

GROSSULAR, VESUVIANITE and ACHTARANDITE MINERALOGY OF THE TALNAKH REGION

Maria S. Alferova

Fersman mineralogical museum RAS, Moscow, alferova.m@gmail.com

Achтарandite, the pseudomorph after unknown mineral is a mineralogical enigma. The second locality of achтарandite described in Talnakh region, Otdel'naya mountain, by its mineral association is an analogue of the type-locality in Yakutia republic, Wiluy river valley. The comprehensive investigation was applied to the rock-forming minerals – grossular, vesuvianite and achтарandite, and also to the mineral and fluid inclusions enclosed.

The experimental modelling of Cl-containing mayenite – the achтарandite proto-mineral synthesis was carried out.

It is established that the specific mineral association containing achтарandite happened during two stages: skarn and apo-skarn. During the first stage there were formed central parts of garnet and vesuvianite crystals, fassaite which remained as inclusions in vesuvianite, and Cl-containing mayenite. During the second stage there were formed edges of garnet and vesuvianite crystals, amesite, titanite, mackinawite, and Cl-containing mayenite was replaced by achтарandite.

7 tables, 8 figures, 28 references.

The mineral composition of grossular, vesuvianite and achтарandite found at Otdel'naya Mountain (Talnakh region) located in the north-western edge part of Siberian platform is similar to that found in the Wiluy river valley. The latter was first described in 1821 by Karl Laksman (Lyakhovich, 1954; Zhabin & Lyakhovich, 1994). The unique rocks containing garnet, vesuvianite and achтарandite were discovered in 2001 not far from the 'Mayak' mine at the foot of Otdel'naya Mountain (Pletnev, Alferova *et al.*, 2001).

Geology-petrological description of the grossular, vesuvianite and achтарandite locality

The plate complex is represented by gently pitching terrigenous, carboniferous limestones, dolomites and marls, sulfate-carboniferous and other sediments of Late Cambrian and Early-Middle Paleozoic (Cambrian – Devonian) periods, with thickness up to 3 km. They are overlapped by terrigenous coal-bearing sediments of Tungussskaya series (Carboniferous-Perm), up to 3.5 km thick. Volcanic trap rocks are associated with multiple intrusions of dolerite and gabbro-dolerites, some of which are enriched with Fe-Cu-Ni-Co

sulfide ores (Godlevsky, 1959). The ore-bearing intrusives are stratified massifs; in the lower part they are represented by picrite gabbro-dolerites saturated with sulfide droplets, in the upper part – by leucocratic gabbro-dolerites with xenoliths of hornfels and schlieren enriched in olivine, chrome-spinels and sulfides. The ore-bearing intrusives are surrounded by a thick aureole of hornfels (pyroxene-hornfels and albite-epidote-hornfels facies), including calcareous-silicate hornfels (skarnoids) and various magnesium and calcareous skarns. The estimated age of the trap formation rocks is $245 \pm 3 - 5$ mln. years, which corresponds to Permian and Triassic periods boundary (Spiridonov *et al.*, 2000).

The grossular, vesuvianite and achтарandite locality is represented by blocks of vastly altered terrigenous rocks of the plate complex (C₃-D₁). These comprise sandstones with dolomitic cement, limestones and dolomites marls. The blocks are enclosed as xenoliths in the front part of the north-eastern branch of Verkhnetalnakhsky taxitic gabbro-dolerite intrusive (T_{1,2}), Leucocratic gabbro-dolerites have undergone albitization and prehnitization processes in conditions of prehnite-pumpellyite facies low-grade metamorphism. They consist of plagioclase,

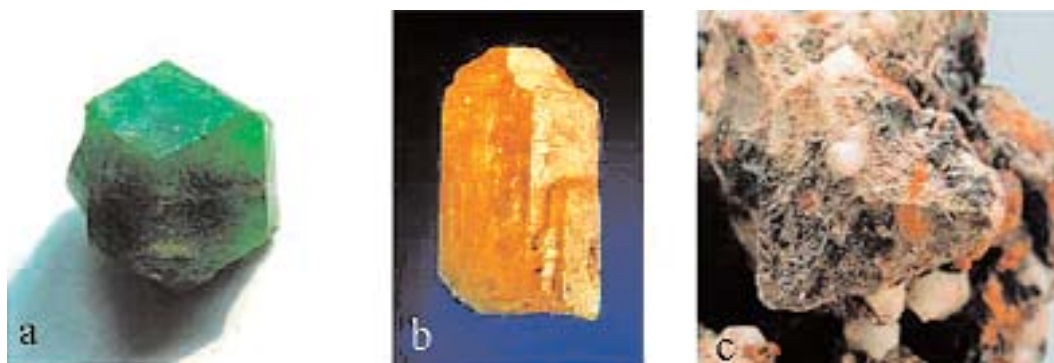


Fig. 1. Mineral association of the Talnakh locality: grossular (crystal size 5 mm), vesuvianite (crystal length 4 mm) and achtarandite (crystal size 6 mm).

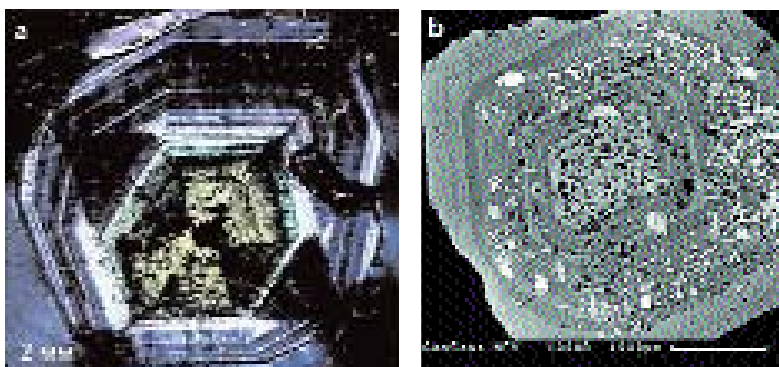


Fig. 2. Internal structure of Cr-Ti-containing grossular crystals from Otdel'naya Mt., Talnakh: a – thin section, b – BSE image

clinopyroxene, sulfides, apatite, titanite and chlorite minerals. Altered hornfels and skarns among leucogabbro are represented by non-equigranular aggregates of white and yellowish grossular, Cr-Ti-containing grossular, vesuvianite, achtarandite, chrome-spinel, calcite, chlorite group minerals, anhydrite, diopside, prehnite, serpentine in association with pyrrhotite, pyrite, sphalerite, chalcopyrite and their alteration products. The size of segregation of these minerals range from millimeter fractions up to 12 mm.

Mineralogy

The main rock-forming minerals at the aforesaid locality are grossular, vesuvianite and achtarandite. Megacrysts of these are set in the fine-grained matrix consisting of grossular, hydrogrossular, pyrite, chalcopyrite and iron oxides. The rocks are often incoherent.

Grossular – is the most common mineral at the locality. Garnet crystals and aggregates form phenocrysts, veinlets and monomineral aggregates in the altered leucogabbro. At the locality near the Otdel'naya Mountain grossu-

lar forms aggregates up to several tens of centimeters composing up to 60–80% of the rock. The mineral is represented by well-terminated crystals from 0.5–1 mm up to 8–10 mm and their aggregates. The main crystal faces are: {110}, {112}, {321} and their combinations. Garnet crystals are normally abruptly zoned; the central part is dark-green, the edge is colourless. The intermediate light-green zone as actually finely zoned with dark-green and colourless zones. In thin section they are anisotropic, sectorial and finely-zoned (Fig.2).

The garnet is chemically heterogeneous: the central dark-green part corresponds to a Cr-Ti-bearing variety of grossular whilst the colourless edge is almost a 'pure' end member (Table 1). The chemical composition of different parts of the garnets is shown in Figure 3. The distribution of the mineral-forming and accessory chemical elements in the zoned Cr-Ti-containing grossular is as follows: the central part of crystals is enriched in Cr, Ti and depleted in Si; the edge is enriched in Ca and Si. The IR spectrum of the edge zone of the garnet crystals corresponds to stoichiometric OH-free grossular.

Table 1. Chemical composition (wt.%) of garnet from Otdel'naya mountain (Talnakh) locality

Comp.	core					edge				
	1	2	3	4	5	6	7	8	9	10
SiO ₂	34.78	36.13	35.90	39.37	39.81	40.40	35.52	36.49	39.89	39.91
TiO ₂	6.47	5.70	5.30	1.38	—	0.21	6.89	5.05	—	0.11
Al ₂ O ₃	11.44	13.06	12.88	20.70	22.23	21.92	10.89	12.45	22.12	21.99
Fe ₂ O ₃	0.51	0.37	0.42	—	0.13	—	0.70	0.45	0.08	0.13
MnO	—	0.10	—	0.02	0.20	0.17	0.06	—	—	—
MgO	1.57	1.69	1.36	1.11	1.07	0.71	1.71	1.25	1.25	1.20
CaO	35.94	35.30	35.72	36.56	36.39	36.51	34.93	34.93	35.86	36.05
Cr ₂ O ₃	8.97	6.91	7.83	0.57	0.02	0.06	9.03	8.94	—	0.15
V ₂ O ₃	0.16	0.33	0.08	0.28	—	—	—	0.07	0.10	0.01
ZnO	0.01	0.25	0.11	—	—	—	0.15	0.12	0.22	0.24
Total	99.85	99.84	99.60	99.99	99.85	99.98	99.88	99.75	99.52	99.79

Notes: 1–6 analyst N.N. Korotaeva, using a CamScan electron microprobe; 7–10 analyst N.N. Kononkova using a Camebax SX-50 electron microprobe.

The central dark-green part of a garnet shows a weak peak in the 3800–3400 cm⁻¹ region indicating the presence of OH-groups in structure. According to thermal analysis of the colourless and light-green (which is a fine interchange of dark-green and colourless zones) parts of a garnet crystal, the weight loss determined were 1.1 wt.% and 1.6 wt.% for these parts respectively. The central part was not studied by this method due to difficulties with sample preparation.

The cell parameter of the edge of the garnet crystals is $a_0 = 11.849\text{\AA}$, which is after Gennady Yu. Shvedenkov's data (Shvedenkov *et al.*, 1974), corresponds to OH-free grossular.

Cr-Ti-containing grossular from the

Talnakh locality is a rare iron-free variety of grossular which, due to its bright green colour, is sometimes called 'siberian tsavolite'. At this locality colour, and hence the decorative features of the material, is due to specific geochemical conditions of high sulphur activity wherein all the Fe is combined as sulfides and not in silicates and chrome-spinel. The difference between tsavolite – V-Cr-containing grossular from Tanzania and grossular samples examined is revealed at their visible spectra. The tsavolite colour is due to Cr³⁺ and V³⁺ ions, which are seen as a double absorption band in 480–580 nm area of the visible spectra. The colour of the Cr-Ti-containing grossular

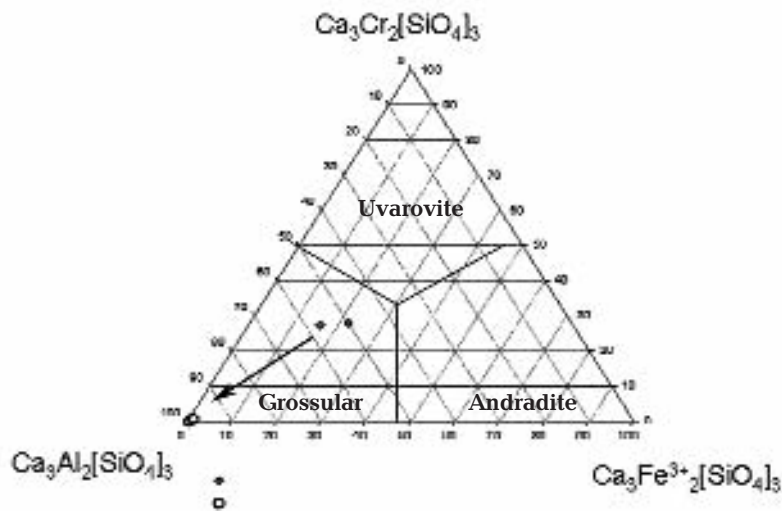


Fig. 3. Chemical composition of Cr-Ti-containing grossular from Otdel'naya Mt., Talnakh

from Talnakh is due to Cr^{3+} ions. In the visible spectra only one absorption band in 480–580 nm region is observed. This is shifted towards the shorter wavelength part of the region compared with that of tsavolite.

Cr-Ti-containing grossular from Talnakh is saturated with numerous mineral inclusions: chrome-spinel, vesuvianite, amesite, stilbite and Fe and Cu sulfides. In addition there are also fluid inclusions.

Chrome-spinel. Garnet crystals from Talnakh mostly contain numerous inclusions of chrome-spinel. Aggregates and chains of isometric brown-red translucent magnesio-chromite crystals are located within both dark-green and colourless zones (Fig. 4). Usually chrom-spinel crystals are themselves finely-zoned. Chemical composition is presented in the Table 2 and corresponds to Al-bearing magnesiochromite – an intermediate member of the MgCr_2O_4 – MgAl_2O_4 system (Table 2). As chrome-spinel does not contain magnetite, chromite and hercynite end members i.e. absolutely iron-free, it can be concluded that this mineral was formed at a relatively low temperatures and high sulphur activity. According to theoretic calculations (Sack & Ghiorso, 1991), there is a continuous solid solutions series in the system MgCr_2O_4 – MgAl_2O_4 at the temperatures above 550°C. Below this temperature chrome-spinels crystallized with chemical composition determined by the MgCr_2O_4 : MgAl_2O_4 ratio (solvus curve). According to Viktor V. Ryabov's data this ratio in chrome-spinels in rodingite garnets from Otdel'naya Mountain can be 4:1 (magnesiochromite) or 1:4 (Al-bearing magne-

siochromite). Chemical composition of the garnets studied are of the 4:1 ratio which corresponds to a temperature of formation between 300–400°C.

Despite the high chromium content (up to 82.2%) of chrome-spinel, there is no local enrichment in Cr around grains, which is typical for many metamorphic minerals formed after chrome-spinel, such as emerald or nephrite etc. Hence, most probably, the chrome-spinel described in this paper is 'new-born', paragenetic to the garnet and has not been altered. According to experimental data (Plyusnina *et al.*, 1993), to fluid inclusions data obtained and theoretical temperatures of formation for Al-bearing magnesio-chromite, the garnet formation temperature is below 400°C. High sulphur activity is corroborated by pyrite and chalcopyrite occurrence together with chrome-spinel.

According to X-Ray tomography performed on several zoned Cr-Ti-containing garnet crystals from Otdel'naya Mountain, Talnakh, the central dark- or bright-green part enriched in Cr and Ti does not contain relics of a connate chrome-spinel, or contains it very rarely.

Troilite $\text{Fe}_{0.64}\text{Ni}_{0.36}\text{Co}_{0.01}\text{S}_{0.99}$ occurs as xenomorphic ingrowths in grossular. Troilite is a typical low-grade metamorphic mineral.

Vesuvianite and amesite. White opaque mineral inclusions with square or rhombic section occur in all of the garnet crystals zones. Sometimes these open-work segregations are spread throughout the garnet crystal making it translucent/opaque with a white tint. More frequently these inclusions are concentrated between colour zones and growth sectors (Fig. 4). The inclusions are fine aggregates of

Table 2. Chemical composition (wt. %) of chrome-spinel inclusion in garnet from Otdel'naya mountain (Talnakh) locality

Comp.	1	2	3	4	5	6	7	8	9	10	11
Al_2O_3	9.87	11.48	10.80	10.30	8.24	10.40	7.78	9.26	10.08	9.96	6.65
FeO	–	0.20	0.36	0.61	1.14	1.53	1.68	1.67	1.77	1.97	1.95
Fe_2O_3	0.73	0.52	–	–	–	–	0.39	–	–	–	–
MnO	0.37	0.59	0.51	0.22	0.62	0.30	0.43	0.95	0.52	0.68	0.74
MgO	21.53	21.15	21.31	20.89	20.34	19.98	20.35	19.84	20.35	19.97	19.94
Cr_2O_3	63.98	64.35	65.64	67.04	68.41	66.10	67.56	67.25	66.13	66.65	70.15
NiO	n.d.	–	–	0.02	–	–	0.24	–	–	–	–
ZnO	0.21	0.20	0.24	0.05	0.18	0.55	0.32	0.36	–	0.29	–
Total	97.56	98.49	98.86	99.13	98.93	98.86	98.75	99.33	98.85	99.52	99.43

Notes: 1 analyst N.N. Kononkova using a Camebax SX-50 electrone microprobe; 2,3,5,6,8–11 – analyst N.N. Korotaeva & 4,7 analyst E.V. Guseva, using a CamScan electrone microprobe«CamScan»

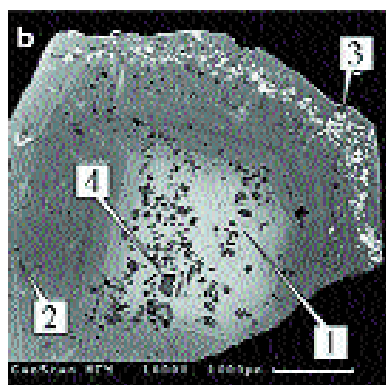
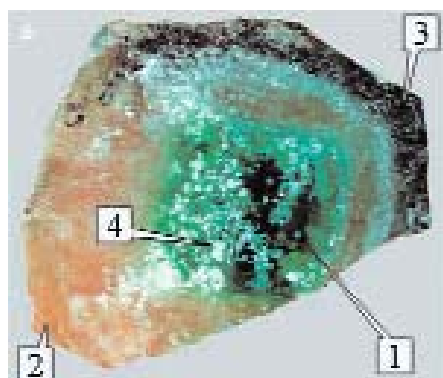


Fig. 4. Mineral inclusions in garnet crystal from Otdel'naya Mt., Talnakh:
a – reflected light, b – BSE image.
1 – Cr-Ti-grossular, 2 – hydrogrossular, 3 – magnesio-chromite, 4 – vesuvian-amesite aggregate

vesuvianite and amesite. Chemical composition of these minerals are presented in Table 3. The theoretical formula of vesuvianite is $\text{Ca}_{19}(\text{Al}, \text{Mg}, \text{Fe}^{2+}, \text{Fe}^{3+})_{13}(\text{B}, \square)_5[\text{SiO}_4]_{10}[\text{Si}_2\text{O}_7]_4(\text{OH}, \text{O}, \text{F})_{10}$. The formula of vesuvianite derived from inclusions and calculated for 50 cations is: $\text{Ca}_{19.00}(\text{Al}_{10.28}\text{Mg}_{2.55}\text{Fe}^{2+}_{0.05}\text{Cr}_{0.05}\text{Ti}_{0.01}\text{Ni}_{0.02}\text{Zn}_{0.06})_{13.02}(\text{B}_{0.66}\square_{4.34})_5[(\text{Si}_{15.66}\text{Al}_{2.34})_{18}\text{O}_{68}](\text{Cl}_{0.68}(\text{OH})_{9.3})_{10}$. Chemical composition of amesite corresponds to the formula $(\text{Mg}_{3.68}\text{Fe}^{2+}_{0.10}\text{Mn}_{0.07}\text{Ni}_{0.02}\text{Zn}_{0.01})_{3.88}(\text{Al}_{1.92}\text{Cr}_{0.02})_{1.94}[(\text{Si}_{2.22}\text{Al}_{1.78})_{4.00}\text{O}_{10}](\text{OH})_8$.

Stilbite. Sometimes different parts of the garnet crystals contain shapeless, curved ingrowths of white opaque stilbite inclusions. Chemical composition of stilbite is represented in the Table 3 and corresponds to the formula $(\text{Ca}_{1.35}\text{Na}_{0.01}\text{Fe}_{0.01})_{1.36}[\text{Al}_{2.53}\text{Si}_{9.42}\text{O}_{24}]\cdot 9(\text{H}_2\text{O})$.

Fluid inclusions. In the vesuvianite crystals

studied multiple fluid inclusions were noted which enabled the estimation of the temperature of formation range. Fluid inclusions studied are primary, primary-secondary and secondary. The size of inclusions is up to 10 – 15 μm . In those fluid inclusions where phase transfer is observed, the composition was determined as $\text{MgCl}_2 - \text{H}_2\text{O}$ with salts concentration 3.23 – 3.39 wt.% eqv. NaCl (Prokof'ev V.Yu. *et al.*, 1999). Results of the study is presented in a Table 4.

Vesuvianite occurs as crystals and crystal aggregates in the rodingite-like rocks of the Talnakh intrusive massif. Crystal sizes vary from 5 to 7 mm along the *c*-axis and from 3 to 4 mm along the *a*-axis. Colour varies from yellowish-green to pistachio-green and crystals are partially transparent. The morphology (block-like constitution, etching channels and

Table 3. Chemical composition (wt.%) of vesuvianite (1–4), amesite (5–6) and stilbite (7–9) inclusions in garnet from Otdel'naya mountain (Talnakh) locality

Comp.	1	2	3	4	5	6	7	8	9
SiO ₂	33.65	34.53	34.00	33.98	25.97	26.79	60.53	59.78	61.08
TiO ₂	0.02	0.08	–	–	0.16	–	0.02	0.02	0.08
Al ₂ O ₃	23.01	20.87	20.05	21.41	41.28	39.75	13.81	14.21	14.87
FeO	0.13	0.09	0.20	0.14	0.87	1.42	0.13	0.11	0.16
MnO	–	–	0.02	0.12	0.44	0.99	0.05	–	–
MgO	3.67	3.90	4.17	3.44	30.55	29.92	0.05	0.09	0.08
CaO	38.11	40.31	40.99	39.70	–	–	8.08	7.87	8.19
Cr ₂ O ₃	0.13	0.17	0.18	0.13	0.11	0.28	–	0.05	–
NiO	0.05	–	–	–	traces	0.22	n.d.	n.d.	n.d.
ZnO	0.17	–	0.39	–	–	0.14	–	–	–
Cl	0.86	n.d.	n.d.	0.86	–	–	–	–	0.01
Total	99.79	99.95	100.0	99.78	99.38	99.51	82.67	82.13	84.47

Notes: 1–6 – CamScan electrone microprobe; 1,4–6 analyst E.V. Guseva & 2,3 analyst N.N. Korotaeva; 7–9 analyst N.N. Kononkova using a Camebax SX-50 electrone microprobe. n.d. – not determined.

Table 4. Temperature conditions estimate of garnet crystals from Otdel'naya mountain (Talnakh) locality formation

Colour, (zone)	T _{hom.} , °C	Number of inclusions	T _{eut.} , °C	T _{ice melt.} , °C
green (core)	243–231	6		
colourless (edge)	206–186	7		
light-grey	215–196	8		
colourless (edge)	286	3	-32	-2.0
colourless (edge)	167–137	17	-33	-2.0–1.9

Notes: Analyst V.Yu Prokof'ev using a THMSG-600 Linkam thermocryocamera

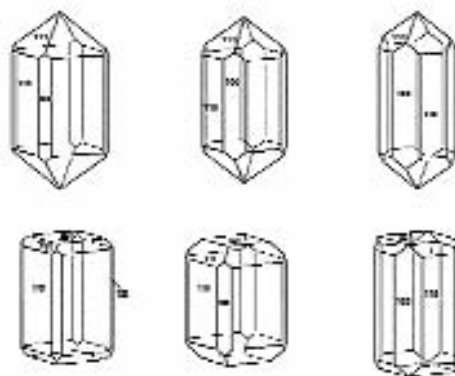


Fig. 5. Simple forms coordinations of vesuvianite crystals from Otdel'naya Mt., Talnakh

cavities) of the vesuvianite crystals are similar to that of wiluite.

Ten crystals were selected for goniometer measurements. Simple forms determined are presented in Fig. 5. Faces of prisms {110} and {100} and dipyrmaid {111} are predominant. Basal pinacoid faces {001} are subordinate or absent.

Vesuvianite crystals in thin sections are similar to the grossular crystals described above; being finely-zonal and sectorial. Sometimes they contain inclusions of bright-green zoned Cr-Ti-bearing grossular and calcite. Crystals show colour zonation across the *c*-axis: the inner zone is normally brownish-green or brownish-yellow containing many fluid and mineral inclusions. The outer zone is yellowish-green and transparent. The outline of the border between zones is normally rounded. Some crystals show splintered constitution across the *c*-axis.

According to EMPA data (Table 5), the chemical composition of the vesuvianite studied is characterized by low Fe content and relatively high Cl and F content. The formulae calculation was based on 50 cations, B and (OH)-group content were calculated according vesuvianite stoichiometry and charge balance. The presence of B was established by IR-spectroscopy.

As shown in Table 5, the Ti, Cr, B content in vesuvianite crystals decreases from the centre to the edge across the *c*-axis whilst the Cl and F content increases. This latter aspect is possi-

bly evidence of increasing Cl and F activity during the final stage of the crystal-forming process. The decrease in Ti and Cr content in vesuvianite crystals, similar to that in zonal grossular garnet, confirms their paragenesis.

The IR-spectra of the Talnakh vesuvianite are similar to the IR-spectra of wiluite (Kurazhkovskaya *et al.*, 2004); they also show [BO₃] and [BO₄] groups vibration bands. According to the EMPA data, vesuvianite from the Otdel'naya Mountain contains up to 1.5 wt.% of F, which is intermediate between the content in vesuvianite from skarns (up to 2 wt.% F) and from rodingites (up to 0.6 wt.% F) (Allen & Burnham, 1992; Armbruster & Gnos, 2000).

Vesuvianite from Talnakh contains mineral inclusions of augite, perovskite, titanite, Cr-Ti-containing grossular, hydrogrossular and iron sulfides.

Augite, perovskite, titanite, hydrogarnet (?)

Inclusions of augite occur in all the vesuvianite crystals (mostly in the central parts) studied. Under electron microscope imaging augite inclusions are seen as well-terminated crystals up to 0.1 μm in size. The typical empiric formula is Ca_{1.00}(Mg_{0.72}Al_{0.23}Ti_{0.05}Cr_{0.01})_{1.01}[Si_{1.67}Al_{0.33}]_{2.00}O₆. Perovskite grains occurring as intergrowths with augite, have the formula (Ca_{0.99}Na_{0.01})_{1.00}Ti_{0.98}O_{2.96}. The ingrowths of titanite ranging from 30–50 μm in size occur mostly in the periphery zone of the augite and perovskite grains. Titanite does not form isolated grains in vesuvianite and is possi-

Table 5. Chemical composition (wt. %) of vesuvianite from Otdel'naya mountain (Talnakh) locality

Comp.	core					edge		core					edge	
	1	2	3	4	5	6	7	8	9	10	11			
SiO ₂	37.58	36.42	37.27	37.04	37.32	37.32	36.66	36.59	35.78	36.39	37.19			
TiO ₂	1.53	1.34	1.64	0.37	0.55	0.94	1.90	1.35	1.08	1.20	0.94			
Al ₂ O ₃	15.14	14.98	15.49	17.23	17.68	17.21	14.23	15.37	16.06	16.03	17.03			
FeO	0.12	0.06	—	0.17	0.17	0.15	0.28	0.11	0.09	0.11	0.21			
MnO	0.06	—	—	traces	0.05	0.03	—	0.03	0.02	0.10	—			
MgO	5.80	6.00	5.75	5.03	4.33	4.73	5.72	5.94	5.23	5.43	5.06			
Na ₂ O	0.01	0.01	—	0.02	0.07	0.02	0.04	0.03	0.01	0.02	0.01			
CaO	35.69	36.04	36.14	36.44	36.85	36.37	36.39	36.28	36.26	36.69	36.80			
Cr ₂ O ₃	0.07	0.17	0.09	0.01	0.05	—	0.05	—	0.01	—	—			
V ₂ O ₃	0.08	0.03	0.09	0.05	0.02	0.02	0.02	0.10	0.15	0.10	0.03			
ZnO	0.16	0.25	—	—	0.11	—	0.12	0.09	—	0.03	—			
Cl	0.05	0.05	0.02	0.10	0.04	0.09	0.04	0.01	0.12	0.06	0.14			
F	0.74	0.98	0.84	0.90	0.81	1.22	0.75	0.91	1.39	1.41	1.47			
B*	1.22	1.14	1.12	1.04	1.02	0.85	1.28	1.10	0.96	0.76	0.55			
OH*	1.75	2.53	1.55	1.60	0.93	1.05	2.52	2.09	2.84	1.67	0.57			
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0			
Apfu calculated for 50 cations														
Ca	18.11	18.33	18.25	18.32	18.48	18.14	18.65	18.37	18.38	18.35	18.15			
Na	0.01	0.01	—	0.02	0.06	0.02	0.03	0.02	0.01	0.02	0.01			
Mg	4.10	4.25	4.04	3.52	3.02	3.28	4.07	4.19	3.69	3.77	3.47			
Mn	0.02	—	—	—	0.02	0.01	—	0.01	0.01	0.04	—			
Zn	0.06	0.09	—	—	0.04	—	0.04	0.03	—	0.01	—			
Fe ²⁺	0.05	0.02	—	0.07	0.07	0.06	0.11	0.04	0.04	0.04	0.08			
Al	8.45	8.38	8.61	9.53	9.75	9.44	8.02	8.56	8.95	8.82	9.24			
Cr	0.03	0.06	0.03	0.01	0.02	—	0.02	—	сл.	—	—			
Ti	0.54	0.48	0.58	0.13	0.19	0.33	0.68	0.48	0.39	0.42	0.33			
V	0.03	0.01	0.04	0.02	0.01	0.01	0.01	0.04	0.06	0.04	0.01			
B*	3.22	3.00	2.95	2.71	2.65	2.20	3.42	2.90	2.57	1.96	1.41			
Si	17.80	17.29	17.56	17.38	17.47	17.38	17.53	17.29	16.93	16.98	17.12			
(OH) ₄ *	0.74	1.07	0.64	0.66	0.77	0.44	1.07	0.87	1.18	0.69	0.24			
Cl	0.04	0.04	0.02	0.08	0.03	0.07	0.03	0.01	0.09	0.05	0.11			
F	0.78	1.04	0.88	0.94	0.85	1.26	0.79	0.96	1.46	1.46	1.50			

Notes: Analyst N.N. Kononkova using a Camebax SX-50 electron microprobe. *Calculated according to valence balance and stoichiometry.

by the alteration product of augite and perovskite. Chemical composition of titanite corresponds to the formula Ca_{1.01}(Ti_{0.75}Al_{0.23}Cr_{0.01})Si_{1.01}O_{4.85}F_{0.09} (Table 6).

Augite and perovskite inclusions (typical minerals of magnesium skarns) in the central zone of vesuvianite crystals are the probably evidence of relatively high-temperature conditions during the crystal-forming process.

Garnet inclusions occur in the periphery

zone of the vesuvianite crystals. According to the thermobarogeochemical data obtained from garnet crystals, the paragenetic late stage vesuvianite-forming process was at a temperature of nearly 250°C.

Sometimes between the two zones in vesuvianite crystals well-terminated inclusions of white opaque micrograin aggregate up to 50 μm in size occur. By chemical composition these correspond to either vesuvianite (formula Ca_{19.29}(Al_{9.17}Mg_{3.25}Fe²⁺_{0.07}Cr_{0.01}Ti_{0.01}Zn_{0.04})_{12.55}

Table 6. Chemical composition (wt. %) of augite (1-2), perovskite (3-4), titanite (5) and vesuvianite-hydrogarnet aggregate (6-8) inclusions in vesuvianite from Otdel'naya mountain (Talnakh) locality

Comp.	1	2	3	4	5	6	7	8
SiO ₂	45.77	46.08	—	—	31.29	35.88	36.02	36.26
TiO ₂	1.85	1.62	57.79	55.01	30.85	0.14	0.03	0.02
Al ₂ O ₃	13.53	12.75	0.29	0.62	5.99	21.90	19.23	17.30
FeO*	0.08	0.05	—	—	0.09	0.58	0.55	0.17
Fe ₂ O ₃ *	—	—	0.07	0.36	—	—	—	—
MnO	0.09	0.01	—	—	0.04	0.27	0.19	0.12
MgO	13.29	13.25	0.01	0.01	ca.	3.90	3.06	4.55
CaO	25.71	25.81	40.79	39.33	29.24	32.41	36.59	37.53
Na ₂ O	0.04	0.02	0.17	ca.	—	0.03	0.01	—
Cr ₂ O ₃	0.22	0.47	0.45	0.80	0.20	0.15	0.06	0.01
V	—	—	0.26	0.13	0.12	0.05	—	0.07
ZnO	—	0.19	—	—	—	0.11	0.15	0.11
Cl	0.01	0.02	0.07	0.02	—	0.03	0.02	0.12
F	—	0.07	0.17	0.40	1.26	0.44	—	—
Total	100.59	100.34	100.07	96.68	99.08	95.89	95.89	96.25

Notes: 1–5 –CamScan electrone microprobe; 1,2,5 analyst E.V. Guseva & 3,4 analyst N.N. Korotaeva; 6–8 analyst N.N. Kononkova using a Camebax SX-50 electrone microprobe.

(B_{4.04}□_{0.96})₅ [(Si_{17.39}Al_{0.61})₁₈O₆₈](Cl_{0.09}(OH)_{9.91})₁₀ or hydrogrossular (formula (Ca_{2.54}Mg_{0.43}Mn_{0.02})_{2.99}(Al_{1.89}Fe³⁺_{0.03}Cr_{0.01}Ti_{0.01})_{1.94}[Si_{2.62}(O₄H₄)_{0.38}]_{3.00}O_{10.48}F_{0.07}). Probably the inclusions are a fine grained mixture of these minerals (Fig. 6).

Pyrite, pyrrhotite

Pyrite and pyrrhotite occur as xenomorphic segregations up to 0.5 mm in size, normally 0.2 mm. Pyrite formula – (Fe_{0.98}Ni_{0.01})_{0.99}S_{2.01}, pyrrhotite formula – (Fe_{6.83}Ni_{0.04})_{6.87}S_{8.13}. Pyrrhotite and pyrite formation indicates high S activity in the mineral system resulting in widespread occurrence of sulfides in the host rocks. Thus, Fe preferentially appears in the sulfides rather than silicates.

Achtarandite occurs as trigon-tristetrahedral crystals (Fig. 7), their twins and aggregates, normally 3–6 mm but up to 9–12 mm in size. As a rule the content of achtarandite in the rocks of Otdel'naya Mountain is approximately 5 vol. %. Achtarandite is unevenly distributed. Separate nests up to 5 cm in size are composed of 50–80 vol.% achtarandite. The achtarandite is colourless. Sometimes achtarandite is characterised by 'stuffed' crystals with multiple inclusions of zoned green

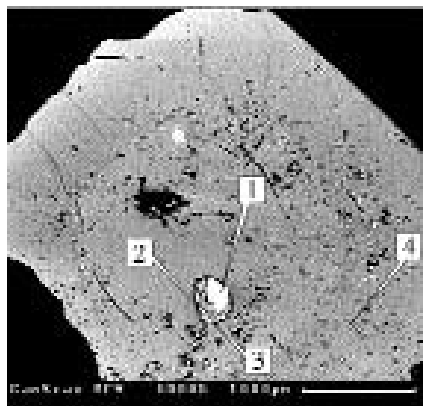


Fig. 6. Mineral inclusions in vesuvianite crystals from Otdel'naya Mt., Talnakh: (1) perovskite, (2) augite, (3) titanite, (4) hydrogrossular



Fig. 7. Achtarandite crystals from Otdel'naya Mt., Talnakh: a – terminated with direct and reverse trigontristetrahedrons, b – in association with zonal Cr-Ti-containing grossular and calcite (thin section)

Table 7. Chemical composition of achtarandite: 1 – achtarandite from Otdel'naya mountain (Talnakh) locality, 2–5 achtarandite from Wiluy river valley

Comp.	1	2	3	4	5
SiO ₂	39.52	39.25	34.70	40.10	34.72
TiO ₂	0.24	–	0.30	–	0.31
Al ₂ O ₃	14.30	11.11	11.17	12.36	13.40
Fe ₂ O ₃	6.71	17.09	7.48	n.d.	5.42
FeO	–	–	1.95	n.d.	2.15
MnO	0.65	–	0.14	–	0.12
MgO	9.77	3.60	19.46	n.o.	19.40
CaO	22.54	12.54	17.03	11.27	16.60
Na ₂ O	0.07	–	n.d.	–	n.d.
K ₂ O	0.01	–	n.d.	–	n.d.
P ₂ O ₅	0.01	–	–	–	–
Cr ₂ O ₃	0.06	–	–	–	–
S	0.12	–	–	–	–
F	0.09	–	–	–	–
Cl	0.04	–	–	–	–
H ₂ O ⁻	–	–	0.56	–	0.83
H ₂ O ⁺ (decrepitation weight loss)	5.93	10.09	7.30	12.27	7.80
CO ₂	–	–	0.54	–	n.d.
Total	100.06	93.68	100.63	76.00	100.75

Notes: 1 – analyst A.I. Yakushev using a Philips PW-2400 XRD; 2, 3 – data after Beck, Hermann (Lyachivich, 1954); 4 – (Lyakhovich, 1954); 5 – (Zhabin & Lyakhovich, 1994). N.d. – not determined

(Cr-Ti-containing) and white (Cr-Ti-free) grossular. In general, achtarandite consists of micro-grained aggregates of garnet, vesuvianite, magnesium rich chlorite and/or serpentine, sphaalerite and chalcopyrite. According to the X-Ray (diffractometer DRON-3.5, $2\theta = 5-120^\circ$) phase analysis data obtained, achtarandite pseudomorphs consist of hydrogrossular ($a_0 = 11.971(2) \text{ \AA}$) for 2/3 volume and of serpentine-7 \AA septechlorite (berthierine) for 1/3 with admixture of calcite, quartz and hematite. These data directly correlates with EMPA data.

Chemical composition of the Talnakh achtarandite (Table 7, analysis 1) is close to that of Wiluy achtarandite (Table 7, analyses 2–4); the latter is enriched in Mg and H₂O, the former is enriched in Ca. Therefore, achtarandite from Wiluy is enriched in minerals of the serpentine and chlorite groups, and from Talnakh – enrichment in hydro- and grossu-

lar. The microelements composition according to RFA is the following (ppm): Cr 417, Ni 73, Co 13, Cu 137, Zn 815, S 1190, F 900, Cl 351, V 22, Sr 14, Ba 36, Y 2, Sc 11, Zr 112, Nb 5, Rb 9 (Pletnev *et al.*, 2001). Relatively high concentration of Zr is due to hydrogrossular enriched in ZrO₂ up to 0.7 wt.% (Ryabov *et al.*, 1996).

Synthesis of achtarandite proto-phase

The first attempts to synthesise high-pressure garnet as a proto-mineral of achtarandite (Gorokhov *et al.*, 1971), were based on a later disproved hypothesis *r* (Pertsev, 1972). Since then scientists made theoretical investigations and speculated about a possible proto-phase (Tchesnokov *et al.*, 1993–1996; Galuskin *et al.*, 1995; Galuskina, 1998; Pavlushin, 2000).

In 1996 Boris V. Tchesnokov *et al.* discovered, in the mineral association of burnt dumps, fumarolitic oxo- and chlorine-bearing garnetoids (those compounds that have structures similar to that of true garnets (McConnell (1942)) – Cl-bearing wadalite and Cl-bearing mayenite, whose crystal shape is similar to that of achtarandite, and assumed that these minerals are the most probable achtarandite proto-phases (Tchesnokov *et al.*, 1996).

Mayenite was first described from Mayen, Eifel Mountains, Germany (Hentschel, 1964). It was found in lava vents which indicates its pneumatolytic origin. This mineral belongs to the so called garnetoids – complex oxides with garnet structure, its formula – Ca₁₂Al₁₄O₃₃, space group – *I*-43d. In natural mayenite oxygen is partially replaced by (F-, Cl-, OH-) which brings it closer to wadalite Ca₆Al₅Si₂O₁₆Cl₃ – an isostructural Cl-bearing mineral (Glasser, 1995). Wadalite and grossular are related to each other structurally (Tsukimura *et al.*, 1993) which was later proven experimentally: wadalite was formed after heat treatment of hydrogrossular (hibschite) in chlorine vapor (Fujita *et al.*, 2001).

In this study the synthesis of the probable proto-phase of achtarandite was performed on the basis of its genetic and structural similarity with grossular-hydrogrossular and the assumption about its pneumatolytic character of a process based on the literature and own analytical data. Method of the synthesis of Cl-bearing garnetoids wadalite-mayenite was based on the

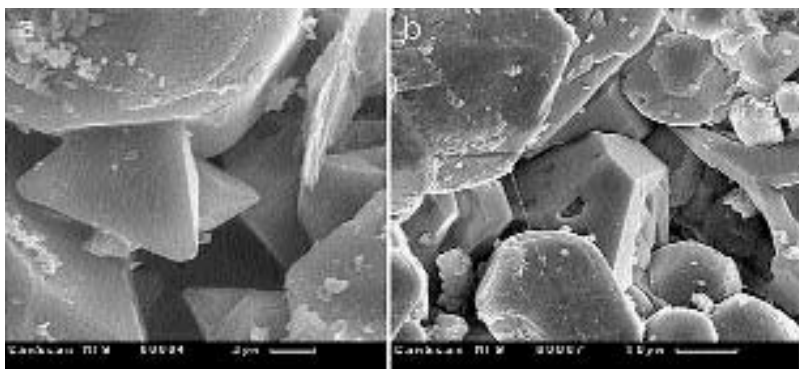
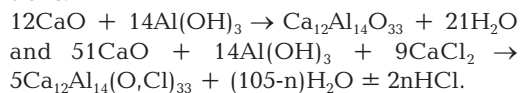


Fig. 8. BSE images of the phases synthesized: a – mayenite ($T=550^{\circ}\text{C}$, $P=1\text{ kb}$), b – Cl-containing mayenite ($T=550^{\circ}\text{C}$, $P=3\text{ kb}$)

data for hydrogrossular synthesis (Shvedenkov *et al.*, 1974). A series of experiment were undertaken in order to obtain the most probable proto-phases of achtearandite: Cl-bearing mayenite, Cl-bearing hibschite, Cl-bearing wadalite and their Cl-free analogues. Experimental conditions were held at 550°C and pressures of 1 kbar and 3 kbar, experiment duration – 14 days. The source materials are: CaO, Al_2O_3 or $\text{Al}(\text{OH})_3$, SiO_2 , CaCl_2 . Synthesis was according to the reactions:



The size of the garnet-like crystals obtained ranged from fractions of a micron up to 20 micron. Among them were trigon-tristetrahedral mayenite crystals with Cl content up to 0.59 wt.% of Cl (Fig. 8). Chemical composition of mayenite synthesized (wt.%): SiO_2 10.56–11.70, Al_2O_3 45.07–45.62, CaO 43.48–42.8 (Alferova, 2004).

The origin of mineral association with achtearandite

As it was noted above, the studied mineral associations at the Otdel'naya Mountain locality for grossular, vesuvianite and achtearandite and those at the Wiluy River deposit for grossular, vesuvianite and achtearandite are similar. They are thought to be of skarn origin (Ryabov, 1996; Lyakhovich, 1954), however mineral paragenesis, IR data, fluid inclusions data and experimental data obtained testify to a more complex process which consisted of at least two stages: a high-temperature skarn and a low-temperature apo-skarn.

During the high-temperature stage augite

and perovskite were formed which can be observed as mineral inclusions in the central parts of vesuvianite crystals, and also the central parts of vesuvianite crystals themselves.

During the low-temperature stage the paragenesis: grossular, hydrogrossular (containing over 10 wt.% of Cr_2O_3 and TiO_2 (Ishimoto *et al.*, 1983)), boron-containing vesuvianite (edge parts of the crystals), amesite, diopside, Al-bearing magnesiochromite, titanite, troilite, chlorite, serpentine were formed. These are typical minerals of the prehnite-pumpellyite facia of low-grade metamorphism.

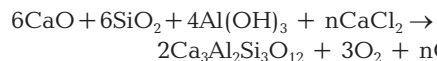
Well-terminated inclusions of aggregates of vesuvianite, amesite and hydrogrossular, occur in grossular and vesuvianite crystals, resemble pseudomorph alike achtearandite which is in the same mineral association. Starting from assumption that these inclusions are achtearandite, one could state that they were altered as well as separate crystals of achtearandite.

Possibly, the mineral forming process was as follows: at the early skarn stage the high-temperature minerals, central parts of vesuvianite crystals and proto-achtearandite (Cl-bearing mayenite) were formed. At the apo-skarn stage the low-temperature minerals were formed, partially as products of alteration of the high-temperature phases: grossular – after plagioclase, Cr-Ti-bearing grossular and Al-bearing magnesiochromite – after primary chome-spinel, low-temperature vesuvianite – after the high-temperature vesuvianite, achtearandite – after Cl-bearing mayenite, titanite – after perovskite. The whole process ended with the formation of thin veinlets of chalcopyrite, troilite and stilbite. We believe that the mineral-forming process at the Wiluy deposit was similar. At the high-temperature stage grossular, wiluite and Cl-bearing mayen-

ite were formed, and at the low-temperature stage the latter was replaced by achtarandite.

In our opinion, the mineral that was later replaced by achtarandite, was initially formed during a distinctive high-temperature skarn process with chlorine-based pneumatolytic influence. The supposed proto-mineral for achtarandite – Cl-bearing mayenite – conforms to the character of the process. The following data indicates the type of pneumatolytic process: 1 – mayenite was first discovered in a post-magmatic fluid-rich lava derivative, 2 – Cl-bearing mayenite with morphology similar to that of achtarandite was found in the burnt dumps of the Chelyabinsk coal basin. This fumarolytic process occurred as a result of human intervention, 3 – synthesis of Cl-bearing mayenite was held in a 'dry' system, after the experiment the excess of HCl was recorded, 4 – transformation of hibschite into wadalite was achieved by the effect of vaporized chlorine phases on hibschite (Fujita *et al.*, 2001).

Grossular and proto-achtarandite – mayenite are structurally and chemically related to each other, and this lead many scientists to consider grossular as a proto-mineral of achtarandite. The first relationship is confirmed by the hibschite-wadalite transformation reaction and isostructural series wadalite-mayenite; the second relationship is proved to be true by obtaining grossular during mayenite and wadalite synthesis according to the chemical reaction:



without free chlorine. Thus achtarandite occurrence is probably, an indicator of a local increased content of Ca in rocks subject to pneumatolysis.

After that the transformation mayenite – wadalite – hydrogrossular took place under the low-temperature process conditions; and the initial morphology was retained. As a result we observe achtarandite represented mainly by hydrogrossular aggregate. During this low-temperature process associated minerals containing Cr- and Ti-bearing grossular, structurally unusual vesuvianite (Otdel'naya Mountain, Talnakh), large grossular and wiluite (Wiluy River, Yakutia) crystals were formed.

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