The Canadian Mineralogist
Vol. 35, pp. 153-165 (1997)

THE VOLTA GRANDE PEGMATITES, MINAS GERAIS, BRAZIL: AN EXAMPLE OF RARE-ELEMENT GRANITIC PEGMATITES EXCEPTIONALLY ENRICHED IN LITHIUM AND RUBIDIUM

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ABSTRACT

The Volta Grande granitic pegmatites are associated with Transamazonian granites (Early Proterozoic) hosted by the Archean greenstone belt of the Rio das Mortes Valley, which is situated at the southern border of the São Francisco Craton, in Minas Gerais, Brazil. The pegmatite bodies, which are usually large, show a dominant intermediate zone containing spodumene, microcline, albite and quartz, with an irregular border of an aplitic facies surrounded by an extensive metasomatic aureole with zinnwaldite, phlogopite and holmquistite. The spodumene-rich core zone is continuous or segmented, and also contains lenses of lepidolite. These pegmatites are characterized chemically by their high Rb and Li content. Rubidium is concentrated in the potassic minerals: microcline, muscovite, lepidolite and zinnwaldite. These minerals show exceptionally low K/Rb weight ratios, from 1.5 to 4.0. In micas, a positive linear correlation exists between fluorine and rubidium. The evolution of the concentrations of Rb and Cs in the minerals, in the core of the pegmatite and in the metasomatic aureole, can be explained using experimentally determined partition coefficients.

Keywords: rare-element-enriched granitic pegmatite, lithium, rubidium, cesium, K/Rb ratios, zinnwaldite, holmquistite, Volta Grande, Minas Gerais, Brazil.

SOMMAIRE

Les pegmatites granitiques de Volta Grande sont associées aux granites transamazoniens (Protérozoïque inférieur) intrusifs dans la ceinture de roches vertes archéennes du Rio das Mortes et localisés à la bordure méridionale du Craton du São Francisco, à Minas Gerais, Brésil. Les corps pegmatitiques, généralement de grandes dimensions, présentent une zone intermédiaire très développée à spodumène, quartz et feldspaths, partiellement entourée d'une zone aplitique aux contours irréguliers. Ils développent une auréole étendue de métasomatose à zinnwaldite, phlogopite et holmquistite. Le coeur riche en spodumène est continu ou segmenté, et contient des lentilles de lépidolite. Chimiquement, ces pegmatites sont caractérisées par leurs teneurs très élevées en rubidium et lithium. Le rubidium est concentré dans les minéraux potassiques: microcline, muscovite, lépidolite et zinnwaldite qui présentent souvent des teneurs exceptionnelles, correspondant à des rapports pondéraux K/Rb très bas, allant de 1,5 à 4,0. Dans les micas, on note une corrélation linéaire entre le rubidium et le fluor. Les coefficients de partage déterminés expérimentalement permettent d'expliquer l'évolution des concentrations en Rb et Cs dans les minéraux des pegmatites et de leur auréole de métasomatose.

Mots-clés: pegmatite granitique à éléments rares, lithium, rubidium, césium, rapport K/Rb, zinnwaldite, holmquistite, Volta Grande, Minas Gerais, Brésil.

INTRODUCTION

A field of large pegmatite bodies is associated with Early Proterozoic granites (Transamazonian, 1930 ± 20 Ma: Quéméneur & Vidal 1989) of the São João del Rei area in southern Minas Gerais, Brazil. One of the pegmatite swarms in this field, the Volta Grande pegmatites, can be described as spodumene-rich bodies displaying a very high degree of fractionation and enrichment of the rare lithophile elements Li and Rb, leading to the precipitation of spodumene and lepidolite, and K-feldspar as well as muscovite rich in Rb. These pegmatites were previously investigated by Heinrich (1964), who was interested in the Sn–Ta mineralization, for which they were being mined at that time. Currently, some of the pegmatites are mined for spodumene.

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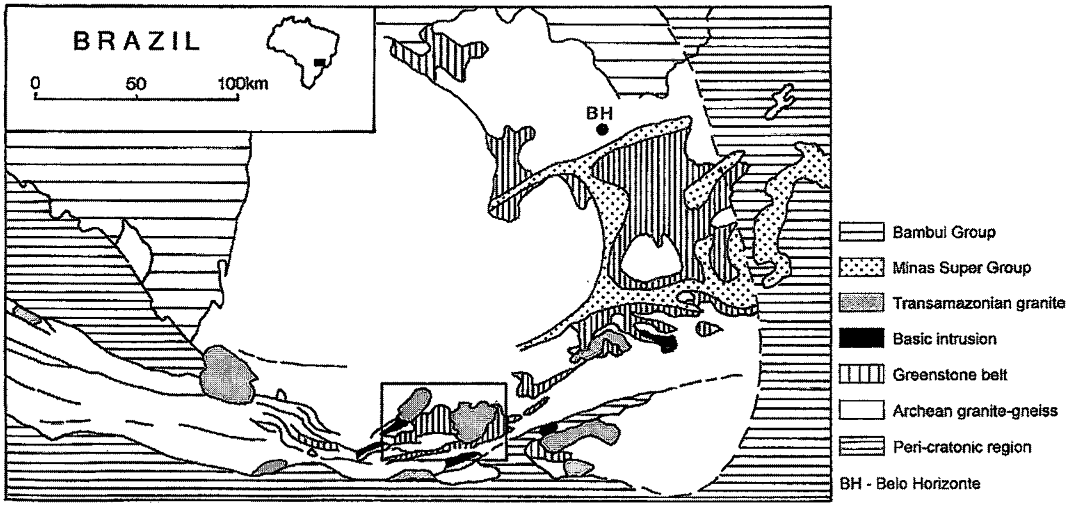

FIG. 1. Location map of the Transamazonian granites at the southern border of the São Francisco Craton. The boxed area corresponds to Figure 2.

The exceptional enrichment of the minerals in rubidium motivated a detailed study of the mineralogy and of the geochemistry of the Volta Grande pegmatites, to characterize the fractionation as well as to evaluate the extent of metasomatic transformations in the exocontact aureole. In addition, the experiments performed by several authors on the determination of partition coefficients of alkali elements between minerals or magma and aqueous fluid allow us to verify if a chemical equilibrium among the solid phases is attained. It will

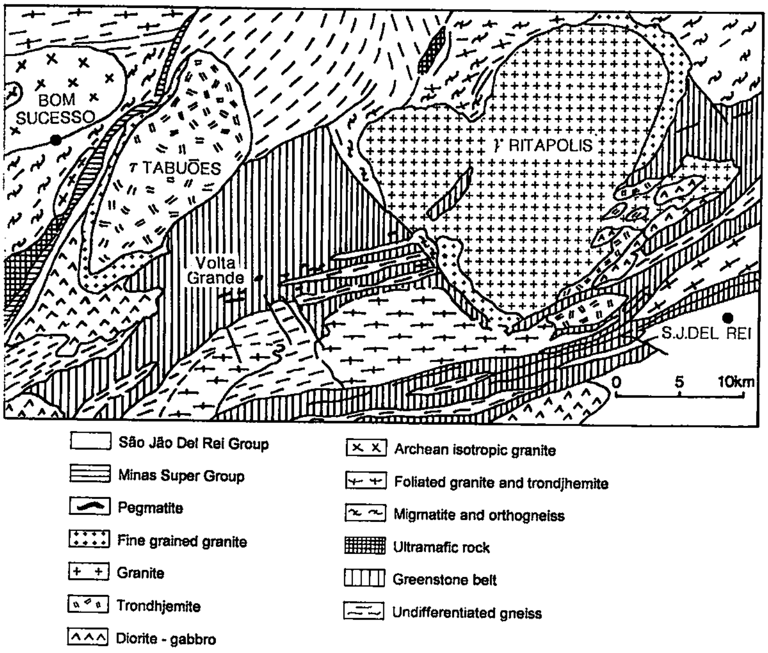

FIG. 2. Sketch map of the geological environment of the Volta Grande pegmatite field.

also be possible to estimate the composition of the fluid present during magmatic crystallization and to follow the metasomatic processes in the exocontact aureole.

REGIONAL GEOLOGICAL SETTING

The São João del Rei area lies on the southern border of the Precambrian (Transamazonian) São Francisco Craton (Fig. 1). This area consists of a series of Archean terranes metamorphosed in the amphibolite facies, and locally in the granulite facies toward the west. The terranes form part of the Rio das Mortes greenstone belt and are comprised of gneisses, amphibolites and meta-ultrabasic rocks. The gneisses are approximately granodioritic to trondhjemitic in composition. They cover large areas to the north and south and represent the oldest pre-greenstone formations.

The Archean terrane is cross-cut by late Archean granite (2700 Ma, Quéméneur & Vidal 1989) and by plutons of the Transamazonian suite. They are aligned in an east–west direction along the entire southern border of the craton, which is approximately 250 km long from the Quilombo granite in the west to the Campolide granite in the east. The Transamazonian plutons are extremely variable in composition: relatively basic rocks such as gabbro, diorite and trondhjemite seem to form zoned intrusions; younger granite, adamellite and granitic pegmatite occur to the north and west of the basic intrusive complexes.

Two large granitic massifs, the Tabuões and the Ritápolis massifs (Fig. 2), as well as two smaller and apparently older basic intrusions, the São Sebastian da Victoria gabbro and the Ibitunga, Rosario and Fazenda Martin diorites and tonalites, are found in the study area. The Ritápolis massif consists predominantly of granite and albite-rich adamellite (Quéméneur & Garcia 1993), and may have been the source of the Volta Grande pegmatites.

THE VOLTA GRANDE PEGMATITES

Pegmatites of the Volta Grande swarm were emplaced as flat subhorizontal sills that form large lenticular bodies elongated parallel to the foliation of the metamorphic host rocks (Fig. 3). The largest intrusion (body A) measured 1000 × 150 × 20 m before exploitation. Neighboring lenticular pegmatites (bodies B, C...) typically had maximum dimensions of approximately 700 × 120 × 10 m.

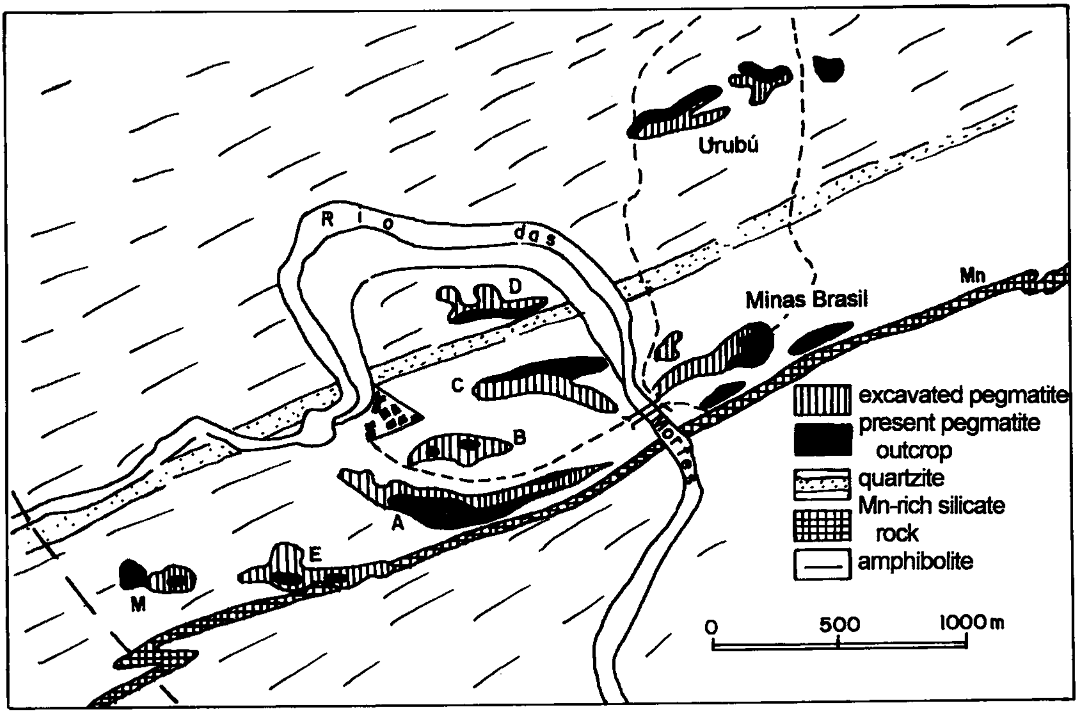

FIG. 3. The pegmatite field of Volta Grande.

Figure 4 shows the distribution of internal pegmatite zones in the remaining parts of pegmatite body A, according to Quéméneur (1987). The subhorizontal attitude of the pegmatites, subparallel to the erosional surface, and the extensive mining activities, render this representation of internal structure rather uninformative. Figure 5 shows a schematic vertical section through the A pegmatite, which can be taken as fairly representative of the internal structure, types of zones and zonal succession in the pegmatites examined. Three principal zones can be distinguished, from the contacts with the amphibolite wallrock inward: (1) wall zone, lower and upper, with (a) aplitic and (b) quartz-spotted facies, (2) intermediate zone, lower and upper, and (3) core zone, continuous or segmented and lenticular. The distribution of the zones is symmetrical in principle, but asymmetrical in terms of dimensions and volumes. The intermediate zone is volumetrically dominant, particularly its lower part.

External to the pegmatite proper, an external metasomatic aureole is developed in the amphibolite wallrock adjacent to the pegmatite contacts.

The wall zone

This zone shows a variable thickness from 0 to 4 m. The main component is an aplitic facies consisting of fine-grained, mm-sized albite with subordinate lenses of quartz (1–2 cm). This aplitic facies is found mainly along the footwall contact, and locally at the roof of the pegmatite. However, the upper wall-zone commonly contains a greater variety of mineral and textural facies than the lower segment. In the A body, a quartz-spotted facies is developed in this location, with rounded blebs of quartz (5–10 cm) in a matrix of K-feldspar, albite and muscovite. In the Minas Brasil body, the common aplitic facies adjoins the upper contact with amphibolite, followed inward by a layer of columnar spodumene (0.8–1.2 m) and quartz.

The inner contact of the aplitic facies usually has a thick border (10–30 cm) of muscovite. In the C body, this border also carries rounded blebs (5–10 cm) of K-feldspar and quartz in a matrix of spodumene, quartz, albite, K-feldspar and muscovite.

The intermediate zone

This zone, which constitutes 75–80% of the A pegmatite, has a coarse-grained granitic texture (0.5–2 cm). It is composed of 20–30% quartz, 20–30% spodumene, 15–20% albite, 10–15% K-feldspar, and 3–5% muscovite. This zone commonly shows a porphyritic aspect, as it contains fairly abundant crystals of spodumene 50 to 100 cm long. The lower segment of this zone is distinctly thicker than the upper one. However, the upper part tends to be texturally more diversified, as it contains numerous lenticular pods of K-feldspar and accessory quartz, 1–5 m long and 0.3–5 m across.

The core zone

This zone is centrally situated in terms of the zonal sequence, but is asymmetrically positioned in the upper central part of the pegmatite, mainly because of the asymmetry in volumes of the lower and upper intermediate zones. It consists of large flat prisms of

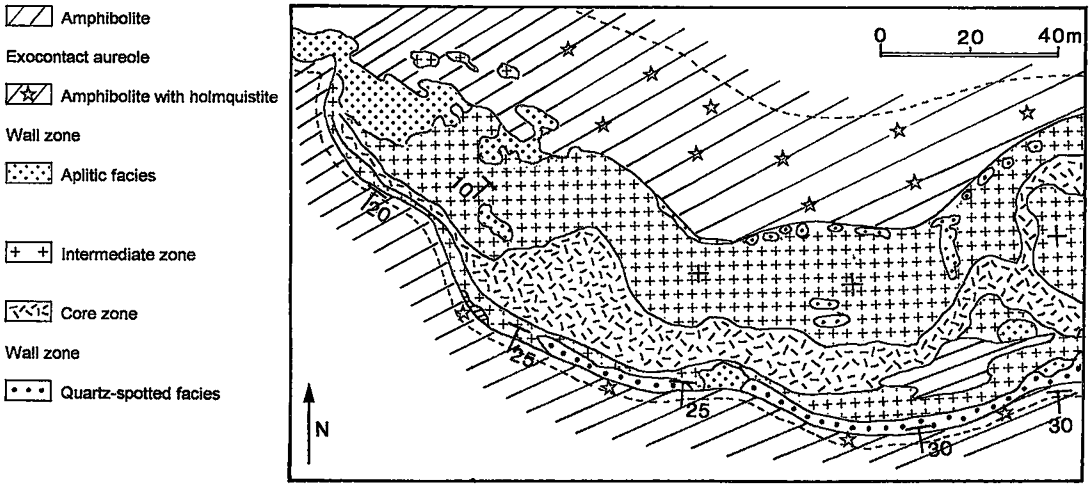

FIG. 4. Sketch of the zoning of the west part of the pegmatite body A, as it is currently preserved.

spodumene, 30 to 100 cm long, which constitute 60–80 vol.% of the core. The interstitial space is filled by quartz and K-feldspar. In the past, lenticular bodies of lepidolite were exposed in the core zone of the B pegmatite. Lepidolite was fine-flaked and compact. Although not currently available in the field, lepidolite was preserved in laboratory samples and examined in the present study.

The exocontact aureole

A metasomatic zone, a few meters across, is developed in the amphibolite wallrock. It consists of two distinct facies. The inner facies is 0–1 m wide; it consists of a compact dark-colored "glimmerite" formed by a complete replacement of hornblende by zinnwaldite and locally by zinnwaldite + holmquistite. The outer facies is 2–3 m thick; the extent of metasomatism of the amphibolite is rather limited, with holmquistite, zinnwaldite and mainly Li-bearing phlogopite dispersed throughout the fairly well preserved country-rock.

Comparison with other pegmatite occurrences

The mineralogy and internal structure of the Volta Grande pegmatites resemble those of other occurrences assembled by Černý (1992) into the category of albite–spodumene type, such as the Weinebene pegmatites of the Koralpe (Göd 1989) and the Kings Mountain pegmatites in the Appalachians (Kunasz 1982). They are all characterized by predominance of a spodumene-

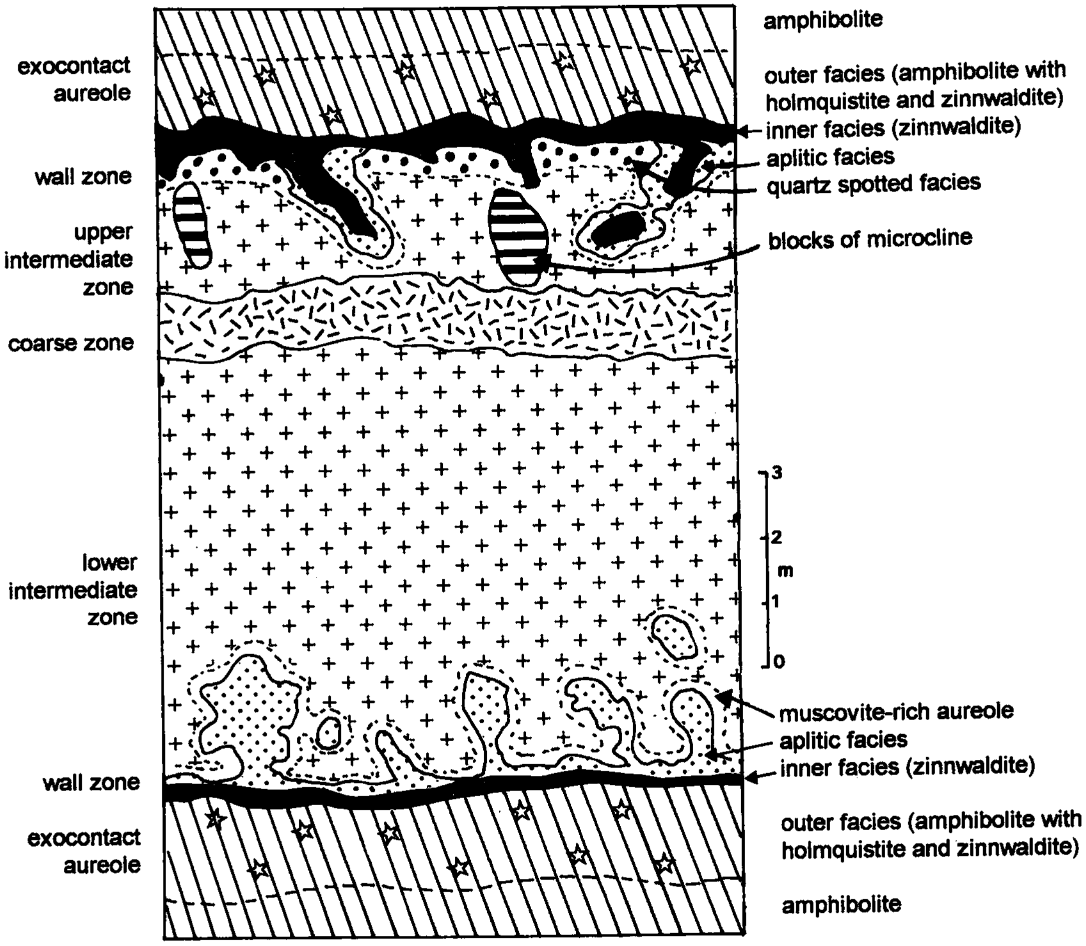

FIG. 5. Schematic vertical cross-section of the pegmatite body A showing a typical sequence of internal zones.

rich zone and the presence of minor aplitic units. However, the Volta Grande pegmatites are distinctly more strongly zoned than the classic near-homogeneous albite–spodumene pegmatites, and they also lack the high degree of preferred orientation of spodumene and K-feldspar typical of most pegmatites in this category. The albite–spodumene pegmatites tend to be steeply dipping to subvertical, but the Volta Grande bodies are subhorizontal; according to this feature, combined with the asymmetrical aspects of internal zoning, the Volta Grande occurrences have the characteristics of layered pegmatite (Černý 1991).

DESCRIPTION OF THE MINERALS

Albite occurs in the aplite zone, mainly as mm-size crystals. It is also present in the intermediate zone as crystals up to a few cm across or as mm-size inclusions in K-feldspar.

The *K-feldspar* is a clear grey perthite-free microcline. It is found in all pegmatite units except in the aplitic zone and in lepidolite lenses. In the C body, rounded blocks of K-feldspar (3 to 10 cm in diameter, in a matrix of quartz, albite, spodumene and muscovite) are present at the contacts with the aplitic zone. Microcline also is found in lenses in association with quartz, where crystals can reach several meters in length. This microcline contains 10 to 15% albite and approximately 5% quartz as discrete micro-inclusions. All the samples studied correspond to maximum microcline, as indicated by the triclinic indicator $\Delta(130)$ proposed by MacKenzie (1954).

Spodumene is present in all pegmatite units except in the aplitic facies of the wall zone and in the lenses of microcline and lepidolite. It is a major constituent of the intermediate zone, where it occurs as acicular or prismatic crystals several centimeters in length. Superimposed on this texture are large rod-shape crystals up to 1 m in length. Spodumene lenses consist of 60 to 80% spodumene, as prisms 0.2 to 1 m long, with the space between crystals filled by quartz and microcline.

Muscovite typically is found in the intermediate zone, particularly at the contact with the aplitic facies of the wall zone. It occurs as mm- to cm-size greenish yellow flakes. It is also locally present (in the western part of bodies A and B) as plates a few centimeters across in a muscovite – quartz – cassiterite assemblage (crystals of cassiterite in this zone attain 10 cm across). A second generation of muscovite is found in fractures and microcavities in the intermediate zone, in the core of the pegmatite, and associated with lepidolite.

Rose-mauve *lepidolite* is relatively rare. It is found in bodies A and B, in lenses of a fine-grained mica (0.1 to 1.0 mm) together with muscovite of the second generation (5%) and scattered quartz.

Accessory minerals are cassiterite, tantalite, microlite, monazite and garnet.

Ferromagnesian micas and *holmquistite* in the exocontact constitute the metasomatic aureole. As shown below, magnesian zinnwaldite is the main mineral in the inner facies of the aureole adjacent to the pegmatite contacts, but it grades into a more or less lithian phlogopite in the outer facies. Holmquistite (Quéméneur & Lagache 1994) is restricted to the outer facies alone.

GEOCHEMISTRY

The chemical composition of minerals was determined by electron microprobe, using Camebax and SX 50 instruments at the Université Pierre et Marie Curie (Paris), by Inductively Coupled Plasma (ICP) spectrometry at École des Mines at Saint-Étienne, and by wet chemistry at the Laboratoire de Géologie de l'École Normale Supérieure de Paris. Representative compositions of each of the major minerals of the pegmatite and of its contact aureole are given in Tables 1 to 5.

Electron-microprobe analysis were performed with the following standards: orthoclase for K, Si and Al, albite for Na, synthetic $MnTiO_3$ for Mn and Ti, synthetic Fe_2O_3 for Fe, diopside for Ca and Mg, topaz for F, synthetic $RbCaF_3$ for Rb, and Cs-rich beryl for Cs. The accelerating voltage was 15 kV, the sample current, 10 nA, and the counting time was 10 seconds for major elements and 20 seconds for minor elements. Data reduction was done using the PAP correction procedure.

Whole-rock compositions

For reasons evident in Figure 5, it is virtually impossible to collect a sample quantitatively representative of the bulk composition of any of the pegmatites studied. However, a few whole-rock analyses were performed on the intermediate zone. It constitutes most of the volume of the pegmatites; it cannot be considered totally representative of the bulk composition, but its modal composition shows good representation of all the mineral components, and its chemistry should be fairly representative of the degree of fractionation and rare-element accumulation in the pegmatite as a whole.

Five samples (3 kg each) of the intermediate zone were crushed, split and analyzed by ICP spectrometry. The results are consistent with the mineral modes and relatively uniform. They show a composition rich in SiO_2 (75 to 78 wt.%), roughly equal proportions of K_2O and Na_2O (2 to 3 wt.% each), and low Fe/Mn weight ratio (between 2 and 3). The most prominent characteristic of the whole-rock compositions is the high Rb content, ranging from 0.7 to 1.2 wt.% Rb_2O. Accordingly, the K/Rb weight ratio averages as low as about 2.5. This is a value rarely encountered even in highly fractionated rare-element pegmatites (Černý *et al.* 1985a), and it comes close to the values characterizing the most differentiated pegmatites analyzed to date. The K/Rb ratio is slightly lower than the approximate value derived for the Tanco pegmatite, in Manitoba (3.6: Černý *et al.* 1996), but the range of Fe/Mn values is higher (0.9 at Tanco). The Volta Grande data are slightly surpassed only by the geochemical signature of the Red Cross Lake pegmatites, also in Manitoba (Rb_2O 0.68–1.55 wt.%, K/Rb 2.6–1; Černý *et al.* 1994).

Mineral compositions

Representative results of electron-microprobe and wet-chemical analyses of *microcline* from two different pegmatite bodies are given in Table 1. Mic1 and Mic2 samples come from lenses of microcline of bodies A and C, and Mic3 comes from the intermediate zone of body C. These compositions have been taken from a batch of about 15 samples. Wet-chemical analyses indicate that the abundance of albite inclusions in microcline is on the order of 10 to 15%, which would enhance the K and Rb abundances in pure microcline. The chemical composition of microcline within individual samples and among the pegmatite bodies is rather uniform. For example, in sample Mic2, K_2O varies from 14.18 to 14.58 wt.%, and Rb_2O varies from 3.03 to 3.39 wt.%. From one sample to another, the variation is of the same order as indicated by the mean values of the three samples chosen. The average K/Rb weight ratio is 4 ± 0.5. This is the same order of magnitude as cited for the Tanco pegmatite (Černý *et al.* 1985a), but is greater than the value of 1.9 reported for feldspar in the lithian pegmatite at Red Cross Lake (Černý *et al.* 1985b, 1994). The average composition of microcline corresponds to $\mathrm{Or}_{0.86}\mathrm{Ab}_{0.04}\mathrm{Rbf}_{0.10}$.

Cesium values are more variable, between 500 and 1400 ppm, which is an average concentration for rare-element granitic pegmatite (Černý 1992), but relatively low compared to the rubidium concentrations. The average Rb/Cs value ranges from 22 to 61, and the average K/Cs value, from 89 to 250 [6–37 and 42–508, respectively, for Tanco; Černý *et al.* (1996)]. The K/Cs range is, however, far from the minimum value of 22.4 given by Černý *et al.* (1985b, 1996). These values suggest a generally low abundance of Cs in the Volta Grande pegmatites, and they may explain the absence of pollucite in these bodies, despite their otherwise high degree of fractionation.

Albite is found in all zones of the pegmatites except in the core zone and lepidolite lenses. The data presented in Table 1 represent the average composition of albite micro-inclusions in microcline. Albite associated with muscovite has the same composition. Albite is very pure and contains neither Ca, Rb nor Cs above the limits of detection of the microprobe (100 ppm).

Analyses of *muscovite* were performed on samples taken from different bodies of the pegmatite field, representative of both types of muscovite described in the preceding section. The first coarsed-grained type is distinguished by elevated contents of Fe (1 to 3 wt.% FeO: Table 2). Among the various samples analyzed and in each sample, rubidium contents are more variable than in microcline, 2.1 to 4.4 wt.% Rb_2O, but the average content is 3.1 wt%, which is of the same order of magnitude as in microcline. The resulting K/Rb weight ratios range from 5.3 to 2.0, with an average of 2.7. The second type of muscovite associated with lepidolite is iron-free and, in comparison to the first generation, has similar Rb but higher Cs contents (0.24 compared to 0.09. wt.% Cs_2O). The Rb/Cs ratio is correspondingly lower, from 33 to 11. The Rb_2O and K/Rb data match those for muscovite and lithian muscovite from Tanco (Černý *et al.* 1996); however, the Cs content of the Tanco micas is higher.

Compositions of two samples of *Li-rich micas* LP1 and LP2 (Table 3) have been determined on various flakes taken in two areas of the pegmatite field. Extensive variations are evident from the microprobe data for each individual flake, which presents a random mixture of compositions. The composition varies from that of the muscovite of the second generation, with which the lithian mica is associated, to that of a lepi-

TABLE 1. AVERAGE COMPOSITION OF ALBITE AND OF MICROCLINE IN THREE SAMPLES

feldspar	albite (4)	Mic1 (6)	Mic1 (chem.)	Mic2 (12)	Mic2 (chem.)	Mic3 (12)	Mic3 (chem.)
SiO_2	68.83	61.73	63.42	62.09	63.14	61.81	64.29
Al_2O_3	19.58	18.25	18.18	18.21	18.00	18.18	17.72
FeO	0.00	0.02	0.06	0.02	0.04	0.05	0.07
Na_2O	11.83	0.35	1.81	0.41	1.80	0.43	1.43
K_2O	0.07	14.41	12.83	14.31	13.28	14.14	13.11
CaO	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Rb_2O	0.00	3.22	2.87	3.14	2.97	3,26	2.65
Cs_2O	0.00	0.09	0.09	0.05	0.06	0.14	0.10
Li_2O	n.d.	n.d.	154ppm	n.d.	148ppm	n.d.	134ppm
Total	100.33	98.07	99.26	98.23	99.29	98.01	99.37

Compositions are obtained from results of electron-microprobe and wet-chemical analyses (chem.). The number of points analyzed by electron microprobe is given in parentheses. n.d.: not determined. Proportion of oxide constituents expressed in weight %, except as noted.

TABLE 2. AVERAGE COMPOSITION OF THREE SAMPLES OF FIRST-GENERATION AND ONE OF SECOND-GENERATION MUSCOVITE

muscovite	MS1 (ICP) 1st gener.	MS2 (5) 1st gener.	MS3 (13) 1st gener.	MS4 (9) 1st gener.	MS5 (3) 2nd gener.
SiO_2	45.74	42.71	44.47	46.34	44.71
Al_2O_3	30.72	39.97	33.89	35.12	34.30
TiO_2	0.04	0.06	0.05	0.07	0.01
FeO	2.35	1.87	2.59	2.75	0.00
MnO	0.52	n.d.	n.d.	0.40	0 08
MgO	0.43	0.02	0.00	0.02	0.03
CaO	0.05	0.02	0.00	0.01	0.01
Na_2O	0.33	0.18	0.34	0.15	0.51
K_2O	8.86	9.15	9.13	8.60	8.83
Rb_2O	3.22	3.18	3.13	2.65	2.70
Cs_2O	0.08	0.11	0.09	0.07	0.24
Li_2O	0.29	n.d.	n.d.	n.d.	n.d.
F	n.d.	n.d.	0.84	n.d.	0.73
H_2O	4.95	n.d.	n.d.	n.d.	n.d.
Total	97.58				

Compositions (expressed in weight %)are obtained by electron microprobe. The results of one ICP-MS analysis of first-generation muscovite (ICP) also are listed.

TABLE 3. AVERAGE COMPOSITION OF TWO MUSCOVITE-LEPIDOLITE SAMPLES

Muscovite -lepidolite	LP1 (chem.)	LP1 (2)	LP1 (11)	LP1 (17)	LP1 (2)	LP2 (chem.)	LP2 (5)	LP2 (4)	LP2 (11)
SiO_2	49.90	43.32	44.91	45.67	47.51	48.56	44.83	45.12	46.17
Al_2O_3	26.14	34.89	28.92	26.02	22.52	26.09	31.03	28.91	26.46
FeO	0.07	0.06	0.02	0.01	0.02	0.12	0.11	0.09	0.11
MnO	n.d.	n.d.	0.38	0.50	0.02	n.d.	n.d.	n.d.	n.d.
MgO	n.d.	n.d.	0.01	0.02	0.01	n.d.	n.d.	n.d.	n.d.
Na_2O	0.38	0.53	0.38	0.29	0.18	0.48	0.34	0.27	0.29
K_2O	7.68	8.96	8.29	8.08	7.90	8.64	8.99	8.88	8.46
Rb_2O	4.65	3.24	4.70	5.29	5.86	4.26	3.95	4.19	4.92
Cs_2O	0.49	0.23	0.52	0.68	1.18	0.38	0.24	0.28	0.29
Li_2O	3.30	n.d.	3.34*	3.55*	4.08*	3.49	n.d.	3.40*	3.70*
F	5.41	1.15	4.56	6.05	8.19	5.62	2.68	4.11	5.70
H_2O	4.10	n.d.	n.d.	n.d.	n.d.	4.26	n.d.	n.d.	n.d.
Total	102.12					101.90			

(*) indicates lithium contents calculated by the method of Tindle & Webb (1990). Note that the higher silica content in the results of the wet-chemical analyses result from the presence of quartz; hence all other elements are relatively depleted. The compositions are quoted in weight %.

dolite. In the absence of data for lithium, fluorine is a good indicator of this variation. The fluorine concentration ranges, for example, from 0.7 wt.% in muscovite of the second generation, to 2 wt.% in Li-poor areas of sample LP1, and can attain 8 wt.%. Representative electron-microprobe data on sample LP1 are therefore reported as averages of four groups, based on their average fluorine concentration. The first group has a very low concentration of F (<2 wt.%), the second corresponds to F between 4 and 5.5 wt.%, the third between 5.5 and 7 wt.%, and the last one to concentrations of 8 wt.%. Members of the first and last groups are rare. The compositions obtained on LP2 are presented in three groups, which average at ~2.7, ~4 and ~5.7 wt.% F.

Wet-chemical analyses, performed on the two samples of mica, show a higher concentration of silica owing to the presence of small quantities of quartz. Hence, all other elements are relatively depleted. It is not possible to quantify a correction because the results of the chemical analysis represent an average composition of intergrown mica aggregates, with unknown proportions of individual phases. The chemical analyses establish an average lithium content at 3.4 wt.% Li_2O. Tindle & Webb (1990) proposed an equation to estimate the Li contents of trioctahedral micas based on silica content. This equation was applied to the F-rich mica compositions, yielding Li_2O contents on the order of 3 to 4 wt.%.

Rubidium contents of the F-poor mica (3.2 wt.% Rb_2O) are slightly greater than those in the second generation of muscovite (2.7 wt.% Rb_2O), but the most F-rich domains contain up to 6.0 wt.% Rb_2O. Figure 6 illustrates the concentration of Rb_2O as a function of fluorine. A positive linear relationship exists between the two elements, and therefore also between lithium and rubidium. The correlation is valid for muscovite, lepidolite and zinnwaldite. The variation of Cs is less consistent, but follows the same trend. The K/Rb weight ratio in lepidolite is between 2.4 and 1.2, whereas the Rb/Cs value is about 10. The Rb content, the K/Rb and Rb/Cs values of the Volta Grande lepidolite are closely comparable to those of the Tanco "lepidolite" (heterogeneous but so far analyzed in bulk: Černý *et al.* 1996). However, the Red Cross lepidolite attains K/Rb and K/Cs values below 0.1 (Černý *et al.* 1994).

It is clear that lepidolite concentrates the larger rare-alkali elements in comparison to muscovite. This is due to the decrease in the tetrahedral rotation angle α from 11.6° in muscovite (Güven & Burnham 1967) to 6° in trilithionite or zinnwaldite (Guggenheim & Bailey 1977) and 3° in polylithionite (Takeda & Burnham 1969); this induces an increase in the K–O bond length in lithium micas and promotes an easier incorporation of Rb and Cs in the lithian micas in general, and polylithionite in particular. The proportion of muscovite, trilithionite and polylithionite can be calculated for each composition. For example, the average composition of sample LP1 corresponds to a mixture of 42% muscovite, 32% trilithionite and 26% polylithionite, with 6 wt.% F. As the fluorine increases, the proportion of muscovite decreases and that of polylithionite increases, in accord with the increasing F content.

A greyish white specimen of *spodumene* from the core zone was analyzed by wet chemistry. The composition is close to the oxide contents calculated from the ideal formula: 64.9% SiO_2, 27.54% Al_2O_3, 7.15% Li_2O and 0.4% wt.% Na_2O. However, Li_2O is lower by 0.9 wt.%, and the deficit cannot be fully compensated by Na_2O, as determined by the analysis. Among the trace elements, spodumene contains 1080 ppm K, 907 ppm Mn

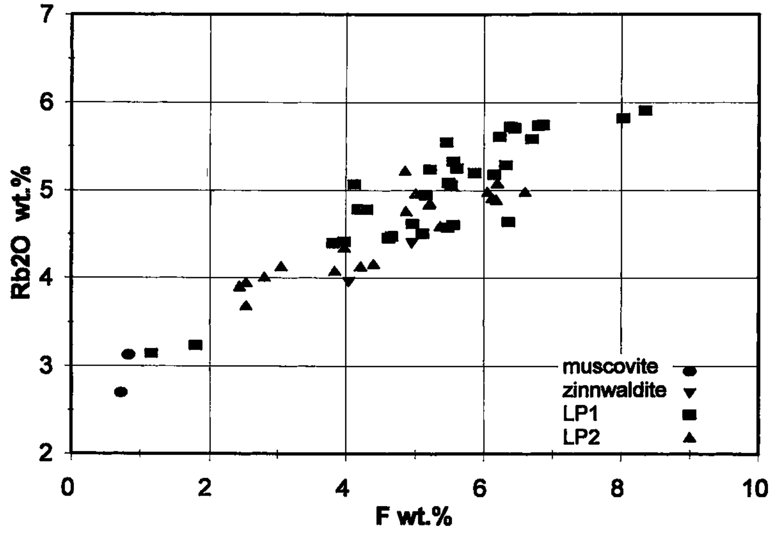

FIG. 6. The Rb_2O wt.% *versus* F wt.% contents of micas from the Volta Grande pegmatites.

and 85 ppm Rb; Fe was not detected. This composition is similar to those cited in the papers of Černý & Ferguson (1972) and Charoy *et al.* (1992), which also are characterized by a deficit in Li.

A few representative compositions of the *exocontact micas* were determined as a function of distance from the pegmatite contact (Table 4). One sample at the contact was analyzed by both electron-microprobe and wet-chemical methods; the results lead to an average structural formula $(Na_{0.02}K_{0.76}Rb_{0.21}Cs_{0.01})_{\Sigma 1.00}(Al_{0.9}Mg_{0.46}Fe^{2+}_{0.47}Mn_{0.02}Li_{1})_{\Sigma 2.85}(Si_{3.1}Al_{0.9})O_{10}(OH_{0.5}F_{1.5})$, corresponding to a Mg-rich zinnwaldite. Its composition can be compared to those of the yellow and brown micas observed by Semenov & Shmakin (1988) in the outer contact of rare-metal pegmatites from the Bastar area (India), and to synthetic Mg-rich zinnwaldite of Monier & Robert (1986). Though we have no data on the Li contents, we can assume that micas are richer in lithium at the contact, as their contents of Mg and Fe increase outward. The mica composition evolves to phlogopite even at a distance of 0.2–0.5 m. Rubidium concentrations also vary as a function of distance, being highest at the contact. Rb abundance decreases from 4 to 2 wt.% Rb_2O within 1 meter, whereas Cs apparently increases from 0.2 to 1 wt.% Cs_2O, but in a rather erratic pattern. Figure 6 shows that Rb and F contents of zinnwaldite follow the same correlation as do those of the micas from the core of the pegmatite. The K/Rb weight ratio ranges from 1.5 to 4, and Rb/Cs values, from 12 to 4. Zinnwaldite and phlogopite clearly replace the primary hornblende by reaction of the rare-alkali-rich pegmatitic fluid.

The exocontact micas of the Volta Grande pegmatites are distinctly more magnesian (Fe/Mg weight ratio 2.2–1.4) than those at Tanco (3.5–2.2; Morgan & London 1987) or Red Cross Lake (5.3–2.1, exceptionally 1.5; P. Černý, pers. comm. 1996). At Tanco, both the Rb and Cs abundances decrease (from 2.0 to 0.4% Rb_2O, and from 1.5 to 0.3% Cs_2O, respectively) with increasing distance from the contact over 3 meters. The K/Rb and K/Cs weight ratios correspondingly increase (from 3.6 to 19.2 and from 4.7 to 25.3, respectively); the Rb/Cs weight ratio oscillates irregularly between 1.2 and 1.5 (Morgan & London 1987). The behavior of Cs is distincly different at Tanco from our observations

TABLE 4. AVERAGE COMPOSITION OF SIX MICA SAMPLES, RANGING FROM Mg-RICH ZINNWALDITE TO PHLOGOPITE

micas of metam. aureole	Mg-rich Zinn. (chem.)	Mg-rich Zinn. (22) contact	Mica 2 (8) contact	Mica 3 (2) 20-50 cm	Mica 4 (5) 50-80 cm	Mica 5 (6) 1m	Mica 6 (8) 1m-2m
SiO_2	44.39	42.60	41.54	40.78	42.25	39.27	38.56
Al_2O_3	20.02	20.90	18.01	16.14	17.25	16.04	16.34
TiO_2	0.83	0.85	1.49	0.56	0.72	1.01	1.10
FeO	6.64	7.50	11.23	15.03	12.15	14.53	16.41
Fe_2O_3	1.49						
MnO	0.37	0.30	0.21	0.33	0.24	0.41	0.24
MgO	3.91	4.05	6.77	12.11	11.47	12.61	11.15
CaO	0.23	0.21	0.01	0.07	0.07	0.00	0.02
Na_2O	0.40	0.12	0.10	0.00	0.06	0.19	0.06
K_2O	9.16	8.20	7.58	6.97	8.41	8.57	7.94
Rb_2O	3.96	4.40	4.82	3.21	1.97	1.91	2.26
Cs_2O	0.21	0.35	0.47	0.51	0.54	0.36	1.04
Li_2O	3.33	2.67(*)	n.d.	n.d.	n.d.	n.d.	n.d.
F	4.04	4.96	n.d.	n.d.	n.d.	n.d.	2.79
H_2O	1.88	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total	100.86						

The samples are arranged, from left to right, in terms of their distance from the pegmatite contact. The symbol * indicates lithium contents estimated for Mg-rich zinnwaldite using the method of Tindle & Webb (1990), which is not valid for the higher concentrations of Mg. The compositions are quoted in weight %.

at Volta Grande. The chemistry of the exocontact mica at Red Cross Lake was not examined in relation to distance from the pegmatite, but the biotite is invariably strongly zoned and attains K/Rb and K/Cs weight ratios as low as 0.18 and 0.05, respectively, in the outer zones (Černý *et al.* 1994). The Rb/Cs ratio is extremely variable.

Five different samples of *holmquistite* (Table 5) were analyzed by electron microprobe, and one was characterized by wet chemistry. The five compositions obtained are very similar (Quéméneur & Lagache 1994), so that only an average composition is given in Table 5. This composition yields the structural formula $(Li_{1.9}Na_{0.1})(Mg_{1.4}Fe_{1.6})(Al_2Si_8)O_{22}(OH,F)_2$, which matches the theoretical formula given by London & Burt (1982). Comparison with compositions published in the literature shows that it is richer in Fe and poorer in Mg than most of the samples studied, but very close to holmquistite from Tanco, Manitoba (Morgan & London 1987). It is very poor in Na, K, Rb and Cs.

As general observations, we have documented that among the pegmatite minerals *sensu stricto,* Rb and Cs are concentrated in the potassic minerals, microcline, muscovite and lepidolite. Li, which is one of the major constituents of spodumene, is also concentrated in the micas. In the metasomatic exocontact assemblage, the micas contain high abundances of Li, Rb and Cs, and Li is also present in holmquistite.

In general, the Rb-rich potassic minerals of the pegmatite have K/Rb weight ratios of approximately 1 to 4, depending on the mineral. As we have stated before, the structural features of zinnwaldite are similar to those of trilithionite, so that the K/Rb values for these two minerals also are similar and close to 1.5–2. In the exocontact aureole, this ratio is observed in the magnesian zinnwaldite proper near the contact, but Rb decreases as a function of distance from the contact, and the K/Rb value increases accordingly. Concerning Cs, the Rb/Cs weight ratio is significantly lower in late minerals such as lepidolite, and it also tends to decrease with distance from the pegmatite into the metasomatic aureole.

TABLE 5. AVERAGE COMPOSITION OF HOLMQUISTITE

holmquistite	5 samples	(chem.)
SiO_2	58.66	59.05
Al_2O_3	12.75	12.29
TiO_2	0.04	0.17
FeO	15.08	10.13
Fe_2O_3		3.66
MnO	0.28	0.22
MgO	6.40	6.60
CaO	0.07	0.56
Na_2O	0.46	0.29
K_2O	0.05	0.06
Rb_2O	n.d.	94ppm
Li_2O	n.d.	2.66
F	0.29	0.10
H_2O	n.d.	2.49
Total		98.28

The average is calculated from the compositions of five samples obtained by electron microprobe. The composition of one of the samples was corrected for the presence of quartz. The average bulk composition is quoted in weight %.

DISCUSSION

In order to explain the above data, we next examine the experimentally determined partition coefficients for Rb and Cs between hydrothermal fluids and minerals, which have been extensively studied for feldspars and micas by several authors. Some experiments performed on equilibria between melt and aqueous fluid have shown that the partition coefficients of Rb and Cs are close to unity for silicate melts ranging from $Qtz_{40}Ab_{60}$ to $Qtz_{40}Or_{60}$ (Carron & Lagache 1980). The partitioning of elements between two solids depends on T and P, but not on the environment (fluid or melt), that led to the equilibration. Experimental data will then provide information on the composition of pairs of minerals in equilibrium and also on the composition of the fluid coexisting with melt during magmatic crystallization or of the fluid that induces re-equilibration of the minerals in the core of the pegmatite or in the exocontact.

Rubidium

The partition coefficient for rubidium between sanidine and hydrothermal solution has been determined experimentally by several authors (Lagache 1968, Volfinger 1969, Beswick 1973, Lagache & Sabatier 1973). These authors have demonstrated that the partition coefficient $C_{san/aq}$ expressed as atomic ratios $(K/Rb)_{san}/(K/Rb)_{aq}$ is constant and equal to 2.22 at 600°C and 1 kbar for concentrations up to 4 wt.% rubidium, *i.e.*, Rb is weakly partitioned in favor of the solution. The potassic feldspars from the Volta Grande pegmatites contain Rb concentrations similar to those of the experimental studies.

In the case of muscovite, the partition coefficient, expressed in the above manner, determined experimentally by Volfinger (1969), is 1.82 for the same experimental conditions. For a given solution, rubidium is thus more concentrated in muscovite than in sanidine. The partition coefficient between muscovite and sanidine $C_{mus/san} = (K/Rb)_{mus}/(K/Rb)_{san}$ is 0.82. In the first-generation muscovite of Volta Grande, the K/Rb atomic ratios ranges from 11.6 to 4.4, with an average of 5.9, whereas this ratio in the microcline is approximately 8.8 (Table 6). The resulting partition coefficient is thus 1.3 to 0.5, values that bracket the experimentally determined value of 0.82. In another rare-element pegmatite in the same area, the Urubu pegmatite, Quéméneur *et al.* (1993) measured a partition coefficient of 1 be-

TABLE 6. AVERAGE WEIGHT (K/Rb AND Rb/Cs) AND ATOMIC (K/Rb) RATIOS FOR PEGMATITE-FORMING MINERALS RICH IN RARE ALKALI ELEMENTS

	K/Rb weight	K/Rb atom.	Rb/Cs weight
microcline	4	8.8	32
muscovite 1 st gener.	2.7 (5.3-2)	5.9 (11.6-4.4)	33
muscovite 2 nd gener.	2.7	5.9	11
lepidolite	2.5-1.4	5.4-3.1	15-7
Mg-rich zinnwaldite (contact)	1.5	3.3	12
phlogopite (20cm-1m)	2-4	4.5-9	4-2

tween muscovite and K-feldspar. Considering all the simplifications inherent to the experimental results (pressure and temperature of equilibration not precisely known in the natural pegmatites, the fact that experiments were performed with sanidine, whereas the pegmatite contains microcline, for example) as well as the heterogeneous distribution of Rb in muscovite, there is good agreement between the experimentally determined partition coefficients and those measured between the minerals of the pegmatite.

In conclusion, a large preferential partitioning of Rb into one specific potassic mineral is not observed. This observation fits well with an equilibrium between the compositions of the two minerals. In contrast, the fluid coexisting in equilibrium with these minerals should be weakly enriched in Rb. An estimation of the composition of this fluid can be calculated by:

$$(\mathrm{K/Rb})_{\mathrm{aq}} = (\mathrm{K/Rb})_{\mathrm{mineral}}/C_{\mathrm{mineral/aq}}$$

which results in a K/Rb value of 4.0 (atomic) for the fluid in equilibrium with the minerals during crystallization.

There are no experimental partition data for lepidolite. However, using the K/Rb ratio measured in the most F-rich compositions of lepidolite from the pegmatite, and the ratio estimated for the fluid above, the partition coefficient for rubidium between lepidolite and solution can be calculated by:

$$C_{\mathrm{lep/aq}} = (\mathrm{K/Rb})_{\mathrm{lep}}/(\mathrm{K/Rb})_{\mathrm{aq}} = 3.1/4 = 0.78$$

Lepidolite thus weakly concentrates rubidium, more than microcline and muscovite. The value calculated is close the coefficient of 0.65 obtained experimentally by Volfinger (1974) for Rb partition between fluid and another trioctahedral mica, phlogopite. Once more, we must recall that the structure of lithian micas is more favorable to the introduction of large alkali cations. Lepidolite and zinnwaldite are among the few minerals which concentrate Rb from aqueous fluid.

The metasomatic aureole is rich in micas. As the partition coefficient favors the micas, the Rb content of the metasomatic fluid must decrease progressively during its flow across the exocontact zone. Table 4 presents the compositions of exocontact micas (zinnwaldite and phlogopite) as a function of distance from the pegmatite contact, from 0.1 to 1.0 m, and illustrates the decrease of rubidium contents in the exocontact.

Cesium

The partition coefficients for cesium between sanidine or muscovite and an aqueous solution have been experimentally determined (Lagache 1969, Volfinger 1969, Carron & Lagache 1980) for the same conditions as for rubidium. In the case of sanidine, the partition coefficient is constant for the concentrations observed in the K-feldspar of the pegmatites, and Cs is concentrated by a factor of 40 in the fluid. In others words, the hydrothermal fluid will be strongly enriched in Cs with progressive crystallization.

For muscovite, the partition coefficient varies with cesium concentration, from 11 at 10 ppm to 28 at 3 wt.% Cs (Volfinger 1969). The muscovite in the Volta Grande pegmatites generally contains 0.1 to 0.2 wt.% Cs; thus we can estimate that Cs concentration in the fluid was approximately 25 times higher.

The increase in Cs concentration in the fluid during the course of crystallization is more pronounced, compared to the modest increases expected for Rb, discussed above. The Rb/Cs value (Table 6) decreases from the first generation of pegmatite-forming minerals (microcline and muscovite) to the lepidolite and muscovite of the second generation, as well as with distance from the contact in the minerals of the metasomatic aureole. It is apparent that the micas most remote from the contact are the most Cs-rich. The Rb/Cs weight ratio attains very low values, down to 4, indicating a gradual depletion of Rb in the fluid due to zinnwaldite crystallization, and an enrichment of Cs, since this element is invariably partitioned in favor of the fluid.

Lithium

Rubidium and cesium never form end-member mineral phases in the Volta Grande pegmatite, but occur in potassic minerals. In contrast, lithium is a major constituent of important minerals in the pegmatite (spodumene and lepidolite) and contact aureole (Mg-rich zinnwaldite and holmquistite). The original magma was very rich in lithium, which resulted in the crystallization of the large mass of spodumene. The fluids that were generated also were Li-rich, which resulted in the crystallization of lithian muscovite and lepidolite in the fractures, and in the transformation of minerals in the contact aureole to lithian micas and holmquistite (Wood & Williams-Jones 1993, Quéméneur & Lagache 1994).

CONCLUSIONS

The Volta Grande pegmatites are fractionated to a degree rarely observed in rare-element granitic pegmatites. The K/Rb weight ratio in potassic minerals ranges from 4.0 to 1.5, both in the pegmatite and in the contact aureole. The partition coefficients for Rb and Cs determined from experimental studies have been successfully used to account for the observed distribution of these elements. In the core of the pegmatites bodies, there is no preferential partitioning of Rb in the potassic minerals. Crystal/melt or crystal/vapor partitioning can explain the enrichment of cesium in the residual fluid and, as a consequence, in the minerals of the aureole of metasomatism. In any event, the total concentration of cesium is too low to permit the crystallization of pollucite, as described in some rare-element pegmatites. In the aureole of metasomatism, rapid decrease of rubidium and relative increase of cesium with increasing distance from the contact depend on the same processes. Finally, the high concentration of Li resulted in the crystallization of spodumene and lepidolite, as well as in the widespread occurrence of magnesium-rich zinnwaldite and holmquistite in the metasomatic aureole.

ACKNOWLEDGEMENTS

This work has been made possible through the financial participation of a CAPES–COFECUB project and of FAPEMIG. We are indebted to the MIBRA Society for giving us facilities in our field work. Technical assistance from N. Catel and L. Mamou are gratefully acknowledged. We also want to thank R. Linnen for the first English version of the manuscript. We are very grateful to P. Černý, who carefully improved the final version of the paper. We benefitted from his knowledge of granitic pegmatites, as applied to a Brazilian pegmatite that deserved to be described. We also gratefully aknowledge many helpful suggestions from R.F. Martin and from an anonymous reviewer.

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Received December 21, 1994, revised manuscript accepted October 13, 1996.