

Article

Copper in Natural Oxide Spinel: The New Mineral Thermaerogenite CuAl_2O_4 , Cuprospinel and Cu-Enriched Varieties of Other Spinel-Group Members from Fumaroles of the Tolbachik Volcano, Kamchatka, Russia

Igor V. Pekov ^{1,*}, Fedor D. Sandalov ¹, Natalia N. Koshlyakova ¹, Marina F. Vigasina ¹, Yury S. Polekhovskiy ^{2,†}, Sergey N. Britvin ^{2,3}, Evgeny G. Sidorov ⁴ and Anna G. Turchkova ¹

¹ Faculty of Geology, Moscow State University, Vorobievy Gory, 119991 Moscow, Russia; fyodor.sandalov@yandex.ru (F.D.S.); nkoshlyakova@gmail.com (N.N.K.); vigasina@geol.msu.ru (M.F.V.); annaturchkova@rambler.ru (A.G.T.)

² Institute of Earth Sciences, St. Petersburg State University, Universitetskaya Nab. 7/9, 199034 St Petersburg, Russia; sbritvin@gmail.com (S.N.B.)

³ Nanomaterials Research Center, Kola Science Centre, Russian Academy of Sciences, Fersman str. 14, 184209 Apatity, Murmansk Region, Russia

⁴ Institute of Volcanology and Seismology, Far Eastern Branch of Russian Academy of Sciences, Piip Boulevard 9, 683006 Petropavlovsk-Kamchatsky, Russia; mineral@kscnet.ru

* Correspondence: igorpekov@mail.ru; Tel.: +7-495-939-4676

† Deceased 28 September 2018.

Received: 11 October 2018; Accepted: 29 October 2018; Published: 1 November 2018



Abstract: This paper is the first description of natural copper-rich oxide spinels. They were found in deposits of oxidizing-type fumaroles related to the Tolbachik volcano, Kamchatka, Russia. This mineralization is represented by nine species with the following maximum contents of CuO (wt.%, given in parentheses): a new mineral thermaerogenite, ideally CuAl_2O_4 (26.9), cuprospinel, ideally $\text{CuFe}^{3+}_2\text{O}_4$ (28.6), gahnite (21.4), magnesioferrite (14.7), spinel (10.9), magnesiochromite (9.0), franklinite (7.9), chromite (5.9), and zincochromite (4.8). Cuprospinel, formerly known only as a phase of anthropogenic origin, turned out to be the Cu-richest natural spinel-type oxide [sample with the composition $(\text{Cu}_{0.831}\text{Zn}_{0.100}\text{Mg}_{0.043}\text{Ni}_{0.022})_{\Sigma 0.996}(\text{Fe}^{3+}_{1.725}\text{Al}_{0.219}\text{Mn}^{3+}_{0.048}\text{Ti}_{0.008})_{\Sigma 2.000}\text{O}_4$ from Tolbachik]. Aluminum and Fe^{3+} -dominant spinels (thermaerogenite, gahnite, spinel, cuprospinel, franklinite, and magnesioferrite) were deposited directly from hot gas as volcanic sublimates. The most probable temperature interval of their crystallization is 600–800 °C. They are associated with each other and with tenorite, hematite, orthoclase, fluorophlogopite, langbeinite, calciolangbeinite, apthitalite, anhydrite, fluoborite, sylvite, halite, pseudobrookite, urusovite, johillerite, ericlxmanite, tilasite, etc. Cu-bearing spinels are among the latest minerals of this assemblage: they occur in cavities and overgrow even alkaline sulfates. Cu-enriched varieties of chrome-spinels (magnesiochromite, chromite, and zincochromite) were likely formed in the course of the metasomatic replacement of a magmatic chrome-spinel in micro-xenoliths of ultrabasic rock under the influence of volcanic gases. The new mineral thermaerogenite, ideally CuAl_2O_4 , was found in the Arsenatnaya fumarole at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption. It forms octahedral crystals up to 0.02 mm typically combined in open-work clusters up to 1 mm across. Thermaerogenite is semitransparent to transparent, with a strong vitreous lustre. Its colour is brown, yellow-brown, red-brown, brown-yellow or brown-red. The mineral is brittle, with the conchoidal fracture, cleavage is none observed. $D(\text{calc.})$ is 4.87 g/cm³. The chemical composition of the holotype (wt.%, electron microprobe) is: CuO 25.01, ZnO 17.45, Al_2O_3 39.43, Cr_2O_3 0.27, Fe_2O_3 17.96, total 100.12 wt.%. The empirical formula calculated on the basis of 4 O *apfu* is:

$(\text{Cu}_{0.619}\text{Zn}_{0.422})_{\Sigma 1.041}(\text{Al}_{1.523}\text{Fe}^{3+}_{0.443}\text{Cr}_{0.007})_{\Sigma 1.973}\text{O}_4$. The mineral is cubic, $Fd-3m$, $a = 8.093(9)$ Å, $V = 530.1(10)$ Å³. Thermaerogenite forms a continuous isomorphous series with gahnite. The strongest lines of the powder X-ray diffraction pattern of thermaerogenite [d , Å (I , %) (hkl)] are: 2.873 (65) (220), 2.451 (100) (311), 2.033 (10) (400), 1.660 (16) (422), 1.565 (28) (511) and 1.438 (30) (440).

Keywords: thermaerogenite; cuprospinel; gahnite; magnesioferrite; CuAl_2O_4 ; CuFe_2O_4 ; copper oxide; new mineral; spinel supergroup; fumarole sublimate; Tolbachik volcano; Kamchatka

1. Introduction

Oxide spinels compose one of the most studied mineral families and have numerous implications in the geosciences, chemistry and materials science [1]. In spite of the apparent simplicity, the spinel-type crystal structure exhibits a remarkable flexibility towards cation and anion substitutions, which results in the appearance of minerals accommodating more than two dozens of chemical elements [2]. Copper-bearing oxide spinels, being well studied as synthetic phases in materials science, are however virtually unknown in nature. The only reported Cu-rich spinel-type oxide mineral, cuprospinel, ideally $\text{CuFe}_2^{3+}\text{O}_4$, is in fact an anthropogenic phase as it has never been found in the natural environments unaffected by anthropogenic influence factors. Cuprospinel was described as a new mineral species from burnt dumps on the property of Consolidated Rambler Mines Limited near Baie Verte, Newfoundland, Canada, where, together with hematite and a Cu-rich (13.9 wt.% CuO) variety of magnesioferrite, it was formed in the result of a spontaneous fire of the mined copper-zinc ore [3]. Thus, these oxides have definite anthropogenic origin, as well as cuprospinel formed as an incidental product of ore processing in ancient and modern smelters [4,5]. Cuprospinel was mentioned in a volcanic material from Mahanadi, Orissa, India [6], and in ores of the Chahnal gold deposit in SE Iran [7], however, no analytical evidences were given and the identification of this mineral from both localities seems doubtful.

In the course of ongoing research of oxidizing-type fumaroles related to the Tolbachik volcano at Kamchatka, Russia, we have encountered more than twenty oxide minerals. Among those, ten mineral species belonging to the spinel supergroup [2] were identified, including the new mineral deltalumite, $(\text{Al}_{0.67}\square_{0.33})\text{Al}_2\text{O}_4$, the delta-alumina dimorphous with corundum [8]. A remarkable chemical feature of Tolbachik spinels is the common presence of a significant amount of copper. CuO contents ranging from 1 to 18 wt.% are typical for spinel, magnesioferrite, gahnite, franklinite, magnesiochromite, chromite and zincochromite. Besides these Cu-rich mineral varieties, two minerals with species-defining copper were therein discovered: the genuine natural cuprospinel and a new mineral first described in the present paper, thermaerogenite, ideally CuAl_2O_4 . The latter was recently approved by the IMA Commission on New Minerals, Nomenclature and Classification (IMA no. 2018-021). The name thermaerogenite (Cyrillic: термаэрогенит) is constructed based on the combination of Greek words θερμός, hot, αέριον, gas, and γενής that means “born by”. Thus, in whole it means *born by hot gas*, that reflects the fumarolic origin of the mineral. This name also contains the allusion that Cu-rich spinel-type oxides form in volcanic fumaroles and their anthropogenic counterparts, unlike Cu-free and Cu-poor oxide spinels, are numerous and widespread in other geological formations. The type specimen of thermaerogenite is deposited in the collections of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, with the registration number 5192/1.

The Mg-Al-Fe oxide spinels, namely magnesioferrite, magnetite and spinel were previously reported from fumaroles of several active volcanoes [9–13]. However, no information on Cu contents in these minerals was published. Moreover, we did not find any references on Cu-enriched (with CuO content higher than 1 wt.%) natural oxide spinels. Thus, this work is the first report on natural copper-rich oxide members of the spinel supergroup.

2. Occurrence and Mineral Associations

The studied material was collected by us during fieldwork in the period of 2012–2018. The majority of studied samples originate from the Arsenatnaya fumarole, one of the brightest in the mineralogical aspect examples in the world of fumaroles belonging to the oxidizing type (in fumaroles of this type, the increase of oxygen fugacity is a result of the mixing of volcanic gases with the atmospheric air [14,15]). Arsenatnaya is located at the apical part of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption (below–NB GTFE), Tolbachik volcano, Kamchatka Peninsula, Far-Eastern Region, Russia (55°41' N 160°14' E, 1200 m asl). This scoria cone, formed in 1975, is a monogenetic volcano about 300 m high and approximately 0.1 km³ in volume [16]. Now, more than 40 years after the eruption, its fumarole fields remain active: numerous gas vents with temperatures up to 490 °C were observed by us in 2012–2018. Now the fumarolic gases at the Second scoria cone are compositionally close to atmospheric air, with the contents of <1 vol.% water vapour and <0.1 vol.% acid species, mainly CO₂, HF and HCl [17], while in 1976–1977 these gases were significantly more enriched in H₂O, CO₂, SO₂, HCl and, in some fumaroles, HF [14].

The Arsenatnaya fumarole was uncovered and first studied by us during fieldworks in July 2012. This active fumarole described in papers [18,19] is a near-meridional linear system of mineralized pockets (up to 10–15 cm wide) and cracks situated between blocks of basalt scoria and volcanic bombs in the near-surface part of the scoria cone. The length of the hot area belonging to Arsenatnaya is about 15 m and its width varies from 1–1.5 m in the southern end to 3–4 m in the northern part. Numerous strongly mineralized pockets occur at depths from 0.3 to 4 m. The sublimate minerals form incrustations in the open space of the pockets, fill cracks and pores or replace basalt. Arsenatnaya is one of the hottest fumaroles at the Second scoria cone of the NB GTFE: the temperature measured by us using chromel–alumel thermocouple in 2012–2018 in different pockets immediately after their partial uncovering varies from 360 to 490 °C and, in general, increases with depth. About 160 valid minerals (including 46 new species first discovered here) and >30 insufficiently studied mineral phases have been identified in this unique mineralogical site.

The Cu-bearing oxide spinels in the Arsenatnaya fumarole were found in two mineral assemblages.

The minerals with Al or Fe³⁺ as species-defining components (spinel, gahnite, thermaerogenite, magnesioferrite, franklinite, and cuprospinel) occur in the intermediate in depth, in the polymineralic zone of the fumarole [19] and are associated with tenorite, hematite, orthoclase (As-bearing variety), fluorophlogopite, langbeinite, calciolangbeinite, apthitalite-type sulfates, anhydrite, krashennikovite, vanthoffite, fluoborite, sylvite, halite, pseudobrookite, rutile, corundum and various arsenates: urusovite, johillerite, ericlxmanite, kozyrevskite, popovite, lammerite, lammerite-β, tilasite, svabite, nickenichite, bradaczekite, dmisokolovite, shchurovskyite, etc. Cu-bearing spinels are among the latest minerals of this assemblage: they occur in cavities and overgrow not only earlier oxides (hematite, tenorite) and silicates but also arsenates and even “saline” sulfates, such as langbeinite-calciolangbeinite series and apthitalite group minerals (Figures 1a–c and 2a,b). Overgrowing of hematite by Cu-rich oxide spinels is very common; these minerals form epitactic intergrowths (the crystal face {111} of a spinel-group member is coplanar to the face {0001} of hematite crystal) or clusters of randomly oriented crystals (Figure 3a–c). Sometimes, spinels cover hematite as massive crusts (Figure 4a,b). Some associations contain two or more spinel-group minerals. In such cases, the Cu-richest species are typically the latest (Figure 4b).

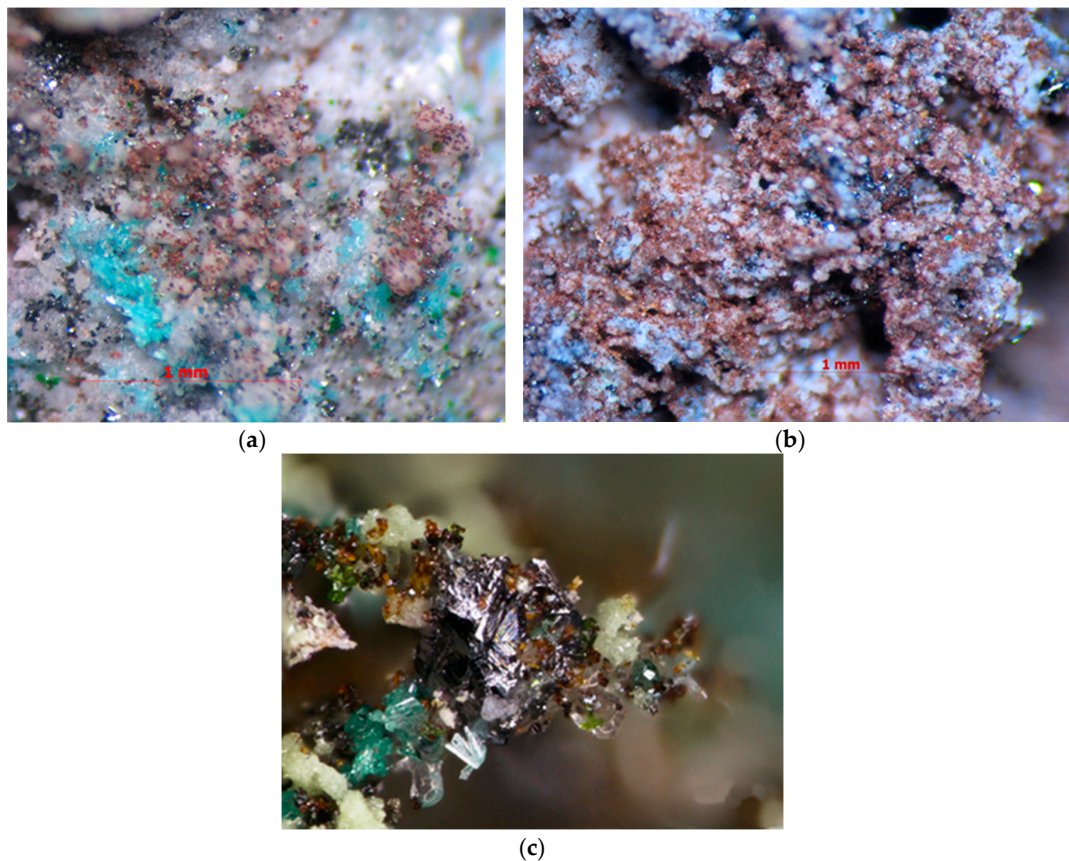


Figure 1. (a) Numerous small brown crystals of thermaerogenite on colourless to white langbeinite with light blue urusovite, iron-black tenorite and minor green ericlxmanite. Field width: 2.2 mm. (b) Abundant small brown crystals of thermaerogenite on white apthitalite and iron-black hematite and tenorite. Field width: 3.5 mm. (c) Small brown crystals of thermaerogenite on colourless calciolangbeinite iron-black tenorite, light blue urusovite and green kozyrevskite. Field width: 0.8 mm.

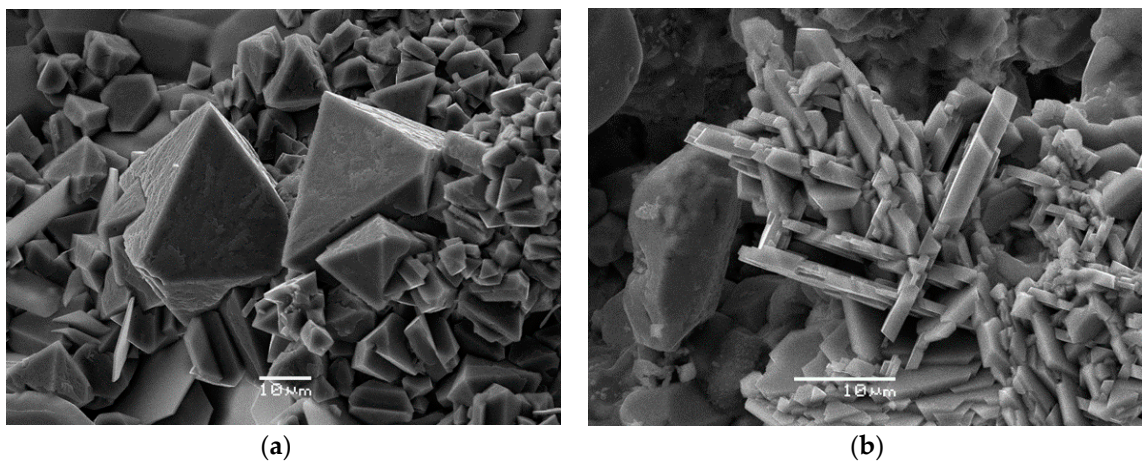


Figure 2. (a) Octahedral crystals of Cu-bearing spinel on crystal crust of tilasite. (b) Flattened spinel-law twins on {111}, additionally combined in complex twinned lattice-like aggregates, of Cu-bearing gahnite on crystal crust of anhydrite. Scanning electron microscopic (SEM)-secondary electron (SE) images.

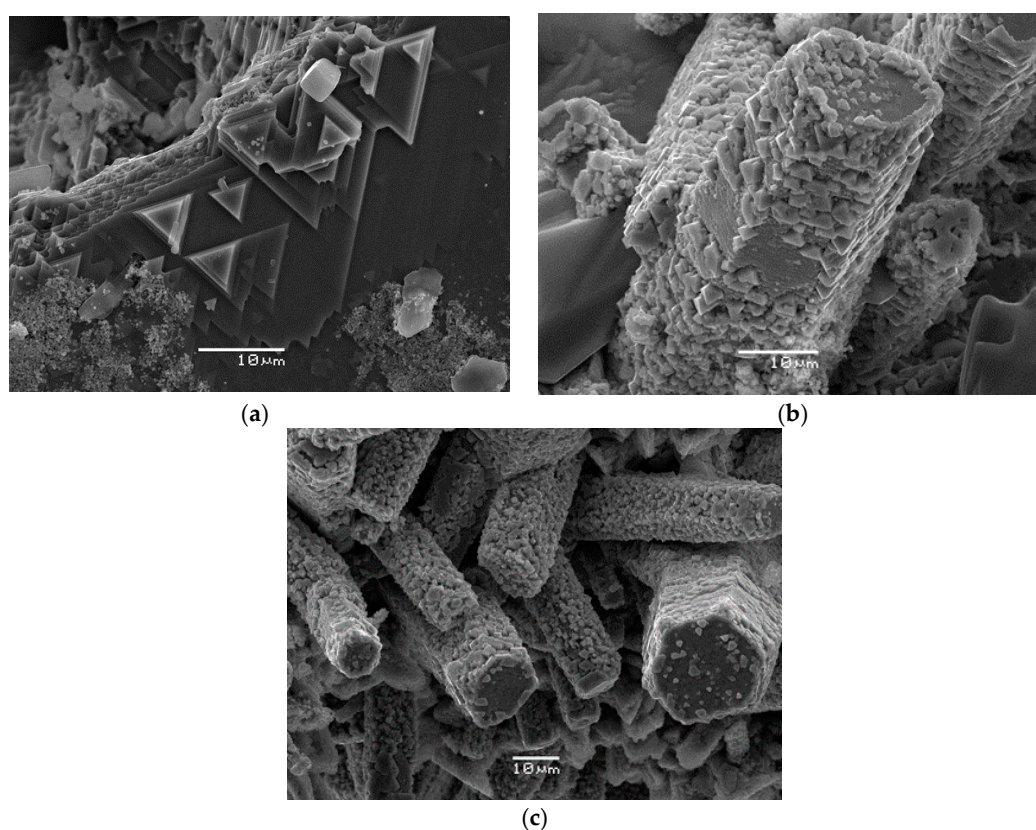


Figure 3. (a) Distorted (flattened on {111}) octahedral crystals of cuprospinel epitactically overgrowing the {0001} face of hematite crystal. (b,c) Octahedral crystals of Cu-bearing gahnite overgrowing columnar hematite crystals. Both epitaxy and random orientation of gahnite crystals on hematite are observed. SEM (SE) images.

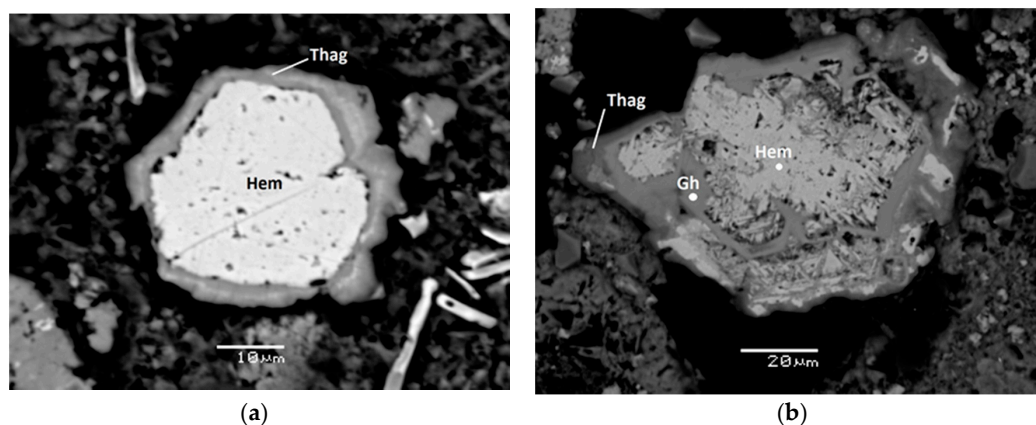


Figure 4. (a) Solid crust of thermaerogenite (Thag) overgrowing hematite (Hem) crystal. (b) Crust consisting of Cu-bearing gahnite (Gh) and later thermaerogenite (Thag) overgrowing skeletal crystal of hematite (Hem). Polished section, SEM-back-scattered electron (BSE) images.

Cu-enriched chrome-spinels were found in Arsenatnaya in several micro-xenoliths (up to 1 mm across) of ultrabasic rock mainly consisting of olivine (F₀83-85). These micro-xenoliths embedded in basalt scoria were strongly altered by fumarolic gases. As a result of gas influence, the peripheral part of olivine grains was significantly replaced by hematite (Figure 5a) and primary, magmatic chrome-spinel (crystals up to 0.06 mm) was altered to Zn- and Cu-bearing species. Figure 5b demonstrates such pseudomorphosed crystal with a core represented by twinned lattice-like aggregates of the newly formed Cu-enriched chromite and a rim consisting of Cu-enriched zincochromite.

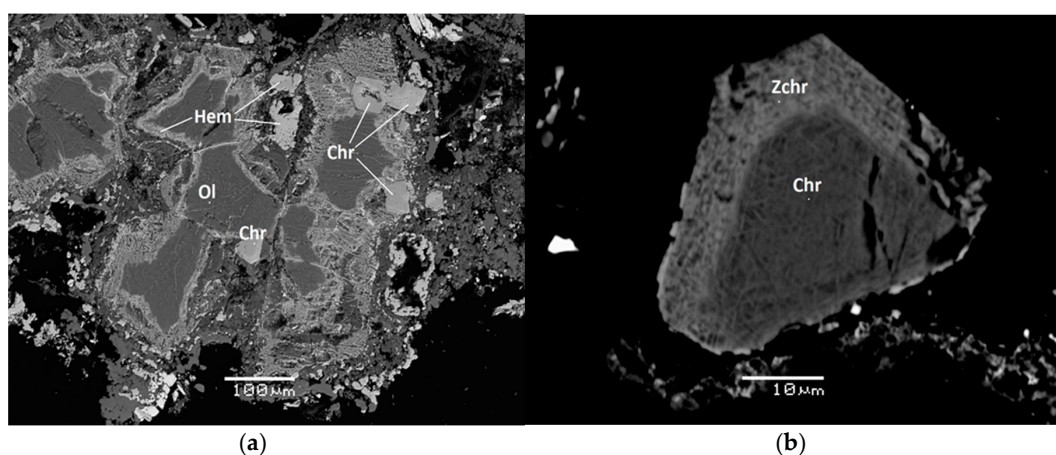


Figure 5. (a) Altered by fumarolic gases, micro-xenolith of ultrabasic rock mainly consisting of olivine (Ol) and containing Cu-bearing chrome-spinels (Chr); Hem—hematite. (b) Crystal of primary, magmatic chrome-spinel replaced by Cu-bearing varieties of chromite (Chr, core) and zincochromite (Zchr, rim). Polished section, SEM (BSE) images.

Besides Arsenatnaya, Cu-bearing varieties of gahnite, magnesioferrite and spinel were found in deposits of extinct fumaroles belonging to the Western paleo-fumarole field at Mountain 1004, a scoria cone located 2 km south of the Second scoria cone of the NB GTFE. Mountain 1004 was formed as a result of an ancient eruption of Tolbachik; the age of this monogenetic volcano and its fumarole fields is evaluated as ca. 2000 years [16]. Spinel occurs here in cavities of basalt scoria altered by fumarolic gas. The associated sublimate minerals are diopside, fluorophlogopite, potassic feldspar, indialite, hematite, tenorite, fluorite, sellaite, anglesite, and baryte.

3. Methods

Reflectance spectra for thermaerogenite were obtained in air using a MSF-21 micro-spectrophotometer (LOMO company, St. Petersburg, Russia) with the monochromator slit width of 0.4 mm and beam diameter of 0.1 mm; SiC (Reflectionstandard 474251, No. 545, Germany) was used as a standard.

The Raman spectrum of thermaerogenite was obtained using an EnSpectr R532 Raman microscope (Department of Mineralogy, Moscow State University, Moscow, Russia) with a solid-state laser diode with green radiation (532 nm) at room temperature. The spectrum was processed in the range from 100 to 4000 cm^{-1} with the use of a holographic diffraction grating with 1800 mm^{-1} and a resolution equal to 6 cm^{-1} . The microscope was focused onto the sample using a PLNC 40X objective (NA = 0.65). Backscattered Raman signals were collected at 1 s exposure time with 400 spectra accumulations. The spectrum was obtained for a randomly oriented crystal with the diameter of the focal spot on the sample about 1 μm . The output laser power was about 12 mW. The power of laser radiation on the surface of the mineral was significantly less. No thermal damage of the sample was observed. Before conducting the experiments, the instrument was calibrated with Raman line of crystalline silicon (520 cm^{-1}).

Scanning electron microscopic (SEM) studies in secondary electron (SE) and back-scattered electron (BSE) modes were carried out and chemical composition was determined for all studied samples using a Jeol JSM-6480LV scanning electron microscope equipped with an INCA-Wave 500 wavelength-dispersive spectrometer (Laboratory of Analytical Techniques of High Spatial Resolution, Department of Petrology, Moscow State University, Moscow, Russia), with an acceleration voltage of 20 kV, a beam current of 20 nA, and a 3 μm beam diameter. The standards used are: MgAl_2O_4 (Mg,Al), Ni (Ni), Cu (Cu), ZnS (Zn), V (V), FeCr_2O_4 (Cr), FeS_2 (Fe), and MnTiO_3 (Mn,Ti).

Powder X-ray diffraction data were collected using a Rigaku RAXIS Rapid II diffractometer with a curved image plate detector, a rotating anode with VariMAX microfocussing optics, using $\text{CoK}\alpha$ radiation, in Debye-Scherrer geometry, at an accelerating voltage of 40 kV, a current of 15 mA and an exposure

time 15 min. The distance between the sample and the detector was 127.4 mm. Data processing was carried out using osc2xrd software [20].

Single-crystal X-ray diffraction studies were carried out using an Xcalibur S diffractometer equipped with a CCD detector (MoK α radiation).

4. Results

4.1. General Appearance and Physical Properties of Thermaerogenite and Other Cu-Rich Oxide Spinel from Tolbachik

Thermaerogenite forms octahedral crystals up to 0.02 mm across, sometimes skeletal, typically combined in open-work clusters (Figure 6a) up to 1 mm across. Areas “sprinkled” by crystals of the new mineral (Figure 1b) are up to 0.5 cm \times 0.5 cm. Besides the major form {111}, narrow {110} faces were observed on some crystals of thermaerogenite. Being visually perfect (Figure 6a), crystals of thermaerogenite have blocky inner structure and these micro-blocks are slightly misoriented, which hampers the single-crystal X-ray diffraction study of the mineral.

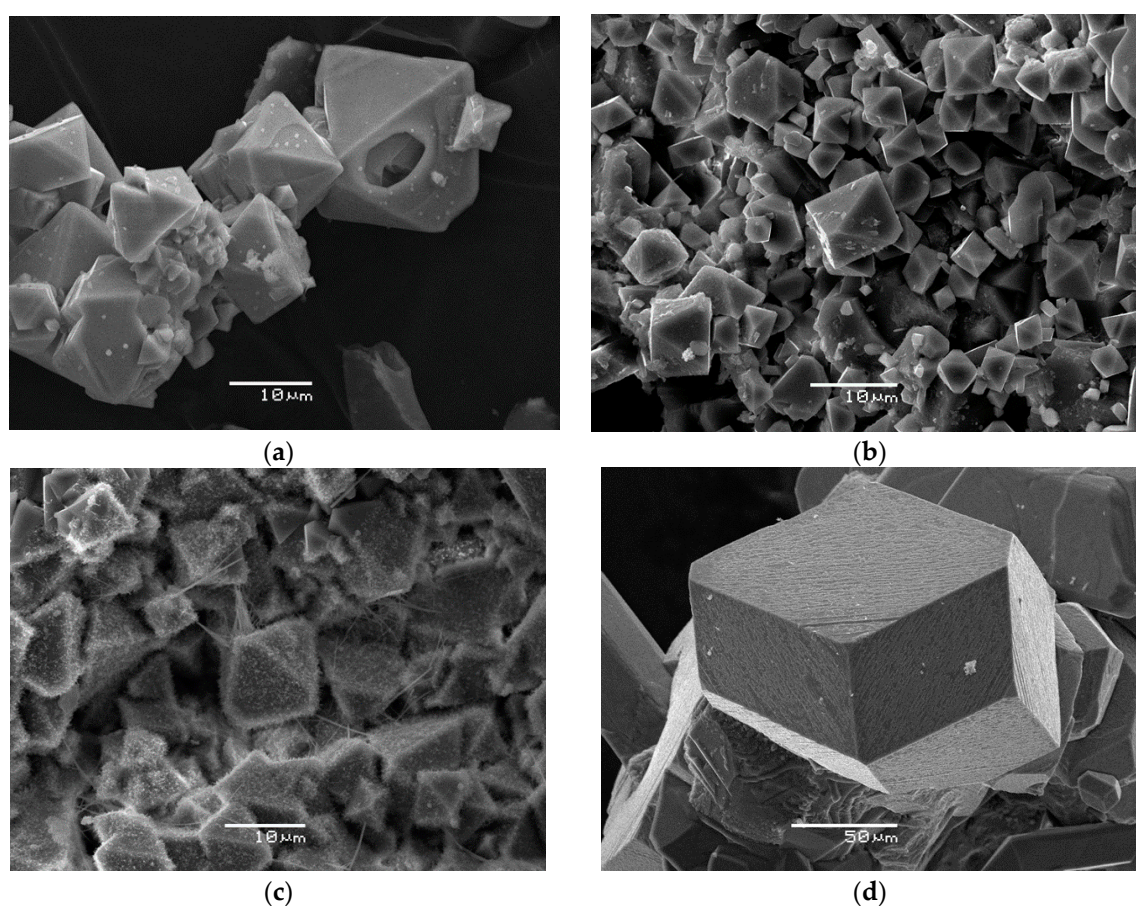


Figure 6. (a) Cluster of octahedral, with minor faces {110}, crystals of thermaerogenite. (b) Crust of octahedral crystals of cuprospinel with minor faces {100}. (c) Aggregate of octahedral crystals of Cu-bearing magnesioferrite partially covered by thin “fluffy” crust of supergene opal from paleo-fumarole (Mountain 1004). (d) Crystal of Cu-bearing magnesioferrite of rhombic dodecahedral shape. SEM (SE) images.

Other Cu-rich Al- and Fe³⁺-dominant spinels in Tolbachik fumaroles occur as octahedral crystals (Figures 2a, 3 and 6a–c), sometimes with minor {110} or/and {100} faces, up to 0.1 mm across, only magnesioferrite was observed as larger (up to 1 mm) crystals, typically rhombic dodecahedra (Figure 6d). Gahnite was also found as flattened spinel-law twins on {111} additionally combined in a

complex lattice-like aggregates (Figure 2b). A similar lattice-like shape was observed for Cu-bearing chromite (Figure 5b). Spinel, magnesioferrite and gahnite sometimes form crusts up to 1 cm across and up to 0.5 mm thick. Solid crusts of cuprospinel (up to 2 mm across) were observed on hematite.

Thermaerogenite is semitransparent to transparent, with a yellowish streak and strong vitreous lustre. Its colour is brown, yellow-brown, red-brown, brown-yellow or brown-red (Figure 1).

Colour, transparency and lustre of other Cu-rich Al- and Fe³⁺-dominant spinels from Tolbachik are in general correlated with the Al:Fe ratio. The Fe-poor varieties are very light (some samples of spinel and gahnite from Mountain 1004 are colourless or greyish-white) with vitreous lustre. Spinel, gahnite and Al-enriched cuprospinel in typical samples from the Arsenatnaya fumarole are visually indistinguishable from the above-described thermaerogenite. Fe-rich cuprospinel is dark reddish-brown with strong vitreous to adamantine lustre. Magnesioferrite has dark brown to iron-black colour and submetallic lustre.

Thermaerogenite is brittle, with conchoidal fracture (observed under the scanning electron microscope); cleavage or parting is not observed. Its Mohs hardness is ca. 7. Density calculated using the empirical formula of the holotype specimen is 4.870 g/cm³.

4.2. Optical Data for Thermaerogenite

In reflected light, thermaerogenite is optically isotropic, grey, with yellowish internal reflections. The reflectance values are given in Table 1.

Table 1. Reflectance data for thermaerogenite. Reflectance values for four wavelengths recommended by the IMA Commission on Ore Microscopy are given in bold type.

λ (nm)	R	λ (nm)	R
400	16.4	560	14.0
420	16.0	580	13.7
440	15.7	589	13.6
460	15.4	600	13.4
470	15.2	620	13.2
480	15.1	640	13.0
500	14.8	650	12.9
520	14.5	660	12.8
540	14.2	680	12.5
546	14.2	700	12.3

4.3. Raman Spectroscopy of Thermaerogenite

The Raman spectrum of thermaerogenite (Figure 7) is typical for spinel-type oxides [21]. It contains four distinct bands with following wavenumbers of maxima (cm⁻¹, s—strong band): 762s, 590, 284, and 125s. They could be assigned based on the data reported for different oxide spinels in [21]. The strongest band at 762 cm⁻¹ could correspond to A_{1g} mode, stretching vibrations of O atoms surrounding Al in tetrahedral coordination. The presence of part of Al in the tetrahedral position (8a) is typical for synthetic Cu-rich members of the series Zn_{1-x}Cu_xAl₂O₄ [22]. Broad band with maximum at 590 cm⁻¹ probably corresponds to $F_{2g}(2)$ or $F_{2g}(3)$ mode involving divalent cations, (Cu,Zn)-O, whereas weak band at 284 cm⁻¹ corresponds to $F_{2g}(1)$ mode. Strong band at 125 cm⁻¹ can be assigned as corresponding to lattice modes.

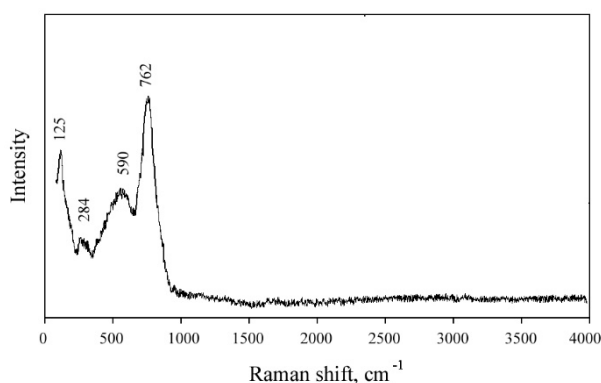


Figure 7. The Raman spectrum of thermaerogenite.

4.4. Chemical Composition of Cu-Rich Oxide Spinel from Tolbachik

Representative electron-microprobe analyses for the studied minerals are given in Table 2 (Cu-bearing Al- and Fe³⁺-dominant spinels) and Table 3 (Cu-bearing chrome-spinels). There are 32 spot analyses of their different chemical varieties which demonstrate chemical variability of Cu-enriched oxide spinels from Tolbachik fumaroles.

Valent states of cations were not determined by direct methods. For properly sublimate minerals (thermaerogenite, cuprospinel, gahnite, spinel, magnesioferrite and franklinite) Fe and Mn are considered as Fe³⁺ and Mn³⁺, respectively, taking into account extremely oxidizing conditions of mineral deposition in Arsenatnaya and similar fumaroles [18]. This is clearly confirmed by the calculation of the empirical formulae using the scheme common for oxide spinels, on the basis of four O atoms per formula unit (*apfu*): Sums of divalent and trivalent cations are close to 2.00 and 3.00 *apfu*, respectively (Tables 2 and 3) that is typical for “2-3 spinels” with the general formula $A^{2+}B^{3+}_2O_4$ [2,23]. For the Cu-bearing chrome-spinels formed in the result of the alteration of a primary, magmatic chrome-spinel, we assume the presence of part of iron in a divalent state (while manganese content is below detection limit in these minerals). Their formulae were calculated on the basis of four O *apfu* with fixing of the cation sum $A^{2+} + B^{3+4+} = 3.00$ *apfu* and the Fe²⁺:Fe³⁺ ratio was calculated by charge balance.

Maximum contents of copper detected in different spinel-group minerals from Tolbachik fumaroles are presented in Table 4 and atomic ratios of the major bivalent (A) and trivalent (B) cations are shown in Figure 8a,b (based on 124 spot electron-microprobe analyses).

Table 2. Chemical composition of Cu-bearing Al- and Fe³⁺-dominant spinel-group oxides from Tolbachik fumaroles: 1–4: thermaerogenite, 5–11: gahnite, 12–16: spinel, 17–20: magnesioferrite, 21: franklinite, and 22–28: cuprospinel.

No.	1 *	2	3	4	5	6	7
	wt.%						
MgO	-	-	-	0.44	-	5.50	-
CuO	25.01 (23.64–26.86)/1.46	25.47	25.67	20.25	20.07	15.00	17.55
ZnO	17.45 (14.46–18.71)/2.00	18.33	17.43	18.99	23.79	18.29	21.71
Al ₂ O ₃	39.43 (34.59–45.43)/4.60	45.43	28.30	22.79	49.05	53.90	56.08
Cr ₂ O ₃	0.27 (0.17–0.33)/0.07	0.17	0.86	-	0.15	0.03	-
Mn ₂ O ₃	-	-	-	0.36	-	0.10	-
Fe ₂ O ₃	17.96 (11.47–22.21)/4.76	11.47	24.48	34.29	7.72	5.99	4.63
TiO ₂	-	-	2.59	2.61	-	0.22	0.24
Total	100.12	100.87	99.33	99.73	100.78	99.03	100.21

Table 2. Cont.

No.	1 *	2	3	4	5	6	7
formula calculated on the basis of 4 O <i>apfu</i>							
Mg	-	-	-	0.023	-	0.242	-
Cu	0.619	0.609	0.673	0.540	0.472	0.334	0.396
Zn	0.422	0.428	0.447	0.496	0.547	0.398	0.479
Al	1.523	1.695	1.156	0.949	1.801	1.874	1.973
Cr	0.007	0.004	0.017	-	0.003	0.001	-
Mn	-	-	-	0.011	-	0.002	-
Fe ³⁺	0.443	0.273	0.639	0.911	0.181	0.133	0.104
Ti	-	-	0.068	0.069	-	0.005	0.006
ΣA^{2+}	1.041	1.037	1.119	1.059	1.019	0.975	0.874
$\Sigma B^{3+,4+}$	1.973	1.972	1.881	1.940	1.984	2.015	2.082
No.	8	9	10	11	12	13	14
wt. %							
MgO	0.42	-	0.59	2.66	13.27	17.54	19.61
NiO	-	-	-	-	0.87	-	-
CuO	13.72	13.06	13.02	2.94	10.89	6.86	4.83
ZnO	30.66	31.91	29.25	35.66	5.98	8.42	9.37
Al ₂ O ₃	44.70	54.11	44.30	55.81	32.93	61.12	48.44
Cr ₂ O ₃	0.19	-	0.18	-	-	-	-
Mn ₂ O ₃	0.16	-	0.10	-	1.88	0.37	0.93
Fe ₂ O ₃	8.82	1.75	11.40	2.11	34.29	4.77	13.88
TiO ₂	1.06	0.11	0.80	-	-	0.41	2.02
Total	99.73	100.94	99.64	99.18	100.11	99.49	99.08
formula calculated on the basis of 4 O <i>apfu</i>							
Mg	0.020	-	0.028	0.119	0.601	0.688	0.807
Ni	-	-	-	-	0.021	-	-
Cu	0.333	0.301	0.314	0.066	0.250	0.136	0.100
Zn	0.726	0.718	0.690	0.789	0.134	0.164	0.191
Al	1.690	1.944	1.669	1.970	1.180	1.897	1.576
Cr	0.004	-	0.004	-	-	-	-
Mn	0.004	-	0.003	-	0.048	0.008	0.022
Fe ³⁺	0.213	0.040	0.274	0.048	0.784	0.094	0.288
Ti	0.025	0.003	0.019	-	-	0.008	0.042
ΣA^{2+}	1.079	1.019	1.033	0.974	1.006	0.989	1.098
$\Sigma B^{3+,4+}$	1.935	1.987	1.969	2.018	2.012	2.008	1.928

Table 2. Cont.

No.	15	16	17	18	19	20	21
wt. %							
MgO	21.94	16.04	17.43	17.65	10.56	20.81	8.54
NiO	-	-	-	-	0.35	-	-
CuO	2.18	4.34	5.90	3.22	14.73	1.26	7.91
ZnO	5.24	12.28	3.09	0.60	0.94	0.60	17.99
Al ₂ O ₃	59.10	58.36	5.30	0.66	5.51	5.72	20.24
Cr ₂ O ₃	-	0.09	0.33	-	-	-	0.17
Mn ₂ O ₃	1.56	0.26	0.24	1.32	1.01	1.24	2.29
Fe ₂ O ₃	8.76	8.10	66.24	77.29	66.64	69.46	36.51
TiO ₂	0.48	0.24	0.92	-	-	-	5.50
Total	99.26	99.70	99.45	100.74	99.74	99.09	99.15
formula calculated on the basis of 4 O <i>apfu</i>							
Mg	0.843	0.640	0.873	0.884	0.552	1.014	0.424
Ni	-	-	-	-	0.010	-	-
Cu	0.042	0.088	0.150	0.082	0.391	0.031	0.199
Zn	0.100	0.243	0.077	0.015	0.024	0.015	0.443
Al	1.796	1.842	0.210	0.026	0.228	0.220	0.795
Cr	-	0.002	0.006	-	-	-	0.005
Mn	0.031	0.005	0.007	0.034	0.027	0.031	0.058
Fe ³⁺	0.170	0.163	1.675	1.953	1.760	1.709	0.915
Ti	0.009	0.005	0.023	-	-	-	0.138
ΣA^{2+}	0.986	0.971	1.099	0.980	0.977	1.060	1.066
$\Sigma B^{3+,4+}$	2.006	2.018	1.922	2.013	2.015	1.960	1.910
No.	22	23	24	25	26	27	28
wt. %							
MgO	0.75	0.63	4.31	3.68	2.32	0.48	5.05
NiO	0.70	-	-	-	-	-	-
CuO	28.55	27.13	24.48	24.36	25.92	20.81	23.44
ZnO	3.51	7.76	3.39	2.48	4.53	18.82	1.94
Al ₂ O ₃	4.82	7.52	3.44	1.69	4.12	18.69	3.46
Cr ₂ O ₃	-	0.22	-	0.23	-	0.24	0.27
Mn ₂ O ₃	1.65	0.94	2.15	0.85	1.38	0.33	1.20
Fe ₂ O ₃	59.49	53.49	59.77	65.82	61.51	37.06	63.40
TiO ₂	0.28	1.75	1.54	-	0.30	2.63	0.41
Total	99.75	99.44	99.08	99.11	100.08	99.06	99.17

Table 2. Cont.

No.	22	23	24	25	26	27	28
formula calculated on the basis of 4 O <i>apfu</i>							
Mg	0.043	0.036	0.244	0.211	0.133	0.026	0.283
Ni	0.022	-	-	-	-	-	-
Cu	0.831	0.781	0.704	0.707	0.748	0.573	0.665
Zn	0.100	0.219	0.096	0.071	0.128	0.506	0.054
Al	0.219	0.338	0.154	0.076	0.185	0.802	0.153
Cr	-	0.005	-	0.006	-	0.005	0.006
Mn	0.048	0.030	0.069	0.027	0.045	0.010	0.038
Fe ³⁺	1.725	1.535	1.711	1.902	1.768	1.016	1.793
Ti	0.008	0.050	0.044	-	0.008	0.072	0.011
ΣA^{2+}	0.996	1.036	1.044	0.988	1.008	1.105	1.002
$\Sigma B^{3+,4+}$	2.000	1.958	1.979	2.012	2.006	1.904	2.002

* The holotype specimen of thermaerogenite: averaged from four spot analyses value (range)/standard deviation; dash means the content below detection limit.

Table 3. Chemical composition of Cu-bearing chrome-spinels from the Arsenatnaya fumarole, Tolbachik: 1–2: magniochromite, 3: chromite, 4: zincchromite.

No.	1	2	3	4
wt.%				
MgO	10.48	7.28	7.52	2.60
FeO	2.30	6.19	16.38	1.07
CuO	8.97	6.25	5.86	3.96
ZnO	8.54	12.83	2.16	27.88
Al ₂ O ₃	11.32	11.52	11.06	10.44
V ₂ O ₃	0.19	0.14	0.16	0.19
Cr ₂ O ₃	47.45	46.06	48.20	43.42
Fe ₂ O ₃	10.73	9.70	7.56	10.61
TiO ₂	0.83	0.89	0.88	0.81
Total	100.82	100.86	99.78	100.98
formula calculated on the basis of 4 O <i>apfu</i> with A + B = 3.00 <i>apfu</i> *				
Mg	0.524	0.374	0.388	0.140
Fe ²⁺	0.058	0.160	0.427	0.029
Cu	0.227	0.163	0.153	0.108
Zn	0.212	0.326	0.056	0.745
Al	0.448	0.467	0.451	0.445
V	0.005	0.004	0.004	0.006
Cr	1.259	1.254	1.319	1.243
Fe ³⁺	0.246	0.228	0.179	0.263
Ti	0.021	0.023	0.023	0.022
ΣA^{2+}	1.021	1.023	1.023	1.022
$\Sigma B^{3+,4+}$	1.979	1.977	1.977	1.978

* Fe²⁺:Fe³⁺ ratio is calculated by charge balance.

Table 4. Maximum contents of copper detected in different spinel-group members from Tolbachik.

Mineral Species	Ideal Formula	CuO, wt.%	Cu, apfu
Cuprospinel	$\text{CuFe}^{3+}_2\text{O}_4$	28.6	0.83
Thermaerogenite	CuAl_2O_4	26.9	0.69
Gahnite	ZnAl_2O_4	21.4	0.51
Magnesioferrite	$\text{MgFe}^{3+}_2\text{O}_4$	14.7	0.39
Spinel	MgAl_2O_4	10.9	0.25
Magnesiochromite	MgCr_2O_4	9.0	0.23
Franklinite	$\text{ZnFe}^{3+}_2\text{O}_4$	7.9	0.20
Chromite	$\text{Fe}^{2+}\text{Cr}_2\text{O}_4$	5.9	0.15
Zincochromite	ZnCr_2O_4	4.8	0.13

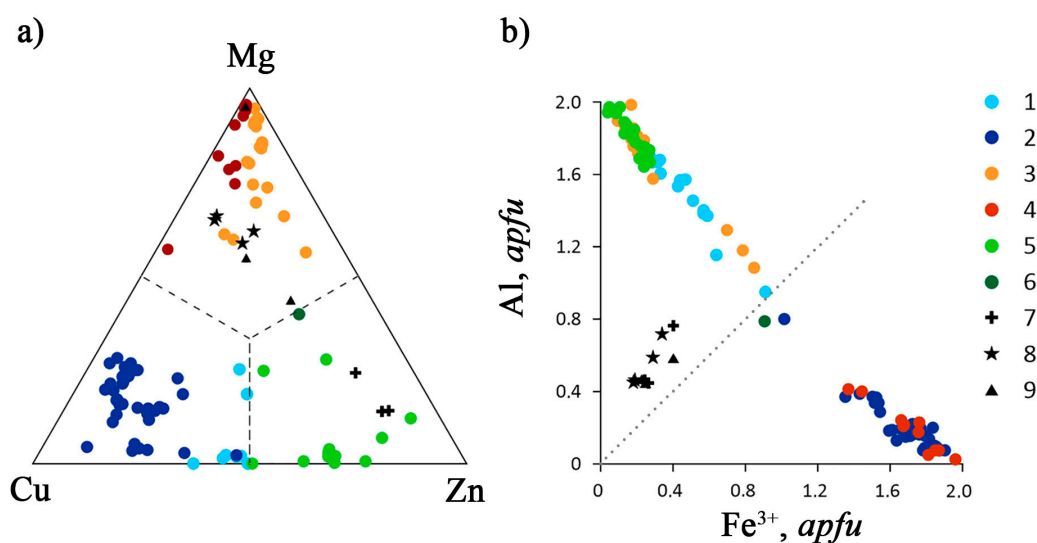


Figure 8. Atomic ratios of the major bivalent (a) and trivalent (b) cations in Cu-bearing spinel-group oxides from Tolbachik fumaroles. Legend: 1—thermaerogenite, 2—cuprospinel, 3—spinel, 4—magnesioferrite, 5—gahnite, 6—franklinite, 7—zincochromite, 8—chromite, 9—magnesiochromite.

4.5. X-ray Diffraction Data of Cu-Rich Oxide Spinel from Tolbachik

Powder X-ray diffraction (XRD) data of thermaerogenite in comparison with the calculated data for synthetic CuAl_2O_4 are given in Table 5. All diffraction reflections are well-indexed in the cubic unit cell, by analogy with common spinel-group minerals [2,23]. Unit-cell dimensions refined from the powder XRD data are presented in Table 6.

Table 5. Powder X-ray diffraction data (d in Å) of thermaerogenite and its synthetic end-member analogue.

Thermaerogenite			Synthetic CuAl_2O_4 *		$h k l$
I_{meas}	d_{meas}	d_{calc}	I_{calc}	d_{calc}	
3	4.659	4.694	2	4.664	111
65	2.873	2.875	51	2.856	220
100	2.451	2.452	100	2.436	311
1	2.329	2.347	0.2	2.332	222
10	2.033	2.033	17	2.020	400
6	1.865	1.865	1	1.853	331
16	1.660	1.660	12	1.649	422
28	1.565	1.565	31	1.555	511
30	1.438	1.437	38	1.428	440
4	1.286	1.286	3	1.277	620
6	1.240	1.240	6	1.232	533
1	1.226	1.226	1	1.218	622
1	1.174	1.174	1	1.166	444

* Calculated from the structure data from [24].

Both single-crystal and powder XRD data for all other studied spinel-group oxides from Tolbachik fumaroles demonstrate their cubic symmetry and systematic absences typical for space group $Fd\bar{3}m$ characteristic for “2-3 spinels” [2,23]. The obtained unit-cell parameters a and V are in agreement with the chemical composition of the minerals (Table 6). The major factor which influences these parameters of the studied spinels is the Al:Fe³⁺ ratio. In particular, unit-cell dimensions and the majority of d -spacings of thermaerogenite are slightly higher in comparison with its synthetic end-member analogue CuAl_2O_4 (Tables 5 and 6) that is mainly caused by admixture of Fe³⁺ which partially substitutes Al in the mineral (Table 2).

Single-crystal XRD data of thermaerogenite allowed to obtain the a parameter of the cubic unit cell (Table 6), however, the crystal structure of the new mineral was not studied due to the low quality of single-crystal diffraction patterns caused by the imperfectness of all tested crystals which consist of slightly misoriented micro-blocks and in fact can be considered as crystal intergrowths.

Table 6. Unit-cell dimension a (Å) and volume (V , Å³) of Cu-rich spinel-group oxides from Tolbachik, cuprospinel from its type locality and synthetic CuAl_2O_4 .

Mineral/Compound	a	V	Method *	Source
Thermaerogenite	8.093(9)	530.1(10)	SCXRD	this work
Thermaerogenite	8.131(1)	537.6(2)	PXRD	this work
Synthetic CuAl_2O_4	8.079(3)	527(3)	SCXRD	[24]
Cuprospinel	8.402(11)	593(1)	SCXRD	this work
Cuprospinel **	8.369	586	PXRD	[3]
Gahnite	8.124(4)	536.2(5)	SCXRD	this work
Gahnite	8.1327(6)	537.9(1)	PXRD	this work
Spinel	8.149(1)	541.2(2)	PXRD	this work
Magnesioferrite	8.344(13)	581(1)	SCXRD	this work

* Abbreviations SCXRD and PXRD mean single-crystal and powder X-ray diffraction methods, respectively; ** type specimen from Consolidated Rambler Mines Limited, Baie Verte, Newfoundland, Canada.

Chemical composition of thermaerogenite varies from crystal to crystal in both Cu:Zn and Al:Fe ratios (Figure 8). The latter is a cause of slight discrepancy between unit-cell parameters of the new mineral obtained from single-crystal and powder X-ray diffraction data (Table 6).

5. Discussion

All spinel-group oxides found in the middle zones of the Arsenatnaya fumarole are copper-bearing and the majority of the studied samples contain >1 wt.% CuO (Tables 2 and 3). The maximum contents of copper in these minerals are reported in Table 4. For Tolbachik cuprospinel, the range 20.8–28.6 wt.% CuO (=0.57–0.83 *apfu* Cu) is found and for thermaerogenite 16.7–26.9 wt.% CuO (=0.41–0.69 *apfu* Cu).

Zinc is the most typical admixture in thermaerogenite. Gahnite and this mineral form here the continuous solid-solution series with the main substitution scheme $\text{Cu}^{2+} \rightarrow \text{Zn}^{2+}$ (Figure 8a). Even the Zn-poorest specimen of thermaerogenite contains 14.5 wt.% ZnO (=0.36 *apfu* Zn), and in the Cu-poorest sample of gahnite from Arsenatnaya, 2.9 wt.% CuO (=0.07 *apfu* Cu) was detected. The continuous isomorphous series with the general formula $\text{Zn}_{1-x}\text{Cu}_x\text{Al}_2\text{O}_4$ was reported for synthetic spinels [22].

Some crystals of thermaerogenite contain significant Mg admixture (up to 5.4 wt.% MgO), however, a continuous solid solution between spinel and the new mineral is not observed (Figure 8a), unlike the synthetic system $\text{Mg}_{1-x}\text{Cu}_x\text{Al}_2\text{O}_4$ with full isomorphism [25]. The solid-solution series between cuprospinel and thermaerogenite, with the main substitution scheme $\text{Al}^{3+} \rightarrow \text{Fe}^{3+}$, also demonstrates a significant gap (Figure 8b). Cuprospinel shows the most stable chemical composition among all studied “2-3 spinels” from Tolbachik fumaroles. It is typically characterized by not very high contents of admixtures, including Mg, Zn and Al, and does not form continuous solid-solution series with other oxide spinels (Table 2, Figure 8).

Cuprospinel was described as a new mineral species from burning dumps [3] and its other finds were related to ore smelters [4,5]. These anthropogenic spinel-forming systems are close in conditions to volcanic fumaroles of the oxidizing type in which copper-rich spinel-type oxides crystallize in a completely natural environment at Tolbachik. The similarity of products formed in both systems, as well as data on the synthesis and thermodynamic stability of these phases [26–28] and the absence of data on such minerals in other geological formations, demonstrate that the physical and chemical conditions in fumaroles are optimal for the formation of Cu-enriched oxide spinels: there is the combination of high temperature, atmospheric pressure and high oxygen fugacity.

It is doubtless that Cu-rich Al- and Fe^{3+} -dominant oxide spinels in fumarole systems of Tolbachik were deposited directly from hot gas as volcanic sublimates. The most convincing evidence of their exhalation origin is the location over crusts of very typical sublimate minerals, especially over alkaline sulfates (Figure 1) in the open space of pockets within a recently formed and still active fumarole at the summit part of a volcanic scoria cone. No sign of occurrence of any other process that could result in the formation of spinels (crystallization from melt or solution, solid-state transformation, etc.) is observed there. Hot volcanic gas was a carrier of “ore” constituents, foremost Cu, Zn and Fe. Basalt scoria which composes the walls of fumarole chambers can be a source of elements having low volatilities in such post-volcanic systems, namely Mg, Al and Ti [29,30]. Our temperature measurements in fumaroles of the Second scoria cone of the NB GTFE and fumaroles born by the Ploskiy Tolbachik eruption of 2012–2013 [31] together with data based on the halite–sylvite solid-solution thermometry [19] show that the mineral assemblages with Cu-bearing oxide spinels were formed at temperatures definitely not lower than 500 °C and probably not higher than 800 °C. This assumption is in agreement with data on synthetic CuAl_2O_4 prepared under the atmospheric pressure in the temperature range 600–1100 °C [28]. Thus, the most probable temperature interval of crystallization of Cu-rich oxide spinels in Tolbachik fumaroles seems to be 600–800 °C.

For the Cu- and Zn-enriched chrome-spinels found in altered micro-xenoliths of ultrabasic rock (Figure 5), we assume the same physical conditions but rather another mechanism of formation. They could be formed due to gas metasomatism, in terminology by Naboko and Glavatskikh [32], i.e., in the result of the replacement of a primary, magmatic chrome-spinel by chemically different spinel-group species under the influence of hot volcanic gas enriched by “ore” components. Chromium, Mg, Al, V and probably part of Fe (which remained as Fe^{2+}) were inherited from the primary chrome-spinel phase whereas Cu and Zn were taken from gas and Fe^{2+} was partly oxidized to Fe^{3+} in this process.

The distribution of cations between tetrahedral and octahedral sites in Cu-rich oxide spinels from Tolbachik fumaroles was not examined by us. We only can consider, based on the Raman spectrum (see above), that thermaerogenite contains part of Al in tetrahedral coordination. The cation distribution is well-studied for synthetic Cu-bearing spinel-type oxides including the end-member CuAl_2O_4 and it was shown that they are “largely normal” spinels (in terminology by [33], i.e., with bivalent cations occupying the tetrahedral site for 2/3 or more) but part of Cu^{2+} typically occurs in the octahedral site and the Cu- B^{3+} disorder in general increases with the temperature increase [22,25,27,28,34]. It should be noted that the distribution of bivalent and trivalent cations between tetrahedral and octahedral sites is not a species-defining sign in the light of the IMA-accepted nomenclature of spinel-supergroup minerals: The classification is based only on chemical formulae as resulting from chemical data only [2].

Copper-rich oxide spinels are extremely rare minerals reliably known in Nature only in Tolbachik fumaroles. Unlike them, the chalcogenide members of the spinel supergroup are not so rare. Nine valid minerals with species-defining Cu belong to the thiospinel and the selenospinel groups [2] and one of them, carrollite CuCo_2S_4 , is a common sulfide in many ore deposits. Such strong difference in diversity and distribution in nature between oxide and chalcogenide Cu-rich spinels is probably caused by the strong chalcophile character (it is worthy to note that the term *chalcophile* originates from Greek word $\chi\alpha\lambda\kappa\acute{o}\varsigma$, copper) of copper.

6. Conclusions

Natural copper-rich oxide spinels are characterized for the first time. They were found in the deposits of active and extinct fumaroles of the oxidizing type related to the Tolbachik volcano, Kamchatka, Russia. This mineralization is represented by nine species belonging to the “2-3 spinels” with the general chemical formula $A^{2+}B^{3+}_2O_4$, i.e., to the spinel subgroup of the oxyspinel group within the spinel supergroup [2]. There are (content of CuO in wt.% is given in parentheses for each mineral) two minerals with species-defining Cu^{2+} , namely cuprospinel (20.8–28.6) and the new species thermaerogenite (16.7–26.9), and Cu-enriched varieties of gahnite (up to 21.4), magnesioferrite (up to 14.7), spinel (up to 10.9), magnesiochromite (up to 9.0), franklinite (up to 7.9), chromite (up to 5.9), and zincochromite (up to 4.8).

The new mineral species thermaerogenite [ideally CuAl_2O_4 , cubic, space group $Fd-3m$, $a = 8.093(9)$ Å, $V = 530.1(10)$ Å³] forms a continuous isomorphous series with gahnite.

Cuprospinel, ideally $\text{CuFe}^{3+}_2\text{O}_4$, earlier reliably known only as a phase of the anthropogenic origin or as a synthetic compound, is a typical oxide mineral in the Arsenatnaya fumarole at Tolbachik. Its sample with composition $(\text{Cu}_{0.831}\text{Zn}_{0.100}\text{Mg}_{0.043}\text{Ni}_{0.022})_{\Sigma 0.996}(\text{Fe}^{3+}_{1.725}\text{Al}_{0.219}\text{Mn}^{3+}_{0.048}\text{Ti}_{0.008})_{\Sigma 2.000}\text{O}_4$ represents the Cu-richest natural spinel-type oxide so far described.

Cu-bearing oxide spinels at Tolbachik have a properly fumarolic origin. Aluminum- and Fe^{3+} -dominant species (thermaerogenite, gahnite, spinel, cuprospinel, franklinite, and magnesioferrite) were deposited directly from hot gas as volcanic sublimates. The most probable temperature interval of their crystallization seems to be 600–800 °C. Copper-enriched varieties of chrome-spinels (magnesiochromite, chromite and zincochromite) were formed probably under the same physical conditions but in the result of the metasomatic replacement of a magmatic chrome-spinel in micro-xenoliths of ultrabasic rock under the influence of volcanic gas.

The rarity of Cu-rich oxide spinels in nature is probably caused by the very specific character of conditions optimal for their formation: there is the combination of high temperature, atmospheric pressure, high oxygen fugacity, rich source of copper and hot gas as effective carrier of this element. Such combination is mostly realized in volcanic fumaroles of the oxidizing type enriched by “ore” components: there are really rare, exotic geological objects. The strong affinity of Cu-rich oxide spinels to such environments is confirmed by earlier reported [3–5] findings of their anthropogenic counterparts in burning copper mine dumps and ore smelters.

Author Contributions: I.V.P. and S.N.B. wrote the paper. N.N.K. and F.D.S. obtained, processed and designed chemical data. I.V.P. and S.N.B. obtained and processed X-ray diffraction data. I.V.P., E.G.S., A.G.T. and F.D.S. collected the material and F.D.S. prepared it for laboratory studies. M.F.V. obtained and processed Raman spectrum. Y.S.P. measured reflectance values.

Funding: This work was supported by the Russian Foundation for Basic Research, grant no. 18-05-00051 (in part of mineralogical studies), and the Russian Science Foundation, grant 14-17-00071 (in part of powder XRD studies).

Acknowledgments: We are grateful to Nadezhda V. Shchipalkina for her assistance in the obtaining of powder XRD data for spinel and to Vasilij O. Yapaskurt for his help with the SEM studies. We thank X-Ray Diffraction Resource Center and Centre for Physical Methods of Surface Investigation of St. Petersburg State University for providing instrumental and computational resources.

Conflicts of Interest: The authors declare no conflict of interest.

References

- Zhao, Q.; Yan, Z.; Chen, C.; Chen, J. Spinel: Controlled preparation, oxygen reduction/evolution reaction application, and beyond. *Chem. Rev.* **2017**, *117*, 10121–10211. [[CrossRef](#)] [[PubMed](#)]
- Bosi, F.; Biagioni, C.; Pasero, M. Nomenclature and classification of the spinel supergroup. *Eur. J. Mineral.* **2018**, in press. [[CrossRef](#)]
- Nickel, E.H. The new mineral cuprospinel {CuFe₂O₄} and other spinels from an oxidized ore dump at Baie Verte, Newfoundland. *Can. Mineral.* **1973**, *11*, 1003–1007.
- Lanteigne, S.; Schindler, M.; McDonald, A.M.; Skeries, K.; Abdu, Y.; Mantha, N.M.; Murayama, M.; Hawthorne, F.C.; Hochella, M.F., Jr. Mineralogy and weathering of smelter-derived spherical particles in soils: Implications for the mobility of Ni and Cu in the surficial environment. *Water Air Soil Pollut.* **2012**, *223*, 3619–3641. [[CrossRef](#)]
- Tropper, P.; Krismer, M.; Goldenberg, G. Recent and ancient copper production in the lower inn valley. An overview of prehistoric mining and primary copper metallurgy in the brixlegg mining. *Mitt. Osterr. Miner. Ges.* **2017**, *163*, 97–115.
- Mallik, B.; Rautray, T.R.; Nayak, P.K. Characterisation of hot material erupted from Mahandi riverbank using EDXRF and XRD techniques. *Indian J. Phys.* **2005**, *79*, 293–296.
- Sholeh, A.; Rastad, E.; Huston, D.; Gemmell, J.B.; Taylor, R.D. The chahaly low-sulfidation epithermal gold deposit, Western Makran Volcanic Arc, Southeast Iran. *Econ. Geol.* **2016**, *111*, 619–639. [[CrossRef](#)]
- Pekov, I.V.; Anikin, L.P.; Chukanov, N.V.; Belakovskiy, D.I.; Yapaskurt, V.O.; Sidorov, E.G.; Britvin, S.N.; Zubkova, N.V. Deltalumite, IMA 2016-027. CNMNC Newsletter No. 32, August 2016, page 919. *Mineral. Mag.* **2016**, *80*, 915–922.
- Rammelsberg, C. Über den sogenannten octaëdrischen Eisenglanz vom Vesuv, und über die Bildung von Magneteisen durch Sublimation. *Ann. Phys. Chem.* **1859**, *107*, 451–454. [[CrossRef](#)]
- Deer, W.A.; Howie, R.A.; Zussman, J. *Rock-Forming Minerals*; Longmans: London, UK, 1962; Volume 5.
- Stoiber, R.E.; Rose, W.I., Jr. Fumarole incrustations at active Central American volcanoes. *Geochim. Cosmochim. Acta* **1974**, *38*, 495–516. [[CrossRef](#)]
- Yudovskaya, M.A.; Distler, V.V.; Chaplygin, I.V.; Mokhov, A.V.; Trubkin, N.V.; Gorbacheva, S.A. Gaseous transport and deposition of gold in magmatic fluid: Evidence from the active Kudryavy volcano, Kurile Islands. *Miner. Deposita* **2006**, *40*, 828–848. [[CrossRef](#)]
- Balić-Žunić, T.; Garavelli, A.; Jakobsson, S.P.; Jonasson, K.; Katerinopoulos, A.; Kyriakopoulos, K.; Acquafredda, P. Fumarolic minerals: An overview of active European volcanoes. In *Updates in Volcanology—From Volcano Modelling to Volcano Geology*; IntechOpen: London, UK, 2016; pp. 267–322.
- Meniaylov, I.A.; Nikitina, L.P.; Shapar', V.N. *Geochemical Features of Exhalations of the Great Tolbachik Fissure Eruption*; Nauka Publishing: Moscow, Russia, 1980. (In Russian)
- Africano, F.; Van Rompaey, G.; Bernard, A.; Le Guern, F. Deposition of trace elements from high temperature gases of Satsuma-Iwojima volcano. *Earth Planets Space* **2002**, *54*, 275–286. [[CrossRef](#)]
- Fedotov, S.A. *The Great Tolbachik Fissure Eruption*; Markhinin, Y.K., Ed.; Cambridge University Press: New York, NY, USA, 1983.
- Zelenski, M.E.; Zubkova, N.V.; Pekov, I.V.; Boldyreva, M.M.; Pushcharovsky, D.Y.; Nekrasov, A.N. Pseudolyonsite, Cu₃(VO₄)₂, a new mineral species from the Tolbachik volcano, Kamchatka Peninsula, Russia. *Eur. J. Mineral.* **2011**, *23*, 475–481. [[CrossRef](#)]

18. Pekov, I.V.; Zubkova, N.V.; Yapaskurt, V.O.; Belakovskiy, D.I.; Lykova, I.S.; Viggasina, M.F.; Sidorov, E.G.; Pushcharovsky, D.Y. New arsenate minerals from the Arsenatnaya fumarole, Tolbachik volcano, Kamchatka, Russia. I. Yurmarinite, $\text{Na}_7(\text{Fe}^{3+}, \text{Mg}, \text{Cu})_4(\text{AsO}_4)_6$. *Mineral. Mag.* **2014**, *78*, 905–917. [[CrossRef](#)]
19. Pekov, I.V.; Koshlyakova, N.N.; Zubkova, N.V.; Lykova, I.S.; Britvin, S.N.; Yapaskurt, V.O.; Agakhanov, A.A.; Shchipalkina, N.V.; Turchkova, A.G.; Sidorov, E.G. Fumarolic arsenates—A special type of arsenic mineralization. *Eur. J. Mineral.* **2018**, *30*, 305–322. [[CrossRef](#)]
20. Britvin, S.N.; Dolivo-Dobrovolsky, D.V.; Krzhizhanovskaya, M.G. Software for processing the X-ray powder diffraction data obtained from the curved image plate detector of Rigaku RAXIS Rapid II diffractometer. *Zap. Ross. Mineral. Obsh.* **2017**, *146*, 104–107. (In Russian)
21. D'Ippolito, V.; Andreozzi, G.B.; Bersani, D.; Lottici, P.P. Raman fingerprint of chromate, aluminate and ferrite spinels. *J. Raman Spectrosc.* **2015**, *46*, 1255–1264. [[CrossRef](#)]
22. Le Nestour, A.; Gaudon, M.; Villeneuve, G.; Andriessen, R.; Demourgues, A. Steric and electronic effects relating to the Cu^{2+} Jahn-Teller distortion in $\text{Zn}_{1-x}\text{Cu}_x\text{Al}_2\text{O}_4$ spinels. *Inorg. Chem.* **2007**, *46*, 2645–2658. [[CrossRef](#)] [[PubMed](#)]
23. Biagioni, C.; Pasero, M. The systematics of the spinel-type minerals: An overview. *Am. Mineral.* **2014**, *99*, 1254–1264. [[CrossRef](#)]
24. Areat, C.O.; Vinuela, J.S.D. Structural study of copper-nickel aluminate ($\text{Cu}_x\text{Ni}_{1-x}\text{Al}_2\text{O}_4$) spinels. *J. Solid State Chem.* **1985**, *60*, 1–5. [[CrossRef](#)]
25. Fregola, R.A.; Bosi, F.; Skogby, S.; Hälenius, U. Cation ordering over short-range and long-range scales in the MgAl_2O_4 - CuAl_2O_4 series. *Am. Mineral.* **2012**, *97*, 1821–1827. [[CrossRef](#)]
26. Jacob, K.T.; Alcock, C.B. Thermodynamics of CuAlO_2 and CuAl_2O_4 and phase-equilibria in system Cu_2O - CuO - Al_2O_3 . *J. Am. Ceram. Soc.* **1975**, *58*, 192–195. [[CrossRef](#)]
27. O'Neill, H.S.C.; Navrotsky, A. Simple spinels: Crystallographic parameters, cation radii, lattice energies, and cation distribution. *Am. Mineral.* **1983**, *68*, 181–194.
28. O'Neill, H.S.C.; James, M.; Dollase, W.A.; Redfern, S.A.T. Temperature dependence of the cation distribution in CuAl_2O_4 spinel. *Eur. J. Mineral.* **2005**, *17*, 581–586. [[CrossRef](#)]
29. Symonds, R.B.; Reed, M.H. Calculation of multicomponent chemical equilibria in gas-solid-liquid systems: Calculation methods, thermochemical data, and applications to studies of high-temperature volcanic gases with examples from Mount St. Helens. *Am. J. Sci.* **1993**, *293*, 758–864. [[CrossRef](#)]
30. Churakov, S.V.; Tkachenko, S.I.; Korzhinskii, M.A.; Bocharnikov, R.E.; Shmulovich, K.I. Evolution of composition of high-temperature fumarolic gases from Kudryavy volcano, Iturup, Kuril Islands: The thermodynamic modeling. *Geochem. Int.* **2000**, *38*, 436–451.
31. Pekov, I.V.; Zubkova, N.V.; Yapaskurt, V.O.; Belakovskiy, D.I.; Chukanov, N.V.; Lykova, I.S.; Saveliev, D.P.; Sidorov, E.G.; Pushcharovsky, D.Y. Wulffite, $\text{K}_3\text{NaCu}_4\text{O}_2(\text{SO}_4)_4$, and parawulffite, $\text{K}_5\text{Na}_3\text{Cu}_8\text{O}_4(\text{SO}_4)_8$, two new minerals from fumarole sublimates of the Tolbachik volcano, Kamchatka, Russia. *Can. Mineral.* **2014**, *52*, 699–716. [[CrossRef](#)]
32. Naboko, S.I.; Glavatskikh, S.F. *Post-Eruptive Metasomatism and Ore Genesis: Great Tolbachik Fissure Eruption of 1975–76 at Kamchatka*; Nauka Publishing: Moscow, Russia, 1983. (In Russian)
33. O'Neill, H.S.C.; Navrotsky, A. Cation distributions and thermodynamic properties of binary spinel solid solutions. *Am. Mineral.* **1984**, *69*, 733–753.
34. Cooley, R.F.; Reed, J.S. Equilibrium cation distribution in NiAl_2O_4 , CuAl_2O_4 and ZnAl_2O_4 spinels. *J. Am. Ceram. Soc.* **1972**, *55*, 395–398. [[CrossRef](#)]

