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Autor: Eisele, Jürgen / Geiger, Sebastian / Rahn, Meinert

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Chemical characterization of metabasites from the Turtmann valley (Valais, Switzerland): implications for their protoliths and geotectonic origin

by *Jürgen Eisele*[1], *Sebastian Geiger*[1] and *Meinert Rahn*[2,3]

Abstract

Within the polymetamorphic basement of the Penninic Siviez-Mischabel nappe, metabasites are widespread occurring as small-scale lenses and layers that locally preserve remnants of a former metamorphic HP event. Metabasites of the eclogite localities (Adlerflüe, Minugrat) in the upper Turtmann valley were investigated by XRF and INAA means. Sampling rocks of different grade of metamorphic overprint enabled to estimate element mobility during amphibolite and Alpine greenschist facies overprint.

Major and trace element contents are consistent with a primary tholeiitic basalt composition that originated from a subducting slab. Rising magma underwent fractional crystallization and/or assimilation of crustal material before and during extrusion within a narrow back arc basin. Despite repeated recrystallization, REE elements behaved immobile in the cores of the lenses and layers independent of metamorphic grade, but were enriched at their periphery due to restricted mobility along the compositional gradient between metabasites and host rock. Metamorphic compositional changes in K, Cr, and P can be explained by mineral breakdown and neoformation during retrogression.

The proposed magmatic model fits well into the situation of the European crust during the Cambro-Ordovician. Therefore, an early Paleozoic age for the metabasites is likely. The proposed model also favours the metabasites as a potential element source for the nearby Co–Ni ore deposits in the Siviez-Mischabel nappe.

Keywords: eclogites, metabasites, REE mobility, pre-Variscan evolution, Siviez-Mischabel nappe, Penninic basement, Valais.

1. Introduction

Eclogites are often assumed to have undergone restricted amount of metasomatism, which makes them interesting objects for geochemical investigations. Within the Alps, eclogites are found in various tectonic settings, but many eclogites occur within thick sequences of paragneisses, e.g. in the Adula nappe (HEINRICH, 1986), in the Silvretta nappe (MAGGETTI and GALETTI, 1988), the Gotthard massif (GEBAUER et al., 1988), and in the Siviez-Mischabel nappe (BEARTH, 1980; THÉLIN et al., 1990; RAHN, 1991). All those eclogites are located within old crystalline basements, that show evidence for polycyclic metamorphic evolution. For this reason, a pre-Alpine age for the HP metamorphic event in these tectonic units was often proposed, and partly confirmed by isotopic investigations. For the eclogites of the Penninic Siviez-Mischabel nappe, isotopic data for the HP event are still missing.

In 1989, ZINGG presented a study on the metabasic rocks of the Siviez-Mischabel nappe, and provided a geochemical and isotopic data set in order to unravel the origin and evolution of the crystalline basement. Additional compositional data were presented by THÉLIN et al. (1990). Why then to present another study on the same problem? We want to focus on four reasons: (1) The data of ZINGG (1989) do only provide a restricted

[1] Geologisches Institut, Albert-Ludwigs-Universität Freiburg, Albertstrasse 23b, D-79104 Freiburg, Germany.
[2] Institut für Mineralogie, Petrologie und Geochemie, Albert-Ludwigs-Universität Freiburg, Albertstrasse 23b, D-79104 Freiburg, Germany (corresponding author). E-mail: rahn@pop3.uni-freiburg.de.
[3] Present address: Department of Geology and Geophysics, Yale University, P.O. Box 208109, New Haven, CT 06520-8109, U.S.A.

amount of information about mineralogy and metamorphic grade of the rocks. Thus, geochemical data cannot be compared to or explained by the existing mineralogy. (2) The application of several classification diagrams does not account for the possibility that some of the elements addressed behaved mobile during polycyclic metamorphic overprint. In particular, THÉLIN et al. (1990) mentioned the fact that their data show no consistent explanation of origin and tectonic context for the protoliths of the metabasites of the Siviez-Mischabel nappe, and thus, every interpretation tends to be selective in the application of the diagrams. (3) With the help of RAHN (1989, 1991), we are able to include compositional data on mineral phases into our investigations. This allows to link mineralogy and bulk rock chemistry. (4) In particular for REE, recent studies have addressed the problem of metamorphic alteration of REE pattern (e.g. PAQUETTE et al., 1989; SHATSKY et al., 1990; TRIBUZIO et al., 1994, 1996), proposing different mechanisms on how REE can behave mobile under the influence of changing P-T conditions. We want to express, however, that this study was markedly stimulated by the preceeding work of ZINGG (1989) and THÉLIN et al. (1990), and that our contribution to the topic should be regarded as a supplement to their contributions.

With the help of a data set on 14 metabasic samples we want to present evidence for the origin, emplacement and metasomatic changes within the metabasic rocks situated in the Siviez-Mischabel nappe crystalline basement of the Turtmann valley. It is important to note that the given interpretations are based on fundamental assumptions. First, the determination of the protolith for the Siviez Mischabel eclogites assumes that no or no relevant chemical changes took place between emplacement of the rocks and the recrystallization under eclogite facies conditions. Second, the assumption is made that the lenses and layers the metabasic rocks form today within their host rock are a primary magmatic feature rather than the result of their structural development. The inferred results will be used to discuss the age of the eclogites in comparison with other regional data.

2. Geological setting

The Penninic Siviez-Mischabel nappe (SMN) is the largest part of the former Bernhard nappe (LUGEON and ARGAND, 1905), that was divided into four smaller, but tectonically distinct units (BEARTH, 1963; ESCHER, 1988). From these four nappes, only the Pontis nappe and the SMN bear crystalline cores of polymetamorphic grade. The SMN crystalline core is dominated by paragneisses with minor amphibolite layers and lenses, and Permian intrusion bodies such as the gneiss of Randa (THÉLIN, 1983; BUSSY et al., 1996a). The polymetamorphic core was subdivided into a lower Ergischhorn series, mainly consisting of monotonous paragneisses and irregularly distributed amphibolite lenses, and an upperlying Barneuza series with a metabasite-dominated basis (called "banded amphibolites") and top (called "banded complex") (THÉLIN et al., 1990). These two layers that show strong regional variation in thickness are intercalated by a series of schists and minor amphibolite lenses, both with characteristic albite blasts (SARTORI and THÉLIN, 1987). Albitization and growth of the blasts within the augen schists are assumed to be an Alpine feature.

Above the polymetamorphic basement, monometamorphic Permo-Carboniferous and Permo-Triassic sediments are followed by a nearly complete series of Mesozoic sediments, ranging in age from middle Triassic to Eocene, that in part were dated by fossil remnants which survived the Alpine greenschist facies overprint. In the eastern part of the SMN, the Barrhorn Series forms a huge Mesozoic cover (SARTORI, 1990), that in the upper Turtmann valley thins drastically from E to W, and is replaced by the more condensed Toûno series towards W (MARTHALER, 1984). Most of the Mesozoic sediment cover of the SMN has been removed during Alpine orogeny, and is assumed to presently be located within the Penninic klippen structure of the Préalpes (SARTORI, 1990).

The present shape of the nappe, a northwards rising recumbent fold, is the result of the Alpine structural and metamorphic evolution. The core of the nappe is formed by the polymetamorphic crystalline basement and the monometamorphic intrusion bodies, surrounded by the remaining sediments that are mainly found in their upright position of the normal limb. At the upper Turtmann valley, the crystalline core (Ergischhorn and Barneuza series) is exposed, together with some small gabbroic intrusion bodies of presumably Permian age (SARTORI et al., 1989). The southern end of the valley provides outcrops (partly covered by glaciation) of the thinning Barrhorn Series that is overlain by a strongly thinned Mont Fort nappe (the uppermost of the four nappes of the former Bernhard nappe) and the South-Penninic ophiolite-bearing Tsaté nappe. The summits of the mountains in the SW are finally composed of leuco-gneisses of the Austroalpine Dent Blanche nappe (Fig. 1).

Several studies on the metabasites of the SMN were undertaken so far. The eclogitic remnants

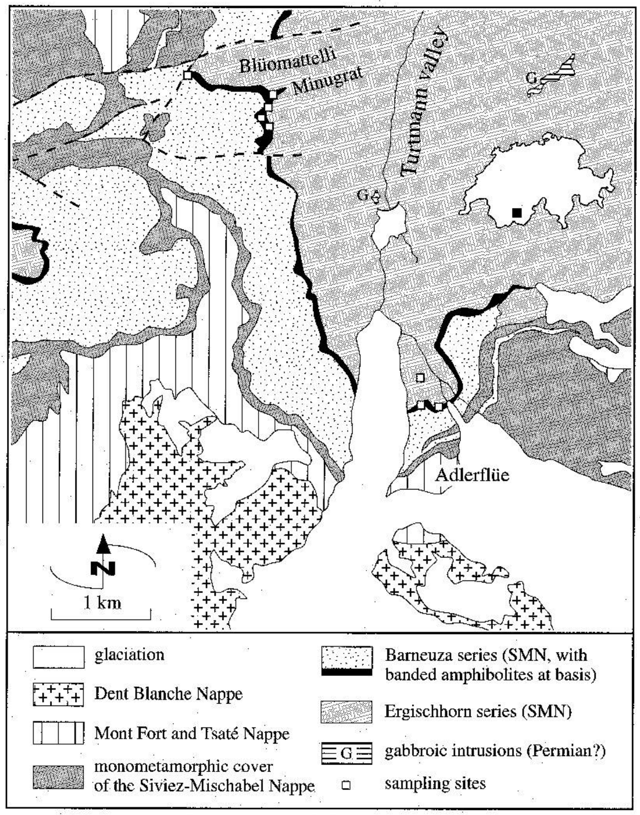

Fig. 1 Tectonic sketch of the upper Turtmann valley (after SARTORI, 1990) with indicated sample localities.

were subject of two contributions by THÉLIN et al. (1990) and RAHN (1991), and eclogitic conditions of 550–650 °C and minimum pressures of 13 kbar were calculated. By a geochemical approach, ZINGG (1989) and THÉLIN et al. (1990) derived a tholeiitic character for the basaltic protolith of the eclogites and amphibolites. Several geologic arguments favour a pre-Alpine age of the eclogitization (THÉLIN et al., 1990; RAHN, 1989), and ZINGG (1989) assumed a Proterozoic age for the polymetamorphic gneisses and most of the banded amphibolites, and a lower Paleozoic age for the emplacement of minor ultrabasic intrusions. Age ranges were assumed to be concordant to ages from basalts of the Berisal complex (STILLE and TATSUMOTO, 1985). For the different metamorphic events, THÉLIN et al. (1990) proposed a Caledonian HP event, followed by Variscan amphibolite facies metamorphism that can be related to a metamorphic event of similar grade and age within the crystalline basement of the Pontis nappe (THÉLIN et al., 1993). Final Alpine greenschist facies overprint was presumably subsequent to a faint second HP event as indicated by the rare presence of crossite relics within the metabasites (RAHN, 1991) and the widespread occurrence of 3T white micas (FREY et al., 1983).

For this study sampling was restricted to the banded amphibolites of the Barneuza unit, and to the two eclogite bearing localities around Minugrat (Kaltenberg, Blüomattelli) and Adlerflüe (Fig. 1). As indicated above, the amphibolites of the overlying albite augen schists are strongly affected by albitization, and the metabasites of the upper banded complex are often thoroughly overprinted. Thus, the amphibolites of the lower banded complex suggest to have undergone the least metamorphic and potentially smallest geochemical overprint. Twelve of the samples are eclogite/amphibolite sample pairs collected within a few metres of distance. Sample JSE-11 is a grt-amph-czo-fels found as a boulder in the moraine gravel below the Adlerflüe. Sample JSE-14 turned out to be a grt and chl bearing quartzite, and was excluded from this study.

3. Methods

14 Samples including 6 pairs of (retro-)eclogite/amphibolite hand specimen were milled in an agate mill for XRF bulk rock major and trace element determinations. For the major element analysis, 1 g of rock powder was mixed with 4 g of a $Li_2B_4O_7/LiBO_2$ mixture and melted at 1100 °C for 8 minutes. For the trace element analysis, 4 g of rock powder were mixed with 1g of wax powder. Measuring conditions on a Philips PW 1450/20 in Freiburg were 40 kV/60 mA and 60 kV/45 mA, respectively.

The rare-earth elements (REE) and most trace elements were analysed by instrumental neutron activation analysis (INAA) at the Radiation Center of the Oregon State University, Corvallis, U.S.A. Pulverized eclogite samples of about 0,5 g were irradiated for 5.717 hours at 10^6 W in a Tigra Mark II nuclear research reactor used as the neutron source. Four multichannel analysers were used with Ge–Li and HPGE detectors, and the Maestro program by EG&G Ortec, while long counts (20.000 sec), lep counts (4.000 sec) and intermediate counts (4.000 sec) were carried out. The data of the gamma ray spectra was reduced with help of the Geligam program, developed by EG&G Ortec. Basalts (SRM688 and CRB IV-1), Coal Fly Ash (SRM1633A), Obsidian (SRM278), Meteorite (Allende) and Granite (SPGa1) were used as standards and monitors for this analysis.

Measured concentrations are given in table 1, together with an estimated average analysis error (expressed as relative percentage). From those elements that have been determined with both methods, the INAA data have been preferred, as generally indicated analysis errors are distinctly

Tab. 1 Compositional data for the Turtmann valley metabasites, measured by XRF and INAA. The column to the right indicates average relative analytical errors (given in %). Sample localities are indicated by x- and y-values from the Swiss map coordinate system.

Sample	JSE-1	JSE-2	JSE-3	JSE-4	JSE-5	JSE-6	JSE-7	JSE-8	JSE-9	JSE-10	JSE-11	JSE-12	JSE-13	JSE-15	analytical error in %
locality	Minugrat	Minugrat	Minugrat	Minugrat	Minugrat	Minugrat	Minugrat	Minugrat	Blüomattelli	Blüomattelli	Adlerflüe	Adlerflüe	Adlerflüe	Adlerflüe	
lithology	retro-ecl.	GS-amph.	retro-ecl.	GS-amph.	eclogite	GS-amph.	eclogite	GS-amph.	eclogite	GS-amph.	Czo-amph.	eclogite	GS-amph.	GS-amph.	
x coordinate	618.340	618.340	618.460	618.460	618.440	618.440	618.365	618.365	617.600	617.600	620.000	620.100	620.100	620.190	
y coordinate	86.130	86.130	86.280	86.280	85.985	85.985	86.080	86.080	86.515	86.515	111.700	111.275	111.275	111.250	
major elements (XRF, in wt%)															
SiO_2	48.67	59.05	55.23	52.19	53.28	51.85	50.52	53.36	51.66	50.60	55.49	50.65	49.48	47.82	1%
TiO_2	2.68	2.32	1.61	1.44	1.40	1.03	1.40	1.29	1.25	1.26	1.64	1.24	1.73	1.34	3%
Al_2O_3	16.31	12.53	16.41	15.76	17.20	16.79	16.91	16.13	16.59	16.48	15.14	16.10	18.52	14.84	1%
Fe_2O_3	13.96	11.42	10.36	10.13	9.58	10.00	9.95	9.17	9.54	10.14	10.32	8.72	12.52	11.46	1%
MnO	0.22	0.20	0.16	0.16	0.19	0.18	0.16	0.16	0.16	0.16	0.17	0.16	0.25	0.18	3%
MgO	4.85	3.70	5.10	6.26	5.85	7.18	7.50	5.05	7.02	6.79	4.82	8.07	4.42	8.71	2%
CaO	9.52	7.03	7.46	8.26	8.56	6.06	9.62	7.79	9.81	8.12	12.60	11.53	7.11	8.94	1%
Na_2O	4.25	3.49	3.69	4.31	4.29	4.16	3.55	3.97	3.16	2.39	0.38	4.12	4.85	3.13	2%
K_2O	0.27	0.33	0.67	0.91	0.39	1.41	0.71	1.31	0.89	2.07	0.04	0.50	0.76	0.91	1%
P_2O_5	0.47	0.25	0.19	0.15	0.19	0.03	0.14	0.15	0.12	0.12	0.23	0.14	0.09	0.08	3%
Σ	101.20	100.32	100.88	99.57	100.93	98.69	100.46	98.38	100.20	98.13	100.83	101.23	99.73	97.41	
trace elements (XRF, in ppm)															
V	349	278	272	230	199	188	207	206	226	233	213	195	176	217	5%
Y	56	51	43	39	34	21	31	36	23	26	43	19	59	16	15%
Zr	201	215	202	151	141	115	99	146	90	119	147	79	391	58	6%
Nb	11	10	7	7	8	7	5	8	5	6	7	6	13	6	50%
Pb	9	8	9	9	8	8	6	17	13	8	10	12	10	8	50%
trace elements (INAA, in ppm)															
Sc	35.30	30.00	36.80	30.90	28.20	30.90	33.80	30.50	32.20	32.30	31.00	29.90	29.10	36.60	3%
Cr	141.00	18.60	325.00	135.00	208.00	254.00	270.00	14.50	280.00	138.00	158.00	536.00	60.90	466.00	10%
Co	36.10	22.20	38.90	33.10	30.70	40.40	39.90	27.20	32.10	34.30	30.80	41.60	25.40	41.60	5%
Ni	60.00	< 110	85.00	88.00	< 96	129.00	81.00	< 100	38.00	42.00	47.00	45.00	42.00	106.00	12%
Rb	9.00	5.00	39.80	25.80	15.20	49.00	25.50	83.00	38.30	71.00	2.00	15.00	11.50	31.90	10%
Sr	242.00	92.00	226.00	201.00	206.00	97.00	110.00	257.00	322.00	230.00	815.00	236.00	131.00	223.00	12%
Cs	0.48	0.48	1.84	1.17	0.63	3.64	1.72	16.60	1.68	4.05	< 0.63	0.51	0.70	1.76	5%
Ba	389.00	176.00	300.00	385.00	464.00	513.00	303.00	677.00	318.00	446.00	230.00	308.00	476.00	310.00	10%
La	11.90	11.10	4.00	11.90	14.90	11.00	6.20	18.50	8.00	8.20	12.00	7.40	19.90	5.20	3%
Ce	32.90	33.90	7.70	34.70	35.30	32.90	12.20	50.60	15.30	16.90	40.20	20.50	49.60	9.60	7%
Nd	15.80	14.50	7.00	20.50	19.30	15.70	9.80	23.00	9.80	11.60	18.40	9.80	24.00	6.80	12%
Sm	5.53	4.69	2.89	4.61	4.66	4.52	3.17	7.11	3.13	3.30	5.18	2.98	6.65	3.06	5%
Eu	2.01	1.53	1.21	1.46	1.64	1.53	1.27	2.75	1.25	1.33	2.05	1.28	2.07	1.27	5%
Tb	1.35	1.13	0.76	0.95	0.89	0.83	0.80	1.47	0.61	0.76	1.19	0.57	1.45	0.79	5%
Yb	4.55	4.88	3.64	3.85	2.97	3.06	3.21	5.28	2.22	2.68	4.04	1.73	4.93	3.14	5%
Lu	0.52	0.71	0.51	0.57	0.44	0.54	0.53	0.65	0.35	0.34	0.58	0.22	0.83	0.47	5%
Hf	5.02	6.85	3.26	4.12	3.84	3.88	3.03	7.19	2.31	4.44	5.35	2.73	10.60	2.96	5%
Ta	0.53	0.62	0.21	0.45	0.44	0.35	0.18	0.81	0.29	0.35	0.43	0.34	0.90	0.19	5%
Th	1.82	2.69	0.39	2.30	1.74	2.06	0.91	2.00	1.03	1.04	1.83	0.54	4.52	0.63	5%
U	2.65	2.24	< 8.4	< 12.00	3.09	3.09	< 9.60	2.18	< 8.10	< 9.00	1.45	< 7.20	3.04	< 9.30	7%

lower compared to XRF. All Fe is given as Fe_2O_3, and therefore the sums tend to be slightly above 100%.

4. Results

4.1. SAMPLE CHARACTERIZATION

In outcrop scale, the amphibolite layers are characterized by varying thickness caused by the strong boudinage, and by various thin quartz and white mica veins (sometimes kyanite bearing), that reflect the layer boundaries. Eclogite and amphibolite facies parageneses are only found in the cores of the lenses, often restricted to volumes markedly less than 1 m^3. Rims and margins of the layers and lenses are dominated by greenschist facies mineral parageneses. Thus, the term "amphibolite" is used here for rocks that actually underwent a nearly complete greenschist facies recrystallization.

With the exception of JSE-11, all samples are relatively fine-grained. In order to compare the stage of overprint with the chemical composition, a careful mineralogical characterization of the samples by thin section study was executed (Tab. 2). Primary eclogite facies minerals include omphacite, garnet, rutile, quartz, rare kyanite, and an ore phase (ilmenite or magnetite). In some samples, white micas lie parallel to the elongation of the omphacite grains, and therefore are thought to be of primary eclogitic age.

The amphibolite facies overprint is rarely displayed in the field. It is characterized by poikiloblastic growth of large amphiboles (pargasites according to THÉLIN et al., 1990), that replace the omphacite and cores of the garnet matrix, and sometimes the growth of large poikiloblastic white mica (RAHN, 1989; THÉLIN et al., 1990). The only real amphibolite facies rock specimen of this study is JSE-11, showing large amphibole crystals that coexist with garnet and clinozoisite. Minor remnants of omphacite grains are rimmed by amphibole.

Retrogression starts by a fine-grained symplectite of bluegreen amphibole and plagioclase, and is, at least locally, exhibited in all eclogites, occurring either as thin symplectitic rims along omphacite grain boundaries or as irregularly distributed patches of omphacite replacement. All "amphibolite" samples display a greenschist facies mineral paragenesis comprising chlorite, green amphibole, titanite, and albite. The former symplectite is still obvious by the fine-grained texture of the matrix, but the bluegreen amphibole is of magnesio-hornblende to actinolite composition, and the former plagioclase is totally replaced by near end-member albite (RAHN, 1989). From the former eclogitic paragenesis only rare relics of garnet or rutile are sometimes found.

4.2. ELEMENT MOBILITY DURING METAMORPHISM

Before using the compositional data for the determination of the protolith, we have to confirm that alteration of the amphibolites did not destroy the original compositional finger prints that would allow to determine the character and origin of the basites. For this purpose, the data of the six sample pairs were used to compare eclogite and amphibolite compositions within these pairs. Ratios amphibolite versus (retro-) eclogite of all elements are presented in figure 2. Most major elements show little or no regular variation between eclogite and neighbouring amphibolite. Systemat-

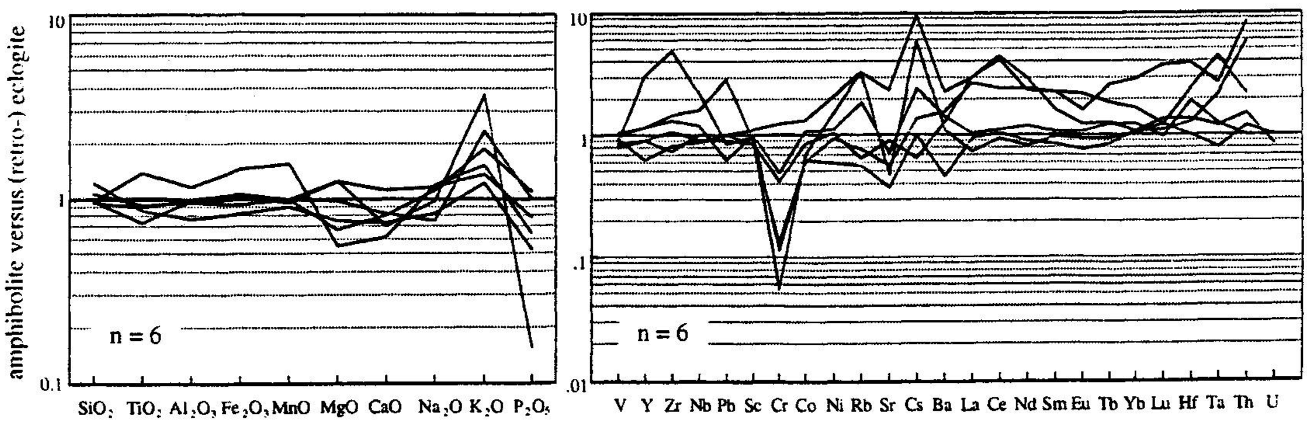

Fig. 2 Estimation of chemical changes during retrograde metamorphism by direct comparison of major (left) and trace element contents (right) within the six amphibolite/(retro-) eclogite sample pairs.

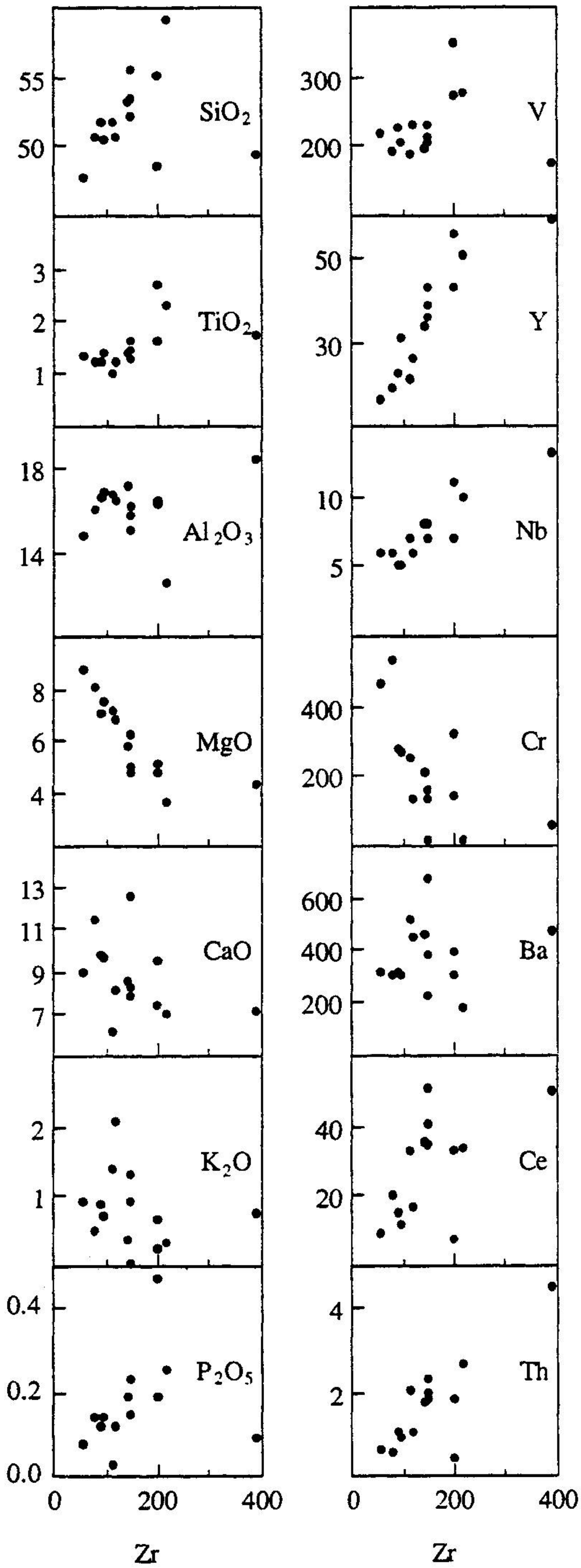

Fig. 3 Comparison of several major (left) and trace elements (right) versus Zr as an immobile reference during metamorphic overprint. In most diagrams, Zr of sample JSE-13 (391 ppm) plots outside the indicated trends, and has to be considered with caution.

ic enrichment, however, is shown by K_2O, slight depletion is indicated for P_2O_5. For the trace elements, enrichments and depletions are stronger, but often not regular in one direction. A strong depletion is indicated for Cr, which can be explained by the release of this element during omphacite breakdown. Omphacite analyses (RAHN, 1989) indicate Cr contents between 0 and 0.2, rarely up to 1 wt%. If we estimate an average content of 0.1 wt%, and consider the fact that omphacite holds 50 or more vol.% within a fresh eclogite, the mineral data fit well with the maximum Cr content (> 500 ppm) from the freshest eclogite sample JSE-12, and suggest that Cr is largely restricted to that phase, and is lost during omphacite breakdown.

Strong enrichment (up to a factor of 10) is indicated for Cs and Th. Zr and Y, that are commonly considered to be very immobile elements, display, with one exception, a very restricted increase or decrease during metamorphism, and thus, Zr was chosen as a reference element in order to test the mobility of all other elements (Fig. 3, cf. PFEIFER et al., 1990).

Good correlations versus Zr are indicated for SiO_2 and MgO, whereas CaO, K_2O, and Na_2O (not shown in Fig. 3) have no correlation at all. For P_2O_5 and TiO_2 correlations are of moderate grade, indicating some restricted mobility. Among the trace elements, good correlations are found for Y, Nb, and Th, correlations of moderate quality for most REE and V, but no correlation for Cr and Ba (Fig. 3). For this reason, discrimination diagrams including Cr, Ba, and V have been avoided or only used with caution.

In three sample pairs, REE are independent of metamorphic grade (Fig. 4), concordant to the suggestion that REE generally behave immobile during metamorphism (e.g. BERNARD-GRIFFITH et al., 1991; PEARCE et al., 1984). However, for the three other pairs, restricted enrichment of up to five times is obvious (JSE-3/4, JSE-7/8, and JSE-12/13), and this enrichment is in part restricted to LREE (JSE-4) suggesting higher rates of mobility for LREE than for HREE. An ongoing debate exists whether the LREE could behave mobile during specific conditions (e.g. SHATSKY et al., 1990; TRIBUZIO et al., 1994, 1996). The key question with respect to REE mobility concerns the different REE carriers and their stability during changing P-T conditions. Grt and cpx (BERNARD-GRIFFITHS et al., 1991) or accessory phases like apatite, titanite or clinozoisite (TRIBUZIO et al., 1994, 1996) were proposed as the main carrier of REE. With the exception of apatite, none of these mineral phases is stable during the whole metamorphic evolution, and also for apatite as the only carrier of P_2O_5, partial dissolution is indicated (Fig. 2). Therefore, a nearly complete redistribution of the REE during metamorphism has to be assumed. A localization of REE within intergranular space as suggested by SHATSKY et al. (1990) would also imply a redistribution of the elements during multistage recrystallization.

If the breakdown of either grt or cpx as the major mineral phases would lead to the loss of the released REE, we would expect to see the pattern to

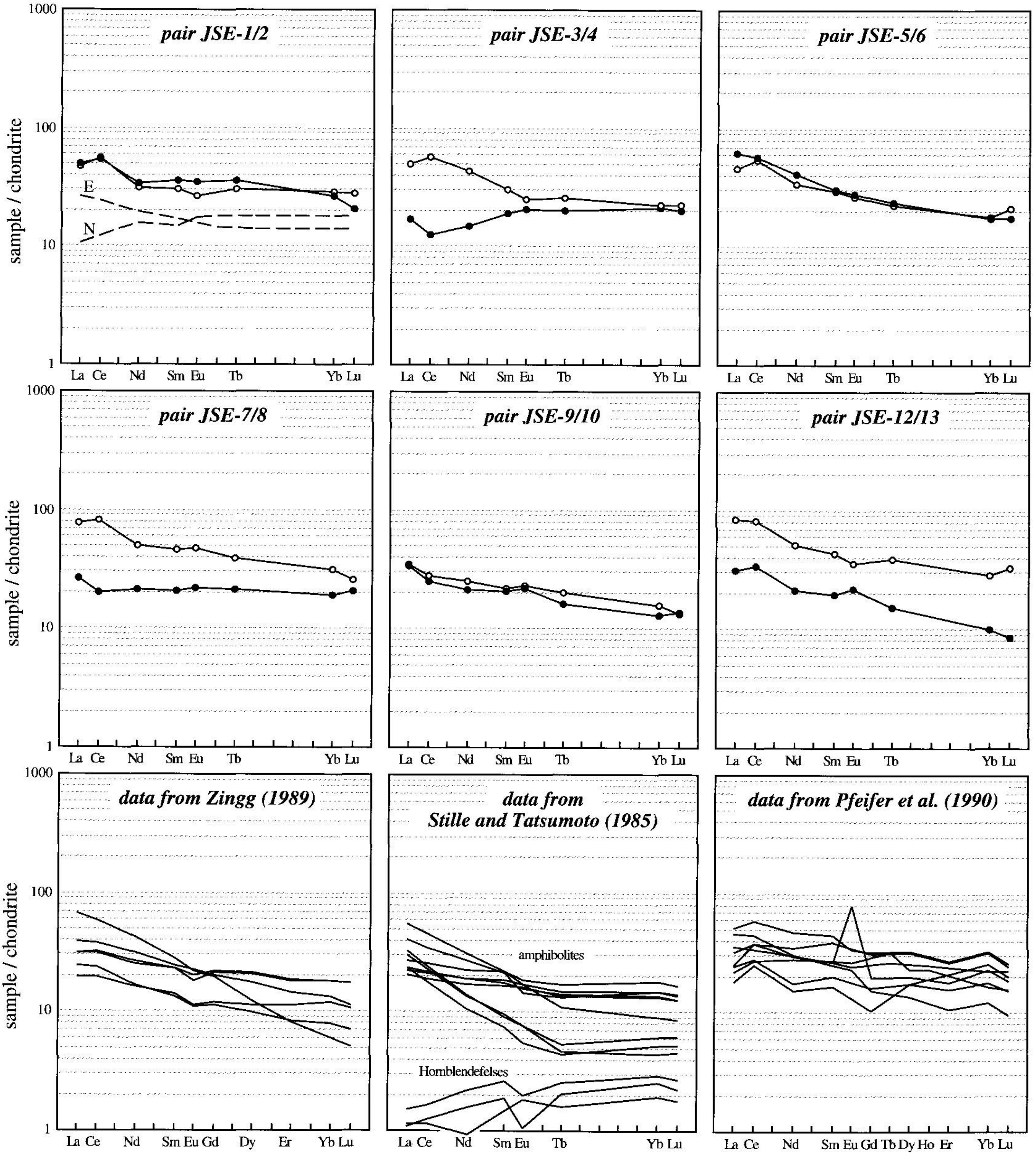

Fig. 4 Chondrite normalized REE contents of the six sample pairs of the banded amphibolites, and comparison with data from SMN amphibolites (ZINGG, 1989), metabasites of the Berisal complex (STILLE and TATSUMOTO, 1985), and metabasites of the Mesozoic Zermatt-Saas ophiolites (PFEIFER et al., 1990). Samples are chondrite normalized after SUN et al. (1979). In the upper left diagram, reference spectra for N- and E-MORB (SUN and MCDONOUGH, 1989) are added to the data of sample pair JSE-1/2. For the six sample pairs, (retro-) eclogites are indicated with filled dots, amphibolites plotted with open circles.

Tab. 2 Mineral content of the Turtmann valley metabasites, as determined by thin section investigations. The observed minerals are divided into three metamorphic facies groups. The division, however, is artificial rather than representative for the indicated metamorphic facies, as most symplectites, formed by either bluegreen amphiboles and plagioclase or green amphiboles and albite, have often strongly been recrystallized during Alpine greenschist facies. The term "others" mainly includes accessory phases such as apatite and zircon.

Sample JSE-	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
eclogitic paragenesis															
omphacite	3				20		35		30		5	50			
garnet	15		15		20		25		30		25	25	10	20	
rutile	3		2	1	3	1	3	1	1	2	3	3			1
phengite	3				8		2		5			3			
quartz	2	10		5	8	5	1	3	5	10	15			20	5
kyanite												2			
ore phase	3	5					1	1	1		1		2		
retrograde / amphibolite facies paragenesis															
pargasite											20				
bluegreen amphibole	35	45	50	45	20	40	20	40	10	30	5	10	35	1	40
plagioclase/albite	20	30	15	32	15	40	10	35	8	30		5	40	42	30
clinozoisite/epidote	2	5	10	5	5	5	3	12	8	15	25		5	10	10
titanite	1	1		3		3		2		1		1			5
sericite		1	2	2		1		5		5			3		6
greenschist facies overprint															
green amphibole	10														
chlorite			3	5		1		1	1	5			3	5	
biotite													1	1	1
carbonate						2									2
others	3	3	3	2	1	2			1	2	1	1	1	1	

be depleted in the corresponding LREE (breakdown of cpx) or HREE (breakdown of grt, BERNARD-GRIFFITHS et al., 1991). Such a hypothesis could be tested e.g. by sample pair JSE-12/13 (Fig. 4), where the amphibolite still bears a considerable amount of relic garnet, but omphacite was lost completely (Tab. 2). However, the pattern of JSE-13 is not depleted in HREE, but shows enrichment of all REE. We therefore conclude that REE elements became released during metamorphic recrystallization and breakdown reactions, but were not depleted at this stage. Due to the lack of single mineral REE data, the mineral reactions and the timing of REE redistribution are not yet revealed.

The pronounced enrichment of LREE found for some of the amphibolites can be assumed to be the result of an obvious REE gradient between metabasites and the surrounding host rocks (ZINGG, 1989): LREE contents of the surrounding paragneisses are in part more than five times higher than for the metabasites. Thus, some amphibolites show an intermediate content between surrounding metasediments and (retro-)eclogites, that is the result of REE migration gradient across the lithological boundary between metabasites and surrounding paragneisses. It is interesting to note that mainly the peripheral amphibolites that underwent the strongest metamorphic overprint, also show the strongest REE enrichment (Fig. 4, Tab. 2).

4.3. CHEMICAL CHARACTERIZATION OF THE FORMER PROTOLITH

Various discrimination systems have been used to characterize the protolith; diagrams based on elements with visible strong mobility have been avoided for this purpose. The chemical characterization of the major elements of the samples points to basalts and basaltic andesites as precursors with 48 to 59 wt% SiO_2 and 0.3 to 2.0 wt% K_2O, except for a small number of samples, after the classification scheme for island arc basaltic rocks (IAB, given in BVSP, 1981). A P_2O_5 versus Zr distribution implies a tholeiitic character (Fig. 5a), and the marked enrichment of Zr with respect to Y indicate a primary process of Zr enrichment from a MORB composition for the Turtmann valley metabasites that might be related to the crust that was passed during ascension of the tholeiitic magma (Fig. 5b). A trend of decreasing Mg number with increasing SiO_2 content is obvious in figure 5c. This feature, however, can account for different processes before or during magma emplacement (see below). Figure 5d reveals a shift of our samples from typical back arc basin (BAB) composition towards average continental crust. In all diagrams of figure 5, trends are independent from metamorphic grade and therefore assumed to represent primary features.

A Zr–Y–TiO_2 ternary system shows a transitional character between N-MORB and within plate basalt (WPB, Fig. 6a). Because TiO_2 is considered to behave slightly mobile (Fig. 3), a shift of the data in a vertical direction is possible, but crucial for the interpretation of the data. In a Zr–Y–Nb ternary plot (Fig. 6b) a transitional character between N-MORB and volcanic arc basalt is displayed, and all three elements of this plot show no mobility (Fig. 3).

CIPW calculations used for the characterization of the protolith yield a calculated mineral assemblage of plg-cpx ± opx ± ol ± qtz ± kfs. The majority of them yield olivine, only a few of them are quartz normative. The general mineral composition is in agreement to their geochemical classification (Fig. 5c), and underlines the rather restricted amount of chemical alteration during polymetamorphic evolution. In correspondence to typical back arc basalts, our metabasites are dominated by an intermediate plagioclase according to the CIPW calculations. Different from typical back arc basalts (BAB), however, some show high amounts of orthoclase (or) which can be explained by the late, i.e. metamorphic K enrichment (Fig. 2). The high amount of qtz-normative sample is uncommon, but in accordance to the trend in figure 5c: SiO_2 increases and Mg decreases, e.g. due to incorporation of crustal or crustal-like material during ascent and emplacement. Assimilation of material of the surrounding host rock would lead to the same feature.

A multivariation diagram of the incompatible elements normalized to N-MORB (Fig. 7) shows two- and threefold enrichment of the more compatible elements P to Lu, where enrichment tends to be parallel to N-MORB. Among these, Zr and Hf show higher enrichment of up to five times. The

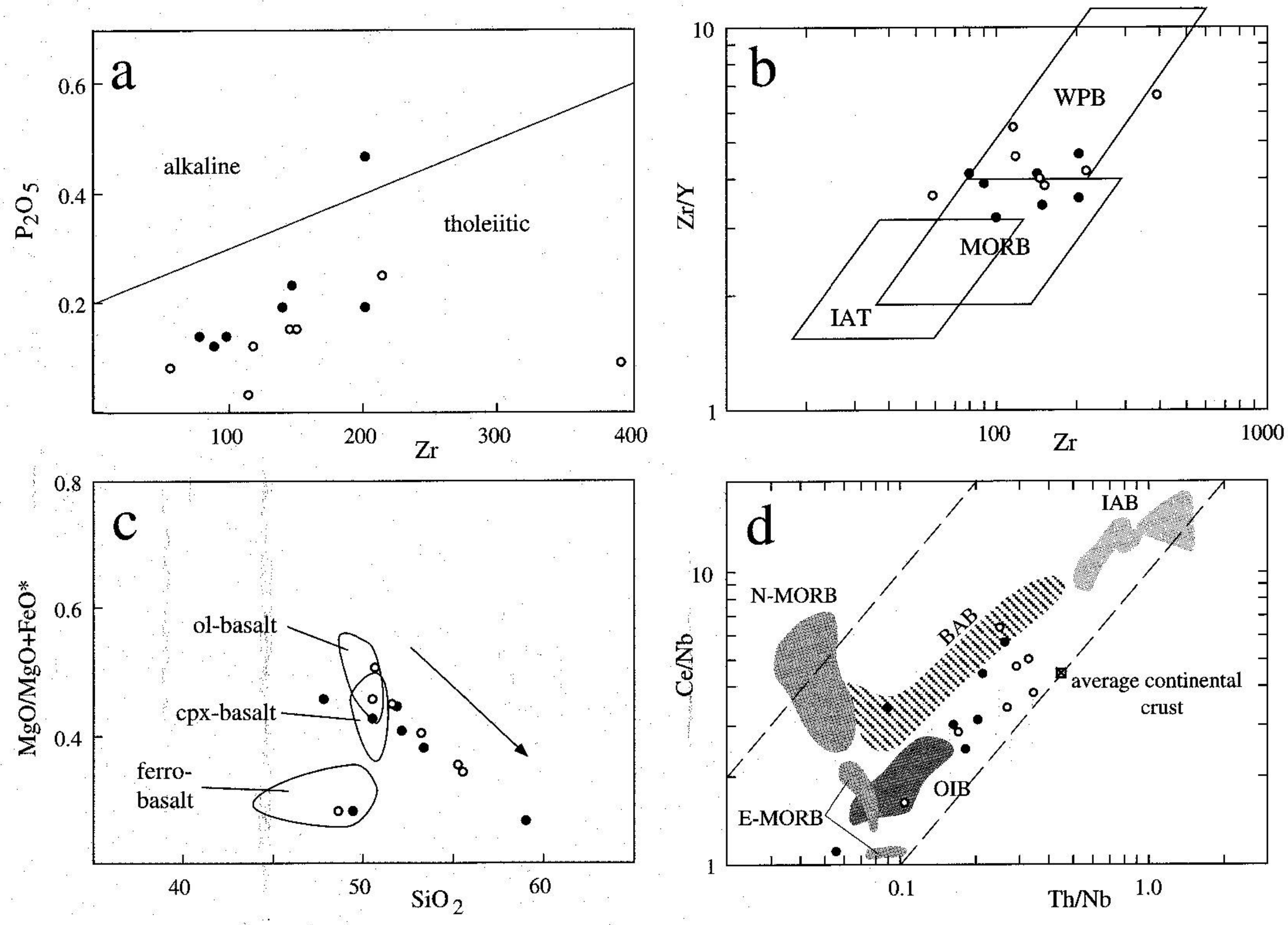

Fig. 5 Discrimination diagrams for the Turtmann valley metabasites: (retro-) eclogites: filled dots, amphibolites: open circles. (a) Zr versus P_2O_5 diagram (after WINCHESTER and FLOYD, 1976), (b) Zr versus Zr/Y diagram (PEARCE and NORRY, 1979), (c) SiO_2 versus Mg' diagram, with typical compositional ranges for olivine, clinopyroxene and ferro-basalts (PFEIFER and COLOMBI, 1989). (d) Th/Nb versus Ce/Nb plot (SAUNDERS and TARNEY, 1991) with indicated ranges for MORB, back arc (BAB) and island arc basalts (IAB).

enrichment of the very incompatible elements Cs to Sr is significant, especially for the highly incompatible elements Cs (70 to 2000 times enriched), Rb, Ba, Th and U (50 times enriched). Furthermore, the plot shows that K and Pb are highly enriched compared to N-MORB. Although the analytical error for Pb is very high (50%), the positive Pb anomaly can be explained by decay of the strongly enriched U. The same is probably also applicable for Sr, that is produced by decay from strongly enriched Rb.

The chondrite normalized REE patterns of the eclogites and some amphibolites display relative magmatic enrichment in the LREE (La/Lu = 0.8 to 3.7) and an enrichment of 20 to 50 times overall (Figs 4 and 7). Eu anomalies are faint, and both positive and negative. Slopes of the eclogites are often parallel to E-MORB, only JSE-3 is similar to N-MORB. All of them display enrichment in REE by a factor of 1–3 compared to standard N- or E-MORB (SUN and MCDONOUGH, 1989).

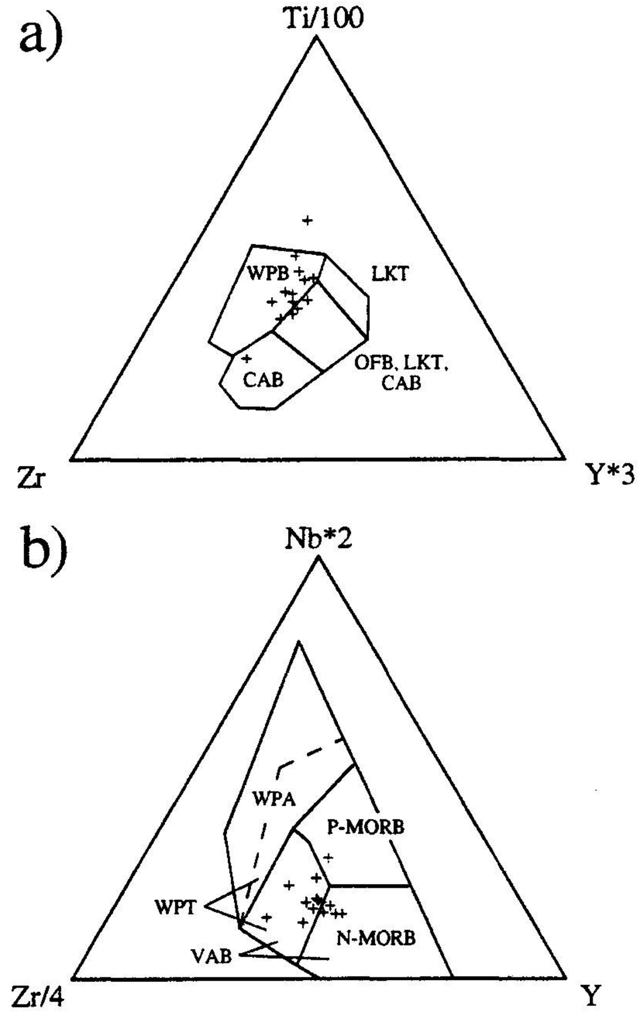

Fig. 6 Ternary discrimination plots for minor and trace elements of basaltic rocks with plotted Turtmann valley metabasites: (a) Ti–Zr–Y plot (after PEARCE and CANN, 1973), and (b) Nd–Zr–Y plot (after MESCHEDE, 1986). CAB = calc-alkaline basalts, LKT = low-K tholeiites, N- and P-MORB = mid ocean ridge basalts with normal and plume signature, OFB = ocean floor basalts, VAB = volcanic arc basalts, WPB = within plate basalts, subdivided into WPA (alkaline basalts) and WPT (tholeiites).

Although the patterns are almost congruent to the REE patterns of ZINGG (1989) and PFEIFER et al. (1990), there are some differences worth to be noted: patterns in ZINGG (1989) show a negative Eu anomaly, while Eu anomalies are faint and not systematic for our patterns. All REE patterns of PFEIFER et al. (1990) display constant La/Ce and Yb/Lu ratios of < 1 and > 1, respectively, while these ratios are not constant in our patterns. For the metabasites of the Zermatt-Saas area (PFEIFER et al., 1990), LREE enrichment is explained by a primary enrichment of these elements within the underlying mantle of the Tethys ocean. A comparison with the metabasites of the Berisal complex suggests a genetic similarity to the REE-rich amphibolites (plagioclase-amphibolites, dark layers of banded amphibolites, STILLE and TATSUMOTO, 1985), while the "hornblendefelses" of the Berisal complex have much lower REE contents.

5. Discussion

5.1. DEVELOPMENT OF A MAGMATIC MODEL

Major and trace elements confirm a tholeiitic basalt precursor for the Turtmann valley metabasites (Fig. 5a; ZINGG, 1989; THÉLIN et al., 1990), and display typical features of an enriched MORB (Fig. 5b). Patterns of enrichment are similar to those of modern back arc basin magmatism (SAUNDERS and TARNEY, 1991). The extensional and magmatic processes within a back arc basin are akin to those occurring in ocean basins. Extension and separation of the lithosphere above a subduction zone allows mantle peridotite to upwell and decompress, and thus produce partial melts, which lead to the formation of basaltic or basalt-like melts. In fact, many back arc basin basalts are transitional in their composition between MORB and island-arc basalts (Fig. 5d) due to the processes discussed below. Support for the back arc basin scenario comes from the fact that the host rocks belong to a thick sequence of former clastic material as typically found in a basin with long-lasting steady subsidence. Considering the formation of a basalt in a back arc basin as our potential precursor, there are several processes that influence its final (i.e. pre-metamorphic) composition:

(a) The contamination of the mantle source by the down-going slab or crust, releasing fluid and triggering off melting in the overlying mantle. The fluid contaminates the mantle source with elements incorporated within the oceanic crust. As a result, back arc basin basalts display higher abundance of the very incompatible soluble (= LIL) elements Cs, Ba, K, Rb (together with Sr), Th, U (with Pb) and light REE, because their source is enriched in these elements (Figs 4 and 7). Thus, the magma first represents the composition of the mantle source and probable contaminating components. The pronounced high enrichment of the LIL elements (Fig. 7), though partly increased by metamorphic processes, can be interpreted as a typical feature for a narrow back arc basin close to a subduction zone (SAUNDERS and TARNEY, 1991).

(b) The solid-liquid fractionation during mantle melting. After SUN et al. (1979) the degree of melting of a pyrolite mantle source can be estimated by the increasing content of Al_2O_3 and decrease of TiO_2. A range of 13–20% of melting can be suggested for our samples that closely follow a trend formed by samples of MORB composition (Fig. 8).

(c) The fractionation processes during ascent. Fractionation can be indicated by the relation between Mg and Si (Fig. 5c). Fractionation can account for a higher proportion of qtz-normative rocks and is one of the distinctions from N-MORB. CIPW calculations assume a qtz-normative protolith for 4 of the 14 samples. However, the CIPW calculations are also thought to be influenced by subsequent processes.

(d) Assimilation of crustal or crustal-like material during ascent and emplacement. Such an assimilation could either be the result of host rock melting (for an intrusive emplacement) or mixing with surrounding sediment during emplacement (for the case of an extrusion). Contamination with host rock material (paragneisses) which is assumed to be close to average continental composition is indicated by the compositional trend in SiO_2 versus Mg number (Fig. 5c). Additional features pointing to such a contamination are the high Zr and Hf contents (Fig. 7), and the trend of the metabasites from a BAB composition towards continental crust by enrichment of Th (Fig. 5d).

According to PFEIFER et al. (1989), the predominantly small grain size of the eclogites could be interpreted to reflect the small grain size of the magmatic precursor which would suggest a volcanic or subvolcanic origin. However, MILLER and THÖNI (1995) report the transition from a coarse

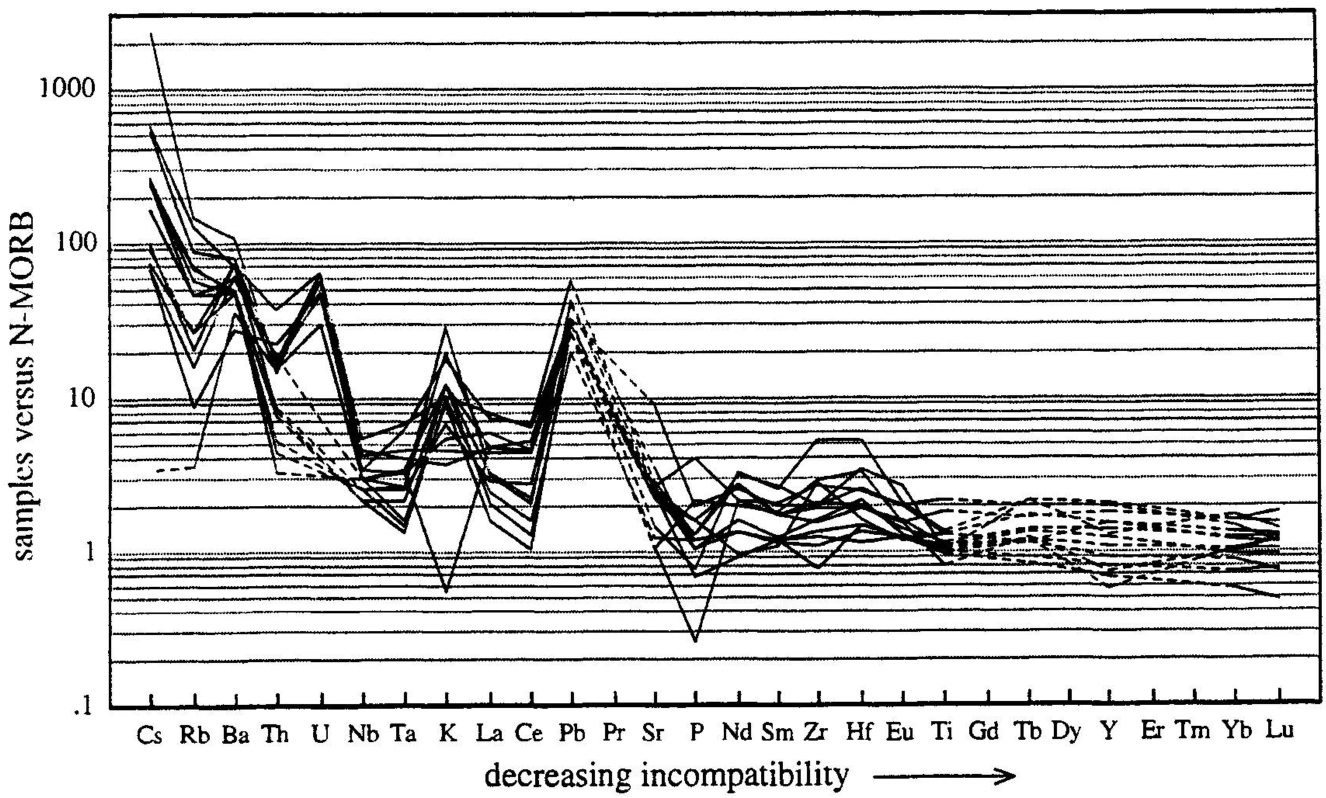

Fig. 7 Multivariation diagram for the Turtmann valley metabasites, normalized to N-MORB (n = 14). Elements are listed according to their decreasing incompatibility (SUN and MCDONOUGH, 1989), dashed lines indicate gaps for elements that have not been measured (Pr, Gd, Tb, Er, Tm), or values below the detection limits (Cs, U).

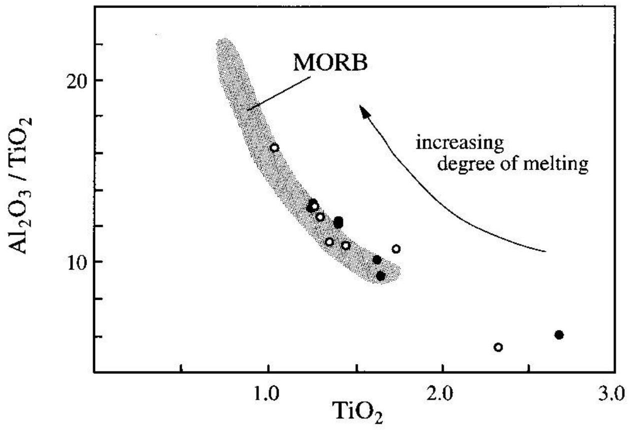

Fig. 8 TiO_2 versus Al_2O_3/TiO_2 diagram (SUN et al., 1979). Typical MORB basalts show decreasing TiO_2 contents (and increasing Al_2O_3) with increasing degree of melting.

grained gabbro into a fine-grained eclogite which would also allow a deep intrusion level for the metabasites. Thus, the small grain size of the eclogites can be taken as a hint, but is not an exclusive argument for a possible tuffaceous precursor or subvolcanic intrusion. An extrusive origin, however, is also supported by the geometry of the amphibolites that often have a pronounced horizontal extension, and small layers are observed that laterally show gradual transition into paragneisses (RAHN, 1989). From this scenario, the paragneisses of the SMN crystalline core can be interpreted in terms of a thick psammitic to sometimes pelitic sediment series within a submarine basin close to an extended continental hinterland.

(e) Metasomatic interaction with seawater during or subsequent to emplacement. The strong enrichment of Rb, Ba and K (Figs 7 and 9) could also be the result of a secondary enrichment by seawater interaction, although other elements such as Na and Ca show no elevated values.

Ba contents are known to increase towards an island arc (Fig. 9), and are sometimes used as an indicator for the distance to the arc (SAUNDERS and TARNEY, 1991). Ba, together with other elements, can also be accumulated by syn-magmatic exhalative processes (black smokers, VON DAMM et al., 1985), and this process has been proposed for the origin of the Ba in several small ore deposits in the upper Turtmann valley (SCHAFER, 1994). In the light of this interpretation, the high Ba contents would also favour an extrusive rather than intrusive protolith.

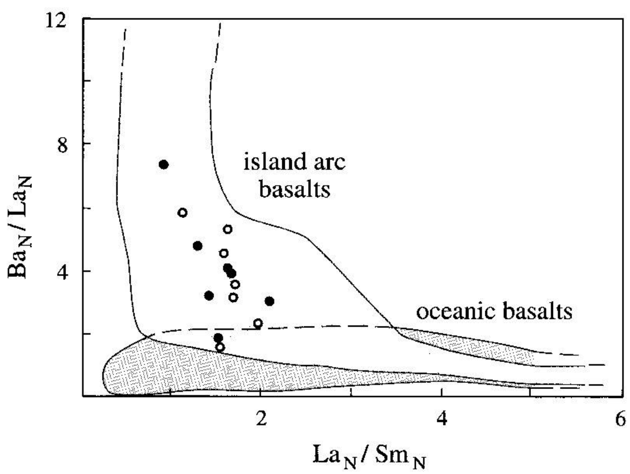

Fig. 9 La/Sm versus Ba/La plot (BVSP, 1981) of the Turtmann valley metabasites with indicated typical ranges for island arc and oceanic basalts. N = chondrite normalized.

5.2. COMPARISON WITH REGIONAL DATA

A compilation of data from the pre-Alpine crystalline basements within the Penninic realm (VON RAUMER and NEUBAUER, 1993) shows a related situation of early Proterozoic and Paleozoic basic magmatism within the Berisal complex (part of the Pontis nappe, STILLE and TATSUMOTO, 1985). There are some striking similarities between Berisal complex metabasites and those of the SMN in terms of occurrence, geometry, and age of the amphibolite bodies, REE patterns (Fig. 4) and metamorphism. It has, however, to be kept in mind, that the isochrones of ZINGG (1989) for the SMN metabasites are, without exception, constructed with the help of the data of STILLE and TATSUMOTO (1985), i.e. are not independently established.

The relative position of pre-Variscan crystalline basement units during Proterozoic and early Paleozoic time is rather speculative (VON RAUMER and NEUBAUER, 1993), but a compilation of reported magmatic events within surrounding Alpine crystalline units during the uppermost Proterozoic and Cambro-Ordovician reveals a dense pattern of different features within the crystalline nappes of the later Helvetic, Penninic and Austroalpine realm of the central and Western Alps (for references before 1993, see VON RAUMER and NEUBAUER, 1993): An overview of Cambro-Ordovician activity indicates a subduction zone south of the later Aar massif and Tauern window crystalline indicating beginning crustal shortening since the Ordovician. From Lake Emosson (Mont Blanc massif), metabasic layers were interpreted to represent subvolcanic sills or dikes of pre-Caledonian age. Basic rocks found in the Adula nappe were dated to have intruded into an oceanic environment during a magmatic event at 461+4/–5 Ma (SANTINI, 1992). In the Silvretta nappe, early Cambrian intrusions of basic to granitic composition formed in a spreading environment (MÜLLER et al., 1996). For the Ötztal eclogites, MILLER and THÖNI (1995) derived a Cambrian age, and an origin within an extensional environment. At the same time widespread acid intrusion activity is indicated for the SMN (ZINGG, 1989; BUSSY et al., 1996b). A comparison of the different compositional data and proposed tectonic models suggests that the geologic pattern of the later Penninic realm was rather complicate and characterized by a large number of small-scale features and processes during the early Paleozoic.

The various intermediate and acid intrusions into the SMN basement of late Cambrian to early Ordovician age (ZINGG, 1989; BUSSY et al., 1996b) point to an evolved continental crust segment in close vicinity to the Turtmann valley metabasites which fits with our scenario of a narrow back arc basin and a nearby evolved continental crust. The eroded material of this continent might be present as metamorphosed psammites of the Ergischhorn Series. Thus, the generation model of the Turtmann valley metabasites is compatible with an early Paleozoic magmatic age. Our investigations rather propose a uniform age for all SMN metabasites instead of two separate events as proposed by ZINGG (1989). It is interesting to note that the hornblendites of the Berisal complex that would be of the same age, show a very different REE pattern suggesting a different tectonic environment for their emplacement. Concordant to the proposed early Paleozoic age the high U contents of the samples run parallel to high Pb values indicating a high degree of U having decayed since extrusion.

The proposed scenario of extrusion of metabasic volcanoes within a back arc regime also bears implications on the genesis of three small ore deposits in the Turtmann valley, and further ore bodies in the neighbouring Val d'Anniviers, that are particularly characterized by the elements Co, Ni, Cu, As, and Ba (WOODTLI, 1987; SARTORI and DELLA VALLE, 1986; SCHAFER, 1994). With the exception of Ba, all elements are typically found in connection with basic to ultrabasic rocks due to their chalcophile affinity. Metamorphic remobilization of these elements probably has resulted in the genesis of the ore deposits of Kaltenberg (Co, Ni, As, Cu), Pipji (Co, Ni, As, Bi) and Plantorin (Ba, Co, Ni). Both Co and Ni show rather low contents of 20–40 ppm and 60–130 ppm, respectively, in the investigated metabasites which might be due to later remobilization. Contemporaneous to the magmatic extrusion of the metabasites, exhalations might have released high amounts of Ba (SCHAFER, 1994). Thus, the proposed model offers a genetic link between all important elements of the nearby ore deposit.

6. Conclusions

The chemical composition of the Turtmann valley metabasites reveal a chemical composition that best fits into a subduction-related MORB-similar magma that underwent fractionation during ascent. Assimilation of crustal or crustal-like material occurred before or during emplacement. Because most eclogites and amphibolites are fine-grained, and the amphibolites form layers and lenses of varying scale within a presumably former clastic sediment pile, the model prefers an extrusive rather than intrusive scenario where assimilation of crustal or crustal-like material is caused by the mixing with sedimentary material during emplacement on the seafloor. The mainly small-scale amphibolite lenses and layers within the Ergischhorn and Barneuza series point to long-lasting magmatic activity that culminated during two events at the base and top of the Barneuza series by generating the banded amphibolites and banded complex. The magmatic activity was presumably driven by tectonic movements along extensional faults within the back arc basin, and profitted from stable tectonic conditions during basin sedimentation. The high content of LIL elements (Fig. 7) within the Turtmann valley basites suggest a rather narrow basin and/or a probable high amount of continental crust that was incorporated into the primary ascending magma before or during emplacement. The high amount of Ba can either be explained by syn-magmatic seawater interaction or syn-magmatic exhalation activity (SCHAFER, 1994).

U–Pb data of the SMN crystalline and related basement nappes show widespread magmatic activity during the Late Cambrian and Ordovician, only small volumes of basic magmatism that might be combined into a large-scale distension zone preceeding the Caledonian Orogeny. From the scenario proposed for the Turtmann valley metabasites, the close vicinity of an evolved continental crust seems likely. Age data from the literature point to such an evolved crust during the Cambro-Ordovician (ZINGG, 1989; BUSSY et al., 1996b). An early Paleozoic magmatic age for the Turtmann valley metabasites is therefore favoured. In comparison with compositional data of the hornblendefelses within the Berisal complex (STILLE and TATSUMOTO, 1985), the proposed age leads to the assumption that the Berisal and SMN crystalline rocks were not in close vicinity to each other during the time of basaltic magmatism in the Cambro-Ordovician.

Some primary geochemical features are blurred by later metamorphic processes. However, especially REE within the cores have shown to be immobile for several of our sample pairs. A moderate element mobility is proposed across the contacts of the metabasite lenses and layers with the surrounding paragneisses due to compositional gradients between the two lithologies. Part of the K mobility (Fig. 2) can be assumed to be synchronous to amphibolite facies overprint, characterized by the neoformation of white mica (RAHN, 1989; THÉLIN et al., 1990). Later Alpine overprint was more penetrating as indicated by the total lack of former eclogite and amphibolite facies minerals within the small metabasite lenses and layers of the Ergischhorn series and other parts of the Barneuza series (RAHN, 1989), and was probably responsible for the remobilization of Co, Ni, As from the basic layers, and Ba from exhalation precipitations that were concentrated within small ore deposits.

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