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REE characteristics in pegmatites and adjacent wallrocks of the calc-alkaline Bergell intrusion (southeastern Central Alps)

by Marc Wenger^{1,2}, Urs Krähenbühl³ and Thomas Armbruster¹

Abstract

Rare-earth element (REE) determinations of pegmatites and adjacent wallrocks of the calcalkaline Bergell intrusion are presented. The pegmatites are derived from a granitic magma produced by AFC contamination of a tonalite with roof pendant material. The geochemical differentiation of the acid dykes is characterized by a depletion of LREE probably caused by fractional crystallization of allanite and minor sphene. According to their REE distribution patterns two different pegmatite groups can be distinguished: The pegmatites intruded in the high metamorphic Gruf unit (group B) reveal contaminated REE distribution patterns, strongly related to their adjacent wallrock, whereas the remaining dykes (group A) have undisturbed patterns. Group A pegmatites can be subdivided into two categories according to their degree of differentiation. A lower fractionated biotite type with $K_2O > Na_2O$ and a less developed negative Eu anomaly can be distinguished from a highly evolved muscovite type with $Na_2O > K_2O$ and a strongly negative Eu anomaly. *Biotite pegmatites* show a differentiation trend towards a lower anorthite component in the feldspars leading to an increase of the Eu anomaly. *Muscovite pegmatites* are strongly depleted in Eu. The remaining low Eu content correlates with the CaO content. Late in situ fractionation and possible multiple injection led to an internal zonation of large pegmatite bodies and lenses. Strong variations of the REE content in this zones can be observed, similar to those observed in large scale lateral differentiation processes.

Keywords: geochemistry, REE analysis, INAA, pegmatite, Bergell/Bregaglia, Switzerland.

Introduction

Studies on trace element behavior in granite genesis are well established (e.g. HANSON, 1978; FOURCADE and ALLÈGRE, 1981; ČERNÝ, 1982; GROMET and SILVER, 1983). Differentiation processes in highly specialized granites and pegmatites are mainly studied using ratios of pairs of chemically coherent elements as Ga/Al, Hf/Zr, Ta/Nb and HREE/LREE. Crystallization of the specialized granitic melts fractionates trace and minor elements between rockforming and accessory minerals and melt. Due to the change in volatile content of the melt and the amount of complexing agents the partition coefficients D are not constant during this fractionation (MÖLLER, 1989). Furthermore, data on REE contents and

partition coefficients D ¹⁾ are only available for few accessory phases in acid rocks as allanite, apatite, monazite, titanite and zircon. Therefore the results of fractional crystallization modelling often contradict the geochemical behavior of compatible and incompatible elements. The aim of this paper is to describe the geochemical behavior of REE in the pegmatites of the calc-alkaline Bergell intrusion related to the assumed source rock and respective wallrocks.

The Bergell intrusion is located at the Swiss-Italian border in the southeast corner of the Cen-

¹⁾ Partition coefficients D are defined according to MAHOOD and HILDRETH (1983) as partitioning of a single component (i) between solid (S) and liquid (L) phases X_i^S/X_i^L , where X_i is the weight fraction of i in each phase.

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Tab. 1 Short description of the analysed rock samples.

No.	sample description (locality, altitude a.s.l.)	CH-coordinates
Val Bondasca		
B-NG1	Gruf-gneiss in contact to pegmatite B-P2 (rock-slide 1972, 1420)	765'800/131'900
B-P2	Gr-Sch bearing Mu-Fsp-Qz-pegmatite (dito B-NG1)	
Vallun da la Trubinasca		
T-PNG1-P	Bi- pegmatite in Gruf-migmatite (entrance of canyon, 1400)	764'700/131'900
T-PNG2-NG	Gruf-migmatite in contact to T-PNG2-P (stream-junction, 1740)	764'650/131'200
T-PNG2-P	Bi-bearing Mu-Gr-pegmatite in Gruf-migmatite (dito T-PNG2-NG)	
Valle Sissone		
S-PNG2-NG	Fine-grained granodiorite (rock-crest E M. Sissone, 2810)	775'900/129'200
Chiavenna (Tanno)		
	Profile through wallrock and zoned pegmatite (ravine, 430)	751'400/131'150
C-NG2-P1	Hanging wall amphibolite	
C-P9-P2	Bi-Mu-Fsp contact zone	
C-P10-P3	Gr-aplitic zone	
C-P11-P4	Assimilated amphibolitic scholle	
C-P12-P5	Coarse-grained Gr-Mu-zone	
C-P13-P6	Aplitic contact zone	
C-NG3-P7	Foot wall amphibolite	

Note: Abbreviations: Gr: garnet; Sch: schorl; Mu: muscovite; Bi: biotite; Fsp: feldspar; Qz: quartz.

tral Alpine metamorphic area. The Bergell massif is a deep-seated igneous body consisting mainly of a zoned structure made up of a frame of tonalite and a granodioritic core. A short description of the investigated rock types is given in table 1. The batholith intruded in Oligocene times (VON BLANCKENBURG, 1990). A separate peraluminous intrusion crosscuts the Bergell units and is according to trace element variations not related to the main Bergell body (REUSSER, 1987). Recent summaries on the geology of the Bergell Alps are given by TROMMSDORFF and NIEVERGELT (1983) and WENK (1986).

Late genetic dykes and lenses with strong variations in general appearance and mineralogy can be observed all over the intrusion and within the neighboring units. The age relation between the different dyke types is not uniform. Pegmatites and aplites crosscut each other without showing distinct generations. These acid dykes can be classified according to their degree of alkali fractionation. A *muscovite type pegmatite*, rich in albite and muscovite (free of biotite) with minerals bearing rare elements (e.g. beryl, columbite, tourmaline, sulfosalts) is distinguished from a *biotite type* with minor muscovite and albite (WENGER and ARMBRUSTER, 1991).

In highly differentiated rocks such as the investigated Bergell pegmatites, fractionation is not reflected in simple relations as e.g. Harker dia-

grams. None of the oxides except Al_2O_3 shows any differentiation with respect to SiO_2 . The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio reflects the modal amount of quartz and feldspar observed in thin sections. A significant evolution trend can be seen in the alkali content of the pegmatites (WENGER and ARMBRUSTER, 1991). The $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratio discloses a linear correlation between the more highly differentiated *muscovite pegmatites* rich in Na_2O , and the K_2O rich *biotite pegmatites*. Feldspars are the main alkali bearing phases in the various pegmatite types. Thus, the differentiation trend is manifested in the variation of the albite/microcline ratio. Major and trace-element geochemistry of these rocks is discussed in detail in WENGER and ARMBRUSTER (1991). For a discussion of the geochemistry of the different wallrocks the reader is referred to WENK et al. (1977), VON BLANCKENBURG (1990) and REUSSER (1987).

Analysed samples and methods

In the course of a detailed mineralogical study on the pegmatites of the Bergell intrusion (WENGER and ARMBRUSTER, 1991), thirteen samples of different pegmatite types and their wallrocks were selected (Tab. 1) and analyzed for major and trace elements (Tab. 2). Analytical details and the major element data set are given in WENGER and

Tab. 2 Whole rock chemistry: concentrations (in ppm) of La, Ce, Nd, Sm, Eu, Tb, Yb and Ta.

whole rock samples														
No.	B-NG1	B-P2	T-PNG1 -P	T-PNG2 -NG	T-PNG2 -P	C-NG2 -P1	C-P9 -P2	C-P10 -P3	C-P11 -P4	C-P12 -P5	C-P13 -P6	C-NG3 -P7	S-PNG2 -NG	Siss7* Bio
Type	Mu	Mu	Bio		Bio		Bio	Mu		Mu	Mu			
La	49	1.7	5.2	51	1.0	5.1	1.0	7.3	4.5	3.0	3.9	4.5	28.9	4.5
Ce	110	6.0	12	93	8.4	16	2.8	20	15	9.1	14	15	63	8.6
Nd	120	4.1	14	76	1.7	13	1.2	18	15	4.4	10	7.6	59	6.4
Sm	38	1.3	5.6	6.7	0.6	4.5	0.5	3.3	7.3	1.5	4.2	3.9	7.3	1.9
Eu	0.8	< 0.1	0.4	1.9	0.1	1.5	< 0.1	< 0.1	1.4	< 0.1	< 0.1	1.4	0.6	0.2
Tb	1.8	0.3	0.6	1.3	< 0.1	0.5	0.1	0.5	0.5	0.4	0.4	0.8	0.9	0.3
Yb	4.7	1.2	3.1	4.7	0.3	8.2	0.5	2.3	4.0	2.5	0.8	7.2	1.4	1.7
Lu	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.2	0.2
Eu/Eu*	0.04	0.025	0.12	0.46	0.20	0.59	0.10	0	0.37	0.011	0.013	0.01	0.14	0.19
Ta	0.9	2.0	1.0	1.5	31	0.3	2.1	7.7	0.2	4.6	2.6	< 0.1	n.d.	n.d.

Note: n.d.: not determined. Type means pegmatite classes introduced in the text; Mu: muscovite pegmatite; Bio: biotite pegmatite. *Sample Siss7 from VON BLANCKENBURG (1990) 1 σ errors: La, Ce, Nd, Eu, Tb, Yb 5–10%; Sm, Lu, Ta 10–15%. Sample numbers see table 1.

ARMBRUSTER (1991). In addition, a columbite (sample C-8) from the Chiavenna profile (rock-sample C-P12-P5) was analyzed for the REE content by ICP-MS and INNA. Chemical data of one *biotite pegmatite* (sample Siss7 from Valle Sissone) were taken from VON BLANCKENBURG (1990). REE and Ta were analyzed by instrumental neutron activation analyses (INAA) after an irradiation with thermal neutrons for two days. The employed procedure (details in SCHALTEGGER and KRÄHENBÜHL (1990) consists of measuring the gamma radiation of the irradiated samples three times after different waiting periods with an HP Ge detector. The evaluations of the concentrations were made relative to the reference materials BCR-1 and BHVO-1 of USGS.

Results

The pegmatites show an enrichment in light REE (LREE) by only 3 to 30 times chondrite, heavy REE (HREE) by 1 to 15 (Fig. 1). All pegmatite patterns reveal strong but varying negative Eu anomalies. Eu/Eu*²⁾ values are below 0.2. (La/Yb)_N range between 0.4 and 3. Flat to slightly increasing plateaus can be observed for LREE and HREE.

The internal distribution of REE in a zoned pegmatite can be seen in the Chiavenna profile (Fig. 1a). This dyke, ca. 5 m in thickness, intruded

into an amphibolite. It has sharp contacts to the wallrock and is internally zoned (Tab. 2). Careful sampling in the different zones was necessary to exclude the possible influence of local REE rich mineral concentrations. Amphibolitic schollen inside the pegmatite show a strong alkali enrichment but are extremely similar in their REE patterns compared to the unaffected wallrock. REE distribution patterns of the different pegmatite zones are similar in shape but vary in the rock/chondrite ratio and the extend of the Eu anomaly. The content of REE ranges between 2 and 12 times chondrite inside the same pegmatitic body. Striking is the REE pattern of the biotite - muscovite - feldspar contactzone (sample C-P9-P2). This *biotite pegmatite* domain is 3 to 4 times depleted relative to the other zones with a less pronounced Eu anomaly of 0.1 Eu/Eu*. This different behavior of the Eu anomaly in *biotite pegmatites* (Tab. 2) compared to the rare mineral bearing muscovite dykes (with Eu/Eu* values below 0.025) is observed in all samples investigated. *Muscovite pegmatites* (Tab. 2) have a pronounced negative Eu anomaly which is not very dependent on the Na₂O/K₂O ratio. In contrast, *biotite pegmatites* show a small range of the alkali ratio with Na₂O/K₂O < 1 (WENGER and ARMBRUSTER, 1991) but strong variations in Eu/Eu* (Tab. 2).

A fine-grained granodiorite from Valle Sissone (sample S-PNG2-NG) was analyzed to distinguish fractionation processes during pegmatite formation from earlier ones. This assumed "source rock" of the acid dykes reveals a REE

²⁾ Eu* was obtained by linear interpolation between Sm and Tb.

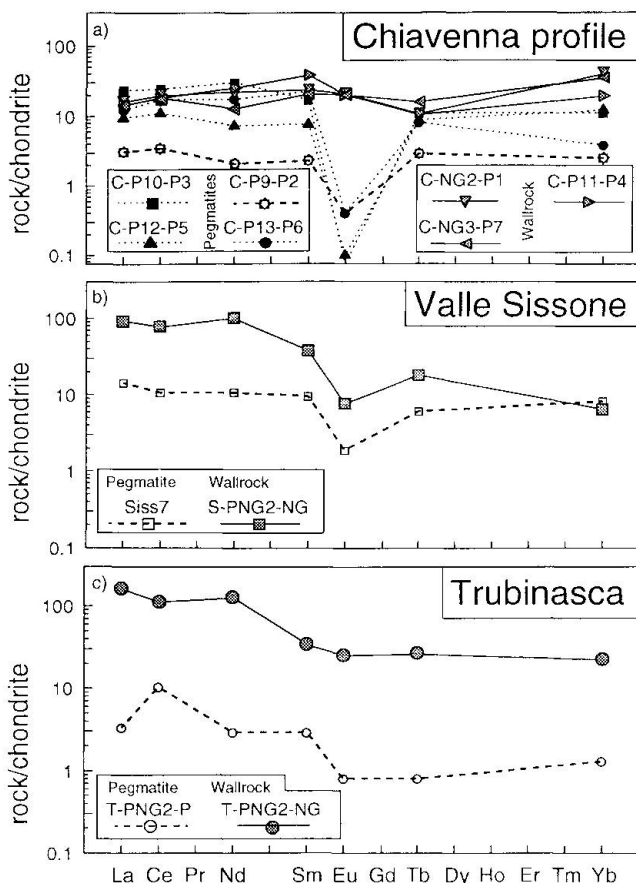


Fig. 1 Chondrite normalized REE variation diagrams of the analyzed pegmatites. Chondrite normalization according to TAYLOR and GORTON (1977).

a) Chiavenna profile – REE profile through a pegmatite intruded in amphibolite near Tanno (Chiavenna) showing the pronounced variations in the REE content due to late in situ fractionation and possible multiple injection. No relevant fluid induced wallrock interaction can be observed.

b) Valle Sissone – Chondrite normalized REE distribution pattern of the assumed granodioritic "source rock" and of an undisturbed dyke from Valle Sissone revealing the LREE depletion of the pegmatites.

c) Trubinasca – Chondrite normalized REE distribution pattern of a contaminated pegmatite and its adjacent wallrock, the high metamorphic Gruf unit (Val Trubinasca).

distribution pattern with $(La/Yb)_N$ of 14 and Eu/Eu^* of 0.14 (Fig. 1b). This is in good correlation with data of the same rocktype by VON BLANCKENBURG (1990). The assumption of choosing sample S-PNG2-NG as a source rock is supported by the pegmatite REE pattern of sample Siss7 (Fig. 1b). The following general trends which can be observed if REE distribution patterns of pegmatites are compared with those of the parental granites: (a) pegmatites are lower in REE contents than the related granites, (b) the

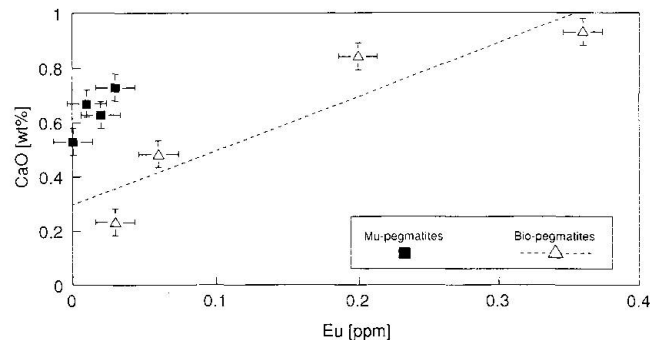


Fig. 2 CaO versus Eu diagram showing the different evolution trends for the two pegmatite types. Only dykes with an undisturbed chondrite normalized REE pattern are used in this diagram.

Mu-pegmatite samples: B-P2, C-P10-P3, C-P12-P5, C-P13-P6.

Bio-pegmatite samples: T-PNG1-P, T-PNG2-P, C-P9-P2, Siss7.

REE patterns are flatter than those of the granites (SIMMONS et al., 1987), (c) both show commonly negative Eu anomalies (ČERNÝ, 1982). Source rock normalized REE pattern of the pegmatites (Fig. 3) reveal strong LREE depletion in a range of 3 to 50. HREE are much less depleted or even slightly enriched. In source rock normalized REE patterns the Eu anomaly is also dependent on the dyke type. *Muscovite pegmatites* show pronounced negative anomalies whereas most of the *biotite pegmatites* have only weak anomalies which tend to be positive.

In our INAA investigation of columbite sample C-8, we tried to evaluate REE concentrations despite the enormous radioactivity of Ta as one of the main elements. The resulting high REE values were subsequently checked by ICP-MS and could not be confirmed (Tab. 3). Thus we tend to accept the ICP-MS results which yielded REE concentrations similar to the ones of the rock sample CP12-P5. This C-8 columbite does not seem to be enriched in REE relative to the pegmatite.

Discussion

INTERPRETATION OF THE WHOLE-ROCK REE PATTERNS

Granodioritic source rock – The assumed "source rock" of the pegmatites, the granodiorite of the Bergell intrusion (sample S-PNG2-P) was probably produced by assimilation and fractional crystallization "(AFC)" of a tonalite contaminated with roof pendant material. Isotopic data exclude hornblende fractionation as sole process (VON

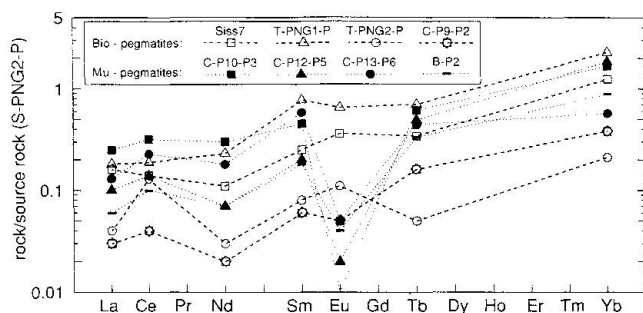


Fig. 3 "Source rock" normalized REE variation patterns of the investigated pegmatites showing the LREE depletion and strong variations in the Eu anomaly. Sample numbers see table 1.

BLANCKENBURG, 1990). This is confirmed by the HREE abundance. Extensive fractional crystallization of hornblende would lead to low HREE concentration in the granitic melt (HANSON, 1978), which is not the case.

Pegmatites – The pegmatite data can be divided into two groups (Fig. 1 a–c): (A) undisturbed REE patterns; and (B) disturbed patterns. Group A includes pegmatites intruded in mafic wallrocks as presented in the Chiavenna profile (Fig. 1a) and the sample Siss7 from Valle Sissone (Fig. 1b). No exchange of REE between pegmatite and wallrock can be observed in this group. E.g. in the Chiavenna profile (Fig. 1a) amphibolitic schollen and wallrock show no negative Eu anomaly. In contrast, pegmatites of group B show patterns related to their adjacent wallrocks. E.g. sample T-PNG2-P (Fig. 1c) has a similar REE distribution profile without significant Eu anomaly as its wallrock T-PNG2-NG consisting of a migmatitic Gruf gneiss.

(A) undisturbed pegmatites – Chondrite normalized REE patterns of group (A) pegmatites (Fig. 1b) are characteristic of granitic pegmatites: flat patterns with low $(La/Yb)_N$ values and negative Eu anomalies. This pattern and the rather low REE content indicate crystallization from fluids that originated from extremely late stages of solidification of a parental melt (MÖLLER, 1989). The negative Eu anomaly is caused by incorporation of Eu^{2+} into feldspar fractionated earlier. This pegmatite group (A) does not disclose important fluid induced wallrock interaction, affecting the REE distribution in both rock types (see Chiavenna profile, Fig. 1a). The REE content of these dykes is a product of internal evolution and/or possible multiple injection.

In the undisturbed pegmatite group (A), a less differentiated biotite type can be distinguished from a highly evolved muscovite type. Allanite,

Tab. 3 REE chemistry of columbite: ICP-MS results of sample C-8 (WENGER and ARMBRUSTER, 1991). Concentrations in ppm.

element	conc.	element	conc.
Cs	2.4	Tb	0.6
Ba	9.2	Dy	3.7
La	1.6	Ho	0.4
Ce	4.7	Er	0.9
Pr	0.8	Tm	0.16
Nd	2.3	Yb	1.3
Sm	1.9	Lu	0.15
Eu	0.01	Th	14
Gd	2.5	U	1400

Note: 2σ error < 20%.

common as accessory mineral is an important REE bearing phase in the *biotite pegmatites*. On the other hand allanite is rare in the more evolved *muscovite pegmatites*. The different internal evolution of the two pegmatite types is reflected in the alkali fractionation and the similar geochemical behavior of Eu and Ca. Eu is already depleted in the granodioritic source rock caused by earlier feldspar fractionation. Thus REE bearing minerals in pegmatites are characterized by inherited strong negative Eu anomalies (MÖLLER, 1989). The remaining Eu content in such highly evolved rocks is very low and several processes are able to influence Eu anomalies or even to alter inherited ones. Important for all these processes is the capability of Eu^{2+} to replace Ca^{2+} in crystal structures. *Biotite pegmatites* show a positive dependence of Eu on the calcium oxide content. *Muscovite pegmatites* have similar Ca concentrations and very low Eu values. Fig. 3 shows a less developed Eu anomaly for the biotite type which confirms the lower degree of differentiation compared to the muscovite type. Furthermore, the biotite type shows an internal differentiation trend including a strong increase of the Eu anomaly together with a small decrease of the Na_2O/K_2O ratio. As shown in an earlier study (WENGER and ARMBRUSTER, 1991), the degree of differentiation is mainly a function of the alkali ratio; a similar correlation can be seen in the extent of the Eu anomaly Eu/Eu^* . *Muscovite pegmatites* already inherited strong Eu anomalies resulting in only small variations of the remaining low Eu content. This confirms that pegmatite domains high in the anorthite component are also high in Eu resulting in a less evolved negative Eu anomaly. Subsolidus exsolution of an early calcic plagioclase component in perthite to form more sodic albite may be the source of this "late stage Ca^{2+} " (MÖLLER, 1989). However, *muscovite peg-*

matites are strongly depleted in Eu and interpretation of the trend observed in figure 2 can only be speculative.

(B) *disturbed pegmatites* – In contrast, group (B) pegmatites (Fig. 1c) have contaminated REE distributions, strongly related to their adjacent wallrocks. These dykes intruded in the deep seated Gruf unit, a migmatitic paragneiss series. The contact to the wallrock changes from sharp in the thicker parts to streaked in the thinner parts, where the pegmatites fade out in schlieren structures. Apophysic off-shooting tongues and assimilation of Gruf-migmatite is common, thus explaining the disturbed REE distribution patterns. This group (B) dykes must be excluded in a discussion on internal dyke evolution. It must be emphasized that not all pegmatites intruded in the Gruf unit show such a disturbed pattern. Several pegmatites in this area are undisturbed (e.g. T-PNGI-P).

BEHAVIOR OF REE DURING DIFFERENTIATION

The pegmatites are depleted in LREE related to the source rock in a range of 3 to 50 (Fig. 3). No major phase including biotite and muscovite in the granodioritic source rock or the pegmatites has partition coefficients $D > 1$. Crystallization of feldspar, quartz and mica would result in an enrichment of LREE in the liquid. Therefore, the observed "anomalous" depletion of LREE in the pegmatites must be attributed to the fractionation of LREE rich accessory phases such as allanite, monazite or titanite (MITTLEFEHLDT and MILLER, 1983). Allanite rich granitic dykes associated with the granodioritic body are very common in the Bergell intrusion. One could argue that the accessory REE rich phases were carried as relic minerals from an earlier crystallization event and therefore disturb the whole rock REE distribution pattern. Idiomorphic habit and missing resorption strongly suggest that the main REE bearing accessories crystallized from components actually dissolved in the melt. Allanite and minor titanite are the only common accessory LREE rich phases in the granodiorite and associated granitic dykes. Thus fractionation of allanite into the granodiorite is probably responsible for the LREE depletion in the pegmatites. Source rock normalized patterns for HREE (Fig. 3) do not reveal any significant differences between granodiorite and pegmatites. Zircon is the only phase in these rocks capable of producing relative fractionation among the middle REE and HREE, resulting in a depletion of HREE (HANSON, 1978).

The low zircon abundance and the even slightly enrichment of HREE contradict a relevant influence of this mineral.

The obtained INAA results first suggested columbite to be an excellent host for LREE. In contrast, ICP-MS analyses led to a low REE content similar to those in the wallrock. A subsequent careful examination of the INAA results showed a problematic influence of the compton background produced by the high Ta concentration in the columbite sample. Thus, columbite does not bear high amounts of REE and has therefore no important influence on REE fractionation processes.

Large pegmatitic lenses or dykes often show asymmetrically zoned textures, lense shaped and layered zonations as well as fluidal structures which may be caused by late in situ fractionation or multiple fluid injection. The occurrence of this pegmatite type in the Bergell area is well documented (SCHMUTZ, 1976). Zoning textures of the Chiavenna pegmatite profile combined with chemical profiles as displayed in figure 2 of WENGER and ARMBRUSTER (1991) reveal late in situ fractionation as the main reason for the internal zonation. Other fractionation processes as liquid state thermogravitational diffusion or loss of a vapor phase can be only of minor importance because they would affect important changes in the shape of the REE distribution patterns (MITTLEFEHLDT and MILLER, 1983) which is not the case. Consequently, in situ fractionation together with a slow cooling rate is able to produce the same pegmatite types as observed in large scale lateral differentiation processes.

Summary and conclusions

1) The pegmatites of the calc-alkaline Bergell intrusion are derived from a granitic magma produced by AFC contamination of a tonalite with roof pendant material. The dykes show an "anomalous" depletion of LREE caused by fractionation of allanite and minor sphene during the crystallization of the granodioritic source rock and associated granitic dykes.

2) The pegmatites intruded in the high metamorphic Gruf unit may reveal contaminated REE distribution patterns (group B), strongly related to their adjacent wallrock whereas the remaining dykes (group A) have undisturbed patterns. Group A pegmatites can be divided in two groups according to their degree of differentiation. A less fractionated biotite type for which WENGER and ARMBRUSTER (1991) determined $K_2O > Na_2O$ has a less developed negative Eu anomaly compared

to a highly evolved muscovite type with $\text{Na}_2\text{O} > \text{K}_2\text{O}$ (WENGER and ARMBRUSTER, 1991) which has a pronounced negative Eu anomaly.

3) *Biotite pegmatites* show a differentiation trend towards a lower anorthite component in the feldspars leading to an increase of the Eu anomaly. The main REE bearing mineral is accessory allanite.

4) *Muscovite pegmatites* are strongly depleted in Eu.

5) Late in situ fractionation and possible multiple injection led to an internal zonation of large pegmatite bodies and lenses. Strong variations of the REE content in this zones can be observed, similar to those observed in large scale lateral differentiation processes.

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