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Minor- and trace-element composition of trioctahedral micas: a review

G. TISCHENDORF¹, H.-J. FÖRSTER^{2,*} AND B. GOTTESMANN²

Bautzner Str. 16, 02763 Zittau, Germany

GeoForschungsZentrum Potsdam, Telegrafenberg, 14473 Potsdam, Germany

ABSTRACT

More than 19,000 analytical data mainly from the literature were used to study statistically the distribution patterns of F and the oxides of minor and trace elements (Ti, Sn, Sc, V, Cr, Ga, Mn, Co, Ni, Zn, Sr, Ba, Rb, Cs) in trioctahedral micas of the system phlogopite-annite/siderophyllite-polyolithionite (PASP), which is divided here into seven varieties, whose compositional ranges are defined by the parameter *mgli* (= octahedral Mg minus Li). Plots of trace-element contents vs. *mgli* reveal that the elements form distinct groups according to the configuration of their distribution patterns. Substitution of most of these elements was established as a function of *mgli*. Micas incorporate the elements in different abundances of up to four orders of magnitude between the concentration highs and lows in micas of 'normal' composition. Only Zn, Sr and Sc are poorly correlated to *mgli*. In compositional extremes, some elements (Zn, Mn, Ba, Sr, Cs, Rb) may be enriched by up to 2–3 orders of magnitude relative to their mean abundance in the respective mica variety. Mica/melt partition coefficients calculated for Variscan granites of the German Erzgebirge demonstrate that trace-element partitioning is strongly dependent on the position of the mica in the PASP system, which has to be considered in petrogenetic modelling.

This review indicates that for a number of trace elements, the concentration ranges are poorly known for some of the mica varieties, as they are for particular host rocks (i.e. igneous rocks of A-type affiliation). The study should help to develop optimal analytical strategies and to provide a tool to distinguish between micas of 'normal' and 'abnormal' trace-element composition.

KEYWORDS: trioctahedral micas, phlogopite, biotite, siderophyllite, lepidolite, trace elements, statistical analysis, partition coefficients.

Introduction

MICA minerals belong to the most important OH-bearing silicates on Earth. Trioctahedral micas in particular are abundant constituents in a wide variety of magmatic, metamorphic and hydrothermal rocks. Ferromagnesian micas are significant mafic minerals in intermediate and basic igneous rocks whereas Li-bearing micas predominate in peraluminous leucogranites, associated pegmatites and ore deposits.

Because of their complex crystal structure, trioctahedral micas may incorporate a large number of elements of different ionic sizes and charges by a variety of isomorphic substitutions. Many of these elements, however, usually occur in concentrations at a low ppm level. Under certain geological conditions, elements such as Ti, F, Li, Rb, Cs, Ba, Mn and Zn may occur in concentrations approaching a few wt.%, even up to 20 wt.%. Micas are useful as monitors of the physicochemical environment, in which they grew, as well as indicators of the metallogenetic potential of their host rock (e.g. Černý and Burt, 1984; Guidotti, 1984; Hewitt and Wones, 1984; Speer, 1984). Moreover, trioctahedral micas in igneous rocks have been used as a discriminating tool in the identification of the nature of their host

* E-mail: forhj@gfz-potsdam.de

granites (e.g. Nachit *et al.*, 1985; Abdel-Rahman, 1994).

Despite the wide distribution of micas in almost all types of rocks and their significance in resolving the *PTX*-conditions during magmatic, metamorphic and metasomatic/hydrothermal processes, no comprehensive outline of their minor- and trace-element composition has been provided in the literature. Several compilation studies on this subject have been published (e.g. Haack, 1969; Ushakova 1971, 1980; Gordiyenko, 1973; Semenov *et al.*, 1974; Mitchell, 1985; Lyakhovich and Lyakhovich, 1987; Bulkin, 1989; Foord *et al.*, 1995; Wise, 1995) that have one or more of the following problems: (1) only a limited spectrum of trace elements was considered; (2) micas from only a single rock type were considered; (3) the review was regional and not global; (4) the study only considered a certain number of trioctahedral micas; or (5) no major element or Li_2O data were reported which preclude identification of the mica variety.

This paper provides a reconnaissance evaluation of the contents of various minor (Ti, Mn, F) and trace elements (Rb, Cs, Sr, Ba, Sc, V, Cr, Co, Ni, Zn, Sn, Ga) in trioctahedral micas from a broad spectrum of rock types, based mainly on data from the literature. Following Rieder *et al.* (1999), trioctahedral micas are discriminated from dioctahedral micas by >5 octahedral cations (per 22 oxygen equivalents). The major goal of this work is to establish and document the levels and ranges of trace-element contents of the system phlogopite-annite/siderophyllite-polyolithionite (PASP), which has been subdivided by Tischendorf *et al.* (1997) into seven varieties (i.e. phlogopite, Mg biotite, Fe biotite, siderophyllite, protolithionite, zinnwaldite, lepidolite).

It is beyond the scope of this paper, and impossible within the limited space available, however, to discuss in detail the physicochemical conditions, under which the extreme compositional variants were formed. Indeed, for many of the elements considered here, these conditions are only poorly known or controversial. Mica compositions are dependent on several factors including crystal-chemical and crystal-physical parameters as well as external factors such as temperature, pressure, oxygen, fluorine and chlorine fugacities, whole-rock composition, and the assemblage of crystallizing phases (i.e. the coexisting mineral association). Separating the influence of the different factors is difficult.

Database

The study considered element contents obtained both from mineral separates and single grains analysed by various methods of local analysis (electron microprobe and, to a lesser extent, ion microprobe, proton microprobe, and laser-ablation inductively coupled plasma-mass spectrometry).

In the past, the vast majority of analyses of minor and trace elements in mica was performed using mineral separates. Bulk analysis of mineral separates permits accurate determination of elements in the low ppm concentration level but suffers from several potential problems. Thus, it can be misleading or unrepresentative because more than one generation of micas may be present in a given sample, and because individual mica grains may be zoned. Furthermore, intergrowths, overgrowths and inclusions of other minerals in mica can affect the results of bulk chemical analysis. For example, in peraluminous granitic rocks, inclusions of zircon (Zr, Hf), apatite (Ca, P, F, *LREE*, Y), monazite (*LREE*, Th), xenotime (Y, *HREE*, U), uraninite (U, Th), thorite (Th, U, *REE*, Y), tourmaline (B), and other accessory minerals are generally responsible for atypically elevated contents of these elements measured in mica separates. All these complications pose no great problems for the diverse local analytical techniques of which the electron microprobe is by far the most commonly used for mica analysis. The electron microprobe, however, was designed for major- and minor-element analyses and is only of limited use for trace-element analysis. Depending on the element, the detection limits typically lie between 200 and 800 ppm, which usually restrict utilization of the electron microprobe for the measurement of Cr, Ni and Ba in ferromagnesian micas (phlogopite, biotite) and Rb and Cs in lithian micas (lepidolite, zinnwaldite). Moreover, under standard analytical conditions, compositional data for elements occurring in concentrations of <0.05 – 0.1 wt.% exhibit large analytical errors. A great portion of the observed data scatter in the low concentration range can probably be ascribed to this factor.

Selection of the minor and trace elements was performed according to the following criteria: (1) analytical data must be available for all varieties of the PASP system in abundances which allow safe conclusions; and (2) the elements are constituents of the mica structure and usually not typical of accessory minerals

which may form potential inclusions in the micas. These conditions are met best by the elements discussed in this paper. However, for mica separates, some contamination because of mineral inclusions (rutile, ilmenite, cassiterite) cannot be excluded, but the effects are considered minor.

The data available for statistical analysis of the 15 elements are listed in Table 1. For the study of the behaviour of Ba, Cr, Cs, F, Mn, Ni, Rb, Ti and Zn, more than 1,000 compositions were selected. For the elements Co, Ga, Sc, Sn, Sr and V, between 1,000 and 500 data could be collected from the literature; the total number of data was 19,619. More than half of the total number refer to the most widespread micas in nature, Mg biotite and Fe biotite. On the other hand, <1,000 analyses define the trace-element distribution patterns in lepidolite. For a number of elements in phlogopite (Cs, Ga, Sc, Sn, V) and lepidolite (Co, Cr, Ga, Ni, Sc, V), 20 or even fewer data could be compiled which seem to have no critical impact on the conclusions drawn, however, because the contents of these elements correspond well with those predicted from the general trend of the individual elements in the PASP system.

The number of analytical data decreased from igneous rocks to metamorphic rocks to hydrothermal/metasomatic rocks. However, investigation of element distribution in micas, performed

separately for these three major groups of rocks, revealed similarity in their patterns. Basically the same holds true for micas from alkaline and peraluminous granites.

Many trace-element data were produced for micas from collisional and subduction-related I- and S-type granites, whereas only a small amount of information was available for those from post-collisional and anorogenic granites of A-type affinity.

Statistical analysis and presentation of data

Interpretation of the trace-element contents was performed as a function of mica composition, i.e. of mica varieties. Subdivision of the PASP system into compositional varieties (phlogopite, Mg biotite, Fe biotite, siderophyllite, protolithionite, zinnwaldite, lepidolite) follows the classification scheme of Tischendorf *et al.* (1997), which is based upon the traditional and widely used mica classification of Foster (1960*a,b*).

We are aware that this classification differs to some extent from that recently proposed by Rieder *et al.* (1999) and approved by the International Mineralogical Association. The Rieder *et al.* (1999) classification is very useful from the viewpoint of species definition and official nomenclature but, in our view, it is not as useful for dealing with compositional varieties of

TABLE 1. Number of data used for determination of the element distribution in the mica varieties.

Oxide/ element	Phlogo- pite	Mg biotite	Fe biotite	Sidero- phyllite	Proto- lithionite	Zinn- waldite	Lepi- dolite	Total
BaO	606	732	615	131	74	64	17	2239
CoO	22	205	367	100	71	34	8	807
Cr ₂ O ₃	509	464	534	127	56	33	8	1731
Cs ₂ O	20	161	356	212	163	183	115	1210
F	359	447	457	294	218	228	167	2170
Ga ₂ O ₃	3	135	202	98	53	60	124	675
MnO	269	306	369	236	161	149	116	1606
NiO	320	309	480	127	67	37	10	1350
Rb ₂ O	170	362	580	291	175	229	153	1960
Sc ₂ O ₃	12	127	237	73	54	32	11	546
SnO ₂	2	90	239	153	98	65	22	669
SrO	37	186	293	85	54	69	33	757
TiO ₂	424	523	396	225	147	116	79	1910
V ₂ O ₃	20	232	423	124	67	41	13	920
ZnO	25	264	437	159	74	87	23	1069
Total	2798	4543	5985	2435	1532	1427	899	19619

micas for petrologic and geochemical purposes. Because this study is aimed primarily at petrologists and geochemists, and to be consistent with the mica subdivision adopted in our previous papers (Tischendorf *et al.* 1997, 1999a), we took advantage of the expanded terminology originally proposed by Foster (1960a,b). To provide the reader with the official names approved by the IMA, Table 2 compares the nomenclature of both mica classifications.

In the classification of Tischendorf *et al.* (1997), the parameter *mgli* (= octahedral Mg minus octahedral Li; Mg–Li) is used as a quantitative measure to classify a mica as a particular variety of the PASP system (see Table 2). In Figs 1–15, the concentrations of the trace elements (mostly as oxides) are plotted as a function of *mgli*. If Li was not analysed, Li₂O has been estimated using empirical equations calculated by Tischendorf *et al.* (1997, 1999a). These equations take advantage of well-established functional relations between SiO₂ and MgO with Li₂O, taking into account the geological environment in which a particular mica was formed. Although indirect estimation of Li₂O may cause errors in the parameter *mgli*, these errors have no impact on the general trace element patterns shown.

One drawback of the parameter *mgli* is that it does not specify the most Fe-rich trioctahedral micas, i.e. annite with octahedral Fe_{tot} >4, which plot in the fields of siderophyllite or Fe biotite in Figs 1–15. Because <5% of the data refer to this particular variety, this disadvantage is negligible.

Although not belonging to the PASP system, compositional extremes with respect to trace-element abundances, e.g. hendricksite

K₂Zn₆Al₂Si₆O₂₀(OH)₄, masutomilite K₂Li₂Al₂Mn²⁺Al₂Si₆O₂₀F₄, anandite Ba₂Fe₆²⁺Fe₃³⁺Si₆O₂₀S₂(OH)₂, kinoshitalite Ba₂Mg₆Al₄Si₄O₂₀(OH)₄, and ferrokinoshitalite Ba₂Fe₆²⁺Al₄Si₄O₂₀(OH)₄, are included in this study for the purposes of completeness, and are specifically mentioned in the text. For the purpose of data presentation, they are plotted according to their *mgli* value in Figs 1–15.

Selection of the most appropriate statistics has considered that, usually, the distribution of the elements or element oxides at a given *mgli* value is not normal (i.e. symmetrical, bell-shaped curves) but is asymmetric or skewed in one way or another (see Figs 1–15). Thus, none of the traditionally-used characteristics of the mean and standard deviation are adequate and they yield seriously biased results. The arithmetic means of such distributions over-estimate the mid-points of their distributions considerably, and the intervals defined by plus-or-minus standard deviations will not contain correct proportions of the distributions.

Because not all the variables have similar distributions, non-parametric statistics were used for the comparisons. The three measures, 15th percentile, 50th percentile, and 85th percentile, are robust non-parametric statistics that express the variability in observations (by the 15th–85th interquartile range) and the central tendency of the observations (by the median or 50th percentile). These measures are comparable directly from one geochemical variable to another, regardless of their distribution pattern.

To focus on the extreme compositions, the 15th–85th interquartile range is considered to characterize micas of ‘normal’ composition with

TABLE 2. Compositional range of mica varieties as function of *mgli* [= Mg – Li octahedral].

Nomenclature this study	Nomenclature IMA 1998	<i>mgli</i>	Mg	Li	Al ^{VI}	Fe ²⁺ +Fe ³⁺
Phlogopite	Phlogopite	6.0..4.0	6.00–4.01	<0.01	<0.2	<1.4
Mg biotite	Ferroan phlogopite	4.0..2.0	4.01–2.09	0.01–0.09	<0.5	1.4–2.6
Fe biotite	Magnesian siderophyllite	2.0..0.6	2.09–0.95	0.09–0.35	0.1–0.8	2.1–4.6
Annite	Annite	2.0..–0.6	2.09–0.20	0.09–0.80	<0.5	3.8–6.0
Siderophyllite	Siderophyllite	0.6..–0.4	0.95–0.35	0.35–0.75	0.5–1.6	2.0–4.0
Protolithionite	Lithian siderophyllite	–0.4..–1.4	0.35–0.10	0.75–1.50	0.8–2.2	1.4–4.0
Zinnwaldite	Ferroan polyolithionite	–1.4..–2.4	0.10–0.02	1.50–2.42	1.6–3.0	0.1–1.8
Lepidolite	Polyolithionite	–2.4..–4.0	<0.02	2.42–4.00	2.0–3.0	<0.8

respect to a particular trace element or oxide. In the x–y diagrams shown in Figs 1–15, this range is dotted. The central solid line represents the median or 50th percentile. In order to keep the diagrams legible, only a selection of those micas that plot well outside the interquartile range, is shown graphically and discussed in the text.

Depending on whether displaying strong enrichment or depletion in a particular element or oxide, the plotted micas are assigned to high (H) or low (L) groups. If micas from various occurrences, but the same type of rock or environment of formation, form compositional extremes with respect to a particular element or oxide, they are combined into single groups for simplification. The more diverse the regimes are in which compositional extremes were formed, the larger is the number of H or L groups distinguished.

The concentrations of the elements in question are plotted in units of weight (percent or ppm) in Figs 1–15. Compared to plotting the abundances in terms of atomic quantities or proportions, our method of data handling may have enlarged the ranges of scatter slightly. The use of atomic quantities, however, would have required calculation or recalculation (if no data for Li are provided) of almost 4,000 mica formulae! Therefore, we used the more consumer-friendly wt.% or ppm values which can be read directly from the plots.

Results

Titanium

Titanium oxide concentration in trioctahedral micas usually ranges over three orders of magnitude from 0.01 wt.% to ~10 wt.% (Fig. 1). Its distribution corresponds in shape to a Gaussian distribution. The maximum TiO₂ contents are contained in Mg and Fe biotites, lowest TiO₂ is shown by the most Li-rich micas. There are several geological environments or single occurrences in which micas formed that, for a specific mica variety, are enriched in TiO₂. They include: (1) protolithionite from alkaline magmatic and metasomatic rocks (Stevens, 1938; Vlasov, 1964; Gamaleya, 1968; Semenov, 1972; Raade and Larsen, 1980; Skosyeva and Vlasova, 1983; Černý and Trueman, 1985; Grew *et al.*, 1993); (2) Ba-rich protolithionite from granulite-facies, metamorphosed iron ores in Montana (Zhu *et al.*, 1994); (3) Ba-rich Mg biotite in marbles from Rogaland (Bol *et al.*, 1989); (4) phlogopite, Mg biotite and subordinate Fe biotite from lampro-

phyric rocks (Jaques and Perkin, 1984; Greenwood, 1998); (5) phlogopite, Mg biotite, and rare Fe biotite from alkaline rocks including leucitites, nephelinites, alkali gabbros, and lamproites (Carmichael, 1967; Velde, 1975; Birch, 1978; 1980; Mansker *et al.*, 1979; Sheraton and Cundari, 1980; Mitchell, 1981, 1985; Ryabchikov *et al.*, 1981; Mitchell *et al.*, 1987; Wagner *et al.*, 1987; Edgar, 1992; Zhang *et al.*, 1993*a,b*; Seifert and Kämpf, 1994; Henderson and Foland, 1996; Ionov *et al.*, 1997); (6) phlogopite from kimberlites (Smith *et al.*, 1978; Scott Smith and Skinner, 1984), and (7) Mg biotite from calc-alkaline mantle xenoliths from Nograd-Gömör, Hungary (Szabo *et al.*, 1996). There are only a few occurrences of micas which are depleted in TiO₂ compared to ‘normal’ composition: (1) protolithionite in A-type granites from the Arabian Shield (du Bray, 1994); and (2) Mg biotite and phlogopite in carbonatite from Chernigov, Russia (Krivdik *et al.*, 1982).

Tin

The concentration of tin in PASP micas from alkaline igneous rocks, metamorphic rocks, and mantle-related mafic rocks is only poorly known. Recent knowledge on the behaviour of tin in these micas comes primarily from intermediate to

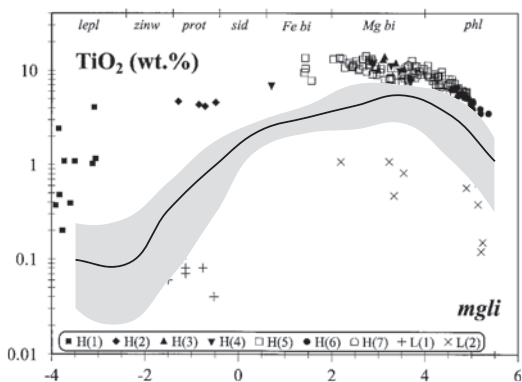
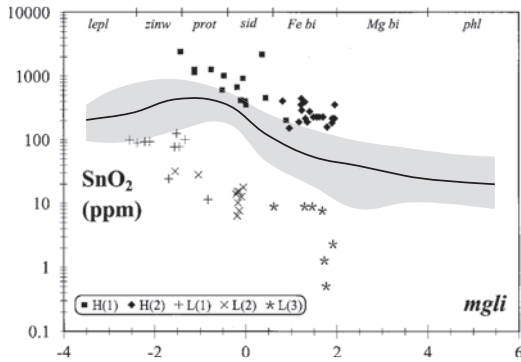


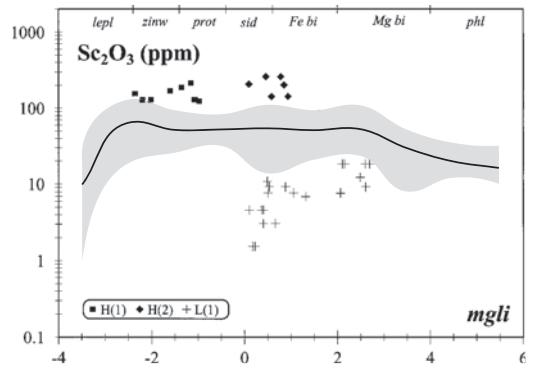
FIG. 1. Plot of TiO₂ vs. *mgli* (= octahedral Mg minus Li) in trioctahedral micas. Solid line represents median or 50th percentile. Dotted area reflects 15th–85th interquartile range. See text for more detailed explanation. lepl = lepidolite, zinw = zinnwaldite, prot = protolithionite, sid = siderophyllite, Fe bi = Fe biotite, Mg bi = Mg biotite, phl = phlogopite. Compositional extremes, whenever possible, are arranged into genetically distinct groups and are shown separately as low (L) and high (H) groups.

FIG. 2. Plot of SnO_2 vs. *mgli*. See Fig. 1 for explanations.

felsic, calc-alkaline to peraluminous I-S-type igneous rocks. In these rocks, the SnO_2 content increases systematically from Mg biotite to zinnwaldite by about three orders of magnitude, from 5 to ~2000 ppm (Fig. 2). Lepidolite from pegmatites is usually less enriched in tin than zinnwaldite from highly fractionated granites with a high potential to generate tin deposits (Barsukov and Pavlenko, 1956; Tischendorf, 1977; and others). Electron-microprobe analyses (Clarke and Beddoe-Stephens, 1987; Nash, 1993) confirm that Sn concentrations of at least 1500 ppm may be present as structural substitutions. Known occurrences of micas particularly rich in Sn comprise: (1) siderophyllite to zinnwaldite in some A-type granites (Gryazev *et al.*, 1985; du Bray, 1994); and (2) Fe biotite from biotite granites from the Erzgebirge, Germany (Tischendorf *et al.*, 1999b). Zinnwaldite and protolithionite poor in Sn are reported from the Cornubian batholith in SW England (group 1, Stone *et al.*, 1988). Protolithionite and siderophyllite in alkali granites from the Eastern Desert, Egypt, make up the low-Sn group 2 (Mohamed *et al.*, 1999). The third population is represented by Fe biotite from contact-metamorphic rocks in Portugal (Neiva, 1980, 1981b).

Scandium

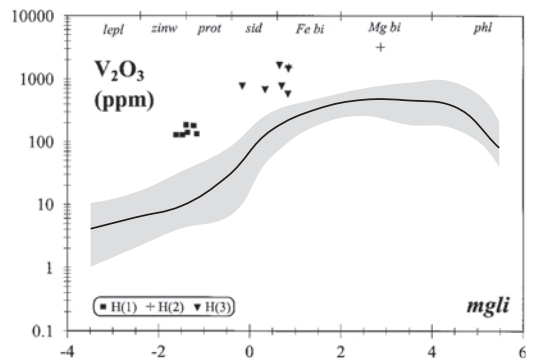
Relatively little is known of the distribution of Sc in trioctahedral micas. Available data define a range in Sc_2O_3 content from 1 ppm to about 300 ppm (Fig. 3). Micas ranging in composition from Mg biotite to zinnwaldite show only minor differences in Sc_2O_3 concentration. Generally, lowest in Sc are phlogopite and lepidolite. Post-

FIG. 3. Plot of Sc_2O_3 vs. *mgli*. See Fig. 1 for explanations.

collisional Li-mica and biotite granites of A-type affinity from Germany contain micas that are rich in this element (Tischendorf *et al.*, 1999b). These are: (1) zinnwaldite and protolithionite from the eastern Erzgebirge; and (2) Fe biotite and siderophyllite from the Harz Mountains. The low-Sc group is made up by Mg biotite to siderophyllite from various I-S-type granite occurrences (Dodge *et al.*, 1969; Lee *et al.*, 1981; Neiva *et al.*, 1987; Neiva and Gomes, 1991; El Shestawi *et al.*, 1993; Neiva, 1993; Neves, 1993).

Vanadium

The distribution of V in trioctahedral micas (Fig. 4) is almost identical to that of Ti. Statistical analysis reveals a common range of V_2O_3 content from 1 ppm in lepidolite to 1000 ppm in Mg biotite. There are only few exceptions from the 'normal' composition noted. Group 1 of V-rich micas comprise those from

FIG. 4. Plot of V_2O_3 vs. *mgli*. See Fig. 1 for explanations.

A-type granite greisens from Bom Futura, Rondônia, Brazil (Lowell and Ahl, 2000). High-V group 2 includes micas from mafic alkaline, mantle-derived rocks: an annitic mica from a lamprophyre at Mt. Woolooma, New South Wales (Jaques and Perkin, 1984) and a Mg biotite from a limburgite in eastern China (Cao and Zhu, 1987). Cao and Zhu determined the highest V_2O_5 content in a mica known to date (not shown), 9.7 wt.% in a phlogopite from garnet lherzolite from the same region. The third high-V group is formed by Fe biotite and siderophyllite from metamorphic rocks of the Erzgebirge, Germany (Rötzler *et al.*, 1998). These data, however, are from electron-microprobe analyses and may be questionable.

Chromium

The distribution of Cr_2O_3 in the studied micas is characterized by a nearly linear decrease in concentration from phlogopite to lepidolite (Fig. 5). Variation in Cr_2O_3 content is large and encompasses more than four orders of magnitude, from ~2 wt.% to <1 ppm. Micas strongly enriched or depleted in chromium occur in a number of environments. Group 1 of Cr-rich micas includes compositionally diverse micas from metasomatically altered rocks: siderophyllite and protolithionite in enclaves in Li-mica granites (Stimac *et al.*, 1995), protolithionite from the exocontact of a Ta-bearing pegmatite (Zagorskij and Makrygin, 1976), siderophyllite from the granite exocontact (Kol'tsov and Rusinova, 1997), Fe biotite from mica schist enclaves in granite (Schödlbauer *et al.*, 1996), and Mg biotite in peridotite xenoliths in granite (Szabo *et al.*, 1996). Group 2 includes micas

with extraordinary compositions, Ba-rich zincian anandite from skarns (Tracy, 1991) and Ba-rich siderophyllite and Mg biotite from Pb-Zn ores (Jiang *et al.*, 1996). Ti-rich siderophyllite to phlogopite from alkaline mantle rocks of syenitic to lamproitic composition represent the third major population of Cr-rich micas (Lalonde and Martin, 1983; Schulze *et al.*, 1985; Brigatti *et al.*, 1991; Rock, 1991; Schneiderman, 1991; Kramer and Seifert, 1994; Lalonde *et al.*, 1996; Jones *et al.*, 2000). Chromium-enrichment (group 4) has also been observed in Mg biotite from a mafic granulite of the Ivrea-Verbano Zone, Italy (D. Harlov and H.-J. Förster, unpublished data). Occurrences of Cr-poor micas can be assigned to four groups: (1) Fe biotite from Alpine pegmatites (Stern, 1966); (2) Mg and Fe biotites in granites of the Sierra Nevada Batholith (Dodge and Moore, 1968; Dodge *et al.*, 1969); (3) Mg biotite from alkali basalts (Ryabchikov *et al.*, 1981; Irving and Frey, 1984); (4) phlogopite from the Grängesberg metamorphosed iron formation in Sweden (Annersten and Eckström, 1971).

Gallium

The evolution of the Ga_2O_3 content in micas of the PASP system is similar to that of Sn but the overall variability is smaller and comprises only two orders of magnitude, from ~10 to 1000 ppm (Fig. 6). Significant deviations from the 'usual' Ga contents are established only for: (1) lepidolite to siderophyllite from pegmatites of Proterozoic anorogenic granites in Colorado (Heinrich, 1967; Foord *et al.*, 1995); and (2) Fe and Mg biotites from Tertiary calc-alkaline volcanic rocks of Hungary (Dobosi, 1987).

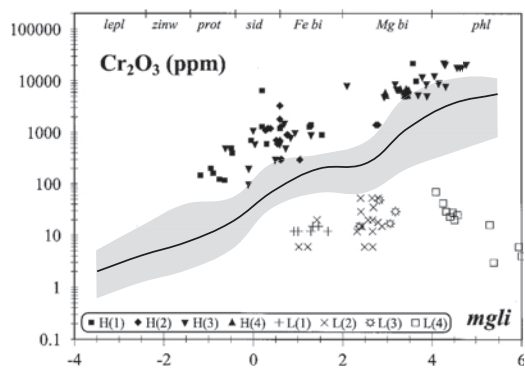


FIG. 5. Plot of Cr_2O_3 vs. *mgli*. See Fig. 1 for explanations.

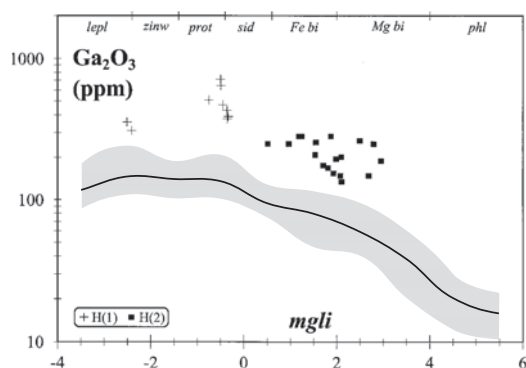
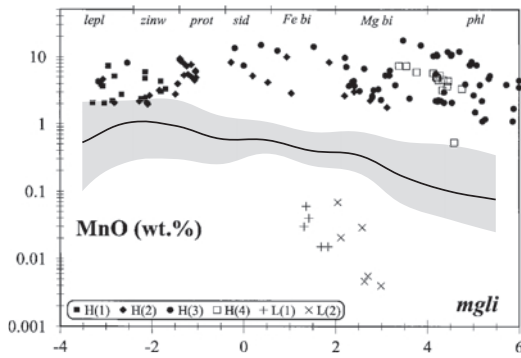
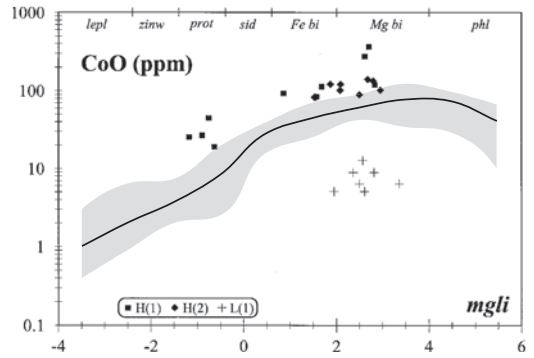


FIG. 6. Plot of Ga_2O_3 vs. *mgli*. See Fig. 1 for explanations.

FIG. 7. Plot of MnO vs. *mgli*. See Fig. 1 for explanations.FIG. 8. Plot of CoO vs. *mgli*. See Fig. 1 for explanations.

Manganese

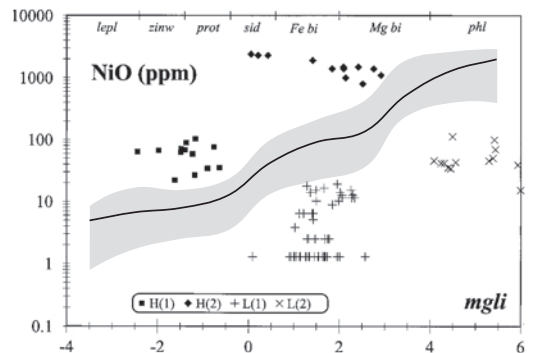
The distribution of Mn is similar, qualitatively, to that of Ga and Sn but its abundance exceeds that of Ga and Sn by three orders of magnitude (Fig. 7). Manganese can be enriched in micas by 10 to 20 times compared to normal composition. The Mn-rich micas are widespread and can be classified into four major groups: (1) masutomilite, lepidolite and zinnwaldite from S-type peraluminous pegmatites (Stevens, 1938; Heinrich, 1967; Guggenheim *et al.*, 1983; Nĕmec, 1983, 1990; Stern *et al.*, 1986; Harada *et al.*, 1976, 1990; Nĕmec and Povondra, 1993); (2) Mg biotite to protolithionite from A-type granites and syenites, associated metasomatic rocks and ore deposits (Lapides *et al.*, 1977; Bailey and Christie, 1978; Robert and Maury, 1979; Gunow *et al.*, 1980; Sklavounos *et al.*, 1986; Chen-Shurong and Wu-Gongbao, 1987; Boggs, 1992; Speer and Becker, 1992; Abdalla *et al.*, 1994; Maslov *et al.*, 1994); (3) manganian biotite, manganian phlogopite, kinoshitalite and hendricksite from Mn skarns and ores (Jacob, 1925; Bilgrami, 1956; Frondel and Ito, 1966; Yoshii *et al.*, 1973*a,b*; Yoshii and Maeda, 1975; Matsubara *et al.*, 1974; Guggenheim *et al.*, 1983; Smith *et al.*, 1983; Craig *et al.*, 1985; Knurr and Bailey, 1986; Kazachenko *et al.*, 1988; Dasgupta *et al.*, 1989); and (4) manganian biotite and manganian phlogopite in highly-oxidized metamorphic rocks (Smith and Albee, 1967; Hiroi *et al.*, 1992). In contrast, micas poor in Mn seem to be rare. Low-Mn group 1 includes Fe biotite from the Bob Ingersoll No.1 pegmatite, Black Hills, South Dakota (Shearer *et al.*, 1986). Low-Mn group 2 comprises Mg biotite from metamorphic rocks in western Labrador (Yang and Rivers, 2000).

Cobalt

The distribution of Co in PASP micas is almost identical to that of Ti and V, with highest contents in Fe and Mg biotites (Fig. 8). Average contents of CoO in the micas span two orders of magnitude, from ~1 to 100 ppm. Cobalt enrichment may be observed in micas formed during interaction of granitic/pegmatitic melt and metamorphic country rock (high-Co group 1). Examples are Fe and Mg biotite from a Portuguese hybrid granite (Neiva, 1981*a*) and from the exocontact of a Russian pegmatite (Zagorskij and Makrygin, 1976). Mg and Fe biotite from granites of the Torredeita region, central Portugal (Neves, 1993) form the low-Co group.

Nickel

The distribution of Ni is almost identical to that of Cr, with a systematic increase of NiO from lepidolite (<<10 ppm) to phlogopite (~2000 ppm) (Fig. 9). Two groups of Ni-enriched micas can be distinguished:

FIG. 9. Plot of NiO vs. *mgli*. See Fig. 1 for explanations.

(1) protolithionite to lepidolite from the endo- and exocontact of pegmatites and greisens (Zagorskij and Makrygin, 1976; Roda *et al.*, 1995; Lowell and Ahl, 2000); and (2) Zn- and Ba-rich siderophyllite to Mg biotite from the Franklin Marble at the Lime Crest quarry and at Sterling Hill, both in New Jersey (Tracy, 1991). Fe and Mg biotite poor in Ni is reported from pegmatites of the Tessin Alps (Hunziker, 1966; Stern, 1966) (low-Ni group 1). Low-Ni group 2 is composed of Cr-poor phlogopite from the Grängesberg metamorphosed iron formation (Annersten and Eckström, 1971).

Zinc

Zinc belongs to that group of elements the content of which is not related to mica composition (Fig. 10). The ZnO concentration is relatively low and only ranges from ~100 to 2000 ppm in PASP micas. However, micas are capable of substituting theoretically up to 45 wt.% ZnO. In nature, such micas, named hendricksite, are known to contain up to 23 wt.% ZnO. Mn-rich hendricksite (which in our diagram plots in the field of siderophyllite!) and Zn-Mn-rich Fe and Mg biotite from complex Mn-Zn skarns and ores (Fron del and Ito, 1966; Fron del and Einaudi, 1968; Guggenheim *et al.*, 1983; Craig *et al.*, 1985; Tracy, 1991) form the H(1) group. A moderate Zn-enrichment is also observed in Fe biotite to protolithionite from some A-type granite occurrences (Sobachenko *et al.*, 1989; du Bray, 1994; Abdalla *et al.*, 1994), which make up the H(2) group. The low-Zn group includes Fe and Mg biotites from the Peña Negra migmatite, Spain (Bea *et al.*, 1994b) and from some Portuguese hybrid granites (Neiva, 1981a)

and contact-metamorphic rocks (Neiva 1980, 1981b). El Shestawi *et al.* (1993) reported Fe biotite (not shown) from the Wadi El-Sheik granite, southwestern Sinai, which contains only 1–2 ppm ZnO.

Strontium

The behaviour of Sr is different from that of the other elements considered in this study (Fig. 11). The lowest average contents of SrO are contained in siderophyllite and Fe biotite (~10 ppm). The most Mg- and Li-rich micas usually have substituted SrO of the order of 50 ppm. Micas with compositions between Mg biotite and phlogopite are highest in SrO. Four groups of Sr-rich micas can be distinguished: (1) protolithionite from A-type granite greisens from Bom Futuro, Rondônia, Brazil (Lowell and Ahl, 2000); (2) Ba-rich Fe biotite from silicate-rich bands within the high-grade, metamorphic banded-iron formation enclosing massive sulphide bodies in the Broken Hill deposit, South Africa (Frimmel *et al.*, 1995); (3) Fe and Mg biotite from submarine exhalative Pb-Zn-Ag and Fe deposits in China (Jiang *et al.*, 1996); and (4) Mg biotite and phlogopite from mafic alkaline rocks (Rimšaitė and Lachance, 1966; Flower, 1971; Rimšaitė, 1971; Ryabchikov *et al.*, 1981; Holm, 1982). Strontium-poor micas are displayed by Mg biotite in metamorphic rocks from Labrador (Yang and Rivers, 2000).

Barium

The variability of BaO content in trioctahedral micas is enormous and reaches six orders of

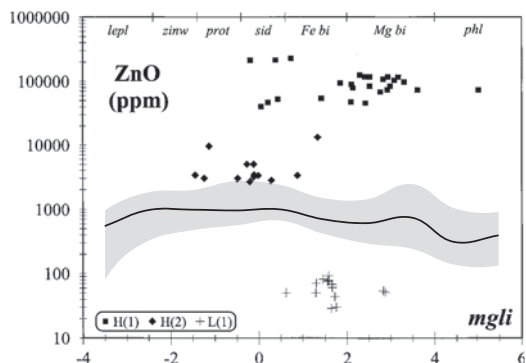


FIG. 10. Plot of ZnO vs. *mgli*. See Fig. 1 for explanations.

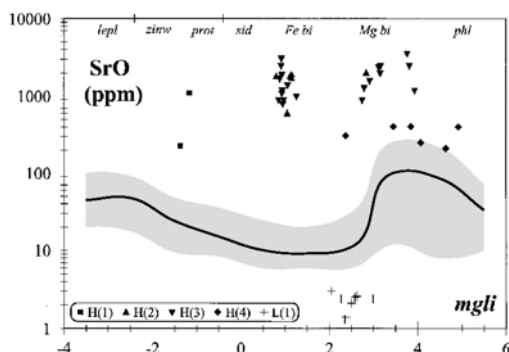


FIG. 11. Plot of SrO vs. *mgli*. See Fig. 1 for explanations.

magnitude, from ~1 ppm to >20 wt.% (Fig. 12). The distribution patterns of BaO are similar to those of V, Co and Ti, with the lowest BaO content found in lepidolite (5–50 ppm) and the highest abundance in Mg biotite (1,000–10,000 ppm). Furthermore, the patterns indicate a continuous transition between PASP micas and the Ba-rich brittle micas anandite and kinoshitalite, respectively. Strong compositional variability is best displayed by the larger number of high and low Ba groups. The Ba-rich micas comprise: (1) zinnwaldite to lepidolite from pegmatites and greisens, mostly related to A-type granites (Bailey and Christie, 1978; Fonteilles, 1987; Černý *et al.*, 1995; Novák and Povondra, 1995; Roda *et al.*, 1995; Lowell and Ahl, 2000); (2) Mn-rich or manganian kinoshitalite (which plots in the fields of Fe and Mg biotite in our diagram!) and Mn-rich Mg biotite and phlogopite from oxidized Mn ores and skarns (Frondel and Ito, 1968; Yoshii *et al.*, 1973a,b; Matsubara *et al.*, 1974; Kazachenko *et al.*, 1988; Dasgupta *et al.*, 1989; Gnos and Armbruster, 2000); (3) Mn-poor kinoshitalite and phlogopite in skarns (Solie and Su, 1987; Bol *et al.*, 1989; Semka *et al.*, 1989); (4) anandite, ferrokinoshitalite (both plotting as siderophyllite!); and Fe biotite from metamorphosed, banded-iron formations and stratiform Pb-Zn and Fe ores and skarns (Pattiaratchi *et al.*, 1967; Lovering and Widdowson, 1968; Orliac *et al.*, 1971; Filut *et al.*, 1985; Frietsch, 1985; Tracy, 1991; Oen and Lustenhouwer, 1992; Grapes, 1993; Zhu *et al.*, 1994; Frimmel *et al.*, 1995; Jiang *et al.*, 1996; Guggenheim and Frimmel, 1999); (5) Fe and Mg biotite from various intermediate, mafic and

ultramafic alkaline rocks (Mitchell, 1972; Thompson, 1977; Wendlandt, 1977; Birch, 1978, 1980; Mansker *et al.*, 1979; Velde, 1979; Sheraton and Cundari, 1980; Baldrige *et al.*, 1981; Holm, 1982; Gaspar and Wyllie, 1982, 1987; Barnett *et al.*, 1984; Boctor and Yoder, 1986; Mitchell *et al.*, 1987; Arima, 1988; Rock, 1991; Edgar, 1992; Brigatti and Poppi, 1993; Zhang *et al.*, 1993a,b; Kramer and Seifert, 1994; Seifert and Kämpf, 1994; Mues-Schumacher *et al.*, 1995; Henderson and Foland, 1996; Shaw and Penczak, 1996; Stoppa *et al.*, 1997; Beard *et al.*, 1998; Greenwood, 1998); and (6) Fe and Mg biotite from mafic, high-grade calc-alkaline rocks (Bigi *et al.*, 1993; Kullerud, 1995). Ba-poor micas are represented by (1) siderophyllite and Fe biotite from Portuguese hybrid granites and their contact-metamorphic aureoles (Neiva 1976, 1980, 1981a,b, 1993; Neiva *et al.*, 1987; Silva and Neiva, 1990; Neiva and Gomes, 1991); and (2) phlogopite from serpentinite from Heřmanov, Czech Republic (Černý, 1972) and from some kimberlites, carbonatites and lherzolites (Delaney *et al.*, 1980; Jones and Smith, 1984; Brigatti *et al.*, 1996).

Rubidium

The Rb₂O content increases continuously from phlogopite (500 ppm on average) to lepidolite (1.2 wt.% on average) (Fig. 13). However, in the PASP system, micas occur displaying substantial Rb-enrichment. These include: (1) Mg biotite to lepidolite from the endo- and exocontact of pegmatites, aplites, greisens and evolved granites (Ukai *et al.*, 1956; Rinaldi *et al.*, 1972; Khvostova

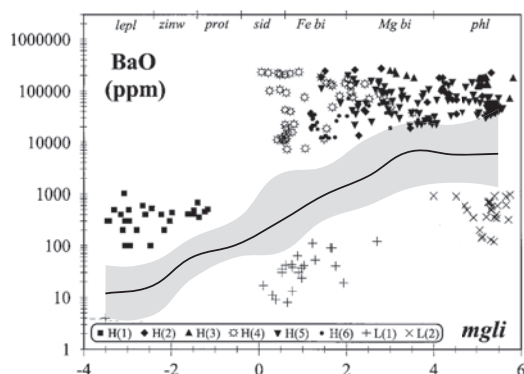


FIG. 12. Plot of BaO vs. *mgli*. See Fig. 1 for explanations.

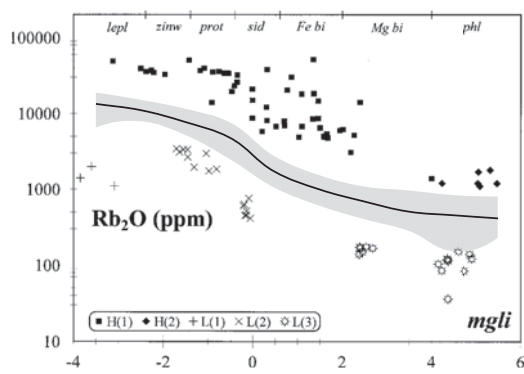


FIG. 13. Plot of Rb₂O vs. *mgli*. See Fig. 1 for explanations.

et al., 1973; Chelishchev *et al.*, 1974; Moloshag and Teremetskaya, 1975; Zagorskiy and Makrygin, 1976; Neiva, 1980; Hawthorne and Černý, 1982; Zaritskiy *et al.*, 1983; Kuznetsova and Zagorskiy, 1984; Morgan and London, 1987; Semenov and Shmakin, 1988; Skosyeva and Vlasova, 1989; Johnston and Chappell, 1992; Lentz, 1992; Icenhower and London, 1995; Lagache and Quéméneur, 1997; Pan and Breaks, 1997; Hawthorne *et al.*, 1999; Tischendorf *et al.*, 1999b); and (2) phlogopite from a South African kimberlite (Aoki, 1974). Polyolithionite from peralkaline granites and pegmatites constitutes group 1 of low-Rb micas (Semenov, 1972; Skosyeva and Vlasova, 1989; Grew *et al.*, 1993). The second group is made up of siderophyllite to zinnwaldite in A-type granites and associated greisens from the Eastern Desert, Egypt (Mohamed *et al.*, 1999). The Mg biotite and phlogopite from mantle xenoliths in alkali basalts and from alkali basalts themselves (Ryabchikov *et al.*, 1981; Ionov *et al.*, 1997) form the third group.

Caesium

The distribution pattern of Cs_2O is identical to that of Rb_2O . However, its absolute abundance is about one order of magnitude lower relative to that of the other rare alkaline element oxide (Fig. 14). Group 1 of the Cs-rich micas is almost identical to group 1 of Rb-rich micas (Hess and Fahey, 1932; Rinaldi *et al.*, 1972; Khvostova *et al.*, 1973; Chelishchev *et al.*, 1974; Moloshag and Teremetskaya, 1975; Zagorskiy and Makrygin, 1976; Hawthorne and Černý, 1982; Zaritskiy *et al.*,

1983; Kuznetsova and Zagorskiy, 1984; Morgan and London, 1987; Semenov and Shmakin, 1988; Icenhower and London, 1995; Pesquera *et al.*, 1999; Tischendorf *et al.*, 1999b). Polyolithionite from alkaline rocks and protolithionite/zinnwaldite from aluminous greisens, all of A-type affinity, may be relatively depleted in Cs (low-Cs group 1; Skosyeva and Vlasova, 1983; Grew *et al.*, 1993; Lowell and Ahl, 2000). The other low-Cs groups consist of siderophyllite to Mg biotite from migmatites and metamorphic rocks (Neiva, 1980, 1981a; Sobachenko *et al.*, 1989; Bea *et al.*, 1994a; Yang and Rivers, 2000) and Mg biotite and phlogopite from some alkaline mantle-derived rocks (Ryabchikov *et al.*, 1981; Carmichael *et al.*, 1996).

Fluorine

The F content ranges through three orders of magnitude, from ~0.01 to 10 wt.% (Fig. 15). High F abundances are observed in zinnwaldite and lepidolite, but phlogopite may also display F enrichment. The Mg biotite and phlogopite are highly variable in F on the scale of more than two orders of magnitude. The following seven groups of particularly F-rich micas can be distinguished: (1) Mg biotite to polyolithionite from the endo- and exocontact of peraluminous and peralkaline pegmatites and granites (Vlasov *et al.*, 1959; Vlasov, 1964; Semenov, 1972; Moloshag and Teremetskaya, 1975; Gunow *et al.*, 1980; Hawthorne and Černý, 1982; Kuznetsova and Zagorskiy, 1984; Semenov and Shmakin, 1988; Sobachenko *et al.*, 1989; Schneiderman, 1991; Lentz, 1992; Speer and Becker, 1992; Grew *et al.*,

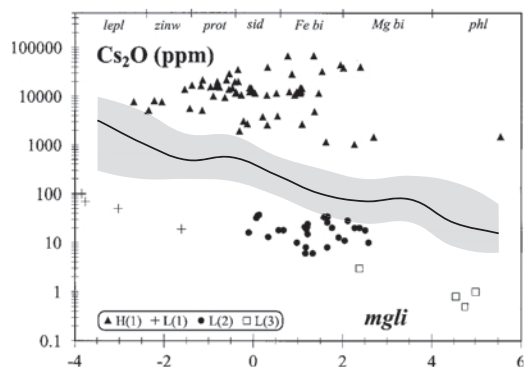


FIG. 14. Plot of Cs_2O vs. *mgli*. See Fig. 1 for explanations.

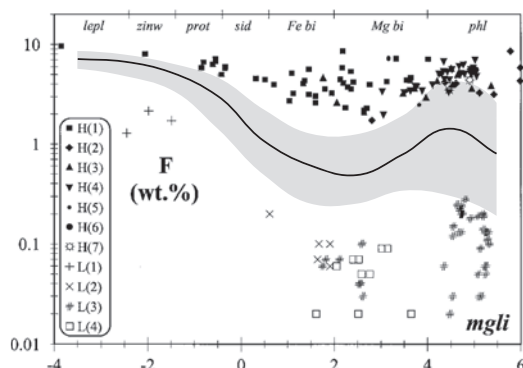


Fig. 15. Plot of F vs. *mgli*. See Fig. 1 for explanations.

1993; Icenhower and London, 1995; Pesquera *et al.*, 1999); (2) Mg biotite and phlogopite from skarns (Němec, 1969; Rimšaitė, 1970; Hazen and Burnham, 1973; Valley *et al.*, 1982; Pomârleanu *et al.*, 1986; van Middelaar and Keith, 1990; Tracy, 1991); (3) Mg biotite and phlogopite from lamprophyric rocks (Kramer and Seifert, 1994; Carmichael *et al.*, 1996; Carlier *et al.*, 1997); (4) Mg biotite and phlogopite from alkaline and peralkaline mafic rocks such as alkaline gabbro, nephelinite, shonkinite, and melilitite (Hazen *et al.*, 1981; Wagner *et al.*, 1987; Malysheonok, 1989; Edgar, 1992; Brigatti and Poppi, 1993; Seifert and Kämpf, 1994; Henderson and Foland, 1996; Conticelli *et al.*, 1997); (5) Mg biotite and phlogopite from carbonatites (Krivdik *et al.*, 1982; Bagdasarov *et al.*, 1985); (6) phlogopite from the Prairie Creek peridotite, Arkansas (Scott Smith and Skinner, 1984); and (7) phlogopite from metasedimentary granulites (Grew *et al.*, 1990).

Micas that are depleted in F are less abundant. These comprise: (1) zinnwaldite from external pegmatites from Fregeneda, Spain (Roda *et al.*, 1995); (2) Fe biotite from contact-metamorphic rocks around Portuguese granites (Neiva, 1980, 1981b); (3) Fe biotite to phlogopite from some ultramafic to mafic alkaline rocks (Exley *et al.*, 1982; Brigatti *et al.*, 1996; Wiese *et al.*, 1996); and (4) Mg and Fe biotite in high-grade mafic metamorphic rocks from the Ivrea-Verbano Zone, Italy (Bigi *et al.*, 1993).

Other elements

Published REE contents, the actinide contents, and high-field strength element (Zr, Hf, Nb, Ta, W, etc.) contents in micas, obtained from the analysis of mineral separates, must be discussed with caution. Particularly in felsic to intermediate igneous and metamorphic rocks as well as in metasedimentary rocks of various metamorphic grade, the contents determined are typically too high, reflecting the modal abundance and assemblage of micro-inclusions. Although a couple of alternative techniques for *in situ* microanalysis of trace elements in minerals such as secondary ion-mass spectrometry (SIMS) and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) have been developed in the last two decades, their application to mica minerals remains limited to date. To demonstrate the low concentrations of many trace components in

phlogopite and biotite, Table 3 provides a review of selected published data obtained by SIMS and LA-ICP-MS. Adequate investigations of micas richer in Li than Fe biotite are lacking.

Our studies have shown that trioctahedral micas typically contain between 10 and 100 ppm PbO, irrespective of the mica variant. Copper may be present occasionally in concentrations approaching the wt.% level. Hiroi *et al.* (1992) reported 5.5 wt.% CuO in phlogopite from a highly oxidized siliceous schist in central Japan.

Discussion

Minor- and trace-element contents as a function of mica variety

The degree of substitution of most of the minor and trace elements in a mica is a function of its *mgli* value. This is shown in Figs 1–15 and also

TABLE 3. Compilation of average compositions of trace elements (in ppm) in micas obtained by LA-ICP-MS (Bea *et al.*, 1994a,b) and SIMS (Carmichael *et al.*, 1996; Ionov *et al.*, 1997). Number of spot analyses given in parentheses.

Element	Phlogopite	Mg-Fe biotite
Be		4.2 (3)
Y		0.1 (3)
Zr	14.9 (10)	17.6 (5)
Nb	143 (10)	24 (8)
Mo		0.23 (3)
La	5.5 (3)	0.18 (7)
Ce	16.7 (3)	0.37 (7)
Pr		0.056 (7)
Nd	7.7 (3)	0.22 (7)
Sm	0.81 (3)	0.041 (7)
Eu	0.25 (3)	0.030 (7)
Gd		0.047 (7)
Tb	0.09 (3)	0.007 (7)
Dy	0.38 (1)	0.034 (7)
Ho		0.0074 (7)
Er		0.018 (7)
Tm		0.0043 (4)
Yb	0.14 (3)	0.018 (7)
Lu		0.0045 (4)
Ta	8.46 (6)	5.24 (3)
W		2.48 (3)
Tl		6.90 (7)
Th	1.83 (3)	0.02 (4)
U	0.19 (3)	0.62 (7)

COMPOSITION OF TRIOCTAHEDRAL MICAS

TABLE 4. Median composition of mica varieties.

	Phlogopite	Mg biotite	Fe biotite	Annite	Sidero- phyllite	Proto- lithionite	Zinnwaldite	Lepidolite
SiO ₂	39.3	36.6	35.1	34.7	36.2	40.6	46.3	50.6
TiO ₂	2.11	43.60	3.10	3.20	1.94	0.56	0.17	0.10
Al ₂ O ₃	13.6	15.0	17.8	12.9	19.7	21.5	21.5	22.1
Fe ₂ O ₃	2.52	2.88	3.07	5.08	3.27	1.97	1.02	0.32
FeO	4.64	15.5	20.8	26.9	21.3	15.5	9.63	0.72
MnO	0.06	0.21	0.34	0.43	0.52	0.60	0.81	0.59
MgO	22.7	12.7	6.64	2.23	1.93	0.47	0.12	0.09
Li ₂ O	0.01	0.05	0.19	0.19	0.63	1.76	3.42	5.39
CaO	0.05	0.23	0.24	0.20	0.22	0.20	0.17	0.15
Na ₂ O	0.31	0.26	0.17	0.16	0.20	0.27	0.28	0.39
K ₂ O	9.81	9.08	8.80	8.67	8.88	9.28	9.76	9.90
Rb ₂ O	0.048	0.065	0.11	0.17	0.26	0.57	0.93	1.23
H ₂ O ⁺	3.10	3.41	3.45	3.30	3.00	2.10	1.51	1.13
F	1.40	0.58	0.74	0.99	1.85	4.20	6.25	6.97
Cl	0.05	0.10	0.07	0.26	0.10	0.04	0.03	0.01
SnO ₂	20	34	77	92	297	452	317	230
Ga ₂ O ₃	20	58	61	123	128	161	131	126
Sc ₂ O ₃	12	52	71	173	58	52	50	12
V ₂ O ₃	168	448	303	169	57	12	6	4
Cr ₂ O ₃	6500	358	131	113	36	11	7	2
CoO	74	64	43	27	16	5	3	1.5
NiO	1700	178	64	30	13	5	8	4
ZnO	235	360	555	672	719	721	847	374
SrO	100	20	10	8	12	24	24	60
BaO	3510	3600	701	800	148	98	50	12
Cs ₂ O	25	65	161	69	318	500	700	2150

SiO₂ to Cl in wt.%, the others in ppm

in Table 4, which lists the median contents of major, minor and trace elements in the individual mica varieties. Their crystal-chemical formulae (cations normalized to 22 oxygen equivalents) are given in Table 5. In Fig. 16, median compositions (in terms of *feal* and *mgli*) of the PASP micas are plotted in the classification diagram of Tischendorf *et al.* (1997).

Trioctahedral micas are capable of substituting minor and trace elements in different concentrations. The elements such as Zn, Mn and Ba, which in PASP micas usually occur in concentrations at the ppm or lower wt.% level, may be enriched to substantial levels that generate separate species: hendricksite (Zn), masutomilite (Mn), and the brittle Ba-micas anandite, kinoshitalite and ferrokinoshitalite.

Minor and trace elements in trioctahedral micas can be grouped according to various aspects.

(I) *Correlation with mgli*

We have to distinguish between elements that show strong correlations with the mica variants (expressed in terms of *mgli*), from those which do not. Chromium and Ni are part of the first group of elements showing a steady decrease in content from phlogopite to lepidolite. The distribution patterns of these and the following elements can be explained from their behaviour in igneous rocks, from which come the majority of mica analyses presented here. Indeed, Cr and Ni always behave compatibly in these rocks. The same trend is observed for Ti, V, Co and, less markedly, for Ba. However, these elements are usually most abundant in Mg biotite, not in phlogopite or close to end-member composition. Three of these elements, Ba, Ti and V, are known to behave incompatibly in magmatic rocks with a low bulk-rock silica content. Change of their behaviour

TABLE 5. Crystal-chemical formulae (cations normalized to 22 oxygens) of mica varieties (based on the medians given in Table 4).

Cation	Phlogopite	Mg biotite	Fe biotite	Annite	Sidero- phyllite	Proto- lithionite	Zinn- waldite	Lepidolite
Si	5.629	5.472	5.363	5.637	5.588	6.089	6.575	6.948
Al ^{IV}	2.279	2.528	2.637	2.363	2.412	1.911	1.425	1.052
Fe ^{3+IV}	0.092							
Ti	0.225	0.405	0.356	0.391	0.225	0.063	0.018	0.010
Sn	0.0001	0.0002	0.0005	0.0006	0.0018	0.0027	0.0018	0.0013
Al ^{VI}	0.000	0.115	0.569	0.107	1.172	1.889	2.174	2.525
Ga	0.0002	0.0006	0.0006	0.0013	0.0013	0.0015	0.0012	0.0011
Sc	0.0001	0.0005	0.0009	0.0024	0.0008	0.0007	0.0006	0.0002
V	0.0029	0.0081	0.0056	0.0033	0.0011	0.0002	0.0001	0.0001
Cr	0.073	0.0042	0.0016	0.0015	0.0004	0.0001	0.0001	0.0000
Fe ³⁺	0.178	0.324	0.353	0.621	0.380	0.222	0.109	0.033
Fe ²⁺	0.552	1.937	2.657	3.654	2.745	1.944	1.143	0.083
Mn	0.007	0.027	0.044	0.059	0.068	0.075	0.097	0.069
Co	0.0008	0.0008	0.0005	0.0004	0.0002	0.0001	0.0000	0.0000
Ni	0.019	0.0021	0.0008	0.0004	0.0002	0.0001	0.0001	0.0000
Zn	0.003	0.004	0.006	0.008	0.008	0.008	0.009	0.004
Mg	4.808	2.829	1.512	0.540	0.444	0.105	0.025	0.018
Li	0.006	0.030	0.117	0.124	0.391	1.062	1.953	2.977
Sum [Y]	5.875	5.688	5.625	5.514	5.439	5.373	5.532	5.722
Ca	0.008	0.037	0.039	0.035	0.036	0.032	0.026	0.022
Sr	0.0008	0.0002	0.0001	0.0001	0.0001	0.0002	0.0002	0.0005
Ba	0.020	0.021	0.0042	0.0051	0.0009	0.0006	0.0003	0.0001
Na	0.085	0.075	0.050	0.050	0.060	0.079	0.077	0.104
K	1.779	1.732	1.715	1.797	1.748	1.775	1.768	1.734
Rb	0.0044	0.0062	0.011	0.018	0.026	0.055	0.085	0.109
Cs	0.0002	0.0004	0.001	0.0005	0.0021	0.0032	0.0042	0.013
Sum [X]	1.897	1.872	1.820	1.905	1.873	1.945	1.961	1.982
OH	2.94	3.40	3.52	3.57	3.09	2.10	1.43	1.03
F	0.63	0.27	0.36	0.51	0.90	1.99	2.81	3.03
Cl	0.012	0.025	0.018	0.072	0.026	0.010	0.007	0.002
<i>mgli</i>	4.80	2.80	1.40	0.42	0.05	-0.96	-1.93	-2.96
<i>feal</i>	1.15	2.58	2.84	4.61	2.25	0.42	-0.86	-2.33
<i>Mg#</i>	0.87	0.56	0.33	0.11	0.12	0.05	0.02	0.13

mgli = Mg–Li (octahedral), *feal* = Fe_{tot} + Mn + Ti–Al^{VI} (octahedral), *Mg#* = Mg/(Mg + Fe_{tot}) (octahedral)

from incompatible to compatible occurs somewhere within the 50–60 wt.% SiO₂ range. In these rocks, where the maximum level of Ti in melts is reached, Mg biotite constitutes the most abundant mica. Therefore, the Ti distribution patterns in the trioctahedral micas simply reflect the Ti distribution patterns in the bulk composition of their igneous hosts.

Rubidium and Cs increase continuously from phlogopite to lepidolite. Both elements are strongly incompatible and became enriched in the most

felsic melts. Only at the latest stages of evolution of pegmatites may the contents of Rb and Cs in a mica drop. Either pollucite exhausts Cs, giving rise to later Cs-poor micas (Gordiyenko, 1973; Černý *et al.*, 1995), or the modal abundance of micas increases to a level where Rb became compatible (Icenhower and London, 1995).

Tin and Ga attain their average concentration maximum in zinnwaldite, and not, as one would expect, in lepidolite. This, in part, may be related to the comparatively minor amount of data

COMPOSITION OF TRIOCTAHEDRAL MICAS

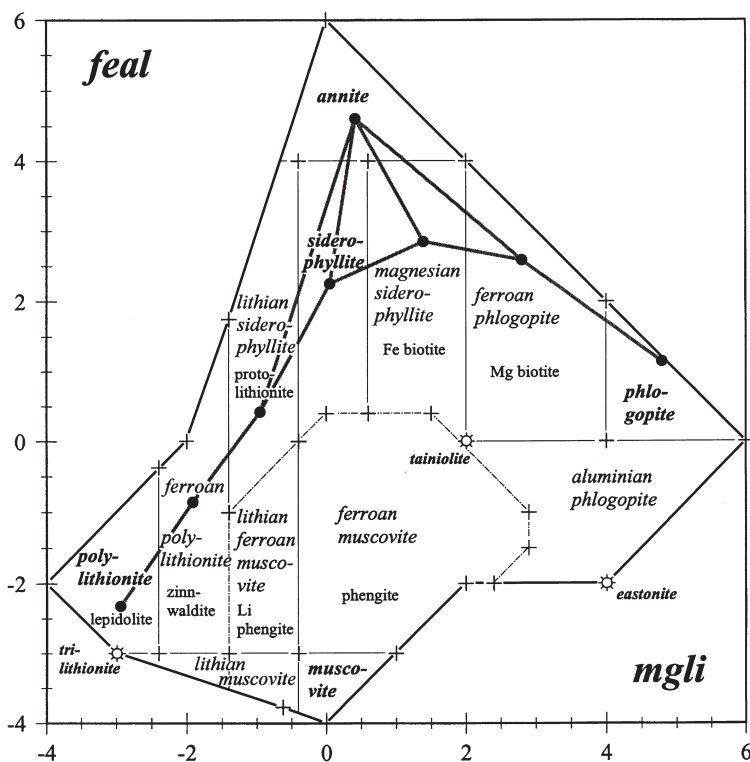


FIG. 16. Median composition (dots) of mica varieties in terms of *feal* vs. *mgli*. Data are from Table 5. IMA approved names are given in italics. Full lines connect micas in the PASP system between which complete miscibility is suggested. *feal* = octahedral (Fe_{tot} + Mn + Ti - Al^{VI}); *mgli* = octahedral (Mg-Li).

available for lepidolite, and because these data do not encompass all environments in which this mica variety forms. However, although Ga and particularly Sn (e.g. Lehmann, 1982) usually behave incompatibly until the final stages of differentiation of peraluminous granite-pegmatite systems, there are exceptions noted for both Ga (Černý *et al.*, 1985) and for Sn (Förster *et al.*, 1999). Precipitation of magmatic cassiterite or dispersion of Sn in accessory Fe-Ti oxides, facilitated by high oxygen fugacities, may deplete the residual melt in Sn (cf. Lehmann, 1990). Moreover, postmagmatic crystallization of lepidolite, after exsolution of the bulk of Sn from a granitic magma into the residual fluid, also may explain the Sn impoverishment in this mica compared to earlier-formed zinnwaldite.

Strontium and F display two concentration peaks, on both sides of the range in *mgli*. Increases of Sr abundances in Mg biotite and phlogopite acknowledge the high Sr contents in

primitive granitoids and mantle-derived material. On the other hand, the slightly increased mean Sr abundances in most Li-rich micas are unexpected from the viewpoint that Sr represents a strongly compatible element in the course of magma differentiation. This can be explained in two different ways. First, and probably most important, a substantial proportion of Sr in (geologically older) Rb-rich micas is secondary, i.e. of a radiogenic nature produced as result of the decay of ⁸⁷Rb (see Clark and Černý, 1987). Second, increased Sr contents may reflect the alteration-induced supply of Sr, which has been recorded in many highly evolved granites and pegmatites (e.g. Raimbault *et al.*, 1995; Förster *et al.*, 1999), and which may have taken place prior to crystallization of postmagmatic lepidolite. Increased concentrations of F in lepidolite directly follow its close chemical relations with Li, Rb, Cs and Sn. Fluorine concentration highs in phlogo-

pite refer to those micas that are contained in igneous rocks derived from enriched mantle domains (Carmichael *et al.*, 1996; Carlier *et al.*, 1997; Conticelli *et al.*, 1997). Phlogopite from rocks of crustal or depleted-mantle affinity, in contrast, is usually poor in F.

The Zn content in a trioctahedral mica is not exactly a function of *mgli*. This is not surprising given the observation that crustal and mantle rocks generally do not differ significantly with respect to Zn. The Sc distribution patterns display only a weak correlation with the mica variety and, given the poor database, is not discussed here in detail.

(2) Extent of variability

The elements differ with respect to their concentration ranges. Excluding the compositional extremes, Ba and Cr extend for an order of four magnitudes in trioctahedral micas, followed by Ni, V and Cs with three orders of magnitude. The Ti, Sn, Co, Rb and Mn concentrations extend for an interval of about two orders of magnitude; F, Sc, Sr, Zn and Ga display a minor variability, on the order of one to two orders of magnitude.

(3) Concentration maxima

The elements can be grouped according to their maximum abundances in micas known to date: >20 wt.% = BaO, ZnO; 10–20 wt.% = TiO₂, MnO; 1–10 wt.% = Cr₂O₃, Rb₂O, Cs₂O, F; 0.1–1 wt.% = SnO₂, NiO, SrO; 0.01–0.1 wt.% = V₂O₃, Ga₂O₃, Sc₂O₃, CoO.

Statistical analysis of the degree of correlation between the studied minor and trace elements and the three oxides in the mica octahedral layer, which are essential for its classification (MgO, FeO_{tot}, Li₂O), reveals the following grouping. For calculation of the linear correlation coefficient R, only element concentrations within the 15th–85th interquartile range are considered.

Minor- and trace-element group with affinity to Mg

This group includes all elements that are most positively correlated with MgO. Expressed as their oxides, these are NiO (R = 0.77; n = 820), Cr₂O₃ (0.72; 833), V₂O₃ (0.72; 620), CoO (0.60; 563), BaO (0.49; 897), and ZnO (0.42; 608).

Minor- and trace-element group with affinity to Li

This group comprises those elements that are most positively correlated with Li₂O. These are Rb₂O (0.96; 1383), F (0.90; 1378), Cs₂O (0.51;

976), SnO₂ (0.50; 522); Ga₂O₃ (0.48; 386), and MnO (0.32; 1246).

Minor- and trace-element group with affinity to Fe

This group is formed by elements that are positively correlated with FeO_{tot} rather than with MgO or Li₂O. These elements show a tendency to be enriched in annitic micas: TiO₂ (0.44; 1196) and Sc₂O₃ (0.42; 278) belong to this group.

The knowledge that the various mica varieties incorporate minor and trace elements in different proportions also has an impact on the use of partition coefficients in modelling igneous processes. Quantitative information on the partitioning of trace elements between crystals and melts can be obtained by calculating element partition coefficients (*D*) between a mica and the coexisting remaining minerals of its host rock. *D* depends on temperature, pressure, the composition of the liquid, and the composition of the solids.

As shown in Table 6 (right side), *D* values for micas are available for only a limited number of trace elements and, more critically, for only a single variety, Mg biotite. The majority of these values are derived from phenocrysts and ground-mass in felsic volcanic rocks. The strong dependence of major-element composition on the trace-element partitioning between a particular trioctahedral mica and the granitic melt, from which it has crystallized, is shown in Table 6 (left side). Granite host rocks considered in this example are late-collisional biotite, two-mica, and Li-mica granites from the Variscan Erzgebirge, Germany (Förster *et al.*, 1999). It is beyond the scope of this paper to provide a detailed discussion of the possible reasons for the differences in *D* ($D = c_{\text{mica}}/c_{\text{(rock-mica)}}$) for the five mica varieties studied. However, it is well demonstrated that for a number of elements (Ti, Sn, V, Cr, Co, Ni, Sr), the *D* values differ on the order of one magnitude or more. On the other hand, the *D* values for Zn, Ga, Ba and Cs display only a weak correlation with the mica variety. The partition coefficients for Mg biotite derived from the Erzgebirge granites show only poor agreement with *D* values obtained for the same variety of mica in felsic volcanic rocks and migmatites.

The enormous scatter in *D*, which is obvious for almost all trace elements for which partition coefficients are available, make petrological interpretations difficult. It has to be considered that the mica/melt partition coefficients for Ba, Rb and Sr are not independent of the mica major-

TABLE 6. Mean element partition coefficients mica/matrix [$c_{\text{mica}}/c_{\text{rock-mica}}$] as function of mica variety. Coefficients were calculated using mica and whole-rock data from Variscan granites (68–76 wt.% SiO₂) of the German Erzgebirge (see Förster *et al.*, 1999).

Element	Mg biotite		Fe biotite		Siderophyllite		Protolithionite		Zinnwaldite		Mg biotite N & C (85) ¹		Mg biotite M & H (83) ²		Mg biotite E & G (94) ³		Mg biotite B <i>et al.</i> (94b) ⁴	
	Mg# = 0.39	$n_{\text{mica}} = 7$ $n_{\text{rock}} = 13$	Mg# = 0.29	$n_{\text{mica}} = 30$ $n_{\text{rock}} = 15$	Mg# = 0.12	$n_{\text{mica}} = 23$ $n_{\text{rock}} = 16$	Mg# = 0.06	$n_{\text{mica}} = 26$ $n_{\text{rock}} = 22$	Mg# = 0.04	$n_{\text{mica}} = 11$ $n_{\text{rock}} = 20$	Mg# = 0.51	Mg# = 0.49	Mg# = 0.38	Mg# = 0.38	Mg# = 0.38	Mg# = 0.38	Mg# = 0.38	Mg# = 0.38
Ti	24		200		26		19		16									
Sn	19		56		32		14		6.2									
Sc	26		30		25		27		15		4.9–20	13.1–18.1					42	
V	26		~200		61		12		8.4		8.3–31	3.7–6.7					79	
Cr	100		21		7.4		3.7		3.6								42	
Ga	1.6		2.7		3.7		4.7		2.9		13.6–205	7.9–13.4						
Mn	18		30		24		19		8.2		42–230	13–19					9.7	
Co	49		123		16		5.7		3.3								2.8	
Ni	70		52		13		2.2		2.0								45	
Zn	14		25		28		27		31									
Li	33		50		79		68		77									
Sr	0.04		0.19		0.30		1.5		2.0		0.29–0.53	3.7–7.0					7.2	0.01
Ba	2.6		3.4		2.3		1.9		3.8		5.6–36	3.0–5.3					0.6	
Rb	4.6		4.3		8.5		9.6		10		2.3–4.1	1.2–4.4					9.6	7.0
Cs	14		13		13		16		19									
F	21		32		21		9.4		6.8									27

¹ = Twin Peaks high-Si rhyolite, Utah (Nash and Crecraft, 1985); ² = Bishop Tuff high-Si rhyolite, California (Mahood and Hildreth, 1983);

³ = Bishop Tuff rhyolite (Ewart and Griffin, 1994); ⁴ = peraluminous migmatites, Peña Negra, Spain (Bea *et al.*, 1994b); Mg# = Mg/(Mg+Fe_{tot})

element composition. These three elements are used widely in quantitatively modelling the evolution of melts during fractional-crystallization differentiation. However, the results of that modelling may differ considerably, depending on the *D* values selected.

Conditions of formation of compositional extremes among the trioctahedral micas

The reasons for crystallization of compositionally anomalous micas are only poorly understood. Firstly, the reasons are complex and include a variety of factors, the relative importance of which is difficult to determine. Furthermore, because of the lack of a data compilation, many authors did not realize that they were working with compositional extremes and, thus, did not study the causes for the unusual mica chemistry. Principally, the reasons for element enrichment in micas are better understood than the conditions, under which micas formed that are low in certain trace elements. Some of the more important processes leading to the growth of micas, which are enriched or depleted in elements relative to what is usually observed in nature, are discussed here briefly.

Ionic radius and charge are fundamental crystallographic factors that determine the spectrum of elements, which can potentially be incorporated into the mica structure. If incorporation is not possible by simple element-element substitution, coupled substitutions may occur. Several substitution mechanisms in different sheets of the mica structure can be active simultaneously in order to balance the total charge. Site occupancy and substitutional schemes are discussed broadly in the literature and are not repeated here. For the minor and trace elements, information is provided by Frondel (1968; Sc), Hazen and Wones (1972; Co, Ni, Zn, Rb, Cs), Mansker *et al.* (1979; Ba, Ti), Mitchell *et al.* (1987; Ti, Ba), Papin *et al.* (1997; F), Brigatti *et al.* (1998; Ba, Ti), and many others.

Although ionic radius and charge are important factors in determining trace-element distribution, there are other energy factors that need to be considered. This is the situation for the transition metals Fe, Ti, Mn, Cr, Ni, Co and V, for which their uptake from a magma may be controlled by crystal-field stabilization-energy of the respective cations (Henderson, 1982)

Regularities of crystal physics and crystal chemistry further influence the incorporation of

an element into the mica structure. The importance of the sequence of cations on octahedrally coordinated sites is stressed by Mason (1992), who explains the Fe-F avoidance in Li-free trioctahedral micas (Munoz, 1984) by a model assuming that F is coordinated to Mg cations only.

In addition to these internal factors, a number of external processes and physicochemical parameters are responsible for the crystallization of micas with atypical enrichment or depletion of minor and trace elements. One of these preconditions is simply that, at the time of mica formation, a specific minor or trace element must have been present at an unusually high or low chemical potential or activity. However, it should be kept in mind that the elements in question may be enriched in the crystallization area but that this enrichment must not be manifested necessarily in the growing mica. Either crystallographic handicaps are evident for the mica itself, or the crystallization assemblage includes minerals other than micas, which preferably accommodate a particular element.

Metalliferous ore deposits are among the geological sites particularly receptive to hosting micas that are enriched in certain trace elements as result of extreme fractionation, fluid-induced mobilization/redeposition of elements, or other processes. Thus, many micas rich in Ba, Ti, Mn and Zn are formed during ore-forming processes or the metamorphic reworking of pre-existing Pb-Zn-Fe-Mn ores (e.g. Craig *et al.*, 1985; Kazachenko *et al.*, 1988; Dasgupta *et al.*, 1989; Tracy, 1991; Frimmel *et al.*, 1995; Jiang *et al.*, 1996). The same is true for Rb- and Cs-rich zinnwaldite and lepidolite in greisens and pegmatites that may have the potential to be mined for rare metals (e.g. Černý *et al.*, 1985).

Physicochemical parameters, which may either encourage or suppress the uptake of elements, include temperature, pressure, and oxygen, HF, and HCl fugacities. High temperatures facilitate the formation of Ti-rich micas in metamorphic rocks (Kwak, 1968). Temperature is thought to be a critical factor in crystallization of Ba-rich phlogopite in contact-metamorphic rocks (Solie and Su, 1987). High oxygen fugacity seems to favour the crystallization of Ti-rich phlogopite in lamproites and mafic alkaline rocks (Mitchell, 1985). Highly oxidizing conditions may be essential for the formation of Mn-rich micas in skarns and ores and their metamorphic equivalents (Hiroi *et al.*, 1992). However, this suggestion is in contradiction to experimental results indicating

that incorporation of Mn in phlogopite is favoured by oxygen fugacities lower than those defined by the Ni-NiO buffer (Papin and Robert, 2000).

For micas growing from a melt, the degree of fractionation as well as the nature of the melt (crustal or mantle) govern their trace-element distribution patterns. Highly fractionated crustal granite-pegmatite melts may produce Rb-Cs-F-Sn-rich micas (Förster *et al.*, 1999). Late-stage mantle-derived magmas may generate Mg-rich micas high in Ba and Ti (Bigi *et al.*, 1993). In mantle rocks, Ba and Ti tend to be concentrated in late-magmatic rather than in early formed micas (Mansker *et al.*, 1979; Barnett *et al.*, 1984). Processes involving fluid-rock interaction seem particularly suited to produce micas of extraordinary composition. Fluids facilitate the exchange of matter between xenoliths or enclaves during interaction with their host rocks (Zhang *et al.*, 1993a). These inclusions act as sponges for mobile elements contained in the surrounding magma. Metasomatic processes involving Ba-rich hydrous fluids are thought to be responsible for formation of barian phlogopite in mafic mantle-derived rocks (Arima, 1988). Interaction of Ba-rich submarine-exhalative hydrothermal solutions with clay minerals are suggested to have generated Ba-rich micas in a stratiform Pb-Zn-Ag deposit in China (Jiang *et al.*, 1996).

Another source for compositionally extreme micas involves granitic melts or pegmatitic liquids that have interacted extensively with the country rock, either during outflow of residual or pegmatic fluids into the country rocks or an influx of (usually metamorphic pore) fluids into (more or less solidified) granite/pegmatite. In the endo- and exocontact of these igneous rocks, micas containing element associations from different sources may be generated. For example, a Li-rich rare-element pegmatitic melt has intruded into Mg-rich rocks either of igneous or sedimentary origin. This melt contains elevated abundances of F, Rb, Cs, Sn and other incompatible elements; the wall rock, in contrast, is enriched in trace elements such as V, Cr, Ba, Ni, Co, Zn and others. Therefore, the Mg-rich micas may contain elevated concentrations of the trace elements accompanying Li, and Li-rich micas contain elevated concentrations of the trace elements coming from the wall rock. As a result, we observe: (1) Li-rich phlogopite (Pomârleanu *et al.*, 1986); (2) zinnwaldite anomalously high in Mg (Semenov and Shmakin, 1988; Lagache and Quéméneur, 1997); (3) high-Li-Rb-Cs-Mg

'siderophyllite' formed at the exocontact of the Tanco pegmatite (Icenhower and London, 1995); and (4) rubidian caesian 'Fe biotite' from pegmatite exocontacts at Red Cross Lake, Manitoba (Hawthorne *et al.*, 1999). Such 'bigenetic' micas may also be present in hybrid granites and their contact aureoles (Neiva 1981a,b).

Summarizing the results of this study, the following rocks are prime candidates to host trioctahedral micas containing 'abnormal' concentrations of minor and trace elements: (1) granitic pegmatites and aplites of strongly peraluminous or alkaline affinity; (2) wall rocks at the endocontact of rare-element pegmatites; (3) mafic alkaline rocks; or (4) volcanogenic-sedimentary and skarn deposits and their metamorphic equivalents.

Concluding remarks

The results of this review will support future studies on the chemistry of trioctahedral micas in a number of ways. Firstly, a broad knowledge of the mica variety may be gained simply from the nature of its host rock and permit the selection of an appropriate strategy of chemical analysis for each element of interest. So it can be predicted easily whether a particular element requires use of an electron microprobe or other microanalytical techniques (SIMS, LA-ICP-MS) that enable a measure of concentrations at the ppm level. Secondly, from compositions measured it can be concluded readily whether a trioctahedral mica contains minor or trace elements at average concentrations or whether one or more of these components are significantly enriched or depleted, thus indicating mica crystallization in a particular physico-chemical environment. Recognition of unusual conditions during mica formation may help to decipher the genesis of the rocks containing these micas. Thirdly, the diagrams presented in this paper are created to encourage other investigators to examine unusual trace-element concentrations as potential analytical artefacts. Finally, the study emphasizes the need for additional data on trace elements for micas from specific environments, e.g. igneous rocks of anorogenic or post-orogenic origin.

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(The complete list of references on which this study is based is available from the authors on request.)

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