

GARNET OF THE PYROPE-MAJORITE SERIES FROM LAMPROPHYRES OF CENTRAL TIMAN

Natalya I. Bryanchaninova, Alexander B. Makeyev

*Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry (IGEM) RAS, Moscow,
ni@igem.ru, abmakeev@igem.ru*

In kersantite and spessartite dikes of Chetlas Kamen' among accessory garnets, that are rather rare in lamprophyres, there was discovered few and for the first time high-majorite pyrope garnet with majorite minal $Mg_3Fe_2[SiO_4]_3$ (26–42%), similar to majorite garnet originating from a meteorite. Majorite discovered in Coorara meteorite (Mason *et al.*, 1968; Smith, Mason, 1970) is very rare in the terrestrial rocks. It is shown, that high-majorite pyrope to variable degree is associated with diamond. On the one hand, it occurs as inclusions in diamond crystals, on the other hand, in rocks, where such garnet is found, microcrystalline diamond is established. Pyrope-majorite garnet in lamprophyres testifies to superdeep origin of lamprophyre magma.
2 tables, 2 figures, 14 references.

Keywords: majorite, pyrope, lamprophyre, Timan, inclusions in diamonds, superdeep mineral parageneses.

Accessory garnets in the Timan lamprophyre attributed to a number of microminerals and occur in autoliths, mantle xenoliths, in olivine and pyroxene phenocrysts, and in the matrix of the rock are very rare and irregular distributed. In chemical composition, garnets from lamprophyre can be divided into three series: grossular-almandine, occasionally containing few pyrope component, andradite-grossular, and pyrope-majorite (Table 1, Fig. 1, 2). Chemical composition of the minerals was determined with a GEOL-733 Superprobe electron microprobe (Vernadsky Institute of Geochemistry and Analytical Chemistry RAS) and JSM-5610LV electron microscope equipped with EDS (Institute of Geology of Ore Deposits, Petrography, Mineralogy and Geochemistry RAS). The results are similar in duplicate measurements. In heavy fractions, content of garnet ranges from a few signs to 0.5%. Yellowish-brown and pinkish pyrope-majorite has rhombo- and pentagon-dodecahedron habit and varies from 0.005 to 0.05 mm in size. Grains of other garnet varieties reach 1.6 mm. Iron-calcium garnets and pyrope-majorite are predominant in lamprophyre of Chetlas Kamen' (Fig. 2).

The garnets from fresh matrix (grossular-almandine, andradite, andradite-grossular) are euhedral, whereas in serpentine-chlorite-calcite and epidote-calcite aggregates, they are significantly corroded and surrounded by kelyphytic rims of variable thickness and composition. These features is favourable for the early deep-seated formation of these garnets. The pyrope with high content majorite component $Mg_3Fe_2[SiO_4]_3$ (26–42%), similar to that described only from meteorites and as

small inclusions in super-deep diamonds (Kaminsky *et al.*, 2001), was found in several samples from three dikes of the kersantite-spessartite series.

Majorite garnets and their mineral assemblages

Majorite garnets were described as inclusions in diamonds (Table 2) from various diamond-bearing provinces worldwide: Juin fields at Brazil, Snap-Lake, Canada, Yakutia province, Russia, Kankan placers, Guinea (Kaminsky *et al.*, 2001; Pokhilenko *et al.*, 2001; Sobolev *et al.*, 2004; Stachel *et al.*, 2000; Moore *et al.*, 1991), and in alnöite lavas of the Malaita Island, Solomon Islands (Collerson *et al.*, 2000). In aforementioned papers, majorite is considered as garnet, in which according to microprobe data SiO_2 is in excess, i.e., there are non-stoichiometry between cations and Si excess at tetrahedral site. Findings of "majorite" garnet are attached much importance, relating its formation to ultrahigh pressure environment in transitional zone of mantle.

According to modern systematics of garnets, ideal formula of majorite is expressed as $Mg_3Fe_2[SiO_4]_3$ (Back, Mandarino, 2008). Majorite end-member is not found in nature. Recalculated microprobe data of majorite grains found in Australian meteorite, give 66% of of majorite component and the remainder of pyrope.

The majorite was firstly described from the Coorara meteorite in 1970. Its formula $Mg_3(Fe_{1.2}, Al_{0.6}, Si_{0.2})_2[SiO_4]_3$, calculated on the basis of electrone microprobe data, suggested partial incorporation of Si at octahedral site.



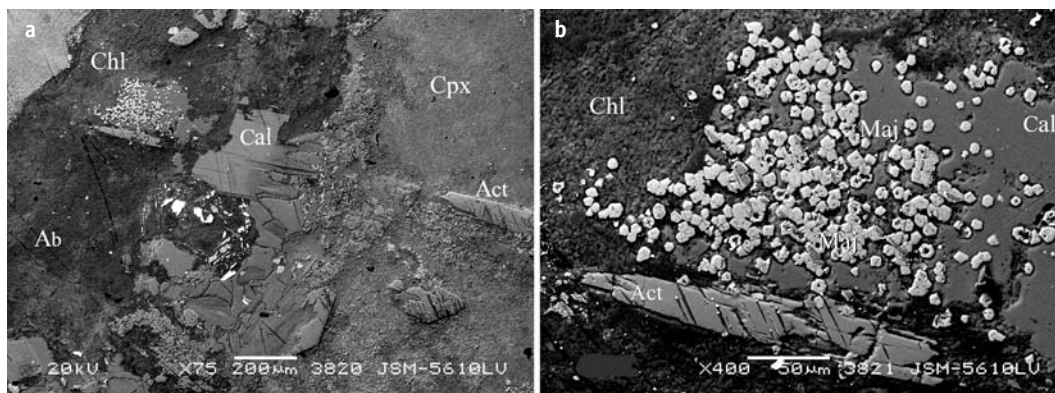


Fig. 1. Scanning-electron microscope image of polished section of lamprophyre-kersantite (spec. 38/180, Kos'yusk Field, Central Timan, Russia. Pyrope-majorite-andradite, andradite, andradite-grossular, and andradite-pyrope-grossular garnets are associated with augite(Cpx), actinolite (Act), chlorite (korundophyllite) (Chl), calcite (Cal), albite (Ab). Rhombododecahedral crystals of garnet (Maj) range from 5 to 15 microns. Magnification (a) 75°, (b) 400°.

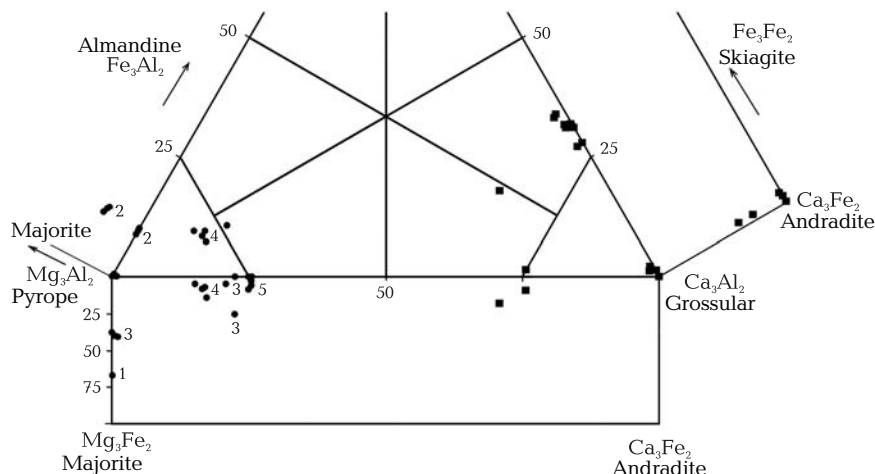


Fig. 2. Composition of garnets plotted on the evolvent of minerals majorite-andradite-skiagite*-pyrope-grossular-almandine trigonal prism: 1 – majorite from the Coorara meteorite (the first composition, approved by CNMNC IMA), 2 – garnets from diamond inclusions in diamonds from kimberlite pipes the Juin Field (Brazil), 3 – from lamprophyres of the Middle Timan (Russia), 4 – from inclusions in diamonds from kimberlite pipes of the region Snap-Lake (Canada), 5 – from xenoliths in alnöite lavas of the Malaita Island (Solomon Islands). Solid squares denote iron-calcium garnets from lamprophyres studied here (Table 1) and associated with the pyrope-majorite.

* – skiagite – hypothetical garnet mineral $Fe_3Fe_2(SiO_4)_3$.

No special X-ray structural study was carried out to support incorporation of Si at octahedral sites of trivalent cations in garnets. Non-stoichiometry and excess of silica in composition of real garnets of minute inclusions (which size rarely exceeds 1–20 microns), most likely could be caused by technical problems of electron microprobe measurements or inhomogeneous sample resulted from microgrowths of pyroxene in garnet. Currently, the latter is received fact. In natural pyrope from garnet-bearing xenoliths of diamond-bearing kimberlites, Haggerty and Sautter (1990) and Sautter *et al.* (1991) described omphacite, diopside-

jadeite solid solution, and showed, that with the clinopyroxene content in garnet of 20 and 30%, SiO_2 was 44–45.5 wt.% and crystallochemical coefficients of Si^{4+} calculated on the basis of 12 O, were 3.14–3.24 (Haggerty, Sautter, 1990; Sautter *et al.*, 1991).

For comparison of majorite garnets from various regions, we calculated available chemical data of the pyrope-majorite garnets by the same way, implying that majorite is the phase $Mg_3Fe_2[SiO_4]_3$, as it was approved by the International Mineralogical Association for the garnet group minerals (Back, Mandarino, 2008).

Table 1. Chemical composition (wt.%) and components (%) of garnets from the lamprophyre of the Central Timan, associated with majorite-bearing pyropes

№№	38/180		Chp-025		116/33				116/43.5		116/47		Chp-036c		Chp-036d	
	1	2	1	2	1	2	3	4	1	2	1	2	1	2	1	2
SiO ₂	35.39	36.80	36.92	38.78	38.98	38.81	38.78	38.98	38.81	38.71	38.91	39.32	38.64	38.83	38.75	38.84
TiO ₂	1.94	1.10	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	0.00	0.00
Al ₂ O ₃	5.97	7.35	8.03	21.97	22.05	21.97	21.97	22.05	21.97	21.94	22.05	18.57	21.87	22.00	21.95	22.00
Cr ₂ O ₃	0.00	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.48	0.19	0.00	0.00	0.00
Fe ₂ O ₃	23.01	21.76	20.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.30	0.00	0.00	0.00	0.00
FeO	0.84	1.20	1.34	14.00	13.47	14.67	14.00	13.47	14.67	15.29	11.92	7.85	13.77	13.71	14.25	13.40
CaO	31.74	26.01	33.25	25.25	24.62	23.96	25.25	24.62	23.96	23.60	27.12	23.29	25.19	24.89	24.89	25.57
MnO	0.46	0.00	0.24	0.00	0.00	0.07	0.00	0.00	0.07	0.00	0.00	0.00	0.28	0.17	0.08	0.05
MgO	0.64	5.79	0.00	0.00	0.88	0.52	0.00	0.88	0.52	0.46	0.00	5.19	0.00	0.39	0.08	0.15
Sum	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	99.99	99.99	100.00	100.01
Si ⁴⁺	2.904	2.939	2.998	3.001	3.002	3.001	3.001	3.002	3.001	2.999	2.998	3.001	2.993	3.000	3.000	3.000
Ti ⁴⁺	0.119	0.066	0.003	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.003	0.000	0.000	0.000
Al ³⁺	0.577	0.691	0.768	2.001	1.999	2.000	2.001	1.999	2.000	2.001	1.999	1.668	1.994	2.000	2.000	2.000
Cr ³⁺	0.000	0.000	0.004	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.029	0.012	0.000	0.000	0.000
Fe ³⁺	1.419	1.306	1.227	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.304	0.000	0.000	0.000	0.000
Fe ²⁺	0.058	0.080	0.091	0.905	0.866	0.947	0.905	0.866	0.947	0.989	0.767	0.500	0.891	0.884	0.921	0.864
Ca ²⁺	2.791	2.225	2.893	2.093	2.031	1.985	2.093	2.031	1.985	1.959	2.239	1.905	2.091	2.060	2.065	2.116
Mn ²⁺	0.032	0.000	0.016	0.000	0.000	0.005	0.000	0.000	0.005	0.000	0.000	0.000	0.018	0.011	0.005	0.003
Mg ²⁺	0.078	0.688	0.000	0.000	0.101	0.060	0.000	0.101	0.060	0.053	0.000	0.590	0.000	0.045	0.009	0.017
Pyr	2.6	22.9	0	0	3.4	2.0	0	3.4	2.0	1.7	0	17.9	0.6	1.5	0.3	0.6
Alm	1.9	2.7	3.0	30.1	28.9	31.6	30.1	28.9	31.6	33.0	25.5	16.7	29.7	29.4	30.7	28.8
Gros	23.5	9.1	34.9	69.9	67.7	66.2	69.9	67.7	66.2	65.3	74.5	48.8	69.7	68.7	68.8	70.5
Andr	71.0	65.3	61.4	0	0	0	0	0	15.2	0	0	0	0	0	0	0

Note: original analyses were normalized to 100%. Content of bivalent and trivalent iron in microprobe analyses is divided on the basis of stoichiometry

Calculation of end-member composition. Formula coefficients (f.c.) are calculated according to standard procedure. Electron microprobe data providing only total iron are corrected; total Fe is redistributed between FeO и Fe₂O₃ taking into account coefficient 1.11 converting FeO to Fe₂O₃. In this case, stoichiometry between sums of bivalent and trivalent cations is 3.000:2.000. Firstly, spessartine end-member Mn₃Al₂[SiO₄]₃ is calculated: 100 (f.c. Mn²⁺)/3 = Spessartine (%). Secondly, almandine end-member Fe₃Al₂[SiO₄]₃ is calculated: 100 (f.c. Fe²⁺)/3 = Almandine (%). In the third place, andradite component Ca₃Fe₂[SiO₄]₃ linking Fe³⁺ with Ca is calculated: 100 (f.c. Fe³⁺)/2 and 100 (f.c. Ca²⁺)/3; an amount of Andradite is determined by the lesser value. In the fourth place, with presence of Cr and Ca excess, uvarovite component Ca₃Cr₂[SiO₄]₃ is calculated. The fifth calculated end-member is knorringite Mg₃Cr₂[SiO₄]₃: 100 (f.c. Cr³⁺)/2 – “Uvarovite” = Knorringite (%). This compo-

nent may be absent at high Ca. In this case, Cr is included into uvarovite end-member. Grossular Ca₃Al₂[SiO₄]₃ is the sixth calculated component: 100 (f.c. Ca²⁺)/3 – “Andradite” – “Uvarovite” = Grossular (%). The seventh end-member is majorite Mg₃Fe₂[SiO₄]₃: 100 (f.c. Fe³⁺)/2 – “Andradite” = Majorite (%). Finally, pyrope Mg₃Al₂[SiO₄]₃ is calculated: 100 (f.c. Al³⁺)/2 – “Almandine” – “Grossular” – “Spessartine” = Pyrope (%). Only such succession of calculation allow estimation majorite content. Majorite end-member estimated from virtual excess of SiO₂ in garnets is invalid.

According to calculation results given in Table 2 and plotted on evolvent of trigonal prism (Fig. 2), not all of described garnets with majorite component really contain it in fair quantity. Pyropes with 26–42% of majorite component from the Central Timan lamprophyre and pyrope inclusions with 24–26% of majorite in diamonds from the Juin Field, Brazil

are the closest to majorite from the the Coorara meteorite. These garnets and majorite from the Coorara meteorite are Cr- and Ca-free. Majorite component in all other garnets is lesser and ranges from from 2 to 15%, but they are Cr- and Ca-bearing. All described garnets are distinguished by high content of magnesium components (pyrope, knorringite and majorite), i.e., Mg # varies from 75 to 100%. It is apparent that this value is an indicator of high-pressure conditions of formation of mineral assemblage. It should be noted, that in diamond-bearing rocks, majorite component is found in garnets of ultramafic assemblage and does not documented in garnets of the eclogite one.

Majorite garnets reported from spinel and garnet-spinel xenoliths and megacrysts from

alnöites of the Malaita Island, Solomon Islands are attributed to the high-pressure mineral assemblage of, where Ca and Mg perovskite, Al silicate phases, and diamond microcrystal are also involved (Collerson *et al.*, 2000). Neal *et al.* (2001) considered this information as untimely and criticized formula coefficients of Si more than 3 calculated on the basis of 12 O. These researchers correctly suggest that most mentioned analyses characterize admixtures of pyroxenes and amphiboles rather than garnets, and they should not assigned to garnets without X-ray diffraction study. We also consider that among analyses of majorite garnets, given by Collerson *et al.* (2000), not all of them correspond to garnet, and among garnets not all correspond to majorite garnet. However, in

Table 2. Chemical composition (wt.%) and components (%) of majorite-bearing garnets

Compo- nents	Coorara	Brazil			Lamprophyre of the Central Timan				Snap-Lake, Canada					Alnöites Malaita Island		
		108a	108b	108c	102/25	116/33	116/47	38/180	SL ₅ -5	SL ₅ -12	SL ₅ -30	SL ₅ -31	SL-133	161	159	CRN136
SiO ₂	43.90	42.46	41.46	40.98	42.28	41.68	41.80	40.74	42.00	41.30	42.30	42.20	41.20	41.03	40.56	40.97
TiO ₂	0.00	1.83	1.95	2.36	0.00	0.00	0.00	0.00	0.06	0.13	0.06	0.19	0.05	3.20	4.09	3.10
Al ₂ O ₃	6.98	17.22	18.82	18.03	14.71	13.90	13.39	11.55	17.20	15.20	9.46	12.30	16.70	16.00	15.60	14.99
Cr ₂ O ₃	0.00	0.10	0.12	0.07	0.00	0.00	0.00	0.00	8.37	10.20	12.80	11.80	7.71	0.01	0.05	0.00
Fe ₂ O ₃	21.88	10.00	10.00	9.00	14.70	15.60	16.25	17.93	1.65	2.20	4.95	3.30	2.20	10.73	11.96	11.47
FeO	0.00	3.59	4.37	5.20	0.00	0.00	0.44	0.00	4.56	4.50	3.14	3.52	5.38	0.00	0.00	0.00
CaO	0.00	0.00	0.00	0.00	0.00	0.28	0.67	8.61	3.73	4.76	5.11	4.68	5.70	9.75	9.45	9.81
MnO	0.00	0.23	0.30	0.25	0.00	0.37	0.34	0.00	0.28	0.32	0.33	0.32	0.33	0.16	0.16	0.16
MgO	27.61	24.48	24.16	24.00	28.31	28.18	27.10	21.17	22.20	21.10	21.20	21.10	20.00	14.54	14.27	14.90
Sum	100.37	99.81	101.18	99.89	100.00	100.00	100.00	100.00	100.05	99.71	99.35	99.41	99.27	95.42	96.14	95.41
Si ⁴⁺	3.176	3.013	2.920	2.930	2.998	2.976	2.998	3.003	3.012	3.008	3.132	3.092	3.010	3.013	2.972	3.022
Ti ⁴⁺	0.000	0.098	0.103	0.127	0.000	0.000	0.000	0.000	0.003	0.007	0.003	0.010	0.003	0.176	0.225	0.172
Al ³⁺	0.594	1.438	1.560	1.517	1.228	1.168	1.130	1.002	1.452	1.303	0.824	1.061	1.436	1.383	1.345	1.301
Cr ³⁺	0.000	0.006	0.007	0.004	0.000	0.000	0.000	0.000	0.474	0.586	0.748	0.683	0.445	0.001	0.003	0.000
Fe ³⁺	1.189	0.533	0.529	0.483	0.783	0.837	0.876	0.993	0.089	0.120	0.275	0.182	0.121	0.592	0.659	0.636
Fe ²⁺	0.000	0.213	0.257	0.310	0.000	0.000	0.027	0.000	0.273	0.274	0.194	0.215	0.328	0.000	0.000	0.000
Ca ²⁺	0.000	0.000	0.000	0.000	0.000	0.021	0.051	0.68	0.287	0.371	0.405	0.367	0.446	0.767	0.742	0.775
Mn ²⁺	0.000	0.014	0.018	0.015	0.000	0.023	0.021	0.000	0.017	0.020	0.021	0.020	0.020	0.010	0.010	0.010
Mg ²⁺	2.974	2.586	2.534	2.555	2.988	2.996	2.894	2.322	2.370	2.288	2.337	2.302	2.176	1.589	1.557	1.636
Pir	33.3	65.0	65.0	65.0	60.9	57.5	54.6	50.0	62.7	54.4	40.2	45.5	59.5	69.0	67.0	65.0
Knor	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	12.7	17.2	23.8	21.7	7.5	0.0	0.0	0.0
Maj	66.6	27.0	26.0	24.0	39.1	41.1	42.1	26.4	4.5	6.0	14.0	9.1	6.0	4.0	8.5	6.0
Uvr	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	9.6	12.3	13.7	12.2	15.0	0.0	0.0	0.0
Alm	0.0	7.0	9.0	10.0	0.0	0.0	0.9	0.0	9.0	9.0	6.3	7.3	11.0	0.0	0.0	0.0
Spes	0.0	0.3	0.7	0.7	0.0	0.7	0.7	0.0	0.7	0.7	0.7	0.7	0.7	0.3	0.3	0.3
Andr	0.0	0.0	0.0	0.0	0.0	0.7	1.7	22.6	0.0	0.0	0.0	0.0	0.0	26.0	25.0	26.0

Note: garnets from lamprophyre of the Central Timan are our data, the remainder taken from the following publications: Coorara meteorite (Smith & Mason, 1970); inclusions in diamonds, Juin region, Brazil (Kaminsky *et al.*, 2001); inclusions in diamonds, Snap-Lake, Canada (Pokhilenko *et al.*, 2001); alnöite, Malaita Island, Solomon Islands, Pacific Ocean (Collerson *et al.*, 2000)

separate pyrope-andradite grains of there is a small amount of majorite component (according to our calculations 4–8.5%).

Formation conditions of mineral assemblage *Ca,Mg-perovskite* + "*majorite*" + *diamond* were estimated by Collerson *et al.* (2000) through empiric barometer using formula coefficient of Si in garnet formula, which is resulted in very high pressure of 22 GPa and consequently, depth of crystallization of this mineral assemblage of 400–670 km. These calculated data are consistent with experiments for Al-free iron-magnesium garnets. According to Kato (1986), majorite is stable at $2000 \pm 200^\circ\text{C}$ and 20 GPa.

Discussion

Non-stoichiometry and excess of SiO_2 in composition of tiny garnet inclusions (size infrequently exceeds 20 microns) in diamond crystals could be caused by: (1) error of microprobe analysis and (2) microinclusions of pyroxenes in garnets. The errors of microprobe analysis might arise due to micrograins of garnets being studied in pyroxene matrix displaying higher Si content in comparison with garnet.

Microinclusions of pyroxenes in garnets are more interesting case. Pyroxene clusters in garnet might be so small that they cannot be detected by conventional techniques and therefore, SiO_2 content can exceed real concentration in garnet. Oriented inclusions of pyroxenes in garnets, which in turn are enclosed in diamond crystals from Brazil and South Africa, are described by many researchers (Moore *et al.*, 1991; Haggerty, Sautter, 1990; Sautter *et al.*, 1991). Experimental study (Ringwood, 1967) suggest that oriented pyroxene inclusions found in natural garnets are resulted from exsolution of hypothetical mantle Fe-Mg-silicate. However, it does not follow that homogeneous phase enriched in pyroxene component should be mineral with the cubic garnet structure. Findings of tetragonal almandine-pyrope phase (TAPP) included in diamonds from the San-Luis placers, Juin district, Brazil (Stachel *et al.*, 2005) support this conclusion. It should be noted that according to cited papers, both tetragonal phases and garnets, containing oriented ingrowths of pyroxenes, are close to almandine-pyrope in composition.

In addition, all the quoted compositions of so called "majorite" with Si excess are characterized by significant Ca, which is not characteristic of original majorite. That is, these

unique pyroxene-garnet assemblages are not related to garnet $\text{Mg}_3\text{Fe}_2[\text{SiO}_4]_3$, for which the International Mineralogical Association approved the name "majorite". Therefore, garnet with Si excess should not be attributed to majorite based only on this feature, in order to avoid dual interpretation of the term majorite.

Conclusions

Majorite was found in nature only in the Coorara meteorite. Similar pyrope with high content of the majorite component $\text{Mg}_3\text{Fe}_2[\text{SiO}_4]_3$ (24–27%) was described as tiny inclusions in superdeep diamonds of Brazil (Kaminsky *et al.*, 2001). We identified further higher content of majorite component in pyropes (up to 42%) in several samples of lamprophyres from the kersantite and spessartite dikes in the Central Timan. These are the highest content of the majorite component in the terrestrial garnet.

Inclusions of pyrope-majorite in diamonds associated with ferripericlaase, perovskite and manganese ilmenite indicate ultrahigh pressure of formation of the garnet. Mantle xenoliths with the pyrope-majorite garnet in volcanic rocks can be served as indicator of deep origin of such rocks. Thus, pyrope with high content of majorite component discovered in the Central Timan lamprophyre for the first time is testimony to superdeep origin of lamprophyre magma, which could be genetically related to primary sources of the Timan diamonds.

Findings of so called tetragonal almandine-pyrope phase suggest that mineralogists are standing at the threshold of discovery of a new mineral species (with lower symmetry than that of garnet or higher, with respect to pyroxene). This mineral in the transformation series pyroxene to garnet would take place similar to wadsleite in the transformation series olivine through wadsleite to ringwoodite.

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