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EXTREME FRACTIONATION IN RARE-ELEMENT GRANITIC PEGMATITES: SELECTED EXAMPLES OF DATA AND MECHANISMS

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ABSTRACT

Granitic pegmatites of the rare-element (and miarolitic) class display extreme fractionation and accumulation of rare lithophile elements, beyond the limits observed in other igneous and postmagmatic assemblages. Enrichment in Li and Cs leads to precipitation of rock-forming spodumene, petalite, Li-phosphates or lepidolite, and pollucite. These species can be interpreted as crystallochemically conditioned Li- and Cs-based feldspathoids, crystallizing along with (and after) the last generations of primary K- and Na-feldspars. Extreme fractionation is encountered in K-feldspar (K/Rb 1.9, K/Cs 22.4, K/Tl 236, Rb/Cs 6.5, Rb/Tl 130 to 35, K/Ba 18,000, Ba/Rb < 0.002); muscovite and lepidolite (K/Rb 1.4, K/Cs 4.0, K/Tl 320, Rb/Cs 4.4, Rb/Tl 80 to 36, Al/Ga 239); pollucite (K/Tl 10, Rb/Tl 60 to 13); microlite, simpsonite and other late oxide minerals of Ta (Nb/Ta < 0.001); manganotantalite (Fe/Mn 0.003); spessartine (Fe/Mn < 0.003); lithiophilite (Fe/Mn < 0.01); hafnon (Zr/Hf 0.014), and hawleyite and černýite (Zn/Cd 0.067). Classic crystallochemical concepts of Goldschmidt and Ringwood alone are not adequate to explain the above values. Selective extraction and transport in a volatile phase (by diffusion or in an exsolved hydrous fluid), complexing stable to relatively low late- to postmagmatic temperatures, and crystallochemical preferences for specific mineral structures operate in conjunction with crystal/melt fractionation; the environment evolves from that of a volatile-saturated residual granitic melt, through that of a melt coexisting with exsolved supercritical fluid, to that of an aqueous solution and possibly a gas phase, in a closed or restricted system.

Keywords: granitic pegmatites, fractionation, rubidium, cesium, thallium, barium, strontium, manganese, gallium, hafnium, tantalum, cadmium.

SOMMAIRE

Les pegmatites granitiques à éléments rares (et miarolitiques) démontrent un degré de fractionation et d'accumulation des éléments lithophiles rares, au delà des limites établies dans les assemblages ignés et postmagmatiques. Un enrichissement en Li et en Cs mène à la précipitation de spodumène, pétalite, phosphates de lithium ou lépidolite, et pollucite. Ces espèces équivaudraient à des feldspathoïdes spécialisés pour accommoder le Li et le Cs, qui cristallisent pendant (et suivant) la formation des dernières générations de feldspaths de K et de Na primaires. La fractionation extrême se voit dans le feldspath potassique (K/Rb 1.9, K/Cs 22.4, K/Tl 236, Rb/Cs 6.5, Rb/Tl de 130 à 35, K/Ba 18,000, Ba/Rb inférieur à 0.002), la muscovite et la lépidolite (K/Rb 1.4, K/Cs 4.0, K/Tl 320, Rb/Cs 4.4, Rb/Tl de 80 à 36, Al/Ga 239), la pollucite (K/Tl 10, Rb/Tl de 60 à 13), la microlite, la simpsonite et autres oxydes tardifs de Ta (Nb/Ta inférieur à 0.001), la manganotantalite (Fe/Mn 0.003), la spessartine (Fe/Mn inférieur à 0.003), la lithiophilite (Fe/Mn inférieur à 0.01), le hafnon (Zr/Hf 0.014) et la hawleyite et la černýite (Zn/Cd 0.067). Les seuls concepts cristallochimiques classiques de Goldschmidt et de Ringwood ne suffisent pas pour expliquer ces valeurs. Une extraction sélective et un transfert dans une phase volatile (par diffusion ou dans une phase fluide exsolvée), une complexation stable à des températures tardi-magmatiques à postmagmatiques relativement basses, et des préférences cristallochimiques pour des structures spécifiques vont de pair avec une fractionation cristal/liquide; le milieu évolue de l'état d'un bain fondu résiduel saturé en composants volatils à celui d'un bain fondu en coexistence avec une phase supercritique exsolvée, et enfin à celui d'une solution aqueuse accompagnée possiblement d'une phase gazeuse, le tout dans un système fermé ou du moins restreint.

(Traduit par la Rédaction)

Mots-clés: pegmatites granitiques, fractionation, rubidium, césium, thallium, baryum, strontium, manganèse, gallium, hafnium, tantale, cadmium.

INTRODUCTION

Granitic pegmatites of the rare-element and, in part, miarolitic classes display extreme fractionation and accumulation of numerous lithophile elements beyond the limits observed in other igneous and postmagmatic assemblages. This fact has been recognized and accepted in general terms since the end of the 19th century. However, there are few modern crystal-chemical studies of major- and trace-element distributions, and the processes promoting the fractionation and accumulation are poorly understood.

The geochemical signatures of rare-element pegmatites are all the more interesting because they represent the extremes of fractionation trends encountered in the final stages of granitic differentiation, in very leucocratic, high-silica, metaluminous to peraluminous granites and rhyolites. Recent

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studies of these intrusive and extrusive rock-types have provoked a healthy interest in the long-neglected extremes of lithophile-element fractionation, and they have produced contrasting or even controversial interpretations (*e.g.*, Hildreth 1979, Michael 1983, Miller & Mittlefehldt 1984). In addition, some recent experimental data relevant to the behavior of rare lithophile elements in granitic melts and supercritical fluids contradict the classic views as put forward by V.M. Goldschmidt and A.E. Ringwood.

The present review is aimed at some selected examples that may best document the extreme character of rare-element fractionation and accumulation in the waning magmatic stages of granitic crystallization, and during the transition into supercritical and "subcritical" regimes. The traditional views of this transition are currently under critical review (London 1982, 1983, 1984a, London *et al.* 1982). Thus a survey of fractionation trends related to the late stages of pegmatite consolidation is desirable to summarize our present understanding and to point out areas of twilight.

Elemental abundances and ratios discussed here come from data on the rare-element and, partly, miarolitic classes of late- and post-tectonic granitic pegmatites of orogenic belts (*cf.* Černý 1982a, 1985 for pegmatite classification). Only rarely is a reference made to the *internal* evolution of anorogenic pegmatites associated with rift-related granitic plutons; the overall geochemistry of these pegmatites and the derivation of their parent melts are fundamentally different from those of the orogenic kindred (*cf.* Martin & Piwinskii 1974, Foord & Martin 1979). Complex granitic pegmatites of the aforementioned classes are treated here as products of extended differentiation of large reservoirs of granitic magma. The present state of arguments in favor of direct metamorphic–anatectic origin of complex rare-element pegmatites and their mineralization does not warrant serious consideration (Norton 1973, 1981, Stewart 1978, Černý 1982b, Gaupp *et al.* 1984).

The fractionation phenomena are demonstrated on selected examples that cover the most extreme data from the available references. A complete coverage of the literature was not attempted but important sources of additional information are quoted wherever appropriate. Similarly, geochemical characteristics of granitoid rocks also are represented only by selected examples, to provide a comparison for the pegmatite data.

Most of the diagrams are of the type A/B *versus* B; these are not particularly suitable for geochemical correlations in general but provide an easy and instantaneous review of absolute abundances and levels of fractionation. However, some other diagrams serve specific purposes, and still other "traditional" types are used here to facilitate comparison with the literature [*e.g.*, Rb *versus* Tl, Mn/(Mn + Fe) *versus* Ta/(Ta + Nb)]. Unless stated otherwise, all the plotted data are given in weight units and ratios.

LITHIUM

During magmatic fractionation, Li does not behave as a typical alkali element (Heier & Billings 1970b). Owing to its suitable ionic radius but lower charge, it is admitted in only negligible amounts into octahedral sites of ferromagnesian minerals and virtually excluded from felsic phases. Notable enrichment is found only in biotite and muscovite of late generations of granitic plutons, such as in two-mica granites and leucogranites (3,000 ppm: Siroonian *et al.* 1959). Nevertheless, the leucogranites quoted above contain only about 250 ppm Li, and the Li content of "normal" granites is much lower (<100 ppm: Beus *et al.* 1968, Stewart 1978), as other rock-forming and accessory minerals present do not accept Li in significant quantities.

The Li content of a granite cannot be taken as necessarily representative of the Li concentration in the parent melt. As the crystallochemical misfit prevents Li from entering the structure of felsic rock-forming minerals, Li is very effectively excluded from solidifying granitic magmas. This is demonstrated by the loss of Li during devitrification of rhyolitic glasses (Burt *et al.* 1982). The Li content of subordinate to accessory mafic minerals such as micas is the only relative indicator of Li enrichment attained by the parent magma (Kosals & Mazurov 1968, Kozlov 1969).

In the course of consolidation of granitic intrusive bodies, exclusion of Li from crystallizing minerals leads to its accumulation in residual magmas. Together with other fluxing agents such as H_2O, F and B, lithium depresses the solidus temperature and increases the range of crystallization temperatures in these residual melts (Wyllie & Tuttle 1964, London 1983). The general geochemical association of Li has led to its designation as a "fluorophile" element (Hildreth 1981, Burt *et al.* 1982). Hildreth (1981) suggested that complexing of Li with H_2O or F (Shawe 1968, Bailey 1977) may assist its extraction from differentiating magmas into residual melts. Besides the obvious crystallochemical reasons, closely related mechanisms of transport of Li and F may promote the crystallization of lithian muscovite, lepidolite and amblygonite.

Solodov (1971) claimed that 5,000 ppm Li (1.07 wt.% Li_2O) is the minimal concentration required to precipitate Li-rich minerals in granitic pegmatites. This threshold value is close to the lower limit of the bulk compositions of homogeneous spodumene- and petalite-rich pegmatites, and of spodumene- and petalite-rich inner zones of texturally heterogeneous, zoned pegmatite bodies (1.0 – 1.2 wt.% Li_2O:

Stewart 1978, Figs. 1, 2). Experimental work in the Ab + Qtz + Ecr system at 2000 bars P(H_2O) confirms that such an accumulation of Li should be expected in granitic melts before the crystallization of Li-rich minerals (Stewart 1963, 1978). Experimental data also indicate that about 2 wt.% Li_2O (equivalent to 25 wt.% spodumene) represents the maximum possible accumulation of Li in solid products of magmatic fractionation. Those values are again in good agreement with observations on Li-rich pegmatites (Stewart 1978). (However, virgilite forms as a liquidus phase in the Peruvian Macusani glass that contains only 2,000 – 3,700 ppm Li: Elliott & Moss 1965, Barnes *et al.* 1970, French *et al.* 1978).

The buildup of Li concentration in a pegmatite melt that precedes the precipitation of Li minerals *sensu stricto* leads to increased contents of Li in early rock-forming phases. Early generations of muscovite may contain as much as 1.5 wt.% Li_2O (*e.g.*, Rinaldi *et al.* 1972), and even quartz shows significant $Li^+ + Al^{3+} \rightarrow Si^{4+}$ substitution (60–225 ppm Li: Stavrov 1963). The crystallochemical role of Li in feldspars is uncertain, and much of their Li is attributed to inclusions of micaceous minerals (Smith 1974). However, Li contents reaching 200 ppm were found in natural feldspars by ion probe (E.E. Foord, pers. comm. 1984), and experimental incorporation of Li into sanidine was shown to be explainable by a local lattice-deformation effect (Iiyama & Volfinger 1976). A well-defined correlation of Li with Rb in K-feldspar from several pegmatite fields containing spodumene- and petalite-bearing pegmatites (Fig. 1) suggests that a similar mechanism may ease the Li incorporation with increasing substitution of K by the large alkalis Rb and Cs. Thus an appreciable quantity of Li becomes incorporated in early crystallizing phases (including early plagioclase, tourmaline and beryl) before its accumulation reaches the level sufficient to trigger the crystallization of Li minerals proper.

Depending on the absolute and relative activities of $(PO_4)^{3-}$, F^-, H^+, Na^+ and K^+, the bulk of Li may become incorporated into three mineral assemblages: (i) anhydrous aluminosilicates, (ii) phosphates, and (iii) (Li,F)-enriched micas.

Spodumene- and petalite-bearing pegmatites

Spodumene or petalite crystallizes as the exclusive or predominant carrier of Li from pegmatite melts and fluids with low $(PO_4)^{3-}$ and F^- contents. Spodumene is typical of relatively high-pressure environments (*e.g.*, Kings Mountain, N.C., Black Hills, S.D. and Yellowknife, N.W.T., pegmatite fields: Kesler 1961, Kunasz 1982, Norton 1975, Meintzer *et al.* 1984). In contrast, petalite occurs in low-P regimes (*e.g.*, Tanco, Manitoba and Bikita, Zimbabwe pegmatites: Černý 1982c, Cooper 1964). The two minerals are related by the reaction Pet ⇌ Spd + 2 Qtz ($LiAlSi_4O_{10} \rightleftharpoons LiAlSi_2O_6 + 2\ SiO_2$), recognized and experimentally explored by Stewart (1963, 1978). The reaction boundary was recently refined by London & Burt (1982b) and London (1984b). London (1984b) also established the stability field of eucryptite $LiAlSiO_4$, which forms only as a product of subsolidus alteration under a restricted range of conditions.

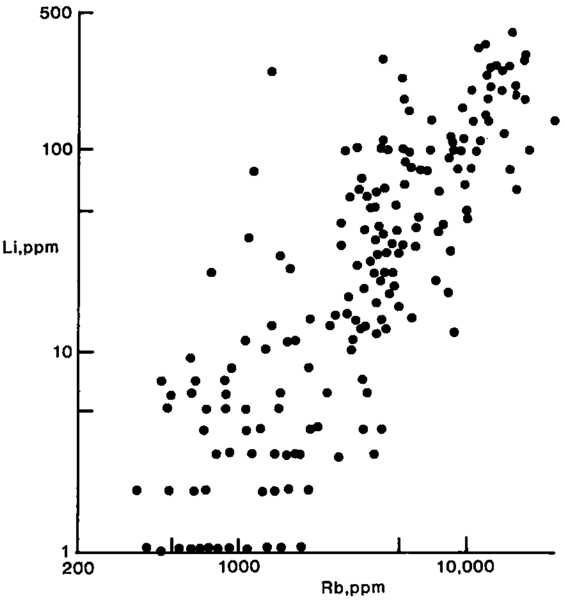


FIG. 1. The Li *versus* Rb contents of K-feldspar from rare-element granitic pegmatites. Data from the Tanco pegmatite (unpubl. data of P.Č.), Yellowknife pegmatite field (unpubl. data of R.E. Meintzer), Borovik-Romanova & Kalita (1958) and Solodov (1960).

The extreme cases of almost exclusive Li-aluminosilicate crystallization are represented by the spodumene pegmatite type (with negligible phosphates and no lepidolite) and by some petalite-bearing pegmatites that display a similar lack of Li-phosphates and lepidolite. In these pegmatites, in which the anionic component of the parent medium is largely represented by silicate and aluminosilicate polymers, Li comes close to the geochemical and crystallochemical role of a true alkali metal. As expressed in Ginsburg's (1960) Na(Ca)–K–Li scheme of alkali succession during primary crystallization of a pegmatite, Li-aluminosilicates generally crystallize simultaneously with and subsequent to the last generations of primary feldspars. They can be interpreted as crystallochemically conditioned Li-based feldspathoids [r_i(Li) being too small for true feldspar structures], extending the crystallization range of anhydrous aluminosilicates of K and Na. It should be noted in this respect that spodumene possesses the clinopyroxene structure, and its Li + Al pair is structurally equivalent to, *e.g.*, Ca + Mg in diopside. However, the petalite structure has some similarities to the framework silicates (Zemann-Hedlik & Zemann 1955, Černý & London 1983).

It should be stressed that the composition of the feldspar-poor core - margin zone of spodumene + quartz is not necessarily representative of the composition expected of a Li-rich melt at its thermal minimum. For this reason, Stewart (1978) advocated crystallization from a supercritical fluid rather than a residual melt for these assemblages. However, Jahns (1982) assigned a different role to a supercritical fluid exsolved during the crystallization of central pegmatite units, and attributed the origin of the "nonmagmatic" assemblages (including quartz cores) to the effects of large-scale mineral segregation; this view was also supported by Norton (1983).

Lithium-phosphate pegmatites

P-rich pegmatites have most of the available Li bound in phosphate minerals. Triphylite–lithiophilite Li(Fe,Mn)PO_4 is commonly the first mineral of lithium to crystallize (Moore 1973), and it is occasionally the only lithium mineral in Li-poor but (Fe,Mn,P)-enriched, beryl–columbite pegmatites (*e.g.*, Hagendorf-Süd in Bavaria, Big Chief and Bull Moose in the Black Hills of South Dakota: Strunz *et al.* 1975, Norton *et al.* 1962, 1964). In the absence (or after the exhaustion) of available Fe and Mn, amblygonite–montebrasite $LiAlPO_4(F,OH)$ forms in acidic P- and F-rich environments. Lithium aluminosilicates are unstable under these conditions (London & Burt 1982b). Given sufficient concentration of $(PO_4)^{3-}$ and F^-, the phosphate association of (triphylite–lithiophilite) + (amblygonite–montebrasite) may become the only primary lithium carrier even in pronouncedly Li-rich pegmatites (*e.g.*, the Peerless pegmatite in the Black Hills, S.D. and Viitaniemi pegmatite in Finland: Sheridan *et al.* 1957, Volborth 1954, 1956, Lahti 1981).

Pegmatites of the above type are scarce, and current classifications do not recognize them as a separate category. Nevertheless, they can be considered a specific paragenetic and geochemical type, *i.e., lithium-phosphate pegmatites.* The crystallochemical role of Li in this type of pegmatite is largely atypical of an alkali metal. Triphylite is, for example, isostructural with the olivine series, and the Li + (Fe,Mn) pair in the phosphate occupies the same octahedral sites as $(Mg,Fe)_2$ in the silicate analogue. Similarly, Li occurs in octahedral coordination in amblygonite, and its substitution by Na is very restricted.

Lepidolite pegmatites

Pegmatite melts and fluids poor in $(PO_4)^{3-}$ but significantly enriched in F^- precipitate most of their Li in the form of lithian muscovite and lepidolite. Lithium aluminosilicates and phosphates are subordinate or entirely absent, whereas the higher activities of F^- and H^+ commonly lead to the precipitation of topaz, fluorite and microlite (London 1982). The lepidolite type of rare-element granitic pegmatites is the extreme representative of P-poor, F-rich pegmatites with lepidolite as almost the only Li-rich phase (*e.g.*, Brown Derby pegmatites in Colorado, the Pidlite deposit in New Mexico, and the Himalaya pegmatite in California: Heinrich 1967, Jahns 1953, Foord 1976). Concentrations of lepidolite close to the pegmatite cores do occur, but the mica is commonly distributed over several textural units. It should be noted here that the crystallochemical role of Li in the lepidolite pegmatites again is analogous to that of ^{VI}(Al,Fe,Mg) rather than to that of the true alkali metals.

Outside the lepidolite type of pegmatite proper, lepidolite units located close to the pegmatite cores are widespread in complex pegmatites (Tanco, Bikita, Stewart, Varuträsk, Mongolian Altai No. 3: Cooper 1964, Jahns & Wright 1951, Quensel 1956, Wang *et al.* 1981, Černý 1982a, Beus 1960). It is generally agreed that they are among the latest units to consolidate, and are interpreted largely as subsolidus metasomatic units formed at the expense of K-feldspar- and Li-aluminosilicate-bearing assemblages (Hutchinson 1959, Ginsburg 1960, Beus 1960, Norton *et al.* 1962, Stewart 1963, Cooper 1964, Černý 1985). However, some authors consider the possibility of precipitation from exsolved immiscible liquid (Melent'yev & Delitsyn 1969, Melentyev *et al.* 1971). Solidification of lepidolite units from residual magma ("magma-like phase", "final aluminous and alkali-rich product of magma") was proposed by Norton (1983).

RUBIDIUM AND THE K/Rb RATIO

The geochemical behavior of Rb is very closely related to that of K, and the distinctly larger r_i of Rb is mainly responsible for their mutual fractionation in igneous processes; their ionization potentials and electronegativities are about equal. In basic to intermediate magmas crystallizing hornblende or plagioclase, the resulting igneous rocks show increasing K/Rb because K is preferred to Rb in these two minerals (Hart & Aldrich 1967, Murthy & Griffin 1970). However, this trend becomes reversed with significant biotite or K-feldspar precipitation. These two phases invariably show K/Rb decreasing with advancing crystallization, owing to rapid depletion of K and relative accumulation of Rb in the residual melt. Most basic–intermediate–acid sequences of igneous differentiates show only a slight reduction in K/Rb [main trend of Shaw (1968), close to K/Rb of 230]. This is possibly a compensation effect resulting from crystallization of both (Ca,Na)- and K-rich phases.

Granites mark a turning point in K/Rb evolution; the ratio begins to rapidly decrease in products of late-magmatic and postmagmatic crystallization [pegmatite-hydrothermal trend of Shaw (1968), extending into low *X*0 values of K/Rb]. Granites average 190 to 276 ppm Rb, and their average K/Rb is quoted as 300 to 160 (Heier & Billings 1970a). However, Turekian & Wedepohl (1961) have already recognized differences between high-Ca and low-Ca granites, as did Heier & Adams (1964): 110 *versus* 170 and 99 *versus* 170 ppm Rb on average, respectively. The rapidly decreasing K/Rb trend from batholithic biotite granites to satellitic two-mica and muscovite granites is now well established (Beus & Oyzerman 1965, Kolbe & Taylor 1966, Stavrov 1971, Blockley 1980, Ayres & Černý 1982, among others). The Archean Lac du Bonnet batholith and associated leucogranites of the Winnipeg River pegmatite district (Goad & Černý 1981) illustrate this trend (Fig. 2).

The Rb content and the K/Rb ratio of granites are controlled mainly by K-feldspar. As shown experimentally (Volfinger 1969, Beswick 1973, Fung & Shaw 1978) and in natural coexisting phases (Heier & Adams 1964, Lange *et al.* 1966, Riber 1972, de Albuquerque 1975, Neiva 1975, 1977), the Rb contents decrease and the K/Rb ratios increase in the sequence biotite – muscovite – K-feldspar. However, the micas are rarely sufficiently abundant in granites to modify the dominant role of the K-feldspar. Thus values of the K/Rb ratio of granitic K-feldspar cover the same range as those of the whole rocks (Fig. 2; Rhodes 1969, Wilson & Coats 1972; *cf.* also Kosals & Mazurov 1968, Kozlov 1969).

The mechanism of sharp Rb-enrichment in high-silica granitic melts and their solidification products is not clear. Thermogravitational diffusion and other forms of liquid fractionation are favored by some authors (Hildreth 1979, 1981, Ludington 1981), aided by the "hydrophile" to "fluorophile" affinity of Rb (Hildreth 1979, Burt *et al.* 1982). Other authors ascribe the enhanced concentration of Rb and related elements to drastic changes in crystal/melt partition coefficients in the course of the bulk-composition shift from average (72–73 wt.% SiO_2) to silicic (75–78 wt.% SiO_2) granitic melts (Michael 1983,

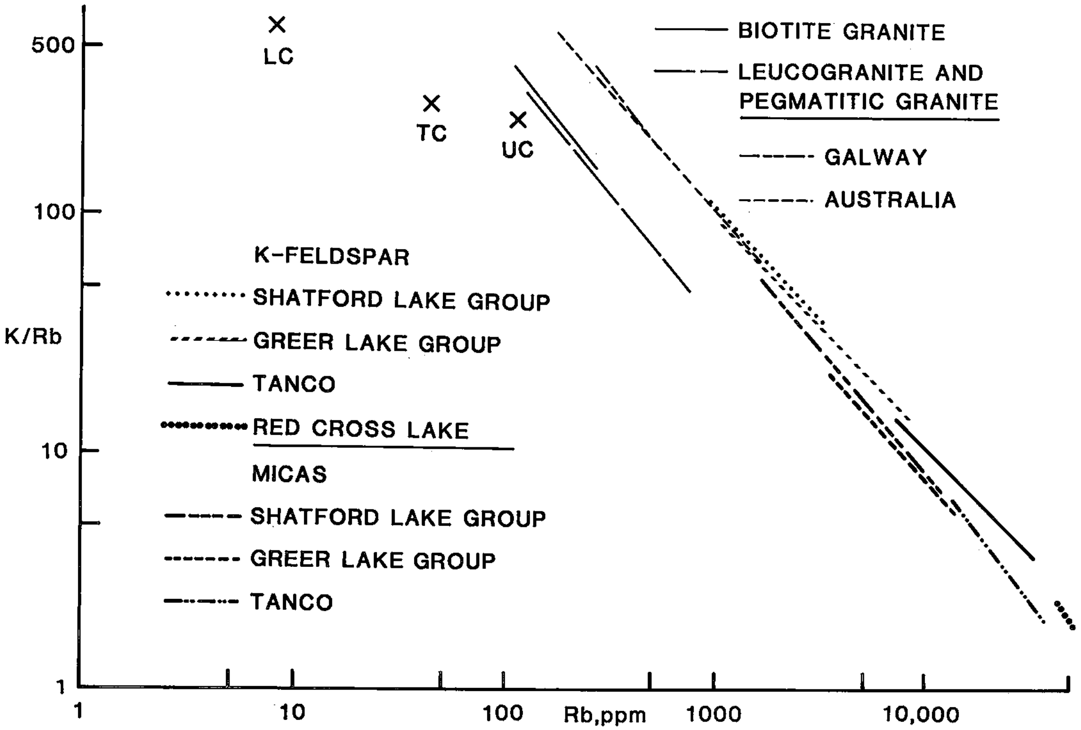


FIG. 2. The K/Rb *versus* Rb trends of granites, K-feldspar and micas. Biotite granite and leucogranite of the Lac du Bonnet batholith, southeastern Manitoba (Černý *et al.* 1981). Granitic K-feldspar from Australia (Rhodes 1969) and Galway (Wilson & Coats 1972). Data for K-feldspar and micas from pegmatites from Černý *et al.* (1981, 1985b) and Černý (1982c). Data for lower crust (LC), upper crust (UC) and total crust (TC) from Taylor & McLennan (1981).

Mittlefehldt & Miller 1983, Miller & Mittlefehldt 1984; *cf.* also McCarthy & Hasty 1975). Whatever the mechanism involved at this stage, the Rb content is increasing at an even faster rate during and after transition from leucogranites and pegmatitic granites to highly fractionated pegmatites (Fig. 2).

Leucogranites and pegmatitic granites parental to groups and fields of complex rare-element pegmatites commonly contain between 170 and 735 ppm Rb, and have a K/Rb ratio as low as 41 (Blockley 1980, Clark & Cheung 1980, Černý *et al.* 1981, Goad & Černý 1981, Černý 1982b). In the pegmatites themselves, the Rb content reaches 4.98 wt.% in K-feldspar, 6.35 wt.% in muscovite and 4.72 wt.% in lepidolite (Jambor & Potter 1967, Rinaldi *et al.* 1972, Gordiyenko 1974, Lopes Nunes 1973, Chaudhry & Howie 1973, Voloshin *et al.* 1977, Khanna 1977, Černý 1982d, Černý *et al.* 1985b, Ferreira 1984); the respective minimal values of the K/Rb ratio are 1.90, 1.15 and 1.37. Considering such a degree of Rb fractionation in these rock-forming and subordinate minerals, it is not surprising that the Rb contents of some pegmatite whole-rock compositions come close to 1.0 wt.% (Jambor & Potter 1967, Kuzmenko 1976).

Besides the extreme *levels* of enrichment in Rb, the steep gradients in fractionation of K/Rb in individual pegmatites are also of interest (Solodov 1960, Correia Neves 1964, Karnin 1980, Lenton 1979, Černý 1982c, Ferreira 1984). Černý *et al.* (1984) found Rb in K-feldspar to range from 180 to 880 ppm (and K/Rb from 390 to 95), over a distance of 1.5 m from border zone to core-margin, in a relatively primitive pegmatite of the beryl–columbite type. In the Tanco pegmatite, K-feldspar ranges from 0.70 to 2.66 wt.% Rb, and from 13.8 to 4.6 in K/Rb, from wall zone to central K-feldspar-bearing zones (Černý 1982c). In individual grains of K-feldspar in a (Li,Rb,Cs)-enriched complex pegmatite, Karnin (1980) described an increase from 0.23 to 0.61 wt.% Rb. Jahns (1982) illustrated a similar case with a Rb range from 0.2 to 0.9 wt.%. Analogous enrichment in Rb is also shown by the micas: in the Tanco pegmatite, muscovite from the wall zone and lepidolite in central parts of the body span 1.60 to 3.60 wt.% Rb, and K/Rb from 4.6 to 2.1 (Černý 1982c; see also Quensel 1956, Vladykin *et al.* 1974, Karnin 1980, Ferreira 1984). Quite commonly, zoned single crystals of mica show extensive core-to-rim K/Rb fractionation as well (Brock 1974, Foord 1976, Lahti 1981).

The spectacular enrichment in Rb in the complex rare-element pegmatites appears to be the ultimate result of continuous fractionation of Rb into the residual melt and emerging vapor phase throughout the leucogranite – pegmatitic granite – pegmatite evolution. Mineral/melt and vapor/melt partition coefficients for Rb never exceed 1 in chloride-based experimental systems (Shaw 1968, Carron & Lagache 1980). However, the vapor/melt distribution of Rb may increase above 1 in fluorine-rich environments, as suggested by the general "fluorophile" behavior of Rb, and by the K/Rb data from unquestionably F-rich assemblages (MacDonald *et al.* 1973). Evolution of supercritical fluid is a typical stage of evolution in volatile-rich granitic magmas, marking the onset of the coarse-grained "pegmatitic" crystallization pattern (Jahns & Burnham 1969, Jahns 1982). Enrichment of the highly mobile supercritical fluid in Rb relative to the melt would promote extraction, transport and final accumulation of Rb in the most fractionated rare-element pegmatites.

In conclusion, it should be noted that the Rb contents of K-feldspar and micas conspicuously decrease after the primary zonal crystallization and formation of most of the metasomatic units. For example, the average Rb is reduced in late K-feldspar veining pollucite (Černý & Simpson 1978). Late muscovite replacing K-feldspar along albitization fronts inherits the K/Rb ratio of the feldspar precursor (Černý 1982c, Černý & Burt 1984). Low-temperature adularia shows a drastic decrease in Rb, even in otherwise extremely fractionated pegmatites (Černý & Chapman 1984). This is probably due to the much reduced molar volume of the mineral structure at low temperatures (*ca.* 300–200°C) compared to that during the main crystallization (about 700–400°C; *cf.* Volfinger 1976).

CESIUM AND THE K/Cs RATIO

Among the major elements, K is the only one for which Cs can substitute. The lower electronegativity and ionization potential of Cs^+ relative to those of K^+ impart a more ionic character to Cs–O bonds. However, the behavior of Cs^+ in igneous and postmagmatic events is governed by its large r_i (1.67 Å) relative to that of K^+ (1.33 Å). Thus Cs^+ is admitted into potassic minerals only reluctantly, much more selectively than Rb^+, and the dispersion of Cs contents in rock-forming minerals is consequently much greater than that of Rb (Ahrens 1966).

As in the case of Rb, the Cs concentration in coexisting phases decreases in the sequence biotite – muscovite – K-feldspar (Volfinger 1969, Carron & Lagache 1972, de Albuquerque 1975, Neiva 1975, 1977), but the relative scarcity of the micas in granites leaves the control of the whole-rock concentration of Cs with K-feldspar. Unfortunately, data on Cs in K-feldspar from plutonic granites are virtually nonexistent.

Due to a very low clarke of Cs (1.7 ppm as compared to 42 ppm for Rb: Taylor & McLennan 1981) and to its extreme partitioning into the melt phase, the Cs content of all igneous rocks is very low. Values also are rather uncertain because of analytical

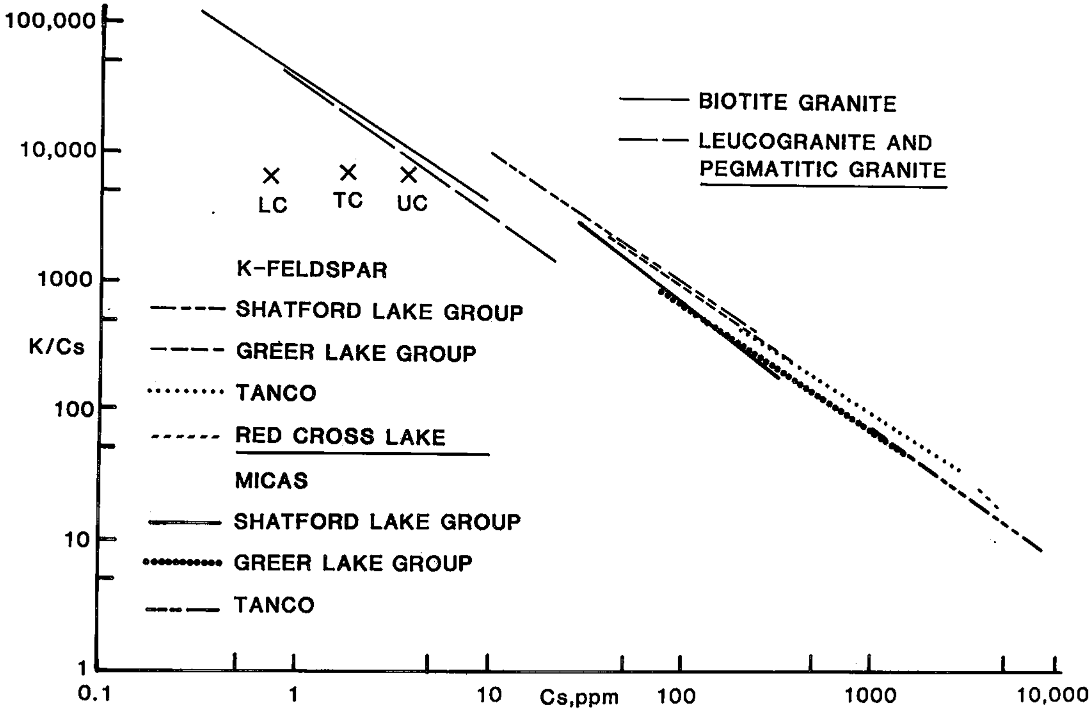


FIG. 3. The K/Cs *versus* Cs trends in granites, K-feldspar and micas. Biotite granite and leucogranite from the Lac du Bonnet batholith, and pegmatitic granites from the Winnipeg River district, southeastern Manitoba (Černý *et al.* 1981). Data for pegmatite micas and feldspars from Černý *et al.* (1981, 1985b) and Černý (1982c). Data for lower crust (LC), upper crust (UC) and total crust (TC) from Taylor & McLennan (1981).

difficulties; estimates of igneous averages vary from 1 to 5 ppm (*e.g.*, Heier & Adams 1964). Concentration of Cs remains at very low levels even in granitoid rocks, including batholithic biotite granites (< 1 to 10 ppm); values of the K/Cs ratio vary from those typical of basalt (~7,500) to about 3,000 in granite (Heier & Adams 1964, Condie & Hunter 1976, Fourcade & Allègre 1981). The high K/Cs ratio and low Cs contents typical of Precambrian granite batholiths are represented in Figure 3 by the Lac du Bonnet biotite granite (Černý *et al.* 1981).

A distinct but still modest enrichment in Cs is found in leucogranites and pegmatitic granites parental to rare-element pegmatites (Fig. 3). Cs contents as high as 10 to 50 (exceptionally reaching 365) ppm and K/Cs ratios decreasing from the 3000 to 500 level are reported (Kuzmenko 1976, Blockley 1980, Černý *et al.* 1981, Goad & Černý 1981). The strong partitioning of Cs into melt and vapor phases, shown experimentally by Carron & Lagache (1980) for chloride-based systems, is evidently responsible. Much more extensive enrichment of Rb in the same rock-types (*cf.* preceding section) corresponds to the more moderate bulk partition-coefficients for this element (Carron & Lagache 1980). The extreme partition of Cs into the melts is also documented by the low partition-coefficient for most mineral/glass pairs in highly evolved rhyolites (Higuchi & Nagasawa 1969, Arth & Hanson 1975, Mahood & Hildreth 1983).

Crystal/melt partitioning does not seem to be the only mechanism leading to the accumulation of Cs in late fractions of melt. Fluoride-bearing systems involving melt, vapor and solid phases systems have not been experimentally investigated, but several authors have expressed the opinion that Cs may follow F rather closely. Cesium is designated a fluorophile element by Hildreth (1979, 1981), Burt *et al.* (1982) and Christiansen *et al.* (1983, 1984), and it is suspected of entering hydrous or fluorine complexes by Hildreth (1981). Some authors advocate a link between Cs and B migration (Stavrov 1963, Kosals & Mazurov 1968). As in the case of Li, and possibly Rb, all these properties would again facilitate fractionation of Cs into silicic granitic melts in the course of different modes of liquid fractionation (thermogravitational diffusion, separation of F-rich immiscible liquids or supercritical fluid). Although all the forms of Cs accumulation and their relative importance remain to be deciphered, their compound effect is well reflected by the Cs enrichment in the rare-element pegmatites.

The process of Cs accumulation into residual systems continues not only from the fertile granites into rare-element pegmatites in general, but it is very strongly expressed even within zoned groups and fields of the pegmatites themselves. A steep increase in Cs occurs only in the most complex (and generally rare) bodies on the outskirts of cogenetic pegmatite swarms, furthest away from their plutonic sources. In order of increasing concentration, the main carriers of Cs are K-feldspar, micas, beryl and pollucite.

In K-feldspar, Cs is mostly restricted to the range of *X* to low *X*00 ppm (Taylor *et al.* 1960, Lopes Nunes 1973, Černý *et al.* 1981, Ucakuwun 1981, Černý *et al.* 1984, Anderson 1984). Only in the complex, rare-alkali enriched, and ultimately pollucite-bearing pegmatites does K-feldspar attain 500–4000 ppm Cs (*e.g.*, Varuträsk, Tanco, Lower Tanco: Quensel 1956, Černý 1982c, Ferreira 1984). The highest Cs content ever recorded seems to be the 4240 ppm in a microcline from northeastern Manitoba, with K/Cs of 22.4 (Černý *et al.* 1985b).

In the mica minerals, the Cs contents remain moderate in most generations of muscovite, increasing to about 0.2 wt.% only in the early muscovite of pollucite-bearing pegmatites (as summarized in the K-feldspar references above, and in Černý & Burt 1984). In lithian muscovite and lepidolite, Cs rapidly increases in good correlation with Li and F (*e.g.*, Gordiyenko 1974, Lopes Nunes 1973, Voloshin *et al.* 1977, Černý 1982c). Cesium reaches its maximum concentration in compositions intermediate between trilithionite and polylithionite, peaking at 1.90 wt.% Cs_2O and K/Cs close to 4.0 (Quensel 1956, Voloshin *et al.* 1977).

The increase of Cs in muscovite of primitive types of pegmatite to (Li,F)-rich lepidolite is several times higher than that in associated K-feldspar. Part of the reason may be the late origin of lepidolite from (Li,Rb,Cs,F)-enriched fluids, but a crystallochemical effect of the changing structure of the mica is also involved. Rotation within the tetrahedral sheets of the mica structure leads to a trigonal distortion of individual 6-membered rings, and reduces their effective inner diameter. This rotation is prominent in muscovite, but becomes progressively reduced with increasing Li substitution into the octahedral sheets (Radoslovich & Norrish 1962, McCawley & Newnham 1971, Bailey 1984). The individual 6-membered rings become much closer to a hexagonal configuration, and their inner diameter increases. Thus the expanded space of the interlayer 12-co-ordinated alkali site in lepidolite becomes more accommodating for large cations such as Cs^+, relative to the constricted size of this site in muscovite.

Beryl accommodates Cs^+ in the channels of its structure. Dimensional relationships of the channel constrictions and bulges permit the entrance of Na^+ and H_2O as well, but the intermediate-size cations such K^+, Rb^+ and Tl^+ are almost eliminated (Hawthorne & Černý 1977). The channel cations are incorporated mainly in response to the substitution of Be^{2+} by Li^+. In the geochemical evolution of consecutive generations of beryl within a zoned body of pegmatite or a group of pegmatites, Na precedes Li in maintaining the electrostatic charge-balance. Cs_2O contents of 1 to 4 wt.% are commonly encountered in beryl from pollucite-bearing pegmatites (Quensel 1956, Beus 1960, Solodov 1960, Feklitchev 1964, Černý 1975, Černý & Simpson 1977).

Pollucite is the ultimate expression of Cs accumulation in the very last residua of granitic fractionation. Solodov (1966) claimed that a concentration of 1.0 wt.% Cs is required in the pegmatite melt to trigger crystallization of pollucite. This limit seems high, as only very few pegmatites approach such a high Cs content in their bulk composition (Černý 1982a,d). However, such a concentration may be attained close to the last stages of pegmatite crystallization.

Occurrence of pollucite in low-pressure petalite-bearing pegmatites, and in the relatively lowest-pressure spodumene-bearing bodies of a given district (Melentyev 1961) attest to the high mobility of Cs. Primary pollucite is typically close to a $Poll_{70-80}Anal_{30-20}$ composition, and contains from 28 to 35 wt.% Cs_2O (Černý 1974, 1979, 1982d). It forms late in the sequence of primary zones in a pegmatite, and commonly is confined to core-margins (Dymkov 1953, Quensel 1956, Neuvonen & Vesasalo 1960, Beus 1960, Solodov 1960, Cooper 1964, Černý & Simpson 1978, Ucakuwun 1981, Černý 1982d). In extreme cases, single bodies of almost monomineralic pollucite may contain up to 87,000 tonnes of Cs_2O (Černý 1982c). It should be kept in mind, however, that rare-element pegmatites containing *any* concentration of pollucite are *extremely* rare.

Precipitation of pollucite may be viewed as the last stage in the progressive crystallization of primary alkali aluminosilicates. After the (Na–Ca)- and K-feldspars and Li-aluminosilicates discussed earlier, pollucite is the last quasi-feldspathic phase to form. Structurally a member of the leucite – analcime – pollucite group, pollucite is *de facto* a feldspathoid with Si/Al in the range 2.20 – 2.50 (Černý 1974). Its crystallization in the presence of excess SiO_2 (commonly in contact with the quartz core) is enforced on crystallochemical grounds. Except for some poorly crystalline products prepared by Borutskaya (1975), end-member cesian feldspar has never been synthesized or found in nature, and it is not expected to form because of the prohibitive size of Cs^+ (Bambauer *et al.* 1974).

In subsolidus supercritical and hydrothermal processes, the Cs contents of feldspars and micas tend to decrease in a manner similar to those of Rb (*cf.* the preceding section for references). The increased contraction of the structures evidently affects Cs^+ even more than Rb^+. Scarcity of Cs^+ in late fluids cannot be a factor, at least not in pollucite-bearing pegmatites. In low-temperature hydrothermal environments, pollucite succumbs to extensive alteration to feldspars, micas, quartz, carbonates and clay minerals, and the Cs is very effectively dispersed in the process (Černý 1978, 1979, 1982d, Černý & Simpson 1978). Significant activity of Cs^+ in late fluids is best documented by the high Cs content of late "alpine" minerals whose structure easily accommodates Cs^+, independent of thermal factors. Late generations of beryl (Hurlbut & Wenden 1951, Evans & Mrose 1966, Černý 1972) and cesian analcime (Černý 1972) contain ~2–11.3 and 6–18 wt.% Cs_2O, respectively.

THALLIUM AND THE K/Tl AND Rb/Tl RATIOS

Thallium has a slightly higher electronegativity and ionization potential than both K and Rb, and its bonding to oxygen is more covalent. However, its ionic radius is virtually equal to that of Rb^+, and consequently about 10% smaller than $r_i(K^+)$. Thus K and Tl exhibit extensive fractionation in geological processes, but Rb and Tl are extremely coherent; enrichment of late phases in Tl is very restricted. The coherency of Rb and Tl applies, however, only to silicate systems. In the presence of sulfur, the chalcophile affinity of thallium and its similarity to Pb and Hg become evident, leading to an effective separation of Tl from K and Rb [although this is apparently not always the case, as reviewed by Fung (1978); sorption of Tl on sulfide gels instead of structural substitution has also been considered by de Albuquerque & Shaw (1972)].

Most continental plutonic rocks including granites have Tl concentrations in the range of 0.01 to 3 ppm, and values of the K/Tl ratio between 150,000 and 30,000 (*e.g.*, Kolbe & Taylor 1966). However, leucogranites, pegmatitic granites and pegmatites exhibit a pronounced enrichment in Tl (to about 4–6 ppm) and consequent rapid reduction of K/Tl (to about 10,000–8,000; *e.g.*, Siedner 1968). This trend is similar to the pegmatitic–hydrothermal trend in K *versus* Rb scattergrams (Shaw 1968, Fung 1978). In view of the similarity of the K–Rb and K–Tl relationships, it is not surprizing that Tl enters the rock-forming silicates in the same order of preference as Rb: biotite > muscovite > K-feldspar (Riber 1972, Fung 1978, Fung & Shaw 1978).

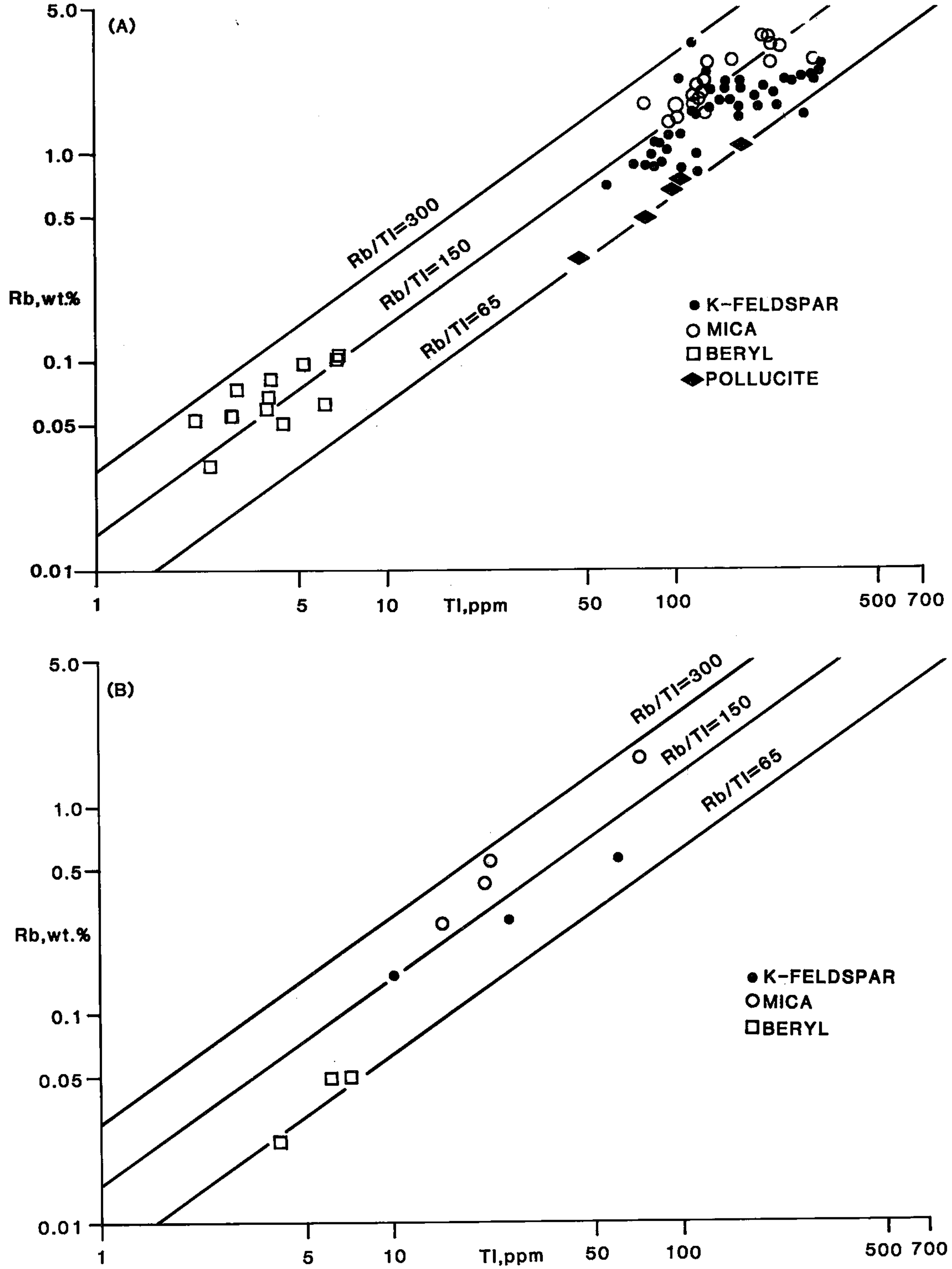
In contrast to the K/Tl fractionation, in continental plutonic rocks, the Rb/Tl ratio is restricted to a relatively narrow and persistent range of 400–65, with no tendency to decrease with increasing abundances of both elements (de Albuquerque & Shaw 1972, Fung 1978). The Rb/Tl ratio in coexisting mineral pairs also shows extensive overlaps (Riber 1972). A very limited range of Rb/Tl fractionation was documented in early studies of pegmatite minerals, and it has been confirmed by more recent data (Heier & Taylor 1959, Borovik-Romanova & Sosedko 1960, Taylor *et al.* 1960, Slepnev 1961, Solodov 1962, Riber 1972, Černý 1982c). With extreme enrichment of potassic pegmatite minerals in Rb, concentration of Tl increases to 20–650 ppm, but the Rb/Tl ratio rarely drops below 60.

No experimental or empirical data are available to model the migration of Tl in crystal–melt–fluid systems. It can only be assumed that Tl closely follows Rb in the advanced stages of fractionation (p. 385). Dietrich & Taylor (1965) and Tauson (1963, 1967) suggested that the Tl distribution in igneous sequences may be influenced by a vapor phase.

Micas and K-feldspar contain the bulk of Tl in any granitic pegmatite. In some cases, the ratio Rb/Tl is higher in the micas than in K-feldspar (Figs. 4A,B; Černý 1982c, Solodov 1962), in orther localities the micas show values intermediate to the range in K-feldspar (Fig. 4C; Borovik-Romanova & Sosedko 1960). The K/Tl ratio ranges from 4,500 to 460 in muscovite, and from 1,500 to 320 in lepidolite (Slepnev 1961, Solodov 1962, unpubl. data of P.Č.). Potassium feldspar shows a general range of 19,600 to 310 (Heier & Taylor 1959, Taylor *et al.* 1960, Slepnev 1961, Solodov 1962, unpubl. data of P.Č.), with an exceptional value of 236 from Manitoba (Černý *et al.* 1985b). More extreme fractionation is suggested by high Tl values from the northern Kola Peninsula, but data for K are not available (Borovik-Romanova & Sosedko 1960).

In rare-element granitic pegmatites, beryl and pollucite are added to the list of the principal Tl carriers. The Rb and Tl concentrations in beryl are one or two orders of magnitude lower than in micas and K-feldspar (*cf.* p. 388), and the Rb/Tl ratio may be equal to, or lower than, those of micas and feldspar (Figs. 4A,B). In contrast, pollucite consistently shows the lowest values of the Rb/Tl ratio (as low as 13), although its absolute Tl content is not necessarily the highest among the minerals of its parent pegmatite (Figs. 4A,C). Both beryl and pollucite fractionate K and Tl very effectively, but only as minor substituents, as neither of them is tailored to the available alkali sites. The K/Tl ranges for Tanco beryl and pollucite are 550–40 and 170–10, respectively (unpubl. data of P.Č.).

In some pegmatites, distinct Rb/Tl fractionation is observed with increasing concentration of both elements, which is at least partly coincident with the progress of pegmatite crystallization. Such a trend


(A)
5.0
1.0
0.5
0.1
0.05
0.01
Rb,wt.%
1
5
10
Tl,ppm
50
100
500
700
Rb/Tl=300
Rb/Tl=150
Rb/Tl=65
● K-FELDSPAR
○ MICA
□ BERYL
◆ POLLUCITE
(B)
5.0
1.0
0.5
0.1
0.05
0.01
Rb,wt.%
1
5
10
Tl,ppm
50
100
500
700
Rb/Tl=300
Rb/Tl=150
Rb/Tl=65
● K-FELDSPAR
○ MICA
□ BERYL

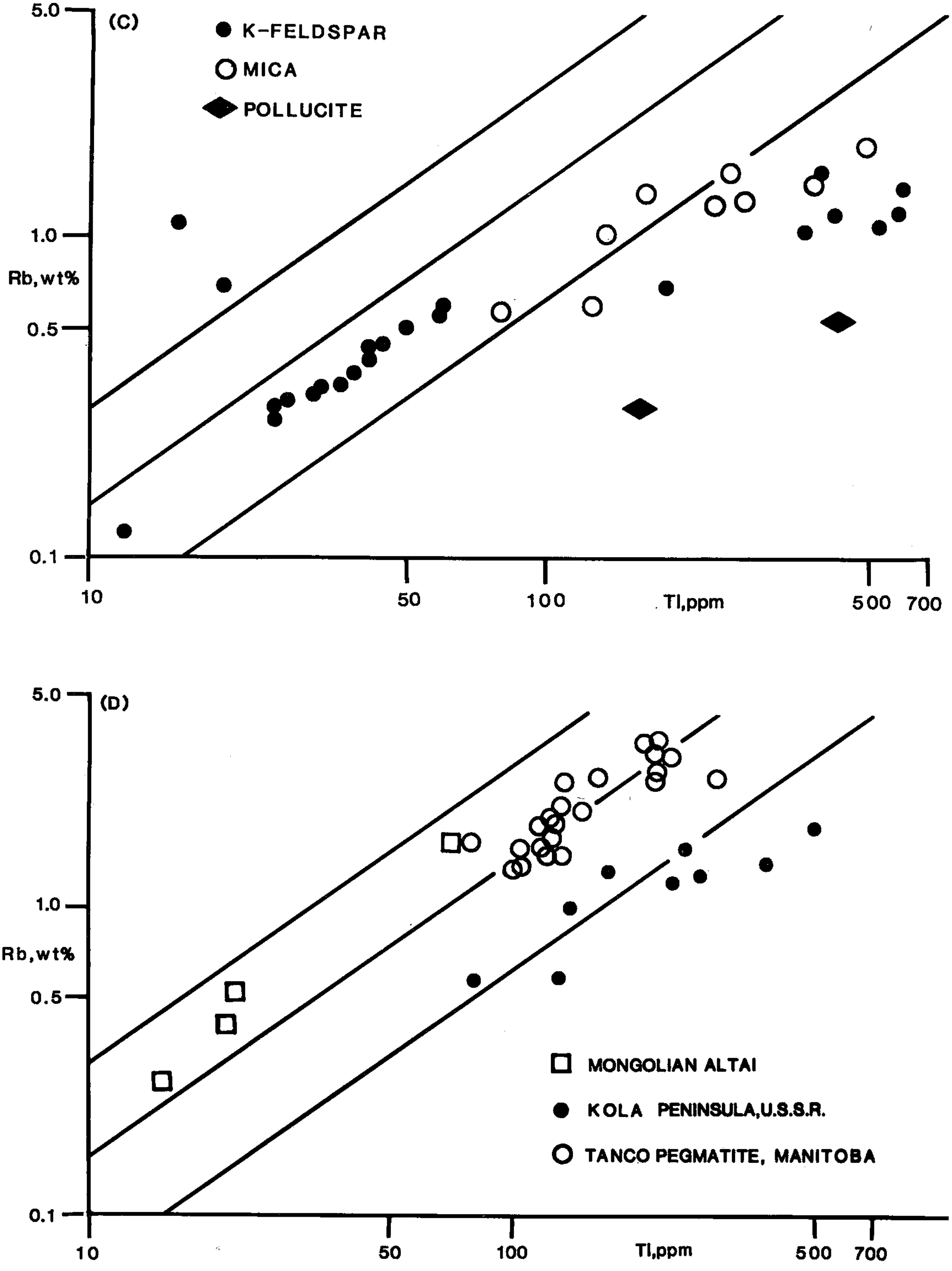


FIG. 4. The Rb *versus* Tl plots for (A) the Tanco pegmatite (unpubl. data of P.Č.; Černý 1982c), (B) the Mongolian Altai pegmatite No. 3 (Solodov 1962), (C) pegmatites of the Kola Peninsula (Borovik-Romanova & Sosedko 1960), and (D) the micas from the above occurrences.

is shown by K-feldspar in the Tanco pegmatite and in the Mongolian Altai No. 3 deposit (Figs. 4A,B). The early to late generations of beryl from Tanco show increasing Rb and Tl and gently decreasing Rb/Tl with increasing Cs content (Fig. 4A; Černý & Simpson 1977, unpubl. data of P.Č.). In contrast, no obvious Rb/Tl fractionation is shown by the diversified mineralogy and bulk composition of the Tanco micas (Fig. 4A). The data for the Kola Peninsula pegmatites (Borovik-Romanova & Sosedko 1960) cover different types of pegmatite from a large district, and an overall Rb/Tl fractionation is evident with increasing concentration of both elements from primitive to highly evolved pegmatites (Fig. 4C).

Despite these local trends of fractionation, it seems that specific levels of Rb and Tl accumulation (and the relatively narrow ranges of their ratios) are characteristic of individual pegmatite fields. For example, Figure 4D shows that the low Rb/Tl value of Kola micas relative to those from Tanco results from both lower Rb and higher Tl concentrations. Similarly, the Rb/Tl ratios of pollucite seem to be fairly constant for samples from a given pegmatite field but distinctly variable among pollucite populations of different fields (unpubl. data of P.Č.).

Partitioning of Tl between silicates and sulfides should not significantly affect granitic pegmatites because of the extreme scarcity of sulfide minerals in them. Nevertheless, the chalcophile tendency of Tl and its partial separation from Rb were observed in the Tanco pegmatite. Late sulfides and sulfosalts of this deposit contain up to 820 ppm Tl (Černý & Harris 1978, unpubl. data of P.Č.).

It can be concluded that the K–Tl pair shows an enormous range of fractionation in igneous-to-pegmatitic differentiation, surpassing by several orders of magnitude that of K and Rb, and it represents one of the most sensitive indicators of fractionation. However, Rb and Tl are confirmed as one of the most coherent pairs of elements in the same environment. This fact emerges clearly from the data obtained for some of the (otherwise) most fractionated pegmatites of the world (Figs. 4A,C). However, the data base is limited, and some of the older information is probably not as reliable as the more recent analytical results. Further systematic study of K, Rb and Tl behavior in primary and alteration stages of granitic pegmatites is desirable.

BARIUM AND THE K/Ba AND Ba/Rb RATIOS

Barium is almost equal to K^+ in size, but it forms a stronger bond with oxygen. Nevertheless, Ba^{2+} behaves according to the classic principle of capture, because of its higher valence. Ba^{2+} tends to be preferred by the K-feldspar structure rather than that

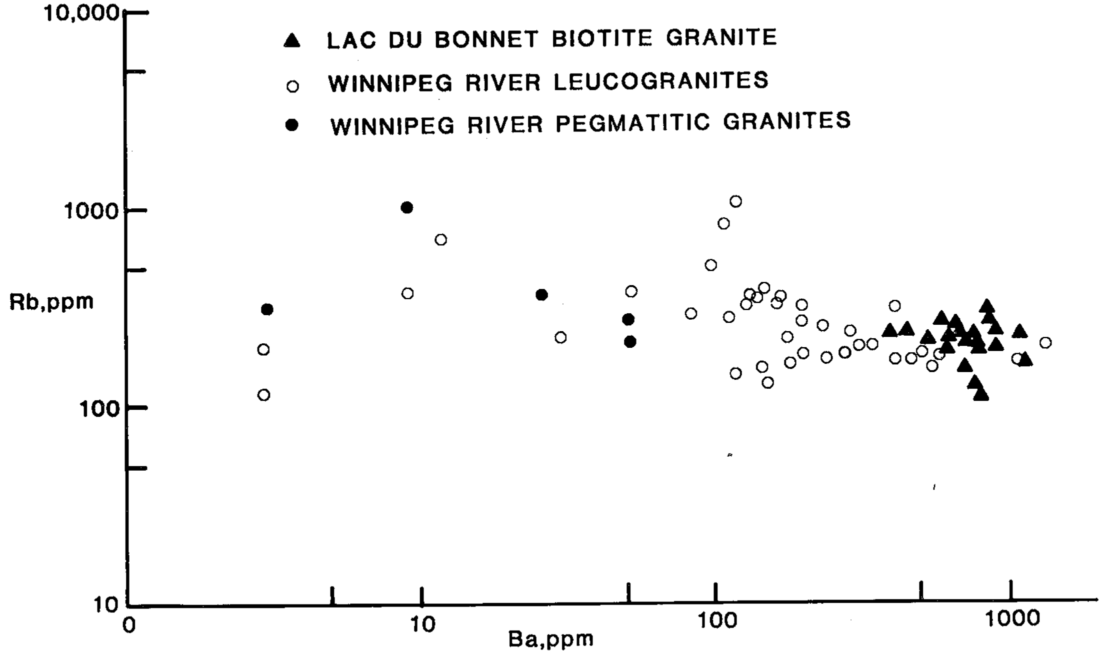


FIG. 5. The Rb *versus* Ba plot for the granitoid rocks of the Lac du Bonnet batholith and the Winnipeg River pegmatite district (after Černý *et al.* 1981).

of biotite (de Albuquerque 1975); consequently, K-feldspar precipitation controls the Ba distribution in differentiated granitic suites.

Barium content increases through peridotite-gabbro-diorite suites from *X* to ~2,000 ppm (K/Ba down to 20) in granodiorites and early granites. However, it becomes rapidly depleted with the onset of significant crystallization of K-rich minerals in granitic rocks proper (Kolbe & Taylor 1966, Vlasov 1966). Late granitic differentiates commonly contain only 900 to 300 ppm Ba, and their K/Ba ratio ranges from 50 to 120 (Fig. 5).

Early precipitation of Ba is reciprocal to the behavior of Rb, and the Ba/Rb ratio rates as one of the most sensitive indicators of fractionation (Taylor & Heier 1960, Taylor 1963). The Ba/Rb ratio of granitoid rocks varies from about 20 in some tonalites to about 2 in biotite granites (*e.g.*, Černý *et al.* 1981). However, the usefulness of Ba/Rb is considerably reduced by the wide scatter of Ba contents even in single units of intrusive complexes, particularly in those with a moderate to low Ba content (*cf.* the leucogranites in Fig. 5).

Steep gradients in Ba, K/Ba and Ba/Rb are observed in highly evolved silicic granites and rhyolites. The controversy in explaining them by either crystal/melt partitioning or liquid fractionation applies here as in the case of Rb enrichment (p. 385). However, crystal/melt fractionation seems to be better supported (McCarthy & Hasty 1976, Michael 1983, Mittlefehldt & Miller 1983, Miller & Mittlefehldt 1984). Hildreth (1979) admitted having difficulties in explaining the behavior of Ba by thermogravitational diffusion, unless a negative Soret coefficient is invoked. In any case, Ba contents of leucogranites and pegmatitic granites are generally less than 500 ppm, and commonly below 100 ppm in the latter (Kolbe & Taylor 1966, Taylor *et al.* 1968). Concentrations as low as 2 ppm have commonly been found (Blockley 1980, Černý *et al.* 1981, Goad & Černý 1981, Černý 1982b). The corresponding K/Ba and Ba/Rb ratios reach the order of 18,000 and 0.002, respectively. In a single fractionated suite, Ba was observed to drop from 287 to 14 ppm, and K/Ba to increase from 162 to 7010, from biotite granite to a garnet + tourmaline-bearing pegmatitic granite (Černý & Brisbin 1982).

Within rare-element pegmatites themselves, steep gradients in Ba content are again the rule, particularly in the less fractionated ones. For example, Shmakin (1979) showed Ba in K-feldspar to decrease from 8800 ppm in the outer zone to 20 ppm in core-margin of the New York mine, Black Hills, whereas Ba/Rb decreases from 23 to 0.03. Černý *et al.* (1984) found Ba in K-feldspar of a beryl–columbite pegmatite type at Věžná, Czechoslovakia, to decrease from 10,000 ppm in the border zone to 40 ppm in miarolitic cavities of the blocky zone. The corresponding values of the K/Ba ratio range from 10 to 1,800. Correia Neves (1964) found a narrow range of Ba contents at lower concentrations, with a wide scatter of Ba/Rb ratios (Fig. 6A). Figure 6B shows the Ba *versus* Rb fields of blocky K-feldspar from two pegmatite series at Cross Lake, central Manitoba (Anderson 1984). The Ba concentrations span three orders of magnitude in both series, and in most of their individual paragenetic zones as well. The variability of Rb is somewhat lower at the level of individual zones. It is interesting to note that the ranges of Ba in both series almost totally overlap,

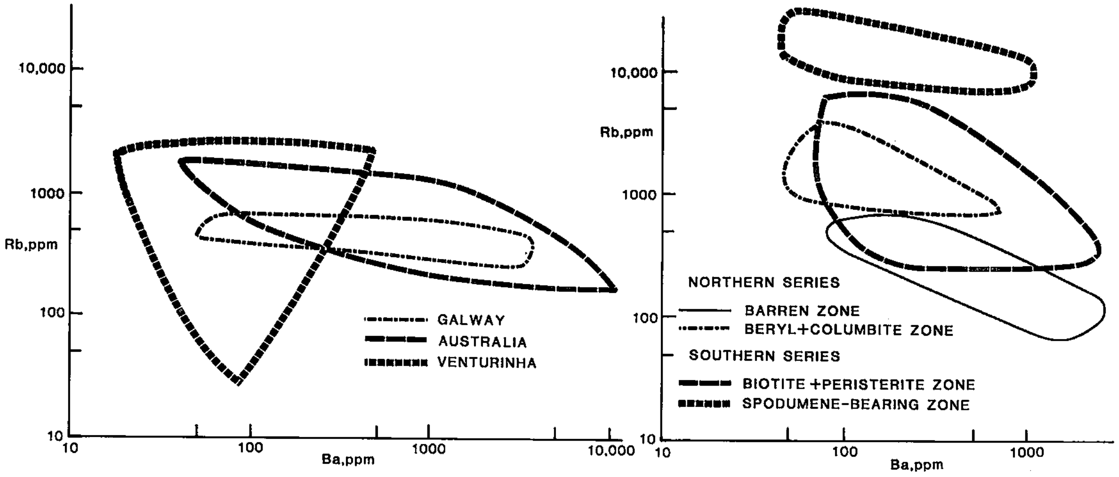


FIG. 6. The Rb *versus* Ba plots of (A) K-feldspar from Australian (Rhodes 1969) and Galway granites (Wilson & Coats 1972), and from the Venturinha pegmatite (Correia Neves 1964); (B) K-feldspar from two zoned pegmatite series of the Cross Lake pegmatite field, central Manitoba (Anderson 1984).

despite the otherwise different geochemical and paragenetic features of the two series. The only decrease to lower Ba concentrations occurs between the barren and mineralized zone of each series (Anderson 1984).

Extensive depletion of Ba in K-feldspar of highly fractionated, rare-alkali-enriched pegmatites is also recorded by Lopes Nunes (1973). This author also provided numerous data on micas that were summarized in a recent review by Černý & Burt (1984). Similar to K-feldspar, Ba in micas spans extensive ranges from high *X*00 ppm in muscovite of the more primitive pegmatites to as low as 15 ppm in lepidolite of complex and pollucite-bearing pegmatite types.

In late hydrothermal stages of pegmatite alteration, Ba becomes somewhat enriched. For example, parabariomicrolite occurs with the late, extremely Ta-rich oxide minerals (Černý & Ercit 1985). Adularia from pegmatite fissures and leaching cavities contains up to 5300 ppm Ba (Černý & Chapman 1984). Also, the Ba-rich phosphates bjarebyite, perloffite, kulanite and samuelsonite are found among products of late alteration (Moore 1982, London & Burt 1982a), and barite is known as a very late exotic rarity from the Tanco pegmatite (Černý 1982c).

Despite the relative abundance of data on the Ba distribution in rare-element granite pegmatites, studies aimed at a systematic and detailed analysis of cogenetic granite-pegmatite assemblages are lacking. Such studies are of critical importance as the overall ranges of Ba concentration seem to be strongly region-dependent (*e.g.*, Shmakin 1979), and mutual comparison of Ba abundances in genetically unrelated granitoid rocks and pegmatites could easily distort geochemical interpretations of pegmatite evolution.

STRONTIUM AND THE Rb–Sr RELATIONSHIP

The complex behavior of Sr in igneous crystallization has been considered by numerous authors (*e.g.*, Taylor & Heier 1960, Heier 1962, Smith 1974). In ionic radius, Sr^{2+} is intermediate between K^+ and Ca^{2+}. Strontium does not enter pyroxenes (or amphiboles) in significant amounts because their 8-co-ordinated Ca sites are too small. In micas, the 12-co-ordinated interlayer K^+ sites are excessively large and rigid. Strontium thus favors feldspar structures with their dimensionally adjustable, 8-fold co-ordination by oxygen around the (K,Na,Ca) sites.

In plagioclase, the Sr–O bond is more ionic than the Ca–O bond, but the effect of the distinctly larger size of Sr^{2+} predominates. Strontium is consequently enriched in late fractions relative to Ca, although the concentration of both elements decreases. In K-feldspar, the higher valency of Sr^{2+} promotes its capture into early precipitates, but the effect is partly offset by the stronger Sr–O bond. The depletion of Sr in K-feldspar with advancing crystallization in granitic systems is slight. Partitioning of Sr between plagioclase and K-feldspar is complex, influenced by competition from other minerals (notably apatite, titanite, hornblende), but close to 1 in most environments (Heier 1962, Smith 1974).

Bulk contents of Sr in differentiated calcalkaline

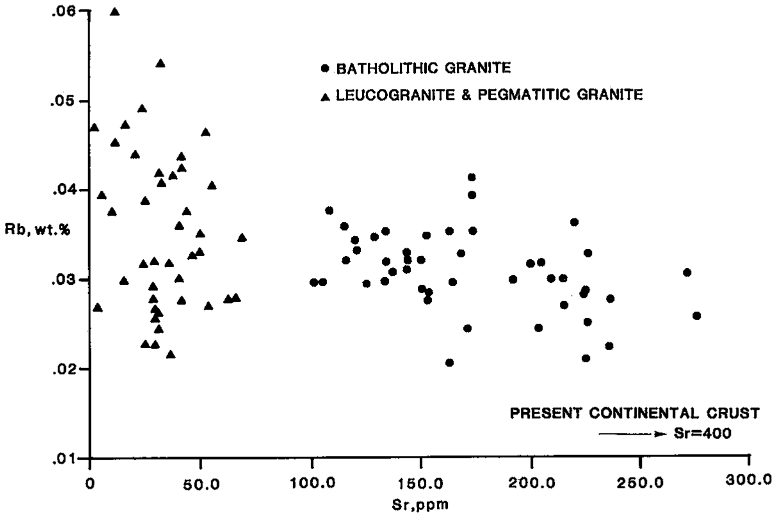


FIG. 7. The Rb *versus* Sr plots of the biotite granite, Lac du Bonnet batholith, and the leucogranites and pegmatitic granites of the Winnipeg River district, southeastern Manitoba (after Černý *et al.* 1981).

systems increase from ultrabasic (low $X0$ ppm) through gabbroic (100–450 ppm) to dioritic and tonalitic compositions (170–800 and 400–1300 ppm, respectively). In granites, the average Sr concentration decreases to lower levels: 440 in high-Ca granites and 100 ppm in low-Ca granites (Turekian & Kulp 1956).

Low Sr contents are particularly characteristic of leucogranites, pegmatitic granites and silicic rhyolites (Kolbe & Taylor 1966, Taylor *et al.* 1968, Clark & Cheung 1980, Jahn *et al.* 1981, Pride & Clark, in prep.). Figure 7 shows the contrasting Sr contents of a typical Archean biotite granite and associated leucogranite of the Lac du Bonnet batholith (Černý *et al.* 1981) as an inverse function of Rb. Leucogranites and pegmatitic granites of the Winnipeg River district have Sr contents from about 100 to 2 ppm (Goad & Černý 1981), as do some occurrences of these rock types in Australia, South Dakota and Colorado (Blockley 1980, Černý 1982b, Shearer *et al.* 1985).

Potassium feldspar of granitic rocks shows 600–150 ppm Sr (*e.g.*, Wilson & Coats 1972), and even less if late leucogranites are included (*e.g.*, 660–65 ppm in Australian granites: Rhodes 1969). The restricted data on plagioclase in granites, summarized by Smith (1974), suggest similar ranges. As in the case of whole-rock compositions, the Sr content of K-feldspar changes antipathetically with its Rb content (Fig. 8). Strontium content of K-feldspar of the Harney Peak pegmatitic granite in the Black Hills of South Dakota ranges from 150 to 60 ppm (Shearer *et al.* 1985). In the Minago series of pegmatitic granites in the Cross Lake field, the K-feldspar carries 290 to 10 ppm Sr (Anderson 1984).

The question concerning the mechanism of rapid Sr depletion in silicic granitic rocks faces the same uncertainty as the Ba depletion discussed earlier (Hildreth 1979). However, most of the evidence available seems to favor feldspar/melt fractionation (McCarthy & Hasty 1976, Michael 1983, Miller & Mittlefehldt 1984); the possibility of liquid fractionation has not been investigated experimentally.

In rare-element pegmatites, Sr concentrations in feldspars of the more primitive types of pegmatite overlap with those of the feldspars from leucogranites and pegmatitic granites and decrease to lower levels. Figure 8 shows the Sr and Rb contents of K-feldspar from the beryl-bearing Venturinha pegmatite, Portugal (Correia Neves 1964); the Sr contents range from 180 to 5 ppm. The ranges of Sr contents in the Be,Nb,Ta-bearing Vėžná pegmatite, Czechoslovakia, are 610–17 ppm for plagioclase and 460–60 ppm for K-feldspar (Černý *et al.* 1984). In both cases the Sr contents rapidly decrease from the early to the late pegmatite units; such a trend is also shown for several localities by Shmakin (1979).

In highly fractionated pegmatites enriched in Li, Rb and Cs, the decreasing trend of Sr as observed in less differentiated bodies seems to be reversed. In the Cross Lake pegmatite field of central Manitoba, the blocky K-feldspar contains 170 to 8 ppm Sr in the more primitive pegmatites (Rb < 5,500 ppm), but a distinct increase in Sr is evident in the spodumene-bearing bodies with increasing Rb (Fig. 9; Anderson 1984). An even more pronounced reversal of an initial (and drastic) Sr depletion was shown by Shearer *et al.* (1985) in the K-feldspar of the Li,Rb,Cs-enriched pegmatites of the Black Hills

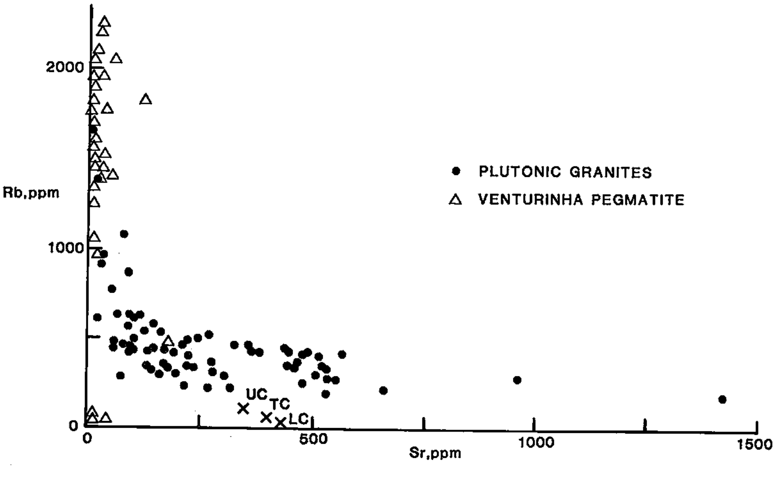


FIG. 8. The Rb *versus* Sr plots for K-feldspar from the Galway and Australian granites (Rhodes 1969, Wilson & Coats 1972), and from the Venturinha pegmatite (Correia Neves 1964). Data for the lower crust (LC), upper crust (UC) and total crust (TC) from Taylor & McLennan (1981).

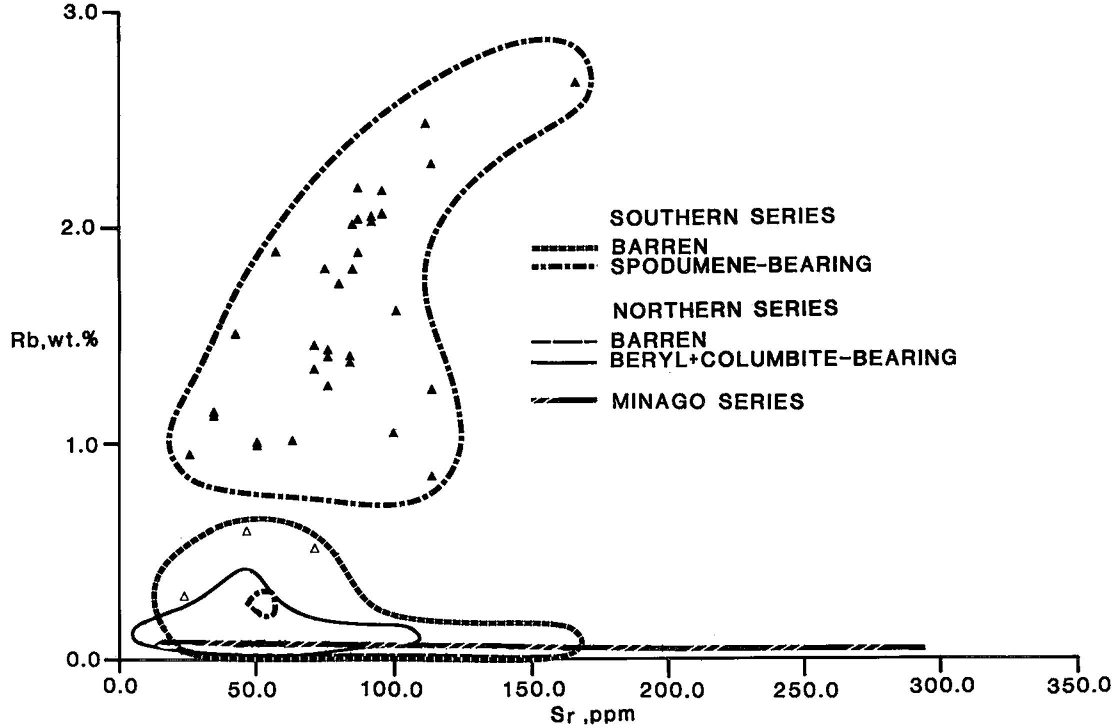


FIG. 9. The Rb *versus* Sr plots of blocky K-feldspar from pegmatitic granites (Minago series) and two zoned pegmatite series of the Cross Lake pegmatite field, central Manitoba (Anderson 1984).

field. However, these trends are strongly exaggerated by (if not entirely due to) the high contents of radiogenic ^{87}Sr in the Rb-rich feldspar.

In Archean and early Proterozoic pegmatitic K-feldspar containing between ~1 and 5 wt.% Rb, the proportion of ^{87}Sr generated by the decay of ^{87}Rb since pegmatite solidification is indeed substantial, and it must be accounted for when crystal/melt fractionation in the consolidating pegmatite is considered. A typical case can be demonstrated using one of the K-feldspar samples from the ~2,600-Ga-old Tanco pegmatite, analyzed by Penner & Clark (1971).

The feldspar contains 21,240 ppm Rb, 12 ppm common Sr, and 226 ppm radiogenic ^{87}Sr. In this case, the radiogenic ^{87}Sr consitutes about 95% of the total Sr and, presumably, 95% more Sr than was present in the feldspar at the time of crystallization (assuming there has been no significant migration of Sr subsequent to crystallization). The shift in the Rb–Sr plots of K-feldspar from the spodumene-bearing pegmatites in Figure 9, introduced by correcting for extreme enrichment in radiogenic ^{87}Sr, would be rather drastic. (The same adjustment should be applied to the Rb–Sr relations in old Rb-rich pegmatite micas, particularly lepidolite). The magnitude of this effect in K-feldspar of different ages and Rb contents is currently being investigated.

Late mobility of Sr in consolidating pegmatite systems was documented, *i.a.*, on Sr isotope distributions, as summarized recently by Clark (1982). It is further shown by the occurrences of late Sr-enriched zoisite and epidote (Vlasov 1966), and late low-T phosphates with substantial Sr (palermoite, goyazite and goedkenite: Moore 1982).

MANGANESE AND THE Fe/Mn RATIO

The Mn^{2+} cation is similar to Fe^{2+}, and it follows this more abundant ion throughout igneous differentiation. The larger size of Mn^{2+} (exceeding that of Fe^{2+} by about 10%) promotes its fractionation into late precipitates. However, this tendency is strongly offset by the distinctly lower electronegativity and ionization potential of Mn^{2+}, resulting in a weaker Mn–O bond relative to Fe–O. In general, increased $f(O_2)$ leads to oxidation of iron and separation of Mn^{2+} from Fe^{3+} in their migration paths and crystallochemical accommodation. However, in granitic pegmatites of orogenic affiliation, the increase in oxygen fugacity is moderate and restricted to late stages of crystallization.

In igneous differentiation, concentrations of both Fe and Mn steadily decrease with the declining percentage of mafic minerals. However, the rate of Mn decrease is slower than that of Fe, and the Fe/Mn ratio is reduced from about 500 in dunites to an average of 25 in granitoid rocks (*e.g.*, Kolbe & Taylor 1966). This ratio is undoubtedly further reduced in leucogranites and pegmatitic granites (*e.g.*, 20–15 in the Winnipeg River district: Goad & Černý 1981), but the available data are probably inaccurate. The absolute Mn concentrations are usually less than 0.05 wt.%, but Mn is routinely analyzed as a major constituent, and the results are subject to a high relative error. A more precise understanding of the variation of the Fe/Mn ratio in the fractionation of high-silica magmas has been achieved in the study of rhyolites (Hildreth 1979, 1981, Smith 1979, Mahood 1981). For example, Hildreth (1979) quoted a reduction in Fe/Mn from 45 to 21 during the fractionation of the Bishop Tuff rhyolitic melt. As indicated by striking analogies in other geochemical features, the Fe/Mn fractionation in silicic rhyolites can be taken as representative of that operating in fertile granitic intrusions.

Shaw (1974) and Hildreth (1979, 1981) quoted Mn^{2+} as one of the cations whose enrichment trend can only be explained by an affinity to upward-diffusing H_2O and other volatile components of silicic magmas; Shawe (1968) and Bailey (1977) proposed complexing of Mn with fluorine. Such a view favoring roofward migration of Mn through a column of melt is supported by its mode of distribution in rare-element pegmatites, as discussed below.

Magnetite and biotite are the most common femic accessory minerals of geochemically primitive granitic pegmatites. The Fe/Mn ratio of magnetite is not comparable with those quoted above for whole-rock compositions; the predominance of Fe^{3+} in magnetite obscures the Fe^{2+}/Mn value. Nevertheless, Hegemann & Albrechts (1954) noted a general increase of Mn in magnetite of pegmatitic origin, relative to other genetic types. Biotite compositions are also affected by the presence of Fe^{3+}, although to a much lesser degree. Unfortunately, the few data available are not statistically meaningful.

During the progressive crystallization of muscovite, lithian muscovite and lepidolite, the Fe/Mn ratio tends to decrease in most localities. For example, Fe/Mn of the Tanco micas drops from 4.57 in early muscovite to 0.13 in the lithium micas (Rinaldi *et al.* 1972). Numerous samples of Li-rich lepidolite

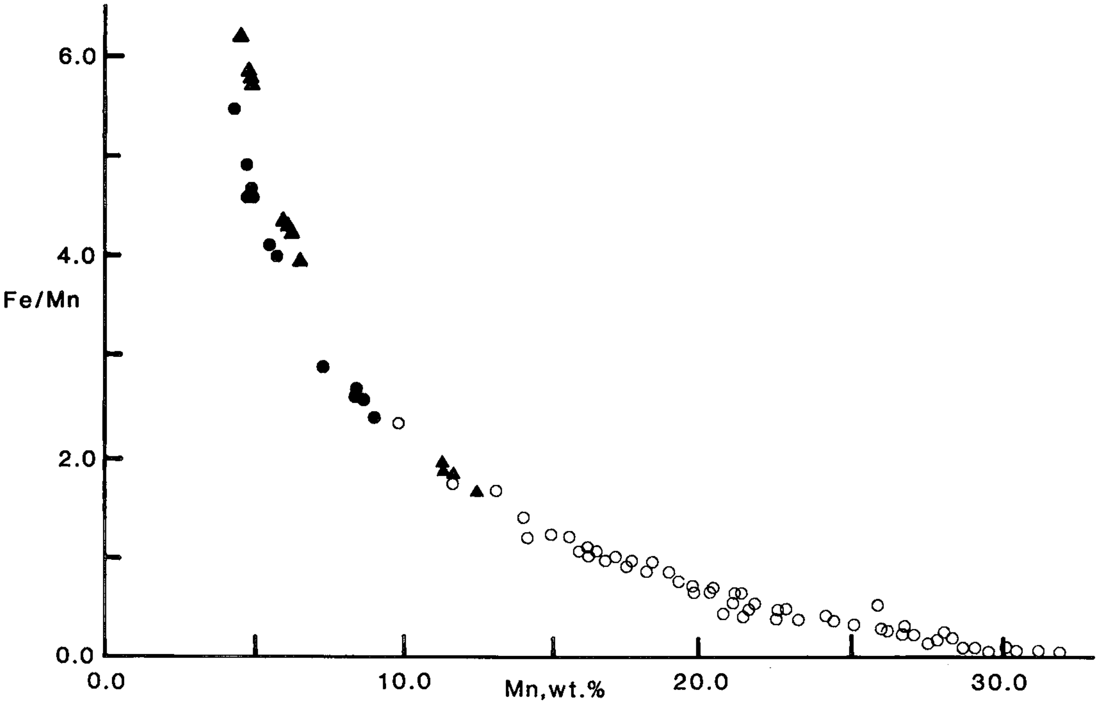


FIG. 10. The Fe/Mn *versus* Mn plots of garnet from Antarctic granitic rocks (solid dots; Vennum & Meyer 1979), pegmatitic granites (Goad & Černý 1981) and pegmatites (Černý *et al.* 1981, Baldwin & von Knorring 1983, unpubl. data of P.Č.).

display some enrichment in Fe and Mn, as compared to the total Fe + Mn in early muscovite (Černý & Burt 1984). Their Fe/Mn ratio is usually less than 1.0; green Fe-dominant lepidolite is rare (Němec 1976). However, extensive enrichment in Fe and Mn that shifts the mica composition to true zinnwaldite (Babu 1969, Němec 1983a, Ferreira 1984) or masutomilite (Harada *et al.* 1976, Němec 1983b) is exceptional in orogenic rare-element pegmatites. In contrast, anorogenic pegmatites carry zinnwaldite as their only Li-bearing mineral (Foord & Martin 1979).

Tourmaline and garnet are widespread in rare-element and miarolitic classes of pegmatites, and they are found through most of their types, including the most fractionated pollucite-bearing and lepidolite categories. As shown by Staatz *et al.* (1955), Slivko (1962), Foord (1976), Sahama *et al.* (1979) and Povondra (1981), both Fe and Mn decrease during tourmaline fractionation, to the virtual exclusion of Fe in late rubellite and achroite. However, verdelite, which usually precedes rubellite in the crystallization sequence, may show considerable enrichment in Mn. The Fe/Mn ratio probably reaches values lower than 0.05.

Garnet shows almandine-dominant compositions in plutonic granitoid rocks, but with distinct Mn enrichment observed even in diorites and granodiorites (Fe/Mn from 5.4 to 2.2, Fig. 10; Vennum & Meyer 1979). Garnet of leucogranites, pegmatitic granites and aplites has a higher Mn content, partly overlapping with that of garnet from relatively primitive pegmatites (Fe/Mn from 6.1 to 1.8, Fig. 10; Černý *et al.* 1981, Anderson 1984). In highly fractionated pegmatites, the Fe/Mn ratio may reach 0.01 or less. Spessartine with 0.30 wt.% Fe from the pollucite-bearing High Grade Dike in southeastern Manitoba, associated with albite and lepidolite, has a Fe/Mn of 0.007 (unpubl. data of P.Č.). As shown by Foord (1976), Černý & Hawthorne (1982) and Baldwin & von Knorring (1983), the Fe/Mn ratio of garnet may span an extensive range in a single pegmatite, from 2.2–1.8 in outer units to 0.05–0.02 in albite- and Li-mica-bearing assemblages.

Individual garnet crystals commonly have Fe-enriched and Mn-depleted outer zones, similar to those in garnet from aplites and plutonic rocks (Hollister 1966, Leake 1967, Baldwin & von Knorring 1983). Rayleigh fractionation or diffusion may be responsible (as reviewed by Meagher 1980).

Triphylite–lithiophilite is the most widespread

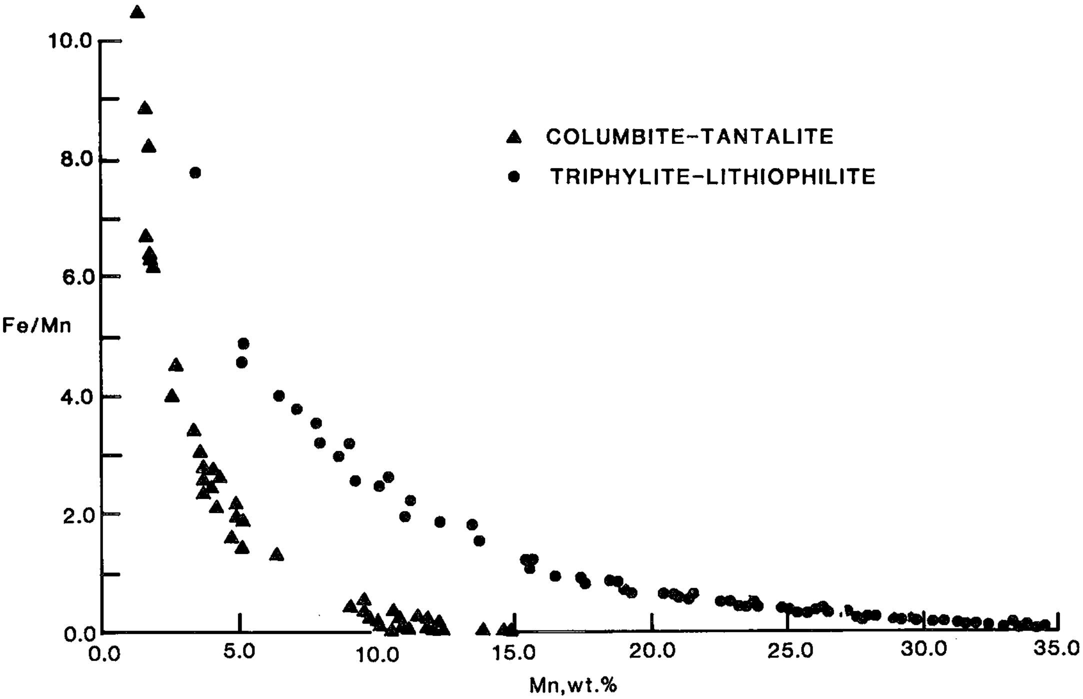


FIG. 11. The Fe/Mn plots for columbite–tantalite (triangles) from African pegmatites (selected from Sahama 1980, von Knorring & Fadipe 1981), Cross Lake pegmatite field (selected from Anderson 1984), the PEG series of the Yellowknife pegmatite field (unpubl. data of M.A. Wise), and from the Winnipeg River district, southeastern Manitoba (unpubl. data of P.Č.; Černý *et al.* 1981). Triphylite–lithiophilite data (dots) from selected localities (Antenucci 1981) and from Tanco (unpubl. data of A.-M. Fransolet *et al.*).

primary Li(Fe,Mn) phosphate, found in all pegmatite categories from the beryl–columbite type with incipient Li-enrichment to the most fractionated complex and lepidolite types. Throughout this pegmatite spectrum, triphylite–lithiophilite shows a wide range of Fe/Mn values (Fig. 11). In highly fractionated complex pegmatites containing multiple generations of this phosphate, the Fe/Mn ratio may vary from 0.95 to <0.01 (unpubl. data of A.-M. Fransolet *et al.* on the Tanco pegmatite). The extreme enrichment in Mn is found in lithiophilite from lepidolite units; its FeO content is below the 0.1 wt.% detection limit of electron microprobe. It is also worth mentioning that early Fe-rich triphylite is commonly enriched in Mg (up to 2.5 wt.% MgO); Mg fades into insignificance in extremely fractionated lithiophilite (<0.05 wt.% MgO; Antenucci 1981, unpubl. data of A.-M. Fransolet *et al.*).

The Fe/Mn ratio of columbite–tantalite covers an even greater range than that of triphylite–lithiophilite (Fig. 11). First ferrocolumbite is encountered in pegmatites that are less fractionated than those in which the Li(Fe,Mn) phosphates begin to crystallize; consequently the Fe/Mn ratio of early ferrocolumbite is higher. Extreme enrichment in Mn is found in complex pegmatites and in the lepidolite type; manganotantalite from Mozambique has a Fe/Mn of 0.003 (von Knorring *et al.* 1966, Sahama 1980). Extensive ranges in Fe/Mn are also encountered in columbite–tantalite from single pegmatite bodies. In the Be + (Nb,Ta)-bearing Plex pegmatite, Baffin Island, the Fe/Mn ratio varies from 3.0 to 0.3 (Černý & Ercit 1985), and in the complex (Be + Li)-rich Peerless deposit of the Black Hills field it ranges from 1.56 to 0.15 (Černý *et al.* 1985c). The enrichment in Mn is particularly conspicuous in columbite–tantalite from lepidolite-rich assemblages.

Wodginite shows a considerable range in Fe/Mn, but in most of its occurrences it is distinctively Mn-rich, up to the virtual exclusion of Fe^{2+} (unpubl. data of T.S. Ercit; Černý & Ercit 1985). Terminating the Mn-enrichment trend of the earlier columbite–tantalite quoted above, a late wodginite from the Peerless pegmatite attains a Fe/Mn of 0.025 (taking into account negligible Fe^{3+}; Černý *et al.* 1985c).

In conclusion, the association of extreme Fe–Mn fractionation with the late stages of pegmatite consolidation, with linings of miarolitic cavities, and with Li,F-rich mineral assemblages must be stressed. From the textural viewpoint, the occurrences of Mn-dominant garnet, tourmaline and columbite in the

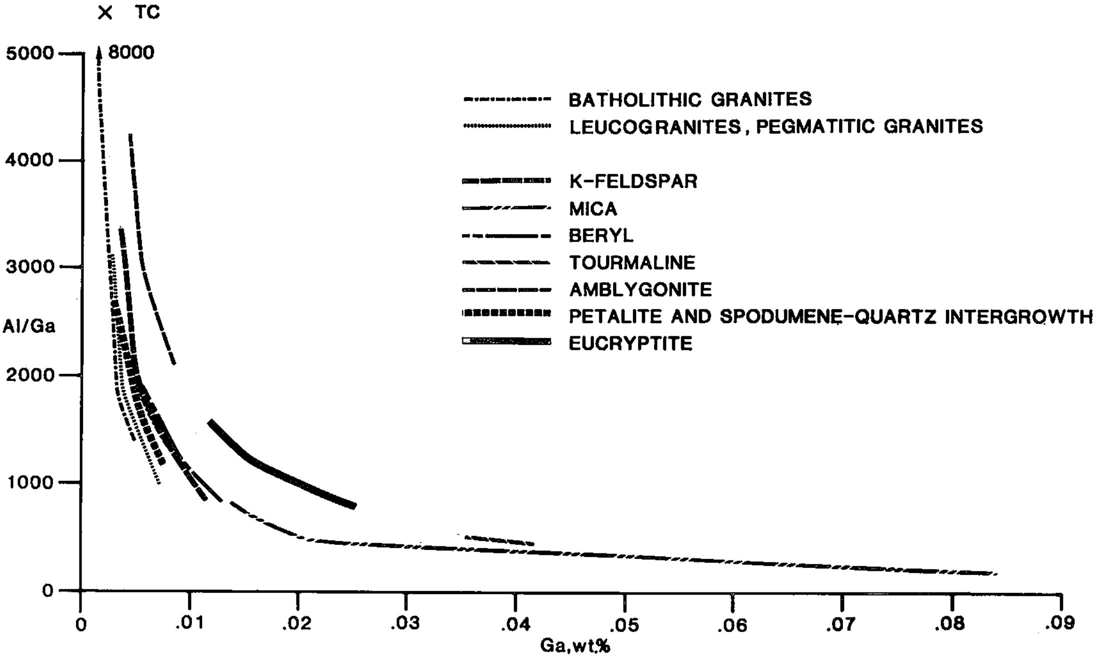


FIG. 12. The Al/Ga *versus* Ga plots for batholithic granites of Azov Sea (Marchenko & Shcherbakov 1966) and of the Lac du Bonnet complex (Černý *et al.* 1981); for the leucogranites and pegmatitic granites of the Winnipeg River district, southeastern Manitoba (Černý *et al.* 1981); and for selected minerals of the Tanco and Lower Tanco pegmatites (unpubl. data of P.Č.; Černý 1982c, Ferreira 1984).

upper pegmatitic parts of the Himalaya dykes near or inside miarolitic pockets are conspicuous (Foord 1976). Similar assemblages are typical for Brazilian gem-bearing pegmatites, such as the Mn-rich wodginite, spessartine and lepidolite in the Lavra Jabuti mine (Dunn *et al.* 1978). From a geochemical viewpoint, extreme Mn-enrichment is typically associated with lepidolite- and microlite-bearing units rich in fluorine: manganocolumbite, manganotantalite, spessartine, lithiophilite and other Fe,Mn phosphates reach here their maximal (and occasionally absolute) levels of fractionation of Mn. The Li-micas themselves commonly show a very low Fe/Mn ratio, and Mn may be enriched in absolute terms, as in the masutomilite + spessartine association from Czechoslovakia (Němec 1983b).

All these relationships suggest a strong tendency of Mn to be selectively extracted into and transported by a hydrous phase, particularly a fluorine-rich supercritical fluid. Such behavior would constitute an extension of the volatile-related transport of Mn diffusion in silicic magmas, as mentioned earlier in this section. The possibility of complexing Mn with F-bearing anions should be examined experimentally.

GALLIUM AND THE Al/Ga RATIO

Trivalent gallium shows some similarity to Fe^{3+}, and it also exhibits chalcophile tendencies. However, its extremely close relationship to Al^{3+} regulates its distribution in igneous rocks. Compared to aluminum, Ga^{3+} has a larger ionic radius, higher electronegativity and ionization potential, and its bond to oxygen is more covalent. All these characteristics contribute to a slight concentration of Ga in residual melts and fluids, and to its preferential entry into late generations of aluminous minerals. However, the effect appears to be very mild throughout the sequence of igneous differentiation. The absolute concentration of Ga in most igneous rocks ($<$ 1 to $\sim$40 ppm) varies with that of Al, and the average Al/Ga ratio decreases only gently from ultramafic and gabbroic rocks to granites (Shaw 1957, Vlasov 1966).

Most igneous rock-types exhibit a broad range of Ga contents that have not yet been interpreted. However, extensive diversity in Ga contents is particularly characteristic of granites that display variability in Al/Ga from 8,000 to about 2,000 (Fig. 12). Concentration of Ga in granites seems to be in many instances a case of "regional specialization," but may also have petrogenetic significance (*cf.* Collins *et al.* 1982). However, Ga content and the Al/Ga ratio commonly show only negligible ranges within individual intrusive phases of granitic batholiths (*e.g.*, Kolbe & Taylor 1966, Černý *et al.* 1981) that are otherwise moderately fractionated, and they may be rather uniform even in extensively differentiated sequences (de Albuquerque 1971, Kolbe & Taylor 1966). Broad ranges in the ratio Al/Ga seem to be typical of alkaline (Bowden 1964) rather than calc-alkaline sequences.

Notable enrichment in Ga is encountered in leucogranites and pegmatitic granites parental to fields of rare-element pegmatites. The Ga contents may reach as high as 50 to 80 ppm, and the Al/Ga ratio drops to the 1,000 level (Fig. 12; Blockley 1980, Goad & Černý 1981, Černý 1982b). Similar Al–Ga relations are also typical of some rhyolite sequences (Ewart *et al.* 1976, 1977, Hildreth 1981) and of highly fractionated granites from anorogenic associations (Anderson & Cullers 1978).

The mechanism of Ga enrichment in leucogranites and pegmatitic granites undoubtedly involves the ionic properties cited above, but other factors may participate as well. The feldspars are the main Ga carriers in granitic rocks but show mild Al/Ga fractionation (*cf.* Hall 1967, Wilson & Coats 1972). The influence of increased Ga contents of accessory biotite, muscovite and tourmaline may well be counterbalanced by low concentrations of Ga typical of garnet, and variable proportions of the micas + tourmaline *versus* garnet may result in erratic trends of Al/Ga values (Shaw 1957, Burton *et al.* 1959, Vlasov 1966). Thus crystal/melt fractionation is not the only means of enrichment in Ga in this environment. Volatile components and fluoride complexing can be expected to participate in the Al–Ga distribution at this stage. Fertile leucogranites and pegmatitic granites solidify under a more extensive influence of (dissolved or exsolved) volatile components than average plutonic granites. Fluoride complexes of Ga^{3+} are stable at magmatic temperatures and should preserve Ga in the melt relative to Al^{3+} (Cotton & Wilkinson 1980, Manning *et al.* 1980). They also are more mobile in acid environments (Borisenok & Saukov 1960), and this may account for the accumulation of Ga observed in late peraluminous and silicic granites.

Large-scale metasomatic processes affecting plutonic granitic rocks have been repeatedly shown to increase the concentrations of Ga (Severov & Vershkovskaya 1960, Ganeev *et al.* 1961, Ganeev & Sechina 1962, Bowden 1964). This is particularly true of albitization and muscovitization, which are generally ascribed to relatively acidic fluids hydrolyzing K-feldspar and calcic plagioclase (Korzhinsky 1953, Beus 1961). Stability of Ga-complexes in late acidic fluids (with Ga residual or scavenged) and their breakdown upon neutralization during the metasomatic reactions would result in enhancement of Ga relative to the primary products of magmatic crystallization (Marchenko & Shcherbakov 1966). Such a mechanism may operate in some leucogranites and pegmatitic granites in fields of rare-element pegmatites, but extensive metasomatism in most of these intrusions cannot be considered proven. Albite and muscovite commonly seem to be primary constituents (Anderson & Rowley 1981, Miller *et al.* 1981), and an increase in Ga may be a consequence of its liquid-state enrichment into more peraluminous and acidic portions of fractionating melts.

In rare-element granitic pegmatites, enrichment in Ga is variable in terms of pegmatite types and mineral species. Gottardi *et al.* (1972) judged the Ga enrichment in granitic pegmatites negligible, in contrast to its prominent increase in alkaline pegmatites. However, their data on calcalkaline pegmatites were restricted to relatively primitive and in part barren types. These pegmatites are indeed at about the same level of Ga fractionation as their parent granites (Shimer 1943, Borisenok & Saukov 1960). However, the Ga concentrations rise considerably in the more fractionated pegmatites of the rare-element class, as shown by Slepnev (1962) and Gordiyenko (1970). Figure 12 shows schematically the Al/Ga ratio *versus* Ga contents of the major mineral constituents of the Tanco pegmatite (Černý 1982c). To the best of our knowledge, the Tanco deposit is the most Ga-enriched pegmatite so far investigated. Thus the data represent the extremes in silicate fractionation of Ga, and they also are representative of the differences among individual species.

Petalite, the spodumene + quartz intergrowth produced by thermal breakdown of petalite, K-feldspar and beryl have similar ranges of Ga content and Al/Ga ratio (generally <100 ppm and 3,000–1,000, respectively). In amblygonite, the Al/Ga range is distinctly higher than in the above minerals, whereas eucryptite displays low Al/Ga (1,500–800) and a conspicuous Ga enrichment (120–250 ppm). As in other pegmatites, tourmaline and the mica minerals are the main concentrators of Ga. Schorl and verdelite have 364 to 415 ppm Ga, and their Al/Ga value varies from 501 to 431. The Ga contents of muscovite, lithian muscovite and lepidolite broadly overlap, extending from 240 to 880 ppm, with a low Al/Ga ratio between 465 and 239. Preliminary data on pollucite indicate 50–60 ppm Ga (Al/Ga 1,800–1,500). The Ga contents of albite seem to be only slightly higher than those of K-feldspar, ranging from 50 to 120 ppm (Al/Ga 2,300–900).

The present understanding of the differential entry of Ga into diverse mineral structures has not advanced beyond the uncertainties expressed by Gottardi *et al.* (1972). The repeatedly stated view that Ga prefers to substitute for ^{VI}Al is contradicted by the low Ga content of amblygonite (^{VI}Al) on one hand, and by the high Ga in eucryptite ($^{IV}Al >> {}^{VI}Al$) on the other. Considering the B, F and OH content of tourmaline and the F,OH-content of ^{VI}Al–O octahedra in micas, it seems possible that Ga is incorporated into these minerals not as free cations but within OH,F-bearing relics of pre-existing octahedral fluorocomplexes. This is also supported by the high Ga content of some samples of polylithionite (Al/Ga as low as 402: Černý & Trueman 1985) that contain only octahedral Al. However, the contrasting Ga contents of amblygonite (^{VI}Al + F,OH) and eucryptite ($^{IV}Al >> {}^{VI}Al$) remain unexplained.

The example of the Tanco pegmatite indicates that the behavior of Ga in complex rare-element pegmatites of granitic parentage has not been sufficiently examined in the past, and interpretation of present data is unsatisfactory. However, it is established now that advanced Al/Ga fractionation can be expected in this type of pegmatite, reaching levels typical of the alkaline pegmatites.

HAFNIUM AND THE Zr/Hf RATIO

Zirconium and hafnium constitute one of the most coherent element pairs in geochemistry. Separated by the lanthanide contraction in the periodic table, Hf is much heavier but otherwise extremely similar to the much more abundant Zr. The electronegativity, ionization potential and ionic radius of Hf^{4+} are slightly lower than those of Zr^{4+}, and they should promote the entry of Hf into early generations of zirconium minerals. However, such a trend appears to be very rare. In general, the Zr/Hf ratio decreases from gabbroic (~ 60) to dioritic and granitic rocks (~ 40–30). The same trend is also documented for individual comagmatic differentiation-sequences (*e.g.*, Kosterin *et al.* 1960, Gottfried & Waring 1964, Gottfried *et. al.* 1968, Condie & Lo 1971).

In peralkaline magmas, Zr(+Hf) form alkali zirconosilicate complexes of variable thermal stability, and their breakdown gives rise to a variety of Zr (+Hf)-bearing minerals (Vlasov 1966, Dietrich 1968, Watson 1979). The concentration of Zr(+Hf) tends to increase in differentiated peralkaline suites, with considerable accumulation of both elements in related pegmatites. In contrast, the mineralogy of Zr(+Hf) in metaluminous to peraluminous igneous series of calcalkaline chemistry is very simple, restricted to an early crystallizing zircon. The Zr(+Hf) content in such igneous sequences drastically decreases with increasing SiO_2 (Dietrich 1968, Watson 1979). The Zr/Hf ratio and Hf content of zircon from the diorites and granites of the Yeoval complex of central New South Wales (Gulson 1970) are shown in Figure 13. They may serve as a typical example of zircon in granitic complexes, although they are slightly above average in Hf enrichment.

No data seem to be available in the literature on the Hf content behavior of zirconium behavior from leucogranites and pegmatitic granites of rare-element pegmatite fields. However, it was shown by Lipova *et al.* (1957) that in leucogranites containing zircon

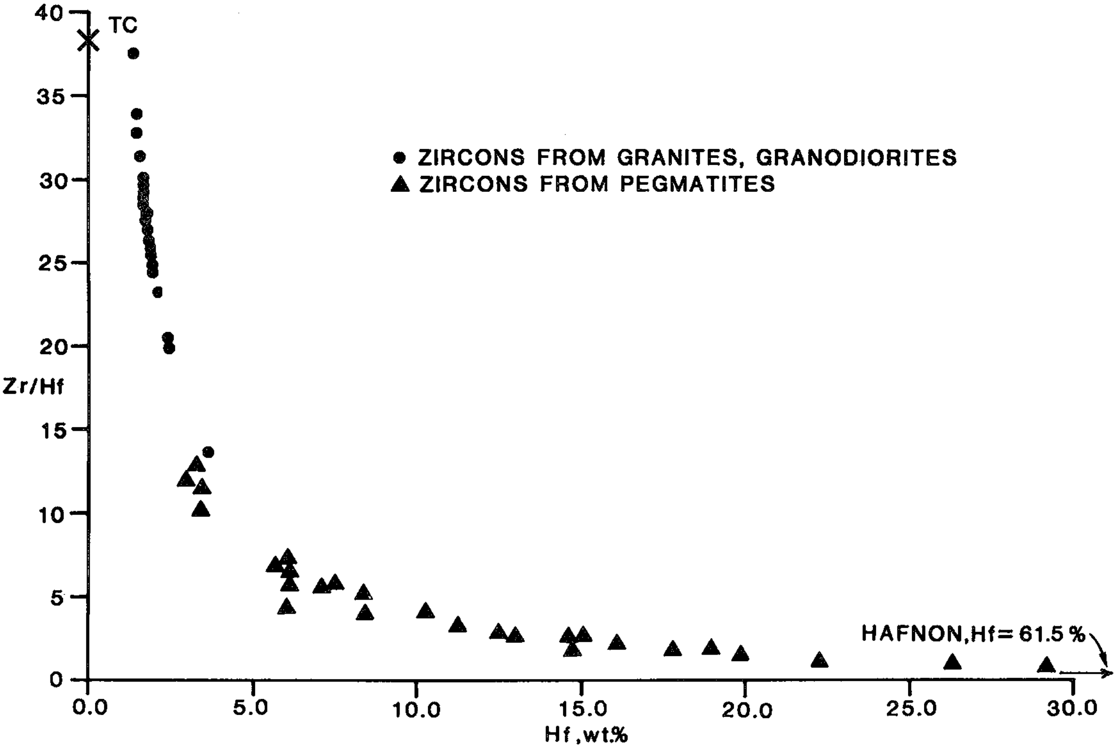


FIG. 13. The Zr/Hf *versus* Hf plots of zircons from the Yeoval complex granitoid rocks (dots; Gulson 1970) and from rare-element pegmatites (triangles; Levinson & Borup 1960, von Knorring & Hornung 1961, Quadrado & Lima de Faria 1966, Correia Neves *et al.* 1974, Fontan *et al.* 1980, Černý & Siivola 1980, Cassedanne *et al.* 1985, Paul 1984, and unpubl. data by P.Č.).

as the only Zr-bearing phase, the concentration of Zr and Hf in the zircon corresponds to that found in the whole rock. Whole-rock Zr/Hf data for leucogranites and pegmatitic granites from southeastern Manitoba vary from 32 to 5, with two exceptionally high values of 62 and 48 (Černý *et al.* 1981, Goad & Černý 1981). The bulk of these data shows a higher degree of Zr/Hf fractionation than average plutonic granites, despite the low absolute Zr and Hf (2–130 and 0.4–4.35 ppm, respectively). The above Zr/Hf data overlap in part the Zr/Hf ranges found in highly evolved silicic rhyolites (*e.g.*, 37 to 24 in the Bishop tuff: Hildreth 1979, 1981).

The low abundance of Zr and Hf in silicic leucogranites parental to rare-element pegmatites is in accord with the behavior of these elements in F-bearing rhyolitic magma undergoing fractionation in a liquid state. Hildreth (1979, 1981) has shown that Zr and Hf show relative to absolute depletion in the most fractionated batches of F-dominant rhyolites, in contrast to an enrichment shown by Cl-rich rhyolites.

Differences in the stabilities and mobilities of Zr- and Hf-bearing complexes may enhance the effects of crystal/melt fractionation at this advanced stage of granitic fractionation. Portnov (1965) emphasized the higher solubility and persistence to lower temperatures of a variety of Hf-complexes relative to those of Zr. Within individual batches of granitic-to-pegmatitic melts, differences in stabilities of complexes and in mass-related rates of diffusion are the primary causes of fractionation (Butler & Thompson 1965); the latter mechanism may particularly apply to zoned crystals of zircon, with progressive core-to-rim enrichment in Hf.

In rare-element granitic pegmatites, zircon and hafnon are the only significant minerals of Zr and Hf (including malacon, alvite, cyrtolite and similar varieties). Thortveitite, showing subordinate Zr and Hf contents with a surprizing Zr/Hf less than 1 (Levinson & Borup 1960), is only of very local significance in *REE*,Nb,Ti-bearing pegmatites of Norway and Madagascar. Garnet probably carries traces of Zr and Hf, as suggested by the similarities between the garnet and zircon structures (Robinson *et al.* 1971) and by the existence of kimzeyite. However, kimzeyite and other Zr-bearing garnets are typical of alkaline parageneses, and no adequate data are available for garnet from the pegmatite types considered in this study.

High contents of Hf in zircon from rare-element pegmatites were first recognized by Fleischer (1955), Vainshtein *et al.* (1959), Levinson & Borup (1960), von Knorring & Hornung (1961) and Quadrado & Lima de Faria (1966). Some of these authors also noted that late generations of zircon are invariably Hf-enriched relative to their early counterparts. The occurrence of hafnon (Correia Neves *et al.* 1974) is so far unique. Nevertheless, it proves that advanced differentiation in highly fractionated, Li,Rb,Cs-rich complex pegmatites can lead to an almost complete separation of Hf and Zr, even if only in the outermost zones of zircon–hafnon crystals (Zr/Hf down to 0.014). The Zr/Hf ratio is generally higher in other complex pegmatites, despite their high overall degree of fractionation. For example, the Zr/Hf value of hafnian zircon from Tanco varies between 3.2 and 1.9 only, and is almost uniform within individual crystals (Černý & Siivola 1980).

Figure 13 summarizes the data for zircon taken from the above-mentioned references and from more recent sources (Robinson 1979, Fontan *et al.* 1980, Ferreira 1984, Paul 1984, Cassedanne *et al.* 1985, unpubl. data of P.Č. from the Greer Lake group of southeastern Manitoba). The scatter of data across the general trend is caused by deviations from stoichiometry. Incorporation of Y,*REE*,P,Th,U with or without Pb disturbs the Zr, Hf and Si contents and their respective ratios in many examples of pegmatitic zircon (Robinson 1979). Metamictization, hydration, leaching and recrystallization are also widespread, affecting the (Zr+Hf)/Si value (*e.g.*, Frondel 1953, Černý & Siivola 1980, Törnroos 1982). Preferential mobility of Hf in hydrothermal environments, postulated by Kosterin *et al.* (1964), would tend to increase the Zr/Hf ratio relative to the original compositions during low-temperature alteration.

TANTALUM AND THE Nb/Ta RATIO

The Nb–Ta pair is analogous to Zr–Hf in being separated by the lanthanide contraction, in having a very close geochemical relationship, and in displaying a fractionation pattern opposite to that expected from ionic properties. Actually, in the main course of gabbro-to-granite differentiation, the Nb/Ta ratio stays close to the value of ~11 characteristic of the average upper-crust abundances of Nb and Ta in calcalkaline igneous rocks (~23 ppm Nb and 2.1 ppm Ta: Flörke *et al.* 1974).

The absolute contents of Nb and Ta increase only slightly from ultramafic to granitic members of calcalkaline sequences, reaching up to 70 ppm Nb and 3.5 ppm Ta (Atkins & Smales 1960, Gottfried & Dinnin 1965). The first marked increase is noted only in silicic leucogranites and pegmatitic granites; Beus *et al.* (1968) quoted 150 ppm Nb and 40 ppm Ta for fertile leucogranites parental to rare-element pegmatites. Compared to the Nb and Ta contents of "ordinary" biotite granites cited above, the leucogranites show an enrichment in both these elements comparable to their enrichment factors in the Bishop Tuff (Beus & Sitnin 1968, Hildreth 1981).

Complexing of Nb and Ta and their response to liquid fractionation, including transport in a hydrous phase, can be expected to operate during the differentiation of a leucogranitic magma as in rhyolitic melts (Hildreth 1979, 1981). Surprizingly, enrichment in Nb and Ta is more pronounced in Cl-dominant rhyolite sequences than in the F-rich magmas (Hildreth 1981) that are typical of pegmatite-generating granites. However, the differences are minimal, and the Cl/F ratio (as analyzed in the *solidified* rhyolites) occasionally becomes reversed in one and the same extrusive sequence. Further examination of these relationships is evidently required.

The enrichment trend is extended into rare-element pegmatites, with maximum contents reaching 550 ppm Nb and ~4,500 Ta (Vlasov 1966, Kuzmenko 1976). These increased abundances also indicate a dramatic change in the Nb/Ta ratio during the evolution of a pegmatite system. As shown by Wang *et al.* (1982), fluorine-based and other complexes of Nb and Ta have different thermal stabilities, the Ta-bearing ones stable to lower temperatures. Thus Nb becomes available for crystallization of solid phases in early stages relative to the bulk of Ta, leading to extensive ranges of the Nb/Ta ratio even in a single body of pegmatite (*e.g.*, Černý *et al.* 1985c). On a local scale of mineral aggregates and individual crystals, a mass-related difference in diffusion rates may be expected, analogous to that proposed for Zr and Hf (Butler & Thompson 1965).

The mineralogy of Ta in granitic rare-element pegmatites is complex; its different aspects were recently reviewed by von Knorring & Fadipe (1981), Foord (1982) and Černý & Ercit (1985). The distribution of individual mineral species among different types of pegmatite is partly governed by the ranges of their Nb/Ta ratio. From the most primitive to the highly fractionated rare-element pegmatites, the following mineral associations are characteristic:

(i) Aeschynite, samarskite, euxenite, polycrase and fersmite are typically niobian species, commonly occurring in relatively primitive types of pegmatite.

(ii) Fergusonite–formanite, yttrocolumbite–yttrotantalite, niobian-tantalian rutile, columbite–tantalite (–tapiolite), pyrochlore–betafite–microlite, stibiocolumbite–stibiotantalite and bismutocolumbite–bismutotantalite have broad ranges of Nb/Ta substitution and are found in most types of pegmatite of the rare-element class. The Nb/Ta ratio of these minerals reflects the level of fractionation attained by the parent melt or by the melts or fluids parental to the individual internal units. Most of the above mineral series are known to cover the full range of Nb–Ta substitution. For example, Figure 14 shows the Nb/Ta *versus* Ta plots of the columbite–tantalite group, from the Mozambique ferrocolumbite with 74.61 wt.% Nb_2O_5 and 2.78 wt.% Ta_2O_5 (von Knorring & Fadipe 1981: Nb/Ta 23.8) to the Mozambique manganotantalite with 0.29 wt.% Nb_2O_5 and 85.8 wt.% Ta_2O_5 (Sahama 1980: Nb/Ta 0.003).

(iii) Largely Ta-dominant species are restricted to the highly fractionated complex type of rare-element pegmatites: wodginite, staringite, ixiolite, rynersonite, the Sn-, Bi-, Pb-, U-, Ba-, Sb- and Cs-based species of microlite, simpsonite, thoreaulite and behierite. Most of these species indicate a high degree of (Fe,Mn) depletion in late metasomatic stages of complex rare-element pegmatite evolution. As a result, minerals containing Ca, Na, Al and Sn are generated.

(iv) The trends of extreme Ta enrichment and (Fe,Mn) depletion are continued in most of the late alteration products that typically replace pre-existing (Ta,Nb)-bearing species in highly fractionated pegmatites: microlite-type minerals, rankamaite, holtite, sosedkoite, alumotantite, natrotantite, calciotantite, lithiotantite and tantite belong to this mineral association, which otherwise includes late generations of manganotantalite, tapiolite and cassiterite (Ercit & Černý 1982, Černý & Ercit 1985).

Some of the minerals quoted in subparagraphs (iii) and (iv) contain but traces of Nb. For example, simpsonite and microlite occasionally show Nb_2O_5 less than 0.1 wt.% (below the detection limit of electron microprobe), indicating a Nb/Ta ratio of 0.001 or less (unpubl. data of T.S. Ercit and P.Č.).

CADMIUM AND THE Zn/Cd RATIO

The fractionation relationship between Zn^{2+} and Cd^{2+} is complicated by discrepancies among their properties. The ionic radius of Cd^{2+} is about 25% larger than that of Zn^{2+}, but most sources quote both ionization potential and electronegativity of Cd as being lower than those of Zn. However, both metals behave as trace elements in silicate magmas, and the degrees of their affinity to major masking elements are more important than their mutual relationship. Both elements substitute predominantly for Fe^{2+}, which is much closer to Zn^{2+} than to Cd^{2+};

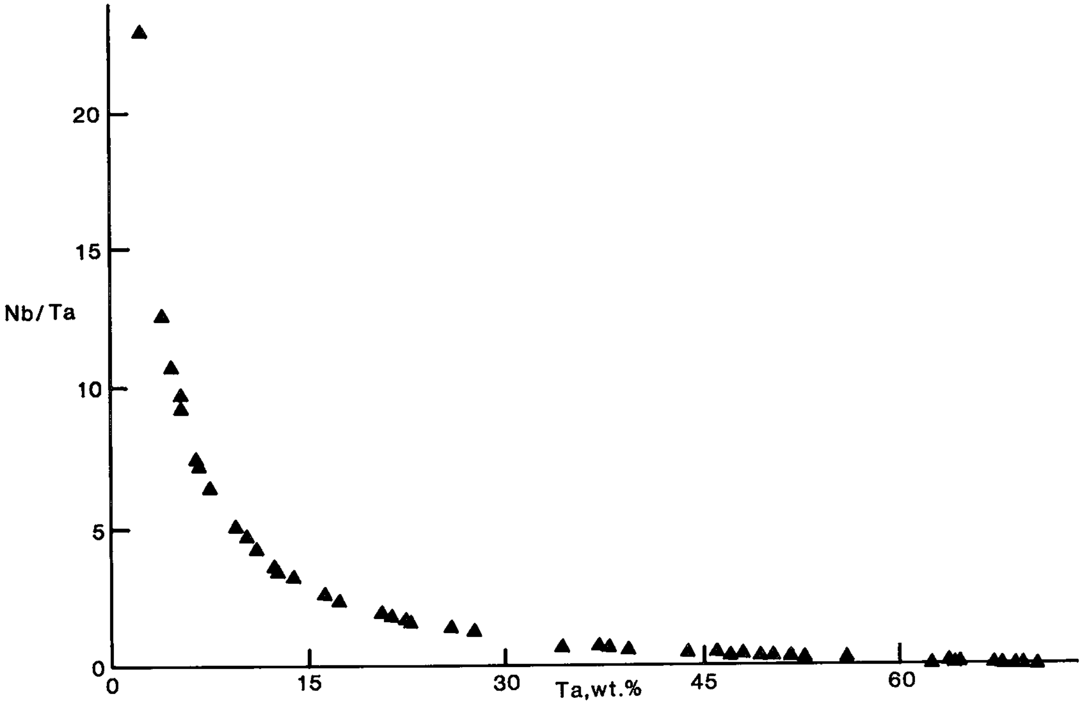


FIG. 14. The Nb/Ta *versus* Ta plots for columbite–tantalite. Data from African pegmatites (selected from Sahama 1980, von Knorring & Fadipe 1981), Cross Lake pegmatite field (Anderson 1984), the PEG series of the Yellowknife pegmatite field (unpubl. data of M.A. Wise) and from the Winnipeg River district, southeastern Manitoba (unpubl. data of P.Č.; Černý *et al.* 1981).

the large radius of Cd^{2+} is probably responsible for a slower rate of its precipitation relative to Zn^{2+}. In most cases examined, both Zn and Cd decrease in abundance with progressing igneous fractionation, but the Zn/Cd ratio changes in favor of Cd (*e.g.*, Vlasov 1966). A further difference between the two metals is based on the greater chalcophile affinity of Cd. Partitioning of Zn and Cd between a silicate melt and liquid or fluid phases carrying sulfide species may affect the Zn/Cd ratio considerably in the ensuing crystallization of silicates (particularly if sphalerite is formed: Taylor 1963). In consequence, it is not surprizing that the data on both Zn and Cd in igneous rocks are considerably variable, owing to regional differences and (to a degree) different analytical techniques (*e.g.*, Marowsky & Wedepohl 1971, Fourcade & Allègre 1981, Collins *et al.* 1982). In general, the average Zn/Cd ratio of igneous rocks is of the order of 900 (30–150 ppm Zn, 25-225 ppb Cd), and approximately 400-500 for granitic lithologies alone (Vlasov 1966, Marowsky & Wedepohl 1971).

During the fractionation of a granitic melt, Zn concentration is rather steady (for example, in the Bishop Tuff sequence: Hildreth 1981). However, Zn shows roofward enrichment in Cl-dominant magma reservoirs, particularly those of peralkaline composition (*cf.* also Christiansen *et al.* 1983). The restricted data on Zn abundances in leucogranites indicate that its concentration decreases compared to the earlier members of presumably comagmatic series (*e.g.*, 96 to 30 and 54 to 33 ppm: Tauson 1967). Nonetheless, gahnite is commonly found as a very minor accessory mineral in peraluminus leucogranites and pegmatitic granites, particularly those parental to rare-element pegmatites (Kuzmenko 1976, Blockley 1980, Tulloch 1981, Černý *et al.* 1981, Goad & Černý 1981). Gahnite probably forms in response to the extremely low concentration of ferromagnesian minerals in the leucogranites, and to the availability of excess Al^{3+}. The considerably covalent nature of the Zn–O bond is much better satisfied in the spinel structure than in biotite or garnet, for example.

Gahnite also is the most common oxide mineral of Zn in granitic pegmatites. It occurs in a wide variety of pegmatites, from the (beryl + columbite)-bearing type to the complex type (as summarized by Černý & Hawthorne 1982). No data are available on the Cd content of gahnite. However, the large size of Cd^{2+} and the more ionic character of the Cd–O bond suggest that the Zn/Cd ratio of gahnite should be very high.

Other oxide minerals of Zn (and Cd), such as

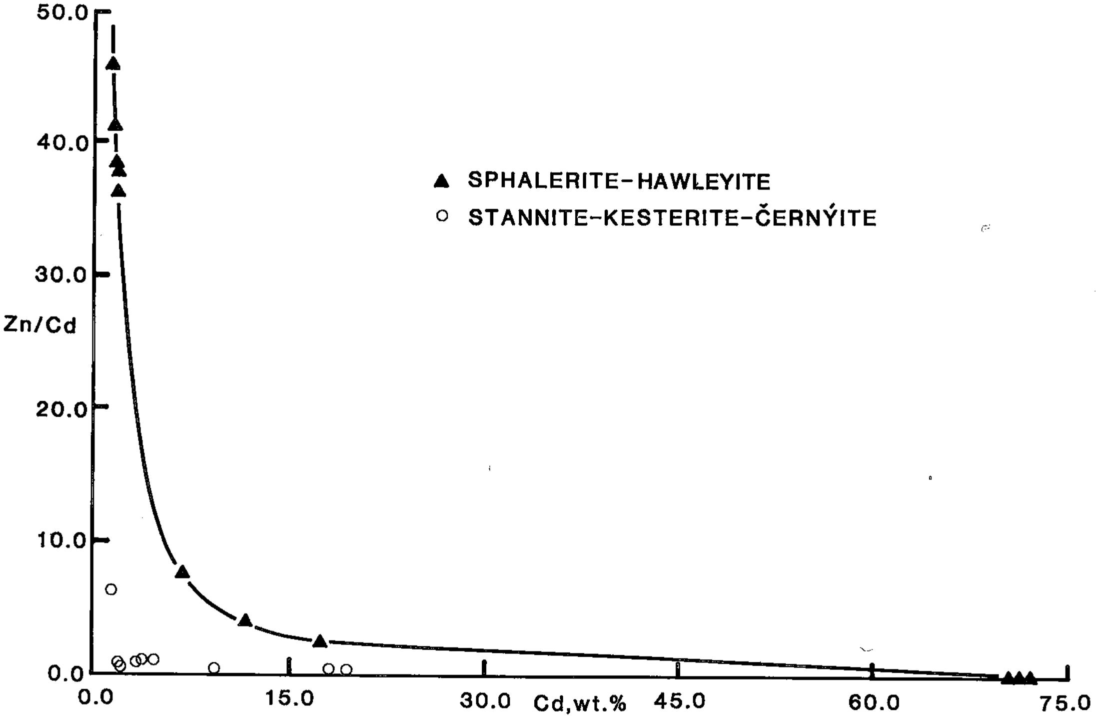


FIG. 15. The Zn/Cd *versus* Cd plots for pegmatitic sphalerite–hawleyite from the Tanco pegmatite (Černý & Harris 1978), and stannite-kesterite-černýite (Kissin *et al.* 1978, Černý & Harris 1978).

genthelvite, nigerite and högbomite, are only exotica of local importance and cannot be considered as important factors in the distribution of Zn (Cd) in granitic pegmatites. However, traces to subordinate quantities of Zn are found in some primary phosphates such as triphylite, graftonite–sarcopside, triplite and zwieselite (up to 0.49 wt.% ZnO: Čech *et al.* 1961, 1962, 1964) and in cordierite (Černý & Povondra 1967). Tourmaline may also carry significant Zn (1.80 wt.% ZnO; Jolliff 1985).

Accessory sphalerite is the most common sulfide of Zn and Cd that also occurs in a variety of pegmatite types. From the very limited data of Kullerud (1953), Vlasov (1966) concluded that calcalkaline granitic pegmatites do not concentrate Cd in sphalerite (in contrast to pegmatites of alkaline kindred). However, recent examination of accessory sulfides from highly fractionated complex pegmatites such as the Tanco, Hugo and Tin Mountain deposits revealed 1.4 to 1.7 wt.% Cd in isolated grains of sphalerite, and 6.9 to 17.6 wt.% Cd in sphalerite from fine-grained sulfide aggregates in which it coexists with hawleyite (70.4 to 72.4 wt.% Cd; Fig. 15; Černý & Harris 1978, W.L. Roberts, pers. comm. 1978). Extensive accumulation of Cd is also shown by the minerals of the stannite group. Stannite shows 2.4 to 4.1 wt.% Cd, kesterite about 2.5 wt.% Cd, and černýite (ideally the cadmium end-member of the group) has up to 19.3 wt.% Cd (Fig. 15; Kissin *et al.* 1978, Černý & Harris 1978). It is evident that the relative rejection of Cd by oxide structures and its affinity for sulfide species lead to its concentration in volatile-saturated, highly fractionated residual pegmatite melts, and finally to its precipitation in very late subsolidus sulfide assemblages.

It is interesting to note that gahnite and sphalerite are mutually exclusive in most of their pegmatite occurrences (Černý & Hawthorne 1982). The fugacity of S^{2-} obviously regulates the form of Zn precipitation. For example, gahnite is a common accessory in the virtually sulfide-free pegmatitic granites and pegmatites in the southern part of the Winnipeg River pegmatite district. In contrast, it is extremely rare (and confined to pegmatitic granites only) in the northern part of the district where sulfides abound in both the granites and pegmatite veins (Goad & Černý 1981).

CORRELATIONS OF FRACTIONATION TRENDS: ACCORDS AND DISCORDS

In the most general way, the fractionation trends discussed in the preceding sections proceed more or less simultaneously during differentiation of fertile granites and their pegmatite aureoles. Fractionation of other element pairs [such as Si/Ge, Th/U, Ti/(Nb,Ta)] and accumulation of additional rare elements (*e.g.*, Be,Sn,U,Th,Y,*REE*,B,P,F) also progress more or less in parallel with the fractionation phenomena considered earlier in this paper. Nevertheless, many investigators have noticed that the fractionations of individual element pairs evi-

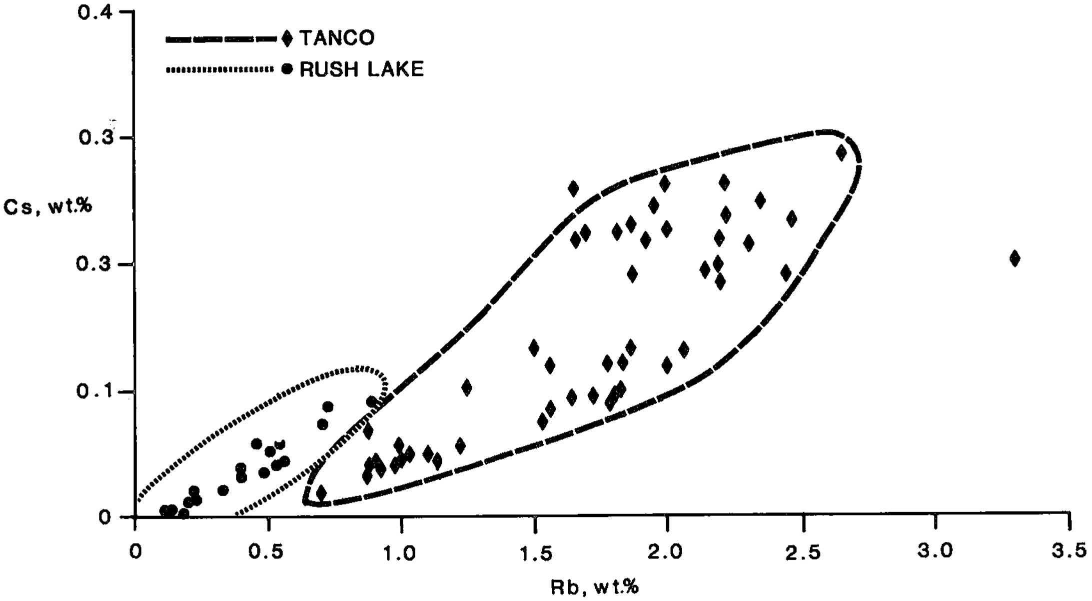


FIG. 16. The Cs *versus* Rb plots for K-feldspar from the Tanco pegmatite (unpubl. data of P.Č.; Černý 1982c) and from the Rush Lake pegmatite group, southeastern Manitoba (Černý *et al.* 1981).

dently proceed at different rates (*e.g.*, von Knorring 1974).

The uneven progress in individual fractionation processes is partly regional but possibly typical of diverse pegmatite types. However, quantitative treatment of these relationships is virtually nonexistent, mainly because of a lack of statistically meaningful numbers of data from properly correlated sample populations. Most geochemical studies of granitic pegmatites have focused on a single characteristic, or a few closely related ones, and mutual correlations of geochemically and crystallochemically unrelated features (such as K/Rb *versus* Zr/Hf) are made only at a very generalized level. Such an approach is sufficient for derivation of criteria of geochemical exploration, but it is decidedly inadequate for a thorough understanding of the geochemical evolution in diverse pegmatite populations or types. The following subsections present several examples of reasonably documented correlations, and comments on others for which no meaningful data are available at present.

Rb versus Cs and K/Rb versus K/Cs

The classic plot of Rb *versus* Cs in granitic and pegmatitic K-feldspar (Taylor & Heier 1960) shows a broadly scattered but essentially linear correlation; no correlation of Rb and Cs has been attempted since that study. Černý *et al.* (1981) used K/Rb *versus* Cs in blocky core-margin K-feldspar for characterization of pegmatite groups and correlation of their alkali fractionation with different types of potentially economic mineralization. They noticed that the K/Rb *versus* Cs trends are largely parallel but not necessarily sequential, suggesting either different sources, or different styles of fractionation, or both. Figure 16 shows the different rates of Rb and Cs accumulation in K-feldspar of the Rush Lake pegmatite group and of the Tanco pegmatite (Bernic Lake group member) in southeastern Manitoba (Černý *et al.* 1981). An even more pronounced separation of the Rb *versus* Cs trends is illustrated in Figure 17, representing two pegmatite series in the Cross Lake field of central Manitoba (Anderson 1984). Muscovite of the same pair of pegmatite series is shown in the K/Rb *versus* K/Cs graph of Figure 18 (Anderson 1984).

It may be significant that the Tanco pegmatite contains gigantic bodies of pollucite, whereas the Rush Lake group is poor in this mineral. Also, the Southern pegmatite series at Cross Lake reaches rare-alkali concentrations suggestive of the presence of pollucite, whereas the Northern series does not match

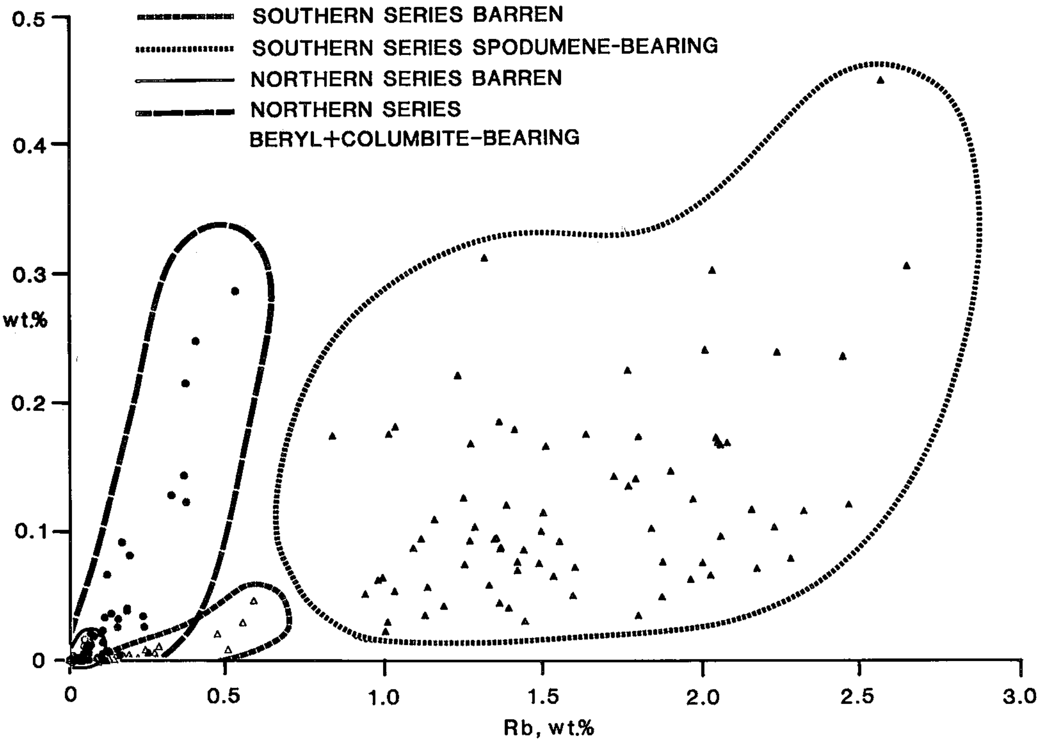


FIG. 17. The Rb *versus* Cs plots for core-margin blocky K-feldspar of the two zoned pegmatite series of the Cross Lake pegmatite field, central Manitoba (Anderson 1984).

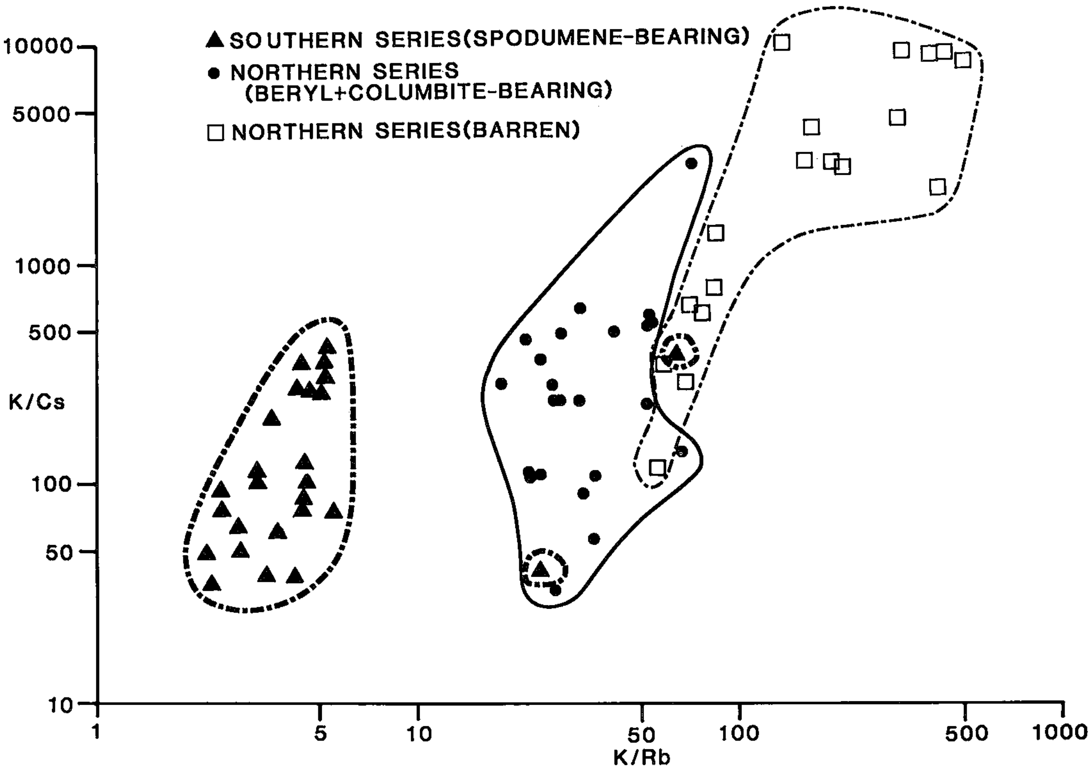


FIG. 18. The K/Cs *versus* K/Rb plots for muscovite of the two zoned pegmatite series of the Cross Lake pegmatite field, central Manitoba (Anderson 1984).

the geochemical signature of pollucite-bearing pegmatites at all. In both cases, the pollucite-rich (or -prone) pegmatites have Cs in K-feldspar distinctly lagging behind the accumulation of Rb, relative to the other regionally associated pegmatite groups. This invites speculation that in some pegmatites a mechanism (complexing ?) may operate that hinders incorporation of the Cs into potassic minerals, retaining it for late crystallization of pollucite, while Rb is entering the K-phases unimpeded. A pegmatite melt with most or all of the Cs^+ available as free cations would consume its supply during the crystallization of K-feldspar and muscovite, as indicated by the higher rate of Cs increase relative to Rb in these minerals. In such a case, the chance of leaving Cs to accumulate for pollucite crystallization would be rather poor. However, many more data are required on closely related pollucite-bearing and pollucite-free pegmatite groups to test this idea.

Al/Ga versus K/Rb and other rare-alkali parameters

Černý & London (1983) have shown a remarkable difference between the Al/Ga ratio of petalite from the Tanco and Bikita deposits (1,900–1,300 and 3,100–2,900, respectively). Trace-element characteristics are not available for the Bikita pegmatite; nevertheless, the near-identical mineral assemblages of both deposits indicate that they are mutually comparable in terms of rare-alkali fractionation (primary petalite, secondary spodumene, lepidolite units, abundant pollucite). A reconnaissance survey of Al/Ga in sodumene, petalite, eucryptite and spodumene + quartz intergrowths after petalite has shown that the Al/Ga ratio is widely variable both among and within different pegmatite fields and types (unpubl. data of P.Č.). As shown in the section on Ga, the Al/Ga relationships in rare-element pegmatites are poorly documented, and their correlation with other fractionation trends is virtually unknown; both subjects warrant thorough study.

Nb/Ta versus Fe/Mn

The columbite–tantalite minerals are the most common (Nb,Ta,Fe,Mn)-bearing phases in granitic pegmatites, complemented by tapiolite, ixiolite and wodginite. With progressive fractionation, they generally show a tendency toward Mn and Ta enrichment, but the mineral populations of individual pegmatites, pegmatite groups and fields rarely show a proportional increase in both elements. Quite to the contrary, Figure 19 shows only one locality (the Peerless pegmatite of the Black Hills, S.D.) with simultaneous Mn and Ta enrichment from ferrocolumbite to manganocolumbite, manganotantalite and wodginite (Černý *et al.* 1985c). All other data sets in Figure 19 show conspicuous discrepancies in the fractionation rates of Nb/Ta and Fe/Mn.

Geochemically primitive pegmatites (such as the Huron Claim deposit, southeastern Manitoba: Paul 1984) tend to carry ferrocolumbite. A similar tendency is shown by the Moose pegmatite, and by the whole Yellowknife, N.W.T., pegmatite field to which the Moose deposit belongs. This pegmatite field reaches its maximum fractionation in spodumene-bearing complex pegmatites having subordinate amblygonite–montebrasite and being depleted in micas and fluorine. The Fe/Mn fractionation rarely progresses to less than 1 whereas the Ta enrichment commonly proceeds from ferrocolumbite to ferrotantalite, tapiolite and rare ixiolite (unpubl. data of M.A. Wise). The Southern pegmatite series at Cross Lake, central Manitoba, belongs to the same pegmatite type, but it shows a notable Mn-enrichment in its more primitive Nb-rich pegmatites, followed by Ta-enrichment in manganotantalite, ixiolite and wodginite in the spodumene-bearing pegmatites proper (Anderson 1984). A manganocolumbite–manganotantalite progression characterizes the whole pegmatite field of the Mongolian Altai (Wang *et al.* 1981).

"Reverse" fractionation leading to Fe or Nb enrichment has been mentioned in the literature but not quantitatively documented (*e.g.*, Fersman 1940, Kornetova 1961). Figure 19 shows one such trend progressing from Ta-rich ixiolite (Fe ≅ Mn) to more niobian manganocolumbite–manganotantalite (Ferreira 1984).

Extreme fractionation of Mn is attained in those F-rich pegmatites in which F persists in the melt and fluid phases until the final phases of consolidation and metasomatism, namely in the lepidolite type of rare-element pegmatites (Černý & Ercit 1985). The Himalaya dyke system of California represents this type (Fig. 19; Foord 1976), and the Brown Derby pegmatite swarm of Colorado as well (Černý *et al.* 1985a). The Peerless mineral sequence, which also reaches maximum Mn enrichment in its late wodginite member, belongs to a pegmatite with sizeable central unit of lithian muscovite (Sheridan *et al.* 1957). Extreme enrichment in Mn is also attained in the complex, lepidolite-rich Tanco deposit; however, its mineralogy of Ta is too complex for graphic representation in a mere columbite–tantalite–tapiolite quadrilateral (unpubl. data of T.S. Ercit).

The close relationship between extreme enrichment in Mn and high activity of fluorine in late fluids is

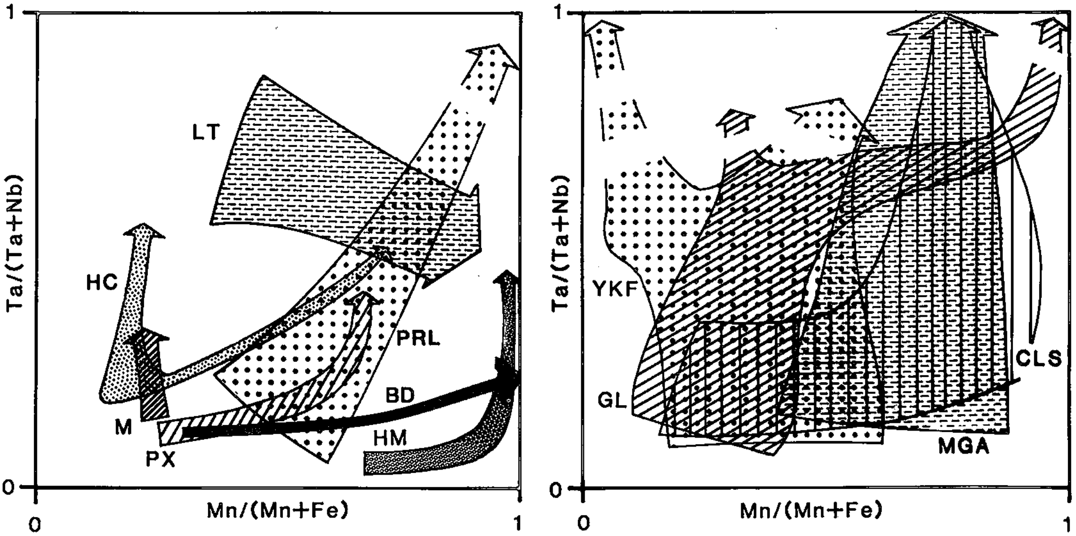


FIG. 19. The Ta/(Ta + Nb) *versus* Mn/(Mn + Fe) ratios (at.) for columbite–tantalite and related species of individual pegmatites (A) and pegmatite groups and fields (B). LT Lower Tanco (Ferreira 1984); HC Huron Claim (Paul 1984); M Moose (M.A. Wise, unpubl. data); PX Plex (unpubl. data of P.Č.and D.L. Trueman); PRL Peerless (Černý *et al.* 1985c); HM Himalaya (Foord 1976); YKF Yellowknife (M.A. Wise, unpubl. data); GL Greer Lake and BD Brown Derby (Černý *et al.* 1985a); MGA Mongolian Altai (Wang *et al.* 1981); CLS Cross Lake Southern series (Anderson 1984). Interrupted arrows indicate compositonal gaps betwen columbite–tantalite and tapiolite or ixiolite.

demonstrated by the evolution of the (Nb,Ta) oxide minerals in the Greer Lake pegmatitic granite (Černý *et al.* 1985a). In the beryl + columbite type of pegmatitic segregations typical of most of the intrusive body, ferrocolumbite and ferrotantalite occur with rare ferroan ixiolite. However, local pegmatite pods of Li-, Rb-, Cs- and F-rich assemblages (with abundant Li,F-micas, to the exclusion of K-feldspar) contain manganotantalite and wodginite with extremely low Fe/Mn values (Fig. 19).

The story of the entire Nb–Ta fractionation as shown in Figure 19 is of course incomplete, being restricted to the (Nb,Ta)- and (Fe,Mn)-bearing phases. For example, microlite is present in most highly fractionated pegmatites or it may even predominate, as in the lepidolite type. Thus the total Ta enrichment in the Himalaya and Brown Derby pegmatites, as illustrated in Figure 19, is considerably underrated. Nevertheless, the data presented here adequately document the extensive diversity in the patterns of Nb–Ta and Fe–Mn fractionation, some of which seem to be typical of different types of pegmatite.

Nb/Ta versus Zr/Hf

Information on the relationship between the Nb/Ta ratio and fractionation in zircon is scarce, and data on truly coexisting columbite-tantalite and zircon are exceptional (Fontan *et al.* 1980). Thus the plots in Figure 20 are a mere first approximation and should be treated with caution. Nevertheless, the data do indicate that there is only a limited range of Hf enrichment in zircon over most of the columbite–tantalite fractionation. Considerable increase in Hf is seen only in the Ta-enriched, lepidolite-bearing pegmatites of the Alto Ligonha field in Mozambique (Correia Neves *et. al.* 1974). The zircon–hafnon crystals from this pegmatite field are extensively zoned, with the extremely low Zr/Hf ratios restricted to their outer zone.

It is interesting to note that in the Greer Lake pegmatite group of southeastern Manitoba, the Zr/Hf ratio in zircon seems to increase with Ta enrichment of columbite–tantalite (in the sequence from GL–8 to GL–9 and GL–2A in Fig. 20; unpubl. data of P.Č.). However, the data base is rather limited, and the relationship could be modified by additional information.

K/Rb (and K/Cs) versus Nb/Ta

Progressive enrichment in Ta has been linked with

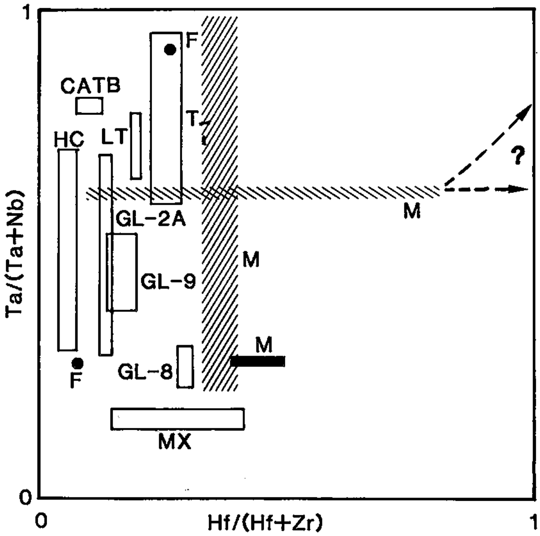


FIG. 20. The Ta/(Ta + Nb) ratio of columbite-tantalite and the Hf/(Hf + Zr) ratio of zircon-hafnon (both atomic) in individual pegmatites of diverse pegmatite fields. HC Huron Claim (Paul 1984); CATB Cat group, GL Greer Lake (both unpubl. data of P.Č.); F Pyrénées (Fontan *et al.* 1980); LT Lower Tanco (Ferreira 1984); T Tanco (Černý & Siivola 1980); MX Mixeriqueira (Cassedanne *et al.* 1985); M Alto Ligonha (Correia Neves *et al.* 1974, Sahama 1980, von Knorring & Fadipe 1981, Törnroos 1982).

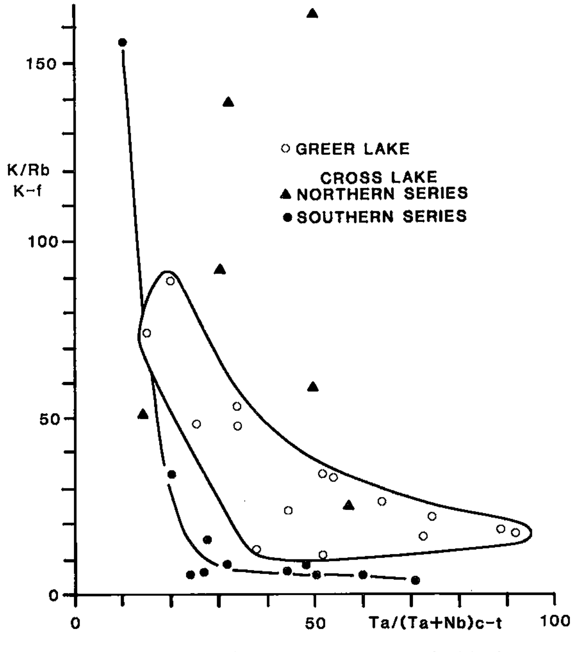


FIG. 21. The K/Rb ratio (wt.) of core-margin blocky K-feldspar and the Ta/(Ta + Nb) ratio (atomic) of columbite-tantalite and related species in the pegmatites of Northern and Southern series of the Cross Lake field (Anderson 1984) and in the Greer Lake group (Černý *et al* 1985a). Individual data-points represent averages of all data from a single pegmatite.

increasing fractionation of rare-alkali elements by many authors (*e.g.*, Ginsburg 1960, Beus *et al.* 1968, Solodov 1971). However, quantitative characterization of this relationship at the level of individual pegmatites and their cogenetic groups is scarce. Figure 21 shows the relationship between the K/Rb ratio in core-margin blocky K-feldspar and the Ta/(Ta + Nb) ratio in columbite–tantalite from three pegmatite groups in Manitoba (Anderson 1984, Černý *et al.* 1985a). Individual plots represent averages of 2 to 6 compositions of each mineral per pegmatite, and the data spread within some individual pegmatites is considerable. Nevertheless, the pegmatite averages show a well-defined linear trend in the Cross Lake Southern series, and a broader trend in the Greer Lake group. In both cases, advanced fractionation of Ta is reached only at a low K/Rb ratio, particularly in the Southern series. In contrast, the data for the Cross Lake Northern series are widely scattered and do not show any systematic change over the whole K/Rb range of 160–25.

A similar relationship is shown by the Nb–Ta fractionation *versus* the K/Cs ratio in core-margin blocky K-feldspar (Anderson 1984). However, data are very scarce at present. Extensive additional documentation is required to define different trends in the correlation of Nb/Ta with both K/Rb and K/Cs, and to decipher the probable causes of the diversity.

CONCLUDING REMARKS

The fractionation paths leading to extreme enrichment of trace components in rare-element granitic pegmatites are extended and complex. They ultimately begin with the concentrations and ratios of trace elements in metamorphic protoliths from which the fertile, pegmatite-generating granites are derived. The style of partial melting and the degree of volatile saturation affect the rare-element concentrations and ratios in the initial magma. Internal evolution of magma reservoirs through crystal–melt fractionation, liquid fractionation and transport of rare elements *via* a hydrous phase (diffuse or exsolved) produces silicic melts greatly enriched in rare elements and volatiles; these melts eventually solidify as late intrusive bodies of fertile, pegmatite-generating leucogranites and pegmatitic granites. Besides extreme crystal–melt partition coefficients of some elements (such as Li, Rb, Cs, Ba, Sr), complexing plays an important role in the accumulation of others (*e.g.*, Nb, Ta, Ga, Zr, Hf and probably also Li, Cs, Tl and Mn).

The diverse processes and mechanisms operating within magma reservoirs and batches of silicic melt also affect the evolution of the pegmatites themselves; the maximal levels of fractionation are finally reached in the rare-element pegmatites, particularly in the most evolved complex and lepidolite types of this class. At the pegmatitic granite to pegmatite stages, the multiphase nature of the parent medium affects the distribution of the rare elements. Volatile components that migrate largely by diffusion during the liquid fractionation of magma reservoirs and less differentiated plutonic intrusions reach saturation limits and exsolve. Rare-element pegmatites consolidate largely from a silicate melt co-existing with an exsolved supercritical fluid, which subsequently reacts extensively with solid phases after the melt is exhausted (Jahns 1982). Recent work on fluid inclusions and Na,Li,B-rich systems suggests the possibility of late homogenization of the melt and fluid in complex pegmatites (London 1984a). A hydrothermal solution finally induces re-equilibration in many earlier mineral assemblages at very low temperatures.

The above complexity of media, processes and mechanisms combine with uncertainties in the crystallochemical relationships of some element pairs (such as Al–Ga, Zr–Hf and Nb–Ta). Fractionation relationships of these and other element pairs are so far based much more on empirical data than theoretical considerations or experimental modeling.

Further progress in undestanding (as opposed to describing) the extreme fractionation and element enrichment in rare-element granitic pegmatites will come from several sources. The recent revival of interest in the geochemistry and petrogenesis of granitic and rhyolitic rocks has already contributed extensively to our understanding of trace-element behavior at the magma-chamber and plutonic level (as summarized in Hildreth 1979, 1981, Mahood & Hildreth 1983, Michael 1983, Miller & Mittlefehldt 1984). The modern study of fluid inclusions in pegmatite minerals has begun to shed light on the nature of parent fluids and the P–T conditions of precipitation (*e.g.*, London *et al.* 1982, London 1983, 1984a, 1984b). However, a systematic collection of quantitative data on elemental abundances in *integrated suites of samples* is also required at several levels; within well-documented *individual pegmatites*, in *cogenetic pegmatite groups and their parent granites*, and in pegmatite groups representative of *different classes and types*. Each of these three approaches will greatly improve our present understanding of the element distributions in pegmatites, which has been shown in the present paper to be rather sketchy in many respects.

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