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Original paper

## The chevkinite group: underestimated accessory phases from a wide range of parageneses

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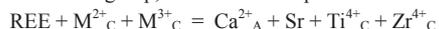
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**Abstract.** Chevkinite-group minerals are widespread in a very wide range of igneous and metamorphic parageneses, forming important components of accessory mineral assemblages. Their presence in a rock may be difficult to establish by standard optical techniques, which has contributed to their importance being underestimated; a combination of SEM and EMPA is recommended here. Currently, there are eleven IMA-approved members of the group but undoubtedly several more will be described in the near future. There is considerable compositional variation in the group, which can be expressed as:



where A and C are structural sites. Chevkinite-group minerals strongly fractionate geochemically coherent pairs, such as LREE-HREE, Nb-Ta, Zr-Hf and Th-U, and thus play a critical role in geochemical modelling.

*Key-words:* chevkinite group minerals, chevkinite, perrierite, chemical composition, classification

### 1. Introduction

Chevkinite is normally considered to be a rare accessory mineral, occurring typically in alkaline rocks, and as a result has been relatively neglected in the literature. For example, in a recent special issue of *Elements* dedicated to rare earth elements (vol. 8, issue 5, 2012), chevkinite, which can contain up to 50wt% REE<sub>2</sub>O<sub>3</sub>, is mentioned only once. However,

much recent work, summarised by Macdonald and Belkin (2002) and Macdonald et al. (2009), has shown that chevkinite and related phases, the chevkinite group of minerals (CGM), occur in a very wide range of igneous and metamorphic parageneses. We know of 250 localities world-wide where members of the group have been recorded and we believe that that number could easily double with further research, even on well-studied suites. For example, we have found chevkinite in such thoroughly studied rocks as the Ilímaussaq agpaitic complex, SW Greenland, and in a majority of the Palaeogene granites of Scotland and Northern Ireland, where it is the dominant REE-bearing phase (Macdonald et al. 2013).

The chevkinite group is important geochemically. They are strong concentrators of the rare earth elements (REE),  $\Sigma\text{REE}_2\text{O}_3$  being up to  $\sim 50\text{wt}\%$ , and they fractionate the LREE from the HREE. Chevkinite minerals can also carry significant concentrations of Zr, Nb, Sc and Th and they fractionate Zr-Hf, Nb-Ta and Th-U relative to mantle and crustal abundances. Any attempts to model the evolution of magmas on the basis of REE or incompatible trace element abundances and behaviour must take account of any CGM present in the rocks. In this paper, we describe the members of the CGM, their modes of occurrence, the compositional variations in the group, some geochemical results of CGM fractionation, and the likelihood of discovering new members of the group.

## 2. Members of the chevkinite group

Eleven members of the chevkinite group are currently accepted by the International Mineralogical Association (Table 1). Two subgroups have been distinguished, the chevkinite and perrierite subgroups (Sokolova et al. 2004), containing 5 and 6 members respectively. Chevkinite-(Ce) and perrierite-(Ce) are overwhelmingly the most abundant, constituting 64% and 32%, respectively, of good-quality analyses of CGM known to us. The compositions of chevkinite and perrierite closely approach the formula  $\text{A}_4\text{BC}_2\text{D}_2\text{Si}_4\text{O}_{22}$  (or alternatively  $\text{A}_4\text{BC}_2\text{D}_2(\text{Si}_2\text{O}_7)_2\text{O}_8$ ), where A = REE, Ca, Sr, Th; B =  $\text{Fe}^{2+}$ ; C =  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ , Mn, Mg, Zr, Nb; and D = Ti (Gottardi 1960; Bonatti, Gottardi 1966; Ito 1967; Ito, Arem 1971) (Table 2). Macdonald, Belkin (2002) presented an empirical discrimination between chevkinite and perrierite using CaO-FeO\* relationships, which was modified by Macdonald et al. (2009) by the addition of SrO to CaO (Fig. 1) to allow other, particularly Sr-rich, CGM members to be included in the scheme. Although empirical, the discriminant also distinguishes phases with  $\beta \sim 100^\circ$  (chevkinite subgroup) and those with  $\beta \sim 113^\circ$  (perrierite subgroup), the angle being the most robust difference between the two subgroups (Haggerty, Mariano 1983). The relationships between other members of the perrierite subgroup are poorly known and no compositional boundaries have yet been proposed, e.g. between perrierite and strontiochevkinite. Furthermore, allocation of cations to specific structural sites becomes more complicated in the Sr-rich members of the perrierite subgroup; rather than the standard  $\text{A}_4\text{BC}_2\text{D}_2\text{Si}_4\text{O}_{22}$  formulation, Miyajima et al. (2001) refer to renegeite as  $\text{Sr}_4\text{ZrTi}_4\text{Si}_4\text{O}_{22}$  and Miyajima et al. (2002) give matsubaraite the formula  $\text{Sr}_4\text{Ti}_5(\text{Si}_2\text{O}_7)_2\text{O}_8$ . Until there is a much fuller understanding of the relationship between mineral structure and composition in the group, the classification in Figure 1 is nevertheless a useful tool, especially in EMPA-based studies.

TABLE 1

Members of the chevkinite group, accepted by the CNMNC-IMA

Mineral	Ideal formula	Reference
<i>Chevkinite subgroup</i>		
Chevkinite-(Ce)	$(\text{REE}, \text{Ca})_4\text{Fe}^{2+}(\text{Ti}, \text{Fe}^{3+}, \text{Fe}^{2+}, \text{Al})_2\text{Ti}_2\text{Si}_4\text{O}_{22}$	Ito, Arem (1971)
Polyakovite-(Ce)	$(\text{REE}, \text{Ca})_4(\text{Mg}, \text{Fe}^{2+})(\text{Cr}, \text{Fe}^{3+})_2(\text{Ti}, \text{Nb})_2\text{Si}_4\text{O}_{22}$	Sokolova et al. (2001)
Maoniupingite-(Ce)	$(\text{REE}, \text{Ca})_4(\text{Fe}^{3+}, \text{Ti}, \text{Fe}^{2+}, \square)(\text{Fe}^{3+}, \text{Fe}^{2+}, \text{Nb}, \text{Ti})_2\text{Ti}_2\text{Si}_4\text{O}_{22}$	Shen et al. (2005)
Dingdaohengite-(Ce)	$\text{Ce}_4\text{Fe}^{2+}\text{Ti}_2\text{Ti}_2(\text{Si}_2\text{O}_7)_2\text{O}_8$	Xu et al. (2008)
Christofschäferite-(Ce)	$(\text{Ce}, \text{La}, \text{Ca})_4\text{Mn}(\text{Ti}, \text{Fe}^{3+})_3(\text{Fe}^{3+}, \text{Fe}^{2+}, \text{Ti})(\text{Si}_2\text{O}_7)_2\text{O}_8$	Chukanov et al. (2012)
<i>Perrierite subgroup</i>		
Perrierite-(Ce)	$(\text{REE}, \text{Ca})_4\text{Fe}^{2+}(\text{Ti}, \text{Fe}^{3+}, \text{Fe}^{2+}, \text{Al})_2\text{Ti}_2\text{Si}_4\text{O}_{22}$	Ito, Arem (1971)
Strontiochevkinite	$(\text{Sr}_2[\text{La}, \text{Ce}]_{1.5}\text{Ca}_{0.5})_4\text{Fe}^{2+}_{0.5}\text{Fe}^{3+}_{0.5}(\text{Ti}, \text{Zr})_2\text{Si}_4\text{O}_{22}$	Haggerty, Mariano (1983)
Rengeite	$\text{Sr}_4\text{ZrTi}_4\text{Si}_4\text{O}_{22}$	Miyajima et al. (2001)
Matsubaraite	$\text{Sr}_4\text{Ti}_5(\text{Si}_2\text{O}_7)_2\text{O}_8$	Miyajima et al. (2002)
Hezuolinite	$(\text{Sr}, \text{REE})_4\text{Zr}(\text{Ti}, \text{Fe}^{3+}, \text{Fe}^{2+})_2\text{Ti}_2\text{O}_8(\text{Si}_2\text{O}_7)_2$	Yang et al. (2012)
Perrierite-(La)	$(\text{La}, \text{Ce}, \text{Ca})_4(\text{Fe}^{2+}, \text{Mn})(\text{Ti}, \text{Fe}^{3+}, \text{Al})_4(\text{Si}_2\text{O}_7)_2\text{O}_8$	Chukanov et al. (2011)

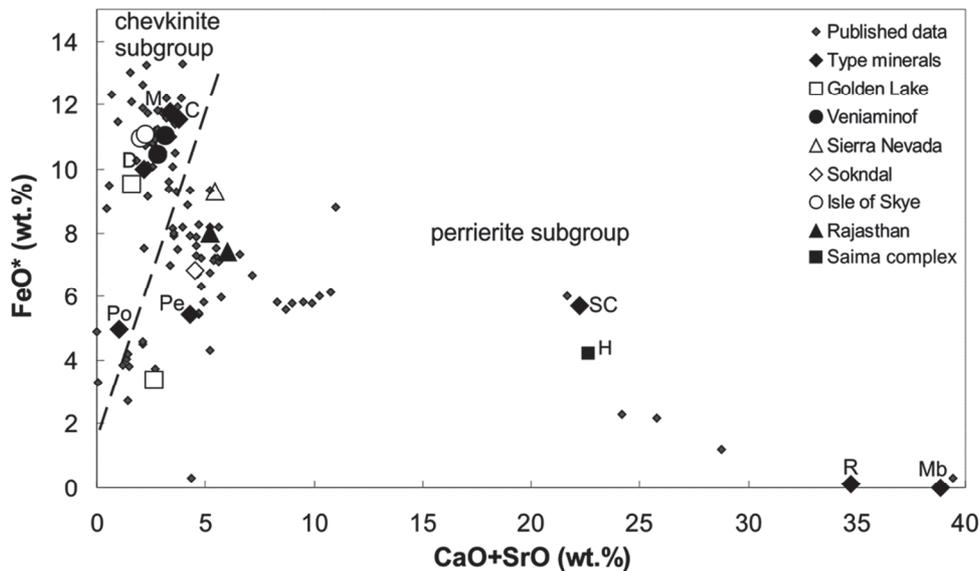


Fig. 1. Selected analyses of CGM plotted on the (CaO+SrO) – FeO\* discriminatory diagram of Macdonald et al. (2009). Members of the group currently accepted by the IMA are (Table 1): M - maoniupingite-(Ce); C - chevkinite-(Ce); D - dingdaohengite-(Ce); H - hezuolinite; Po - polyakovite-(Ce); Pe - perrierite-(Ce); SC - strontio-chevkinite; R - rengeite; Mb - matsubaraite. Analyses of perrierite-(La) and christofschäferite-(Ce) (Table 1) have not yet been published. Other symbols are for CGM from a range of localities, from Macdonald et al. (2009).

TABLE 2

Composition of type minerals in the chevkinite group

Sample	Chevkinite subgroup					Perrierite subgroup		
	1	2	3	4	5	6	7	8
Nb <sub>2</sub> O <sub>5</sub>	1.90	3.98	0.47	2.79	0.08	<0.01	0.24	0.00
SiO <sub>2</sub>	20.62	19.09	19.29	20.03	20.43	19.71	22.58	22.60
TiO <sub>2</sub>	15.16	9.49	18.26	16.05	18.81	22.78	29.88	39.06
ZrO <sub>2</sub>	0.31	-	-	-	0.62	10.60	9.49	0.00
ThO <sub>2</sub>	3.48	2.79	0.16	0.41	2.87	<0.01	-	0.00
Al <sub>2</sub> O <sub>3</sub>	0.50	-	0.04	0.17	3.93	0.11	0.20	0.00
Cr <sub>2</sub> O <sub>3</sub>	-	7.42	-	-	-	0.46	-	-
Y <sub>2</sub> O <sub>3</sub>	0.13	0.38	0.00	0.02	0.35	<0.01	-	0.00
La <sub>2</sub> O <sub>3</sub>	15.19	15.94	19.53	12.73	11.01	8.79	0.00	0.00
Ce <sub>2</sub> O <sub>3</sub>	20.52	24.24	28.08	23.03	21.53	8.33	0.38	0.00
Pr <sub>2</sub> O <sub>3</sub>	1.32	2.01	-	1.58	1.95	-	0.10	0.00
Nd <sub>2</sub> O <sub>3</sub>	3.37	4.76	-	5.64	6.22	-	0.29	0.00
Sm <sub>2</sub> O <sub>3</sub>	-	0.38	-	0.37	0.58	-	0.04	0.00
FeO*	11.55	4.96	10.00	11.78	5.41	5.70	0.10	0.00
MnO	0.73	0.05	-	0.32	0.04	0.11	-	0.00
MgO	0.24	2.61	1.32	0.17	0.87	<0.01	0.00	0.00
CaO	3.62	1.06	2.17	3.39	4.26	1.78	0.43	0.00
SrO	0.17	-	-	-	0.03	20.48	34.32	38.84
BaO	0.07	-	-	-	-	0.31	0.13	0.00
Na <sub>2</sub> O	0.05	-	0.00	-	b.d.	0.05	-	0.00
Total	98.93	99.16	99.32	98.48	98.99	100.37*	98.18	100.50

b.d., below detection. -, not reported. FeO\*, total Fe as Fe<sup>2+</sup>. \* total includes other REE = 1.16 wt.%.

Samples: 1 - chevkinite, near Miass, Urals, Russia (Macdonald, Belkin 2002); 2 - polyakovite, Ilmen Mts, Urals, Russia (Popov et al. 2001); 3 - dingdaohengite, Bayan Obo, China; 4 - maoniupingite, Mianning, Sichuan, China (Shen et al. 2005; 5 - perrierite, Nettuno, Italy (Macdonald et al. 2009); 6 - strontio-chevkinite, Sarambi, Paraguay (Haggerty, Mariano 1983); 7 - renegeite, Itoigawa-Ohmi district, Japan (Miyajima et al. 2001); 8 - matsubaraite, Itoigawa-Ohmi district, Japan (Miyajima et al. 2002). All analyses given as in original publications.

### 3. Difficulties of recognition

Chevkinite group minerals are sorosilicates, normally crystallising in the monoclinic system. They range in colour from brownish black to deep red, lack cleavage and show very brittle fracture. When fresh, they have a strong lustre but on alteration or metamictisation appear earthy. Although CGM from pegmatites can form large, handsome, prismatic crystals (Fig. 2), in the majority of occurrences they are much smaller, 10 µm to 1 mm (Fig. 3-5). This, plus very strong absorption, can make them difficult to recognise under the optical microscope and the CGM have been confused with, *inter alia*, allanite, aenigmatite, ilmenite and rutile. However, in back-scattered electron (BSE) images, CGM are very bright, often the brightest phase in the thin section (Fig. 4a). In our experience, CGM are best located using SEM scans followed by electron microprobe analysis. The process can be time-consuming but usually guarantees that any CGM present are not

overlooked. The existence of REE-free species, such as rengerite and matsubaraitite, means that the REE cannot always be used as a “prospecting tool”.

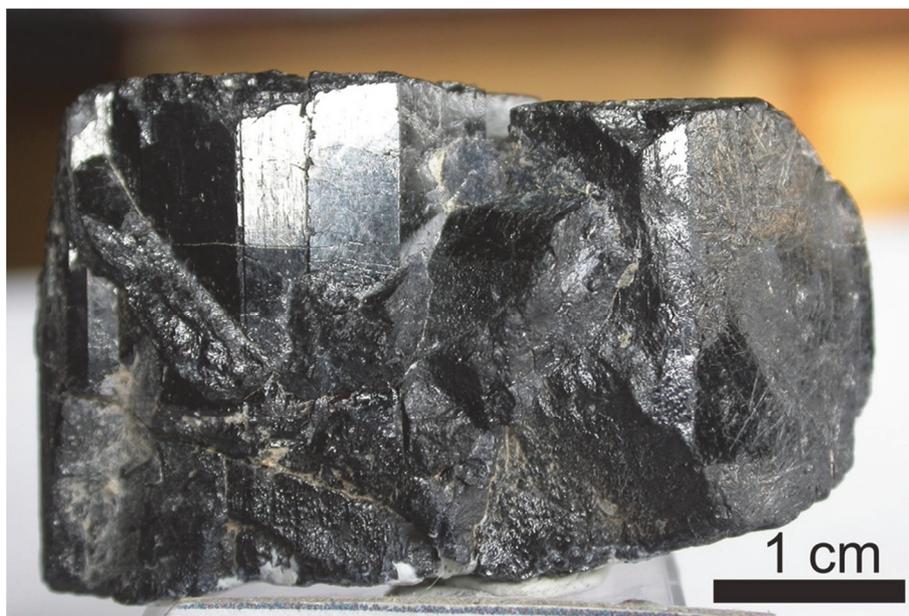


Fig. 2. Gem-quality crystal of chevkinite from Haramosh, Pakistan (B. Bagiński, collection).

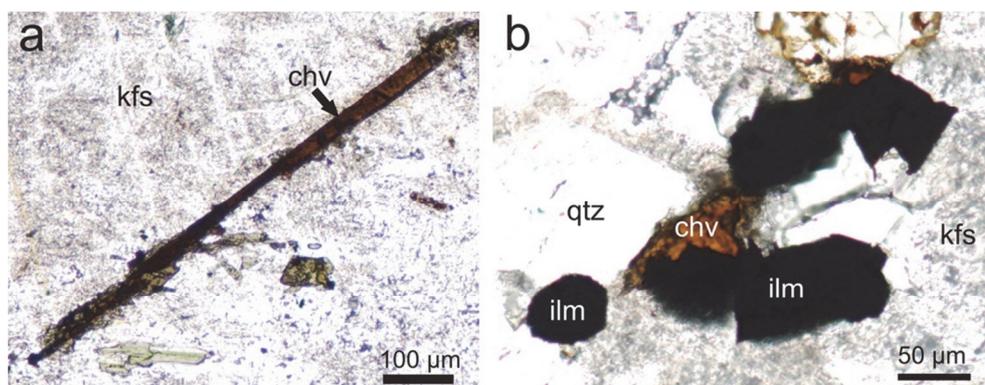


Fig. 3. (a) Acicular, reddish-brown chevkinite-(Ce) crystal in Creag Strollamus Granite, Skye, Scotland (plane polarised light). (b) Anhedral chevkinite-(Ce) mantling ilmenite in granophyre vein, Centre II, Ardnamurchan, Scotland (plane polarised light).

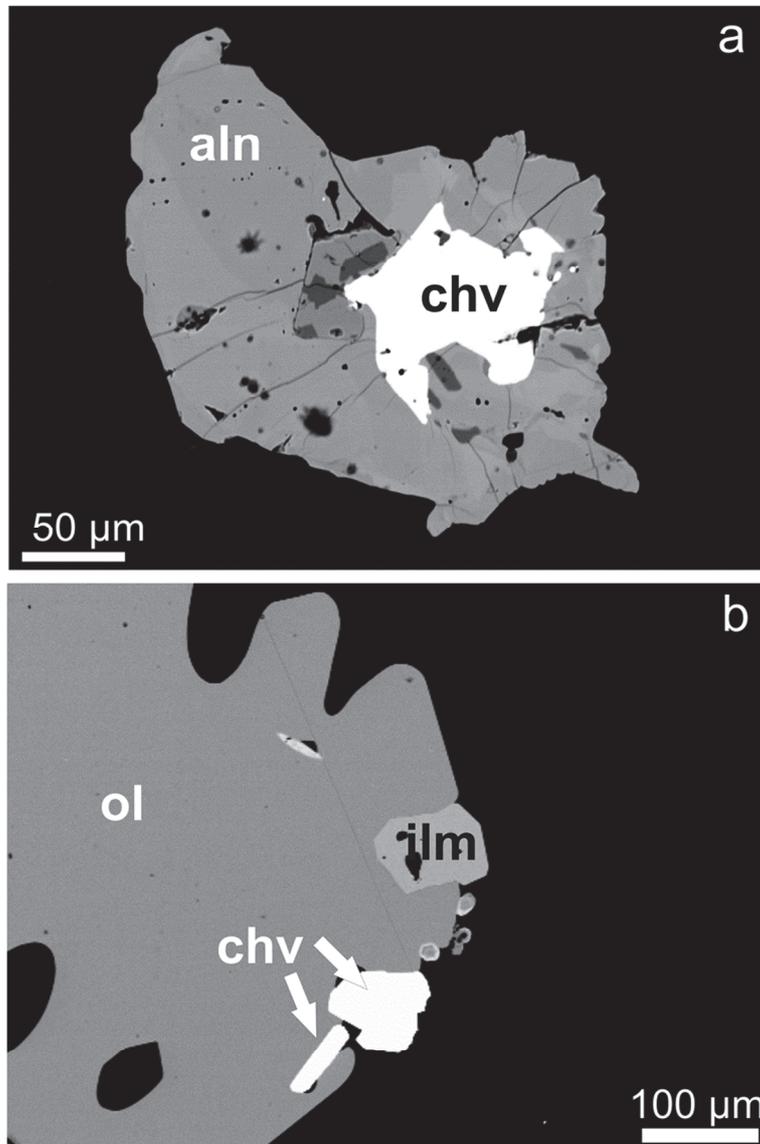


Fig. 4. (a) Chevkinite-(Ce) crystal mantled by allanite-(Ce). Note the brightness of chevkinite on this BSE image. Cumulate in G1 Granite, Mourne Mountains, Northern Ireland. (b) Chevkinite-(Ce) crystals associated with olivine phenocryst, peralkaline rhyolite, Olkaria complex, Kenya; BSE image.

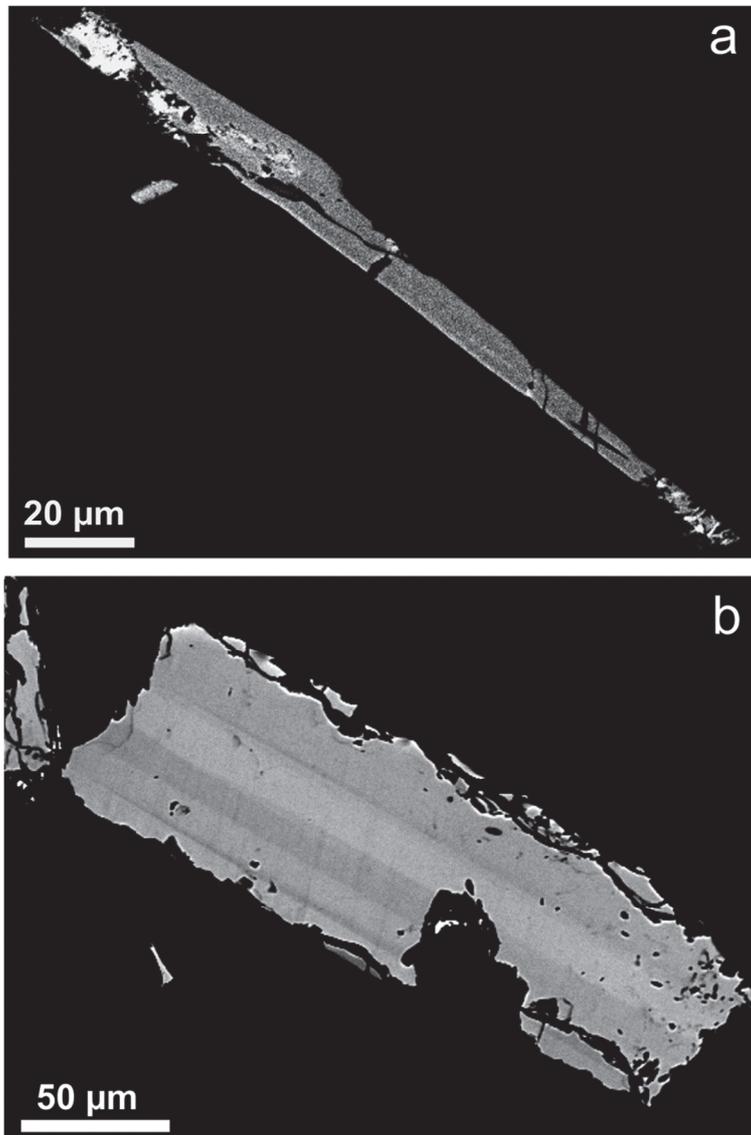


Fig. 5. (a) Acicular chevkinite in quartz crystal, Loch Ainort Granite, Skye, Scotland. (b) Zoned, partly resorbed, prismatic chevkinite-(Ce), Lava Creek Tuff, Yellowstone, USA. BSE images.

Minerals of the chevkinite group show a very wide range of habits (Fig. 3-5). One of the more common, and rather distinctive, is the acicular form shown in Figure 3a and Figure 5a. Where they occur as phenocrysts in eruptive rocks, CGM are very often associated with the other phenocryst phases (Fig. 4b, Fig. 5b). In Figure 3b, chevkinite-(Ce) mantles ilmenite, presumably in a reaction relationship. Figure 3a also depicts a reaction relationship, this time of chevkinite-(Ce) to allanite-(Ce) (see more details in Macdonald et al. 2012).

#### 4. Modes of occurrence

*Chevkinite* is found in a wide range of rock types, including: metaluminous to peralkaline rhyolites, granites and syenites and associated pegmatites; albitites; fenites associated with carbonatite complexes; metasomatic rocks; and ore deposits. We know of only one metamorphic occurrence, in a metacarbonate at Golden Lake, Ontario (Macdonald et al. 2009). In igneous parageneses, it ranges from phenocrysts in rhyolites to late- or post-magmatic phases in the matrix of syenites and granites and in miarolitic cavities. It appears that chevkinite crystallization is restricted to relatively low temperatures, < 900°C.

*Perrierite* occurs in a wider range of environments than chevkinite (Table 3). Igneous parageneses include: metaluminous rhyolites, dacites, granites, granodiorites and diorites; quartz- and nepheline-syenites and associated pegmatites; mafic-intermediate members of potassic volcanic suites; gabbroic complexes (perhaps in quartz-rich lenses); albitites; and carbonatites and associated rocks. It has been recorded, however, from only one peralkaline rhyolite, the scarcely peralkaline Tortoise Shell Mountain rhyolite, California (McCurry 1988). Perrierite has also been recorded from a range of granulite-facies rocks and associated pegmatites from Antarctica and South India. It appears that perrierite crystallizes over a considerable P-T range, up to 1180°C and 10 kbar in some Antarctic examples, and perhaps down to T < 500°C at upper crustal pressures for some ore deposits. Neither chevkinite or perrierite seems to be particularly sensitive to oxygen fugacity; Macdonald and Belkin (2002) collated literature data on a variety of geothermobarometers and phase equilibria studies to show that they crystallised in  $fO_2$  conditions varying from below the fayalite+magnetite+quartz (FMQ) buffer to above the nickel-nickel oxide (NNO) buffer.

The ranges of occurrence of other CGM are more restricted. *Strontiochevkinite* is known from two localities, in rheomorphic fenites (sanidine-aegirine-nepheline dykes) associated with carbonatite plugs at Sarambi, Paraguay (Haggerty, Mariano 1983) and in nepheline syenitic pegmatites at Pegmatite Peak, Bearpaw Mountains, Montana (Chakhmouradian, Mitchell 1999). *Polyakovite-(Ce)* has been recorded from two very different parageneses: from a carbonatite vein of hydrothermal origin at the contact between fenites and metasomatised ultramafic rocks in the Ilmen Mountains, southern Urals, Russia (Popov et al. 2001) and as radioactive inclusions in diamonds from the River Ranch kimberlite pipe, Zimbabwe (Kopylova et al. 1997). Clearly, polyakovite-(Ce) has a very wide stability field. *Rengeite* was first discovered in jadeitic rocks occurring as tectonic inclusions in a serpentinite melange in the Ohmi-Itoigawa region, Japan (Miyajima et al. 2001); a second occurrence of rengeite was recorded in an albite-anorthoclase hornfels from Mt Kaskasnyunchorr, Khibiny complex, Kola, Russia by Yakovenchuk et al. (2005). An orthorhombic form of rengeite has been described by Mashima et al. (2008) from secondary veins associated with jadeitic rocks from Ohmi-Itoigawa. The same suite of rocks hosts *matsubaraitite*, forming a prismatic crystal ~ 0.3 mm long (Miyajima et al. 2002). *Dingdaohengite-(Ce)* is known only from magnesian skarns at the contact of granite and dolomitic marble in the Bayan Obo ore deposit in Inner Mongolia, China (Xu et al. 2008). *Maoniupingite-(Ce)* was identified in carbonatitic veins and alkaline rocks from the Maoniuping rare-earth deposit, Mianning, Sichuan, China (Shen et al. 2005). *Hezuolinite* occurs in a peralkaline nepheline syenite in the Saima alkaline complex, Liaoning Province,

China (Yang et al. 2012). Full descriptions of perrierite-(La) and christofschäferite-(Ce), both from Mendig, Laacher See area, Germany, have not yet been published (Chukanov et al. 2011, 2012).

TABLE 3

Examples of modes of occurrence of chevkinite and perrierite

Locality	Occurrence	Mineral name*	Ref.
<b>Magmatic</b>			
Olkaria complex, Kenya	phenocryst in rhyolite	chevkinite-(Ce)	1
Golden Lake, Labrador	accessory in metacarbonate	chevkinite-(Ce)	2
Timedjelalen, Mali	accessory in syenite	chevkinite-(Ce)	3
Oroscocha, Peru	accessory in kersantite	<i>perrierite-(Ca)</i>	4
Organ Needle pluton	accessory in syenite	perrierite-(Ce)	5
Joe Lott Tuff, Utah	phenocryst in rhyolite	perrierite-(Ce)	6
<b>Late- or post-magmatic</b>			
Roccamonfina, Italy	in miarolitic cavities	<i>perrierite-(Ca)</i>	7
Sabatini volcano, Italy	In miarolitic cavities	<i>perrierite-(Ca)</i>	8
<b>Pegmatitic</b>			
Oslofjord, Norway	syenite	chevkinite-(Ce)	9
Burley Farm, Virginia	granitoid pegmatite	perrierite-(Ce)	2
Mt Charles, E. Antarctica	cutting gneisses	<i>Al-dom. anal. of perr-(Ce)</i>	10
<b>Metasomatic</b>			
Russian Platform	alkaline 'metasomite'	chevkinite-(Ce)	11
Burpala massif, Russia	aegirinitised syenite pegmatite	perrierite-(Ce)	12
<b>Metamorphic</b>			
Golden Lake, Labrador	accessory in metacarbonate	<i>perrierite-(La)</i>	2
Granulites, E. Antarctica	in sillimanite-garnet gneiss	<i>Al-dom. anal. of perr-(Ce)</i>	10

\* Mineral names in italics have not been IMA-approved. Names are based on the dominant cation in the A site. Al-dom. anal. of perr-(Ce) = Al-dominant analogue of perrierite-(Ce). Table modified from table 1 in Macdonald et al. (2009). References: 1 - Macdonald et al. (2002); 2 - Macdonald et al. (2009); 3 - Macdonald, Belkin (2002); 4 - Carlier, Lorand (2008); 5 - Verplanck et al. (1999); 6 - Budding et al. (1987); 7 - Della Ventura et al. (2001); 8 - Parodi et al. (1994); 9 - Segalstad, Larsen (1978); 10 - Belkin et al. (2009); 11 - Povarennikh, Ganseeva (1972); 12 - Portnov (1964).

It appears that CGM are potentially present in a very wide spectrum of igneous or metamorphic rocks and we would be loath to rule out any specific lithology as a potential host. For example, Macdonald et al. (2009) have noted that perrierite has been recorded in metaluminous granites, granodiorites and diorites (and extrusive equivalents) from at least 30 localities and have suggested that careful search will show it to be a very common, if never very abundant, phase in such rocks. In the Polish context, chevkinite group minerals

occur in the Variscan granites in the Sudetes and in the Carboniferous alkaline intrusions of Mazury (Bagiński et al. in preparation).

## 5. Some geochemical issues

Table 4 presents analyses of chevkinite and perrierite, selected to show some of the compositional range. Despite the large ranges in individual oxides, the compositional variation in the CGM follows the general coupled substitution scheme:



(Della Ventura et al. 2001; Vlach, Gualda 2007; Macdonald et al. 2009). For simplicity, the scheme is shown in Figure 6 for the perrierite subgroup only but it is also an excellent representation of variation in the chevkinite subgroup. Symbols on Figure 6 relate to the occurrences of the plotted points, stressing the wide range of parageneses in which the CGM are found.

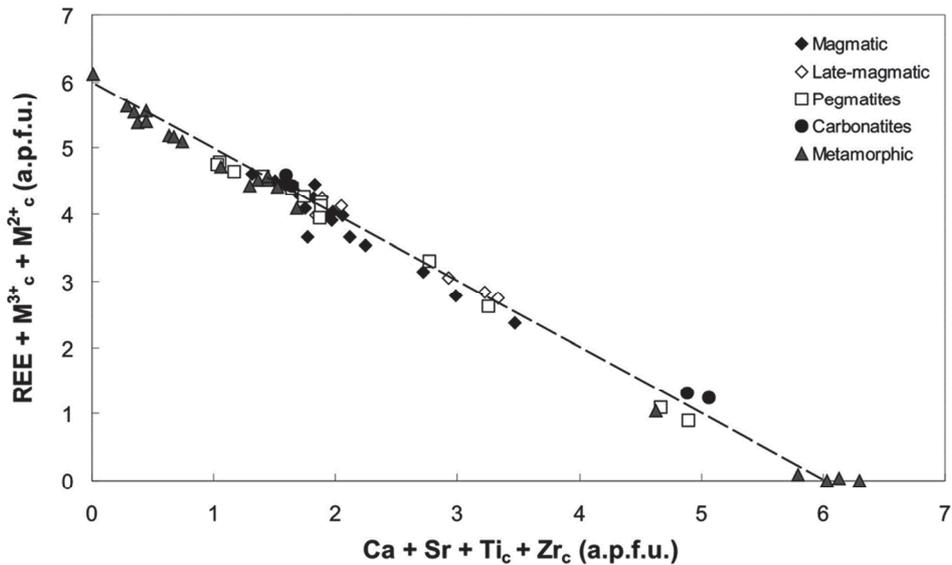


Fig. 6. Generalised coupled substitution scheme for minerals of the perrierite subgroup (from Macdonald et al. 2009). The scheme applies equally to minerals of the chevkinite subgroup.

The list (Table 4) includes three potentially new species. According to the IMA-CNMNC dominant-constituent rule (Hatert, Burke 2008), perrierite with  $(\text{Ca}+\text{Sr}) > (\text{REE}+\text{Y})$  and  $\text{Ca} > \text{Sr}$  in the A site is potentially perrierite-Ca, e.g. the phase from the Oroscocha volcano, Peru (Carlier, Lorand 2008). Where  $(\text{REE}+\text{Y}) > (\text{Ca}+\text{Sr})$  and La is the dominant cation, the mineral could qualify as chevkinite-(La). A mineral from Mt Cronus in the Antarctic has Y as the dominant cation in the A site and Al dominant in the C site; it is potentially the Al-dominant analogue of perrierite-(Y) (Belkin et al. 2009). Confirmation of these names, or introduction of a new terminology, must await a systematic review of chevkinite-group nomenclature by a subcommittee of the IMA-CNMNC.

TABLE 4

Analyses of chevkinite and perrierite, to show some of the compositional range

	Chevkinite subgroup			Perrierite subgroup				
	1	2	3	4	5	6	7	8
Nb <sub>2</sub> O <sub>5</sub>	3.82	3.12	0.23	-	b.d.	0.20	0.74	0.09
SiO <sub>2</sub>	20.18	19.01	19.73	20.30	19.92	18.34	23.15	21.18
TiO <sub>2</sub>	13.77	14.95	17.63	22.09	18.91	18.63	22.19	12.09
ZrO <sub>2</sub>	0.22	0.68	1.34	4.85	0.03	0.15	7.20	b.d.
ThO <sub>2</sub>	1.22	1.59	3.03	0.54	b.d.	0.62	0.48	4.13
Al <sub>2</sub> O <sub>3</sub>	0.30	-	0.53	0.48	2.06	0.38	2.15	8.76
Y <sub>2</sub> O <sub>3</sub>	0.91	0.80	1.47	0.90	0.09	-	b.d.	8.47
La <sub>2</sub> O <sub>3</sub>	12.92	11.70	10.13	11.63	22.83	16.44	9.95	2.17
Ce <sub>2</sub> O <sub>3</sub>	22.16	19.20	20.74	16.27	21.00	21.51	13.21	8.11
Pr <sub>2</sub> O <sub>3</sub>	1.97	1.95	2.12	0.92	1.20	3.11	1.63	1.54
Nd <sub>2</sub> O <sub>3</sub>	6.39	6.16	6.31	2.17	3.17	3.79	1.61	9.84
Sm <sub>2</sub> O <sub>3</sub>	-	0.83	0.73	-	b.d.	-	0.10	5.40
Gd <sub>2</sub> O <sub>3</sub>	-	0.51	0.51	0.04	b.d.	-	0.03	5.79
Dy <sub>2</sub> O <sub>3</sub>	-	0.23	0.13	-	b.d.	-	b.d.	2.76
Yb <sub>2</sub> O <sub>3</sub>	-	0.09	0.15	0.04	b.d.	-	b.d.	0.09
FeO*	13.26	11.40	11.03	6.13	3.37	8.17	6.10	4.04
MnO	0.48	0.15	0.21	0.93	0.01	0.48	b.d.	b.d.
MgO	0.06	b.d.	0.22	0.11	2.99	b.d.	0.22	1.69
CaO	2.30	3.29	3.14	3.06	2.52	1.26	10.83	1.37
SrO	b.d.	b.d.	0.03	7.73	0.12	4.36	-	-
Na <sub>2</sub> O	b.d.	-	b.d.	0.72	b.d.	b.d.	b.d.	b.d.
Total	99.96	95.91*	99.41	98.91	98.22	97.44	99.59	98.79**

*Formulae based on 22 oxygens*

Ca	0.515	0.763	0.694	0.644	0.547	0.292	2.073	0.289
Sr	0.000	0.000	0.004	0.880	0.014	0.546	0.000	0.000
Na	-	-	-	0.274	0.000	0.000	0.000	0.000
Th	0.058	0.078	0.143	0.024	0.000	0.031	0.020	0.185
Y	0.100	0.092	0.161	0.094	0.010	0.000	0.000	0.889

La	0.997	0.933	0.771	0.842	1.706	1.311	0.656	0.158
Ce	1.695	1.521	1.567	1.169	1.558	1.702	0.864	0.586
Pr	0.151	0.153	0.160	0.066	0.089	0.245	0.106	0.111
Nd	0.477	0.476	0.465	0.152	0.229	0.293	0.103	0.694
Sm	-	0.062	0.052	0.000	0.000	0.000	0.006	0.367
Gd	-	0.036	0.035	0.003	0.000	-	0.000	0.379
Dy	-	0.016	0.009	0.000	-	-	-	0.176
Sum A	3.99	4.13	4.06	4.18	4.15	4.42	3.83	3.83
Fe <sup>2+</sup>	1.000	1.000	1.000	1.000	0.571	1.000	0.911	0.666
Mn	0.000	0.000	0.000	0.000	0.002	-	0.059	0.000
Mg	0.000	0.000	0.000	0.000	0.427	0.000	-	0.334
Sum B	1.00	1.00	1.00	1.00	1.00	1.00	0.97	1.00
Fe <sup>2+</sup>	1.318	1.063	0.903	0.006	0.000	0.477	0.000	0.000
Mn	0.085	0.027	0.037	0.155	0.002	0.088	0.000	0.000
Mg	0.019	0.000	0.068	0.032	0.475	0.000	0.000	0.163
Ti	0.163	0.432	0.737	1.261	0.881	1.028	0.981	0.000
Al	0.073	-	0.129	0.096	0.492	0.061	0.453	2.033
Zr	0.023	0.072	0.135	0.464	0.003	0.016	0.627	0.000
Nb	0.362	0.306	0.021	0.000	0.000	0.020	0.060	0.009
Sum C	2.04	1.90	2.03	2.01	1.85	1.69	2.12	2.21
Ti (=D)	2.00	2.00	2.00	2.00	2.00	2.00	2.00	1.79
Si	4.216	4.113	4.071	3.985	4.035	3.964	4.135	4.162
Al	0.000	0.000	0.000	0.015	0.000	0.036	0.000	0.000
Sum T	4.22	4.11	4.07	4.00	4.04	4.00	4.14	4.16
CatSum	13.2	13.2***	13.2	13.2	13.0	13.1	13.1	13.1****

b.d., below detection. Blank, not determined. FeO\*, total Fe as Fe<sup>2+</sup>. CatSum - sum of cations.

\* - total includes Tb<sub>2</sub>O<sub>3</sub> 0.05, Ho<sub>2</sub>O<sub>3</sub> 0.04, Er<sub>2</sub>O<sub>3</sub> 0.08, Tm<sub>2</sub>O<sub>3</sub> 0.01, UO<sub>2</sub> 0.03. HfO<sub>2</sub> 0.03, ZnO 0.01

\*\* - total includes Eu<sub>2</sub>O<sub>3</sub> 0.49, Ho<sub>2</sub>O<sub>3</sub> 0.23, PbO 0.55.

\*\*\* - sum includes (Tb + Ho + Er + Tm + U + Hf + Zn) = 0.026

\*\*\*\* - sum includes Eu 0.033, Ho 0.014. Pb 0.029

Samples: 1 - Nb-rich chevkinite-(Ce), Cerro Toledo, New Mexico (Macdonald, Belkin 2002); 2 - chevkinite-(Ce), Olkaria complex, Kenya (Macdonald et al. 2007); 3 - Th-rich chevkinite-(Ce), Veniaminoff volcano, Alaska (Macdonald et al. 2009); 4 - Sr-Zr-rich perrierite-(Ce), Burpala, Russia (Portnov 1964); 5 - potentially perrierite-(La), Golden Lake, Ontario (Macdonald et al. 2009); 6 - Sr-rich perrierite-(Ce), Bearpaws, Montana (Chakhmouradian, Mitchell 1999); 7 - Ca-rich perrierite-(Ce), Oroscocha volcano, Peru (Carlier, Lorand 2008); 8 - potentially Al-dominant analogue of perrierite-(Y), Mt Cronus, East Antarctica (Belkin et al. 2009)

The ranges of the more abundant minor elements in chevkinite and perrierite are presented in Table 5. The high concentrations provide some optimism that further new species will eventually be recorded. For example, Doelter (1931) presented an analysis of a phase from the Ilmen Mountain, Urals, that he termed thoriochevkinite. With Th =

1.01 apfu (20.91wt% ThO<sub>2</sub>), this is strictly thorian chevkinite. Similarly, the so-called niobochevkinite reported from the Ilmen Mountain by Makarochkin et al. (1959) has 0.71 apfu Nb (7.40wt% Nb<sub>2</sub>O<sub>5</sub>) and is niobian chevkinite-(Ce). Semenov et al. (1966) described scandium-perrierite from pegmatites in southeastern Kazakhstan, with Sc<sub>2</sub>O<sub>3</sub> = 4.14wt% but the quality of their analysis has been questioned by Macdonald et al. (2009).

TABLE 5

Compositional ranges of selected elements in chevkinite group minerals

	chevkinite		perrierite	
	oxide, wt%	a.p.f.u.	oxide, wt%	a.p.f.u.
Mn	0.04 – 5.00	0.00 – 0.90	0.01 – 1.96	0.00 – 0.35
Nb	0.05 – 7.40	0.00 – 0.71	0.04 – 3.96	0.00 – 0.35
Sc	0.02 – 4.14	0.00 – 0.76	0.03 – 3.26	0.00 – 0.57
Th	0.05 – 20.91	0.00 – 1.01	0.03 – 4.60	0.00 – 0.20
Zr	0.01 – 2.71	0.00 – 0.27	0.03 – 7.20	0.00 – 0.62

The REE-bearing accessory phases show large compositional differences between different lithologies and in individual rocks as crystallization proceeded. They show, however, differing REE fractionation patterns. For example, chevkinite and allanite, with which it may be confused during routine petrographic examination, both fractionate the LREE relative to the MREE and HREE. LREE/MREE and LREE/HREE ratios in allanite are about three times those in chevkinite, such that residual melts from fractional crystallization of allanite become LREE-depleted more rapidly than through chevkinite fractionation. Misidentifying chevkinite as allanite, or missing its presence in the rock altogether, will lead to significant errors in geochemical models based on the REE. The ability of both phases to deplete residual melts in REE, and to fractionate the REE, is obviously maximised when they occur as phenocryst phases.

The ranges of selected trace element ratios in chevkinite and perrierite and average concentrations in primitive mantle (Sun, MacDonough 1989) and bulk continental crust (Taylor, McLennan 1985) are: Zr/Hf ~ 2-184, 36.2, 33.3; Nb/Ta ~ 1-113, 17.4, 11.0; Th/U ~ 2-93, 4.0, 3.8). Although some of these ranges may be due to the uncertainties inherent in analysing Hf, Ta and U at low concentrations (down to hundreds of ppm), it is nevertheless clear that chevkinite and perrierite have the potential to fractionate these geochemically coherent pairs of elements relative to their mantle and crustal values. Chevkinite-(Ce) is also a strong concentrator of Ge; phenocrysts from a peralkaline rhyolite from the Olkaria volcanic complex, Kenya, had a Ge concentration of 309 ppm and an apparent mineral/melt partition coefficient of 124 (Macdonald et al. 2007). Another rhyolite from the same complex contains chevkinite-(Ce) phenocrysts with 364 ppm Ga and an apparent partition coefficient of 12 (Macdonald et al. 2010). The CGM may have important, and as yet poorly understood, roles to play in the sequestering of rare elements during crystal fractionation and partial melting.

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