

## Beryllium in Metamorphic Environments (emphasis on aluminous compositions)

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### INTRODUCTION

Beryllium is an element thought to be largely associated with igneous and hydrothermal processes and the world's major economic Be deposits are largely igneous or hydrothermal. However, metamorphic rocks also play a major role in the Be budget of the Earth's crust. Beryllium enrichments in pegmatites and hydrothermal deposits are associated with granitic systems that many geoscientists think are derived from melting of metasedimentary rocks, with metapelites being the most fertile for Be (e.g., London and Evensen, this volume). Consequently, metamorphism plays an important role in the cycling beryllium from sediments to granitic systems.

The emphasis of my chapter is on rocks of pelitic composition or otherwise relatively rich in aluminum such as bauxite and metamorphosed peraluminous pegmatites (see also Franz and Morteani, this volume) and on the minerals making up these rocks. It concerns beryllium in metamorphic environments where beryllium was not introduced *during* metamorphism. Two major questions are addressed: (1) average and range of Be contents of metamorphic rocks, and (2) the effect of metamorphism on their beryllium content. Addressing both questions requires not only extensive data on metamorphic rocks, but also a comparable database of beryllium contents of unmetamorphosed precursor sediments. In general, beryllium is analyzed much less often than other trace elements, and as far as I am aware, there have been no systematic large-scale studies of Be in pelitic rocks or any other rock type. For example, Terry Plank (pers. comm. 2001) finds that there still is not enough high quality data to consider its behavior in marine sediments as has been done for other trace elements (Plank and Langmuir 1998).

Beryllium minerals, including both silicates and oxides, are rare in most metamorphic rocks, although a surprisingly large number of species has been found. This scarcity undoubtedly reflects the low abundance of Be in these rocks, including metapelites, metapsammities, carbonates, and metabauxites, in which Be contents rarely exceed 10 ppm. At this low concentration, Be can be accommodated in some common rock-forming minerals, notably muscovite, staurolite and cordierite, so that minerals containing essential beryllium, e.g., beryl or chrysoberyl, are relatively rare. In contrast, the situation with boron, another element characteristic of the upper continental crust and the subject of the companion *Reviews in Mineralogy*, Volume 33, is very different. Borosilicates are widespread (Henry and Dutrow 1996; Grew 1996) and B contents averaging 100 ppm are not rare in non-metasomatic metapelites (e.g., Leeman and Sisson 1996). This amount of boron generally cannot be accommodated either in quartz or in the most abundant minerals of the mica, feldspar, amphibole and pyroxene groups, so that a boron phase, in most cases a tourmaline-group mineral, is present.

Although well over half the known beryllium minerals (see Grew, Chapter 1, Appendix 1) have been found in metamorphic environments, I will not discuss all of them in the chapter on metamorphism, but refer the reader to the Introduction for the necessary information. I have selected only those minerals (Table 1) that are predominantly metamorphic and sufficiently studied that coverage in Appendix 1 of the Introduction is inadequate. Beryl and chrysoberyl, which are the two most widespread Be minerals, are being covered in this volume by Černý, London and Evensen, Franz and Morteani (Chapters 10, 11 and 13, respectively).

### BERYLLIUM CONTENTS OF NON-PELITIC METAMORPHIC ROCKS

Carbonate sediments contain less Be than pelitic sediments, e.g., <0.2 to 4 ppm (Warner et al. 1959; Beus 1966; Hörmann 1978; Gao et al. 1991). Nonetheless, many metasomatic beryllium deposits have formed by replacement of carbonate rocks, e.g., the Yermakovskoye phenakite-bertrandite-fluorite deposit in Buratiya, Transbaikalia, Russia (Novikova et al. 1994).

Low-grade metamorphosed oolitic ironstone and ferruginous sandstone from Sardinia contain 0.24-7.29 ppm Be; the most abundant minerals are chamosite, siderite, and magnetite (Franceschelli et al. 2000).

Beryllium is not particularly enriched in many manganese deposits and Mn-rich rocks, e.g., <0.2-0.84 ppm Be, Franciscan Complex, California, (Huebner and Flohr 1990; Huebner et al. 1992); 2-5 ppm in Mn-rich metapelites ("redschiefer") and associated spessartine-quartzites ("coticules") from the Ardennes Mountains, Belgium (Krosse and Schreyer 1993). However, relatively elevated Be contents have been reported as the following Mn-bearing rocks, minerals, and deposits:

- 2-15 ppm Be in Mn nodules (Ryan, Chapter 3, this volume)
- 20-200 ppm Be in residual manganese ore concentrated from several U.S. manganese deposits associated with quartzite and dolomite (Warner et al. 1959)
- 0.04-0.4 wt % BeO in tilasite (CaMgAsO<sub>4</sub>F), garnet and mineralized arkose from Guettara, Algeria (Agard 1965)
- 0.22-0.25 wt % BeO in rhodochrosite in a supergene deposit formed over a Be-bearing greisen (Grigor'yev 1967)
- 2-34 ppm Be in cryptomelane, the most abundant Mn oxide in volcanogenic-hydrothermal Mn deposits of the Calatrava Volcanic Field, Spain (Crespo and Lunar 1997).

Beryllium enrichment is also reported in some metamorphic manganese deposits, of which the most famous is Långban, Sweden (e.g., Magnusson 1930; Moore 1971; Sandström and Holtstam 1999). Metamorphosed manganese deposits with beryllium mineralization have been described from localities near Långban (e.g., Harstigen, Moore 1971), central French Pyrenees (Ragu 1994) and Val Ferrera, eastern Swiss Alps (Brugger and Gieré 1999; Brugger et al. 1998); Be contents range from <0.2 to 175 ppm in Fe-Mn deposits of Val Ferrera (Brugger and Gieré 2000). Prevailing opinion is that Be was introduced hydrothermally from granites into these manganese deposits during or after metamorphism (e.g., Moore 1971; Ragu 1994). However, the possibility of a pre-metamorphic origin of Be from volcanic exhalations cannot be excluded; such an origin has been proposed for As, Pb, U and other elements at Långban (Boström et al. 1979; Bollbark 1999) and for Be and W in the eastern Swiss Alps (Brugger and Gieré 1999, 2000). Krosse and Schreyer (1993) inferred a similar origin for Fe-Mn enrichment in the Mn-rich metasediments from the Ardennes, Belgium.

Table 1. Minerals containing major beryllium and mineral abbreviations used in this chapter.

<i>Mineral (abbreviation)</i>	<i>Symmetry</i>	<i>Formula plus exchange introducing Be</i>
<b>AENIGMATITE GROUP AND RELATED MINERALS</b>		
Hogtuvaite	Triclinic	$(Ca_{1.8}Na_{0.2})(Fe^{2+}_{3.55}Fe^{3+}_{2.2}Ti_{0.25}O)_2[Si_{4.5}BeAl_{0.5}O_{18}]$
“Makarochkinite”	Triclinic	$(Ca_{1.76}Na_{0.19}Mn_{0.05})(Fe^{2+}_{3.66}Fe^{3+}_{1.36}Ti_{0.54}Mg_{0.25}Mn_{0.10}Nb_{0.06}Sb_{0.02}Ta_{0.01})O_2-[Si_{4.43}BeAl_{0.49}Fe^{3+}_{0.06}B_{0.01}O_{18}]$
Welshite	Triclinic	$Ca_2Mg_{3.8}Mn^{2+}_{0.6}Fe^{2+}_{0.1}Sb^{5+}_{1.5}O_2[Si_{2.3}Be_{1.7}Fe^{3+}_{0.65}Al_{0.7}As_{0.17}O_{18}]$
Sapphire (Spr) – khamralite (Khm)	Monoclinic	$(Al,Mg,Fe)_8O_2[(Al,Si,Fe^{3+})_6O_{18}]$ plus up to 0.78 BeSiAl <sub>2</sub>
Surinamite (Sur)	Monoclinic	$(Mg_1Fe^{2+})_3(Al_1Fe^{3+})_3O_4[AlBeSi_3O_{15}]$
<b>OTHER SILICATES</b>		
Cordierite (Mg>Fe, Crd) – sekaminaite (Fe>Mg)	Orthorhombic	$\square(Mg,Fe)_2Al_4Si_5O_{18} \cdot nH_2O$ plus NaBe( $\square$ Al) <sub>1</sub> and/or BeSiAl <sub>2</sub>
Euclase	Monoclinic	BeAlSiO <sub>4</sub> (OH)
<b>TAAFFEITE GROUP (OXIDES)</b>		
Magnesiotaaffeite-6N°3S, formerly “musgravite” (Mgr)	Hexagonal	$(Mg,Fe,Zn)_2Al_6BeO_{12}$
Ferrotaaffeite-6N°3S, formerly “pehrmanite”	Hexagonal	$(Fe,Zn,Mg)_2Al_6BeO_{12}$
Magnesiotaaffeite-2N°2S, formerly “taaffeite” (Tff)	Hexagonal	$(Mg,Fe,Zn)_3Al_8BeO_{16}$
<p><i>Note:</i> Minerals in bold contain essential beryllium. Other abbreviations (based on Kretz 1983) used in this chapter are: Ab – albite, Alm – almandine, An – anorthite; And – andalusite; Ap – apatite; Bor – borasilite, Brl – beryl, Bt – biotite, Cal – calcite, Ch – chrysoberyl, BeAl<sub>2</sub>O<sub>3</sub>; Chl – chlorite, Crn – corundum, Di – diopside, Fl – fluorite, Grt – garnet; Gdd – granddierite, Hc – hercynite, Hem – hematite, Hg – hggomite, Hg – hggomite, Ilm – ilmenite, Kis – K-feldspar; Ky – kyanite, Mc – microcline, Mgr – magnetite, Ms – muscovite, Mnz – monazite, Oam – orthoamphibole; Ol – olivine; Opx – orthopyroxene; Pg – paraonite, Phl – phlogopite, Pl – plagioclase, Prp – pyrope, Qtz – quartz, Rt – rutile, Sil – sillimanite; Spl – spinel, St – staurolite, Tur – tourmaline, Wrd – werdingite.</p>		

### BERYLLIUM CONTENTS OF SEMI-PELITIC, PELITIC AND OTHER ALUMINOUS ROCKS

In brief, the great majority of pelitic and semipelitic sediments and their metamorphic equivalents contain 0.2 to 5 ppm Be and average near 3 ppm Be for all grades of metamorphism. Ten ppm Be represents a maximum for unmineralized pelite not associated with bauxite or metasediments unusually enriched in Be.

#### Unmetamorphosed rocks

Available data on pelitic sediments represent a random sampling of different lithologic types whose Be content depends on the environment of deposition. The beryllium content of pelagic clays and other marine sediments has been reported to vary within a narrow range of 0.3 to 3 ppm Be (Merrill et al 1961; Ryan and Langmuir 1988; Johnson and Plank 1999; summarized in Table 2 and Figure 1a; see also Hörmann 1978 and Ryan, this volume). In contrast, near-shore clays from Trinidad and redeposited terrestrial clays from different areas in the former USSR show a much greater range.

Carbonaceous sediments in some cases contain more beryllium than other sediments. Coal ash can have relatively high Be contents, although these vary locally, regionally and temporally, e.g., in the U.S., Late Paleozoic Appalachian coal ash averages 62 ppm Be, nearly three times the average in the Great Plains and Rocky Mountains of Mesozoic-Cenozoic age (Warner et al. 1959; Stadnichenko et al. 1961). Hörmann (1978) concluded that variations were too great to calculate a meaningful average for coal ash overall. On the other hand, carbonaceous shales are rarely enriched in Be. A comprehensive survey of U.S. black shales gave a median content of 1 ppm Be and very few contents above 10 ppm Be (Vine and Tourtelot 1970); Warner et al. (1959) reported several lignitic and carbonaceous shales and clays containing 7-14 ppm Be.

Be contents of pelites are higher than those of sands, sandstone and carbonate rocks (Hörmann 1978; Gao et al. 1991, 1998). Hörmann (1978) suggested an average of 5 ppm Be for bauxites, but a wide range of Be contents has been reported (Table 2).

Taylor and McLennan (1985 1995) noted that beryllium is one of the elements with a very small seawater-upper crust partition coefficient and relatively short residence time in seawater, and thus, its abundance in terrigenous sedimentary rocks (i.e., shales and related rocks, which constitute an estimated 70% of all sedimentary rocks) should approach the average Be content of the upper continental crust. This conclusion, which is largely based on the compilations of Hörmann (1978), is supported by the trends based on new, not yet published data in Figure 1a, which shows that Be increases with Al. Wedepohl (1995) calculated 3.1 ppm Be for the upper crust using the average compositions of crustal rocks (mostly from the compilations of Hörmann 1978) multiplied by their proportion in the upper crust. Gao et al. (1998) calculated 1.95 ppm Be as the average content for the upper crust of central East China (sedimentary carbonate rock-free basis). The lower value for Be could reflect real differences between central East China and the Earth as a whole; Gao et al. (1998) noted that relatively low Al<sub>2</sub>O<sub>3</sub> in East China reflects such differences.

#### Metamorphosed rocks

Wedepohl (1995) noted that for Be "reliable literature data on common rocks, especially on metamorphic rocks, are rather rare", and this observation still holds despite a spate of studies reporting Be data since 1995 (Table 2, Fig. 1b). Available data do not suggest that beryllium is lost from pelitic rocks during metamorphism (e.g., Lebedev and Nagaytsev 1980). The studies by Bebout et al. (1993 1999) of the Catalina Schist, California are the most systematic for low to middle-grade metapelites. Beryllium content

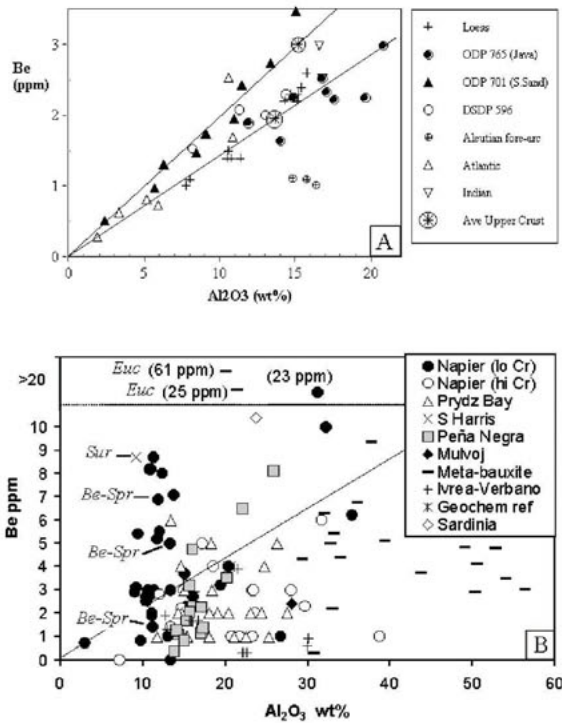
Table 2. Beryllium contents of rocks

Rock types and localities	Metamorphic zone (or other information)	Be, ppm		Source
		Range*	Average (n)	
<b>UNMETAMORPHOSED PELITIC ROCKS</b>				
Pelagic clays in 5 sediment cores		2.0-3.0	2.6 (32)	Merrill et al. (1960)
Pelagic clay in one core		2.1-3.9	2.75(4)	
Red pelagic clay		2.16-2.53	2.32(5)	Johnson & Plank (1999)
Marine sediments		0.282-2.83	1.45 (19)	Ryan & Langmuir (1988)
Calcareous argillite, Paris basin		2.23-2.64	2.48 (3)	Henry et al. (1996)
Clays, Gulf of Paria, between Trinidad and Venezuela		1.0-8.7	6.2 (12)	Hirst (1962)
Limonitic concretions, Gulf of Paria		9.8-18	12.5(4)	
Clays, miscellaneous from former USSR		0.2-1.0	1.5-3(60) <sup>y</sup>	Beus (1966, Table 142)
Miscellaneous shale and clay, including carbonaceous varieties, U.S.		Mostly <4; maximum 14	<4 (181)	Warner et al. (1959)
Shale		0.5-2	4 (36)	Goldschmidt & Peters (1932)
Miscellaneous shale not cited above			(5)	Hörmann (1978)
<b>METAMORPHOSED PELITIC ROCKS</b>				
Geochemical reference slate				
Metasediments with Mn deposit, Franciscan Complex, Calif.	Blueschist facies	Shale	4 (1)	Flanagan (1973)
		Graywacke:	2.90 (1)	Huebner et al. (1992)
Metamorphosed shales and sandstones, Catalina Schist, California	Lawsonite-albite Blueschist Greenschist & Epidote-amphibolite Amphibolite Chivor and Gachala districts Muza mine	0.67-1.20	0.96 (7)	
		0.34-1.3	0.95 (14)	
		0.19-1.4	0.77 (8)	
		0.3-1.1 (4.1- 5.4)	0.73 (16+2)	Bebout et al. (1993, 1999)
		0.41-1.15	0.70 (10)	
Very weakly metamorphosed carbonate-rich and siliceous black shales, emerald deposits, Colombia		3.00-4.00	3.73(7)	Giuliani et al. (1999)
			3 ± 0.5	Ottaway et al. (1994)
Low-grade metapelites, western Alps Black metapelite associated with oolitic ironstones, Nurra region, NW Sardinia, Italy		1.36-4.38	4.0(38)	Beus (1979)
			3.1(11)	Henry et al. (1996)
			10.4	Franceschelli et al. (2000)

Aluminous metasediments, Quebec			1.8 (5)	Shaw et al. (1967)
Aluminous metasediments, Baffin Island			1.5 ± 1.3 (20)	
Schists from "geosynclinal" regions of the former USSR	1-8		3.8 (22)	Beus (1966, Table 142)
Schists from eastern Transbaikalia, Russia	1-5		3.5 (10)	Hietanen (1969)
Mica schist, different grades	0-8		~1 (7)	
Biotite and biotite-muscovite schists with porphyroblasts of garnet, staurolite and andalusite, Ladoga complex, NW Russia	2.5-6.5		4.1 (16)	Sergeyev et al. (1967)
Garnet			2.9 (5)	
Staurolite-andalusite			2.6 (11)	
Sillimanite-muscovite			3.5 (7)	Lebedev & Nagaytsev (1980)
Sillimanite-K feldspar			3.0 (30)	
Hyperssthene			2.3 (28)	
Phyllite, schist, shale, greenschist- and amphibolite-facies, Urals	0.5-8		2.6 (40)	Bushlyakov & Grigor'yev (1989)
Metapelites, Kinzigite Formation, Ivrea-Verbano, Italy				
"Kinzigite" = amphibolite facies	1.3-3.9		2.34 (5)	
Transitional	1.6-1.7		1.65 (2)	Bea & Montero (1999)
"Stronalite" = granulite facies	0.3-0.9		0.48 (5)	
Mesosomes	1.13-4.75		2.34 (5)	
Melanosomes	3.51-8.10		6.04 (3)	Bea et al. (1994)
Leucosomes	0.37-2.04		1.20 (6)	
Migmatites, undifferentiated	1.13-3.16		1.98(4)	Pereira Gómez & Rodríguez Alonso (2000)
Restites	1.66-3.17		2.40(3)	Grew (unpub. data)
Whiteschist (taic-kyanite), Mulvoj, Tajikistan			2.4 (1)	
Amphibolite facies with relict granulite and eclogite facies, Zerendin Series, Kokchetav massif, Kazakhstan				
Metasedimentary mica schists with Grt and Sil			3.4 (33)	Rozen & Serykh (1972)
Gneisses derived from feldspathization of the above			3.2 (20)	
Amphibolite-facies inclusions in granitic intrusives, N. Victoria Land, Antarctica				
Biotite-schist xenoliths	2-5		3 (9) <sup>†</sup>	Sheraton et al. (1987a)
Biotite-rich restite			4 (2)	

Miscellaneous pelitic granulites, Prydz Bay, East Antarctica	1-6	2.4 (22)	Sheraton et al. (1984), Sheraton (unpubl. data)
Ultrahigh- <i>T</i> granulite-facies Napier complex, Enderby Land, East Antarctica	Miscellaneous pelitic granulites, S. and E. of Amundsen Bay	0-10 (23)	Sheraton (1980, 1985, unpubl. data); Sheraton et al. (1982)
	Quartzofeldspathic granulite	5 (1)	Grew (1998)
Granulite-facies metapelite in lower crustal xenoliths in the Hannuoba basalt, Zhouba, North China craton	Quartz rich-granulites, Khmara Bay and Mt. Pardoe	0.8-8.7	Grew et al. (2000, 2001b, unpubl. data)
		0.33-0.67	Liu et al. (2001)
Miscellaneous claylate, phyllite, schist, gneiss, not cited above	0.8-10.5		Hörmann (1978)
Clastic metasediments, (anchizone to Bt zone), Cinco Villas massif, Spain	<1-7	5.4 (45)	Pesquera and Velasco (1997)
Tur-rich metapelite and metapsammite, Broken Hill district, Australia	1-3	2 (3)	Slack et al. (1993)
<b>BAUXITE AND ASSOCIATED ROCKS, UNMETAMORPHOSED AND METAMORPHOSED AT LOW-<i>T</i> CONDITIONS</b>			
Bauxite, Jamaica, unmetamorphosed		180 (1)	Wamer et al. (1959)
	Bauxite, Dutch Guiana	4 (1)	
Metabauxite and chloritoid schists, Tuscany, Italy	0.32-6.75	4.06 (10)	Franceschelli et al. (1998)
Metabauxite and meta-aluminous argillites, western Alps, Switzerland and France	3.47-9.38	5.06 (7)	Poinssot et al. (1997)
Miscellaneous bauxite, unmetamorphosed, not cited above	0-36		Hörmann (1978)
<b>ROCKS CONTAINING A Bf-RICH MINERAL (IN SMALL CAPITALS)</b>			
Granulite-facies quartzofeldspathic gneiss, South Harris, Scotland (SURINAMITE)		8.7, 9 (1)	Baba et al. (2000)
Quartz-rich granulites (2) and quartzofeldspathic gneiss, Napier complex, East Antarctica (SAPPHIRE with 0.2-1.34 wt % BeO), a subset of the Napier Complex data cited above	1.4-6.9	4.4 (3)	Grew (1998);
			Grew et al. (2000);
Chloritoid-chlorite phyllite, Aiguille du Fruit, Vanoise (W. Alps), France (EUCLASE)	25, 61		Sheraton (1985, unpubl. data)
Spinel-phylogopite rock, Mt. Painter, South Australia (MAGNESIOTAAFFEITE-2N75)		5.3 (1)	Goffé (1980, 1982); Catel & Goffé (pers. comm. 2001)
			Teale (1980)

Note: n – number of samples. \*Exceptional values (in italics) are not included in average. †Range of averages on 4 groups of samples.



**Figure 1.** (a) Beryllium contents of marine and other sediments (compiled by Terry Plank; cf. Plank and Langmuir 1998). Loess is a good estimate of upper crust (Taylor et al. 1983). ODP Site 765 (Java) – Al from Plank and Ludden (1992); Be from Plank (unpublished ICP-MS data). ODP Site 701 (South Sandwich) – Al from Plank and Langmuir (1998); Be from Plank (unpubl. ICP-MS data). DSDP 596 refers to Tonga sediments from DSDP 595&6 – Al from Plank and Langmuir (1998); Be from Plank (unpublished ICP-MS data). Aleutian fore-arc sediments are dominated by arc volcanics, which explains their anomalous low Be contents (data from Ryan 1989). Atlantic sediments are also from Ryan (1989), whereas the Indian Ocean sediments are from Plank (unpublished ICP-MS data). The average upper crustal values of 3.0 and 1.95 ppm Be are from Taylor and McLennan (1985) and Gao et al. (1998), respectively. (b) Whole-rock Be and Al<sub>2</sub>O<sub>3</sub> contents of metamorphic rocks listed in Table 2, where sources of data are given. Lo Cr and Hi Cr refer to average Cr contents of Napier Complex metapelites, respectively 6 ppm and 674 ppm Cr (Sheraton 1980). Points for rocks containing euclase (Euc), surinamite (Sur) or sapphirine containing  $\geq 0.2$  wt % BeO, Be-Spr (Table 2) are labeled. The line is a reference passing through the estimated Be (3 ppm) and Al<sub>2</sub>O<sub>3</sub> (15.2 wt %) contents of the upper continental crust (Taylor and McLennan 1985, 1995).

decreases with increasing grade from an average of  $0.95 \pm 0.31$  ppm Be to  $0.70 \pm 0.26$  (see also Ryan, this volume). However, by the authors' (Bebout et al. 1993) own admission, the overlap of Be contents from grade to grade is too great for this difference to indicate Be loss with metamorphic grade. In their comprehensive study of central East China, Gao et al. (1991 1998) reported a difference in the Be contents between unmetamorphosed, greenschist-facies and amphibolite-facies post-Archean pelites (2.69



ppm Be) and arenites (1.78 ppm Be) and metapelites and meta-arenites in amphibolite- and granulite-facies Archean complexes, respectively, 2.08 and 1.18 ppm Be. Being of different ages, the rocks are not exactly comparable, and the overall higher metamorphic grade of the Archean rocks may be only one factor behind their lower Be contents.

Co-variance of Be with Al is not evident in the metamorphic rocks overall (Fig. 1b), as it is in the unmetamorphosed sediments (Fig. 1a); nonetheless, samples from certain areas do show trends, e.g., migmatites from the Peña Negra complex, Spain, and the low-Cr metapelites from Napier Complex, Antarctica. The co-variance of Be with Al in the Peña Negra migmatites could be a relic of the original sediments, but a substantial influence of anatexis cannot be discounted.

The very weakly metamorphosed carbonaceous shales in the emerald deposits, Colombia (see Franz and Morteani, this volume) contain 3-4 ppm Be on the average, i.e., the same as shale overall, but this amount is deemed sufficient to supply Be for emerald formation (e.g., Beus 1979; Ottaway et al. 1994; Giuliani et al. 1999).

Low-grade metabauxites and associated aluminum-rich rocks on the whole contain more Be than metapelites, i.e., 5-10 ppm Be are not unusual (Table 2), whereas the 25-61 ppm Be measured in two euclase-chloritoid-chlorite rocks from the western Alps (Goffé 1982; Catel and Goffé, pers. comm. 2001) are exceptional (Fig. 1b), albeit non-metasomatic (see below under euclase).

The granulite facies is a special case. Citing older data supplemented by new results on rocks from the Brazilian shield, Sighinolfi (1973) concluded that there was no evidence for Be depletion in granulite facies rocks overall, though "acid" granulites appeared to be depleted relative to other rocks of granitic composition. Consequently, Sighinolfi (op. cit.) proposed two scenarios: (1) the Be concentrations measured in granulites represent Be concentrations of the precursors (metamorphism was isochemical) (2) Be was redistributed by dehydration reactions or anatexis during metamorphism resulting in depletions in some rocks, but enrichments in others. Overall, Be contents of granulite-facies metapelites rocks are not lower than in lower-grade rocks (Table 2, Fig. 1b), and thus are consistent with Sighinolfi's (1973) general conclusion and supportive of his first scenario. However, a closer look indicates that there are some depletions and enrichments suggesting that the second scenario might be more appropriate. For example, data of Bea and Montero (1999) for the Kinzigite Formation of Ivrea-Verbano, Italy show a decrease in Be in the granulite facies "stronalites" (0.3-0.9 ppm Be) relative to the upper-amphibolite facies "kinzigites" and transitional to granulite-facies (NB. This conclusion is based on Bea and Montero's Table 2 and not on these authors' statement in the text on p. 1137 reporting that the granulite-facies "stronalites to be significantly richer in Be"). On the other hand, the South Harris surimanite-bearing gneiss and many low-Cr Napier Complex metapelites are somewhat enriched in Be relative to most pelites. Redistribution of Be by anatexis under granulite-facies conditions is also suggested by slight enrichment in Be in two anatectic pegmatites in the Napier Complex, 11.2-11.4 ppm Be (Grew et al. 2001b and unpublished data) vs. an average of 3.9 ppm in associated granulites (Table 2).

Mica schists in the aureoles of the Be-enriched Beauvoir granite, Massif Central, France (Burnol 1974; Monier et al. 1987; Rossi et al. 1987; Piantone and Burnol 1987) deserve a brief mention. Earlier studies cited by Piantone and Burnol (1987) reported that average Be contents of metapelites in aureoles around the Beauvoir and related granites range from 3 to 6 ppm, values not much greater than for the pelites listed in Table 2. Higher Be contents were found in mica schist from the aureoles cut by the Échassières drill hole, i.e., 2 to 277 ppm; average  $12 \pm 32$  ppm (77 samples, Piantone and Burnol

1987). Although the 277 ppm maximum represents an extraordinary enrichment of Be adjacent to the granite, Be on the whole does not vary significantly as a function of distance in the drill core from the Beauvoir granite. Multivariant statistical treatment shows that Be behaves independently of F, Li, Sn, and Rb in the aureoles.

Another example of Be enrichment are muscovite schists (10.7-71.9 ppm Be) associated with emerald deposits in Habachtal, Austria, but it is possible these are volcanogenic rocks enriched in Be prior to metamorphism (Grundmann and Morteani 1982, 1989; Franz and Morteani, this volume).

### **Relationship between whole-rock Be content and mineral assemblage**

The observed variations in Be content with metamorphic grade can be rationalized in terms of the minerals present. White mica, which is relatively abundant in nearly all low- and medium-grade metapelites, should be able to carry the amount of Be normally present in pelites, i.e.,  $\leq 5$  ppm whole-rock vs. 20-120 ppm present in some muscovite. Thus, as long as muscovite is present in reasonable abundance, no loss of Be would be expected, and none has been conclusively demonstrated in muscovite-bearing rocks. However, at temperatures above the breakdown of muscovite, retention of beryllium most likely depends on biotite or plagioclase unless a major Be sink such as cordierite or sapphirine is present. For example, cordierite and sapphirine are absent from the Ivrea-Verbano granulite-facies "stronalites"; which are richer in garnet and poorer in biotite (and to a lesser extent, poorer in plagioclase) than the lower-grade "kinzigites" (Bea and Montero 1999). Thus, loss of Be could be explained by the increase in modal garnet, a phase poor in Be, at the expense of biotite and plagioclase. In contrast, cordierite is present in all the Peña Negra (Spain) migmatites (Bea et al. 1994; Pereira Gómez and Rodríguez Alonso 2000) and in all but two of the Prydz Bay (Antarctica) metapelites (the two cordierite-free Prydz Bay rocks have only 1 ppm Be, Sheraton, unpublished data). Thus, the retention of Be in these metapelites can be attributed to the presence of cordierite. The situation with the Napier Complex is less clearly defined. Most of the Napier Complex metapelites contain cordierite or sapphirine or both, and the Be contents of these metapelites average somewhat higher than Napier Complex metapelites lacking these minerals. However, the difference is less than  $1\sigma$  of the average and in the rocks lacking sapphirine and cordierite, there could be another carrier for Be that has not been elucidated to date.

In contrast to euclase-bearing rocks containing 25-61 ppm Be, other pelitic and Al-rich metamorphic rocks containing Be-rich phases are only modestly, if at all, enriched in Be (Table 2, Fig. 1b), implying that Be content is not the sole factor determining whether a discrete Be-rich phase appears. Its appearance in rocks containing only a few ppm Be could result from the very low Be concentrations accepted in the major constituents of the rock such as quartz, alkali feldspar and garnet. In rocks containing a few ppm to few tens ppm Be and abundant muscovite, a Be-rich phase would not appear because this amount of Be could be accommodated in muscovite. If a Be "sink" such as cordierite or sapphirine were present in trace amounts only with quartz, alkali feldspar and garnet, Be could reach substantial concentrations in these "sinks". One example appears to be the Napier Complex metapelites unusually poor in Cr (6 ppm Cr on the average, Sheraton 1980), V, and Ni (Fig. 1b). Because these are relatively poor in alumina and the modal amount of sapphirine correspondingly low, Be is concentrated in sapphirine. Anatexis is another process by which Be enrichments might appear in association with pelites themselves not unusually enriched in Be. Bea et al. (1994) reported substantial enrichment of Be in Peña Negra melanosomes (Table 2; Fig. 1b). Partial melting at ultrahigh temperatures (the most recent estimate at one locality is 1120 °C, Harley and Motoyoshi 2000) of Napier Complex quartz-rich granulites in Khmara Bay and Mt.

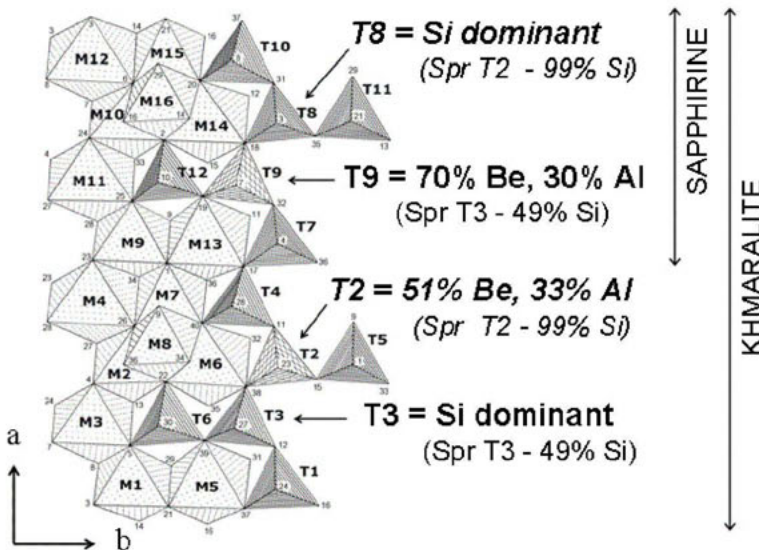
Pardoe (Table 2) has resulted in pegmatites containing beryllian sapphirine-khmaralite (Grew 1981 1998; Grew et al. 2000). Another example is the Almgjothei, Norway, pegmatite, which contains Be-bearing sillimanite, werdingite and boralsilite. Grew et al. (1998c) suggested that B in these phases could have originated from graphite-rich layers in the metapelitic host rocks to the pegmatite, and that Be had been remobilized with B. As noted above, carbonaceous sediments can contain more Be than average metapelite, and thus, graphite-rich layers could have been a source for Be as well as B.

## DESCRIPTION OF SELECTED MINERALS WITH MAJOR BERYLLIUM

### Aenigmatite group and related minerals

Surinamite and sapphirine-khmaralite, two major carriers of Be in high-grade Al-rich metamorphic rocks, are related to the aenigmatite group, which includes two rare minerals found in metamorphic environments, høgtuvaite and welshite (Table 1). Aenigmatite-group minerals are triclinic chain silicates having the general formula  $^{[8]}A_2^{[6]}B_6O_2^{[4]}T_6O_{18}$ , where A = Ca, Na; B = Al, Cr, Fe<sup>3+</sup>, Fe<sup>2+</sup>, Mg, Sb, Ti; T = Al, Si, B, Be, and Fe<sup>3+</sup> (e.g., Cannillo et al. 1971; Deer et al. 1978; Burt 1994; Mandarino 1999; Kunzmann 1999; Hawthorne and Huminicki this volume). Sapphirine and khmaralite differ from the aenigmatite-group minerals in that the A site is octahedral and is occupied dominantly by Mg and Fe<sup>2+</sup> (e.g., Moore 1969; Barbier et al. 1999; Fig. 2).

The six-membered tetrahedral chains in aenigmatite-group minerals, sapphirine and khmaralite differ from tetrahedral chains in pyroxene by the presence of wings of single tetrahedra sharing a corner with half the chain tetrahedra. As a result, two tetrahedra



**Figure 2.** Crystal structure of khmaralite showing the relationship between sapphirine (Spr) and khmaralite and occupancies of the tetrahedra sharing three corners with other tetrahedra (the so called Q<sup>3</sup> tetrahedra). Italics emphasize the alternation of ordering schemes from one sapphirine subcell to the next, resulting in the doubling of the unit cell in khmaralite. Modified from Barbier et al. (1999).

share three corners with other tetrahedra; these are the most highly polymerized, so called  $Q^3$  tetrahedra (Fig. 2). Two tetrahedra share two corners with other tetrahedra as in pyroxenes, and the two wing tetrahedra share only one corner with a tetrahedron. Beryllium is found to reside exclusively in the tetrahedra sharing three corners. In surinamite, only every fourth tetrahedron has a wing so that only one tetrahedron in the five-membered chain shares three corners with tetrahedra (Moore and Araki 1983). Barbier (1998) noted that tetrahedral order in surinamite is nearly complete, whereas the tetrahedral sites in sapphirine and khmaralite are never completely ordered, so that surinamite is a more favorable host for beryllium. The partial disorder in sapphirine-khmaralite could result from the availability of two competing  $Q^3$  tetrahedra. Beryllium cannot occupy the two  $Q^3$  tetrahedra simultaneously because the bridging oxygen between them would be seriously undersaturated (Be-O-Be bridge); this complication does not arise with the single  $Q^3$  tetrahedron in surinamite. The need to avoid Be-O-Be bridges also limits the maximum Be content in the double-winged chain to one Be per 6 tetrahedra, i.e., 1 Be per 20 O. Be contents of høgtuvaite, "makarochkinite", synthetic beryllian sapphirine and khmaralite do not exceed 1 Be per 20 O, but welshite composition appears to violate this constraint.

**Høgtuvaite and "makarochkinite".** Høgtuvaite, ideally  $Ca_2(Fe^{2+}_5Ti)(Si_5Be)O_{20}$  (Burt 1994), was first reported as a metamorphic mineral in granitic gneiss and mafic pegmatites near the eponymous Høgtuva, Mo i Rana, Nordland, Norway (Grauch et al. 1994). In the absence of a crystal structure determination, which was impossible due to pervasive polysynthetic twinning, defining høgtuvaite as a mineral distinct from rhönite was justified by the vector analysis method, whereby høgtuvaite is related to rhönite by the vector  $BeSiAl_2$  (Burt 1994). To date, høgtuvaite has only been reported from the Høgtuva area. However, another aenigmatite-group mineral, "makarochkinite", was described from a granite pegmatite in the Ilmeny Natural Reserve, south Urals, Russia (Polyakov et al. 1986). Grauch et al. (1994) equated it with høgtuvaite, but "makarochkinite" is untwinned and its crystal structure could be refined (Yakubovich et al. 1990; Barbier et al. 2001 and in preparation). Because no proposal for "makarochkinite" had been submitted to the IMA Commission on New Minerals and Mineral Names, it now must be demonstrated that "makarochkinite" is distinct from høgtuvaite in order for it to qualify for species status (see Hawthorne and Huminicki, this volume).

Høgtuvaite forms prismatic crystals up to 4 cm long and 6 mm across, and tends to be porphyroblastic (Grauch et al. 1994). It is nearly opaque, and its strong brown to green pleochroism was detectable only in ultra-thin sections <10- $\mu$ m thick. Refractive indices had to be estimated from reflected light. The difference between calculated and measured density was attributed to inclusions and chemical heterogeneity. "Makarochkinite" forms masses 5-50 mm across. Optically, it is weakly pleochroic, shows anomalous interference colors and does not extinguish;  $\gamma = 1.860$ ,  $\alpha = 1.799$  (thickness of studied fragments not specified, Polyakov et al. 1986).

Burt (1994) proposed  $Ca_2(Fe^{2+}_5Ti)(Si_5Be)O_{20}$  as the ideal formula for end-member høgtuvaite, whereas the analyses reported by Grauch et al. (1994) are closer to  $(Ca_{1.8}Na_{0.2})(Fe^{2+}_{3.55}Fe^{3+}_{2.2}Ti_{0.25})(Si_{4.5}BeAl_{0.5})O_{20}$ . Høgtuvaite varies somewhat in BeO (2.47-2.75 wt %),  $Na_2O$ , and  $TiO_2$  contents. Høgtuvaite is enriched in a large number of trace elements, e.g., B (95 ppm), Y (1250 ppm), Nb (1110 ppm), REE (e.g., Ce 350 ppm), Th (570 ppm) and U (205 ppm).

Electron microprobe analysis of "makarochkinite" together with a crystal structure refinement gave



(Barbier et al. 2001 and in preparation), which compares favorably to the wet chemical analysis reported by Polyakov et al. (1986). "Makarochkinite" contains more divalent and high-valence cations (Ti, Nb) and less  $\text{Fe}^{3+}$  and Na than høgтуvaite, but its status as a distinct species would depend on whether one M site is dominated by Ti (see Hawthorne and Huminicki, this volume). Available crystallographic data (Yakubovich et al. 1990; Barbier et al. 2001 and in preparation) do not provide convincing evidence for such dominance.

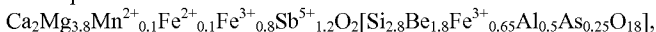
Høgтуvaite is found in the distinctive Bordvedåga mineralized quartzofeldspathic gneiss and associated pegmatites of Early Proterozoic age in the Høgтуva window, Norway (Lindahl and Grauch 1988; Grauch et al. 1994). These rocks were metamorphosed to at least lower-amphibolite-facies grade by the Caledonian event, and the pegmatites have a "metamorphic origin". Precursors to the høgтуvaite-bearing rocks could have been a stratabound beryllium deposit hosted by a highly evolved igneous suite. Associated minerals the gneisses and pegmatites include quartz, microcline, albite, biotite, epidote, magnetite, fluorite, zircon, allanite and other REE minerals, and calcic amphibole with overgrowths of sodic amphibole. The most important associated Be mineral is phenakite; gadolinite, danalite and genthelvite are minor. The gneisses are unusually enriched in trace elements such as Zr, Y, Nb, Th, U; some layers contain 0.19–0.42% Be, an enrichment that could be pre-metamorphic. In contrast to the highly aluminous rocks containing surinamite, sapphirine and khmaralite, høgтуvaite-bearing rocks have a slightly alkaline character.

"Makarochkinite" is found in a granite pegmatite; associated minerals include helvite, gadolinite and phenakite, as well as samarskite-(Y), columbite and allanite (Polyakov et al. 1986), i.e., an assemblage virtually identical to that in the Bordvedåga gneiss.

**Welshite.** Welshite,  $\text{Ca}_2\text{Mg}_{3.8}\text{Mn}^{2+}_{0.6}\text{Fe}^{2+}_{0.1}\text{Sb}^{5+}_{1.5}\text{O}_2[\text{Si}_{2.8}\text{Be}_{1.7}\text{Fe}^{3+}_{0.65}\text{Al}_{0.7}\text{As}_{0.17}\text{O}_{18}]$ , was originally described from Långban, Sweden, the only known locality, where it occurs in dolomite filling fractures in hematite ore or in calcite veinlets cutting hematite ore (Moore 1967 1971 1978; Nysten et al. 1999; Grew et al. 2001a). Associated minerals include arsenates (e.g., adelite, tilasite, manganese-hörnesite),  $\text{Sb}^{5+}$  oxides (e.g., roméite) and silicates, serpentine, and barite. It is not associated with any Be mineral other than rare swedenborgite. Moore (1971) included welshite among the Magnusson's (1930) period C or "vug minerals," for which Grew et al. (1994b), citing circumstantial evidence, inferred temperatures in the range of 500–600°C and P as low as 2 kbar.

Moore (1978) described welshite as being deep reddish-brown to reddish black; in transmitted light, brownish-orange and not discernibly pleochroic with low birefringence and high refringence ( $\alpha = 1.81, \gamma = 1.83$ ), whereas optical absorption spectra are consistent with weak pleochroism, absorption  $\alpha \approx \gamma < \beta$  (Grew et al. 2001a).

Like høgтуvaite, welshite is polysynthetically twinned, foiling attempts to refine of its crystal structure, and thus its chemical composition has been difficult to characterize. By analogy with the aenigmatite group, Moore (1978) proposed the end-member formula  $\text{Ca}_2\text{Mg}_4\text{Fe}^{3+}\text{Sb}^{5+}\text{O}_2[\text{Si}_4\text{Be}_2\text{O}_{18}]$ , which is a reasonable simplification of his empirical formula,  $\text{Ca}_{2.35}\text{Mg}_{3.53}\text{Mn}_{0.13}\text{Fe}^{3+}_{1.06}\text{Sb}_{1.42}\text{As}_{0.29}\text{Al}_{0.38}\text{Si}_{3.03}\text{Be}_{1.49}\text{O}_{20}$ , based on an electron microprobe analysis (plus a BeO determination by an unspecified wet chemical method) totaling only 93.7 wt %. New microprobe data, in conjunction with Mössbauer spectroscopy, optical absorption spectroscopy and ion microprobe data, gave reasonable analytical totals and the formula cited above for one sample (Grew et al. 2001a). A second sample has the formula

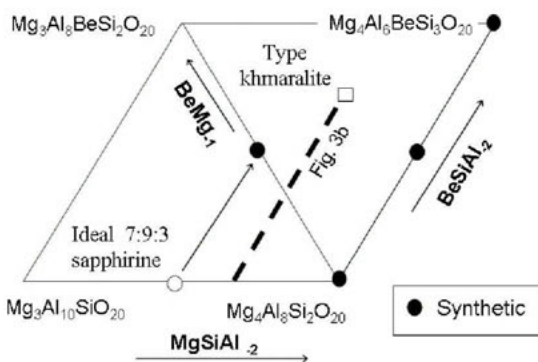


which is related to the first by the substitution of approximately  $0.6^{[6 \text{ and } 4]}(\text{Fe,Al})^{3+}$  for  $0.4^{[6]}(\text{Mg,Mn,Fe})^{2+} + 0.2^{[6]\text{Sb},[4]\text{As}}^{5+}$ , i.e.,  $3^{[\text{vi},\text{iv}]}M^{3+} = 2^{[\text{vi}]}M^{2+} + ^{[\text{vi},\text{iv}]}M^{5+}$  (cf. Kunzmann 1999).

**Khmaralite and Be-bearing sapphire.** Wilson and Hudson (1967) were the first to report significant beryllium in sapphire,  $\sim(\text{Mg,Fe})_{3.5}(\text{Al,Fe})_9\text{Si}_{1.5}\text{O}_{20}$ : 0.65 wt % BeO in a sample from the Musgrave Ranges, Australia, and Povondra and Langer (1971b) synthesized sapphire suspected to contain Be because of its smaller cell volume. Recognition of a “sapphire” containing 2.5 wt % BeO from Khmara Bay (part of Casey Bay), Antarctica (Grew 1981, 1998) as the new mineral khmaralite (Barbier et al. 1999) had to wait for single-crystal X-ray technology capable of measuring the very faint superstructure reflections first seen by Christy (1988) in electron diffraction diagrams. Grew et al. (2000) reported that 0.5 Be/20 O appears to be the minimum needed for the superstructure reflections to appear.

The presence of these superstructure reflections is the critical feature distinguishing khmaralite from sapphire. Christy et al. (2002) found no superstructure reflections in TEM images of the synthetic sapphire with 1 Be/20 O (vs. 0.78 Be/20 O in type khmaralite, Fig. 3a). It is likely that ordering of Be into the most polymerized tetrahedral sites is as extensive in synthetic beryllian sapphire as it is in khmaralite, but unlike khmaralite, there is no regular alternation of different ordering schemes from one chain segment to the next. The regular alternation of ordering schemes, which results in the doubling of the unit cell (Fig. 2), is undoubtedly due to annealing, either during a superimposed metamorphic event or during cooling following metamorphism.

#### Sapphire Compositions in $(\text{Mg,Fe})\text{O}-\text{BeO}-\text{Al}_2\text{O}_3-\text{SiO}_2$

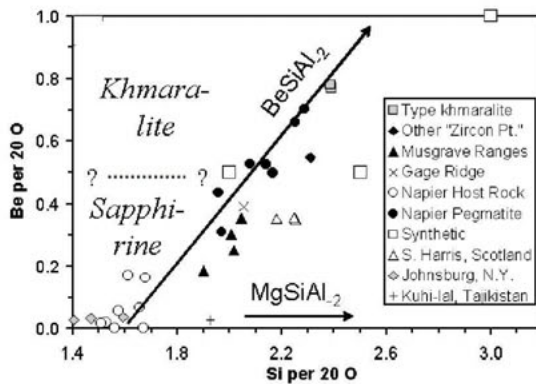


**Figure 3.** (a) A planar section of compositional space in the  $\text{MgO}-\text{BeO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  system showing the relative positions of the beryllian sapphirines synthesized by Hölscher (1987) and khmaralite with  $\text{Fe}^{2+}$  combined with Mg and  $\text{Fe}^{3+}$  combined with Al (modified from Christy et al. 2002).

Khmaralite forms masses 3–5 cm across that are deeply embayed by minerals formed from its breakdown. It is indistinguishable from iron-rich sapphire both in hand specimen and thin section, i.e., it is nearly opaque in large pieces, blue when powdered and moderately pleochroic in shades of blue and green.

Khmaralite composition is equivalent to that of a sapphire of composition  $\sim(\text{Mg,Fe})_{3.6}(\text{Al,Fe})_{8.8}\text{Si}_{1.6}\text{O}_{20}$  to which 0.78BeSiAl<sub>2</sub> has been added (Grew et al. 2000;

Barbier et al. 2002). Ion probe (SIMS) analyses of Be-bearing sapphirine (Be > 0.1 per 20 O or about 0.3 wt % BeO) and khmaralite from several localities and different rock types suggest a continuum of compositions along a pseudobinary between  $\sim(\text{Mg,Fe}^{2+})_{3,6}(\text{Al,Fe}^{3+})_{8,8}\text{Si}_{1,6}\text{O}_{20}$  and  $\sim(\text{Mg,Fe}^{2+})_{3,6}(\text{Al,Fe}^{3+})_{7,2}\text{Be}_{0,8}\text{Si}_{2,4}\text{O}_{20}$  with no discernible break between the fields of sapphirine and khmaralite (Fig. 3b). The close approach to this pseudobinary is surprising given that sapphirine-khmaralite from both silica-saturated (Napier Complex) and silica-undersaturated assemblages (Musgrave Ranges) are included. However, several compositions of sapphirine suspected to contain about 0.35Be per 20 O (but not analyzed for Be) from silica-saturated rocks from S. Harris, Scotland, do not plot close to this pseudobinary (Fig. 3b); they are richer in the  $\text{MgSiAl}_2$  component (Baba et al. 2000). Compositions of synthetic beryllian sapphirine also vary in  $\text{MgSiAl}_2$  (Fig. 3a).



**Figure 3.** (b) Composition of natural and synthetic sapphirine for which ion microprobe Be measurements are available except South Harris, for which Be content was estimated, and synthetic, for which Be content was assumed to be the same as in the starting gel (extensively modified from Grew et al. 2000, their Fig. 12). The dashed line marking a tentative boundary between khmaralite and sapphirine in natural material is based on the appearance of superstructure reflections in a natural sample containing 0.52 Be/20 O (Grew et al. 2000). Type khmaralite, other "Zircon Point", Gage Ridge, Napier Host Rock and Napier Pegmatite all refer to samples from the Napier Complex, Enderby Land, East Antarctica. Sources of data are given in Table 3; also Baba et al. (2000) for South Harris, Scotland.

Sapphirine is a sink for beryllium. Its Be content can be substantial even in rocks with a modest bulk Be content if sapphirine is present in trace amounts; e.g., its Be content ranges from 60 to 1000 times whole-rock Be content in Napier Complex metamorphic rocks (Table 3). Only kornerupine-prismatine and cordierite incorporate a comparable amount of Be (see below).

Sapphirine containing more than 1Be per 20 O could not be synthesized (Hölscher 1987; Christy et al. 2002), and khmaralite in Be-rich assemblages contains even less (0.78 Be/20 O), consistent with the constraint on Be incorporation discussed above under aenigmatite-group minerals.

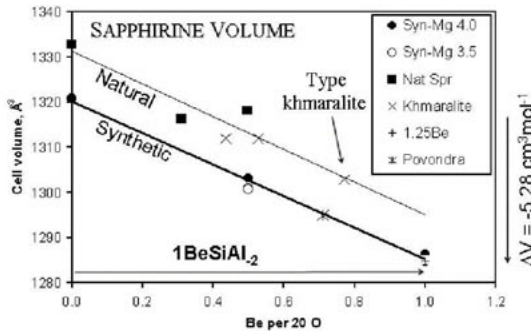
In both synthetic Fe-free sapphirine, and in natural Fe-rich sapphirine-khmaralite of comparable total Fe content, cell volume decreases 2.7 % from Be = 0 to Be = 1 per 20 O, i.e., the component  $\text{BeSiAl}_2$  has a molar volume of  $-5.28 \text{ cm}^3 \text{ mol}^{-1}$  (Fig. 4).

Table 3. Beryllium content of sapphirine and khmaralite.

<i>Rock type, grade</i>	<i>Host rock Be, ppm (n)</i>	<i>Spr. Khm Be*(n) ppm Be</i>	<i>Source</i>	
Napier Complex, East Antarctica.	Beryllium pegmatites, Khmara Bay	—	1.07-2.77 (6) wt % BeO Barbier et al. (1999); Grew et al. (2000); Grew & Yates (unpubl. data); Barbier et al. (2002)	
	Quartz granulite hosting pegmatite, "Christmas Point"	1.4-7.1 (5)	790-2200 (5) Grew et al. (2000, 2001b and unpubl. data)	
	Quartz granulite hosting pegmatite, Mt. Pardoe	3.7	240	Grew et al. (2000)
		—	30	
	Quartzofeldspathic granulite, Gage Ridge	5	1.34 wt % BeO	Grew (1981, 1998), Grew et al. (2000)
Quartz-bearing granulite, Mt. Riser-Larsen	—	~0.1 wt % BeO	Christy (1989)	
"Musgravite" nodule, Musgrave Ranges, Australia (Fig. 6)	—	0.04-2.10 (8) wt % BeO	Hudson (1968); Wilson & Hudson (1967); Grew et al. (2000); Grew (unpubl. data)	
Serendibite-bearing metasomatic zones, Johnsbury, NY, USA	—	330-430 (3)	Grew et al. (1991a, 1992)	
Ultramagessian metamorphic rocks, SW Pamirs, Tajikistan	—	0-300 (5)	Grew et al. (1994a, 1998b)	
Komerupine-bearing rocks, various localities	—	0-100 (14)	Grew et al. (1990, 1991b); Grew (1986)	
Sapphirine-enstatite-hornblende rock, Mautia Hill, Tanzania	—	22	McKie (1963)	
Sapphirine-cordierite-biotite-garnet-hypersthene rock, Val Codera, Italy	—	3	Barker (1964)	

Note: n – number of samples. \* 0.1 wt % BeO  $\equiv$  360 ppm Be



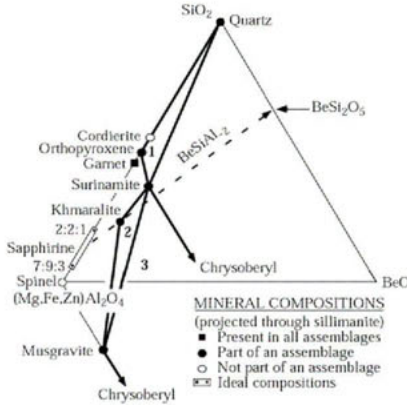


**Figure 4.** Effect of beryllium on sapphire unit-cell volume for synthetic sapphire (Hölscher 1987; Christy et al. 2002) and for natural sapphire and khmaralite containing 8–10 wt % Fe (Sahama et al. 1974; Barbier et al. 1999; Grew et al. 2000). The lines are least-square fits to the natural data (filled squares and “X’s”) and the synthetics containing 4 Mg/20 O (filled circles).  $\Delta V$  applies to the synthetic sapphire (Christy et al. 2002). The Be contents of sapphire synthesized by Povondra and Langer (1971b) and by Hölscher (1987) from a gel containing 1.25 Be/20 O were calculated by Christy et al. (2002) from cell volume and the least-square fit for the synthetics.

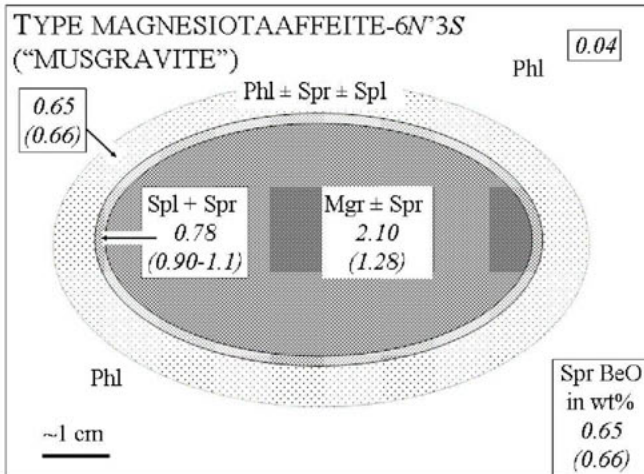
Khmaralite and beryllian sapphire ( $\geq 1$  wt % BeO) has been reported to date from two pegmatites metamorphosed under granulite-facies conditions in the Archean Napier Complex (Table 3). In the original description of khmaralite I interpreted it to be a metamorphic mineral that crystallized in the “Zircon Point” assemblage khmaralite + sillimanite + surinamite + magnesiotaaffeite-6N<sup>3</sup>S (“musgravite”) + garnet + biotite + rutile at  $T \geq 820^\circ\text{C}$ ,  $P \geq 10$  kbar (Barbier et al. 1999), conditions sufficient to stabilize sillimanite + orthopyroxene (Grew 1998). However, textural relations of coarse grained khmaralite and beryllian sapphire from “Christmas Point” suggest that these minerals crystallized from a pegmatitic magma with sillimanite in prisms up to 10 cm long and 4 cm across, quartz, alkali feldspar, biotite and wagnerite (Grew et al. 2000). The pegmatites were emplaced at the peak of metamorphism possibly at 1000–1100°C at 9–11 kbar. During subsequent metamorphism, khmaralite and beryllian sapphire reacted with quartz to form sillimanite, surinamite and garnet, or where isolated from quartz, broke down to chrysoberyl- or magnesiotaaffeite-6N<sup>3</sup>S-bearing assemblages. Nonetheless, sapphire-khmaralite could have equilibrated with its breakdown products to form stable metamorphic assemblages, some of which are shown in Figure 5. An alternative scenario is that these minerals formed by reaction of sapphire and khmaralite with the pegmatitic melt prior to crystallization of quartz (Grew et al. 2001b).

Other sapphire relatively rich in Be (Fig. 3b) has been reported from quartz-bearing rocks in the Napier Complex, including host rocks to the beryllium pegmatites in Khmara Bay, and from quartz free rocks in the Musgrave Ranges, Australia (Table 3; Fig. 6). Napier Complex metamorphic sapphire was stable with quartz at ultrahigh temperatures (e.g., Sheraton et al. 1987b), i.e., in the range 1000–1100°C at pressures from 7 to 11 kbar according to Harley (1998). The Musgrave Ranges sapphire is associated with a magnesiotaaffeite-6N<sup>3</sup>S (“musgravite”) nodule enclosed in phlogopite replacing pyroxenite (Fig. 6). Sapphire BeO content decreases progressively outward from the nodule to the phlogopite enclosing it. Wilson and Hudson (1967) suggested that beryllium may have been introduced metasomatically with K, F, and P in the contact

aureole of the nearby Emabella ferrohypersthene-adamellite; temperatures of crystallization could have been ca. 700°C, the value estimated for a similar complex about 100 km west of the sapphirine locality (Maboko et al. 1989 1991; cf. oxygen isotope temperature of 550°C reported by Wilson et al. 1970 for the sapphirine locality).



**Figure 5.** Possible assemblages of Be minerals (all with sillimanite) in the system  $(\text{Mg,Fe,Zn})\text{Al}_2\text{O}_4\text{-BeO-SiO}_2$  in Be-bearing assemblages, e.g., pegmatites (no. 3, Grew 1981; no. 2 without garnet, Grew et al. 2000) and quartzofeldspathic gneiss (no. 1 without garnet, Baba et al. 2000). The dashed line marked  $\text{BeSiAl}_2$  is one of an array of lines converging on the point  $\text{BeSi}_2\text{O}_5$ . Copied from Barbier et al. (1999, Fig. 1).



**Figure 6.** Schematic representation of a 10×9×5 cm nodule of magnesiotaaffeite-6N<sup>3</sup>S (Mgr) described by Wilson and Hudson (1967), Hudson et al. (1967) and Hudson (1968) from the Musgrave Ranges, Australia. The spinel (Spl)-sapphirine (Spr) rim around magnesiotaaffeite-6N<sup>3</sup>S is mostly 0.5–2 mm thick. Sapphirine BeO contents were measured both spectrographically (Wilson and Hudson 1967; Hudson 1968) and by ion microprobe (values in parentheses, Grew et al. 2000 on Hudson’s sample 14820). The 0.04 wt % BeO value was obtained on sapphirine 20 cm from the magnesiotaaffeite-6N<sup>3</sup>S nodule (Hudson 1968).

Two studies reported experimental syntheses of beryllian sapphirine. Povondra and Langer (1971b) reported beryllian sapphirine in run products from glasses on the join  $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}\text{--NaMg}_2\text{Al}_3\text{BeSi}_5\text{O}_{18}$  at  $T \geq 900^\circ\text{C}$  for  $P$  up to 3 kbar. Hölscher (1987) synthesized sapphirine from gels having several starting compositions in a reconnaissance study at  $T$  from 700 to  $1350^\circ\text{C}$  and  $P$  from 1–13 kbar, which is being written up by Christy et al. (2002). Hölscher's (1987) syntheses lie within the stability field of sapphirine in the Be-free  $\text{MgO--Al}_2\text{O}_3\text{--SiO}_2\text{--H}_2\text{O}$  system (Seifert 1974; Ackermann et al. 1975) except for one synthesis at  $750^\circ\text{C}$  and 13 kbar, about  $30^\circ\text{C}$  below the minimum  $T$  at 13 kbar given by Ackermann et al. (1975). Determining whether Be expands the stability range of sapphirine would require systematic studies involving reversed experiments of sapphirine breakdown to surinamite and cordierite.

**Surinamite.** Surinamite,  $(\text{Mg}, \text{Fe}^{2+})_3(\text{Al}, \text{Fe}^{3+})_3\text{O}(\text{AlBeSi}_3\text{O}_{15})$ , was first described in a granulite-facies metapelite from the Bakhuis Mountains, Surinam, as a ferromagnesian aluminosilicate that closely resembled sapphirine in thin section and in crystal structure (de Roever et al. 1976; Moore 1976). Grew (1981) and de Roever et al. (1981) independently discovered that Be was a major constituent, and de Roever et al. (1981) demonstrated that Be was essential for synthesizing an Fe-bearing surinamite at 20 kbar and  $800^\circ\text{C}$ . Moore and Araki (1983) successfully refined the crystal structure and confirmed the stoichiometry in the formula proposed by de Roever et al. (1981),  $(\text{Mg}, \text{Fe}^{2+})_3(\text{Al}, \text{Fe}^{3+})_3(\text{AlBeSi}_3\text{O}_{16})$ . Hölscher et al. (1986) made a comprehensive study of surinamite stability in the  $\text{MgO--Al}_2\text{O}_3\text{--BeO--SiO}_2\text{--H}_2\text{O}$  system and showed that it formed at high temperature ( $\geq 650^\circ\text{C}$ ) and relatively high pressure ( $\sim 4$  kbar). Barbier (1996 1998) has synthesized several Ga and Ge, but Be-free, analogues of surinamite and refined their crystal structures.

Surinamite is generally too fine-grained to be seen in hand specimen. The cm-sized surinamite-rich aggregates in beryllium pegmatites from Casey Bay in Antarctica are exceptional; these are nearly black, but show blue in powder, which distinguishes them from other dark ferromagnesian silicates other than sapphirine. In thin section surinamite resembles iron-bearing sapphirine in its platy habit, high refractive indices, low birefringence, strong dispersion, and strong color. It differs from sapphirine-khmaralite (e.g., Grew 1998, Fig. 3, where khmaralite is labeled as sapphirine) in its distinctive pleochroism, which is violet parallel to  $Y$  and ranges from greenish blue to colorless or very light greenish brown perpendicular to  $Y$  (de Roever et al. 1976; Barbier et al. 2002). The orientation of the indicatrix is  $X \wedge c \approx 20^\circ$ ,  $Y = b$ , and  $Z \wedge a \approx 5^\circ$ , but the axes of the indicatrix do not correspond to those of the absorption surface in (010).

The most important variable in natural surinamite is Fe, which ranges from 5.25 to 14.17 wt % as FeO (e.g., Baba et al. 2000; Grew et al. 2000). A room-temperature Mössbauer spectrum and crystal structure refinement gave  $\text{Fe}^{3+}/\Sigma\text{Fe} = 0.31, 0.35$ , respectively, for two surinamite specimens from Khmara Bay for which 0.30, 0.35, respectively, were calculated by assuming 16 O and 11 cations (Barbier et al. 2002). These results indicate that calculating  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio from stoichiometry is a servicable approximation. Surinamite  $\text{Fe}^{3+}/\Sigma\text{Fe}$  increases with increasing  $\text{Fe}^{3+}$  content in associated sillimanite and reaches 0.54 in samples from "Christmas Point" (Khmara Bay), where associated oxide is ilmeneo-hematite and magnetite (Grew et al. 2000).

A new crystal-structure refinement of a Khmara Bay surinamite (Barbier et al. 2002) gave exactly 1 Be per 16 O (vs. 0.945 reported by Moore and Araki 1983). Within analytical uncertainty, ion microprobe measurements are consistent with the ideal 1Be per formula in other Khmara Bay surinamite (Grew et al. 2000), but only 0.766–0.824 Be was found in South Harris surinamite. Baba et al. (2000) attributed this deficiency in Be to the coupled substitution of  $^{14}\text{Al}$  for  $^{14}\text{Be}$  and  $^{16}\text{Mg}$  for  $^{16}\text{Al}$ , summing to  $\text{MgBe}_{-1}$ . No

other surinamite has been quantitatively analyzed for Be.

Other constituents reported in surinamite include MnO ( $\leq 2$  wt %), P<sub>2</sub>O<sub>5</sub> ( $\leq 0.33$  wt %), K<sub>2</sub>O, CaO and ZnO ( $\leq 0.2$  wt %), Na<sub>2</sub>O ( $< 0.1$  wt %), and Cu, Pb, Sn, and V (0.01-0.05 wt %)(de Roever et al. 1976, Hålenius 1980; Grew 1981; Grew et al. 2000). Ion microprobe boron contents range from 3-12 ppm B in surinamite from quartzofeldspathic gneiss (Baba et al. 2000) to 0.09-0.15 wt % B<sub>2</sub>O<sub>3</sub> in surinamite from metamorphosed pegmatite (Grew et al. 2000).

The tetrahedral sites of Khmara Bay surinamite are highly ordered, and the octahedral sites show no mixing between divalent and trivalent cations, although there is Mg-Fe<sup>2+</sup> mixing on some sites and Al-Fe<sup>3+</sup> mixing on others (Moore and Araki 1983; Barbier et al. 2002). The greater cation order in surinamite compared to sapphirine is reflected in the more restricted compositional variation in terms of the Tschermarks substitution, MgSiAl<sub>2</sub>, e.g., 2.89-3.07 Si per 16 O (Baba et al. 2000; Grew et al. 2000) vs. 1.13-1.57 Si per 16 O for Be-free sapphirine (Christy 1989).

Surinamite preferentially fractionates Mg relative to Fe<sup>2+</sup> compared to associated minerals except cordierite: X(Mg) increases Grt  $\ll$  Spr and khmaralite  $<$  surinamite  $\leq$  Crd in samples from Casey Bay and South Harris (Baba et al. 2000; Grew et al. 2000); some ambiguity results from the large error in estimating Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio in surinamite from stoichiometry.

Surinamite is exclusively a metamorphic mineral reported only from metapelites and metapegmatites metamorphosed under upper-amphibolite or granulite-facies conditions (Table 4). Ramesh Kumar et al. (1995) reported surinamite rich in B and Ga from an eighth locality, the Eastern Ghats belt, India, but this identification could not be confirmed; it appears that hypersthene was misidentified as surinamite (Grew et al. 2001c). Surinamite is invariably associated with Al-rich minerals, e.g., sillimanite, kyanite, and cordierite, but never with primary muscovite. Almost all assemblages are quartz saturated, but surinamite also occurs with corundum in isolation from quartz at "Christmas Point" (Grew et al. 2000). Al<sub>2</sub>SiO<sub>5</sub> + K-feldspar assemblages are characteristic of most surinamite-bearing rocks. Ferromagnesian minerals associated with surinamite typically have relatively high X(Mg), e.g., garnet (Fig. 7). In the MgO-BeO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> model system, surinamite is equivalent to pyrope + chrysoberyl: Mg<sub>3</sub>Al<sub>4</sub>BeSi<sub>3</sub>O<sub>16</sub> = Mg<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> + Al<sub>2</sub>BeO<sub>4</sub>, and the assemblage Grt + Cb + Sur thus theoretically defines the limit of Fe<sup>2+</sup> substitution for Mg in surinamite at a given pressure and temperature. Observed compositions for Antarctic garnet and surinamite are not entirely consistent with this relationship: several garnet-surinamite pairs in assemblages lacking chrysoberyl are more ferroan than the pair associated with chrysoberyl (Fig. 7).

The temperature estimated for surinamite formation mostly exceeds 800°C, although temperature for the upper-amphibolite-facies Chimwala, Zambia occurrence was more likely in the 600-700°C range. Estimated pressure exceeds 8 kbar. These conditions lie within the stability field Hölscher et al. (1986) determined for the Mg-end member, T  $\geq 650^\circ\text{C}$ , P  $\geq 4$  kbar (see also Franz and Morteani, this volume). Table 4 summarizes reactions proposed for surinamite formation from Be-bearing cordierite, generally due to an increase in pressure, and from Be-bearing sapphirine-khmaralite due a nearly isobaric temperature decrease. Theoretically, surinamite is expected to break down at high pressure to pyrope + chrysoberyl, which is denser, but Hölscher et al. (1986) encountered unidentified phases and anomalies in the XRD pattern of chrysoberyl formed from surinamite breakdown at 45 kbar.

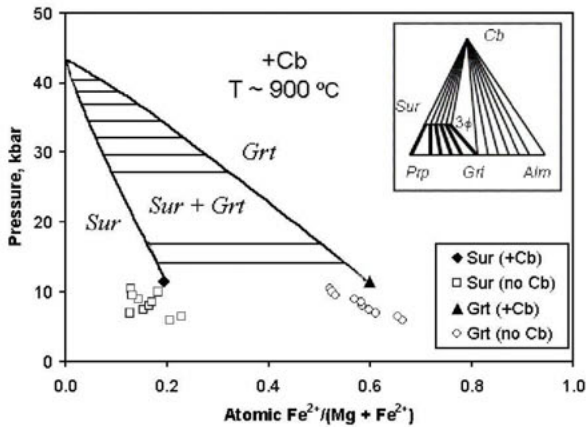
Hölscher et al. (1986) noted that most pegmatites, if hydrous, would crystallize at too low a temperature for surinamite; in addition, their bulk X(Mg) is too low for its

Table 4. Surinamite occurrences.

Locality	Host rock	Associated minerals	T, P conditions
		Reactions for surinamite formation	
1. Bakhuis Mtns., Surinam	Mylonitic mesoperthite gneiss	Qtz, Kfs, Pl, Bt, Sil, Ky, Spl	Granulite facies
		$Crd \rightarrow Sur + Al_2SiO_5 + Qtz$	
2. Strangways Ranges, central Australia	Aluminous granulite	Included in Crd. Also Qtz, Spl, Spr, Phl, Opx, Sil, opaque oxide	$T < 900-950^\circ C,$ $P = 8-9$ kbar
3. "Christmas Point", Casey Bay, Antarctica	Meta- pegmatite	Qtz, Kfs, Sil, Spr, khmaralite, wagnerite, Grt, Opx, Bt, Hem, Mgt; Spl, Mgr, Crm; 2 <sup>nd</sup> Crd, And, Ky	$T = 800-$ $900^\circ C, P = 8-9$ kbar
		$Khm-Spr + Qtz \rightarrow Sur + Grt + Sil$ and $Khm-Spr \rightarrow Mgr + Sil + Sur$	
4. "Zircon Point", Casey Bay, Antarctica	Meta- pegmatite	Qtz, Kfs, Pl, Sil, Ky, Khm, Mgr, dumortierite, Cb, Grt, Bt, Rt	
5. Mount Pardoe, Amundsen Bay, Antarctica	Meta- pegmatite	Enclosed in 2 <sup>nd</sup> Crd with Sil, Bt. Also Qtz, Kfs, wagnerite, Grt, Opx, And, Ky	
6. Chimwala area, Zambia	Cordierite granulite	Qtz, Kfs, Pl, Bt, Ky, Grt, Mgt. Crd and a Sil-like mineral are completely replaced	Amphibolite, transitional to granulite, facies
		$Crd + Kfs + H_2O \rightarrow Sur + Qtz + Ky$ $+ Bt + Ab$	
7. South Harris, Scotland, U.K.	Gneiss	Qtz, Kfs, Spr, Opx, Ky, Sil, 2 <sup>nd</sup> Crd	$T = 850-900^\circ C,$ $P > 12$ kbar: M2 stage
		First $BeSiAl_2$ (in Spr) + 3 Sil + 3 Opx $\rightarrow Sur + 4 Qtz$ , then $Mg_{7.4}Al_{15.7}Be_{0.7}Si_{4.2}O_{40}$ (Be Spr) + 9.65 $Qtz \rightarrow 0.7 Sur + 5.3 Opx + 6.45 Ky$ , which is (Crd) in Figure 8	

Note: Sources of information on surinamite localities: 1-de Roever (1973), de Roever et al. (1976). 2-Woodford and Wilson (1976), Goscombe (1992). 3, 4, 5-Grew (1981, 1998), Grew et al. (2000). 6-Vavrdka and Vrána (1972), de Roever and Vrána (1985). 7- Baba (1998a,b, 1999), Baba et al. (2000). Table format modified from Baba et al. (2000).

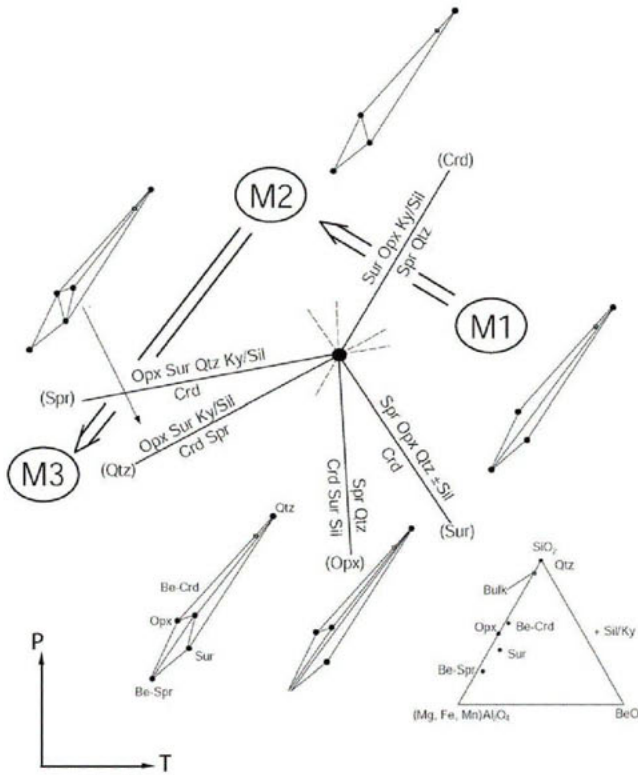
stability. Thus, the presence of magmatic surinamite in a granite pegmatite is unlikely, and none has been reported to date. The garnet + chrysoberyl assemblage apparently takes the place of surinamite in most pegmatites, and indeed almandine-spessartine garnet and chrysoberyl are often reported from the same pegmatite (e.g., Okrusch 1971, Franz and Morteani 1984; Soman and Druzhinin 1987; Černý et al. 1992; Černý, this volume). Franz and Morteani (1984) presented evidence that many of the chrysoberyl-bearing pegmatites have been metamorphosed after emplacement. However, it is less obvious that garnet and chrysoberyl coexisted in all cases. A clear cut example of a metamorphic garnet + chrysoberyl assemblage was illustrated by Černý et al. (1992) from a muscovite pegmatite at Maršíkov, Czech Republic, which was metamorphosed at 600°C, 4-6 kbar ( $P_{fluid} < P_{total}$ ), i.e., conditions only slightly outside the surinamite stability field reported



**Figure 7.** Schematic and hypothetical pressure-composition section for the system surinamite- $\text{Fe}^{2+}$  analogue of surinamite modified from Hölscher et al. (1986, Fig. 13a) with compositions of a surinamite-garnet pair (+ chrysoberyl) from “Zircon Point”, Khmara Bay, Antarctica (Grew 1981) and of 8 surinamite-garnet pairs (no chrysoberyl) from “Christmas Point”, Khmara Bay and from Mt. Pardoe, Amundsen Bay, Antarctica (Grew 1981; Grew et al. 2000 and unpublished data). All nine pairs are presumed to have formed at the same pressure, but are plotted at slightly different pressures to show regularity of Fe-Mg distribution; scatter in surinamite data is due to uncertainties in calculating  $\text{Fe}^{2+}$  from stoichiometry. Inset shows sketch of the ternary system almandine (Alm)-pyrope (Prp)-chrysoberyl (Cb). Three-phase field Grt + Sur + Cb (3 $\phi$ ) corresponds to filled symbols and the 2-phase field Grt + Sur (heavy tielines) corresponds to unfilled symbols.

by Hölscher et al. (1986). Given the marked enrichment of  $\text{Fe}^{2+}$  and Mn in garnet, the Maršikov assemblage is not a compositional equivalent to surinamite, and thus the Maršikov assemblage is not a definitive test of the stability field proposed by Hölscher et al. (1986). A closer alternative to surinamite in quartz- and sillimanite-bearing pegmatites would be garnet + cordierite + chrysoberyl, but this assemblage has not yet been reported.

Most high-temperature metapelites and many peraluminous meta-pegmatites do not contain chrysoberyl. Thus, a petrogenetic grid restricted to assemblages with chrysoberyl (Hölscher et al. 1986, their Fig. 11) has limited applicability to Be-bearing assemblages in metamorphic rocks. Instead, compositional relationships can be simplified by projection through sillimanite (Fig. 5). A P-T diagram (Fig. 8) based on this projection is constructed so that surinamite is a high-pressure mineral relative to sapphirine-khmaralite and cordierite consistent with the formation of surinamite in nature (Table 4) and experiment (Hölscher et al. 1986). For example, Baba et al. (2000) reported surinamite formation from beryllian sapphirine during a pressure increase as temperature decreased between the first and second metamorphic events at South Harris, Scotland (M1  $\rightarrow$  M2, Fig. 8) and its breakdown to cordierite as pressure decreased following the second event (M2  $\rightarrow$  M3, Fig. 8). These observations are consistent with calculations involving molar volumes of surinamite, beryllian sapphirine and anhydrous beryllian cordierite (Christy and Grew in preparation). Because natural Na-Be-bearing cordierite is commonly hydrous, the breakdown of cordierite to surinamite would be a dehydration, and the reactions labeled (Qtz) and (Spr) in Figure 8 could have negative slopes.



**Figure 8.** Pressure-temperature diagram based on a Schreinemaker net for phase relations in the system  $\text{MgAl}_2\text{O}_4\text{-BeO-SiO}_2$  (cf. Fig. 5) for assemblages containing  $\text{Al}_2\text{SiO}_5$ . Reactions are labeled by the non-participating phase in parenthesis. Arrow indicates  $P$ - $T$  path inferred for the surinamite-bearing rock at South Harris, Scotland (see text). Slopes of the Qtz-absent and Spr-absent reactions are shown positive as cordierite is presumed to be anhydrous. Copied from Baba et al. (2000, their Fig. 7).

Surinamite is indicative of a distinctive metamorphic environment and history. Surinamite-bearing rocks are typically polymetamorphic; in most cases, there is evidence for pre-existing cordierite or sapphirine enriched in beryllium. Mylonitic textures are characteristic of several examples, notably, South Harris and Bakhuis Mountains. In all cases, surinamite formed with an increase in pressure and/or decrease in temperature; no examples are known of surinamite forming as pressure decreased isothermally. Surinamite is not restricted to rocks enriched in Be and scarcity of Be in metamorphic systems is not the only factor controlling surinamite formation. Surinamite formation apparently depends on a mechanism for concentrating disseminated beryllium. This mechanism appears to be formation of a mineral such as cordierite or sapphirine that can scavenge Be from a large mass of rock and becomes the locus of surinamite crystallization during a succeeding metamorphic event. Conditions during this event must be such that Be is not newly dispersed. Low water activities probably restrict its mobility.

**Table 5.** Beryllium content of cordierite and sekaninaite ( $\text{BeO} \leq 0.55 \text{ wt\%}$ , i.e.,  $\text{Be} \leq 2000 \text{ ppm}$ ).

Rock type		Host rock Be, ppm (n)	Crd Be ppm (n)	Source
<b>METAMORPHIC</b>				
Miscellaneous metasediments		—	0-140 (6)	Ginzburg & Stavrov (1961)
Miscellaneous gneiss		—	10-30 (6)	Griffitts & Cooley (1961)
Migmatite, Bavarian Forest, Germany		—	1-49 (—)	Kalt et al. (1999)
Contact metapelite T = 508 to 762°C, P = 2 kbar, Kos, Greece		—	7-30 (15)	Kalt et al. (1998)
Ladoga complex, NW Russia	Sil + Kfs zone	3.0 (30)	40 (5)	Lebedev & Nagaytsev (1980) <sup>1</sup>
	Hypersthene zone	2.3 (28)	18 (3)	
Rocks with kornepine-prismatine	Ellamankovilpatti, India (granulite facies)	—	20-170 (3)	Grew et al. (1987, 1990)
	Miscellaneous (granulite facies)	—	0-30 (5)	Grew et al. (1990, 1991b)
“Kinzigite” (amphibolite-facies metapelite), Ivrea-Verbano, Italy		1.7	12.3	Bea & Montero (1999); Bea (pers comm. 2001)
Migmatite, Peña Negra Complex, Spain		0.37-8.1	1.9-16.2 (7)	Bea et al. (1994); Bea (pers comm. 2001)
		—	22	Malcherek et al. (2001)
“Cordierite” formed by an anatectic process, El Pílon, Soto, Argentina		—	40-65 (2)	Schreyer et al. (1979)
Sapphirine-cordierite-biotite-garnet-hypersthene rock, Val Codera, Italy		—	5	Barker (1964)
Cordierite-bearing gneiss, Bamble Sector, South Norway		—	<2-257 (20)	Visser et al. (1994)
<b>PEGMATITE, VEIN AND UNSPECIFIED</b>				
Pegmatites, Murzinka, Urals, Russia and Turkestan Mtns., Kazakhstan		—	190-580 (2)	Ginzburg & Stavrov (1961)
Miscellaneous veins and pegmatites (unaltered only)		—	1.5-2000 (6)	Griffitts & Cooley (1961)
Pegmatite, Bjordammen (“Bjordan”), Bamble, Norway		—	430	Newton (1966)
Pegmatitic sekaninaite, Dolní Bory, Czech Republic		—	4-30 (8)	Černý et al. (1997)
		—	0 (2)	Malcherek et al. (2001)
Pegmatite, Sri Lanka		44	290	Grew et al. (1995)
Miscellaneous, possibly vein or pegmatite		—	0-270 (9)	Malcherek et al. (2001)

Note: n – number of samples. <sup>1</sup> Values are averages; individual analyses were not given.



It should not be forgotten that surinamite occurs very sparsely except in the pegmatites at "Christmas Point" and "Zircon Point" and could be easily overlooked because of its close resemblance to sapphirine.

#### **Be-bearing cordierite (Mg > Fe)–sekaninaite (Fe > Mg)**

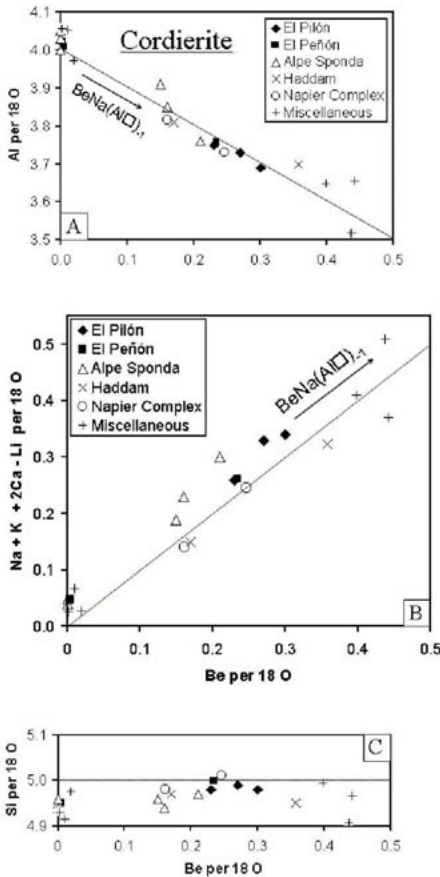
The structural relationship between beryl and cordierite (indialite, the high-temperature hexagonal form of cordierite, is isostructural with beryl) and the frequent presence of cordierite in contact zones and pegmatites prompted Ginzburg and Stavrov (1961) and Griffiths and Cooley (1961) to search cordierite for beryllium. As much as 2000 ppm Be were found in pegmatitic cordierite (Table 5, see also Černý, this volume and London and Evensen, this volume). The structural relationship between cordierite and beryl also led investigators to look for evidence of solid solution between them, both in natural phases and experimentally (e.g., Newton 1966; Borchert et al. 1970; Povondra and Langer 1971a,b; Franz and Morteani, this volume). Several substitutions involving Be, Mg, Al and Si have been proposed for cordierite, notably  $\text{Be} + \text{Si} = 2\text{Al}$  (Schreyer 1964) and  $3\text{Be} + \text{Si} = 2\text{Mg} + 2\text{Al}$ , which relates cordierite and beryl (Newton 1966). Povondra and Langer's (1971a,b) failure to confirm early evidence for extensive solid solution between beryl and cordierite is not surprising. The substitution  $(\text{Be}_3\text{Si})(\text{Al}_2\text{Mg}_2)$  linking cordierite and beryl is equivalent to  $2\text{Al}_2(\text{MgSi})_{-1}$  (Tschermaks) +  $3\text{BeSiAl}_2$ , and the former substitution is virtually unknown in both cordierite and beryl (e.g., Deer et al. 1986; Aurisicchio et al. 1988). Some authors (e.g., Vrána 1979) have suggested solid solution of beryl towards cordierite, but it has not been confirmed by systematic studies (e.g., Aurisicchio et al. 1988; Demina and Mikhaylov 2000; Černý, this volume, p. 405ff.; Franz and Morteani, this volume, p. 551ff.).

Černý and Povondra (1966) concluded that  $\text{Na} + \text{Be} \rightarrow \square + \text{Al}$  is the most important substitution in natural cordierite, and this has been confirmed by crystal structure refinements (e.g., Armbruster 1986) and subsequent analytical studies summarized in Figure 9 in which K and 2Ca are added to Na. Povondra and Langer (1971b) showed experimentally that considerable Be could be incorporated by  $\text{Na} + \text{Be} \rightarrow \square + \text{Al}$  at geologically reasonable temperatures of 700–880°C at  $P_{\text{H}_2\text{O}} = 1\text{--}3$  kbar. Even when corrected for incorporation of Li by the substitution  $(\text{Na,K})\text{Li}(\square\text{Mg})_{-1}$  (e.g., Gordillo et al. 1985), the sum  $(\text{Na} + \text{K} + 2\text{Ca})$  generally exceeds Be, so this sum cannot be used as a proxy to estimate Be + Li content.

It is possible that Schreyer's (1964) proposed substitution  $\text{BeSiAl}_2$  could play a limited role under conditions comparable to those under which synthetic cordierite incorporates Be by this substitution, i.e., at very high temperatures in the absence of Na, K and Ca (Hölscher and Schreyer 1989). Baba et al. (2000) reported cordierite with excess Si as a corona around surinamite and estimated that it contains about 12% of the  $\text{Na}(\text{Mg,Fe})_2\text{Al}_3\text{BeSi}_5\text{O}_{18}$  end member and 12% of Hölscher and Schreyer's (1989)  $\text{Mg}_2[\text{Al}_2\text{BeSi}_6\text{O}_{18}]$  end member, but had no Be analysis to substantiate this estimate.

The reduction in volume afforded by  $1(\text{NaBe})(\square\text{Al})_{-1}$  is ~2% of the volume of the Mg end member in synthetic cordierite (Povondra and Langer 1971b) and 1.49% in natural cordierite, which is the same as the effect of Fe substitution for Mg, +1.54% for  $1\text{FeMg}_{-1}$  (Armbruster and Irouschek 1983). It is thus not surprising that the volume reduction due to Be incorporation in the samples for which compositional (Fig. 9) and XRD data are available is obscured by variations in FeO, which ranges from 3.6 to 14.1 wt % (sekaninaite) in these samples. In contrast, the reduction afforded by  $1\text{BeSiAl}_2$  is 4.2% (Hölscher and Schreyer 1989), greater than in sapphirine, 2.7% (Fig. 4).

Most cordierite (and all sekaninaite) containing  $\text{BeO} > 0.1$  wt % is reported from pegmatites (both unmetamorphosed and metamorphosed) and related vein deposits



**Figure 9.** Plots of compositional variables vs. Be content of cordierite and sekaninaite from pegmatites and metamorphic rocks. (A) Aluminum. (B) Alkali and calcium. (C) Silicon. Sources of data: El Pílon, near Soto, Argentina – Schreyer et al. (1979); El Peñón, Sierras de Córdoba, Argentina—Gordillo et al. (1985); Alpe Sponda, Switzerland (includes data from nearby Miregn)—Armbruster and Irouschek (1983); Haddam, Connecticut – Armbruster and Irouschek (1983), Povondra and Čech (1978); Napier Complex, Antarctica—Grew et al. (2000); Miscellaneous—Povondra et al. (1984), Černý and Povondra (1966), Piyar et al. (1966), Malcherek et al. (2001).

(Tables 5 and 6; Černý, this volume). At El Peñón, Sierras de Córdoba, 65 km west of Córdoba City and south of Tala Cañada (Edgardo Baldo, pers. comm. 2001), Argentina, beryllian sekaninaite is a major constituent of some nodules in pegmatites cutting a roof pendant in the Achala Batholith (Gordillo et al. 1985), while in the El Pílon complex near Soto, about 50 km to the west-northwest of El Peñón, beryllian cordierite is a porphyroblast in biotite-rich “cordierite” a few meters from a pegmatite (Schreyer et al. 1979). The origin of the “cordierites” (mostly Be-poor) in the Soto area, which contain subordinate biotite, quartz, fibrolite and plagioclase, is under continuing investigation by Carlos Rapela and colleagues; formation by low-pressure (garnet-absent) partial melting of metasediments in the roof zone of granite was proposed by Rapela et al. (1995 1997 1998). It has not been specified whether Be in the cordierite-sekaninaite originated from nearby pegmatites at either locality. The first and still most noteworthy metamorphic occurrence of beryllian cordierite, i.e., with no evidence for introduction of Be from an external source such as pegmatite, is kyanite-paragonite-staurolite schist from Alpe Sponda, Switzerland (Armbruster and Irouschek 1983). But there could be other

**Table 6.** Occurrences of beryllian cordierite and sekaninaite (BeO > 0.5 wt %)

<i>Locality</i>	<i>Host rock</i>	<i>Associated minerals</i>	<i>T, P conditions</i>	<i>BeO wt % (n)</i>
1. Alpe Sponda, Ticino, Switzerland	Mica schist	Pg, St, Ky, Pl, Bt, Tur	$T = 600\text{-}650^{\circ}\text{C}$ , $P = 6\text{-}10$ kbar	0.60-0.81 (3)
2. El Pilón, Soto, Argentina	Porphyroblast in "cordierite"	Qtz, Bt, Pl	Upper amphibolite	0.93
3. El Peñon, Argentina (sekaninaite)	Nodules in pegmatite	Qtz, Kfs, Pl, Ms, Bt, Ap, And, Sil, Brl, Tur, uraninite, 2 <sup>nd</sup> Chl	Upper amphibolite	0.87-1.16 (3)
4. Ukraine (exact locality unknown)	Vein formed by reaction of pegmatitic magma and ultramafic rock	Grt, Pl, Mc, Sil, Qtz, Spl, Mgt, Ap		1.77
5. Vezná, Czech Republic	Metasomatic zones in pegmatite	Qtz, Kfs, Pl, Rt, columbite, Brl, Mnz, Tur, Ap		1.70-1.94 (-)
6. Haddam, Connecticut, USA	Pegmatite	Qtz, Mc, Ab, Tur, Grt, Cb, columbite		0.52-1.44 (3)
7. Micanite, Colorado, USA (sekaninaite?)	Pegmatite	Qtz, Mc, Ms, Bt, Tur		0.70
8. Kemiö Island, Finland (sekaninaite)	Pegmatite	Qtz; 2 <sup>nd</sup> Qtz, Ms, Pg, Chl, Brl		1.55
9. Sugamo, Japan (sekaninaite)	Pegmatite	Qtz, Pl, Kfs, Ms, Sil, Tur, Grt		~1
10. "Christmas Point", Antarctica	Metamorphosed pegmatite	Qtz, Sil, Grt, Sur, Opx	$T = 600\text{-}650^{\circ}\text{C}$ , $P = 2\text{-}5$ kbar	1.00
11. Mt. Pardoe, Antarctica		Qtz, Sil, Grt, Sur, Opx		0.64

*Note:* n – number of samples. Sources of information on cordierite composition, paragenesis and *P-T* estimates: 1-Irouschek-Zumthor (1983), Armbruster and Irouschek (1983), Armbruster, 1986. 2-Schreyer et al. (1979). 3-Gordillo et al. (1985). 4-Piyar et al. (1968). 5- Černý and Povondra (1966, 1967). 6-Newton (1966), Povondra and Čech (1978), Armbruster and Irouschek (1983), Heinrich (1950). 7-Newton (1966), Heinrich (1950). 8-Povondra et al. (1984). 9-Sambonsugi (1957), Miyashiro (1957), Selkregg and Bloss (1980). 10, 11-Grew et al. (2000); Harley (1985), Sandiford (1985).

examples of metamorphic beryllian cordierite but not yet analyzed, e.g., the cordierite that had broken down to surinamite (Bakhuis, Mtns., Strangways Ranges, Chimwala, Table 4). In other metamorphic rocks, cordierite is not rich in Be; nonetheless, its Be content is several times the host-rock bulk Be content (Table 5), implying that like sapphirine, cordierite is a sink for Be (see below and Evensen and London 1999, in press; London and Evensen, this volume).

## Euclase

Since its discovery by Haüy (see Delamétherie 1792, 1797; Haüy 1799; Dana 1892), euclase,  $\text{AlBeSiO}_4(\text{OH})$ , was long considered to be a relatively rare mineral, but now it has been found in a variety of environments, including granite pegmatites, greisens, alpine fissures and metamorphic rocks (Introduction, Appendix 1; Černý, this volume).

**Composition.** Most wet chemical analyses (e.g., Damour 1855; von Knorring et al. 1964) and electron microprobe analyses (e.g., Goffé 1980; Barton 1986; Hemingway et al. 1986) confirm ideal stoichiometry and the minimal presence of impurities. Nonetheless, minor amounts of Na, Ca, Fe, Ti, Ga, Ge, and Sn have been reported, e.g.,  $\text{Fe}_2\text{O}_3$  to 0.47 wt %, Fe as FeO to 0.28 wt % (respectively, Yegorov 1967; Graziani and Guidi 1980); 0.02 wt %  $\text{TiO}_2$  (Mattson and Rossman 1987), and from 0.084 to about 0.15 wt % Ge (Yegorov 1967; Sharp 1961). Fluorine was reported in the first analysis to establish the presence of water (0.38 wt % F, Damour 1855), but few authors have sought fluorine since. Impurities such as included fluorite, which was found in euclase from Colombia (Notari et al. 2000), pose a problem when assessing the reliability of wet chemical analysis of F, e.g., Popov's (1998) report of 0.09 and 1.35 wt % in euclase from the Mariin emerald deposit (Urals, Russia). Electron microprobe analysis avoids the problem of impurities, but detection limits can be high, e.g., 0.5 wt % F in a study reporting no F detected (Hemingway et al. 1986). Hsu (1983) reported that synthetic euclase incorporated little, if any, F in the presence of HF, whereas bertrandite in this environment became F dominant.

**Occurrence.** Euclase has been reported from low-grade metamorphic environments. In some cases, formation of euclase is associated with hydrothermal activity and such occurrences are not strictly metamorphic. For example, Dana (1892, p. 509) mentioned an occurrence of euclase "with topaz in chloritic schist" in the mining district of Villa Rica (now Ouro Preto, possibly the type locality or near it, see Cassedanne 1989), Minas Gerais, Brazil. The origin of euclase and topaz in this area is controversial, i.e., whether they formed in a pegmatite or by metamorphism of a stratabound deposit affected by hydrothermal fluids (e.g., Olsen 1971 1972; Fleischer 1972; Keller 1983; Cassedanne 1989). According to Cassedanne (1989), who reviewed literature on the Ouro Preto topaz deposits, euclase has been found only as loose crystals in association with topaz, which is restricted to a single, endogenic horizon dominated by muscovite, sericite and quartz. In Yakutiya, Russia, euclase is found in chlorite-quartz zones that cut coarse-grained granite and are associated with its cataclasis (Yegorov 1967). Formation of euclase in these zones is attributed to low-temperature hydrothermal activity under conditions of high acidity. A third example is the development of beautifully faceted euclase crystals with quartz, rutile, albite ("pericline"), calcite, ankerite, muscovite and chlorite in fissures cutting metamorphic rocks at several localities in the Alps (e.g., Meixner 1957); these occurrences are related to postmetamorphic activity. Lastly, euclase occurs sparingly in emerald-bearing veins cutting Cretaceous sediments in Colombia (Rubiano 1990; Notari et al. 2000); these emerald deposits are now thought to be metamorphic-hydrothermal in origin (see Franz and Morteani, this volume, for a review of the Colombian emerald deposits).

Examples of metamorphic euclase include Goffé's (1980 1982) report of relatively abundant (3.6 modal % in the studied section) euclase in a Fe-rich chlorite-rich rock from Aiguille du Fruit, Vanoise, Briançonnais zone, France (W Alps) containing chloritoid and quartz. Both ferromagnesian silicates approach their respective Fe end members. The chlorite rock is associated with metabauxite and rocks containing the high-pressure/low-temperature phase magnesiocarpholite (sample Chanrossa B2, Henry et al. 1996) and resulted from metamorphism estimated at 10-11 kbar, 330-350°C by the method of Goffé

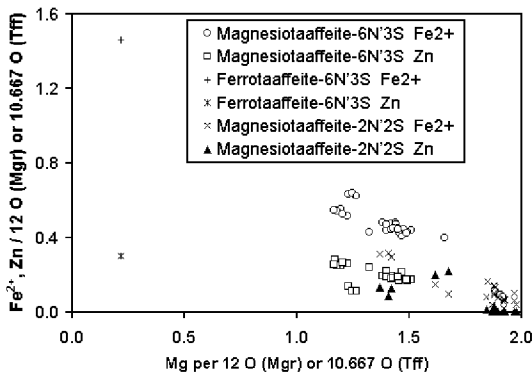
and Bousquet (1997; Goffé, pers. comm. 2001). That is, euclase is also high-pressure/low-temperature phase in these rocks. This rock and a second one with the same assemblage later found on the Aiguille du Fruit contain 25-61 ppm Be (Catel and Goffé, pers. comm. 2001). Nonetheless, Goffé (1982) and Poinssot et al. (1997) inferred a sedimentary origin for this remarkable, if localized, Be enrichment; the Be-enriched rocks and associated bauxites are Al-rich materials formed by alteration of a granitic basement and subsequently washed away, transported and redeposited.

Hanson (1985) reported euclase in a quartz vein with pyrophyllite, ottrelite and davreuxite that cuts phyllites containing chloritoid, andalusite and spessartine, at Otrré, Ardennes Mountains, Belgium. The vein was emplaced during the later stages of metamorphism, which peaked near 380°C and 1-2 kbar. Beryllium could have been remobilized from the host Mn-rich metasediments, in which 2-5 ppm Be have been reported (Krosse and Schreyer 1993), and concentrated in the vein; a magmatic source of Be is unlikely because as such rocks are absent in the Otrré area.

### Taaffeite group

There are three mineral species in the taaffeite group: magnesiotaaaffeite-2*N*'2*S* ( $Mg_3BeAl_3O_{16}$ ), magnesiotaaaffeite-6*N*'3*S* ( $Mg_2BeAl_6O_{16}$ ) and the  $Fe^{2+}$  analogue of the latter, ferrotaaaffeite-6*N*'3*S* (Armbruster 2002). These minerals are polysomes consisting of modified nolanite (*N*') and spinel (*S*) modules, respectively  $Be(Mg,Fe)Al_4O_8$  and  $(Mg,Fe)Al_2O_4$  (see also Hawthorne and Huminicki, this volume). The suffix in the mineral name gives the proportions of the modified nolanite and spinel modules, whereas the chemical prefix specifies the dominant divalent cation. The taaffeite group is closely related to the högbomite and nigerite groups, which are Fe-Mg-Zn-Al oxide minerals forming polysomatic series and containing significant amounts of Ti and Sn, respectively (Armbruster 2002).

Magnesiotaaaffeite-2*N*'2*S* was originally described as "taaffeite" (Anderson et al. 1951) from a cut gemstone from Sri Lanka, whereas magnesiotaaaffeite-6*N*'3*S* ("musgravite") was first found by Hudson et al. (1967) in granulite-facies rocks from the Musgrave Ranges, Australia and its  $Fe^{2+}$  analogue, ferrotaaaffeite-6*N*'3*S* ("pehrmanite") from a pegmatite in Finland (Burke and Lustenhouwer 1981). The compositional and structural similarity of these minerals to one another and problems in the original analysis of magnesiotaaaffeite-2*N*'2*S* resulted in considerable confusion that was finally clarified by Schmetzer (1983a,b).



**Figure 10.** Ferrous iron and zinc contents of taaffeite-group minerals. Formulae of magnesiotaaaffeite-2*N*'2*S* have been recalculated to a 10.667 O basis so as to be directly comparable to magnesiotaaaffeite-6*N*'3*S* and ferrotaaaffeite-6*N*'3*S*, i.e., with divalent cations totalling close to 2. Sources of data: Hudson et al. (1967), Teale (1980), Burke and Lustenouwer (1981), Grew (1981), Moor et al. (1981), Schmetzer (1983a), Schmetzer and Bank (1985), Chadwick et al. (1993), Rakotondrazafy (1999), Grew et al. (2000).

**Composition.** The three oxides are largely  $\text{Fe}^{2+}$ -Mg-Zn solid solutions (Fig. 10). Nuber and Schmetzer (1983) found no isomorphous replacement of Be and Mg, and thus Be content is fixed for each of the three minerals. Most analyses are by electron microprobe, and thus few direct determinations of ferric/ferrous ratio have been reported. In most samples, the sum of trivalent cations excluding Fe approaches the ideal 6 and 8 atoms per formula units for magnesiotaaaffeite- $6N^73S$  and magnesiotaaaffeite- $2N^22S$ , respectively, implying that ferric iron contents are low; this is consistent with wet chemical determination on the type magnesiotaaaffeite- $6N^73S$  (0.4 wt %  $\text{Fe}_2\text{O}_3$ , Hudson et al. 1967). Higher  $\text{Fe}_2\text{O}_3$  contents, 1.5-2.0 wt %, equivalent to 0.11-0.13  $\text{Fe}^{3+}$  per formula unit, were calculated by stoichiometry from electron microprobe analyses of magnesiotaaaffeite- $6N^73S$  associated with hematite-ilmenite, which implies a relatively oxidizing environment with high  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratios (Grew et al. 2000). Huang et al. (1988) reported wet chemical analyses of magnesiotaaaffeite- $2N^22S$  from the Hsianghualing deposit, China, in which the iron is dominantly ferric, i.e., 7.15-8.14 wt %  $\text{Fe}_2\text{O}_3$  and 0-0.45 wt % FeO. However, these values give an excess of trivalent cations, 8.27-8.34 per formula unit and my recalculation of the analysis assuming stoichiometry gave 0.10-0.16  $\text{Fe}^{3+}$  per formula unit, more in accord with Schmetzer's (1983a) electron microprobe analyses of magnesiotaaaffeite- $2N^22S$  from this deposit.

Maximum contents reported for other constituents include 3.03 wt % MnO, 0.64 wt %  $\text{Ga}_2\text{O}_3$ , 0.33 wt %  $\text{Cr}_2\text{O}_3$ , 0.15 wt %  $\text{V}_2\text{O}_5$  (Schmetzer 1983a; Schmetzer et al. 2000).

The data plotted in Figure 10 suggest that Zn and  $\text{Fe}^{2+}$  increase together, e.g., the highly magnesian Sakeny magnesiotaaaffeite- $6N^73S$  contains negligible Zn (Devouard, pers. comm., 2001; Devouard et al. 2002; Rakotondrazafy, Raith, Devouard Nicolle, in preparation) as does highly magnesian magnesiotaaaffeite- $2N^22S$ . In addition, magnesiotaaaffeite- $6N^73S$  appears to incorporate more  $\text{Fe}^{2+}$  and Zn than magnesiotaaaffeite- $2N^22S$ . However, these trends could result from the geochemical environments from which the analyzed samples happen to originate rather than from crystallographic controls on the incorporation of  $\text{Fe}^{2+}$  and Zn. An assemblage of both magnesiotaaaffeite minerals has yet to be found, and thus distribution of elements between them cannot be determined directly. When compared to spinel from separate assemblages, magnesiotaaaffeite- $6N^73S$  fractionates Mg relative to  $\text{Fe}^{2+}$  slightly more than magnesiotaaaffeite- $2N^22S$  does, i.e.,  $(\text{Mg}/\text{Fe}^{2+})_{\text{Mgf}}/(\text{Mg}/\text{Fe}^{2+})_{\text{Spl}} = 1.70\text{-}2.85$  vs.  $(\text{Mg}/\text{Fe}^{2+})_{\text{Tff}}/(\text{Mg}/\text{Fe}^{2+})_{\text{Spl}} = 1.48$  (Wilson and Hudson 1967; Teale 1980; Rakotondrazafy 1999; Grew et al. 2000).

**Occurrence.** Both magnesiotaaaffeite minerals are found in calcareous and non-calcareous silica-undersaturated environments (Table 7). Three of the four known magnesiotaaaffeite- $2N^22S$ -bearing deposits, i.e., Hsianghualing (China), Sakhir-Shulutynsky and Pitkäranta (Russia), are carbonate rocks or magnesian ("apocarbonate") skarns that have been metasomatized by hydrothermal fluids rich in F and Be, as well as Sn or Li associated with granites. Magnesiotaaaffeite- $2N^22S$  probably formed at temperatures below 400°C at these three deposits although I am not aware of temperature-pressure estimates specifically for magnesiotaaaffeite- $2N^22S$  formation at any of them. For example, temperature of beryllium mineralization at similar deposits (e.g., Yermakovskoye fluorite-phenakite-bertrandite deposit in the Transbaikal region, Russia) are estimated from fluid inclusions to have ranged from 340°C at the start to 140°C at the end at depths not exceeding 1.5 km (Bulnaev 1996; cf. 400-140°C range at  $P < 1$  kbar reported by Kosals et al. 1973). Although phenakite and bertrandite are not found with magnesiotaaaffeite- $2N^22S$ , both minerals are present elsewhere in the Pitkäranta and Hsianghualing deposits (Nefedov 1967; Pekov 1994, Huang et al. 1988), and phenakite is

Table 7. Occurrences of taaffeite-group beryllium oxides.

Locality	Associated minerals	T, P	Source ( <i>italics</i> – P-T data only)
<b>MAGNESIOTAFFEITE-6N°3S (“MUSGRAVITE”)</b>			
Musgrave Ranges, Australia (type)	Spl, Spr	~550°C (probably too low)	Hudson et al. (1967); Wilson & Hudson (1967); <i>Wilson et al. (1970)</i>
“Zircon Point”, Khmara Bay, East Antarctica	Sil, Sur, Khm, Cb, Grt, Bt, Rt, Qtz	~800-900°C, ~8-9 kbar	Grew (1981, 1998); Grew et al. (2000)
“Christmas Point”, Khmara Bay, East Antarctica	Sil, Sur, Spr-Khm, Ilm- Hem, Spl, Crn, Bt, wagnerite		
Dove Bugt, North-East Greenland	Cal, Norbergite, Spl <sup>†</sup> , Phl, Ap, Fl, arsenopyrite, 2 <sup>nd</sup> Chl		Chadwick et al. (1993); Jensen & Stendal (1994); Jensen (1994)
Pegmatite P30, Antsofimbato, Sahatany, Madagascar	Tur, spessartine, beryl, Cb		Ranoroosa (1986)
Sakeny, ~100 km NW of Ihosy, southern Madagascar	An, Spl, Di, Crn, Spr, 2 <sup>nd</sup> Ms	<~700°C, 4-5 kbar	Rakotondrazafy (1999); Rakotondrazafy & Raith (2000); Devouard et al. (2002)
<b>FERROTAFFEITE-6N°3S (“PEHRMANITE”)</b>			
Rosendale pegmatite, Kemiö Island, Finland	Sil, Ms, Grt, Hc, Cb, Tur, Crn, nigerite		Burke et al. (1977); Burke & Lustenhower (1981)
<b>MAGNESIOTAFFEITE-2N°2S (“TAAFFEITE”)</b>			
Hsianghualing deposit, Hunan Province, China	Fl, Cal, Li mica, Phl, nigerite, Spl, Cb, cassiterite, cancrinite		Peng & Wang (1963), Beus (1966), Vlasov (1966); Huang et al. (1988)
Sakhir-Shulutynskiy pluton*, E. Sayan, Russia	Li mica, Fl		Kozhevnikov et al. (1975a); locality from N.N. Pertsev (pers. comm. 2000)
Mount Painter, South Australia	Spl, Rt, Crn; 2 <sup>nd</sup> högbomite		Teale (1980)
Pitkäranta, Karelia, Russia	Spl		Schmetzer (1983a); Pekov (1994)

Note: The great majority of reported “taaffeites” are gemstones of unknown provenance from Sri Lanka (type) and, in a few cases, Myanmar (Burma) and Tunduru, Tanzania; rare “musgravite” gemstones are also found in Sri Lanka. \*For background, see Kozhevnikov et al. (1975b), Kozhevnikov and Perelyayev (1987). <sup>†</sup>Spinel identified optically in sample #339313 from the Greenland Geological Survey

reported in metasomatites in the aureole of the Sakhir-Shulutynskiy pluton (Kozhevnikov et al. 1975a). The Dove Bugt magnesiotaaffeite-6N°3S paragenesis is also a skarn, which resulted from metasomatic action of a sheet of granite, which introduced Be into underlying calcite marble (Chadwick et al. 1993; Jensen 1994; Jensen and Stendal 1994).

This metasomatic activity probably post-dates the regional upper amphibolite-facies metamorphism during which sillimanite, garnet and cordierite developed in schist and paragneiss in the Dove Bugt area (Chadwick and Friend 1991; Chadwick et al. 1990; 1993), and thus there is little information bearing on the *P-T* conditions for magnesio-taaffeite-6 $N^3S$  formation. Chadwick et al. (1993) inferred that magnesio-taaffeite-6 $N^3S$  predated introduction of F-rich fluid, but the association of magnesio-taaffeite-2 $N^2S$  and fluorite at other localities (and the association of Be and F mineralization in general) suggests that magnesio-taaffeite-6 $N^3S$  at Dove Bugt is more likely coeval with fluorite and F-rich fluid activity.

In the case of the non-calcareous environments, magnesio-taaffeite minerals are found with the Al-rich minerals, chrysoberyl, spinel or sapphirine-khmaralite, mostly in high-temperature, deep-seated rocks. At the type locality magnesio-taaffeite-6 $N^3S$  constitutes a nearly monomineralic nodule 10×9×5 cm in a phlogopite replacement zone (Fig. 6). Wilson and Hudson (1967) and Hudson et al. (1967) inferred that magnesio-taaffeite-6 $N^3S$  formed from replacement of corundum during metasomatic introduction of Be (see above under *Khmaralite-sapphirine*). Parageneses in the Khmara Bay pegmatites differ in that magnesio-taaffeite-6 $N^3S$  occurs in beryllium-rich aggregates formed by reaction of sapphirine-khmaralite with quartz during a high-temperature metamorphic event following intrusion; Be enrichment is clearly premetamorphic (Grew et al. 2000; see above under *Surinamite*). Magmatic sapphirine-khmaralite reacted with quartz to form sillimanite-surinamite-garnet coronas; magnesio-taaffeite-6 $N^3S$  formed where breakdown of sapphirine-khmaralite proceeded in isolation from quartz. The single exception to silica-undersaturation in parageneses with either magnesio-taaffeite mineral is a magnesio-taaffeite-6 $N^3S$  grain enclosed in quartz in the pegmatite at “Zircon Point” (Grew 1981). At Mt. Painter, South Australia, metamorphic magnesio-taaffeite-2 $N^2S$  and corundum are completely enclosed in spinel porphyroblasts and isolated from the phlogopite matrix; a magnesiohögbonite mineral formed from magnesio-taaffeite-2 $N^2S$  during a later metamorphic event (Teale 1980). Teale (1980) reported no evidence for metasomatic activity at Mt. Painter and inferred that Be had been present in the sedimentary precursor to the magnesio-taaffeite-2 $N^2S$ -bearing rock. Ranoroso (1986) reported from the Sahatany pegmatite district a “taaffeite” with a powder X-ray diffraction pattern similar to that of magnesio-taaffeite-6 $N^3S$ . Apart from the minerals listed in Table 7, no details on the paragenesis were reported, and it is not clear whether magnesio-taaffeite-6 $N^3S$  at Sahatany is strictly pegmatitic or like ferrotaaffeite-6 $N^3S$ , a late, hydrothermal phase.

The Sakeny, Madagascar, magnesio-taaffeite-6 $N^3S$  paragenesis in “sakénite” (anorthite-rich rocks containing spinel, sapphirine or corundum, Lacroix 1939) is both Ca- and Al-rich, but calcite is absent (Rakotondrazafy 1999). Anorthite and phlogopite constitute the matrix; corundum is often isolated by coronas of spinel and/or sapphirine. Magnesio-taaffeite-6 $N^3S$  forms platelets up to 0.5×0.1 mm enclosed in a spinel corona and almost touches diopside (Rakotondrazafy 1999) or in spinel ± sapphirine + anorthite symplectite between spinel and anorthite (C. Nicollet, pers. comm. 2001; Rakotondrazafy, Raith, Devouard and Nicollet, in preparation). Both igneous (anorthosite) and sedimentary precursors have been suggested for “sakénite”; Rakotondrazafy and Raith (1997) and Rakotondrazafy (1999) cited geochemical evidence for metasomatic introduction of Si and Mg as critical in their development from sediments containing clayey and calcareous intercalations. Devouard et al. (2002) propose that Be was introduced by infiltration metasomatism related to emplacement of Be- and B-rich pegmatites associated with the Ranotsara ductile shear zone at temperatures below ~700°C and pressures of 4-5 kbar, i.e., less than the >700°C, 5.0-5.5 kbar estimated for pelitic gneiss in Ihosy, 100 km distant (Nicollet 1985, 1990).



Ferrotaafeite-6N<sup>3</sup>S is found in aggregates of sillimanite, garnet, muscovite, columbite-tantalite, zirconian Hercynite, nigerite-group minerals, chrysoberyl, corundum, tourmaline, apatite, and zirconian staurolite in the wall zone of the Rosendal pegmatite, Finland (Burke et al. 1977; Burke and Lustenhouwer 1981). Ferrotaafeite-6N<sup>3</sup>S overgrows and replaces the nigerite-group minerals, which in turn replace Hercynite. The above authors attributed formation of ferrotaafeite-6N<sup>3</sup>S and nigerite-group minerals to the action on Hercynite of late-stage Sn- and Be-bearing hydrothermal solutions that separated from the pegmatitic melt. Although quartz and sodic plagioclase are also present in the wall zone, there is no evidence ferrotaafeite-6N<sup>3</sup>S coexisted with either.

The relative stabilities of the magnesiotaaffeite minerals are unknown (see also Franz and Morteani, this volume). Both minerals are found over a comparable range of *P-T* conditions in similar geochemical environments, and the difference in Be:Mg:Al ratio between them would in principle allow stable coexistence, yet the two phases have not been found together. It remains unclear which conditions favor one over the other, and experimental work sheds little light on the problem. Syntheses of both minerals have been reported in the ceramic literature (Geller et al. 1946; Reeve et al. 1969; Kawakami et al. 1986; Franz and Morteani, this volume) and gemological literature (Schmetzer et al. 1999), but at temperatures above those encountered in the crustal environments where these minerals are found, i.e., 1200 °C and higher. In addition, Hölscher (1987) listed "Taaffeit 9R", i.e., magnesiotaaffeite-6N<sup>3</sup>S, with beryllian sapphirine and cordierite as phases synthesized at 1200°C and 1 kbar from a gel of (Mg<sub>3.5</sub>Al<sub>4.5</sub>)(Al<sub>3.5</sub>Be<sub>0.5</sub>Si<sub>2.0</sub>)O<sub>20</sub> composition but did not report any details on how the magnesiotaaffeite-6N<sup>3</sup>S was identified or on its physical properties. To date, the magnesiotaaffeite minerals are the only ternary compounds found in the MgO-BeO-Al<sub>2</sub>O<sub>3</sub> system at near-liquidus temperatures. Although crystallization of a melt has yielded only magnesiotaaffeite-6N<sup>3</sup>S, both minerals formed by exsolution from a MgAl<sub>2</sub>O<sub>4</sub>-BeAl<sub>2</sub>O<sub>4</sub> spinel solid solution on cooling. Whether spinel can incorporate sufficient beryllium at geologically reasonable temperatures to exsolve magnesiotaaffeite minerals is another question that needs further study. The presence of magnesiotaaffeite-6N<sup>3</sup>S as lamellae in spinel and spinel + anorthite symplectite at Sakeny, Madagascar suggests the possibility that musgravite resulted from exsolution of the Be component from an originally high-temperature beryllian spinel.

The provenance of the alluvial magnesiotaaffeite minerals that are highly prized as gemstones from Sri Lanka, Myanmar (Burma) and Tanzania has yet to be elucidated (e.g., Kampf 1991; Demartin et al. 1993; Burford 1998; Kiefert and Schmetzer 1998; Schmetzer et al. 2000).

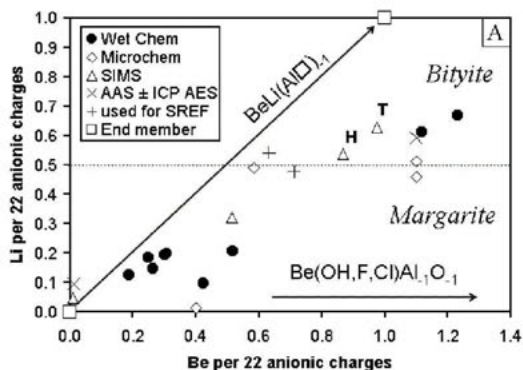
## BERYLLIUM CONTENTS OF SELECTED ROCK-FORMING MINERALS

### General statement

Beryllium contents of rock-forming minerals are less often determined than the contents of other trace elements, and there have been even fewer systematic studies of the distribution of beryllium among common rock-forming minerals in metamorphic rocks, indeed in any rock type. The older studies of Be contents, which began with Goldschmidt and Peters (1932) and Goldschmidt (1958), are based on spectrographic analyses of mineral separates (e.g., Pearson and Shaw 1960; Petrova and Petrov 1965; Wenk et al. 1963; Schwander et al. 1968). The Russian-language literature on Be geochemistry is relatively large, and I have made no attempt to cover it entirely. More recent studies using mineral separates have made use of atomic absorption spectrophotometry (e.g., Lahti 1988), inductively coupled plasma emission spectroscopy (e.g., Bebout et al. 1993; Dahl et al. 1993) or direct current plasma emission spectroscopy (Kretz et al. 1989).

Investigators have also increasingly resorted to microbeam techniques of individual grains or zones in a given grain, including nuclear (e.g., particle-induced X-ray or gamma-ray emission, i.e., PIXE or PIGE, Lahlafl 1997), ion microprobe (e.g., Hervig, this volume; Domanik et al. 1993; Černý et al. 1995; Grew et al. 1998a,b,c), and laser ablation inductively coupled plasma emission mass spectroscopy, LA-ICP-MS (Bea et al. 1994; Bea, unpublished data).

The present review, while not confined to samples found in metamorphic rocks, emphasizes those minerals occurring in metapelites. The large number of studies of minerals in alkalic systems has not been covered; it should be noted that compared to metasedimentary and calc-alkalic rocks, amphiboles and pyroxenes are more enriched in Be in nepheline syenite pegmatites (reviewed by Hörmann 1978).

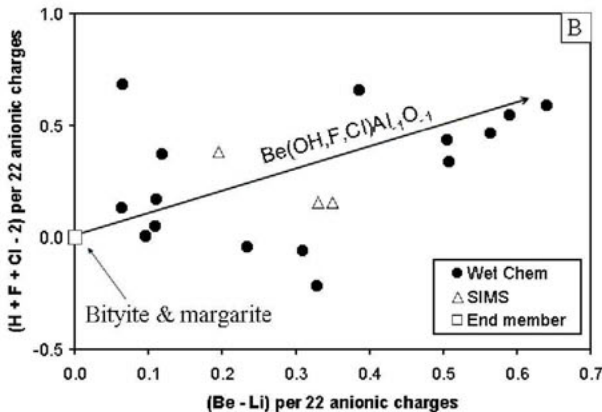


**Figure 11.** (a) Beryllium and lithium contents of bityte-margarite solid solutions. The substitution  $\text{BeLi}(\text{Al}\square)_1$  joins the end-member compositions of margarite and bityte, respectively,  $\text{Ca}\square\text{Al}_2(\text{Al}_2\text{Si}_2\text{O}_{10})(\text{OH})_2$  and  $\text{CaLiAl}_2(\text{BeAlSi}_2\text{O}_{10})(\text{OH})_2$ . Beryllium and lithium data were obtained by wet chemistry on mineral separates (Wet Chem, microchemical, atomic absorption spectrophotometry, AAS and inductively coupled plasma-atomic emission spectroscopy, ICP-AES), secondary ion mass spectroscopy (SIMS or ion microprobe), or by single crystal structural refinement (SREF). Sources of data: Arnaudov et al. (1982, wet chem), Bayrakov (1973, wet chem, one used by Sokolova et al. 1979 for SREF), Beus (1966, wet), Evensen (pers. comm. 2000, SIMS), Gallagher and Hawkes (1966, microchemical analyses), Grew et al. (1986, SIMS), Kupriyanova (1976, wet), Kutukova (1959, wet), Lahti (1988, AAS), Lahti and Saikkonen (1985, AAS and ICP-AES), Lin and Guggenheim (1983, microchem from Gallagher and Hawkes 1966, corrected for quartz; used for SREF), Rowledge and Hayton (1948, wet), Lin and Guggenheim (1983) used the same sample from the Mops pegmatite, Zimbabwe as Gallagher and Hawkes (1966). H = holotype specimen; T = specimen from near type locality in Sahatany Valley, Madagascar (J. Evensen, pers. comm.).

### Mica group

Among naturally occurring micas only margarite-bityte solid solutions are known to contain a significant amount of beryllium (Fig. 11a). The Mica Subcommittee of the Commission on New Minerals and New Mineral Names (International Mineralogical Association) defined bityte as a trioctahedral brittle mica with  $^{6}\text{Li} > ^{7}\text{Li}$  and with an end-member formula  $\text{CaLiAl}_2(\text{AlBeSi}_2)\text{O}_{10}(\text{OH})_2$  (e.g., Can. Mineral. 36: 905-912 1998). This composition is linked to end-member margarite,  $\text{Ca}\square\text{Al}_2(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2$ , by the exchange vector,  $\text{BeLi}(\text{Al}\square)_1$  (Lin and Guggenheim 1983). Most micas plotting in the

bityite field have more Be and less Li than predicted by this exchange, e.g., the most beryllian bityite contains 1.23 Be and 0.67 Li per formula unit. Grigor'yev and Pal'guyeva (1980) reported "beryllium margarite", a variety in which only Be is present (Table 8). However, it is not clear whether Li was sought and not found, or simply not sought, so the possibility of a Li-free, Be-rich component in margarite remains to be demonstrated. Ginzburg (1957) suggested that Be could also be introduced with hydroxyl via  $\text{Be}(\text{OH})\text{Al}_1\text{O}_{1.1}$ , whence his formula for margarite-bityite solid solutions,  $\text{CaLi}_{x-y}\text{Al}_2[\text{Al}_{2-x}\text{Be}_x\text{Si}_2(\text{OH})_y]\text{O}_{10-y}(\text{OH})_2$ ; Grigor'yev and Pal'guyeva (1980) reported that this substitution was consistent with analytical data on "beryllium margarite". Albeit scattered, the data plotted in Figure 11b lend some credence to this suggestion if F and Cl are included with OH in computing anionic composition. Nonetheless, a crystallographic study of bityite with significant excess of Be over Li or of a Li-free "beryllium margarite" would be needed to confirm it. A similar substitution is implicit in the conclusions reached by Robert et al. (1995), who reported infrared and thermogravimetric evidence that the charge deficiency resulting from Be replacement of Si in micas synthesized in the system  $\text{K}_2\text{O}-\text{MgO}-\text{BeO}-\text{SiO}_2-\text{H}_2\text{O}$  was largely balanced by incorporation of extra OH, i.e., the most important substitution could be  $\text{Be}(\text{OH})_2\text{Si}_1\text{O}_2$ .



**Figure 11 (b)**  
Anion compositions of bityite-margarite solid solutions (wet chemical and SIMS data). Square marks end-member compositions.

Few investigators have sought B in bityite, but the amounts reported suggest that B could be a significant constituent, i.e., 0.48 wt %  $\text{B}_2\text{O}_3$  in a sample from Finland (Lahti and Saikkonen 1985) and 1.45-1.51 wt %  $\text{B}_2\text{O}_3$  in samples from the Sahatany Valley, Madagascar, including holotype material (J. Evensen, pers. comm.).

The compositions plotted in Figure 11 are for pegmatitic micas, except for the Be-poor metamorphic margarite reported from amphibolite-facies rocks in Antarctica by Grew et al. (1986) and metasomatic beryllian lithian margarite reported from the Harding Pegmatite (New Mexico) by J. Evensen (pers. comm. 2000). This bityite is an exocontact phase in a tourmalinized zone of amphibolite from 0 to about 6 cm from the pegmatite contact. The beryllium content of metamorphic margarite has overall received little attention (Table 8), although it probably contains more Be than associated paragonite (one pair reported) and muscovite.

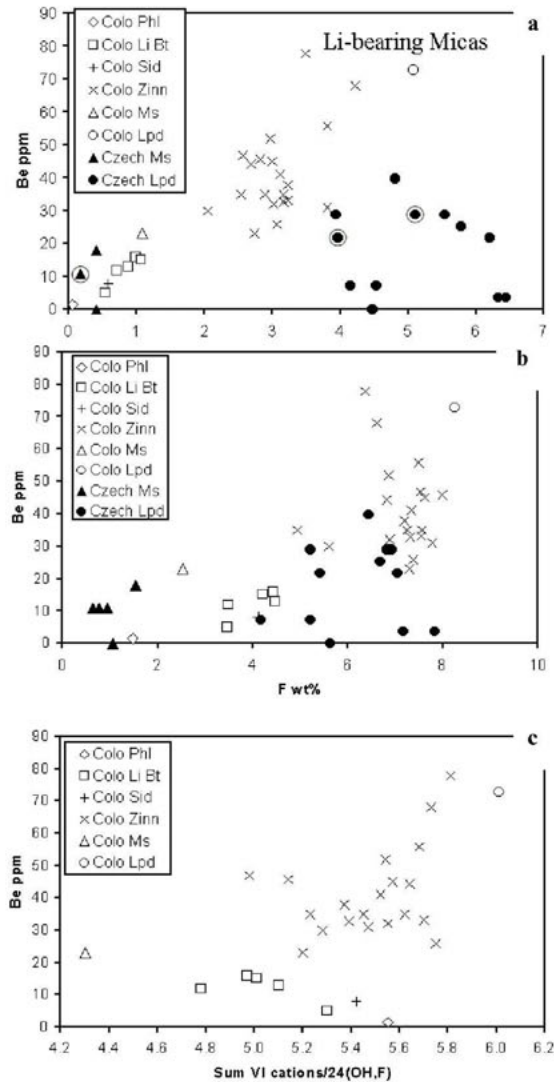
Muscovite, paragonite and potassic lithium micas rarely contain more than 100 ppm Be even in environments rich in Be (Table 8, Fig. 12), e.g., 19-68 ppm Be in muscovite from mica schists containing 10-61 ppm Be from the Habachtal emerald deposit, Austria

Table 8. Beryllium contents of micas (excluding bitityte)

<i>Rock Type</i>	<i>Be, ppm (n)</i>	<i>Source</i>
<b>MUSCOVITE AND PHENGITE</b>		
Amphibolite-facies metasediment, Catalina Schist, Calif., USA	0.69 (1)	Bebout et al. (1993)
Pegmatite, Catalina Schist, Calif., USA	0.92-4.0 (3)	
Eclogite, Tressolmen, Central Alps, Switzerland	0.27-2.47 (7)	Zack (2000)
Mica schist, different grades	0-5 (3)	Hietanen (1969)
Amphibolite-facies metamorphic, Ural, Russia	2.5-4.0 (2)	Bushlyakov & Grigor'yev (1989)
Metamorphics, St + And + Sil grade, Ladoga, Russia	31 (-) <sup>1</sup>	Lebedev & Nagaytsev (1980)
Metagraywacke, metabasalt, etc.	0.6-6.2 (74)	Domanik et al. (1993)
Rožná pegmatite, Czech Republic (beryl)	11-18 (4)	
Dobrá Voda pegmatite, Czech Republic	0 (1)	Černý et al. (1995)
Miarolitic pegmatites, Pikes Peak, Colorado, USA	23 (1)	Foord et al. (1995)
Granite, Yellowknife, Canada	11 (1)	Kretz et al. (1989)
Pegmatite, Yellowknife, Canada	17 (1)	
Miscellaneous metamorphics, Tessin Alps, Switzerland	1-7 (55)	
Pegmatite, Tessin Alps, Switzerland	<2-15(15)	Schwander et al. (1968), cf. Wenk et al. (1963)
Schist and gneiss from Habachtal emerald deposit, Austria	19-68 (12)	Grundmann & Morteani (1989)
Staurilite zone schists, Black Hills, South Dakota, USA	2.1-17.7 (31)	
Sillimanite zone schists, Black Hills, South Dakota, USA	0-14.2 (16)	Dahl et al. (1993); Dahl (pers. comm. 1999)
Aurosoles of pegmatite	16.9-42.5 (2)	
Yermakovskoye hydrothermal Be deposit, Transbaikalia, Russia	101	Novikova et al. (1994)
Miscellaneous granite pegmatites	12-120 (7)	Goldschmidt (1958)
Pegmatites containing beryllium minerals	20-108 (30)	Beus (1966, Table 129)
Metamorphic borian Ms in meta-pegmatite, Koralpe, Austria	49-140 (5)	Bernhardt et al. (1999); Kalt et al. (2001)
Muscovite replacing topaz and Tur in pegmatite, Orivesi, Finland	6-63 (6)	Lahri (1988)
Muscovite, pegmatite, Stoneham, Maine, USA	35 (SIMS)	Dyar et al. (2001)
	43 (ICP-AES)	

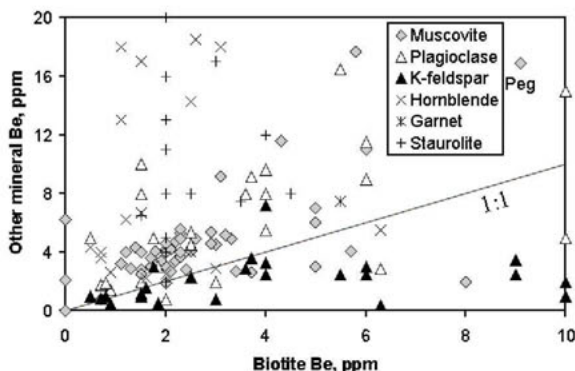
<b>PARAGONITE</b>				
Eclogite, Trescolmen, Central Alps, Switzerland		7.0-9.7 (3)	Zack (2000)	
Mt. Bernstein, N. Victoria Land, Antarctica		30 <sup>2</sup>	Grew et al. (1986)	
<b>MARGARITE</b>				
Miscellaneous margarite		Between 4 and 36 (3)	Schaller et al. (1967) semi-quantitative spectrographic analysis	
Lithian, sodian margarite, pegmatite, Orivesi, Finland		700-1000(2)	Lahti (1988)	
Mt. Bernstein, N. Victoria Land, Antarctica		255	Grew et al. (1986)	
"Beryllium margarite" in weathering residua from pegmatite, Urals, Russia		200 <sup>2</sup>	Grigor'yev (1980); Grigor'yev & Pal'guyeva (1980)	
		1.12 - 2.91 wt% BeO (2)		
<b>BIOTITE AND PHLOGOPITE</b>				
Amphibolite-facies metamorphic, Urals, Russia		1.5-13 (6)	Bushlyakov & Grigor'yev (1989)	
with St		~2-4.5 (16)	Sergeyev et al. (1967)	
Metamorphics, Ladoga, Russia		0.5-4.2 (5) <sup>3</sup>	Lebedev & Nagayisev (1980)	
Grt to Opx zone				
Metamorphic, in amphibolite wallrock of Harding pegmatite (also bityite), New Mexico, USA		17	J. Evensen (pers. comm., 2000)	
Metasedimentary and mafic migmatites, California, USA		0.5-2.0 (5)	Domanik et al. (1993)	
Pegmatite, Madagascar		~0-0.4 (2)	Grew et al. (1998c)	
Whiteschist, SW Pamirs, Tajikistan		0-1 (6)	Grew et al. (1994, 1998b)	
Miarolitic pegmatites, Pikes Peak, Colorado, USA		1 (1)	Foord et al. (1995)	
Granite, Yellowknife, Canada		6 (1)	Kretz et al. (1989)	
Granite, syenite, diorite (Dzhida complex, Trans-Baikal, Russia)		0.3-4.0 (40)	Petrova & Petrov (1965); Kostetskaya et al. (1969)	
		6-10 (3)	Kosals & Mazurov (1968)	
Miscellaneous plutonics, Russia, Kazakhstan		0.9-4 (5)	Petrov (1973)	
Schist and gneiss from emerald deposit, Habachtal, Austria		~0-18 (38)	Grundmann & Moriteani (1989)	
Migmatites, Peña Negra Complex, Spain		0.11-1.43 (7)	Bea et al. (1994); Bea (pers. comm., 2001)	
Metapelites, Ivrea-Verbano, Italy		0-6.14 (10)	Bea & Montero (1999); Bea (pers. comm., 2001)	

Staurolite zone schists, Black Hills, South Dakota, USA	0-5.8 (31) 0-5.7 (12)	Dahl et al. (1993), Dahl (pers. comm., 1999)
Sillimanite zone schists, Black Hills, South Dakota, USA	9.1-12.3 (2) 35.1-75.3 (4)	
Granite pegmatites, Norway	2 (2)	Goldschmidt (1958)
Phlogopite from fringe of beryl-bearing vein	30-600 (10) <sup>4</sup>	
"Lepidomelane" from nepheline syenite	3-30 (-) 4-36 (-)	Beus (1966, Tables 132, 134) Goldschmidt & Peters (1932)
Pegmatite, Tessin Alps, Switzerland	<5 to 7 (5)	Wenk et al. (1963); cf. Schwander et al. (1968)
Bavono granite, Italy	<5 & 20 (2)	
Gneisses and few schists, Tessin Alps, Switzerland	Mostly <5; 8(1)	
With surinamite, pegmatite, Enderby Land, Antarctica	5	Grew (unpublished data)
<b>LITHIUM MICAS</b>		
Lepidolite, Rožná pegmatite, Czech Republic (beryl)	22-40 (7)	Černý et al. (1995)
Lepidolite, Dobrá Voda pegmatite, Czech Republic	0-7 (5)	
Miscellaneous, miarolitic pegmatites, Pikes Peak, Colorado, USA	5-78 (27) 38-237(7)	Foord et al. (1995) Monier et al. (1987)
Lepidolite-zinnwaldite, Beauvoir granite, France	<20-512 (29)	Volfinger & Robert (1994)
Lepidolite in granite pegmatite	16-126 (10)	Beus (1966, Table 129)
Zinnwaldite, Bom Futuro tin mine, Brazil	19-26 (6)	Lowell & Ahl (2000)
Note: n – number of samples. <sup>1</sup> Average of an unspecified number of samples. <sup>2</sup> Be contents reported in original sources have been corrected for revised surinamite standardization, Grew et al. (2000). <sup>3</sup> The ppm values given are themselves averages of 5 to 28 samples. <sup>4</sup> The reported Be contents are so high (average 60 ppm) that contamination is highly likely.		



**Figure 12.** Beryllium,  $\text{Li}_2\text{O}$ , and F contents, as well as octahedral occupancy of Li-bearing micas from miarolitic pegmatites, Pikes Peak, Colo., USA (Foord et al. 1995) and Rožná and Dobrá Voda pegmatites, Czech Republic (Černý et al. 1995). Circled points are two coexisting muscovite-lepidolite pairs (muscovite points are superimposed). Abbreviations not in Table 1 are: Sid = siderophyllite, Zinn = zinnwaldite, Lpd = lepidolite.

(Grundmann and Morteani 1989). An exception is lepidolite with up to 512 ppm Be from the Beauvoir granite, which contains from less than 60 to more than 250 ppm Be (Monier et al. 1987; Rossi et al. 1987; Volfinger and Robert 1994). Grundmann and Morteani (1989) noted that 20 ppm could be a natural limit for biotite because with increasing whole-rock Be content in the Habachtal emerald deposit (Austria), biotite Be content increases to 20 ppm and then levels out, an observation consistent with data reported elsewhere except for "lepidomelane" (Fe-rich biotite) from nepheline syenite (Table 8). In most pelitic rocks, where bulk Be rarely exceeds 10 ppm, muscovite and biotite Be contents rarely exceed 20 ppm and 10 ppm, respectively (Figs. 13, 14). Paragonite is an important host for Be in high-pressure rocks from Syros, Cyclades, Greece (Marschall et al. 2001); Zack (2000) reported five- to sixfold enrichment of Be in paragonite relative to phengite in two eclogites from the Central Alps.

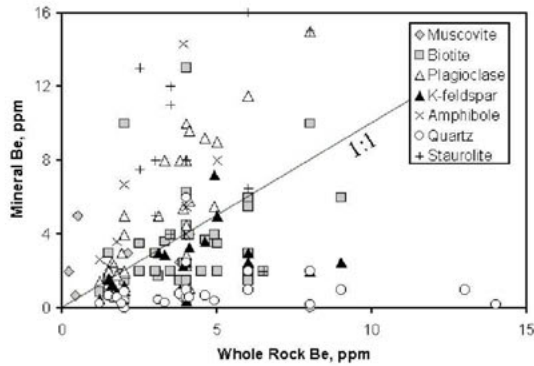


**Figure 13.** Mineral Be contents for plutonic and metamorphic rocks for biotite Be contents not exceeding 10 ppm. Peg refers to biotite-muscovite pair from aureole of pegmatite; a second pair, not plotted, is Bt 12.3 ppm, Ms 42.6 ppm, Dahl et al. 1993 and Dahl, pers. comm. 1999). Kosals and Mazurov (1968) reported oligoclase Be contents of 28-50 ppm, which are not plotted; neither are staurolite Be contents of 24-45 ppm (Sergeyev et al. 1967). Sources of data: Beus and Sazhina (1956; cf. Beus 1966, Table 123), Bushlaykova and Grigor'yeva (1989), Dahl et al. (1993), Dominik et al. (1993), Hügi and Röwe (1970), Kosals and Mazurov (1968), Kostetskaya et al. (1969), Kretz et al. (1989), Moxham (1965), Petrov (1973), Petrova and Petrov (1965), Sandell (1952), Schwander et al. (1968), Sergeyev et al. (1967), Wenk et al. (1963; only biotite containing measurable Be, i.e.,  $\geq 5$  ppm).

Nonetheless, syntheses of K-Mg-Be mica with up to 0.5 Be per formula unit and excess hydroxyl and K-Al-Mg and K-Al-Li micas with up to 1 Be per formula unit suggests the possibility of significant Be incorporation in potassic micas (Robert et al. 1995; Lahlafı 1997). Lahlafı (1997) reported experiments during which relatively significant amounts of Be were incorporated in muscovite and biotite neofomed from mica seeds in the presence of granitic melts, including a suite of melts doped in Li, Be and F, that is, the ready availability of F and Li in the environment enhances the incorporation of Be in mica. Higher F activity in pegmatites could also contribute to incorporation of Be by facilitating mobility of Be.

Figure 12 suggests that both geochemical environment and crystallographic constraint could be important controls on Be content in Li-bearing micas. Beryllium





**Figure 14.** Mineral and whole-rock Be contents for plutonic and metamorphic rocks containing up to 16 ppm Be. Staurolite Be contents of 17–45 ppm (Sergeyev et al. 1967; Hietanen 1969) are not plotted. Sources of data: Bebout et al. (1993), Beus (1966), Beus and Sazhina (1956; cf. Beus 1966, Table 123), Bushlaykova and Grigor'yeva (1989), Hietanen (1969), Hügi and Röwe (1970), Kosals and Mazurov (1968), Kretz et al. (1989), Petrov (1973), Petrova and Petrov (1965), Sandell (1952), Sergeyev et al. (1967).

content of the micas from Pikes Peak (Colorado, USA) increases almost linearly with their Li content and less regularly with F content, both of which increased as the Pikes Peak miarolitic pegmatites evolved (Foord et al. 1995), that is, mica Be content is a function of the timing of crystallization of the mica in the Pikes Peak pegmatites. However, such an evolution is not obvious in two pegmatites from the Czech Republic (Fig. 12). Data on bulk lepidolite-zinnwaldite separates indicate simultaneous Be-Li-F enrichment in the Beauvoir granite, France, but analyses of individual lepidolite-zinnwaldite flakes in thin section showed no co-variance of Be with Li (Monier et al. 1987; Volfinger and Robert 1994).

The rather imperfect correlation of Be with F compared to the Be-Li correlation suggests another factor at work. Increasing Li content could create a crystallographic environment more conducive to Be incorporation. Because Be replaces the more highly charged Al and Si on tetrahedral sites, additional charge is needed to make up the deficit. This could be accomplished in part by filling of vacant octahedral sites by Li as in bityite. A weak correlation of Be and octahedral occupancy in the Pikes Peak, Colorado, zinnwaldite and lepidolite is consistent with this interpretation, but data on the biotite and muscovite lend no support to it (Fig. 12).

In general, receptivity to Be incorporation increases as follows: biotite < muscovite < lepidolite << margarite-bityite (Černý et al. 1995; this paper, Figs. 13 and 14). The preference for Be ↔ Al miscibility over Be ↔ Si miscibility (e.g., Barbier et al. 1999; Hawthorne and Huminicki, this volume) could explain the high receptivity in margarite-bityite, which has the most tetrahedrally coordinated Al. Refinement of tetrahedral occupancies in micas intermediate between bityite and margarite (Fig. 11) is consistent with this because two tetrahedral sites are occupied nearly exclusively by Be and Al, and these sites alternate with Si dominated sites (Sokolova et al. 1979; Lin and Guggenheim 1983). As in the case of sapphirine-khmaralite, this arrangement eliminates possible Be-O-Be bridges, minimizes the number of Be-O-Al bridges and maximizes the number of Be-O-Si bridges. In addition, predominance of Ca in the interlayer site could supply

charge needed to make up the deficit resulting from  $\text{Be}^{2+}$  substituting for  $\text{Al}^{3+}$  in margarite-bityite. J.-L. Robert (pers. comm. to Černý et al. 1995) suggested that preferred incorporation of Be in lepidolite over muscovite is due to weak interaction of OH groups with tetrahedral oxygens in lepidolite.

### Feldspar group

There are more Be measurements for feldspars than for any other mineral, and these data have been comprehensively reviewed by Smith (1974) and Smith and Brown (1988). In general, feldspar Be contents rarely exceed 20 ppm, even in pegmatites, and Be preferentially enters sodic plagioclase relative to calcic plagioclase and K-feldspar (see also London and Evensen, this volume). For example, in a study of plagioclase from anorthosite, “basalt”, granite, and pegmatite, Steele et al. (1980; discussed in Smith 1974) found that Be content determined by ion probe increased by nearly three orders of magnitude from calcic plagioclase (~0-1 ppm Be) to sodic plagioclase (~3-30 ppm Be) with a maximum ~200 ppm in Be oligoclase from beryl-bearing pegmatite, the most Be reported in a feldspar. In addition, Be increased with albite content for anorthosite and “basalt” considered individually. While the marked trend is more likely due to structural factors, the observations do not preclude a possible role for a geochemical association of Be and Na in the host rocks of the analyzed plagioclase. More recent studies of plagioclase include Kalt et al. (2001), who reported 79-169 ppm Be (ion probe analyses) in sodian oligoclase in a metapegmatite from Koralmpe, Austria in which Be-bearing muscovite (Table 8) and tourmaline (see below) are also present.

The maximum Be content in K-feldspar cited in the above compilations is 40 ppm in microcline from pegmatite. Roda Robles et al. (1999) reported 1-15 ppm Be in pegmatitic K-feldspar from Salamanca, Spain, and Foord et al. (1989) reported 6.1 ppm Be in pegmatitic microcline (ion probe) from San Diego, California, USA.

Because incorporation of Be in feldspar involves heterovalent substitutions  $\text{Be} \rightarrow \text{Al}$  or  $\text{Be} \rightarrow \text{Si}$ , investigators have proposed coupling with incorporation of rare earth elements for K, Na and Ca (Beus 1956, 1966) or highly charged species such as  $\text{As}^{5+}$  for Si (Smith 1974; Smith and Brown 1988).

### Staurolite

Available data, albeit limited, suggest that staurolite is potentially a major carrier of Be in pelitic rocks:

- An average of 13 ppm Be for 16 staurolite samples (range: ~2 to 45 ppm Be) from mica schist containing porphyroblastic staurolite, garnet and andalusite in the Ladoga formation, Russia (Sergeyev et al. 1967). Average Be contents of the host rocks and of associated biotite are 4 and 3 ppm, respectively (Tables 2, 8). A later study of the same area reported an average of 12 ppm Be in five staurolite samples from the staurolite-andalusite zone and 4 ppm Be in one staurolite sample from sillimanite-muscovite zone (Lebedev and Nagaytsev 1980).
- From 14 to over 30 ppm Be in 22 of 27 staurolite samples from the Keivsky Block, Kola Peninsula, Russia (Shcheglova et al. 2000)
- 15-40 ppm Be in two staurolite samples from pelitic schist north of the Idaho Batholith (Hietanen 1969)
- 14-16 ppm Be in staurolite from a talc-tourmaline schist, northern Victoria Land, Antarctica and 30-40 ppm in staurolite from metapelitic schist, Alpe Sponda, Ticino, Switzerland (Armbruster and Irouschek 1983; Grew et al. 1986; Grew and Shearer, preliminary ion microprobe analyses with a surinamite standard)
- 70-140 ppm Be in Li-bearing Fe-dominant staurolite from Truchas Mountains, New

Mexico, USA; ~0 ppm Be in zincostaurolite from the Zermatt valley, Swiss western Alps; and between ~40 and ~220 ppm Be in magnesiostaurolite from the Dora-Maira massif, Italian western Alps (Holdaway et al. 1986; Chopin et al. in preparation; C. Chopin, pers. comm., ion microprobe analyses with a beryl standard). The last value could be the highest reported for staurolite, but it should be noted that the measurement is based on a scan in which the  $^9\text{Be}^+$  peak was not completely resolved from the  $^{27}\text{Al}^{3+}$  peak (see Hervig, this volume), and the calibration was not direct.

Hölscher (1987) attempted synthesizing a Be-bearing staurolite from gels of two compositions in the  $\text{MgO-BeO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  system at 800°C, 15 kbar and obtained staurolite, yoderite, corundum, chlorite or quartz (?), and a trace of chrysoberyl. That is, staurolite and/or yoderite must have incorporated some Be as the amount of chrysoberyl was insufficient to contain the beryllium in the starting mixture. The cell volumes of the two product staurolites (Hölscher 1987) were only  $3 \text{ \AA}^3$  (or 0.4%) smaller than that of synthetic Be-free magnesiostaurolite (Schreyer and Seifert 1969), i.e.,  $732.4(2)$  to  $732.7(3) \text{ \AA}^3$  vs.  $735.6(3) \text{ \AA}^3$ . Assuming that the observed reduction of the staurolite cell volume is due entirely to incorporation of Be via  $\text{BeSiAl}_2$  and that this substitution shrinks staurolite cell volume by about the same amount as it does sapphirine cell volume (Fig. 4), the 0.4 % reduction in cell volume translates into 2000 ppm Be in Hölscher's (1987) synthetic staurolite. Thus, staurolite Be content merits further investigation with microbeam methods so the problem of inclusions can be avoided.

### Almandine

Although up to 0.19 wt % BeO has been reported in grossular-andradite (e.g., Glass et al. 1944; Warner et al. 1959), available evidence suggests that garnet is not a favorable host for beryllium in metamorphic and most plutonic rocks, i.e., below detection to 5 ppm on average (Hietanen 1969; Lebedev and Nagaytsev 1980, Lyakhovich and Lyakhovich 1983; Zack 2000) and 0.12-1.81 ppm (Bea et al. 1994; Bea and Montero 1999; Bea, pers. comm. 2001). Even in granite pegmatites, no more than 20 ppm Be has been found (Beus 1966, Table 129). Compositions of the analyzed garnets were not given, but presumably they are dominantly almandine in the metamorphic and non-pegmatitic plutonic rocks, but could be spessartine-rich in the pegmatites. Beryllium contents of pyrope-almandine in 5 samples of Napier complex (Antarctica) pelitic granulites are less than 1 ppm (Grew and Shearer, unpublished ion microprobe data).

### Orthopyroxene

Orthopyroxene is a potential carrier of Be in granulite-facies metapelites. In ultramafic nodules containing spinel, diopside, enstatite and olivine from the Eifel, Germany it concentrates Be to some extent: Ol (0.25-0.6 ppm Be) < Opx (0.4-1.1 ppm Be) < Di (0.6-1.2 ppm Be)  $\approx$  Spl (1.0-1.1) (Hörmann 1966).

Pelitic orthopyroxene Be content is expected to be greater because pelitic rocks are richer in Be than ultramafics, which is borne out by preliminary analyses of orthopyroxene in Napier Complex metapelites. Be content of this orthopyroxene ranges from 0.1 to 16 ppm, in some cases, exceeding the Be content of the rock as a whole (Grew et al. 2001b and unpublished ion microprobe data, see below).

### Miscellaneous calcium silicates

Overall, Ca silicates could be somewhat more favorable hosts for Be than the most abundant rock-forming minerals in metapelites, e.g.,

- Scapolite: trace-37 ppm Be
- Clinopyroxene: trace-19 ppm Be
- Amphibole: trace-18 ppm Be; rarely 25-85 ppm

- Amphibole and clinopyroxene incorporate comparable amounts of Be, but less than scapolite

(Bushlyakov and Grigor'yev 1989; Dodge and Ross 1971; Dodge et al. 1968; Domanik et al. 1993; Grew et al. 1991a; Hepp et al. 2001; Hietanen 1971; Kostetskaya et al. 1969; Moxham 1960 1965; Petrov 1973; Petrova and Petrov 1965; Rao 1976; Shaw 1960; Shaw et al. 1963; Wenk et al. 1974). Clinopyroxene (largely omphacite and containing 1.79-4.07 ppm Be) is the main carrier of Be in eclogite from the Central Alps (Zack 2000). One of the more studied minerals with respect to Be content is vesuvianite, yet the amount that can be incorporated in this mineral remains a moot point and newer studies have failed to confirm old reports of high Be contents (Introduction, this volume).

### **Kyanite**

In most cases, Be contents of kyanite are negligible (Table 9), e.g., spectrographic analyses of kyanite separates turned up 2.2 and 22 ppm Be in two samples out of 30 analyzed spectroscopically; Be was near ("trace") or below detection in the other 28. Pomirleanu et al. (1965) reported Be contents between 10 and 1000 ppm (plus an exceptional 10 000 ppm Be in one lot) in kyanite from mica schist in the Sebeş Mountains, southern Carpathian range, Romania and attributed the high Be contents to solutions emanating from nearby beryl-bearing pegmatites. However, contamination from beryl impurities in the kyanite samples cannot be excluded in this case.

### **Distribution of beryllium among common rock-forming minerals**

Analytical difficulties, low concentrations and possible impurities undoubtedly contribute to the scatter in the Be data in Figures 13 and 14. The plotted data are for mineral separates. Data on plutonic rocks have been included because the data on metamorphic rocks are relatively sparse. Although some of the data are contradictory, a definite pattern emerges whether Be contents of rock-forming minerals are compared to whole-rock (Fig. 14) or to biotite (Fig. 13) Be contents (cf. London and Evensen, this volume; Ryan, Fig. 6b, this volume):

staurolite, amphibole > muscovite > plagioclase > biotite  $\approx$  K-feldspar  $\approx$  whole rock > quartz  
 Steppan et al. (2001) reported a similar sequence in amphibolite-facies metapelites from Greece and Switzerland (presumably based on ion microprobe data):

staurolite > plagioclase > muscovite > biotite > tourmaline > garnet > kyanite  
 This sequence is consistent with the negligible Be contents reported in most almandine-rich garnet and kyanite (see above) and schorl-dravite lacking tetrahedral boron (see below).

The data obtained using laser-ablation ICP-MS for *in situ* analyses of minerals in upper-amphibolite- and granulite-facies metamorphic rocks from Peña Negra, Spain, and the Ivrea-Verbano, Italy (Fig. 15) gave a somewhat different sequence, albeit with exceptions:

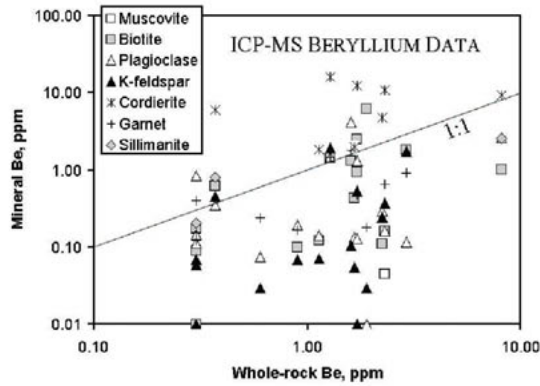
cordierite >> whole-rock  $\approx$  sillimanite  $\geq$  biotite  $\approx$  garnet > plagioclase > K-feldspar

That many of the minerals contain less Be than the rock as a whole could be interpreted to indicate the presence of another carrier of Be, e.g., quartz, which was not analyzed. However, a significant role for quartz is not indicated by preliminary ion microprobe data on Napier complex granulite-facies rocks in which sapphirine takes the place of cordierite as the major carrier of Be (Grew et al. 2001b and unpublished data):

sapphirine (29-2200 ppm Be) >> orthopyroxene (0.1-16 ppm Be)  $\approx$  sillimanite (0.1-15 ppm Be) > garnet (0.06-0.2 ppm Be)  $\approx$  quartz (0.01-0.8 ppm Be); the position of the rock as a whole is variable (1.4-7.1 ppm Be).

**Table 9.** Beryllium and boron contents of  $\text{Al}_2\text{SiO}_5$  and related phases.

Mineral, locality	B, ppm	Be, ppm (n)	Source
<b>METAMORPHIC <math>\text{Al}_2\text{SiO}_5</math> PHASES</b>			
Sillimanite, miscellaneous	30-170	Trace-25 (3)	Pearson & Shaw (1960)
Andalusite, miscellaneous	<10-25	<0.5-2 (6)	
Kyanite, miscellaneous		<0.5-trace (11)	
Kyanite, miscellaneous, Brazil		<2-22 (17)	Herz & Dutra (1964)
Kyanite, Franciscan-Catalina, Calif., USA		0	Domanik et al. (1993)
Kyanite, Carpathian Mtns., Romania		between 10 and 1000(1)	Pomirleanu et al. (1965)
Kyanite, andalusite, Boehls Butte, Idaho, USA		0 (3)	Hietanen (1956)
Kyanite, whiteschist, Zambia and Tajikistan		0 (3)	Grew et al. (1998b)
Sillimanite, Urungwe, Zimbabwe	1400	12 <sup>†</sup>	Grew et al. (1997)
Sillimanite, Port Shepstone, South Africa	1000	16	Grew et al. (1990); Grew (unpublished data)
Sillimanite, Bok se Puts, South Africa	1200	21	Grew (unpubl. data)
Sillimanite, Napier Complex, Antarctica	<1 (?)	0.1-15 (7)	Grew & Shearer (unpublished data)
Sillimanite, migmatite, Peña Negra, Spain		0.8-2.6 (2)	Bea (pers. comm.. 2001)
Sillimanite, Ivrea-Verbano, Italy		0.2	
<b>PEGMATITIC <math>\text{Al}_2\text{SiO}_5</math> PHASES, NO ASSOCIATED BE PHASES</b>			
Sillimanite, Almgjotheii, Norway and Andrahomana, Madagascar	1100-2000	290-480(5) <sup>†</sup>	Grew et al. (1998c)
Andalusite, ditto	10-60	<0.4(2) <sup>†</sup>	
<b>PEGMATITIC <math>\text{Al}_2\text{SiO}_5</math> PHASE ASSOCIATED WITH A BE PHASE</b>			
Sillimanite, "Christmas Point" (Napier Complex), Antarctica	6	23	Grew (unpublished data). Associated with surinamite.
Sillimanite, "Zircon Point" (Napier Complex), Antarctica	170-200	100-140(2)	
Sillimanite, Taseyevskoye muscovite deposit, Russia		20	Saltykova (1959). Possibly associated with chrysoberyl (see Beus 1960, p. 206)
<b>BOROALUMINOSILICATES</b>			
Boralsilite, miscellaneous		12-990(8) <sup>†</sup>	Grew et al. (1998a)
Weringite, miscellaneous		40-2200(10) <sup>†</sup>	Grew et al. (1997, 1998c)
Grandidierite, miscellaneous		<0.4-8(3) <sup>†</sup>	
Note: n – number of samples. <sup>†</sup> Be contents reported in original sources have been corrected for revised surinamite standardization, Grew et al. (2000).			



**Figure 15.** Mineral and whole-rock Be contents for high-grade metamorphic rocks from Peña Negra, Spain, and the Ivrea-Verbano, Italy (Bea et al. 1994; Bea and Montero 1999; F. Bea, pers. comm. 2001). Whole-rock Be contents were obtained by ICP-MS (mass spectrometry) and mineral Be contents, by laser-ablation ICP-MS. The latter are averages of analyses at several points per sample. Detection level should have been close to 0.05 ppm Be. Amounts reported as being below detection were not included in the average, unless all were, in which case, the amount was plotted as 0.01 ppm Be.

Orthopyroxene and sillimanite Be contents increase regularly with increasing sapphirine Be content, but not with whole-rock Be content, a situation consistent with approach to an equilibrium distribution of Be among the three minerals. Most likely, bulk Be content of cordierite- and sapphirine-bearing rocks is determined by the modal amount and Be content of cordierite and sapphirine, which concentrate Be so markedly relative to associated minerals.

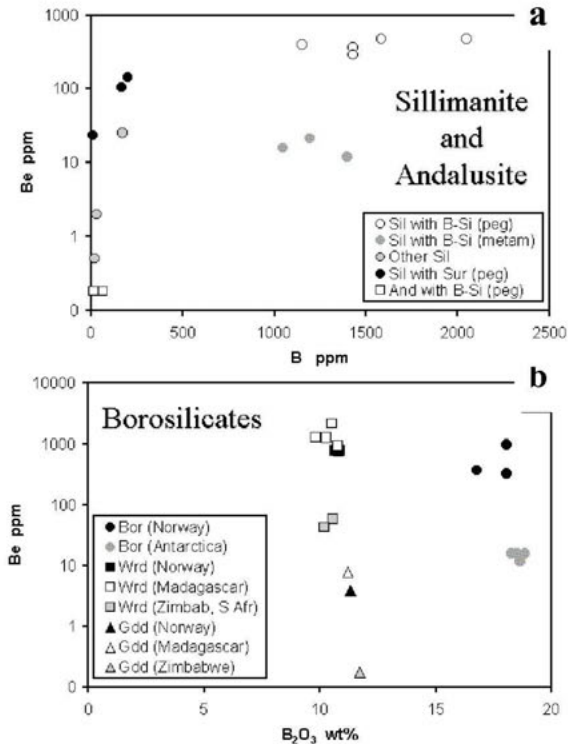
Kornerupine-prismatine (see below) is another potential “sink” for Be in metamorphic rocks. Available data, albeit somewhat contradictory, suggest that sequence of fractionation is most likely sapphirine  $\approx$  kornerupine-prismatine > cordierite (Grew et al. 1987, 1990, 1995, 1998b).

### The special case of boron

Compared to other silicates, several borosilicates and minerals containing significant non-essential boron incorporate a relatively large amounts of Be, the converse of significant B in some beryllosilicates, e.g., bityite (see above).

**Sillimanite, andalusite and related borosaluminosilicate phases.** The borosilicates boralsilite,  $\text{Al}_{16}\text{B}_6\text{Si}_2\text{O}_{37}$ , werdingite,  $(\text{Mg},\text{Fe})_2\text{Al}_{14}\text{B}_4\text{Si}_4\text{O}_{37}$ , and grandidierite,  $(\text{Mg},\text{Fe})\text{Al}_3\text{BSiO}_9$ , together with sillimanite and andalusite, constitute a family of borosaluminosilicates based on chains of edge-sharing  $\text{AlO}_6$  octahedra (Peacor et al. 1999). Pearson and Shaw (1960) suggested that sillimanite incorporates more Be than either andalusite or kyanite, which has been confirmed by later analyses (Table 9), including those of sillimanite and andalusite associated with borosilicates in pegmatites and metamorphic rocks (Fig. 16a). Incorporation of beryllium appears to be greater in B-bearing sillimanite, e.g., B-poor sillimanite associated with surinamite in beryllium pegmatites of the Napier Complex, Antarctica contains less beryllium than pegmatitic sillimanite richer in B, but not associated with any Be phase. However, andalusite

associated with the Be- and B-bearing sillimanite from pegmatites contains negligible Be and B (Fig. 16a). Hölscher (1987) attempted synthesizing a Be-bearing sillimanite using a starting composition of  $0.875\text{Al}_2\text{SiO}_5 + 0.125\text{BeSiAl}_2$  at  $780^\circ\text{C}$ , 6 kbar; no B was present. Cell parameters of the product sillimanite, which had formed with chrysoberyl, corundum and quartz, are identical to Be-free sillimanite, which led her to conclude that very little beryllium was incorporated in the synthetic sillimanite. In contrast Gelsdorf et al. (1958) reported that as much as 1.5 wt % BeO could be incorporated in synthetic mullite at  $1500^\circ\text{C}$ , which resulted in a 0.38% reduction in the cell volume, largely in the c direction.



**Figure 16.** Beryllium (log scale) and boron contents of borosilicates. Be contents reported in original Grew et al. sources have been corrected for revised surinamite standardization, Grew et al. (2000). (A) Sillimanite (Sil) and andalusite (And) in association with borosilicate minerals (B-Si) from pegmatites and metamorphic rocks in Norway, Madagascar, Zimbabwe and South Africa (Grew et al. 1997, 1998c, unpublished data) or with surinamite (Sur) in Napier Complex beryllium pegmatites (Grew unpublished data); "other" refers to assemblages in which no mention is made of associated B or Be minerals (Pearson and Shaw 1960). (B) Boralsilite (Bor), werdingite (Wrd) and grandidierite (Gdd) from pegmatites in Norway and Madagascar and from metamorphic rocks in Zimbabwe and South Africa (Grew et al. 1997 1998a,c). The Be contents of associated werdingite and grandidierite increase as follows: Zimbabwe metamorphic rock < Norway pegmatite < Madagascar pegmatite.

Boralsilite and werdingite from pegmatites in Norway and Madagascar contain about

1000 ppm Be, over two orders of magnitude more than granddierite from these two pegmatites (Fig. 16b), i.e., the relationship between the Be signatures of boralsilite-werdingite and granddierite mirrors the relationship between the Be signatures of sillimanite and andalusite. Available data suggest that boralsilite and werdingite are more closely related in structure to one another and to sillimanite, e.g., werdingite-boralsilite intergrowths suggestive of exsolution (Grew et al. 1998a) and the presence of werdingite-like domains in sillimanite (Niven et al. 1991; Werding and Schreyer 1992). Granddierite and andalusite are closer in structure to one another than either to sillimanite (Stephenson and Moore 1968; Niven et al. 1991). In summary, the crystallographic differences between boralsilite, werdingite, sillimanite, and mullite on the one hand, and andalusite and granddierite on the other, are reflected in the amount of Be incorporated in a Be-bearing environment.

**Tourmaline group.** Beryllium contents of tourmaline-group minerals are generally low, including samples from pegmatites (Henry and Dutrow 1996; this paper, Table 10). The high, presumably wet-chemical (but method not specified) Be contents reported by Otrashchenko et al. (1971) should be viewed with caution given anomalies in other aspects of the reported compositions (high SiO<sub>2</sub> or K<sub>2</sub>O, low H<sub>2</sub>O). Instead, the highest Be content (120 ppm by SIMS, A. Kalt, pers. comm.) reported in lithian excess-boron olenite containing significant <sup>14</sup>B from a metapegmatite at Koralmpe, Austria (Kalt et al. 2001) is probably a better measure of the maximum amount of Be accepted in tourmaline-group minerals. Beryllium content tends to increase with <sup>14</sup>B in the Koralmpe tourmalines, which range from Mg-rich schorl lacking <sup>14</sup>B to lithian olenite with <sup>14</sup>B/(<sup>14</sup>B+<sup>14</sup>Al+Si) = 0.15, a further indication that minerals containing variable amounts of tetrahedral B are more receptive to Be incorporation than the same mineral lacking tetrahedral B.

**Kornerupine-prismatine series.** The highest BeO contents reported in this series, (□,Fe,Mg)(Al,Mg,Fe)<sub>5</sub>(Si,Al,B)<sub>5</sub>O<sub>21</sub>(OH,F), are 0.32 and 0.74 wt % in kornerupine from whiteschists from Tajikistan and Zambia, respectively (Grew 1996; Grew et al. 1998b; corrected for revised surinamite standardization, Grew et al. 2000). In a crystal structure refinement of the kornerupine containing 0.74 wt % BeO, which corresponds to 0.22 Be/21.5 O, Mark Cooper (pers. comm. 2001) reports that Be is found only at the third of three T sites for which he determined a preliminary occupancy of 0.17Si, 0.19Al, 0.44B, and 0.20Be. Given the absence of a Be-saturating phase in whiteschist, it is likely that kornerupine-prismatine could incorporate significantly more Be. Hölscher (1987) attempted to synthesize a Be-bearing, B-free kornerupine at 780°C, 6 kbar using a starting composition of Mg<sub>3.5</sub>Al<sub>6</sub>Be<sub>0.5</sub>Si<sub>4</sub>O<sub>20</sub>(OH)<sub>2</sub>, but obtained only a trace of kornerupine among the products.

### Crystallographic features favoring incorporation of Be in minerals

Beryllium incorporation appears to be very site specific; substantial amounts are incorporated on certain sites, but not on others (Hawthorne and Huminicki, this volume). Because of the large difference in charge between Be<sup>2+</sup> and Si<sup>4+</sup>, Be would be expected to share sites with B or Al instead of Si despite the greater disparity in size (Si 0.26, Be 0.27, B 0.11, Al 0.39 Å, Shannon 1976). Nonetheless, Be-Si miscibility is observed in several minerals, particularly when Al or B is also present, e.g., khmaralite, kornerupine. Availability of abundant tetrahedral Al in margarite and tetrahedral B in olenitic tourmaline could explain the preference of Be for these minerals over micas containing less tetrahedral Al and tourmaline containing negligible tetrahedral B.

Similar constraints may be controlling the incorporation of Be in borooalumino-silicates. Boralsilite, werdingite and sillimanite contain <sup>14</sup>B or <sup>14</sup>Al, which are absent in



Table 10. Beryllium content of tourmaline

Tourmaline species	Rock Type, Locality	Be, ppm (n)	Source
“Black” (schorl?)	Pegmatite, Snares., Norway	4	Goldschmidt (1958)
“Red” (elbaite?)	Pegmatite, San Diego, California, USA	120	
Not specified	Miscellaneous plutonic rocks	5.0(2)-17.4(9)	Lyakhovich & Lyakhovich (1983) Averages only
	Altered granites	31.2(5)	
	Pegmatite	21.8(8)	
Schorl (?)	Quartz veins	3.2	Otroschenko et al. (1971)
	Quartz veins, Uzbekistan	220-360 (2)	
Uvite	Skarn, Talas Mtns., Kyrgyzstan	360 (1)	Grew et al. (1998b)
Dravite	Whiteschist, Zambia and Tajikistan	0-3 (3)	
Schorl-foitite	Granulite-facies pegmatite, I. Arsenmann Hills, Antarctica & Almgjotheii, Norway	0.4-7(8)	Grew et al. (1998a)
Mg-rich schorl	Meta-pegmatite and contact-metasomatic tourmalinite, Koralpe, Austria	6-25	Kalt et al. (2001); A. Kalt (pers. comm.)
Lithian excess-boron olenite		40-120	
Dravite	Pegmatite(?), Madagascar	13	Dyar et al. (2001)
Schorl	Pegmatite, Mozambique	22	
Elbaite	Pegmatite, Brazil	19	

Note: n – number of samples.

andalusite and grandierite (Peacor et al. 1999), and Be may be more readily accommodated at these sites rather than at  $^{[4]}\text{Si}$ , thereby explaining the fractionation of Be into boralsilite, werdingite and sillimanite relative to associated andalusite and grandierite. In addition, the greater variety of polyhedra cross-linking the octahedral chains in boralsilite, werdingite and in the werdingite-like domains in B-bearing sillimanite, could play an important role by providing a flexibility that allows heterovalent substitutions involving Be, B and Al.

### CONCLUSION

As noted in the Introduction to this chapter, metamorphic rocks are a critical link in the crustal Be budget, that is, getting Be from sediments to granites, where igneous processes concentrate Be (London and Evensen, this volume) into economic deposits, both pegmatitic and volcanogenic. Retention of beryllium in sediments during burial and heating depends on the minerals constituting metasedimentary rocks. Data summarized in this chapter suggest that the few ppm Be present in most terrigenous sediments could be easily accommodated in common rock-forming silicates, most importantly, muscovite, so beryllium is not expected to be lost at low to medium grades of metamorphism where muscovite is stable. Staurolite could also play a significant role in medium-grade rocks, particularly in rocks with little or no muscovite. At temperatures above which muscovite and staurolite break down, beryllium retention depends on the presence of another suitable host, such as cordierite. The breakdown of muscovite is often accompanied by anatexis, and this is a critical juncture in the fate of beryllium in buried sediments. As noted by Sighinolfi (1973), there is a possibility of both Be depletion and Be enrichment associated with anatexis (or fluid movement) in the upper amphibolite-facies and granulite-facies conditions. London and Evensen (this volume) suggest that at lower pressures, cordierite could form and would be the only common-rock forming mineral to retain Be in the restite, resulting in melts depleted at Be. Conversely, at higher pressures, where cordierite is not stable, garnet-sillimanite-biotite restites may not be able to retain Be, which would be lost to the melt. At greater depths, a potential host is sapphirine, so again Be could be retained in the restite. Thus, it is possible beryllium could be retained in metasediments buried to lower crustal depths. The ultrahigh-temperature Napier Complex is an example of sapphirine-bearing lower crustal metasediments that have retained Be, indeed, Fig. 1b suggests a modest enrichment. Evidently, the Napier metapelites never experienced a melting event that depleted them in Be, i.e., these rocks most likely followed a P-T path within the stability fields of cordierite and sapphirine. However, there are anatectic Be-bearing pegmatites in the Napier. If sapphirine retains Be, how could it be released into an anatectic melt? The Strona granulites lack cordierite and sapphirine and are depleted in Be; could these have lost Be-bearing melts similar to those discussed by London and Evensen (this volume)?

The evolution outlined above is very sketchy. There are many aspects that need more detailed study. One is the Be content of the starting material. What are the average Be contents of the major sedimentary rocks? Distribution of Be among minerals and between minerals and melt is still very imperfectly known, as evident in the scatter in Figures 13-15 and in London and Evensen (this volume). Low Be concentrations and contamination has stymied the acquisition of the requisite compositional data; these studies require microbeam technologies such as LA-ICP-MS, PIGE or SIMS. More consideration needs to be given to possible Be enrichments and mobility in situations not involving obvious Be metasomatism such as greisens. For example, Figure 6 shows a decrease in sapphirine BeO content away from a nodule of magnesiotaaffeite- $6N'3S$  ("musgravite"), implying outward migration of Be. A fourth aspect needing attention is the behavior of Be in the anatectic process, itself currently a popular field of research. Rocks undoubtedly undergo

melting over a protracted extent of their metamorphic evolution at depth, resulting in many opportunities for Be loss or exchange. In order to understand how Be gets into a granitic system, one must understand how Be distributed between anatectic melts, fluid phase and the sediments undergoing metamorphism and anatexis.

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