

The distribution of minerals in hyper-aggpaitic rocks in terms of symmetry: evolution of views on the number and symmetry of minerals

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Among the unique mineral localities of the Earth the complexes of nepheline syenites with hyper-aggpaitic differentiates are of special interest due to their extreme diversity of mineral species. The four best studied complexes of this type – Khibina, Lovozero, Ilímaussaq and Mont Saint-Hilaire – have yielded more than 700 mineral species of which about 200 are new. The great mineral diversity is due to the combination of several factors, the most important of which is the extremely high alkalinity of aggpaitic magmas, causing about half of the elements of the periodic table to be concentrated together. Minerals from hyper-aggpaitic rocks are characterised by the predominance of highly ordered, low-symmetry crystal structures resulting, in particular, from the markedly extended temperature range of crystallisation. Generalisation of available data for unique mineral localities underpins the hypothesis that there is no natural limit to the number of mineral species. It is predicted that by the middle of the 21st century, the overall number of minerals recorded in nature will exceed 10 000, with the proportion of triclinic species increasing from the present 9% to 14.5%, and that of cubic species decreasing from 10% to 5%.

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The development of mineralogy in the latter half of the 20th century has been marked by an accelerating pace of new mineral discoveries. The number of minerals discovered worldwide since 1970 is roughly equal to that recorded throughout the preceding historic time. This dramatic acceleration has radically changed our views on the chemical and structural diversity of minerals and on the distribution patterns of various elements in rocks and mineral deposits. It also provides a powerful stimulus for further advancement of mineralogy and allied sciences and challenges long-held theories of the mineral system, its limits, symmetry features, and prospects for further mineralogical discoveries.

The main sources of new mineral discoveries during the last few decades were unique deposits, in particular the mineral-rich complexes of aggpaitic nepheline syenites. The best known of these are Ilímaussaq in South Greenland, Khibina and Lovozero on the Kola

Peninsula in Russia and Mont Saint-Hilaire, Quebec in Canada. Between 1970 and 2000, more than 150 IMA-approved minerals were discovered in these four complexes. The overall list of new mineral species described from these complexes includes approximately 200 entries (Semenov 1972, 1997; Kostyleva-Labunstova *et al.* 1978; Khomyakov 1980, 1990, 1995; Sørensen *et al.* 1981; Horváth & Gault 1990; Petersen & Secher 1993; Sørensen 1997). In all, more than 700 mineral species have been identified in these complexes.

About two-thirds of the aforementioned 150 IMA-approved minerals were described from the Khibina and Lovozero complexes (94 species), which have been the main target of the author's research over the last 30 years and presented in a monograph (Khomyakov 1990, 1995). The vast majority of these minerals were discovered in a special type of silicate-salt pegmatoid, supersaturated in alkaline, volatile and rare elements.

Rocks of this type, distinguished as hyper-agpaitic (Khomyakov 1977, 1995; Sokolova 1986, see also Sørensen & Larsen 2001, this volume), contain accumulations of maximally alkaline minerals; an indication of the extreme peralkalinity which is the principal factor controlling the extraordinary mineral diversity of nepheline syenite complexes with hyper-agpaitic rocks.

The mineral discoveries in the Khibina and Lovozero complexes are briefly reviewed in the first section of this paper. The data, supplemented by new facts and ideas, provide the basis for subsequent generalisations which are summarised in the second and third sections of the paper.

The Khibina and Lovozero complexes and their new minerals

The Khibina and Lovozero complexes are the world's largest localities of agpaitic alkaline rocks outside the Ilímaussaq complex where they were originally described (Ussing 1912; see Sørensen 2001, this volume). Situated in the centre of the Kola Peninsula, these adjacent complexes occupy about 2000 km² in area. They are the type localities of 126 minerals whose discovery began with the expeditions of the Finnish geologist W. Ramsay in the 1890s.

A vast array of compositionally unusual minerals were discovered by members of A.E. Fersman's expeditions conducted under the auspices of the Academy of Sciences of the USSR before World War II. Fersman demonstrated the significance of the two complexes as a unique ore-bearing and mineralogical province. They hold the world's largest deposits of apatite and rare metals in which an unprecedented number of new minerals has been identified.

Fersman (1937) listed 111 mineral species and varieties that were then known in Khibina and Lovozero. In the postwar years, Fersman's students and followers successfully continued and expanded the achievements of their predecessors, considerably increasing the number of new minerals described from the complexes. The overall list of mineral species has now reached about 500 entries, far surpassing any other complex or deposit in the world, including such famous ones as the Ilmen and Vishnevye mountains in the Urals, Ilímaussaq in Greenland, Mont Saint-Hilaire in Canada, Franklin in the United States, Långban in Sweden and Tsumeb in Namibia (each with 200 to 350 species).

The history of discovery of new minerals in the

Khibina and Lovozero complexes may be divided into three major periods.

1. 1890–1941: 11 new minerals were discovered.
2. 1950–1969: 21 new minerals were discovered.
3. 1970–1999: 94 minerals were identified.

Table 1 brings a list of the rare minerals mentioned in this paper.

The enormous increase in the number of new minerals was brought about by the discovery (Khomyakov 1977, 1980, 1990, 1993, 1995) that the deep zones of the complexes (below the zone of weathering) are very rich in hyper-agpaitic rocks. These are enriched in half the elements of the periodic table and contain previously unknown persodic minerals which are readily soluble in water and are therefore not encountered under near-surface conditions. These minerals tend to occur near phosphate (apatite) and rare-element (loparite and eudialyte) deposits.

In particular, these rocks contain water-soluble Na carbonates, making them candidates for commercial extraction of soda (Khomyakov 1985). The most important clue to the origin of Na carbonate mineralisa-

Table 1. The major rock types of the Ilímaussaq alkaline complex

Rock type	Texture	Essential minerals*	Minor minerals
Augite syenite	hypidiomorphic to xenomorphic granular, massive or layered, medium to coarse	alkali feldspar, hedenbergite, titanomagnetite, ferropargasite, olivine, biotite	ternary feldspar, apatite, pyrrhotite, nepheline
Pulaskite and foyaite	massive, medium to coarse, platy feldspars	alkali feldspar, nepheline, hedenbergite, fayalite, aegirine-augite to aegirine, katophorite	titanomagnetite, apatite, aenigmatite, biotite, fluorite, eudialyte
Sodalite foyaite	foyalitic, coarse	alkali feldspar, nepheline, sodalite, aegirine-augite to aegirine, katophorite, arvedsonite	fayalite, hedenbergite, apatite, aenigmatite, titanomagnetite, eudialyte, rinkite, fluorite, biotite
Naujaite	poikilitic, coarse to pegmatitic	sodalite, alkali feldspar, nepheline, aegirine, arvedsonite, eudialyte	aenigmatite, hedenbergite, aegirine-augite, fayalite, apatite, katophorite, rinkite, polyolithionite, biotite, sphalerite, pectolite, williamite, fluorite, titanomagnetite
Kakortokite	laminated, layered, medium to coarse	alkali feldspar, nepheline, aegirine, arvedsonite, eudialyte	sodalite, aenigmatite, magnetite, rinkite, fluorite, löllingite, sphalerite, galena
Lujavrite [†]	laminated, fine-grained; sometimes layered or massive, medium to coarse	microcline, albite, nepheline, sodalite, analcime, naujakasite, aegirine, arvedsonite, eudialyte	monazite, britholite, williamite, sphalerite, pectolite, steenstrupine, lovozerite, vitusite, polyolithionite, ussingite, lueshite, neptunite
Alkali granite, quartz syenite	hypidiomorphic granular, medium to coarse	alkali feldspar, quartz, aegirine, arvedsonite	aenigmatite, elpidite, zircon, ilmenite, pyrochlore, neptunite, fluorite, sphalerite

* Analcime and natrolite are secondary minerals in most rocks.

† There are several types of lujavrites. Three major groups may be distinguished: *aegirine* or *green lujavrite* with aegirine being the dominant mafic mineral; *arvedsonite* or *black lujavrite*, fine grained, often laminated with arvedsonite as the dominant mafic mineral; *medium- to coarse-grained lujavrite* (*M-C lujavrite*) with arvedsonite as the dominant mafic mineral and generally showing foyalic textures. *Naujakasite lujavrite* is a variety of arvedsonite lujavrite containing naujakasite instead of nepheline and with steenstrupine instead of eudialyte.

tion of this highly unusual type was provided by the discovery, deep within the complexes, of the new mineral natrite which is an anhydrous Na carbonate, a natural analogue of soda ash, which is produced industrially by fusing limestone and common salt. In addition to natrite, hyper-agpaitic rocks contain more than 20 minerals that are sodium salts, including the most alkaline silicate (natrosilite) and phosphate (olympite) encountered in nature (Khomyakov 1987). Silicate melts and supercritical aqueous solutions saturated with these salts show an exceedingly high reactivity which is used, in particular, in the hydrothermal synthesis of many insoluble compounds (Litvin 1975). Prior to their discovery, the very possibility of these salts separating as crystalline phases of rocks was difficult to predict on the basis of traditional theories. Now, the existence of natrite, natrosilite, and olympite as magma-related minerals is beyond question.

It is quite possible that further research on hyper-agpaitic rocks will reveal even more highly alkaline salt minerals, e.g. hydroxides such as NaOH and KOH. This possibility is indirectly confirmed by the fact that these hydroxides constitute the 'side chain' (according to V.I. Vernadsky) in the formulas of some minerals that are peculiar to hyper-agpaitic rocks, such as ussingite $\text{NaAlSi}_3\text{O}_8 \cdot \text{NaOH}$ (albite + NaOH) and lithosite $2\text{KAlSi}_2\text{O}_6 \cdot \text{KOH}$ (leucite + KOH), which have the highest known agpaicity in sodic and potassic phases ($\text{Na}/\text{Al} = 2$, $\text{K}/\text{Al} = 1.5$). Another indication is provided by experiments in which crystals of $\text{Na}_2\text{TiSiO}_5$ (the composition of the mineral natisite which is a characteristic mineral of hyper-agpaitic rocks) were synthesised in titanosilicate systems (Litvin 1975) only at NaOH concentrations ranging from 38 to 100%, whereas lower NaOH concentrations produced lorenzenite $\text{Na}_2\text{Ti}_2\text{Si}_2\text{O}_9$, which contains relatively less Na than natisite. Similarly, the synthesis of steenstrupine, a characteristic mineral of hyper-agpaitic rocks, only takes place in a system oversaturated in Na (Sørensen *et al.* 1985).

The new minerals of the Kola Peninsula are dominated by highly alkaline compounds of P (e.g. arctite and nacaphite) and rare elements: Li (lintisite, olympite), Be (lovdarite), Sr (crawfordite, olgite), REE (laplandite, sazhinite), Zr (khibinskite, umbite), and Nb (borne-manite, sobolevite), see Table 1. Some of these minerals have turned out to be the first representatives of new compound types. An example is provided by hydrous zirconosilicates of K (e.g. umbite) which are particularly remarkable because all attempts to synthesise them in laboratories had long been unsuccessful. Lithosite and kalborsite contain more K than all other

known alkaline aluminosilicates. The list of compositional groups was supplemented by silicato-phosphates (phosinaite), hydrophosphates (nastrophite) and manganoferrrosilicates (shafranovskite). New members were added to the mineral groups of apatite, bradleyite, cancrinite, eudialyte, hilairite, keldyshite, labuntsovite–nenadkevichite, lomonosovite and lovozerite.

The discovery of this vast array of new minerals and the concomitant investigation of their crystal structures have furthered the development of structural mineralogy. Khibina and Lovozero minerals have been used to elucidate some 80 crystal structures. These studies have extended the list of structure types with a wide variety of ring, chain, layer and framework radicals, such as the framework formed by three-membered rings of Be and Si tetrahedra in lovdarite, the huge 18-membered cycloradical in megacyclite, and the multirow (six Si tetrahedra wide) branched amphibole band in nafertisite. The structure determinations also led to the prediction or explanation of pronounced ion-exchange, molecular-sieve, and other technologically important properties in many minerals, stimulating research aimed at synthesising the equivalents of naturally occurring phases and using the latter (e.g. lovdarite) as prototypes for creating new materials with desired properties.

The mineralogical investigations in Khibina and Lovozero greatly influenced work in analogous complexes elsewhere, in particular in the Gardar and Montereian alkaline provinces. In the latter, in addition to the main site of alkaline rocks at Mont Saint-Hilaire, a whole series of nepheline syenite sills with peralkaline mineral associations have been studied. One of them, the Saint-Amable Sill, yielded more than 100 minerals, including a large group of species characteristic of Khibina–Lovozero hyper-agpaitic suites (Horváth *et al.* 1998). An important contribution to the investigation of agpaitic rocks of pronounced potassic character was made in recent years by investigators of the Murun alkaline complex, situated in Yakutia within the Aldan Shield (Konev *et al.* 1996).

Symmetry of minerals from hyper-agpaitic rocks and symmetry trend in the mineral world

The statistical distribution of mineral species over crystal systems, symmetry classes, space groups and other symmetry ranks shows certain consistent regularities (Povarennykh 1966b; Shafranovsky & Feklichev 1982;

Table 3. Analyses of rocks representing Ilímaussaq liquids

	1 augite syenite, chilled margin	2 evolved augite syenite, av. of 3	3 Cl-poor sodalite teyuite, av. of 3	4 Fe-rich phonolite dyke	5 Fe-rich phonolite dyke	6 aegirine lujavrite av. of 3	7 arfvedsonite lujavrite av. of 2	8 medium- to coarse-grained lujavrite weighted av.
SiO ₂ (wt%)	53.24	62.33	61.01	51.83	52.27	52.38	52.25	52.71
TiO ₂	2.44	0.50	0.34	0.55	0.25	0.25	0.25	0.35
Al ₂ O ₃	0.34	0.11	0.73	0.55	0.75	0.25	0.25	0.13
FeO*	14.79	15.65	17.58	14.57	14.09	13.20	12.23	13.29
MnO	0.24	2.35	4.73	7.55	1.03	10.90	5.03	3.04
MgO	8.66	3.54	4.62	4.61	1.15	1.95	8.72	8.21
ZnO	0.00	0.16	0.28	0.48	0.30	0.37	0.64	0.60
CaO	1.60	0.31	0.13	0.14	0.07	0.10	0.12	0.12
Na ₂ O	4.94	1.89	1.97	2.54	3.27	10.72	9.25	9.20
K ₂ O	4.68	6.74	10.08	5.81	3.27	2.82	3.23	4.69
Li ₂ O	4.26	5.53	3.93	4.87	4.15	2.44	3.53	3.70
CO ₂	0.74	0.68	0.68	0.68	1.15†	0.18	0.24	0.18
H ₂ O	0.29†	0.19	0.15	1.56†	1.15†	0.44	3.53	4.69
Total	0.19	0.20	0.17	0.47	0.36	0.25	0.24	0.15
TOF	0.15	0.23	0.07	0.12	0.03	0.09	0.19	0.07
—	0.03	0.01	0.09	0.23	0.08	0.05	0.03	0.05
F	0.10	0.15	0.31	0.34	1.50	0.03	0.14	0.15
others	0.46	0.08	0.31	0.42	0.71	0.89	1.64	1.47
—	98.59	100.71	100.10	100.33	99.85	99.89	99.74	99.77
—	0.12	0.07	0.20	0.49	0.79	0.07	0.10	0.15
—	98.57	100.64	99.90	99.84	99.06	99.82	99.64	99.62
A.I.	0.83	1.09	1.20	1.36	1.40	1.57	1.53	1.52
FeO*	11.04	9.45	8.88	11.41	11.08	11.77	14.17	11.66
Zr (ppm)	264	838	2590	4040	5740	7010	1650	939

Analysts: J. Kystol, J.C. Bailey and F. Fuge.

A.I.: Loss on ignition corrected for other volatiles where known.

A.I.: Apatite index, (Na₂O+K₂O)/Al₂O₃ mol.

FeO*: Total Fe as FeO.

1: GGU 153394 (new analysis of sample U-106 from Ussing's collection in the Geological Museum, Copenhagen).

2: Average of GGU 152122, 152130, 154375.

3: Average of GGU 57079, 154303, 154317.

4: Sample GGU 42475 (Larsen & Steenfelt 1974), new analysis.

5: Sample ARM 62/3010 (Martin 1985), new analysis.

6: Average of GGU 152128, 154302, 66143.

7: Average of GGU 152127, 154363.

8: 1:1 average of (a) 3 large surface samples (GGU 154397, 154399, 154724) and (b) 21 smaller samples from drill cores.

GGU prefixed to sample numbers; samples in the collections of the Geological Survey of Denmark and Greenland.

* Fleischer & Mandarino (1995).

† The first number relates to the data set of 250 characteristic minerals; the second (in parentheses) relates to the data set of 173 minerals whose type localities are at Khibina, Lovozero, Ilímaussaq and Mont Saint-Hilaire.

Fedorov–Groth law). In order to assess the importance of this factor, Table 3 presents data similar to those in Table 2, but relating solely to silicates (911 out of the 3534 species). It can be seen that, in terms of their symmetry distinctions, silicates of hyper-apatitic rocks resemble minerals of all classes. The monoclinic anomaly that is typical of silicates as a whole (41.6%) is due to the very high proportion of amphiboles, pyroxenes, and micas (about 120 species out of 911 in the data set), the vast majority of which belong to the monoclinic system. The triclinic minerals show a nearly 20-fold predominance over cubic ones in the data set of 122 new silicates described from the four complexes (Table 3). This data set contains only one cubic mineral, sodalite.

The effect of a highly alkaline environment on the lowering of the symmetry of crystallising minerals can be illustrated by the apatite group. The most characteristic representatives of this group in the Khibina complex form the following evolutionary sequence: REE,Sr-bearing fluorapatite, (Ca,REE,Sr)₅(PO₄)₃F – fluorcaphite, Ca(Sr,Na,Ca)(Ca,Sr,REE)₃(PO₄)₃F – belovite-(Ce), NaSr₃Ce(PO₄)₃F – deloneite-(Ce), NaCa₂SrCe(PO₄)₃F, with the corresponding sequential lowering of the space group symmetries: P6₃/m–P6₃–P3–P3 (Khomyakov *et al.* 1996, 1997). The highest symmetry mineral of this series – fluorapatite – is characteristic of the moderately alkaline rocks of the principal intrusive phases and their closely associated apatite deposits, whereas the remaining members of the series are found only in bodies of hyper-apatitic pegmatites and their hydrothermal equivalents, in which fluorapatite is not stable.

Phosphates with the compositions of belovite and

deloneite synthesised under laboratory conditions share the high-symmetry space group P6₃/m with fluorapatite. This can be attributed to the much higher temperatures (1100°C; Mayer *et al.* 1974) and shorter duration of the processes in experiments than the temperature range 150–300°C within which deloneite and belovite are assumed to have formed in nature. This sequence of apatite-group phosphates is an example of early higher symmetry members being successively transformed into lower symmetry members, a sequence already demonstrated by Fersman (1940, p. 336) for minerals in granite pegmatites.

There is no doubt that the differentiated complexes of nepheline syenites will continue to make a contribution to the overall mineral system, thereby reducing the average symmetry of the mineral world as a whole. The change in the triclinic to cubic ratio over the last 100 years speaks for itself: in 1891, it equaled 0.3; in 1966, 0.6; in 1991, 0.9; and now it is steadily approaching 1.0. According to the predictions of Khomyakov (1998a, b) based on correlation diagrams (the number of species versus time), the total number of known minerals will approach 11 000 by the year 2050, with the proportion of triclinic minerals increasing from the present 9.1 to 14.5%, and that of cubic minerals decreasing from 10 to 5%. The cubic–triclinic ‘inversion’ of the mineral world is expected to occur near the year 2005.

Recent mineralogical discoveries and the number of mineral species

At present the number of naturally occurring minerals is in the order of 4000 whereas the number of artificial compounds amounts to many millions. According to Fersman (1938), the limited number of mineral species existing in the Earth's crust, despite the astronomical number of theoretically possible combinations of chemical elements, is due mainly to the pattern of geochemical distribution of elements and the relatively narrow range of physicochemical parameters realised during the mineral-forming processes. Because of these and other limiting factors it has been suggested (Povarennykh 1966c; Urusov 1983) that the discovery of new minerals would soon be a very rare event. The last few decades, however, have witnessed an unprecedented expansion of the number of minerals, with 50–100 new minerals annually approved by the International Mineralogical Association.

What are the limits to the mineral world as a whole? Analysis of the long-held theory that there is a natural limit to the number of mineral species (Fersman 1938; Saukov 1946; Povarennykh 1966c; Kostov 1968; Yushkin 1977; Urusov 1983) shows that this theory is mainly valid for ordinary types of rocks and mineral deposits. The principal source of new mineral discoveries is in unusual deposits formed in anomalous geotectonic and geochemical environments. The conditions of formation of these deposits encompass virtually the entire range of physicochemical parameters (T , P , X , pH, Eh, etc.) accessible to modern experimental mineralogy and also involve geological time and other factors unattainable in experiments. This serves to remove barriers to the diversity of natural crystalline phases and allows the presentation of a hypothesis of an in-

finite diversity of mineral species in the mineral world (Khomyakov 1986, 1990, 1994, 1995, 1996, 1998b).

According to general theories of physical chemistry, one peculiar property of peralkaline aluminosilicate melts and solutions is that all dissolved electropositive elements less basic than Na are made to behave as amphoteric elements, stimulating their transition from the cationic part to the much more capacious anionic part of the melt structure. Furthermore, a rise in the alkalinity of these melts causes a substantial increase in the solubility of H_2O and other volatile components such as F, Cl, S, and CO_2 (Kogarko 1977). Therefore, agpaiteic magmas can be regarded as universal solvents, capable of concentrating, in addition to alkalis and volatiles, virtually all other chemical elements. This may explain the unique ability of these magmas to extract diverse elements, including those that form mineral deposits of P, Nb, Ta, Zr, Hf, Ti, REE, Sr, etc. from sources such as deep transmigmatic fluids. Hence, economically important deposits of the alkaline series tend to occur near ultra-deep faults which were figuratively described by Ovchinnikov (1985) as 'punctures' in the Earth's hot spots.

Data for the four best-studied complexes of this type – Khibina, Lovozero, Ilímaussaq and Mont Saint-Hilaire – indicate that, in addition to the petrogenetically important elements O, Si, Al, Na, K, Ca, Fe, Mg, Mn and Ti, there are approximately 30 other elements that form their own minerals: Li, Be, Sr, Ba, B, Ce, La, Nd, Y, Zr, Nb, P, Th, U, Ag, Au, Tl, Cu, Zn, Sn, Pb, As, Sb, Mo, W, Co, Ni, as well as F, S, Cl, C and H. A large number of the minerals have very complex compositions with as many as 10 elements occupying separate structural sites.

Table 4 shows the calculated number of theoretically possible combinations (C^m) of a known number

TABLE 4 (continued)

Mineral	Formula	Reference
Riesbeckite	$Na_4(Fe^{2+}, Mg)(Fe^{3+})_2Si_2O_{10}(OH)_2F$	Using (1994)
Riesbeckite var. crocidolite (crocidolite)	$Na_4(Fe^{2+}, Mg)(Fe^{3+})_2Si_2O_{10}(OH)_2F$	1959 (Chesnokov)††
Rutile	$(Na, Ca)_{10}(Cu, Co)_2(Ti, Nb)_6(Si, O)_2(C, F)_2$	Lorenson (1983a)
Tinkaitite †	$(Ti, Fe, K), Cu, Sb, S$	Simonov (1955)
Rosendushchito	$(Ca, Na), (Zr, Cs), (Tl, Mn)(Si, O)_2(F, OH)_2$	Karup-Møller (1976a)
Saite	TiO_2	Using (1912)
Schizolite see pectolite (manganian)	$Na_2Zr_2(Si, Al)_2O_{10}(OH)_2 \cdot 4H_2O$	Semerov (1955)
Schizolite	$(Fe, Ni)(Sb, As)$	Simonov (1955)
Semrenovite	$(Na, Ca)_4F_6(Co, La), (Si, B)_2(O, OH)_{10}$	Karup-Møller (1976b)
Sennarndite	Si_2O_2	Petersen & Ronsbo (1972)
Sopocuite	$Mg_3Si_2O_7(OH)_2 \cdot 6H_2O$	Karup-Møller (1974)
Suzuro	$FeCO_3$	Simonov (1955)
Silver	Ag	1808 (Lomonosov)††
Sklarerite	$Cu_2Sb_2S_5$	Simonov <i>et al.</i> (1977)
Sklarerite	$Cu_2Sb_2S_5$	Karup-Møller & Makovicky (1974)
Sodalite	$Na_4(Si, Al)_3O_{14}Cl_2$	Karup-Møller (1964)
Sodalite (sodalite-tris-hydrate)	$CH_3COONa \cdot 5H_2O$	Thomson (1811)
Sorrensenite	$Na_2S_2O_7$	Simonov <i>et al.</i> (1955)
Sphaerobondite †	$Na_2S_2O_7(Si, O)_2 \cdot 2H_2O$	Semerov & Sorenson (1966)
Sphalerite	ZnS	Frank (1898)
Stafolite see carbonate-fluorapatite		
Stannite	$Cu_2FeSb_2S_7$	Cun & Sorenson (1964)
Stannite	$Na_2(Cu, Mn, Fe, F)_2(PO_4)_2(Si, O)_2(OH)_2 \cdot 3H_2O$	Larsen (1963)
Stannite (stannite)	$Na_2(Cu, Mn, Fe, F)_2(PO_4)_2(Si, O)_2(OH)_2 \cdot 3H_2O$	Karup-Møller (1974)
Stibnite	$(Ca, La, Ce)BSiO_3$	Gren & Mielas (1960), Gric (2001)
Stibvolite	SnS	Anderson <i>et al.</i> (1959)
Sthomsonite †	$Ca(Ce, La)(CO_3)F$	Anderson & Sorenson (1958)
Synchysite I	$Ca_2(Sr, Ba)(SO_4)F$	Karup-Møller (1978b)
Talc	Si_2O_4	Hamilton (1924)
Tenonite	$Na_2Zr(H, Si, O)_{10}$	Larsen (1976)
Tenonite	$(Cu, Fe)_{10}(Sb, S)_{10}$	Simonov (1955)
Tetrahedrite † see Sennarndite		
Tetrahedrite	Cu_4FeTeS_4	Karup-Møller & Makovicky (2001)
Thomsonite	$Na_2CO_3 \cdot H_2O$	Karup-Møller (1974)
Thorianite	ThO_2	Quon (1964)
Tiagite	Sn	Makovicky <i>et al.</i> (1989)
Tin	Sn	Bondam & Sorenson (1958)
Titanite	$(Ca, Sr, Na)(Ti, Ta, Al, Nb, Sb)SiO_6(O, F)$	Karup-Møller (1978b)
Titanomagnesianite	$(Nb, Ca, K, Ba, Sr), (Mn, Mg, Al)_2O_2 \cdot 3-4H_2O$	Hamilton (1924)
Tolansite	Na_2CO_3	Larsen (1976)
Troilite	FeS	Karup-Møller (1978b)
Tungstite	$Na_2(HCO_3)(CO_3) \cdot 2H_2O$	Sorenson <i>et al.</i> (1970)
Tungstite (Nd)	$Na_2CaTi_2Si_2O_{10}(CO_3)$	Simonov <i>et al.</i> (1957a)
Tungstite (Nd)	$Na_2CaTi_2Si_2O_{10}(CO_3)$	Simonov <i>et al.</i> (1957a)
Upernivassite	$NaFe_2Si_2O_7(OH)_2 \cdot 5H_2O$	Simonov <i>et al.</i> (1959)
Upernivassite	$NaFe_2Si_2O_7(OH)_2 \cdot 5H_2O$	Karup-Møller & Petersen (1984)
Uvöspingit	$Fe_2Ti_2Si_2O_{10}(OH)_2 \cdot 2H_2O$	Simonov <i>et al.</i> (1959)
Uvöspingit	$Fe_2Ti_2Si_2O_{10}(OH)_2 \cdot 2H_2O$	Karup-Møller (1978b)
Uvöspingit	$Fe_2Ti_2Si_2O_{10}(OH)_2 \cdot 2H_2O$	Makovicky <i>et al.</i> (1980)
Uschmidtite	$Fe_2Ti_2Si_2O_{10}(OH)_2 \cdot 2H_2O$	Beggid (1915)
Uvöspingit	$Fe_2Ti_2Si_2O_{10}(OH)_2 \cdot 2H_2O$	Karup-Møller (1974)
Uvöspingit T	$Na_2(Na)_{10}(Al, Mg, Fe)_{10}(SiO_4)_{10}(Si_2O_7)_2(OH, F, O)_{10}$	Rodd & Ferguson (1962)
Villaviejaite	NaF	

of chemical elements (n) in a system and the actual number of significant elements in each individual mineral (m) according to the formula $(C^m) = n!/m!(n-m)!$. Two sets of calculations were carried out. One set included approximately one-third of the elements in the periodic table ($n = 30$) that form relatively simple compounds ($m \leq 5$); the other set involved a narrow range of the most characteristic elements of alkaline rocks ($n = 17$) that form more complex compounds ($m \leq 8$). The calculations show that, when $n = 30$ and m ranges from 2 to 5, the number of combinations equals 174 406; when $n = 17$ and m ranges from 2 to 8, the result is 65 518. Even though this approach is fairly arbitrary, the number of possible minerals of alkaline rocks can nevertheless be estimated to be of the order of 10^4 – 10^5 species.

The diversity of the crystal structures of alkaline minerals can be illustrated by compounds of the type $\text{Na}_x\text{M}_y\text{Si}_p\text{O}_q$, where M = Ti, Zr, Be, and other amphoteric elements. The special features of the atomic arrangements of these compounds and their more complex analogues have been examined in detail elsewhere (Belov 1961, 1976; Povarennykh 1966a; Sandomirsky & Belov 1984; Voronkov *et al.* 1975, 1978; Pyatenko *et al.* 1976; Egorov-Tismenko & Sokolova 1990; Ferraris, 1997; Ferraris *et al.* 1997; Merlino & Pasero 1997). In the crystal structures, Ti and other high-charge elements together with Si form mixed radicals whose negative charge is compensated by alkali cations. The presence of Na is important because, as a large cation, it performs the function of a 'rigid fragment' relative to the more flexible MSiO radicals and, as a strong base, it helps amphoteric elements play their anion-forming role (Belov 1961, 1976). Na is characterised by a unique range in co-ordination numbers (from 4 to 12) and shapes of the corresponding polyhedra. Na atoms are capable of off-centre displacements within co-ordination polyhedra and of forming highly unequal Na–O bond lengths, thus ensuring complete charge balance for the Na-linked anions. Na polyhedra are able to link by corner-, edge-, or face-sharing with each other, producing diverse structural units, including one-dimensional (chains and columns) and two-dimensional (sheet and net) structures, and each type of association can have several different topologies.

In these structural arrangements, the variety of M–O and Si–O fragments is complex and varied. For example, Ti polyhedra characteristically form (in addition to single and coupled octahedra) geometrically diverse rings, chains, bands, one- and multilevel layers, and

intricate frameworks. An additional factor controlling the diversity of Ti–O structural units is the ability of Ti to lower its co-ordination number from six to five.

The polymorphism of Si–O fragments is well known: for example, the same metasilicate formula $[\text{SiO}_3]_n$, with $n = \infty$, may represent the pyroxene chain Si_2O_6 or any of more than ten topologically different bands; the dimetasilicate formula $[\text{Si}_2\text{O}_5]_n$ may represent a variety of cyclogroups, bands, sheets and frameworks. Along with homogeneous Si–O structural units, some structures involve heterogeneous Si–O fragments, such as three- and nine-membered rings in eudialyte or chains and bands in vinogradovite.

The mutual combinations of Na–, M–, and Si–O structural units in $\text{Na}_x\text{M}_y\text{Si}_p\text{O}_q$ compounds are no less diverse than the structural units themselves, and the diversity of MSiO combinations markedly increases with the degree of polymerisation. According to Sandomirsky & Belov (1984), among mixed radicals, only one finite radical is known; there are 10-odd known band (or chain) radicals and about 50 layer radicals, whereas framework radicals run into the hundreds. The great variety of cationic and anionic motifs and their combinations explain the abundance of distinct structure types of alkaline amphoteric silicates (silicates with amphoteric elements) and, in particular, the existence of vast families of Ti, Nb, Zr and Be silicates that have similar compositions but differ in stoichiometry or structural features (or both). The majority of titanosilicates and their analogues recently discovered in differentiated nepheline syenite complexes represent hitherto unknown structure types. A large number of new structure types have also been identified in other silicates (Bokii 1996), as well as in phosphates (Yakubovich & Urusov 1996), carbonates (Pobedimskaya & Trinh 1985), and complex sulphides (Makovicky 1997). These facts, which fully agree with Yushkin's (1977) observation that the structural diversity of minerals steadily increases as the mineral system expands, highlight the role of the structural factor as a determinant of the hypothesised infinite diversity of mineral species. This hypothesis is in agreement with the conclusions of Skinner & Skinner (1980), based on their analysis of other factors, that there are no predictable limits to the number of minerals.

It stands to reason that most of the minerals that form large crystals and grains – more than 10 cm across – have already been discovered. The majority of species yet undiscovered can be broadly divided according to size into objects of the binocular level (0.1–1 mm), microscopic level (0.001–0.1 mm), and nanolevel

(< 0.001 mm). The number of minerals of the binocular level alone appears to exceed that of the currently known minerals by at least one order of magnitude. Although the great majority of these will be mineralogical rarities, the identification and study of the yet undescribed natural phases is not only of interest from a purely scientific point of view, but also has practical implications. Among the future minerals, there will undoubtedly be various types of commercial ores and compounds with unique structures and technologically useful properties.

Conclusions

The deep zones of Khibina and Lovozero contain abundant hyper-aggaitic rocks – essentially a new type of silicate-salt pegmatoid, supersaturated in alkaline, volatile and rare elements. Rocks of this type contain very large amounts of the most alkaline minerals of various classes ever recorded in nature. These rocks and minerals are indicators of special physicochemical conditions of agpaitic magma differentiation, which promote the accumulation of most of the less common elements and the crystallisation of an enormous number of minerals.

The unusual physicochemical conditions under which hyper-aggaitic rocks form predetermine the prevalence of complexly built minerals with highly ordered low-symmetry structures, characterised by a substantial predominance of triclinic species over cubic ones. In the future, the number of minerals from hyper-aggaitic rocks will undoubtedly continue to grow and, in turn, will serve to reduce the average symmetry of the mineral world. It is also clear that, regardless of the source of new species, they will be increasingly dominated by micro- and nanominerals, most of which crystallise after macrominerals at lower temperatures, thus being generally of lower symmetry. It can be predicted that, in the near future, the proportion of triclinic minerals in the mineral world will become equal to, and subsequently exceed, that of cubic minerals.

The long-held thesis that there is a limit to the number of mineral species is valid only for ordinary types of rocks and mineral deposits. The principal sources of new mineral discoveries are deposits formed in anomalous geotectonic and geochemical environments under conditions that encompass virtually the entire range of physicochemical parameters (T , P , X , pH, Eh, etc.) accessible to modern experimental mineralogy

and, moreover, include geological time and other factors unattainable experimentally in the laboratory. All this serves to remove any barriers that limit the number of mineral species.

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