz-rich schists (piemontite-bearing) from the east Otago area (filled squares; 30 analyses, Roser, 1983; Coombs *et al.*, 1985); and metacherts (non piemontite-bearing) from the Southern Alps and Otago areas (filled diamonds; 25 analyses; Grapes *et al.*, 1982; Roser, 1983). Inset diagram shows the expected trend line shifts from samples with a mainly terriginous Ba content (i.e. detrital feldspars and micas) to those with increasing amounts of hydrothermal–hydrogenous Ba. Filled circle = Average of 20 metalliferous sediments, East Pacific Rise (Marchig and Gundlach, 1982).

sulphide and the correspondingly low oxidation ratios of the two Ba-rich metacherts (mol $2Fe_2O_3 \times 100/[2Fe_2O_3 + FeO]$ = 8 in 28666 and 5 in 29170; Table 2) suggests that Ba-enrichment of the muscovite rims could have resulted from the high-temperature breakdown of baryte under reducing conditions according to the reaction, $BaSO_4 = Ba_{(in\,mica)} + S_{(in\,sulphide)} + 2O_2$ during recrystallisation of the metacherts under amphibolite facies conditions.

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