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COMPOSITION OF BARIUM-RICH WHITE MICAS FROM THE BERISAL COMPLEX, SIMPLON REGION, SWITZERLAND

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Abstract

The chemistry of barian muscovite and ganterite in metamorphosed basement rocks from the Berisal Complex, Simplon Region, Switzerland, is described. Analysis of white micas from several Ba-enriched localities in this complex established an extensive solid-solution between ganterite and muscovite. Thus, the material is excellent for studying the crystal-chemical consequences of introducing Ba into the dioctahedral muscovite structure. The Ba-rich white micas are found in two lithologic units with whole-rock chemical compositions dominated by $SiO_2 + Al_2O_3 + BaO + K_2O \pm Na_2O$ and $SiO_2 + Al_2O_3 + BaO + CaO$. The first is a white-mica schist that consists of white mica + quartz + epidote-group minerals, and occurs as lenses or bands interlayered in garnet-bearing two-mica augen gneiss, zoisite–biotite gneiss or zoisite–celsian gneiss. The second host-rock type is a zoisite–celsian gneiss that is characterized by the assemblage white mica + zoisite + celsian + quartz + margarite. In both lithologies, the Ba-rich white micas are synkinematic, and petrographic observations suggest that Ba was present in the rocks prior to, or introduced during the peak of Alpine metamorphism. Concentrations of Ba in the white micas range from 3.6 to 18.2 wt.% BaO. Higher Ba content is always associated with higher Al, and lower K and Si concentrations. The highest Ba contents are also coupled to increases in Na, but there are no similar correlations observed for Fe or Mg. Accommodation of Ba^{2+} ions in micas is generally achieved by exchange vectors (1) $[Ba][^{[IV]}Al][K]_{-1}[Si]_{-1}$ or (2) $[Ba][Fe,Mg][K]_{-1}[Al]_{-1}$. The data presented here show that vector (2) plays no part in the solid solution between muscovite and ganterite. Furthermore, vector (1) operates only if $K > 0.53$ *apfu*, *i.e.*, $Ba < 0.32$. At higher Ba concentrations, a second, distinct exchange-vector $[Na][K]_{-1}$ also operates in the interlayer site. It appears that at higher Ba concentrations in dioctahedral white micas, there is extensive solid-solution involving Na^+, K^+, and Ba^{2+}. In minerals where exchange between alkali and alkaline-earth elements is observed (*e.g.,* feldspar system), a miscibility gap generally exists. Such a miscibility gap, however, was not observed in the system ganterite – muscovite – paragonite, making the system possibly unique. The reasons for such exchanges being possible are not fully understood, but it is shown that whole-rock composition does not play a significant role.

Keywords: barium, white mica, ganterite, chemical exchange, Berisal Complex, Switzerland.

Sommaire

Nous avons étudié la composition chimique de la muscovite riche en barium et de la gantérite provenant du socle cristallin du complexe du Bérisal et de la région du Simplon, en Suisse. Les compositions de mica blanc provenant de différentes localités où la teneur en Ba est élevée montrent l'existence d'une solution solide étendue entre la gantérite et la muscovite. Ainsi le matériel est idéal pour l'étude des conséquences cristallochimiques liées à l'introduction de barium dans la muscovite dioctaédrique. On trouve les micas blancs riches en barium dans deux unités lithologiques à composition chimique dominées par $SiO_2 + Al_2O_3 + BaO + K_2O \pm Na_2O$ et $SiO_2 + Al_2O_3 + BaO + CaO$. La première est un schiste à mica blanc composé de mica blanc + quartz + minéraux du groupe de l'épidote et se présentant sous forme de lentilles ou de couches intercalées dans des gneiss à œillets à deux micas et grenat, des gneiss à zoïsite et biotite et des gneiss à zoïsite et celsiane. Le deuxième type de roche propice est un gneiss à zoïsite et celsiane caractérisé par l'assemblage minéralogique mica blanc + zoïsite + celsiane + quartz + margarite. Au sein des

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deux lithologies, les micas blancs riches en barium sont syncinématiques, et d'après les observations pétrologiques, le barium était présent dans ces roches au départ, ou introduit durant le paroxysme métamorphique alpin. Les concentrations en Ba des micas blancs varient entre 3.6 et 18.2% de BaO (poids). Une forte teneur en Ba est toujours associée à une forte teneur en Al, et de faibles concentrations en K et Si. La plus forte teneur en Ba est accouplée à un enrichissement en Na, mais des corrélations similaires pour le Fe ou le Mg ne sont pas observées. L'accomodation des ions Ba^{2+} dans les micas est généralement accomplie selon les vecteurs d'échange (1) $[Ba][^{[IV]}Al][K]_{-1}[Si]_{-1}$ ou (2) $[Ba][Fe,Mg][K]_{-1}[Al]_{-1}$. Pourtant, les données présentées ici montrent que le vecteur d'échange (2) n'est pas important dans la solution solide entre la muscovite et la gantérite. En outre, le vecteur (1) n'opère que si K dépasse 0.53 atomes par unité formulaire (Ba < 0.32). Pour de plus fortes concentrations en Ba, un deuxième vecteur d'échange distinct $[Na][K]_{-1}$ opère également dans le site interfoliaire. Pour de fortes concentrations en Ba dans les micas blancs dioctaédriques, il y a une solution solide d'échange étendue impliquant les ions Na^+, K^+, et Ba^{2+}. Dans les minéraux où l'échange entre les éléments alcalins et alcalino-terreux est observé (exemple: les feldspaths), une lacune de miscibilité existe, en général. Une telle lacune n'est pas observée dans le système gantérite – muscovite – paragonite, rendant le système probablement unique. Les raisons permettant de tels échanges ne sont pas entièrement comprises. D'ailleurs, la composition de la roche totale ne joue pas de rôle important.

Mots-clés: barium, mica blanc, gantérite, échange chimique, complexe de Bérisal, Suisse.

INTRODUCTION

Barium-rich micas occur in igneous and metamorphic rocks at several localities (Brigatti & Poppi 1993, and references therein), and metasomatic effects are also widely quoted as being of great importance in their formation (Harlow 1995, and references therein). Prior to the description of ganterite, $[Ba_{0.5}(Na + K)_{0.5}]Al_2(Si_{2.5}Al_{1.5}O_{10})(OH)$ (Graeser *et al.* 2003), none of the known Ba-bearing dioctahedral micas attained Ba contents exceeding 12 wt.% BaO, and the occupancy of the interlayer site (*I* site) was invariably dominated by K (see Table 1 in Graeser *et al.* 2003).

In this paper, we present results from a study of the composition of Ba-enriched white micas occurring in the Berisal Complex, Simplon Region, Switzerland. In that area, the metamorphic rocks at many localities are unusually rich in Ba; the concentrations of Ba may be 200 times greater than that reported for average continental crust. Ba-rich white micas, including ganterite, are common at all of these localities. The $2M_1$ dioctahedral micas exhibit a vast range of Ba contents, ranging from 3.6 to 18.2 wt.% BaO, and Ba^{2+} is commonly the dominant interlayer cation. The data presented here reveal a nearly complete solid-solution series between muscovite and ganterite (Hetherington 2001). We document the compositional variability of these unusual dioctahedral micas and discuss possible reasons for their formation.

BARIUM ACCOMMODATION IN MICAS

Various mechanisms of substitution can be invoked to describe the accommodation of Ba in muscovite. The simplest case may be expressed by the exchange vector

$$[Ba][^{[IV]}Al][K]_{-1}[Si]_{-1} \quad (1).$$

Another commonly reported mechanism of substitution in Ba-rich white micas is

$$[Ba][Fe,Mg][K]_{-1}[^{[VI]}Al]_{-1} \quad (2),$$

which ultimately leads to formation of the trioctahedral brittle micas kinoshitalite or ferrokinoshitalite (Brigatti & Poppi 1993). This substitution is a combination of exchange vector (1) and

$$[Fe,Mg][Si][^{[VI]}Al]_{-1}[^{[IV]}Al]_{-1} \quad (3),$$

the classic Tschermak substitution describing the muscovite–phengite solid solution.

The goodness of fit and stacking arrangement of the sheets that controls the interatomic distances as well as the volume of both the octahedrally coordinated *M* site and the interlayer *I* site are affected by α, the rotation angle of tetrahedra. This angle represents the rotation of a $(Si,Al)O_4^{4-}$ tetrahedron within the plane of the sheet of tetrahedra (Bailey 1984). The magnitude of α controls the structure, and hence symmetry, of the sheets of tetrahedra, and in turn, the size of the *I* and *M* sites. The size of these sites determines which elements are preferentially accommodated (Guidotti *et al.* 2000). In trioctahedral micas, the presence of Mg^{2+} or Fe^{2+} in the *M* site is coupled with a smaller α angle, generating a larger *I* site, which in turn promotes accommodation of larger cations, such as Ba^{2+}. Several of the reported examples of Ba-rich muscovite contain relatively high amounts of Cr^{3+}, V^{3+} and Mn^{2+} (*i.e.*, Tracy 1991, Pan & Fleet 1991, Morand 1990, Ankinovich *et al.* 1973, Snetsinger 1966); because these cations are all larger than Al^{3+}, their accommodation in the *M* site reduces α, thereby increasing the size of the *I* site and promoting incorporation of Ba^{2+}. However, at the same time, there appears to be no increase in the total occupancy of the *M* site.

The most Ba-rich examples of ganterite conform to a chemical formula resembling that of the brittle mica margarite (Graeser *et al.* 2003). Brittle micas are characterized by a layer charge per formula unit of –2.0 owing to the presence of a divalent cation in the *I* site.

Margarite, the most common brittle mica, contains Ca^{2+} at the *I* site, and Al^{3+} at the *M* site; charge balance is achieved *via* replacement of Si by Al at the tetrahedral site (*T* site). In Ba-dominant brittle micas, Ba^{2+} dominates the *I* site, whereas the *M* site is filled by up to three divalent cations (Mg^{2+} or Fe^{2+}); these micas thus are trioctahedral. Characterization of dioctahedral Ba-rich micas has been performed from different points of view, and various parameters, including crystal structure (Harlow 1995), stacking of silicate sheets (Bailey 1984), host-rock composition (Pan & Fleet 1991), and conditions of crystal growth (Shmakin 1984), have been found to influence the level of Ba incorporation.

GEOLOGICAL FEATURES

The Berisal Complex is structurally the uppermost unit of the Western Lepontine dome (Fig. 1), which is made up of a series of large crystalline nappes enveloped by Mesozoic sediments metamorphosed during the Alpine orogeny. The Berisal Complex is a lower Penninic unit, and is bounded to the southwest by the Simplon Line (Simplon Fault Zone), and on all other sides by the Monte Leone nappe, structurally the next lowest Lepontine nappe (Fig. 1). The crystalline basement rocks of the Berisal Complex consist of orthogneisses, garnet – biotite – muscovite gneiss, and orthoamphibolites. Barium enrichment is found in the first two rock types.

The metamorphic grade observed in the Lepontine nappes ranges between greenschist facies on the northern periphery and eclogite facies in the Central Adula nappe. The Alpine metamorphic isograds in the lower Penninic area are quite steep and cut across nappe boundaries (Todd & Engi 1997). In the Berisal Complex, the metamorphic grade ranges between the upper greenschist and middle amphibolite facies (Stille 1980).

OCCURRENCE OF BA-RICH WHITE MICAS

In the lower Penninic Berisal Complex, Frank (1979) first noted the presence of Ba-rich white micas, and Köhn (1993) reported additional localities. During an extensive study of the basement rocks of the Berisal Complex, unusual enrichments in Ba were found in several outcrops where ganterite or barian muscovite occurs as a rock-forming mineral in two lithologic units, white-mica schist and zoisite–celsian gneiss (Hetherington 2001).

The schist is characterized by white-mica contents of up to 90 vol.%. This rock also contains some quartz and an epidote-group mineral, and the accessory phases zircon and apatite (Fig. 2a). The white-mica schist is found throughout the Berisal Complex, and occurs as lenses and thin bands interlayered with garnet-bearing two-mica augen gneiss, zoisite–biotite gneiss, or zoisite–celsian gneiss. At some localities, the white-mica schist is highly enriched in Ba (up to 8 wt.% BaO), and it is here that it contains Ba-rich white mica or ganterite. The white micas occur in two generations, as inferred from their orientations. The first, and more abundant, generation is oriented parallel to the dominant Alpine foliation, and thus is inferred to be synkinematic, whereas the second is much less abundant and postkinematic (Fig. 2a). Both generations are chemically identical.

Barian muscovite and ganterite are also present in zoisite–celsian gneiss, which is characterized by the metamorphic assemblage white mica + zoisite + celsian + margarite + quartz (Fig. 2b). The textural relationship between the two Ba silicate minerals celsian and ganterite indicates that they grew synkinematically with respect to the main Alpine deformation (Fig. 2b).

All Ba-rich silicate minerals, in both the white-mica schist and the gneiss, are chemically homogeneous, suggesting that Ba enrichment of the rocks predates, or is coeval with, the peak of Alpine metamorphism, and that post-Alpine alteration was not an important process in their genesis (Hetherington 2001, Hetherington *et al.* 2001).

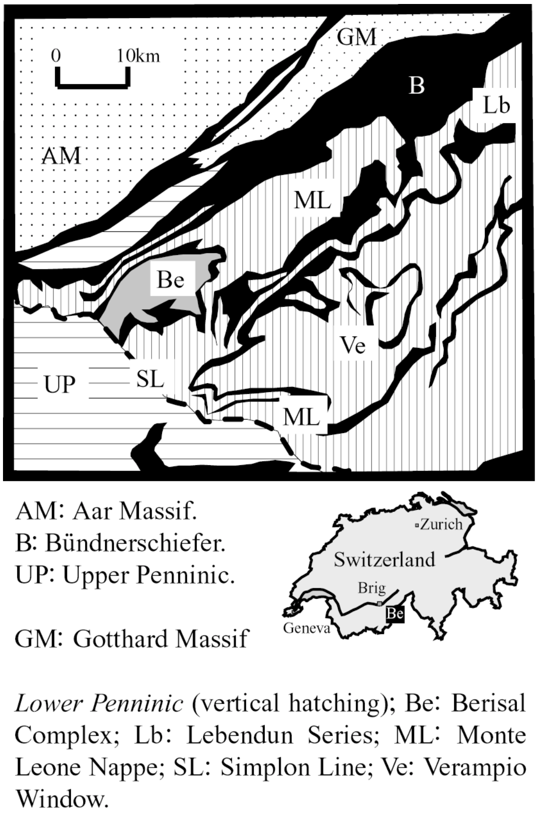

FIG. 1. Map of the Berisal Complex and the western Lepontine Alps.

ANALYTICAL PROCEDURES

Whole-rock chemical analyses of the two host-rock types were made at the Geochemistry Laboratories, University of Basel. Two preparations of each sample were made. For the major elements, a fused glass bead, with a diameter of 20 mm, was prepared. Each bead contains a mixture of 300 mg sample powder and 4700 mg lithium tetraborate. For the analysis of these rocks for trace elements, a pressed powder pellet 20 mm in diameter, containing 800 or 1000 mg of rock powder and an organic fixing agent was prepared and mounted in a Plexiglas ring. The compositions of the glass beads and the pressed powder pellets were measured with a Siemens SRS3000 wavelength- dispersion sequential X-ray spectrometer equipped with a Rh end-window tube (4 kV). The results were collected and evaluated using the Bruker AXS Spectraplus standardless evaluation program.

Mineral compositions were determined by electron probe micro-analysis (EPMA) using a JEOL JXA–8600 instrument at the University of Basel. The instrument is equipped with four crystal spectrometers and the Voyager software of Noran Instruments. The mica analyses were made with a focussed electron beam, which scanned over an area of 26 μm^2. The accelerating voltage was 15 kV, the beam current was 10 nA, and the counting times were between 10 and 20 seconds. Calibrations were performed with the following standards: sanbornite (Ba), orthoclase (K, Si), forsterite (Mg, Fe), gehlenite (Al), wollastonite (Ca), albite (Na), titanite (Ti), and graftonite (Mn). A ZAF-type correction procedure was used for all data reduction, and all Fe was assumed to be ferrous.

BULK COMPOSITION OF THE HOST ROCKS

The two types of rock containing the Ba-rich white micas are characterized by unusually high concentrations of Ba (Table 1). Despite that, there is a considerable variation in the bulk Ba content of the hand specimens. The highest values were observed in the zoisite–celsian gneiss (up to 15.3 wt.% BaO). The observed concentrations represent a huge geochemical anomaly for crustal silicate rocks, which typically contain between 300 and 750 ppm Ba (Taylor & McLennan 1981). Previously reported Ba anomalies in silicate rocks only rarely exceed 5 wt.% BaO; moreover, those were observed in rocks closely associated with barite-bearing metasedimentary rocks (*e.g.*, Fortey & Beddoe-Stephens 1982), or in rocks that have been hydrothermally altered (*e.g.*, Seki 1992, Polliand & Moritz 1999).

The Ba-rich rocks studied also contain considerable amounts of Sr, and generally, the Ba and Sr contents correlate positively with each other (Hetherington 2001). There are no discernible enrichments in other trace elements, including Cr, V, Pb and Zn (Table 1). In general, the white-mica schists are richer in Mg and K, but significantly poorer in Ca than the gneisses. On the other hand, the concentration of Na varies widely in both rock types.

Compared to other rocks that host Ba-rich white mica, the rocks of the Berisal Complex are geochemically distinct. Regionally metamorphosed sedimentary units appear to be the most common host-rocks for Ba-rich white mica, and in each of the reported occurrences, these rocks exhibit higher concentrations of base metals (Snetsinger 1966, Ankinovich *et al.* 1973, Fortey & Beddoe-Stephens 1982, Green *et al.* 1986, Morand 1990, Chabu & Boulègue 1992, Grapes 1993, Jiang *et al.* 1996). In many cases, the host rocks also contain graphite, but this phase was not detected in the rocks studied here. The rocks of the Berisal Complex are also significantly different from the jadeitites and altered jadeitites of the serpentinite and serpentinite-matrix mélange on the Motagua Fault, Motagua Valley, Guatemala (Harlow 1995) and the Franklin marble at Lime

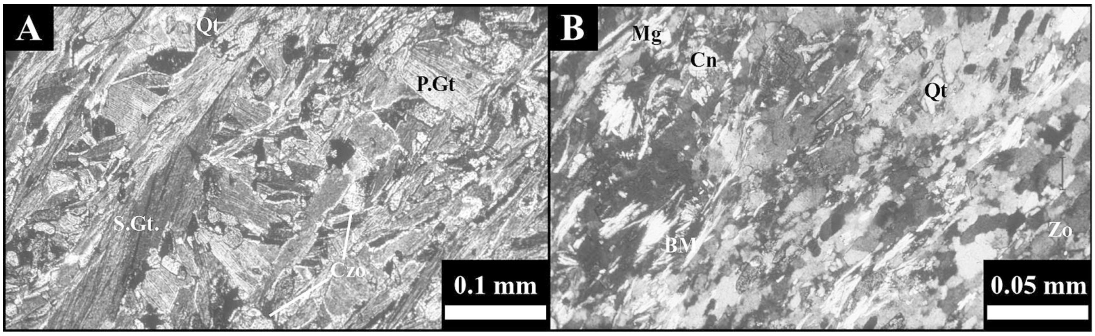

FIG. 2. A) Micrograph of ganterite in white mica schist (sample SS9787) (S.Gt: synkinematic ganterite; P.Gt: postkinematic ganterite, Qt: quartz, Czo: clinozoisite). B) Micrograph of barian muscovite in zoisite–celsian gneiss (sample SS9854/1A) (Cn: celsian; Zo: zoisite, Qt: quartz; Mg: margarite, BM: synkinematic crystals of barian muscovite).

Crest and Sterling Hill, New Jersey (Tracy 1991), where metasomatism was invoked as the important process leading to formation of the micas.

CHEMICAL CHARACTERISTICS OF THE WHITE MICAS

The data reported here pertain to micas occurring in both the white-mica schist and the zoisite–celsian gneiss. The hand specimens studied were collected at several outcrops in the Berisal Complex. The Ba content of white mica is generally relatively constant at hand-specimen scale, but displays wide variation among different samples (Fig. 3). Inspection of Figure 3 suggests that the Ba content of the white micas increases with the bulk Ba concentration in the host rock. This trend, however, is not very pronounced ($r^2 = 0.40$). On the other hand, EPMA data were available for only eight rocks that were analyzed for their bulk composition.

The chemical formula of the micas was calculated on the basis of 11 atoms of oxygen (Tables 2, 3). The *T* sites were assumed to be completely filled by Si and Al. The remaining Al, as well as all Ti, Fe^{2+}, Mg and Mn^{2+}, were assigned to the octahedrally coordinated *M* site. The *M*-site occupancy is close to 2.000 atoms per formula unit (*apfu*), consistent with that of dioctahedral micas (average Σcations at the *M* site = 2.015 *apfu*, range +0.065, –0.045). All Ba^{2+}, K^+, Na^+ and any Ca^{2+} present were assigned to the *I* site, which similarly, is nearly always completely filled (average Σcations at the *I* site 0.97 *apfu*, range +0.08, –0.115).

TABLE 1. REPRESENTATIVE BULK COMPOSITION OF THE Ba-ENRICHED HOST ROCKS, BERISAL COMPLEX

	White-mica schist		Zoisite–celsian gneiss		
	1	2	3	4	5
Na_2O wt.%	1.54	<0.05	0.86	<0.05	2.85
MgO	1.94	3.38	0.54	0.15	1.36
Al_2O_3	14.8	10.8	18.8	13.3	14.9
SiO_2	64.2	74.4	64.4	74.4	57.5
P_2O_5	0.39	0.29	1.90	0.37	0.60
K_2O	2.65	2.19	0.42	0.29	0.56
CaO	1.26	0.35	9.30	5.75	4.97
TiO_2	0.69	<0.04	0.17	0.25	0.50
MnO	0.06	<0.02	0.03	0.03	0.04
FeO	4.66	0.64	0.56	0.18	2.06
LOI	1.68	2.84	1.62	1.03	1.12
Total	93.9	94.2	98.7	95.7	86.5
Cl ppm	160	149	167	144	144
V	81	<83	<83	<83	<83
Cr	131	104	154	<4	72
Co	67	<40	<40	137	<40
Ni	75	<37	122	<37	95
Cu	57	65	96	<38	91
Zn	<78	<78	109	<78	<78
Rb	267	96	85	<9	<9
Sr	286	64	2618	750	4094
Y	<14	38	140	47	145
Zr	508	124	1071	111	86
Nb	60	34	79	15	<15
Ba	43766	37794	8023	40200	128507
Pb	<40	<40	<40	<40	<40

LOI: loss on ignition. < denotes element, if present, is below detection limits of the XRF measurement routine.

The chemical variation plots shown in Figures 4 through 8 were constructed using results of 278 analyses of 51 crystals of Ba-rich white mica and ganterite. The dataset has been divided into three sets on the following basis: ganterite, *i.e.,* all compositions where Ba is the dominant *I*-site cation (filled triangles); compositions where the K content exceeds 0.53 *apfu* (diamonds), and compositions where the K content is ≤0.53 *apfu*, but Ba is not dominant (grey squares). In the K > 0.53 *apfu* dataset, several points are significantly displaced

TABLE 2. REPRESENTATIVE ELECTRON-MICROPROBE DATA FOR Ba-RICH WHITE MICAS AND GANTERITE IN WHITE-MICA SCHIST, BERISAL COMPLEX

	1	2	3	4	5	6	7
BaO wt.%	5.18	7.73	8.73	8.94	10.9	12.1	16.1
K_2O	8.05	7.36	7.05	7.23	6.47	5.79	2.86
MgO	0.33	0.97	1.44	1.68	1.51	1.31	0.65
Al_2O_3	37.6	36.2	34.6	33.7	34.9	34.3	37.4
SiO_2	42.7	41.8	41.8	42.5	41.3	38.9	36.5
FeO	0.58	0.86	1.47	1.48	1.65	1.39	0.83
CaO	<0.06	0.02	0.03	<0.06	0.01	0.03	0.03
Na_2O	1.38	0.98	1.02	0.97	0.95	0.84	1.88
TiO_2	0.19	0.51	1.01	1.06	0.97	0.75	0.35
MnO	<0.02	<0.02	0.14	0.01	0.08	0.15	<0.02
Total	96.0	96.4	97.4	97.6	98.8	95.5	96.7
Number of cations on the basis of 11 atoms of oxygen							
Ba *apfu*	0.138	0.209	0.237	0.242	0.296	0.342	0.459
K	0.699	0.649	0.623	0.638	0.572	0.535	0.265
Na	0.182	0.131	0.137	0.130	0.128	0.118	0.265
Ca	0.000	0.001	0.002	0.000	0.001	0.002	0.002
I site	1.020	0.990	0.999	1.010	0.996	0.997	0.991
Mn	0.000	0.000	0.008	0.001	0.005	0.009	0.000
Mg	0.034	0.100	0.149	0.173	0.156	0.141	0.070
Fe	0.033	0.050	0.085	0.086	0.096	0.084	0.050
Ti	0.010	0.026	0.053	0.055	0.051	0.041	0.019
^{VI}Al	1.921	1.834	1.723	1.689	1.710	1.737	1.858
M site	1.997	2.011	2.018	2.004	2.017	2.013	1.998
Si	2.906	2.889	2.897	2.939	2.862	2.813	2.654
^{IV}Al	1.094	1.111	1.103	1.061	1.138	1.187	1.346
T site	4.000	4.000	4.000	4.000	4.000	4.000	4.000
Σcations	7.017	7.001	7.017	7.014	7.012	7.010	6.989

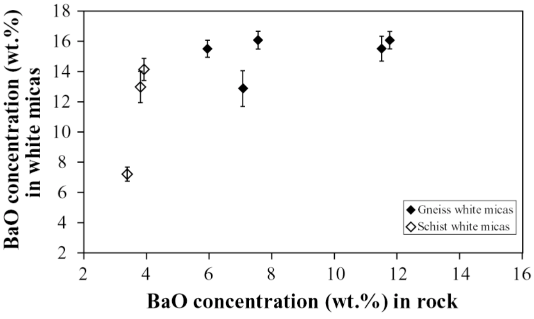

FIG. 3. Variation of Ba concentration in white micas *versus* whole-rock Ba concentration. Error bars show standard deviation for mica compositions from a single sample (n = 21 or greater; $r^2 = 0.40$).

from the general trend exhibited by the other points in the set (filled diamonds). These points represent a small number of analytical results from seven crystals. Their chemical behavior is anomalous, and they are treated as a separate subset (not included in any calculations of regression coefficients). Typical error bars are displayed on each diagram for one composition from each set.

The first subdivision discriminates between ganterite and barian muscovite (Fig. 4). The second subdivision of the Ba-rich mica compositions has been made because of an observed variation in the behavior of Na where K ≤ 0.53 *apfu* (Fig. 5). This arbitrary subdivision is based entirely on observations made in the discrimination diagrams. Where K exceeds 0.53 *apfu*, there is no correlation between K and Na (Fig. 5), irrespective of the Ba content. Where K ≤ 0.53 *apfu*, the Na content of the micas has a strong correlation with both Ba and K (Figs. 4, 5).

The plots of $\mathrm{Al}_{(\mathrm{tot})}$ *versus* Si, Ba *versus* Si, and Ba *versus* $\mathrm{Al}_{(\mathrm{tot})}$ show relatively simple linear relationships between each of the components (Figs. 6, 7). The data points depicted by the filled diamonds have higher than expected total Al, lower $\Sigma^{\mathrm{VI}}Me^{2+}$, and slightly lower Si contents (Figs. 6A, 7, 8). These compositions appear to have a chemical profile that is influenced by the Tschermak substitution (exchange vector 3), which, however, has not influenced the quantities of Ba, Na and K (Figs. 4, 5). In all other cases, it is clear that with an increasing Ba content in the micas, the total Al content also increases, whereas the concentration of Si decreases. The linear regression lines displayed in Figures 6 and 7 show that there is a good coherence among the three cations across the entire compositional range.

The plot of Ba *versus* octahedrally coordinated Me^{2+} (Fig. 8) shows that along with the increase in Ba (*i.e.*, decrease in Si) content, there is a decrease in the number of divalent cations present in the *M* site. Thus, as the Ba content increases and ganterite is formed, the micas become more strongly dioctahedral in character. This is contrary to what is seen in the barian trioctahedral micas kinoshitalite and ferrokinoshitalite. No correlation between Ba and Ti has been observed ($r^2 = 0.04$).

DISCUSSION

For the mica compositions reported here, an [Al][Si]$_{-1}$ substitution is in operation over the complete range of Ba contents (Fig. 6A). This is balanced by, and can be partially correlated with, a [Ba][K]$_{-1}$ substitution at the *I* site (Fig. 4). Therefore, exchange vector (1) is primarily responsible for the solid-solution series between muscovite and ganterite. The variation in Ba and K, however, does not exhibit a true linear distribution (Fig. 4). Thus the mechanism of Ba incorporation must be more complicated, particularly at high Ba contents. From Figures 4 and 5, it is clear that the nature of the interlayer cation-exchange is modified where the K content of the mica decreases to ≤0.53 *apfu*. In the ganterite

TABLE 3. REPRESENTATIVE ELECTRON-MICROPROBE DATA FOR Ba-RICH WHITE MICAS AND GANTERITE IN ZOISITE–CELSIAN GNEISS, BERISAL COMPLEX

	8	9	10	11	12	13	14
BaO wt.%	8.42	9.10	11.5	12.2	14.4	15.2	16.8
K_2O	6.90	6.80	5.34	5.81	4.33	2.53	2.81
MgO	0.68	0.78	1.15	1.07	0.64	0.63	0.87
Al_2O_3	36.3	36.1	35.1	34.7	37.7	38.0	36.6
SiO_2	39.3	39.2	38.8	38.1	36.6	37.5	35.7
FeO	1.32	1.06	0.93	0.95	0.74	0.61	0.70
CaO	0.04	0.04	0.04	0.01	<0.02	0.05	0.03
Na_2O	0.91	0.8	1.02	0.96	1.25	2.37	1.65
TiO_2	0.21	<0.15	1.80	1.85	0.78	0.38	0.65
MnO	0.09	<0.02	0.02	0.10	0.02	<0.02	<0.02
Total	94.2	93.9	95.7	95.7	96.4	97.2	95.8
Number of cations on the basis of 11 atoms of oxygen							
Ba *apfu*	0.236	0.256	0.322	0.345	0.409	0.426	0.487
K	0.629	0.624	0.487	0.536	0.399	0.230	0.265
Na	0.126	0.112	0.141	0.134	0.175	0.328	0.236
Ca	0.003	0.003	0.003	0.001	0.000	0.004	0.002
I site	0.994	0.995	0.954	1.016	0.984	0.988	0.991
Mn	0.005	0.000	0.001	0.006	0.001	0.000	0.000
Mg	0.072	0.084	0.123	0.115	0.069	0.067	0.096
Fe	0.079	0.064	0.056	0.057	0.045	0.036	0.043
Ti	0.011	0.000	0.097	0.101	0.042	0.020	0.036
^{VI}Al	1.866	1.877	1.733	1.708	1.854	1.872	1.820
M site	2.034	2.024	2.009	1.988	2.011	1.996	1.995
Si	2.808	2.820	2.776	2.753	2.646	2.677	2.636
^{IV}Al	1.192	1.180	1.224	1.247	1.354	1.323	1.364
T site	4.000	4.000	4.000	4.000	4.000	4.000	4.000
Σ cations	7.029	7.019	6.963	7.003	6.995	6.984	6.986

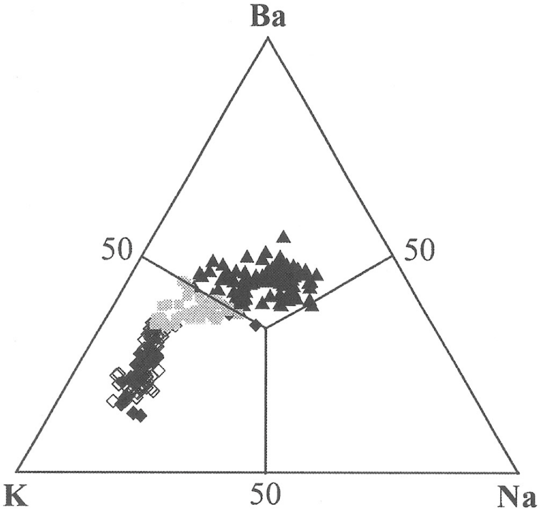

FIG. 4. Distribution of the three most important *I*-site cations in Ba-rich white mica and ganterite from the Berisal Complex, Switzerland. Symbols: filled triangles: ganterite; grey squares: K ≤ 0.53 *apfu*, diamonds: K > 0.53 *apfu*.

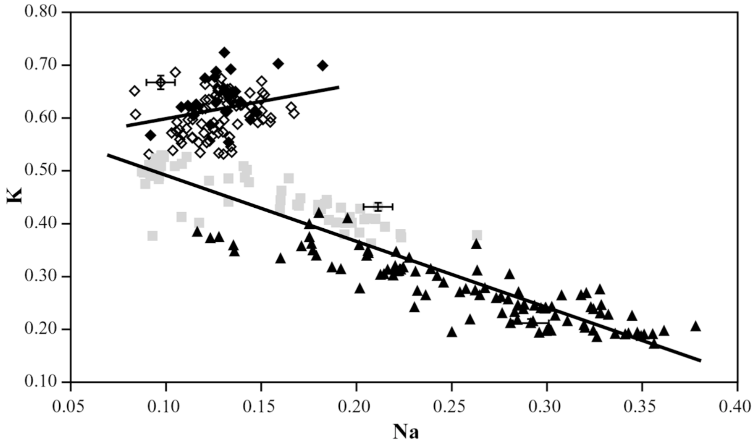

FIG. 5. Variation of K *versus* Na in Ba-rich white micas and ganterite from the Berisal Complex, Switzerland (for K > 0.53: $y = -1.23x + 0.61$ and $r^2 = 0.08$; for ganterite and $K \leq 0.53$: $y = 0.90x + 0.49$ and $r^2 = 0.85$). Same symbols as in Figure 4. Filled diamonds are influenced by different exchange-vectors and are not included in the linear regression lines plotted.

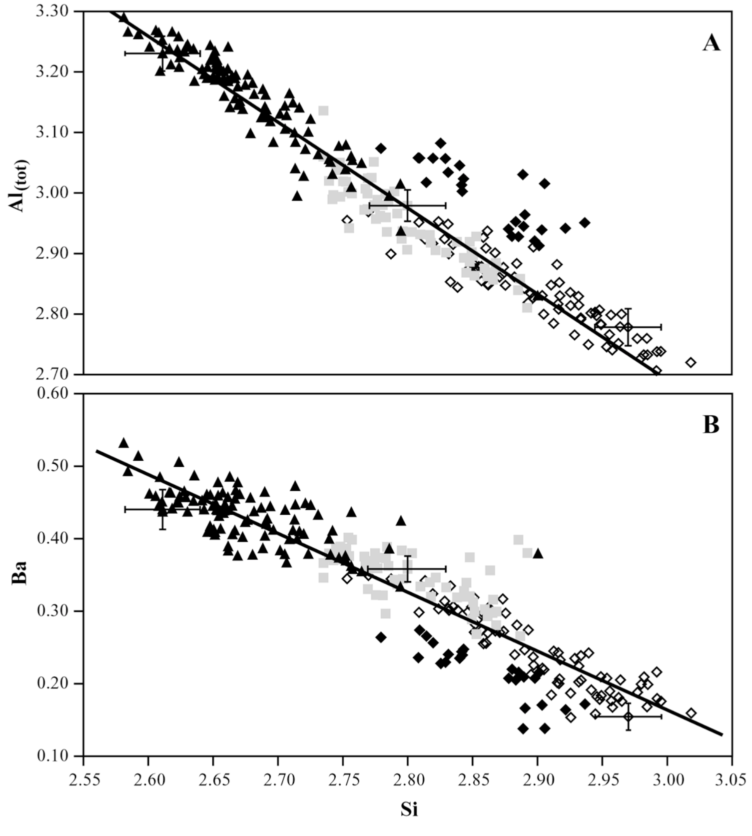

FIG. 6. Variation plots for Ba-rich white micas and ganterite from the Berisal Complex, Switzerland. A) $Al_{(tot)}$ *versus* Si ($y = -1.42x + 6.95$; $r^2 = 0.96$); B) Ba *versus* Si ($y = -0.85x - 2.60$; $r^2 = 0.85$). Same symbols as in Figure 4. Filled diamonds are influenced by different exchange-vectors and are not included in the linear regression lines plotted.

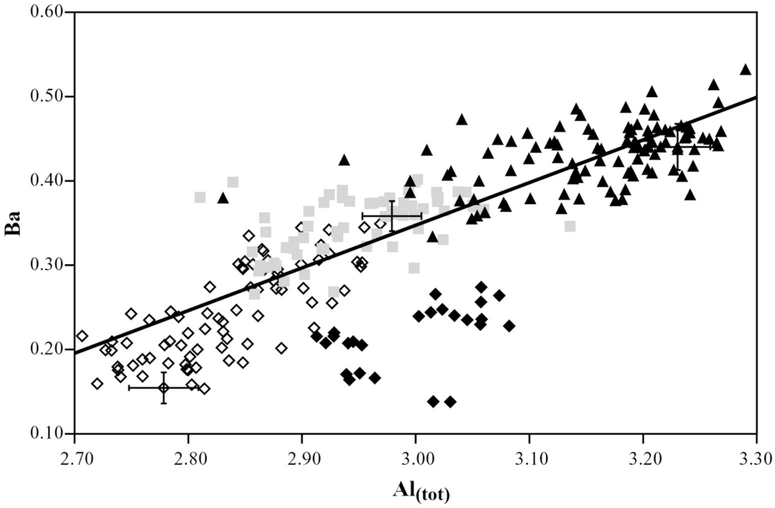

FIG. 7. Variation of Ba *versus* Al in Ba-rich white micas and ganterite from the Berisal Complex, Switzerland ($y = 0.51x - 1.17$; $r^2 = 0.79$). Same symbols as in Figure 4. Filled diamonds are influenced by different exchange-vectors and are not included in the linear regression lines plotted.

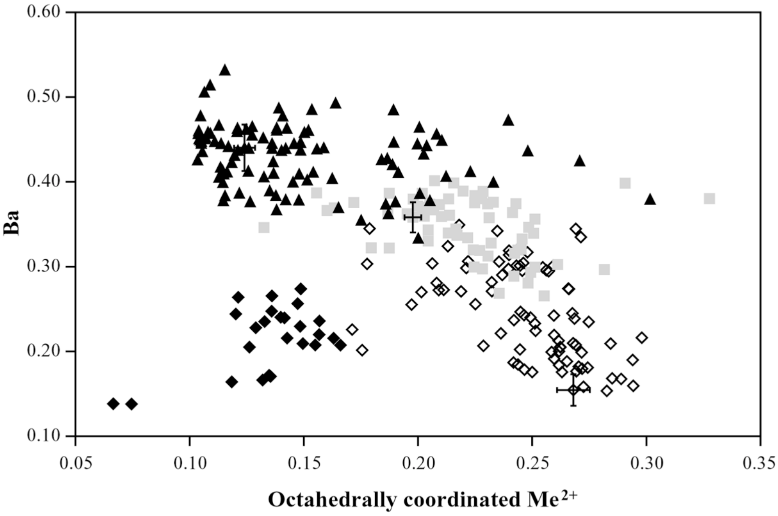

FIG. 8. Variation of Ba *versus* octahedrally coordinated Me^{2+} (Mg + Fe + Mn) in Ba-rich white micas and ganterite from the Berisal Complex, Switzerland. Same symbols as in Figure 4.

field, the Ba concentration remains relatively constant compared to the wide range of K/(K + Na) values observed (Fig. 4). Thus Na also must be involved in the chemical exchanges. We infer that two substitutions are operating simultaneously and, to some degree, independently: a coupled substitution described by $[\mathrm{Ba}][\mathrm{Al}][\mathrm{K}]_{-1}[\mathrm{Si}]_{-1}$ (vector 1), and a simple $[\mathrm{Na}][\mathrm{K}]_{-1}$ exchange operating at the I site, which would explain the good correlation between K and Na observed for compositions with K ≤ 0.53 *apfu* (Fig. 5). As the *I* sites in all micas are identical (Bailey 1984), Ba^{2+}, K^{+} and Na^{+} should be randomly distributed and interchangeable, and this is documented by our data with K ≤ 0.53 *apfu* (Fig. 4).

The results obtained for the Ba-rich micas with $K \leq 0.53$ *apfu* and ganterite in the Berisal Complex are intriguing for two reasons. Firstly, the described characteristics are possibly unique, because in minerals where exchange between alkali and alkaline-earth elements is observed, such as in the albite – orthoclase – celsian, albite – orthoclase – anorthite or muscovite – paragonite – margarite systems, a ternary solid-solution is, under most geological conditions, not observed or is very limited in extent (Smith & Brown 1988, Hewitt & Wones 1984). Secondly, ganterite is capable of simultaneously accommodating atoms so far considered to be incompatible without altering the occupancy of the *M* site. For example, Harlow (1995) noted that there were no occurrences of Ba-dominant dioctahedral micas, *i.e.,* Ba analogues of margarite, because the presence of $^{[VI]}Al$ requires a large α angle, and thus a small *I* site, making accommodation of high quantities of a large cation such as Ba^{2+} impossible. The study of Graeser *et al.* (2003) and this work demonstrate, however, that such a species occurs naturally, forming a solid solution with muscovite.

The explanation for these unusual features may perhaps be found in the bulk composition of the host rocks. The chemical composition of the white-mica schists and leucocratic gneisses in which the Ba-rich micas are found is essentially given by $SiO_2 + Al_2O_3 + BaO + K_2O \pm Na_2O$ and $SiO_2 + Al_2O_3 + BaO + CaO$, respectively; the total ($FeO + MgO + MnO + TiO_2$) concentration rarely exceeds 3 wt.% in either rock type (Table 1). One might therefore conclude that the dioctahedral Ba-dominant micas may have formed because there was insufficient Fe or Mg available for the growth of trioctahedral Ba-rich brittle mica. However, Fe–Mg minerals such as chlorite and garnet are found occasionally as part of the assemblage of synkinematic minerals, and thus Fe and Mg must have been available during formation the Ba-rich micas and ganterite, but they were not incorporated in substantial amounts (Fig. 8).

At the peak of Alpine metamorphism (~600°C and 7 kbar, Todd & Engi 1997), plagioclase (albite) growth or exsolution of paragonite could be expected, and is indeed observed in samples of Ba-poor white-mica schist in the Berisal Complex (Hetherington 2001). In ganterite-bearing samples, however, exsolution textures in either plagioclase, or muscovite–paragonite or ganterite–paragonite are not observed. Therefore, we conclude that in rocks with exceptionally high Ba concentrations, where Na is available, Na is being preferentially accommodated in barian muscovite and ganterite.

Structure refinements for some of the barian mica crystals have shown that the presence of Na^+ and Ba^{2+} in dioctahedral micas results in similar interlayer distances (Armbruster *et al.* 2002). This observation provides a crystallographic reason for accommodation of Ba^{2+} and Na^+ in identical structural sites of dioctahedral $2M_1$ micas. However, high bulk-rock concentrations of Na are not a prerequisite for ganterite formation, since ganterite is also found in rocks poorer in Na (Table 1).

Accommodation of Mg and Fe^{2+} in the *M* site of normal white micas is promoted by elevated pressure (P), as observed in the muscovite–phengite series (Bailey 1984, Guidotti *et al.* 2000). By invoking exchange vector 2, one might conclude that elevated P may also increase the Ba content of white micas growing in Ba-enriched rocks. The possible role of P, and its effects on crystal structure, *M*-site occupancy and composition of Ba-rich white micas have been discussed previously. Harlow (1995) stated that the data from the locality in Guatemala did not permit a clear interpretation of the P-dependency of Ba in phengite, despite the availability of a suite of rocks from a wide range in P. Similarly, Jiang *et al.* (1996) found no clear relationship between Ba content and pressure in the muscovite–phengite series; they concluded that Ba uptake is controlled primarily by $[Ba][Al][K]_{-1}[Si]_{-1}$, and that the quantities of Fe^{2+} and Mg in barian mica are dictated by phengite formation. The influence of elevated P in the formation of Ba-rich micas has also been suggested by Shmakin (1984), and evidence for dioctahedral Ba-rich white micas has more recently been reported from ultrahigh-P rocks in the Erzgebirge (Massonne & Burchard 2000). As proposed by Stille (1980), the Berisal Complex underwent high-P metamorphism during early Alpine orogenesis, and hence pressure may have played a part in the formation of ganterite in the samples studied here.

The suite of samples from the Berisal Complex, which exhibits a continuous range of Ba concentrations, was collected from a restricted geographical area, and all of the rocks have a similar metamorphic history, with peak conditions at *ca.* 600°C and 7 kbar (Todd & Engi 1997). Hence, the role of elevated P in the formation of these Ba-rich white micas may be approached from the perspective of variable Ba content of the micas and elevated, but constant pressure. The data presented here show that in the mica samples studied, formed at amphibolite-facies conditions, the concentrations of Mg and Fe decrease as the Ba content increases (Fig. 8). A similar pattern was also noted by Grapes (1993) for micas in metacherts and quartzofeldspathic schists in the Southern Alps, New Zealand. From the behavior of the divalent *M*-site cations in the Berisal white micas, we conclude that the high Ba content of these micas was not the result of elevated pressure. Some of the crystals, though, do seem to have been affected by the phengite substitution (3), which, however, has had no visible effect on the Ba content (filled diamonds in Figs. 4 and 5).

A full explanation of why the supposedly incompatible elements Ba and Na are accommodated in dioctahedral $2M_1$ micas, in identical structural sites, and why Mg and Fe^{2+} are progressively excluded from the *M*-site is still sought. The structure-refinement study of Ba-rich white micas of Armbruster *et al.* (2002) indicates that ternary occupancy of the *I* site by the contrasting ions may stabilize the structure. The study also showed that lower Mg and Fe^{2+} contents in the mica and, by inference, higher Ba ± Na contents, result in a decrease in the thickness of the layer of octahedra, promoting $^{[VI]}Al^{3+}$ stability. If a similar argument holds true for the micas richest in Ba presented in this study, then it might provide one possible reason for the occurrence of dioctahedral micas with such an unusual composition.

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