

## Barium-rich phengite in eclogites from the Voltri Group (northwestern Italy)§

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**ABSTRACT.** — A white mica with high barium content has been found for the first time in eclogites from a single body cropping out near the village of Vara Inferiore (Voltri Group, Italy). Petrographic observations reveal that the modal abundance of mica is low and that its crystallisation took place after the climax of the eclogite-facies metamorphism. This study reports data on bulk rock chemistry, obtained by ICP-MS, as well as the results of EMP and LA-ICP-MS analyses on major and selected trace elements carried out *in situ* on handpicked separate grains of mica. The most significant features of the bulk rock chemistry are the high content of Na<sub>2</sub>O and the enrichment in LILE elements (Ba and Cs over K and Rb) compared with other eclogites of the area. The white mica is a "phengite" that contains 3.17 - 3.30 Si a.p.f.u, and 0.19 - 0.31 Mg a.p.f.u. All the analysed grains show marked heterogeneities in both major and trace element distribution. In particular, the content of BaO varies from 1.65 to 4.55 wt% and from 2.46 to 4.59 wt% in two examined samples, thus leading to a range of ≈ 4-12 % Ba atoms in the cation interlayer (*I*) of the mica. The high barium content in white mica is coupled with a high abundance in other LILE (Cs, Rb) and light elements such as Li and B. On the contrary, mica has low concentration

of REE, Sr, P and HFSE (e.g. Nb, Zr, Ti, Y). Phengite chemistry indicates that its trace element signature is controlled by a fluid activity that also prevented the achievement of complete homogenisation.

**RIASSUNTO.** — In un affioramento di rocce eclogitiche situato vicino alla località di Vara Inferiore (Gruppo di Voltri, Italia) sono stati riscontrati cristalli di mica bianca contenenti un elevato tenore di bario. Dalle osservazioni petrografiche è emerso che tale mica è presente in quantità molto limitata (pochi cristalli per sezione sottile) e che la sua cristallizzazione è successiva all'evento eclogitico. Questo studio riporta i dati geochimici di roccia totale (ottenuti mediante ICP-MS) e i risultati di analisi EMP e LA-ICP-MS su elementi maggiori e in tracce eseguite *in situ* su cristalli di mica bianca opportunamente selezionati. Le rocce analizzate sono caratterizzate da un contenuto di Na<sub>2</sub>O e di elementi litofili a grande raggio ionico (LILE: Ba, Cs, K, Rb) più elevato rispetto a quelli di altre eclogiti del Gruppo di Voltri. La mica bianca è una "phengite" che contiene 3,17 - 3,30 Si a.p.f.u e 0,19 - 0,31 Mg a.p.f.u. Tutti i cristalli analizzati mostrano una certa disomogeneità composizionale sia per quanto riguarda gli elementi maggiori che per quelli in tracce. In particolare, il contenuto di BaO nei due campioni di mica bianca esaminati varia da 1,65 a 4,55 e da 2,46 a 4,59 % in peso, rispettivamente. L'alto contenuto di bario

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è accompagnato da un significativo arricchimento in altri LILE (Cs, Rb) e in alcuni elementi leggeri come Li e B. Viceversa, entrambi i campioni di mica risultano impoveriti in REE, Sr, P e in altri elementi ad alta forza di campo (HFSE) come Nb, Zr, Ti e Y. Il chimismo delle fengiti analizzate indica che il loro contenuto in elementi in tracce è controllato dalla presenza di fluidi che hanno probabilmente favorito l'elevata disomogeneità composizionale.

KEY-WORDS: *eclogite, white mica, barium, LA-IC-MS data, trace elements, Voltri Group, Italy.*

### INTRODUCTION

According to the original definition of *eclogite* (from the Greek word *εκλογη*, meaning *choice*) given by Haüy (1822), white mica is not included in the mineral assemblage of this rock type. Nevertheless, it is now known to be widespread in eclogites as accessory hydrous mineral, both as a primary phase in textural equilibrium with garnet and omphacite and as secondary one crystallised at some stage of the rock's history. The analyses of white mica reported in literature for eclogites from all around the world, indicate the presence of two dominant compositions: muscovite (Mu) - with a variable amount of "phengitic substitution" [*i.e.* the substitution of (Mg,Fe)Si for Al<sup>iv</sup>Al<sup>vi</sup>] - and paragonite (Pg), sometimes also closely associated. More rarely, paragonite also coexists with margarite (Ma) as described, for example, in the pseudomorphs on lawsonite porphyroblasts occurring in the amphibolitised eclogites from the Betic Cordilleras, Spain (Gomez-Pugnaire *et al.*, 1985). Na-(Mg,Fe)-margarite and preiswerkite [a rare sodic trioctahedral mica with the ideal formula NaMg<sub>2</sub>Al(Si<sub>2</sub>Al<sub>2</sub>) O<sub>10</sub>(OH)<sub>2</sub>] have been exceptionally observed as retrogression products in two eclogites occurrences from France and Norway (Godard and Smith, 1999 and references therein).

In the course of the electron microprobe analyses of main minerals forming a small eclogite outcrop (1.70 x 2 m ca) near Vara Inferiore, a village at the geographical centre of the Voltri Group (Western Liguria, Italy), phengitic muscovites with high Ba content (by

EMP: up to BaO = 4.59 wt%) were discovered. BaO was found to vary significantly within individual grains, between different grains within the same sample and between different rock samples.

Barium, besides K, Na, and possibly Ca, is the most abundant large ion in white micas from metamorphic rocks but it is often omitted during chemical analyses, mainly because of its generally small amount in the bulk (Guidotti, 1984). A review of the literature on barian dioctahedral micas, muscovites and phengites, is reported by Harlow (1995): most of them coexist with a Ba phase (for example barite, celsian or hyalophane) and are generally formed at high P/T conditions. In recent years, Graeser *et al.* (2003) have presented a description of ganterite, a dioctahedral mica from the leucocratic gneisses of Berisal Complex (Switzerland) with the occupancy of the interlayer site (*I* site) dominated by Ba.

As regards the occurrence of Ba-rich white mica in eclogites from subduction zone settings, a phengite with significant Ba content (BaO = 14.51 wt%) and associated with other exotic minerals (cymrite, apatite) is reported from the eclogites of the Erzgebirge Massif (Massonne and Burchard, 2000). The assemblage is interpreted as a clear evidence that H<sub>2</sub>O-CO<sub>2</sub> fluid phase rich in elements such as Ba, K, P, Ti, Sr, Cl penetrated the UHP metamorphic rocks at level of deep orogenic roots; possibly, these fluids were also responsible for the fast exhumation of the rocks.

The eclogites examined in this study are partially retrogressed to epidote-amphibolite facies (Bocchio and Liborio, 1996). The Ba-rich white mica occurs only as an accessory mineral both in contact with garnet and in aggregates consisting of amphibole, chlorite, quartz and opaques. However, its trace element signature can be a significant parameter to be considered when assessing the origin and the evolution of the subduction-related rocks of the Voltri Group.

## PETROGRAPHIC OUTLINE

The Voltri Group represents the largest ophiolitic complex in the Alpine belt and contains the most "spectacular" occurrence of eclogites of the Alps (Ernst, 1976). Extensive geologic and petrologic studies on these eclogitic bodies have been carried out by many authors (*e.g.* Mottana and Bocchio, 1975; Ernst, 1976; Cortesogno *et al.*, 1977; Ernst *et al.*, 1983; Messiga and Scambelluri, 1991; Messiga *et al.*, 1995; Tribuzio *et al.*, 1996). Two main types of eclogites were recognised on petrographic and textural grounds: the most common are the "*flaser-eclogites*" showing a corona texture where large crystals of clinopyroxene are rimmed by euhedral and fine grained garnets. A second type (named "*bimineralic-eclogites*" by Mottana and Bocchio, 1975) displays a fine-grained foliated to mylonitic fabric, with euhedral garnet embedded in a recrystallised matrix of clinopyroxene. The eclogite from the body of Vara Inferiore (Italian map 82, Tav.III, N.E., U.T.M. coord. 32TMQ69182390) belongs to this second type. Bocchio and Liborio (1996) already described it in detail and therefore only the main features are reported.

The six samples (91-GV-1 to 6) examined by Bocchio and Liborio (*op. cit.*) were collected in different parts of the outcrop, at intervals of 20-30 cm from the northern border. The serpentinites crop out only a few meters away but the contact is unclear and covered by a thick sedimentary deposit. Anyhow, sample 91-GV-6 is the closest to the contact with the serpentinites. Macroscopically, the eclogites are massive and dark green to black in colour and contain alternating patches of silvery pyrrhotine and violet rutile. In thin section, these rocks are composed predominantly by garnet (30-35 vol%) of variable dimension in a fine-grained matrix (sometimes strongly mylonitised) made up mainly by clinopyroxene (25-30 vol%) and symplectite (10-15 vol%). The matrix also contains amphibole (15-20 vol%), rutile (4-5 vol%) and small abundances of epidote group minerals, plagioclase, quartz, and opaque grains (<10 vol%). A few crystals of white mica per thin section (<1 vol %) occur in all the samples, with the unique exception of sample 91-GV-1. They are irregularly distributed within the rock as isolated, small and euhedral flakes in contact with garnet or filling necks between boudinaged garnet porphyroblasts. In this occurrence, mica is occasionally associated with quartz and amphibole. In the most retrograded portion of eclogite samples, white mica is also present inside fractures cutting the

garnet as sheaf- or fan-like aggregates together with amphibole and chlorite.

## ANALYTICAL TECHNIQUES

As mentioned, the eclogite of Vara Inferiore has already been studied. Bocchio and Liborio (1996) performed a detailed microprobe study on the compositional variations of garnet, which proved to be related with the grain size. In the present work, whole-rock chemistry of the main eclogitic blocks (91-GV-1, 2 and 6: hereafter 1, 2 and 6 for simplicity), was investigated by the ICP-MS technique at the Acme Analytical Laboratories, Vancouver. The FeO content was determined by potentiometric titration with  $K_2Cr_2O_7$  and loss on ignition (LOI), corrected for FeO oxidation, by gravimetry on powders. Handpicked separate grains of white mica from samples 2 and 6 were embedded in epoxy resin and then analysed in situ for major and minor elements (also including Ba) with a CAMSCAN MX 2500 wave-length-dispersion microprobe at the "Dipartimento di Scienze Mineralogiche e Petrografiche" of the University of Padova. Operating conditions were 15 kV and 15 nA on the brass. Natural silicates and oxides were used as standards. Ba and Ti were also measured on three crystals of each sample by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) at the "C.N.R.-I.G.G." (Pavia) together with other selected trace elements (Li, B, P, Sc, V, Cr, Co, Ni, Zn, Rb, Sr, Y, Zr, Nb, Cs, Pb). REE were also analysed but their abundances, with the exception of a few elements (La, Ce, Eu), were below the detection levels. The laser source consists of a Nd:YAG laser whose fundamental emission in the near-IR region (1064 nm) is converted into 266 nm by two harmonic generators and then focussed on the sample with a petrographic microscope. The laser was operated with a frequency of 10 Hz and with a power of 2.5 mW. The spot size was set to 40 microns. The ablated material was analyzed for selected elements by a quadrupole ICP-MS (DRCe-Perkin Elmer). Each analysis consisted in the acquisition of 60 seconds of background and 60 seconds of mica ablation signal. Data reduction and element concentrations were obtained with the software "Glitter" (van Achterbergh *et al.*, 2001)

using NIST SRM 612 and  $^{43}\text{Ca}$  as external and internal standard, respectively. The precision and the accuracy estimated on the basaltic glass BCR2 (USGS) were better than 10%.

#### BULK COMPOSITION OF THE HOST ROCK

Major and selected trace and rare-earth elements data on the eclogites from Vara Inferiore are reported in Table 1. As a whole, the resulting chemical compositions resemble that of all the eclogites from the Voltri Group from literature, which appear to be the metamorphic equivalent of Fe-Ti oxide gabbroic tholeiites. As a common feature, the Voltri eclogites display high contents of  $\text{FeO}_{\text{tot}}$  and  $\text{TiO}_2$  derived from the high modal Fe-Ti oxides in the primary igneous assemblage. In the present case,  $\text{FeO}_{\text{tot}}$  ranges from 15.93 to 18.40 and  $\text{TiO}_2$  from 2.40 to 3.57, respectively. As a whole, the data (Table 1) compare quite well with the published average bulk analysis of eclogites from the Voltri Group but with a slight depletion in  $\text{TiO}_2$  content (cfr. Mottana and Bocchio, 1975 and Cortesogno *et al.*, 1977). On the contrary, all the samples from Vara Inferiore display a significant enrichment in sodium [ $\text{Na}_2\text{O} = 6.12\text{--}6.59$  wt% vs. the values of 3.26 wt% and 4.33 wt% calculated by Mottana and Bocchio (*op. cit.*) from the analyses of twelve “*flaser*” and four “*bimineralic*” eclogites, respectively]. MnO ranges from 0.37 to 0.49 and is higher than the content determined in all the eclogites from the Voltri Group reported in literature. Two white mica-bearing eclogites (samples 2 and 6), have a  $\text{Mg}\#$  value [ $=100 \cdot \text{Mg}/(\text{Mg} + \text{Fe}^{2+}_{\text{tot}})$ ] higher than sample 1 that is white mica-free (30.3 and 30.6 vs. 26.5, respectively).

The spider-diagram of whole-rock minor and trace elements normalised to N-MORB and arranged in order of decreasing incompatibility (Fig. 1a), shows that the examined samples are enriched in LIL elements such as Ba and Cs and, in a minor amount, in Rb and K compared with the normalizing values of Sun and McDonough (1989). When the present data are compared with the gross mean given by Mottana and Bocchio (1975) and by Morten *et al.* (1978), both for the “*flaser*” (Ba = 80 ppm; Cs = 0.095 ppm; Rb = 0.16 ppm;  $\text{K}_2\text{O} = 0.08$  wt%) and the “*bimineralic*” eclogites of the Voltri Group (Ba = 140 ppm; Cs = 0.11 ppm;

TABLE 1  
*Bulk composition of eclogites from Vara Inferiore (Voltri Group, Italy).  $\text{Mg}\# = 100 \cdot \text{Mg}/(\text{Mg} + \text{Fe}^{2+}_{\text{tot}})$*

sample	1	6	
	phe-free	phe-bearing	
$\text{SiO}_2$ (wt%)	47.50	47.10	47.46
$\text{TiO}_2$	2.40	3.54	3.57
$\text{Al}_2\text{O}_3$	13.29	10.50	11.67
$\text{Fe}_2\text{O}_3$	7.59	8.63	6.27
FeO	10.07	8.71	10.29
MnO	0.37	0.49	0.42
MgO	3.50	4.03	3.97
CaO	7.04	8.09	8.23
$\text{Na}_2\text{O}$	6.36	6.59	6.12
$\text{K}_2\text{O}$	0.09	0.09	0.21
$\text{P}_2\text{O}_5$	0.55	0.48	0.47
LOI (loss on ignition)	1.22	1.57	1.24
Total	99.98	99.82	99.92
$\text{Mg}\#$	26.5	30.3	30.6
Ba (ppm)	135.4	179.6	503.8
Be	1	2	1
Co	19.9	34.8	19.8
Cs	0.3	0.6	0.6
Cu	7.5	9.4	16.3
Ga	27.4	21.2	23.7
Hf	3.3	4.4	4.7
Nb	5.9	9.7	12.4
Ni	19	43	16
Pb	2.1	0.4	0.3
Rb	1.9	2	4.3
Sc	35	41	39
Sr	62.6	53.5	61.5
V	30	200	150
Y	136.3	150.8	142.2
Zr	118.5	160.4	179.4
La (ppm)	12.1	6.8	2.2
Ce	46.5	27.8	10.1
Pr	8.93	5.09	2.03
Nd	55.1	30.5	13.3
Sm	16.5	10.9	7
Eu	5.47	4.18	3.18
Gd	22.82	18.59	17.29
Tb	3.97	3.88	3.78
Dy	23.66	26.08	24.96
Ho	4.84	5.44	5.1
Er	13.57	16.32	14.8
Tm	1.81	2.43	1.99
Yb	10.88	14.27	12.2
Lu	1.71	2.27	2.13
Eu/Eu*	0.87	0.90	0.89
(La/Yb) <sub>N</sub>	0.77	0.32	0.12

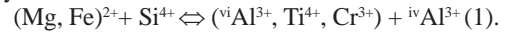
Rb = 0.36 ppm; K<sub>2</sub>O = 0.10 wt%), all the samples from Vara Inferiore appear to be enriched in LIL elements (Table 1). Fig. 1a also shows that these eclogites display a rather flat pattern and a higher abundance in REE, high field strength elements (HFSE, *e.g.* Nb, Zr, Ti, Y) and P compared with MORB. The unique exception is sample 2, which has a moderate light (L) REE depletion. Both white mica-bearing eclogites (2, 6) have a MORB-like content of Pb that is, on the contrary, higher in sample 1. Pb abundance is controlled mainly by phengite and epidote-group minerals (Becker *et al.*, 2000). The somewhat higher Pb content in sample 1 could be related to the presence in this rock of a substantial amount of epidote-group minerals that could play a significant role in retaining Pb in substitution of Ca. The different abundance in the examined samples of epidote-group minerals could also explain the scattering in LREE (Fig. 1b and Table 1) and confirms the control played by accessory minerals on the redistribution of REE in subduction-related eclogites (Tribuzio *et al.*, 1996). In contrast with the scattering content of LREE, the content of HREE clusters in a narrow band (70-100 x C1) in the C1-normalised patterns (Fig. 1b). The REE patterns of the samples examined in this paper do not show the positive Eu anomaly observed in the “*flaser*” eclogites from the Voltri Group but match the patterns of the fine-grained (or “*bimineralic*”) type showing a comparable range of Mg# (24.4 -33.6; Morten *et al.*, 1979).

## WHITE MICA CHEMISTRY

### Major and minor elements

The chemical compositions of the two white micas found in the Vara Inferiore eclogitic body, obtained by EMP analyses, are reported in Table 2 together with the structural formulae. Individual spots in some grains of both samples do not show systematic intragrain zoning for major and minor elements. However, they exhibit broad to moderate variations that are in most cases (Al, Fe, Mg, Na, K, Ba) over the limit of the analytical error. Given that two main phases occurring in these rocks (*i.e.* garnet and clinopyroxene) exhibit major element zoning and evidence for disequilibrium between major elements (Bocchio and Liborio, 1996), the scatter in mica composition is not surprising.

The (Si + Al) cations are sufficient to completely fill the tetrahedrally-coordinated sites (*T*). The remaining Al is assigned, as well as Ti, Fe<sup>2+</sup>, Mg, Cr, to the octahedrally coordinated *M* site. The presence in *M* site of other cations than Al implies the occurrence in white mica of the “*phengitic*” substitution deviating from the ideal muscovite by



In the present case, the amount of this substitution is approximately 25-30 % of the *M* site.

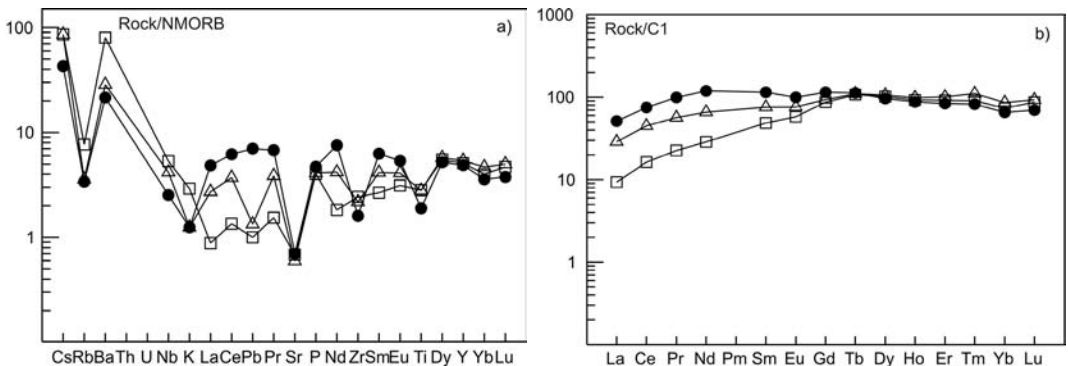


Fig. 1 – (a) Multi-element diagram normalized to N-MORB (Sun and McDonough, 1989) and (b) C1-normalized REE abundances (Anders and Grevesse, 1989) for eclogites of Vara Inferiore (Voltri Group, Italy). Solid circles: phengite-free sample (1); triangles and squares: phengite-bearing samples (2 and 6, respectively).

TABLE 2 — Major element composition and structural formulae of white mica in eclogites from Vara Inferiore (Voltri Group, Italy)

sample	2													
	grain/spot analysis	a1	b1	b2	b3	c1	c2	c3	d1	d2	e1	e2	e3	e4
SiO <sub>2</sub> (wt%)	45.97	46.22	46.15	46.61	47.39	47.50	46.46	47.66	47.45	47.48	47.16	46.79	47.15	46.34
TiO <sub>2</sub>	0.36	0.31	0.27	0.27	0.30	0.35	0.29	0.36	0.36	0.36	0.47	0.36	0.22	0.40
Al <sub>2</sub> O <sub>3</sub>	27.10	29.13	29.93	29.49	27.15	26.87	27.23	27.38	26.91	27.01	27.48	27.61	27.64	26.78
Cr <sub>2</sub> O <sub>3</sub>	0.00	0.08	0.00	0.00	0.06	0.03	0.04	0.06	0.05	0.03	0.00	0.00	0.12	0.03
FeO	4.63	4.57	4.88	4.65	4.42	4.73	4.67	4.10	4.28	4.29	4.61	4.56	4.65	4.44
MgO	2.83	2.08	1.90	2.12	2.96	3.05	3.00	2.73	2.55	2.94	2.80	2.60	2.57	2.50
MnO	0.00	0.00	0.09	0.04	0.04	0.00	0.00	0.00	0.04	0.06	0.00	0.00	0.01	0.00
CaO	0.00	0.01	0.00	0.00	0.00	0.04	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BaO	3.59	1.92	1.65	1.75	4.20	4.55	4.13	4.39	3.02	2.66	3.28	3.18	2.70	4.18
Na <sub>2</sub> O	0.39	0.97	0.78	0.79	0.29	0.30	0.35	0.39	0.55	0.48	0.48	0.44	0.51	0.51
K <sub>2</sub> O	8.96	9.07	9.34	9.40	8.91	8.66	9.22	9.00	9.33	9.43	9.16	9.20	9.33	9.05
Total	93.85	94.37	95.00	95.12	95.73	96.07	95.39	96.06	94.54	94.74	95.45	94.73	94.90	94.09
Formulae calculated on the basis of 11 O atoms														
Si a.p.f.u.	3.242	3.199	3.173	3.199	3.277	3.282	3.239	3.284	3.300	3.288	3.258	3.254	3.265	3.270
<sup>IV</sup> Al	0.758	0.801	0.827	0.801	0.723	0.718	0.761	0.716	0.700	0.712	0.742	0.746	0.735	0.730
T site	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000
Ti	0.019	0.016	0.014	0.014	0.016	0.018	0.015	0.019	0.019	0.019	0.024	0.019	0.011	0.021
<sup>VI</sup> Al	1.494	1.576	1.599	1.584	1.490	1.470	1.477	1.506	1.506	1.493	1.495	1.517	1.520	1.498
Cr	0.000	0.004	0.000	0.000	0.003	0.002	0.002	0.003	0.003	0.002	0.000	0.000	0.006	0.002
Fe <sup>2+</sup>	0.273	0.265	0.281	0.267	0.255	0.273	0.273	0.236	0.249	0.248	0.267	0.265	0.269	0.262
Mn	0.000	0.000	0.005	0.002	0.003	0.000	0.000	0.000	0.002	0.003	0.000	0.000	0.001	0.000
Mg	0.298	0.215	0.195	0.217	0.306	0.314	0.311	0.280	0.264	0.303	0.289	0.270	0.265	0.263
M site	2.084	2.076	2.094	2.084	2.073	2.077	2.078	2.044	2.043	2.068	2.075	2.071	2.072	2.047
Ca	0.000	0.001	0.000	0.000	0.000	0.003	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Na	0.053	0.131	0.104	0.106	0.040	0.040	0.047	0.052	0.074	0.065	0.065	0.059	0.069	0.047
K	0.806	0.801	0.820	0.823	0.786	0.763	0.820	0.791	0.828	0.833	0.807	0.816	0.824	0.815
Ba	0.099	0.052	0.045	0.047	0.114	0.123	0.113	0.119	0.082	0.072	0.089	0.087	0.073	0.116
I site	0.958	0.985	0.969	0.976	0.940	0.929	0.981	0.962	0.984	0.970	0.961	0.962	0.966	0.978
Σ cations	7.042	7.061	7.063	7.060	7.013	7.006	7.059	7.006	7.027	7.038	7.036	7.033	7.038	7.025
TiO <sub>2</sub>		0.28* - 0.39**						0.36* - 0.51**		0.35* - 0.30**				
BaO		1.77* - 1.83**						3.70* - 3.95**		2.96* - 2.98**				

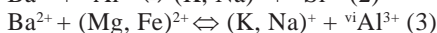
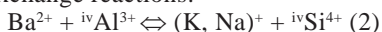
\*EMP analyses average (wt%); \*\*LAM data (wt%).

TABLE 2 — *continued...*

6																				
a1	a2	a3	b1	b2	c1	c2	d1	d2	d3	e1	e2	e3	f1	f2	g1	g2	h1			
46.32	47.09	47.09	46.07	46.31	46.83	46.79	46.33	46.27	47.17	47.59	46.81	45.94	46.00	45.88	46.57	47.34	45.82			
0.39	0.43	0.33	0.24	0.38	0.31	0.14	0.31	0.42	0.31	0.24	0.39	0.32	0.41	0.44	0.33	0.23	0.34			
27.16	27.19	28.10	26.88	27.63	27.86	27.98	26.89	27.01	27.55	27.75	27.94	27.51	27.21	27.04	27.99	26.99	27.57			
0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.07	0.00	0.12	0.00	0.00	0.09	0.04	0.01	0.00	0.02	0.09			
4.83	5.19	4.63	4.58	4.72	5.15	5.08	4.61	5.07	4.26	4.65	4.52	4.89	5.17	5.23	5.14	4.87	4.88			
2.60	2.48	2.28	2.82	2.55	2.26	2.11	2.51	2.54	2.59	2.34	2.48	2.57	2.79	2.75	2.27	2.45	2.67			
0.07	0.00	0.00	0.07	0.04	0.01	0.00	0.00	0.00	0.00	0.04	0.05	0.00	0.00	0.00	0.00	0.08	0.04			
0.00	0.00	0.00	0.07	0.06	0.03	0.01	0.00	0.01	0.01	0.00	0.00	0.00	0.02	0.01	0.00	0.01	0.06			
3.86	3.31	3.47	4.31	3.95	3.88	3.14	3.27	3.33	3.40	2.46	3.59	2.88	3.81	4.59	3.43	3.27	4.17			
0.43	0.58	0.61	0.38	0.48	0.67	0.51	0.45	0.46	0.56	0.50	0.57	0.51	0.35	0.39	0.57	0.34	0.56			
8.88	9.29	8.96	8.75	8.95	8.87	9.13	9.32	9.06	9.40	9.23	8.81	8.98	8.92	8.87	9.12	8.93	8.86			
94.53	95.57	95.47	94.18	95.07	95.87	94.87	93.76	94.17	95.38	94.79	95.15	93.70	94.71	95.21	95.42	94.53	95.05			
Formulae calculated on the basis of 11 O atoms.																				
3.249	3.264	3.252	3.252	3.232	3.241	3.253	3.267	3.253	3.264	3.285	3.245	3.232	3.227	3.224	3.231	3.298	3.211			
0.751	0.736	0.748	0.748	0.768	0.759	0.747	0.733	0.747	0.736	0.715	0.755	0.768	0.773	0.776	0.769	0.702	0.789			
4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000	4.000			
0.020	0.022	0.017	0.013	0.020	0.016	0.007	0.016	0.022	0.016	0.012	0.020	0.017	0.022	0.023	0.017	0.012	0.018			
1.495	1.485	1.539	1.488	1.505	1.514	1.546	1.501	1.490	1.511	1.543	1.527	1.512	1.477	1.463	1.521	1.515	1.488			
0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.004	0.000	0.007	0.000	0.000	0.005	0.002	0.000	0.000	0.001	0.005			
0.283	0.301	0.267	0.270	0.276	0.298	0.295	0.272	0.298	0.246	0.269	0.262	0.288	0.303	0.307	0.298	0.284	0.286			
0.004	0.000	0.000	0.004	0.002	0.001	0.000	0.000	0.000	0.000	0.002	0.003	0.000	0.000	0.000	0.000	0.005	0.002			
0.272	0.256	0.235	0.297	0.266	0.233	0.218	0.264	0.267	0.267	0.241	0.257	0.269	0.291	0.288	0.235	0.254	0.279			
2.074	2.064	2.058	2.073	2.069	2.062	2.066	2.057	2.077	2.047	2.067	2.069	2.091	2.095	2.081	2.071	2.071	2.078			
0.000	0.000	0.000	0.006	0.005	0.002	0.000	0.000	0.000	0.001	0.000	0.000	0.000	0.001	0.001	0.000	0.000	0.004			
0.058	0.078	0.081	0.052	0.065	0.090	0.068	0.062	0.063	0.075	0.067	0.077	0.070	0.048	0.054	0.077	0.046	0.076			
0.794	0.822	0.789	0.788	0.797	0.783	0.810	0.838	0.812	0.830	0.813	0.779	0.806	0.799	0.795	0.807	0.794	0.792			
0.106	0.090	0.094	0.119	0.108	0.105	0.086	0.090	0.092	0.092	0.067	0.098	0.079	0.105	0.126	0.093	0.089	0.115			
0.958	0.990	0.964	0.965	0.975	0.980	0.964	0.990	0.967	0.998	0.947	0.954	0.955	0.953	0.976	0.977	0.929	0.987			
7.032	7.054	7.022	7.038	7.044	7.042	7.030	7.047	7.044	7.045	7.014	7.023	7.046	7.048	7.057	7.048	7.000	7.065			
0.38* - 0.43**									0.35* - 0.37**			0.32* - 0.29**								
3.55* - 3.05**									3.33* - 2.84**			2.98* - 2.39**								

\*EMP analyses average (wt%);\*\*LAM data (wt%).

The content of BaO varies from 1.65 to 4.55 wt% and from 2.46 to 4.59 wt% in samples 2 and 6, respectively, thus evidencing a range of 4-12 % Ba atoms in the cation interlayer (*I*) of the mica. Ba is assigned in this site together with the dominant K, and also with Na and any Ca, the latest in more cases below the detection limits. An inhomogeneous distribution of BaO can be observed between different grains (compare, for example, the content of BaO in crystals *b* and *d* of sample 2) and within the same grains, in both rock samples. According to the data reported in literature, the substitution scheme for Ba incorporation occurs by one of the following exchange reactions:



Reaction (3) is a combination of (1) and (2).

The well-defined negative correlations shown in Figs. 2a and b suggest that, in the present case, both substitutions (2) and (3) are responsible for the incorporation of Ba in these micas. In addition, as already observed by Jiang *et al.* (1996) in some Ba-rich muscovites from Pb-Zn-Ag and Fe deposit of northwestern China, also a general correlation between the  $\text{ivAl}^{3+}$  and

alkaline earth (Ba+Ca) contents (not shown, for simplicity) reflects the reaction (3) and the reaction:  $\text{Ca}^{2+} + \text{Al}^{3+} \Leftrightarrow \text{K}^+ + \text{Si}^{4+}$ . The slight deficit in the cation interlayer (the occupancy of *I* site ranges from 0.93 to 0.99) could imply also the occurrence of the substitution scheme  $\text{Ba} + \text{vacancy} \Leftrightarrow 2(\text{K} + \text{Na})$ , reported by Guidotti (1984) and observed by Bocchio *et al.* (1996) in phengites from eclogitic rocks of Isla Margarita (Venezuela).

#### Minor (Ba and Ti) and trace elements

The LA-ICP-MS data for Ba and Ti (also determined by EMP) and trace elements (Li, B, P, Sc, V, Cr, Co, Ni, Zn, Rb, Sr, Y, Zr, Nb, Cs, La, Ce, Eu, Pb), measured on six selected grains of the same mount used for EMP analyses, are listed in Table 3 in order of increasing atomic number. The spot analysis was close to the centre of each crystal. The standard deviations calculated for most elements are higher than those of typical analytical precision (~10% as derived from measurement of reproducibility on international standards). Thus the observed scatter is ascribed to real inhomogeneity within the data set. The abundance of Ba and Ti is also reported in Table 2 (expressed as oxide wt%): the comparison

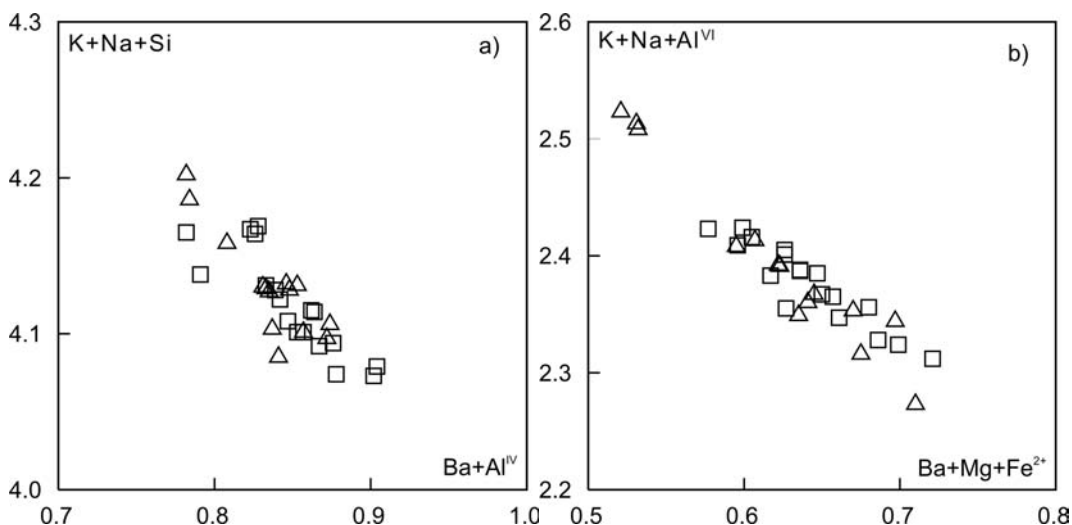


Fig. 2 – Variation plot of Ba-rich white mica (“phengite”) from the eclogite body of Vara Inferiore.

(a) Ba +  $\text{Al}^{\text{IV}}$  versus K + Na + Si ; (b) Ba + Mg +  $\text{Fe}^{2+}$  versus K + Na +  $\text{Al}^{\text{VI}}$ . Triangles and squares: sample 2 and 6, respectively.



with the results obtained by EMP for both these elements suggests a general agreement of the two sets of analytical data. In addition, it also confirms the compositional variation of barium and emphasises its inhomogenous distribution in the various grains.

The multi-element diagram normalised to N-MORB (Sun and McDonough, 1989) shows that all the crystals display a strong enrichment in LILE (Cs, Rb, Ba, K) and a moderate abundance of Pb (Fig. 3). On the contrary, they are depleted in REE, Sr, P and HFSE (*e.g.* Nb, Zr, Ti, Y), with the unique exception of Nb that is close to unity.

The inspection of Table 3 suggests that both samples 2 and 6 contain a significant

amount of the light elements (Li and B). The grains of both samples display considerable variations in the content of these elements but their distribution is different: sample 2 shows Li > B whereas in sample 6 the content of B is higher than that of Li. Both examined white micas are also an important host phase for V (86 and 66 ppm on average in sample 2 and 6, respectively) as well as for other trace elements of the transition group such as Cr, Co, Ni, Cu that very likely enter the octahedral *M* sites. Their concentration in two samples follows the same sequence of abundance (V > Ni > Cr > Co) but the content varies significantly among the samples and among the various grains.

TABLE 3

*Trace elements in the selected grains of white mica in eclogites from Vara Inferiore (Voltri Group, Italy)*

sample grain	2			average	st.dev.	6			average	st.dev.
	b	d	e			a	d	e		
Li (ppm)	154.79	150.18	180.08	161.68	16.10	178.65	220.42	231.45	210.17	27.85
B	157.67	187.08	240.57	195.11	42.03	171.47	205.26	135.56	170.76	34.86
P	5.52	7.81	7.85	7.06	1.33	7.41	5.39	6.41	6.40	1.01
Sc	15.32	4.88	5.67	8.62	5.81	7.09	13.27	10.14	10.17	3.09
Ti	2320.89	3065.87	2027.94	2471.57	535.12	2560.34	2195.42	1723.39	2159.72	419.62
V	109.75	74.41	72.48	85.55	20.98	71.28	80.68	45.92	65.96	17.98
Cr	7.68	21.91	30.53	20.04	11.54	6.93	2.62	2.84	4.13	2.43
Co	3.87	10.73	4.89	6.50	3.70	3.01	4.70	2.60	3.44	1.11
Ni	26.09	98.08	73.40	65.86	36.58	17.61	12.72	8.43	12.92	4.59
Zn	46.17	93.24	61.91	67.11	23.96	84.07	67.16	55.77	69.00	14.24
Rb	171.52	203.64	188.03	187.73	16.06	163.88	164.73	154.99	161.20	5.39
Sr	20.72	23.02	33.03	25.59	6.55	23.56	22.82	24.7	23.69	0.95
Y	0.35	0.99	0.02	0.45	0.49	10.60	0.55	0.61	3.92	5.79
Zr	0.28	0.72	0.51	0.50	0.22	0.20	0.129	0.56	0.30	0.23
Nb	1.02	0.77	0.63	0.81	0.20	1.59	0.97	2.11	1.56	0.57
Cs	5.70	9.08	5.48	6.75	2.02	6.91	5.89	5.89	6.23	0.59
Ba	16404.45	35456.02	26694.08	26184.85	9535.99	27279.71	25481.87	21401.67	24721.08	3011.97
La	0.020	0.071	0.022	0.04	0.03	0.024	0.069	0.055	0.05	0.02
Ce	0.072	0.041	0.000	0.04	0.04	0.102	0.043	0.045	0.06	0.03
Eu	0.25	0.37	0.28	0.30	0.06	0.185	0.46	0.22	0.29	0.15
Pb	1.33	2.99	1.59	1.97	0.89	1.31	0.99	1.53	1.28	0.27

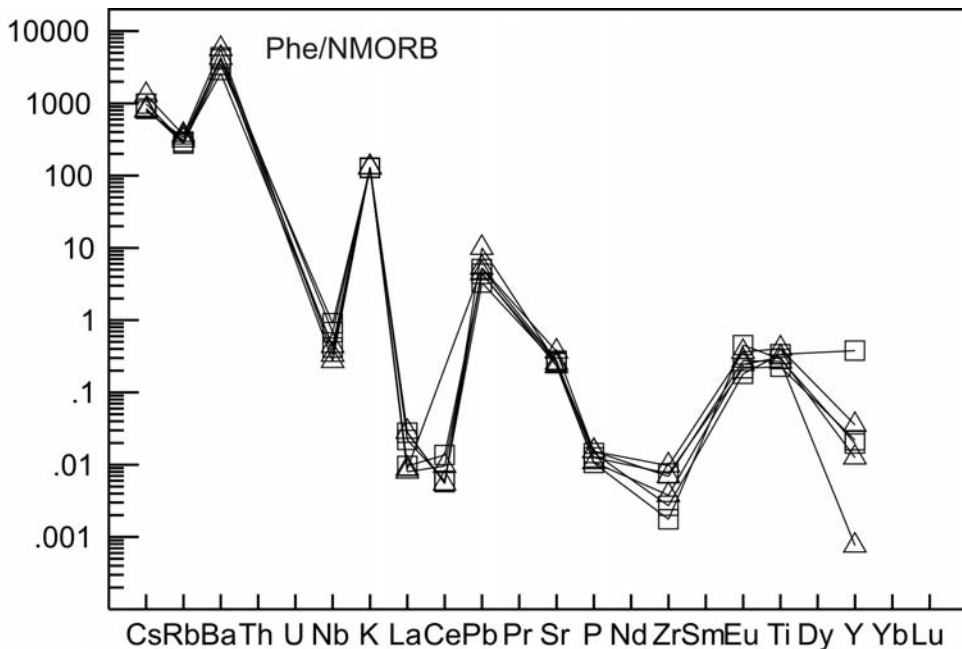


Fig. 3 – Multi-element diagram normalized to N-MORB (Sun and McDonough, 1989) for selected grains of white mica (“phengite”) from samples 2 and 6. Symbols as in Fig. 2.

### DISCUSSION

The eclogites of the Voltri Group still preserve evidence in the bulk as well as in the mineral chemistry of their complex history, starting from ocean-floor metamorphism of the parental Fe-Ti gabbros to eclogite- and subsequent greenschist facies metamorphism. All these stages involved episodes of fluid flow favouring both the growth of hydrous minerals and the formation of aqueous fluid inclusion in the quartz veins and in apatites (Morten *et al.*, 1985; Scambelluri, 1992; Vallis and Scambelluri, 1996). In some occurrences, the fluid flow also favoured metasomatic exchanges between the mafic bodies and the ultramafic country rocks (Liou *et al.* (1998). In particular, metasomatism probably in the vicinity of a spreading center or oceanic fracture zone resulted in local development of a shallow-level chemical alteration (rodingitisation) during serpentinisation of the enclosing Beigua peridotite (Messiga *et al.*, 1983).

The eclogite body of Vara Inferiore does not show any petrographic or chemical evidences

typical of rodingites (*i.e.* enrichment by CaO and depletion in Na<sub>2</sub>O). However, its chemistry seems to record significant metasomatism. All the samples are enriched in sodium (up to Na<sub>2</sub>O = 6.59 wt%) compared with the mean composition for all the eclogites of the Voltri Group reported in literature. This result could be explained by suggesting that bulk chemistry of the eclogite protolith may have suffered post-magmatic alteration processes, including spilitisation (*i.e.* Na-enrichment). According to Zack *et al.* (2002) further evidence for spilitisation is provided by the enrichment in Li and LREE concentrations. The authors also showed that clinopyroxene plays a dominant role for Li budget in eclogites, whereas phengite incorporates <10% of the whole-rock concentration. Unfortunately, no whole-rock and clinopyroxene data on Li are available for the examined eclogites, as well as for other occurrences in the Voltri Group. However, the content of Li determined in both phengites (Table 3) is significantly higher than that reported in literature for samples from Bohemian Massif and Central Alps (Woodland *et al.*, 2002; Zack *et al.*, 2002). Thus, it is possible that even the Li budget of

whole rock may have been influenced by these alteration episodes before subduction.

The eclogites analysed in this study are also characterised by a higher abundance of LILE (Ba and Cs over K and Rb) compared with other eclogites of the area (Fig. 1a). However, the content of these elements varies across the body and the phengite-free sample is slightly depleted compared with samples 2 and 6, which contain phengite. According to Becker *et al.* (2000) the high content of K, Ba, Rb and Cs in low-temperature eclogites supports the evidence for localised influx of fluid. Moreover, the enrichment in Ba and Cs over K and Rb is a characteristic feature of this type of metasomatic fluid, derived from the dehydration of surrounding metasediments under subduction zone metamorphic conditions (Sorensen *et al.*, 1997). The phengite-bearing eclogite 6, which is close to the contact with serpentinites, contains more Ba and other LILE than the two other samples. Thus, the possibility that local fluid flows could have favoured the inward migration in the studied eclogites of LILE elements from the surrounding rocks must be considered.

The microstructural study of the examined samples suggests that the crystallisation of white mica did not occur at the climax of the eclogitic metamorphic stage. Moreover, the Si content of white mica varies from 3.17 to 3.30 atoms p.f.u. and is typical of phengites crystallised at rather low-pressure and moderate temperature (Salot and Velde, 1982). The eclogites of the Voltri Group display the *Alm-rich garnet + Fe<sup>3+</sup>-omphacite + rutile* assemblage. Hence, the growth of a secondary hydrous mineral such as white mica requires the addition of a sufficient amount of K to the eclogite mineral assemblage and an aqueous fluid-rich environment. In addition, the high content of Ba, coupled with appreciable abundance of other LILE (Cs, Rb) and light-elements (Li, B) determined in the examined phengites implies that all these elements were available for this neoblastic phase. The bulk rock Ba abundance, as well as that of Cs and Rb, is significantly lower than the content determined in phengites but it is higher than that of the phengite-free sample and of the other eclogites of this area. Therefore, it is reasonable to infer that in these rocks mica served as sink for all these elements

while its growth proceeded. Moreover, it is worth noting that both the examined phengites display grains showing different BaO content as well as patchy trace elements distribution. These results imply that the phengite chemistry was controlled by irregular episodes of fluid infiltration that occurred during the incipient stages of eclogite retrogression. It is likely that these fluids were also responsible for deposition in the eclogite body of Vara of sulphide minerals (pyrrhotine) and contributed to change the oxygen fugacity of the chemical system (Grapes, 1993; Jiang *et al.*, 1996). Such a changing physical and chemical environment probably gave rise to the broad compositional scatter of the white mica and prevented the achievement of complete homogenisation.

#### CONCLUSIONS

On the basis of the results presented and discussed above, it is possible to draw the following conclusions:

1. The bulk chemistry of the eclogite body of Vara Inferiore shows evidence for inward migration of fluid-mobile elements such as LILE (Ba and Cs over K and Rb).

2. The white mica, actually a “*phengite*”, is not an ubiquitous mineral throughout the eclogite body and, in any case, its abundance is limited to few grains per each thin sections. The high barium content detected in this mineral by EMP is confirmed by LA-ICP-MS measurements on selected grains of the same mount. Both examined samples reveal to be an important host also for Cs, Rb and light elements such as Li and B. However, the distribution of barium, as well as of other trace elements, is not homogeneous.

3. The phengite plays an important role in storing LILE, whose enrichment could be related to episodes of fluid-rock interaction probably occurred during the first stages of eclogite retrogression.

4. The inhomogeneous composition of white mica emphasises the existence, at least at a very local scale, of chemical disequilibrium.

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§ Dedicated to the memory of Luciano Cortesogno and Lauro Morten.

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