

Specificity of Pyrometamorphic Minerals of the Ellestadite Group

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Abstract—Numerous rare and new mineral species are synthesized during the process of pyrometamorphism (Gross, 1977; Chesnokov et al., 1987; Chesnokov and Shcherbakova, 1991; Chesnokov, 1999), including silicoxides, chloride-, fluoride, and sulfate-silicates, carbonate-sulfides, chloride-oxides, etc. Having made sense of numerous findings of compounds of this type, Chesnokov (1999) set forth the concept of the crystallochemical transition at extreme temperatures attaining 1200–1450°C in pyrogenic systems. First of all, intertype transitions (oxygen-bearing–oxygen-free) and interclass transitions (chloride–silicate, carbonate–sulfide, chloride–oxide) are realized. The specificity of pyrometamorphic mineral assemblages consists in the abundance of silicates with additional anions (F^- , Cl^- , $(CO_3)^{2-}$) (Sokol et al., 2005). Minerals of the ellestadite group $Ca_{10}(SiO_4)_{3-x}(SO_4)_{3-x}(PO_4)_{2x}(OH,F,Cl)_2$ are a spectacular example of these features. In the general case, they are silicate-sulfate-phosphate-hydroxide-chlorides-fluorides. The detailed description of these minerals based on the study of the original collection of pyrometamorphic minerals is presented in this paper.

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*In loving memory, the authors dedicate this study to Boris
Valentinovich Chesnokov—the man who extended frames of
mineralogical commonness through his hands and mind.*

INTRODUCTION

Ellestadite is an extremely rare mineral pertaining to the structural type of apatite and corresponding to the formula $Ca_{10}(SiO_4)_{3-x}(SO_4)_{3-x}(PO_4)_{2x}(OH,F,Cl)_2$, where x varies from 0 (ellestadite) to 3 (apatite) (Rouse and Dunn, 1982). Three main end members $Ca_{10}(SiO_4)_3(SO_4)_3Z_2$ are recognized: hydroxyllellestadite ($Z = OH$), fluorellestadite ($Z = F$), and chlorellestadite ($Z = Cl$). Its space group $P6_3/m$ coincides with that of apatite (Harada et al., 1971; Rouse and Dunn, 1982; Chesnokov et al., 1987; Neubauer and Pollmann, 1992; Sejkora et al., 1999). However, space group $P2_1$ was determined for hydroxyllellestadite (Litsarev et al., 1998) and group $P2_1/m$ for synthetic samples of a similar composition (Organova et al., 1994). The mineral was first found in calc-skarn of Crestmore, the United States (McConnell, 1937). All subsequent findings of hydroxyllellestadite were related to the same type of rocks (Table 1). The Cl-bearing variety was found in supergene cave deposits (Onac et al., 2002) and in burnt waste piles near Brno in the Czech Republic. Fluorellestadite is regularly found in burnt waste piles, where carbonaceous or bituminous clayey and carbonate rocks are stored. In all cases, carbonate rocks were a protolith for its formation (Chesnokov et al., 1987;

Sejkora et al., 1999; Potapov et al., 2005; Eytier et al., 2004).

OVERVIEW OF BURNT WASTE PILES

The high porosity of waste piles, which attains 30%, provides their active gas blowing that results in large-scale and long-term burning. The pelitic rocks are predominant in waste piles, while fragments of petrified wood, siderite nodules, and marlstone are of subordinate importance. The fuel is carbonaceous and bituminous materials and pyrite. The waste pile has a bedded structure. The coarse-clastic beds are convenient ways for the movement of air within the pile and the removal gases to its surface. Precisely within these beds, the materials experience the highest temperature reworking and the layer of dump sinter (burnt rocks) is formed therein. The fragments of trunks of petrified wood 10–20 to 30–50 cm in diameter are second in terms of the abundance of dump mass components. Ankerite and siderite varieties are predominant; dolomite and rhodochrosite trunks and branches occur occasionally. Calcite is rare and commonly fills separate veinlets. The burning of petrified wood results in the formation of specific “nuts” that have a loose core and a more compact shell mainly consisting of anhydrite (Fig. 1). The cores of the “nuts” differ in composition. Products of

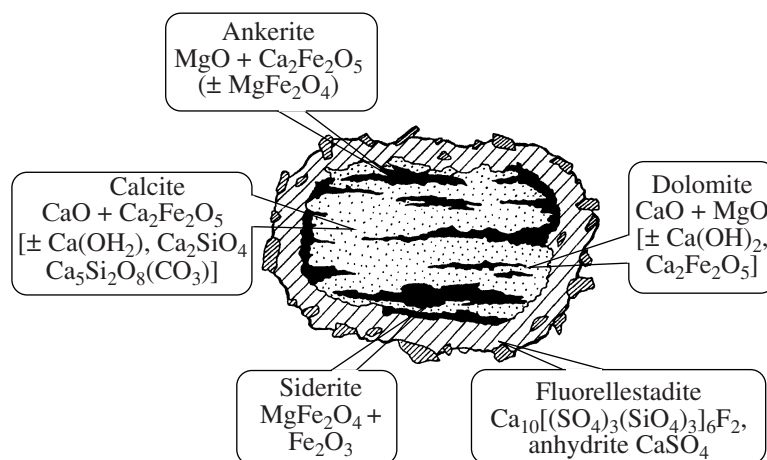


Fig. 1. Main product of the calcination of carbonate rocks from the waste piles of the Chelyabinsk coal basin; data from Chesnokov and Shcherbakova (1991) have been used.

calcite and dolomite decomposition and their subsequent hydration—lime, portlandite, brucite, and periclase—are common. If the petrified wood contained iron carbonate, then hematite, magnesioferrite, and srebrodolskite arise in the core. The “nuts” from the highest-temperature zones of the waste piles are transformed by the greatest degree. Rhönite, melilite, Cl-replaced analogs of hydrogarnet, fluorsilicates, various calcium ferrites, esseneite, as well as larnite and extremely rare spurrite and rankinite are formed here as index-minerals of the sanidinite facies (Chesnokov and Shcherbakova, 1991; Sokol et al., 2005) (Table 2).

In general, the pyrometamorphism, or combustion metamorphism of sedimentary rocks under the effect of coal fires proceeds at 600–1250°C and under a pressure that does not exceed a few atmospheres. The extremely low water pressure ($P_{\text{H}_2\text{O}} \ll 1$ bar) determines the complete absence of OH-bearing phases, and F- and Cl-replaced analogs occupy their place in pyrogenic assemblages (Chesnokov, 1999; 2001a, 2001b, Sokol et al., 2002, 2005). Fluorellestadite pertains to this category.

MATERIALS AND RESEARCH METHODS

The collections of pyrogenic ellestadite-bearing rocks (about 40 samples) were taken from waste piles of the Kopeisk and Yemanzhelinsk districts in the Chelyabinsk coal basin and from burnt dumps in the Kizel basin (Klyuchevsky Mine) and the Kuznetsk basin (Abashevo Mine). The samples were examined on a LEO 420 SEM at the Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences (IGM SB RAS, analysts Ya.L. Luk'yanov and S.V. Letov), as well as with Camebax-Micro and a JXA-8100 microprobes at the IGM SB RAS (analysts V.N. Korolyuk and E.N. Nigmatulina). Measurements on a Camebax-Micro were performed at an accelerat-

ing voltage of 20 kV and a current of absorbed electrons of 30 nA, the angle of sorting was 40°, the duration of the impulse count was 10 s, and the diameter of the beam was 2–3 μm. The superposition of analytical line $\text{Ca}_{K\beta}$ on line $\text{P}_{K\alpha}$ was taken into account. Cl and F were determined with a JXA-8100 microprobe at an accelerating voltage of 20 kV and a current of absorbed electrons of 30 nA; the angle of sorting was 40°, the duration of the impulse count was 10 s, and the diameter of the beam was 2–3 μm. Uncertainties in the determination of all major components were <2% and <5% for F. IR spectra of powder samples pressed into KBr tablets were recorded in the regime of transmittance in the region 400–4000 cm^{-1} on a Specord 75 IR and Bruker Vertex 70 FTIR spectrometers (analyst I.N. Kupriyanov). The proton contents in the ellestadites were determined with SIMS on a CAMECA IMS-4F at the Institute of Microelectronics and Informatics, Russian Academy of Sciences in Yaroslavl.

PYROMETAMORPHIC ASSEMBLAGES OF ELLESTADITES

The Chelyabinsk coal basin. The most significant and spectacular segregations of bright blue fluorellestadite were found as constituents of the petrified wood in the waste pile of the Baturinsky-1,2 East Mine near the town of Yemanzhelinsk. The anhydrite shell in this case is absent. The cavernous core is largely composed of magnesioferrite, srebrodolskite, and anhydrite with inclusions of larnite, cuspidine, fluorellestadite, rustumite, hematite, apatite, and chlormayenite. The minerals mostly make up zonal kidney-like aggregates. Larnite $\text{Ca}_2(\text{SiO}_4)$, cuspidine $\text{Ca}_4(\text{Si}_2\text{O}_7)\text{F}_2$, fluorellestadite $\text{Ca}_{10}[(\text{SO}_4)_3(\text{SiO}_4)_3]\text{F}_2$, and finally, srebrodolskite intergrown with anhydrite CaSO_4 appear, following one another, from the center to the margin of the aggregates (Figs. 2a–2c). The individuals vary from 5 μm to 0.5 mm in size. The structural pattern of the petrified

Table 1. Natural and technogenic occurrences of ellestadite

Occurrence and source	Host rock	Mineral assemblage	Morphology, color, and chemical composition of ellestadite
Arimao Norte, Cienfuegos Province, Cuba (Litsarev et al., 1998)	Garnet–wollastonite skarn	Wollastonite, garnet, vesuvianite, and diopside	Hydroxyllelestadite; dispersed grains and small segregations; crystal faces are poorly delineated; colorless
Crestmore, California, the United States (McConnel, 1937)	Calc skarn	Garnet, pyrite, stilpnomelane, thaumasite, jennite, and magnetite	Hydroxyllelestadite; monomineralic rock, lenses up to 1.5–2.0 m thick; colorless
Doshinkudo deposit, Chichibu Mine, Japan (Harada et al., 1971)	"	Diopside, wollastonite, calcite, monticellite, okenite, and vesuvianite	Hydroxyllelestadite; veinlets; pink and pale pink
Chichibu Mine, Japan (Harada et al., 1971)	"	Diopside, wollastonite, calcite, xanthophyllite, and vesuvianite	Hydroxyllelestadite; aggregates up to 100 kg in weight; separate chips up to 2 cm in size; purple and pale purple
Cerboia Valley, Cornet Hill, the Carpathians, Romania (Pascal et al., 2001)	Calc exoskarn	Vesuvianite and calcite	Wikeite; grains as small as 1 mm; aggregates, pink
Gumeshevo, the central Urals (Grabeshev, 2004)	Copper-bearing metasomatic rocks in skarn	Calcite, wollastonite, melilite, and Ti-garnet	High-P hydroxyllelestadite; light gray
Kopeisk district, Chelyabinsk coal basin (Chesnokov et al., 1987, 1991)	Burnt waste pile of coal mine. Fragments of burnt siderite fossil wood	Calcite, wollastonite, tilleyite, melilite, spurrite, perovskite, cuspidine, monticellite, vesuvianite, and hydrogrossular	Hydroxyllelestadite; very small crystals included in a rim of melilite crystals; light gray
Zastavka near Brno, Czech Republic (Sejkora et al., 1999)	Burnt dumps of coal mine. Fragments of burnt carbonate-bearing mudstone	Calcite, pyroxene, titanite, gypsum, chlorite, fukalite, chalcopyrite, garnet, sphalerite, vallerite, and pyrite	Hydroxyllelestadite; aggregate of grains 0.1–1.5 mm in size; occasionally, poorly expressed tabular morphology of individuals; simple and polysynthetic twins; colorless
Aveuron, France (Eytier et al., 2004)	Burnt waste piles of bituminous rocks	Magnesian ferrite, periclas, srebrodolskite, anhydrite, hematite, and lime	Fluorellestadite; crystals with poorly expressed faces in veinlets; color varies from bright blue and blue to light bluish green
Hatruhim Basin, Israel (Gross, 1984)	Burnt bituminous shale ($T = 850\text{--}1000^\circ\text{C}$)	No data	Fluor-hydroxyl-chlorellestadite; acicular crystals up to 1 mm in size and granular aggregates up to 1 cm across; pale blue
Cioclovina Cave, Romania (Onac et al., 2002)	Products of spontaneous oxidation and subsequent burning of guano	Fluorite, cuspidine, and ettringite	Fluorellestadite; parallel-columnar aggregates and perfectly faceted crystals; blue, pale blue, pale green, and yellow
		Larnite, brownmillerite, and ye'elimite	Fluorellestadite; grains from 90 μm to 0.2 mm in size with larnite and brownmillerite inclusions; colorless
		Berlinite, vogtite, sampleite, monelite, burbankite, churchite, paratacamite, leucophosphate, collinsite, todorokite, and romanechite	Chlorellestadite

Table 2. List of minerals from pyrometamorphic rocks

Mineral	Abbreviation	Formula	Symmetry
Anhydrite	<i>Anh</i>	$\text{Ca}(\text{SO}_4)$	Orthorhombic
Apatite	<i>Ap</i>	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH}, \text{F})_2$	Hexagonal
Brownmillerite		$\text{Ca}_2(\text{Al}, \text{Fe})_2\text{O}_5$	Orthorhombic
Brucite		$\text{Mg}(\text{OH})_2$	Trigonal
Hematite	<i>Hem</i>	$\alpha\text{-Fe}_2\text{O}_3$	"
Ellestadite	<i>Ell</i>	$\text{Ca}_{10}[(\text{SO}_4)_3(\text{SiO}_4)_3](\text{OH}, \text{F}, \text{Cl})_2$	Monoclinic
Lime		CaO	Cubic
Ye'elimite		$\text{Ca}_4\text{Al}_6\text{O}_{12}(\text{SO}_4)$	"
Cupsidine	<i>Cusp</i>	$\text{Ca}_4[\text{Si}_2\text{O}_7]\text{F}_2$	Monoclinic
Larnite	<i>Lar</i>	$\beta\text{-Ca}_2[\text{SiO}_4]$	"
Magnesioferrite		MgFe_2O_4	Cubic
Mayenite		$\text{Ca}_{12}\text{Al}_{14}\text{O}_{13}$	"
Melilite		$(\text{Ca}, \text{Al})_2(\text{Al}, \text{Mg}, \text{Fe})[(\text{Si}, \text{Al})_2\text{O}_7]$	Triclinic
Merwinite		$\text{Ca}_3\text{Mg}[\text{SiO}_4]_2$	Monoclinic
Periclase	<i>Per</i>	MgO	Cubic
Portlandite		$\text{Ca}(\text{OH})_2$	Trigonal
Rankinite		$\text{Ca}_3[\text{Si}_2\text{O}_7]$	Monoclinic
Rhönite		$\text{Ca}_2(\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Mg}, \text{Ti})_6[(\text{Si}, \text{Al})_6\text{O}_{20}]$	Tetragonal
Rustumite	<i>Rust</i>	$\text{Ca}_{10}(\text{Si}_2\text{O}_7)_2(\text{SiO}_4)\text{Cl}_2(\text{OH})_2$	Monoclinic
Silicochormayenite	<i>Cl-May</i>	$\text{Ca}_{13}\text{Al}_{14}(\text{SiO}_4)_4\text{O}_{24}\text{Cl}_4$	Cubic
Spurrite		$\text{Ca}_4[\text{SiO}_4]_2 \cdot \text{Ca}(\text{CO}_3)$	Monoclinic
Srebrodolskite	<i>Sreb</i>	$\text{Ca}_2\text{Fe}_2^{3+}\text{O}_5$	Orthorhombic
Tilleyite		$\text{Ca}_5\text{Si}_2\text{O}_7(\text{CO}_3)_2$	Monoclinic
Fluorellestadite		$\text{Ca}_{10}[(\text{SO}_4)_3(\text{SiO}_4)_3]\text{F}_2$	"
Fluorapatite	<i>Ap</i>	$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$	Hexagonal
Chlorcupsidine		$\text{Ca}_4[\text{Si}_2\text{O}_7](\text{F}, \text{Cl})_2$	Monoclinic
Chlormayenite		$\text{Ca}_{13}\text{Al}_{14}(\text{SiO}_4)_{0.5}\text{O}_{32}\text{Cl}_2$	Cubic
Chlorellestadite		$\text{Ca}_{10}[(\text{SO}_4)_3(\text{SiO}_4)_3]\text{Cl}_2$	Monoclinic
Esseneite		$\text{CaFe}^{3+}[\text{SiAlO}_6]$	"

wood is retained only in local segments marked by segregations of acicular fluorellestadite and anhydrite crystals.

In the Kopeisk coal district, fluorellestadite was found in sinter blocks from the burnt waste piles of mines nos. 43, 44, 47, and 1-2. The metacarbonate "nuts" show here a typically zonal structure (Fig. 1). Their cores are composed of anhydrite, srebrodolskite, magnesioferrite, periclase, calcite, portlandite, cuspidine, and apatite. The segregations of the columnar fluorellestadite emphasize the structural pattern of the petrified wood.

The mineral assemblages of metacarbonate rocks from the waste piles of the Chelyabinsk basin have been studied and described in detail (see below). The representative analyses of the minerals are given in Tables 3 and 4.

Fluor- and chlorellestadites are characterized by acicular individuals pale and bright blue in color with greenish and yellowish hues. They make up radiated and parallel columnar aggregates that fill the cavities in anhydrite pseudomorphs after the fibers of petrified wood (Figs. 3c–3f). The ellestadite individuals are not plane-faced crystals. The plane faces of the crown and prismatic girdle in the absence of linear edges were noted only in some crystals (Figs. 4e–4h). The sheath crystals, as well as individuals with a corroded surface and dissolution sculpture are common.

Ellestadites are heterogeneous in anatomy and composition as expressed in the wide variations in the concentrations of anion-forming cations (P, S, Si) and, to a lesser extent, F and Cl (Table 4; Fig. 5). In particular, for the Yemanzhelinsk ellestadites, these variations are as follows (wt %): 2.39–28.05 SiO_2 , 1.38–22.20 SO_3 ,

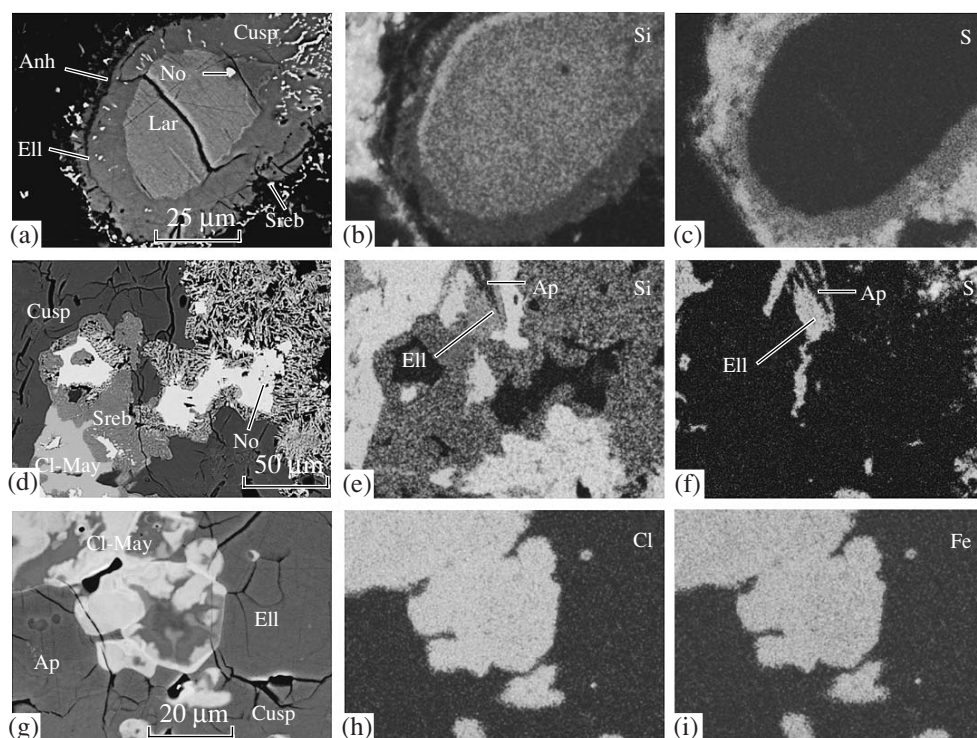


Fig. 2. Mineral assemblages of ellestadite-bearing pyrogenic rocks from the Yemanzhelinsk district, the Chelyabinsk coal basin: (a–c) zonal aggregate of the products of calcination of carbonate petrified wood; the following minerals occur in the aggregate from its core toward the margin: larnite, cuspidine, chlor-fluorellestadite, and srebrodolskite intergrown with anhydrite: (a) BSE image, (b, c) images in characteristic radiation of Si and S, respectively; (d–f) hematite, srebrodolskite, chlormayenite, and cuspidine in ellestadite-bearing samples: (d) BSE image, (e, f) images in characteristic radiation of Si and S, respectively; (g–i) cuspidine intergrown with fluorellestadite, chlormayenite and apatite: (g) BSE image, (h, i) images in characteristic radiation of Cl and Fe, respectively.

0.00–38.18 P₂O₅, 2.03–3.58 Cl, and 0.04–2.02 F. The Cl and F contents in the Kopeisk ellestadites vary within wider ranges (wt %): 0.15–2.62 Cl and 1.91–3.19 F. In fact, calcium is the single cation in all ellestadites. Examination with an ion microprobe has shown that the H₂O content does not exceed 0.24 wt % (commonly 0.02–0.03 wt %).

As a rule, several zones different in Si, P, and S contents are recognized in individuals. Two opposite types of zoning are observed. In one case, the core is sharply enriched in P up to the appearance of an apatite core (Fig. 6). In another case, the P content in the core is minimal and reaches a maximum in the shell. Virtually all intermediate members of the ellestadite–apatite series have been detected.

According to the results of IR spectroscopy, the incorporation of significant amounts of (CO₃)²⁻ into the ellestadite structure is not characteristic. The low-intense diffuse absorption bands of (CO₃)²⁻ groups in the IR spectra of the Kopeisk ellestadites are reasonably explained by CaCO₃ ingrowths. The reliable occurrence of (OH)⁻ groups was not established. The diffuse absorption bands ($\nu = 3550\text{--}3300\text{ cm}^{-1}$ and 1625 cm^{-1}) are caused by the occurrence of absorbed molecular H₂O.

Magnesioferrite occurs as crystallites (<1 mm) with habit octahedral {111} and rhombic-dodecahedral {110} faces (Figs. 3a, 3b, and 4a), which make up a cavernous aggregate that serves as a substrate for anhydrite needles and nodules (Fig. 4b). In some cases, magnesioferrite crystals grow on anhydrite needles. This mineral is a complex ferrite of Ca, Mg, and Mn.

Srebrodolskite makes up the cores of “nuts” together with magnesioferrite. The tabular crystals (<0.5 mm) grow over hematite and occur as isolated segregations. The association with anhydrite is typical (Fig. 2). In the Kopeisk samples, srebrodolskite is close to pure Ca₂Fe₂³⁺O₅, forms intergrowths with fluorellestadite, and contains periclase inclusions. Srebrodolskite from Yemanzhelinsk has a complex cation composition.

Hematite occurs as single grains (<70 μm), commonly as inclusions in cuspidine, srebrodolskite, larnite, and fluorellestadite (Figs. 2d–2f).

The morphology of *anhydrite* is diverse (Figs. 2–4). This mineral forms outer zones of kidney-shaped aggregates that grow over a cavernous aggregate of ore minerals. The size of mineral grains in nodules varies from 5 μm to 0.5 mm. Segregations of acicular anhydrite crystals up to 5 mm long are confined to cavities. Separate anhydrite “needles” are actually sheath crys-

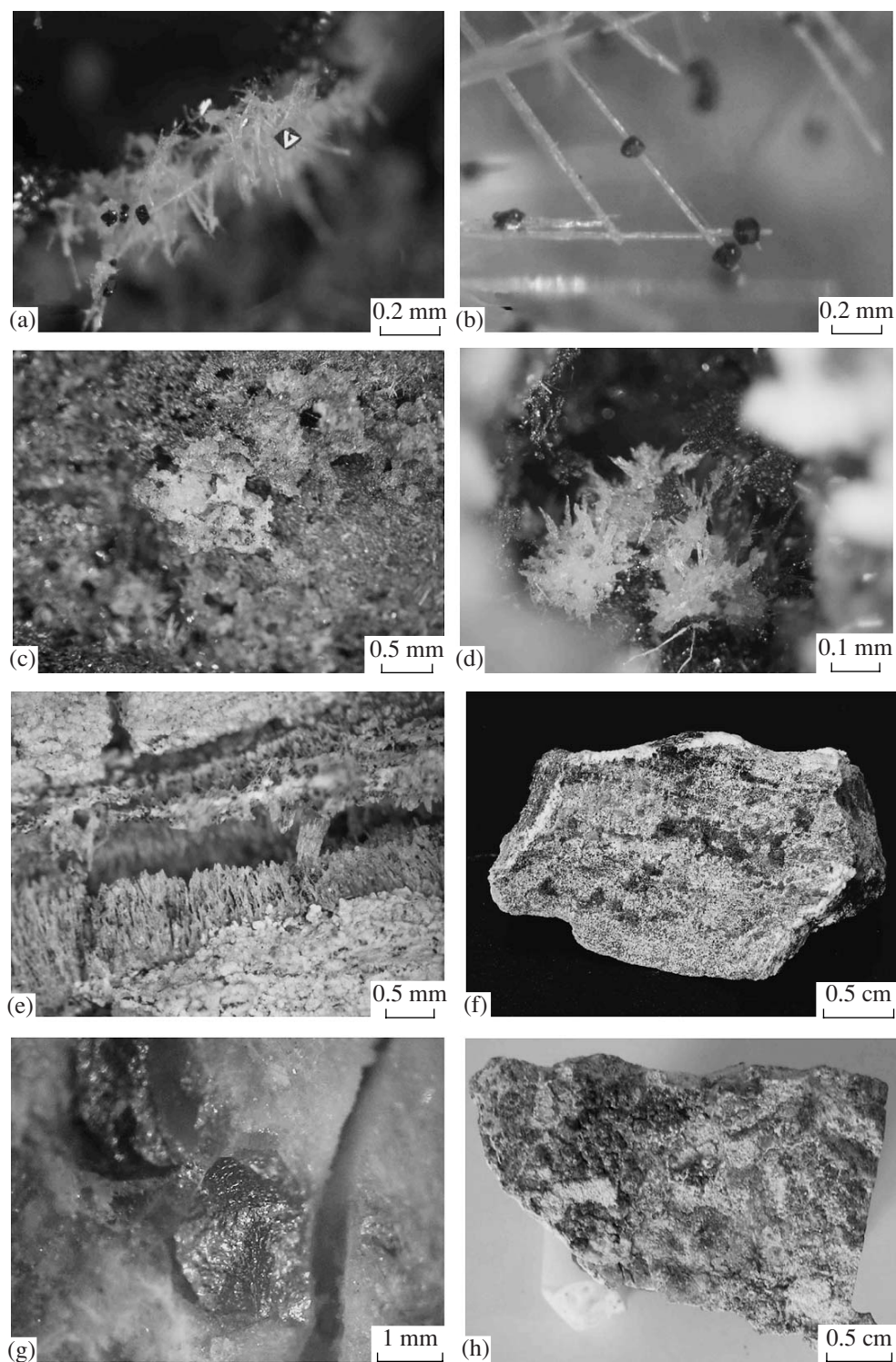


Fig. 3. The outward appearance of magnesioferrite and chlor-fluorellestadites from metacarbonate rocks in the burnt waste piles of the Chelyabinsk, Kizel, and Kuznetsk coal basins: (a, b) acicular anhydrite with octahedral and rhombic-dodecahedral magnesioferrite crystals (Yemanzhelinsk district, Chelyabinsk basin); (c, d) chlor-fluorellestadite from metacarbonate rocks (Yemanzhelinsk district, Chelyabinsk basin): (c) cavernous ellestadite aggregates on the magnesioferrite-srebrodolskite aggregate with inclusions of the same ore minerals, (d) radiated ellestadite on the magnesioferrite-srebrodolskite aggregate; (e, f) chlor-fluorellestadite from metacarbonate rocks (Kopeisk district, Chelyabinsk coal basin): (e) columnar ellestadite crystals on the granular substrate consisting of anhydrite, magnesioferrite, and srebrodolskite; (f) ellestadite segregation in the core of the “nut” consisting of magnesioferrite, srebrodolskite, anhydrite, larnite, cuspidine, chlormayenite, rustumite, hematite, and apatite; (g) fluorellestadite from metacarbonate rocks in the waste pile of the Klyuchevsky Mine (Kizel coal basin), photo by S.S. Potapov; (h) fluorellestadite from the contact zone of the metacarbonate core and anhydrite shell (waste pile of the Abashevo Mine, Kuznetsk coal basin).

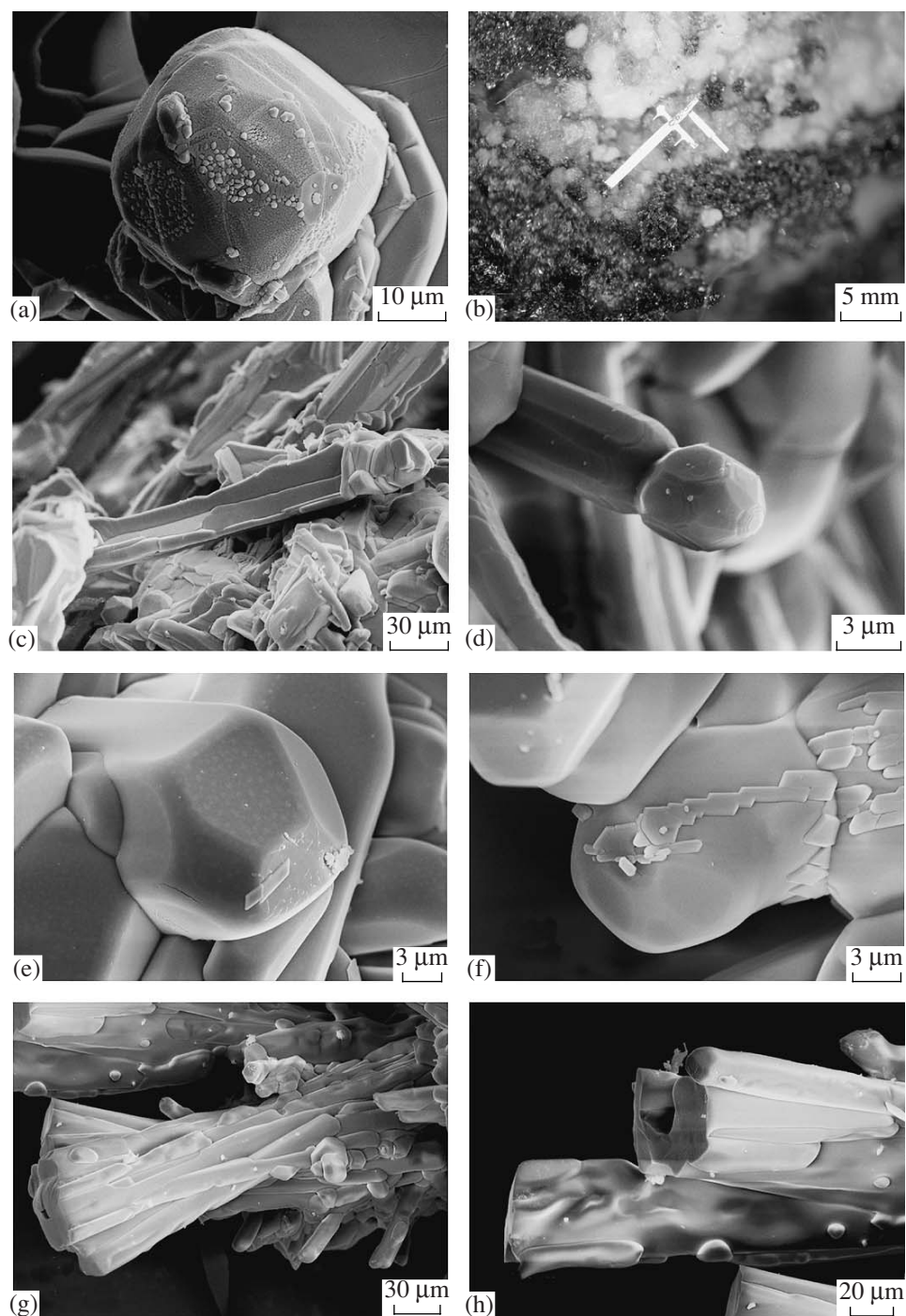


Fig. 4. Anhydrite, magnesioferrite, and chlor-fluorellestadite from the metacarbonate rocks of the Yemanzhelinsk district, Chelyabinsk coal basin: (a) morphology of the magnesioferrite crystal, (b) large skeletal anhydrite crystal, (c) sheath anhydrite crystal, (d) scepterlike anhydrite individual, (e) faceted microindividual of fluorellestadite, (f) autoepitaxial overgrowth of microindividuals of fluorellestadite on its large imperfect crystals, (g) sheaflike intergrowth of fluorellestadite individuals, and (h) sheath fluorellestadite individuals. Images made on a LEO 420 SEM.

tals or their sheaflike aggregates. The growth of anhydrite needles over radiated fluorellestadite aggregates is typical. In some cases, anhydrite occurs as large (up to 1 cm in length) tabular or skeletal crystals. The composition of mineral is close to CaSO_4 .

Larnite is commonly observed as round and xenomorphic grains up to 100 μm in size captured by cuspidine. The mineral is identified by a high refractive index and characteristic striation of polysynthetic twinning along $\{100\}$ (Fig. 2a) and clear cleavage along $\{100\}$.

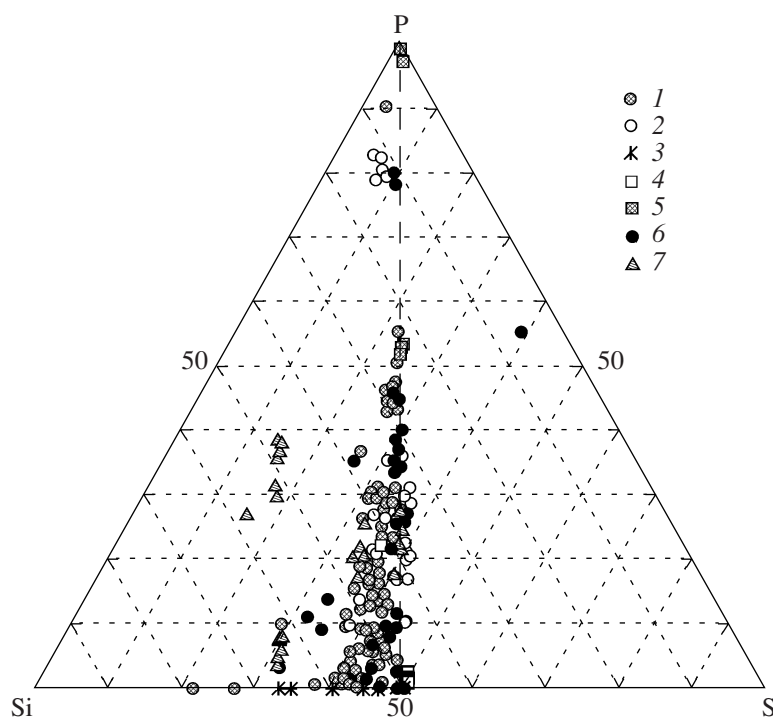


Fig. 5. Compositions of ellestadites plotted on the Si–P–S diagram. (1) chlor-fluorellestadites from the Yemanzhelinsk district, Chelyabinsk coal basin; (2) chlor-fluorellestadites from the Kopeisk district, Chelyabinsk coal basin; (3) fluorellestadites from the Kizel coal basin; (4) fluorellestadites from metacarbonate rocks, the Kuznetsk coal basin; (5) fluorellestadites from the clinker, the Kuznetsk coal basin; (6) compositions of pyrogenic and skarn ellestadites published in the literature (Harada et al. 1971; Rouse and Dunn, 1982; Chesnokov et al., 1987; Neubauer and Pollmann, 1992; Organova et al., 1994; Litsarev et al., 1998; Sejkora et al., 1999; Paskal et al., 2001; Eytier et al., 2004); and (7) fluorellestadite from the Hatrurim Formation, Israel (original data).

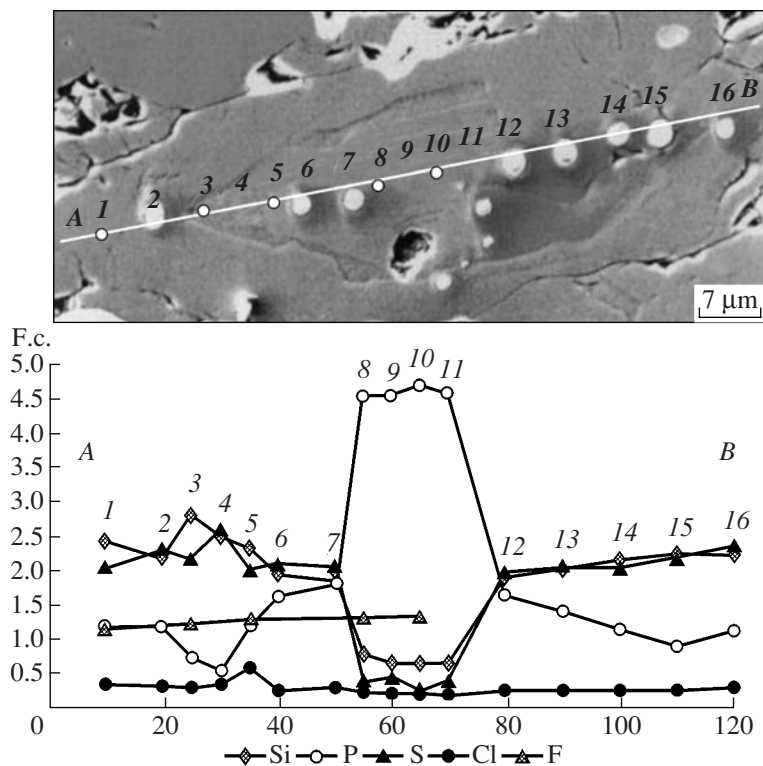


Fig. 6. A zonal individual of chlor-fluorellestadite and the profile across this grain. Contents of the elements are given in the formula coefficients. The Kopeisk district of the Chelyabinsk coal basin.

Table 3. Representative analyses, wt % of minerals coexisting with minerals of the ellestadite series in pyrometamorphic rocks

Component	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
	E-28	E-28	E-17	E-25	E-21	E-10	E-9	44-2	43-5	43-3c	43-3c	43-4c	47-1-2	kiz-1	kiz-1	kiz-1
SiO ₂	34.18	32.20	3.69	36.17	0.04	0.01	0.00	32.20	3.22	0.00	0.02	0.07	0.05	0.14	0.22	0.00
P ₂ O ₅	0.18	0.30	–	0.00	0.00	0.01	0.00	0.03	0.00	0.00	0.00	0.00	0.02	0.00	0.00	0.00
SO ₃	0.00	0.05	0.02	0.23	57.94	0.00	0.00	0.02	0.14	0.02	0.14	0.00	0.01	0.09	13.07	58.88
TiO ₂	0.05	–	0.02	0.02	0.02	0.00	0.00	–	0.13	0.00	0.01	0.00	0.00	0.98	0.01	–
Cr ₂ O ₃	–	0.01	0.00	–	–	–	–	0.00	–	–	–	–	–	0.02	0.00	–
Al ₂ O ₃	–	0.01	33.08	–	–	–	–	0.00	35.63	0.00	0.00	0.33	0.87	10.29	48.25	–
FeO	0.00	0.07	–	0.11	0.03	–	–	0.06	–	0.02	0.00	–	–	–	–	–
Fe ₂ O ₃ *	–	–	11.08	–	–	91.5	71.00	–	10.43	–	–	57.20	75.00	44.96	1.64	–
MnO	–	–	–	–	–	2.34	2.74	0.00	0.02	0.02	0.03	0.39	2.21	–	–	–
MgO	0.02	0.09	0.05	0.07	0.05	0.22	0.04	0.07	0.18	99.6	0.01	0.45	19.5	0.72	0.13	–
CaO	65.1	62.17	44.89	58.02	41.85	6.07	25.3	62.38	44.00	0.32	80.3	41.90	0.75	43.85	36.69	41.14
SrO	0.00	–	–	0.00	0.00	0.02	0.00	–	0.00	0.00	0.00	0.00	0.03	0.00	0.00	–
Na ₂ O	0.03	–	–	0.00	0.01	0.02	0.00	–	0.00	0.01	0.03	0.03	0.00	0.00	0.00	–
K ₂ O	–	–	–	–	–	–	–	–	0.03	–	0.00	0.01	0.00	0.00	0.00	–
F	–	8.35	0.35	–	–	–	–	8.13	–	–	–	–	–	–	–	0.00
Cl	–	0.00	7.58	7.05	0.01	–	–	0.02	6.52	0.00	0.00	0.00	0.00	–	–	0.00
Total	99.63	103.37	99.77	101.76	99.94	100.26	99.09	102.91	99.36	100.02	80.56	100.38	98.50	99.06	100.04	100.02
O-(F, Cl) ₂	–	3.52	1.86	1.59	–	–	–	3.43	1.47	–	–	–	–	–	–	–
Total	99.63	99.85	98.92	100.17	99.94	100.26	99.09	99.48	98.61	100.02	80.56	100.38	98.50	99.06	100.04	100.02

Note: (1–7) samples from the waste piles of the Yemanzhelinsk district: (1) larnite, (2) cuspidine, (3) chlormayenite, (4) rustumite, (5) anhydrite, (6) magnesioferrite, (7) srebrodolskite; (8–13) samples from the waste piles of the Kopeisk district: (8) cuspidine, (9) chlormayenite, (10) periclase, (11) portlandite, (12) srebrodolskite, (13) magnesioferrite; (14–16) samples from the waste piles of the Kizel coal basin: (14) brownmillerite, (15) ye'elimite, (16) anhydrite.

Table 4. Representative analyses, wt % of minerals of the ellestadite series from pyrometamorphic rocks of the Chelyabinsk, Kizel, and Kuznetsk coal basins

Component	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
	E-4	E-4	E-18	E-20	E-20	43-3	43-5	43-7C	47-1-1	kiz-3	kiz-2-6	kiz-1-2	05-82-1	05-82-1	05-81-1	05-81-1
SiO ₂	28.03	18.00	2.39	17.02	20.42	21.66	20.52	4.15	19.46	24.26	18.62	17.64	17.01	17.48	8.14	0.06
P ₂ O ₅	0.00	0.27	38.18	6.27	0.46	0.76	0.41	33.64	3.11	0.00	0.03	0.03	1.05	0.33	22.46	41.35
SO ₃	10.29	22.20	1.38	16.62	20.54	18.09	19.56	2.29	18.29	16.13	23.26	23.65	23.44	24.30	11.40	0.25
CaO	59.86	57.90	55.99	57.00	57.31	56.90	57.24	56.44	56.13	57.63	56.17	57.09	56.73	56.23	56.46	56.30
F	–	–	2.90	2.03	3.58	2.53	3.19	2.60	2.07	–	3.21	2.92	3.03	3.99	3.19	3.23
Cl	0.27	0.63	0.30	2.02	0.16	1.53	0.15	0.82	2.62	–	0.03	0.01	0.02	0.02	0.02	0.00
Total	98.60	99.10	101.33	101.05	102.66	101.69	101.13	100.16	101.77	98.21	101.44	101.42	100.11	100.90	100.36	100.06
O-(F, Cl) ₂	0.06	0.14	1.29	1.31	1.54	1.41	1.38	1.28	1.46	–	1.36	1.23	1.28	1.69	1.35	1.36
Total	98.54	98.95	100.04	99.74	101.12	100.28	99.75	98.88	100.30	98.21	100.08	100.18	98.83	99.21	99.01	98.70

Formula coefficients calculated on the basis of 10 Ca ²⁺ cations																
Si	4.36	2.89	0.40	2.78	3.31	3.55	3.43	0.75	3.23	3.91	3.09	2.88	2.79	2.90	1.34	0.01
P	0.00	0.04	5.37	0.87	0.06	0.11	0.06	4.71	0.44	0.00	0.01	0.01	0.15	0.05	3.14	5.79
S	1.20	2.68	0.17	2.04	2.50	2.23	2.39	0.28	2.28	1.95	2.89	2.89	2.89	3.02	1.41	0.03
Ca	9.98	9.98	9.98	9.98	9.97	10.00	10.00	10.00	10.00	9.96	10.00	10.00	10.00	10.00	10.00	10.00
F	–	–	1.52	1.05	1.84	1.31	1.64	1.36	1.09	–	1.69	1.51	1.58	2.09	1.67	1.69
Cl	0.07	0.17	0.08	0.56	0.05	0.46	0.04	0.23	0.74	–	0.01	0.00	0.01	0.01	0.01	0.00
O	1.93	1.83	0.39	0.39	0.12	0.26	0.32	0.41	0.18	2.00	0.31	0.49	0.42	0.09	0.33	0.31

Note: (1–5) chlor-fluorellestadites from the waste piles of the Yemanzhelsk district; (6–9) chlor-fluorellestadites from the waste piles of the Kopeisk district; (10–12) fluorellestadites from the waste pile of the Klyuchevsky Mine, the Kizel coal basin; (13–16) fluorellestadites from the waste pile of the Abashevo Mine, the Kuznetsk coal basin: (13, 14) blue and green fluorellestadites from the metacarbonate material, (15) fluorellestadite found in the clinker, (16) fluorapatite found in clinker.

Cuspidine together with anhydrite, fluorellestadite, chlormayenite, srebrodolskite, and larnite occurs as a fine-grained aggregate in intermediate zones of nodules (Fig. 2) and separate crusts. Cuspidine and larnite are distinguished by pure compositions and contain only an insignificant admixture of phosphorus.

Chlormayenite forms aggregates of round grains (5–40 μm) in association with fluorellestadite, cuspidine, and apatite (Figs. 2d–2i). The Cl content in the Yemanzhinsk chlormayenite is close to the limiting value (7.58 wt %) and is somewhat lower in the Kopeisk sample (6.5 wt %). Since SiO_2 always enters into the composition of the mineral (up to 3.69 wt %), it has to be defined as silicochlormayenite. This mineral was described for the first time by Chesnokov (1999). Since it contains a significant amount (up to 10.4 wt %) of FeO, iron may be considered among the major cations of minerals from the mayenite series.

Rustumite occurs as small (up to 30 μm) round grains dispersed within cuspidine. The mineral contains more than 7 wt % Cl and, hence, is the utmost Cl-replaced analogue of rustumite. Minerals of such composition are as yet unknown in other assemblages.

Apatite does not form separate grains and occurs only in cores (5–25 μm) of zonal fluorellestadite crystals (Figs. 2d–2f). The Ba^{2+} and Sr^{2+} contents are not higher than 0.16 and 0.02 wt %, respectively.

Portlandite is associated with chlormayenite, cuspidine, and periclase. Small (20–30 μm) inclusions in the fluorellestadite matrix are common. The mineral contains 80.3 wt % CaO and is practically devoid of admixtures and most likely is a product of lime hydration that arose through the calcination of carbonates.

Periclase along with fluorellestadite also make up granular segregations in srebrodolskite and is close to pure MgO in composition.

The Kizel coal basin. Fluorellestadite was found in fragments of calcinated limestone in the sinter from waste pile of the Klyuchevsky Mine near the town of Gubakha. The loose mineral aggregate consists largely of anhydrite; ye'elimite, fluorellestadite, brownmillerite, and mayenite occur in subordinate amounts.

Fluorellestadite is blue in color and forms compact monomineralic aggregates that appear as spots in the loose core (Fig. 3g). The mineral is uniform in composition (Table 4). The CaO content varies from 56.02 to 58.16 wt %. Variations in the sulfur and silica contents are not large as well: 17.40–24.26 wt % SiO_2 and 16.13–24.05 wt % SO_3 . The absence of P is typical. The amount of F ranges from 2.62 to 3.21 wt %; the Cl content is minimal (0.01–0.06 wt %). No $(\text{OH})^-$ groups were detected with IR spectroscopy; the bands of $(\text{CO}_3)^{2-}$ absorption are expressed extremely poorly.

Anhydrite forms a matrix and occurs as discrete crystals in ye'elimite. Its composition is close to the theoretical.

Brownmillerite is associated with anhydrite and characterized by a high purity in its composition. Only TiO_2 (~1 wt %) and MgO (0.72 wt %) were detected as admixtures.

Mayenite and ye'elimite are intimately intergrown with fluorellestadite. Ye'elimite is observed as fine disseminations in calcite and, in turn, contains anhydrite grains. FeO (1.64 wt %) is only an admixture.

The Kuznetsk coal basin. Two types of mineral aggregates containing fluorellestadite were found in the waste pile of the Abashevo Mine near Novokuznetsk. The first one is a typical metacarbonate “nut” enveloped by a dense anhydrite crust. The core consists of a loose aggregate of anhydrite, calcite, periclase, lime, and srebrodolskite; the grain size is not larger than 2–4 μm and does not allow us to obtain proper microprobe analyses. Fluorellestadite is turquoise green in color and a bright blue color makes up large granular segregations (Fig. 3h). The CaO content varies from 56.25 to 56.73 wt %. Phosphorus is a trace element (0.14–1.05 wt % P_2O_5). Variations in the S and Si concentrations are not wide: 23.44–24.33 wt % SO_3 and 16.95–17.67 wt % SiO_2 . The F content ranges from 2.87 to 3.99 wt %; the Cl concentration is minimal (0.02–0.05 wt %). The $(\text{OH})^-$ group was not detected.

The second finding of bright blue fluorellestadite was made in an unusual setting among welded fragments of pelitic clinker without any relation to the calcinated carbonates. This mineral occurs here as monomineralic ribbonlike segregations. The typical feature is a high P_2O_5 content from 21.74 to 41.35 wt % against a background of low and variable contents of SiO_2 (0.06–8.44 wt %) and SO_3 (0.25–1.57 wt %) (Table 4; Fig. 5). The amount of F is close to its limit (3.19–3.69 wt %); Cl < 0.02%. The H_2O content was not estimated. Thus, fluorapatite occurs together with fluorellestadite in samples from burnt metapelitic rocks in the waste pile of the Abashevo Mine. Isomorphism according to the scheme $2(\text{PO}_4)^{3-} \rightarrow (\text{SO}_4)^{2-} + (\text{SiO}_4)^{4-}$ is completed in this case by the appearance of the $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ end member devoid of Si and admixtures (Fig. 5).

DISCUSSION

Chemical composition. The minerals of the ellestadite group from the Chelyabinsk basin correspond to fluorellestadite and chlorellestadite in composition and are characterized by contrasting zoning in the distribution of P, S, Si, and to a lesser extent, F and Cl as a response to the abrupt changes in the chemical composition of the crystallization medium. Chlorides and chloresilicates are absent in these mineral assemblages. In the Kuznetsk and Kizel basins, only fluorellestadite has been identified; chlorellestadite was not detected. Most likely, this is explained by the appearance of other Cl-bearing phases—chlormayenite and Cl-replaced analogue of rustumite—instead of chlorellestadite.

Thus, all pyrogenic ellestadites are halogen-replaced derivatives of hydroxyllelestadite consistent with the anhydrite specificity of the mineral assemblages of pyrometamorphic systems with an unusually high contribution of fluor- and chlorsilicates (9 and 6%) (Chesnokov, 2001a, 2001b, Sokol et al., 2005).

Although the apatite structure admits the incorporation of the $(\text{CO}_3)^{2-}$ ion therein, no ellestadites with any significant content of this ion were detected. It is quite explicable for pyrogenic systems, because, under low-pressure conditions, a rise in the temperature stimulates the breakdown of all carbonate compounds (Bowen, 1940; Reverdatto, 1970; Gross, 1977; Chesnokov and Shcherbakova, 1991; Sokol et al., 2005). While ellestadite compositions are plotted on the Si–P–S triangle (Fig. 5), one can clearly see a shift of many samples from stoichiometry toward enrichment in silica. A deficiency in F and Cl may be suggested as the simplest scheme for compensation of the negative charge. This is indicated by the fact that, in the absence of $(\text{OH})^-$ groups, the sum of the formula coefficients of F and Cl is less than 2 in all of the samples (Table 4).

Formation conditions of ellestadite-bearing assemblages. The high-temperature and low-pressure transformation of any carbonate rocks is a succession of reactions of the progressive removal of CO_2 from the solid phases. The three highest-temperature mineral transformations, which result in the consecutive formation of spurrite, merwinite, and larnite, correspond to the conditions of sanidine-facies metamorphism and pyrometamorphism as its particular case (Bowen, 1940; Reverdatto, 1970). Spurrite accompanies ellestadite in specific assemblages of the Cornet Hill deposit in Romania (Table 1). The mineralogical features of their mineralogy allow interpretation of these aureoles as composite assemblages where skarn mineralization (calcite, vesuvianite, and hydrogrossular) is superimposed on high-temperature tilite- and spurrite-bearing rocks of contact metamorphism.

The findings of ellestadite in the technogenic pyrometamorphic systems and its discovery in pyrogenic rocks of the Hatrurim Formation, Israel (Gross, 1977), directly demonstrate the possibility of this mineral to form at *PT* parameters of sanidine metamorphic facies. In the studied pyrogenic assemblages, fluorellestadite coexists with larnite, lime, or portlandite as a product of its hydration. At the minimum P_{CO_2} , this assemblage is stable at $T \geq 950^\circ\text{C}$ (Reverdatto, 1970). The ellestadite-bearing assemblages (mayenite + anhydrite + ye'elimite + calcite + brownmillerite) of the Kizel basin as products of limestone calcination are identical to the pyrogenic assemblages in rocks from the Hatrurim Formation, Israel, where these assemblages were developed after chalk and limestone were contaminated by pelitic materials (Gross, 1977).

During the process of calcination at $P \approx 1$ bar and $T = 600\text{--}1000^\circ\text{C}$, all carbonates are decomposed according to the scheme $\text{MeCO}_3 \rightarrow \text{MeO} + \text{CO}_2\uparrow$. Calcite is

decarbonated at $700\text{--}900^\circ\text{C}$. Dolomite breaks down at $T < 750^\circ\text{C}$ with the formation of CO_2 , periclase, and calcite, and the latter, in turn, is decomposed at a higher temperature with the formation of lime (CaO). The lowest breakdown temperature is characteristic of siderite, which readily dissociates beginning from 600°C . In general, the dissociation temperature of carbonates is directly related to the partial CO_2 pressure in the gas phase and appreciably decreases at $P_{\text{CO}_2} < 0.8P_{\text{tot}}$. The real possibility of spurrite, tilleyite, merwinite, and rankinite formation in contact aureoles appears only at $P_{\text{CO}_2} \leq 0.5P_{\text{tot}}$ (Reverdatto, 1970). In the burnt coal dumps, where carbonates do not occur in large amounts and the total pressure is not higher than a few atmospheres, the phase transformations are realized under the conditions of an extremely low partial pressure of CO_2 , which feature the calcination of raw materials during the production of cement (Toropov, 1956). In general, the transformation of carbonates in burnt coal dumps is characterized by complete decarbonation at $T > 600\text{--}800^\circ\text{C}$ accompanied by the formation of simple oxides and ferrites and the intense alteration of these phases by high-temperature pneumatolysis (Chesnokov and Shcherbakova, 1991; Chesnokov, 1997, 1999; Sokol et al., 2002, 2005). As a result, the mineral assemblages of unique compositions with complex anions containing fluorine-, chlorine-, sulfate-, phosphate-, and less frequently, sulfide-ions are formed on the place of carbonate rocks.

Source of material. The composition of pyrogenic ellestadite and coexisting minerals is set by the composition of carbonate and silicate protoliths that underwent calcination. The iron carbonates are the main source of phosphorus in the studied pyrogenic systems (Sokol et al., 2005). Apatite and high-F fluorellestadite are typical of the metacarbonate association of waste piles in the Chelyabinsk basin. In the Kizel ellestadites resulting from the calcination of limestones, phosphorus is commonly absent. The main sulfur sources in coal-bearing sequences are related to the dispersed pyrite and the carbonaceous matter itself, where sulfur occurs as sulfide, sulfate, and native species. In the Chelyabinsk basin, the sulfur content in coal is about 1 wt % (Sokol et al., 2005). Micas and hydromicas of pelitic rocks are the main source of fluorine (Sokol et al., 2002), whereas coal is the major source of chlorine (Chesnokov, 2001a, 2001b).

Gas transport is the main mechanism of heat and mass transfer in burning and cooling waste piles. This mechanism provides the redistribution of elements between areas with different regimes of burning and make it possible to remove some elements out of a dump as fumarole streams. As the intensity of the thermal transformation increases, the hypocenters of burning are displaced toward deep-seated zones, and new blocks of sedimentary rocks are progressively involved in the gas release providing a steady gas flow. This fea-

ture of the burning of large dumps causes widespread telescoping, i.e., the superposition of one mineral assemblage on others (Chesnokov, 1997, 1999).

The gas transfer in dumps is especially striking while carbonate rocks are calcinated. A two-stage scheme of the transformation of these rocks was offered by Chesnokov (1995, 1999). The decarbonation mentioned above occurs at the first stage, whereas, at the second stage, the newly formed oxides (CaO, MgO, and FeO) interact with components of hot gas streams. Lime is an effective precipitating agent for a wide range of anions: S^{2-} , $(SO_4)^{2-}$, Cl^- , and F^- . Periclase behaves in the same manner with regard to fluorine (Sokol et al., 2002, 2005).

Oldhamite (CaS) and ovchinnikovite ($4FeS \cdot FeO \cdot 3CaO$) are formed as products of the high-temperature ($T \sim 1000\text{--}1200^\circ\text{C}$) interaction of the decarbonated substrate with gas that contains sulfide sulfur (Chesnokov 1995, 1999). If a gas stream largely transports sulfate sulfur, anhydrite originates on the place of the metacarbonate rocks. If chlorine is predominant in the gas phase, $CaCl_2$, Cl-bearing silicooxides, and silicate-chlorides are the products of the exchange reactions (Chesnokov, 1995, 1999). The formation of polyanionic compounds (fluor- or chlorellestadites, in particular) is feasible only with the participation of gas streams that provide the joint transport of several anion-forming elements (F, Cl, S). Thus, the long-term action of gas streams with relatively low F, Cl, and S contents removed from the hypocenter of burning results in the formation of minerals enriched in these elements in the discharge areas.

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