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Abstract: Pyrometamorphic rocks generated during spontaneous burning of spoil-heaps in the Chelyabinsk coal basin, South Urals, contain a variety of high-temperature minerals, some with diverse and unusual compositons. Optical microscopy, X-ray diffraction, X-ray fluorescence, and microprobe analyses were performed to study the mineralogy of annealed and fused waste rocks. A wide spectrum of rare minerals was found, including tridymite, crystobalite, mullite, K-bearing cordierite, K-Mg-osumilite, and Fe^{3+},Al-rich Ca-clinopyroxene, as well as hexagonal and orthorhombic analogues of anorthite. It is suggested that the mineralogy of pyrometamorphic rocks is mainly governed by bulk chemical composition, annealing temperature, and oxygen fugacity; moreover, varying degrees of disequilibrium melting, mixing, crystallization, volatilization and a variety of reaction mechanisms influence the formation, structure and chemistry of the constituent minerals.

Key-words: pyrometamorphic rocks, spoil-heap, clinker, paralava, Chelyabinsk coal basin.

Introduction

Pyrometamorphic annealed, melted and slag-like rocks formed during the natural burning of coal are well known in the neighbourhood of many coal deposits (Venkatesh, 1952; Miyashiro, 1957; Bentor *et al.*, 1981; Foit *et al.*, 1987; Cosca *et al.*, 1989; Kalugin *et al.*, 1991). The spontaneous combustion of coal is a common phenomenon not only in near-surface coal beds, but also in spoil-heaps.

Coal-fire baked but unmelted sedimentary rocks, or *clinkers*, and pyrometamorphic melt-rocks, or *paralavas*, are unique geological systems formed under conditions which may be considered as intermediate between laboratory experiments and natural metamorphic processes. Their formation is determined by a combination of the following factors: a) extreme parameters of annealing (high temperatures, very low pressures, and very short duration of thermal exposure); b) extreme chemical heterogeneity of waste mass; c) aggressive gaseous atmosphere; d) high and transient temperature gradients and oxidation-reduction potential gradients. All these factors lead to the generation of a wide variety of specific minerals and mineral associations.

Burning spoil-heaps in the Chelyabinsk coal basin (the South Urals, Russia) are a very suitable subject for addressing many problems of industrial mineralogy. A major contribution to the study on mineralogy of these heaps was made by Chesnokov & Tsherbakova (1991). The present paper presents the result of our continuing studies on pyrometamorphic rocks from the studied region.

Occurrence of pyrometamorphic rocks in burned spoil-heaps

There are about 50 pit-heaps in the Chelyabinsk brown coal basin (Geology of coal…, 1967), located in the vicinity of Chelyabinsk. The majority of the heaps are 40–70 m in height, with volumes reaching 1 000 000 m^3. Fresh material supplied to

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the wastes contains mudstones, siltstones, siderite concretions, sandstones and pieces of petrified wood. Spontaneous oxidation of coal material in the heaps, which began with smouldering and lasted for 10–15 years, infrequently passed through the phase of flame combustion (T = 1000–1200°C). At present, coal combustion is complete and the heaps are composed of rocks that have suffered variable extents of pyrometamorphic alteration. So far, one can observe the emissions of hot gases (T = 200–500°C) accompanied by the precipitation of sulphate and chloride minerals.

The products of the highest temperature baking under conditions of free access to oxygen are represented by reddish-brown baked sedimentary rocks – cherry and red clinker. The less thermally altered layers, appearing as a loose mass, are composed of fragments of annealed mudstones of pink to yellow colour.

During excavator stripping of deep-seated zones of the heaps, segments were exposed around 10–20 m in size that had been annealed away from oxygen. These have been termed "black blocks" (Chesnokov & Tsherbakova, 1991). The processes proceeded in them are likely to be similar to the dry refining of coal, when combustible gases are produced, containing up to 1–20% of CO and 10% of H_2. The "black blocks" are commonly isolated from the main part of the heaps by a dense weakly permeable crust of fine-grained clayish material. During the annealing process within "black-blocks", carbonate dissociation reactions were taking place. These reactions proceeded with the release of a great amount of carbonaceous material, similar to gas carbon black, which did not move away from the block and which uniformly penetrated the entire rock volume.

Besides the annealed sedimentary rocks constituting the main part of the waste mass, basalt-like crystalline melted rocks (paralava) and cordierite nodules were found in a larger heaps, where combustion had proceeded more intensively.

Analytical methods

The phase composition of paralavas and crystalline cordierite rocks was analysed using the electron microprobe, chemical and X-ray methods, and also by microscopic study. The annealed mudstones are too fine-grained to permit the determination of their modal mineralogical composition by optical means, so in this case the X-ray diffraction method was the most effective. Quantitative mineral analyses were performed using a Camebax electron microprobe. Conditions were optimized with an accelerating potential of 20 kV and sample current of 10 nA.

The X-ray diffraction data were collected on a DRON-3 powder X-ray diffractometer. Lattice parameters of minerals were obtained by least-squares refinement of $Cu_{K\alpha}$ diffractometer data, which were internally calibrated with metallic Si. The degree of variation of the cordierite lattice from hexagonal symmetry was measured by the distortion index Δ (Miyashiro, 1957). The whole-rock chemistry was determined for a representative 5 g sample by X-ray fluorescence analysis. The instrument used for photographs was a JSM-35 electron scanning microscope.

Whole-rock composition of pyrometamorphic rocks

The chemical compositions of initial sedimentary rocks discarded into wastes, and the products of their thermal alteration, including clinkers and paralavas, are given in Table 1.

The initial sediments are represented by the three general rock types: mudstones, siderite concretions, and calcareous mudstones. Their LOI content is very high, usually more than 10%. Water, however, would have been largely expelled from the rocks during the heating event, well before the start of melting, together with CO_2 resulting from the dissociation of carbonates.

The annealed rocks are characterised by the approximate composition of the parent mudstones (recalculated on LOI-free basis), but differ in having significantly lower sodium content, which has evidently been expelled in the earlier stages of the combustion process.

Finally, the paralavas are depleted in silica, alumina and alkalis with respect to the initial mudstones (the Na_2O content decreases to less than 0.2 wt%) and enriched in total iron, magnesium and calcium. There are strong grounds to believe that siderite-bearing material was the major contributor of iron to paralavas, while calcareous clays may be considered as a source of magnesium and calcium. Thus, the examined basalt-like rocks are thought to be formed by the melting of all three parent rock types. Moreover, field observations suggest that the zones of initial partial melting are commonly confined to siderite-bearing parts of the heaps. This may be due to the ear-

Table 1. Chemical compositions of initial and pyrometamorphic rocks from burned spoil-heaps of the Chelyabinsk coal basin.

N	1	2	3	4	5	6	7	8	9	10	11	`12	13	14
Sample	C-1	Ap-1	99-1	99-2	54-37	54-37b	54-37a	54-38	45/7	55-29	54-157	KP	KP-5	55-29
SiO_2	5.36	21.60	58.28	57.48	60.57	63.38	62.24	52.65	55.76	54.58	62.17	45.65	44.06	52.89
TiO_2	0.14	0.44	1.21	1.30	1.08	1.14	0.97	1.01	1.19	1.22	1.36	1.07	0.93	0.92
Al_2O_3	2.17	9.71	19.59	18.74	27.23	26.25	25.48	21.46	21.29	30.05	20.75	17.91	17.26	20.08
Fe_2O_3	3.19	5.66	1.01	0.73	2.85*	2.69*	4.45*	12.78*	10.93*	5.08*	6.11*	1.19	13.49*	13.39*
FeO	49.57	2.06	2.65	3.76	–	–	–	–	–	–	–	12.64	–	–
MnO	0.58	0.11	0.04	0.06	0.01	0.11	0.01	0.16	0.25	0.13	0.13	0.27	0.21	0.21
MgO	0.94	9.08	1.99	2.13	0.50	2.01	0.70	4.52	4.58	1.62	1.66	4.62	5.67	5.07
CaO	2.36	18.51	0.40	1.27	0.25	0.40	0.89	2.71	2.41	0.97	0.43	13.86	16.39	5.98
Na_2O	0.25	0.48	1.03	1.23	0.25	0.64	0.33	0.24	0.48	0.65	0.49	0.20	0.00	0.00
K_2O	0.27	1.55	2.00	1.88	4.88	2.00	2.80	2.28	0.84	4.23	4.09	1.37	1.48	0.47
H_2O	2.67	0.44	1.48	1.28	0.60	–	0.24	–	–	–	–	0.25	–	–
LOI	–	29.66	9.76	10.23	1.40	1.18	0.96	1.29	1.40	1.25	2.57	–	0.00	0.44
P_2O_5	0.48	0.37	0.19	0.38	0.14	0.15	0.38	0.86	0.86	0.21	0.23	0.68	0.51	0.53
F	–	–	0.04	0.06	<0.01	–	<0.01	–	–	–	–	–	–	–
Cl	–	–	0.04	0.01	<0.01	–	<0.01	–	–	–	–	–	–	–
CO_2	32.00	25.48	–	–	–	–	–	–	–	–	–	–	–	–
Total	99.98	99.67	99.71	100.54	99.76	99.95	99.55	99.96	99.99	99.99	99.99	99.71	100.00	99.98

Note: **1-4– initial sedimentary rocks**: 1– siderite concretions, 2– carbonaceous mudstone, 3-4– mudstones; **5-11– annealed mudstones**: 5-6– yellow "mudstone", 7– "mudstone" from pink zone, 8– "mudstone" from red clinker, 9– "mudstone" from cherry clinker, 10– "mudstone" from xenolith in cordierite nodule; 11– "mudstone" from "black blocks"; **12–13– basalt-like paralava**; **14– cordierite nodule**.

* All Fe as Fe_2O_3. Dash denotes "not analyzed".

1-5, 7, 12 – from Chesnokov & Tsherbakova (1991); 6, 8–11, 13–14 – original data.

lier siderite dissociation and rather low temperature conditions of the melting of highly reducing high-ferric systems.

Fine-grained products of the burning of mudstones are the main constituents of the considered heaps. We studied samples mainly from high-temperature red and cherry-coloured clinkers. X-ray powder diffraction analysis of clinkers revealed the presence of cordierite (Δ = 0.10–0.25), mullite, tridymite (rarely quartz, α-cristobalite), hematite and magnetite. Annealed mudstones from pink-coloured zones of the heaps correspond to the lower temperature formations. They are characterized by low content or absence of cordierite, and by the presence of quartz, hercynite and mullite (Table 2).

Yellow annealed "mudstones" correspond to the initial stage of burning. From X-ray diffraction analysis data, quartz, altered muscovite and a small amount of mullite are predominant in their mineral composition.

Of special interest are the rocks making up the "black blocks", in which layered and porcelain-like burned mudstones are contaminated by "soot" and are black in colour. Here we identified cordierite (Δ = 0.00–0.15), quartz, sanidine and K-Mg-osumilite (Table 2).

Cordierite nodules less than 20 cm in size are found in the cherry clinker in the highest temperature parts of the heaps, being commonly adjacent to channels of hot gas jets. They are grey-violet and grey crystalline rocks with abundant cavities, containing cemented fragments of annealed mudstones and infrequently associated with a black slag like mass which is a product of siderite burning. Their mineral composition is rather uniform (Table 2): cordierite, plagioclase, tridymite (sometimes associated with quartz and α-cristobalite) and mullite are predominant; biotite, hermatite and rarely magnetite also occur (ore minerals can constitute up to 50% of the rock volume).

As a rule, walls of gas vesicles are covered by small (< 1 mm) crystals of hematite, pseudobrookite, mullite, cordierite, and aggregates of thin plates of tridymite, plagioclase and mica. On the surfaces of baked mudstones, we found crusts

Table 2. Mineral assemblages of pyrometamorphic rocks from spoil-heaps of the Chelyabinsk coal basin.

Rock type	Sample	Assemblage
Annealed mudstones		
a)pink-coloured zones	45/6; MC-1; MC-2	Qtz,Mul,Hc,(±Crd)
b) "black blocks"	54-326	Crd,Qtz,Trd,Osm,Sa
	45/10	Crd,Qtz,Mul,Sa
	45/11	Crd,Qtz,Sa(?)
	45/7	Crd,Qtz,Crs,Trd
c) cherry clinker	45/7; 54-39	Crd,Mul,Trd,Crs(?),Hem,(± Qtz)
	204; 55-27	Crd,Mul,Trd,Hem,(± Qtz)
d) xenoliths of annealed	55E-27; 204/6; 204/1	Crd, Mul, Qtz (± Hem)
mudstones in cordierite	54-15; 55-29	Crd, Mul, Trd, Hem
nodules	204	Crd, Mul,Trd,Qtz,Hem,Psb
	55-27	Crd, Mul, Trd, Pl, Wo
	204/4; 204/5	Crd, Mul, Qtz, Crs, Mag
Cordierite nodules	55	Pl,Crd,Trd,Mul,Bt,Hem,Mag
	204	Pl,Crd,Trd,Mul,Bt,Hem,Mag,Psb
	55-27	Pl,Crd,Trd,Mul,Bt,Hem
	55E-27	Pl,Crd,Trd,Crs,Mul,Bt,Hem,Psb,Fl
	55-29	Pl,Crd,Trd,Crs,Mul(?),Hem
	204/6	Pl(?),Crd,Crs,Qtz,Mul
	204/4;204/5	Pl,Crd,Trd,Mul,Bt,Opx,Hem
	204/1; 1-2; 2	Pl,Crd,Trd,Crs,Mul,Bt,Hem
	54-15	Pl,Crd,Trd,Crs,Mul,Bt,Opx,Hem
	55-22	Pl,Crd,Trd,Mul,Bt,Cpx,Hem,Psb
Basalt-like paralava	KP-1/3; KP-2; 42-17	Cpx, Opx, Pl, glass
	KP-3;KP-5;KP-6	Cpx,Ol,Pl, Lct, Mag, glass

Note: Bt – biotite; Cpx – clinopyroxene; Crd – cordierite; Crs – cristobalite; Fl – fluorite; Hc – hercynite; Hem – hematite; Lct – leucite; Mag – magnetite; Mul – mullite; Ol – olivine; Opx – orthopyroxene; Osm – osumilite; Pl – plagioclase; Psb – pseudobrookite; Qtz – quartz; Sa – sanidine; Trd – tridymite; Wo – wollastonite.

composed of a fine-grained mixture of plagioclase and wollastonite, and small yellowish-brown crystals of clinopyroxene of unusual chemical composition (Table 3).

Completely melted basal-like rocks occur as distinct zones within the surrounding clinker as dike-shaped bodies and drop-stone forms, similar to stalactites and stalagmites. The size of the blocks ranges up to several cubic metres. The rocks are greyish-green-coloured, fine- and medium-grained, massive, and akin to basalts in their appearance. Within the blocks, there are large (up to 20 cm) fragments of annealed mudstones, making up to 50% of the rock volume. It is thought that the melt source was a low-melting mixture of mudstone and carbonate material (Chesnokov & Tsherbakova, 1991). The main rock-forming minerals are plagioclase, olivine, clinopyroxene, and rare orthopyroxene (Table 2). On the walls of cavities within the basalt-like rocks, there are crystals of diopside, olivine, leucite and mullite needles. Moreover, Chesnokov & Tsherbakova (1991) discovered natural iron, pyrrhotite, troilite, oldhamite, magnetite, magnesioferrite, melilite and inclusions of shungite-like material.

A wide spectrum of rare minerals was found by Chesnokov & Tsherbakova (1991) in fragments of **roasted petrified wood**. Burning of this material has resulted in the formation of a concentrically-zoned aggregates of minerals resembling a peculiar nut with a dense anhydrite shell and a loose core. The mineral assemblage of the cores is controlled by the original composition of the petrified wood: thus, the prevalent mineral in calcitic varieties is portlandite, the product of the hydration of initial quick lime; while in siderite varieties the assemblage is hematite, magnesioferrite and magnetite. Spurrite and larnite are also found in cores, while apatite, chondrodite, fluorite, forsterite, anorthite and wollastonite occur in anhydrite shells.

Mineralogy of pyrometamorphic rocks

SiO_2 polymorphs. Pyrometamorphic rocks may contain any one or two of the SiO_2 polymorphs – quartz, tridymite, and cristobalite. In cordierite nodules, tridymite is the predominant SiO_2 phase. In gas vesicles, many tridymite crystals form well-shaped hexagonal platelets. However, in polarized light, the crystals display an intricate intergrowth pattern of sectors. Intergrowths of small crystals of α-cristobalite sometimes also occur here. In the annealed mudstones, enclosed within cordierite nodules and basalt-like rocks, tridymite and quartz occur commonly; α-cristobalite is scarce. In the annealed mudstones from pink zones of the heaps, as well as in the "black blocks" the predominant SiO_2 phase is quartz.

The small amounts of FeO and Al_2O_3 (0.3 wt.%) are incorporated into the tridymite of cordierite nodules. Cosca *et al.* (1989) point out that even minor additional components in the SiO_2 phases may markedly affect the phase diagram. Therefore, solid solutions combined with rapidly varying temperatures may lead to the metastable formation of any of the polymorphs. From the aforesaid, the pyrometamorphic rocks may be correctly subdivided into relatively low-temperature quartz-bearing assemblages, and rather higher-temperature tridymite-bearing assemblages.

Olivine is a rock-forming mineral of the basalt-like paralavas. It occurs as euhedral grains in the groundmass or forms prismatic crystals in cavities. It varies in composition from fayalite to intermediate Fe-Mg olivine and is characterized by a comparatively high Ca content (Table 3). Skeletal crystals, typical of paralavas of the Powder River Basin (Cosca *et al.*, 1989), are not found in the studied heaps, which may be indicative of the relatively slow cooling of the basalt-like rocks. Forsterite and fayalite crystals are found in cracks in the so-called "black blocks" (Chesnokov & Tsherbakova, 1991).

Pyroxene. Pyroxenes in pyrometamorphic rocks are extremely varied. Clinopyroxenes belonging to the diopside-hedenbergite series occur in olivine-bearing basalt-like paralavas in association with anorthite, leucite, mullite and acid K-rich glass. Fe-Mg orthopyroxenes and fassaite as-

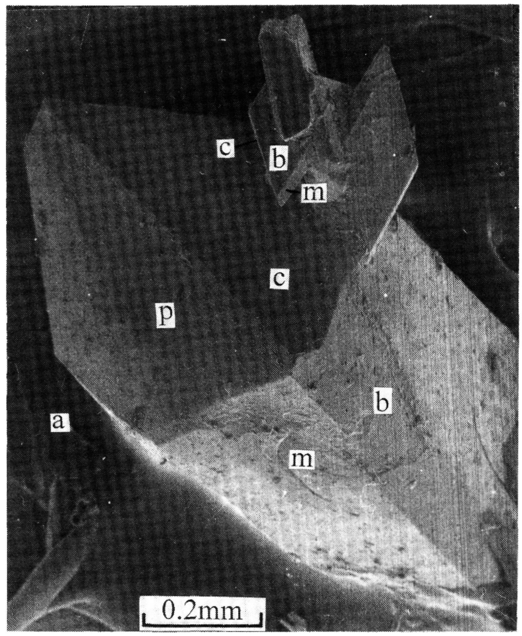

Fig. 1. Intergrowth of lamellar individuals of anorthite on the surface of a large crystal of diopside. Diopside faces: a {100}, b {010}, c {001}, m {110}, p {$\bar{1}$01}. Anorthite is flattened along (010); habit form is pinacoid, b {010}; complementary forms are c {001} and m {110}. Sample KP-3 from cavity in a basalt-like rock.

sociated with anorthite, melilite and acid K-rich glass are common in olivine-free paralavas (Table 3, Fig. 1).

Nevertheless, unusual Fe^{3+},Al-rich Ca-clinopyroxene is the most widespread representative of this family of minerals in pyrometamorphic rocks (see sample 204/1 in Table 3). Along with anorthite and wollastonite, this mineral makes up crusts at the surface of annealed mudstones; it is also found in cordierite nodules and in highly roasted petrified wood. Crystals of diopside habit are quite common. The colour is an intense yellow. The strongest XRD peaks are typical of a mineral, that has been described as esseneite according to the empirical formula (Cosca & Peacor, 1987). Recently, Kabalov *et al.* (1997) carried out Mössbauer spectroscopy and Rietveld refinement of the site occupancies of a similar pyroxene from the Chelyabinsk coal basin. They established that, in contrast to ideal esseneite ($CaFe^{3+}AlSiO_6$), Fe^{3+} ions in the mineral structure are partitioned between the octahedral and tetrahedral site, and con-

Table 3. Representative mineral compositions of pyrometamorphic rocks from burned spoil-heaps of the Chelyabinsk coal basin.

Rock	3	1	1	1	1	3	1	1	4	2	1	3
Sample	54-328	KP-3	0107	KP-6	KP-2	54-252	KP-5	42-17	204/1	55	0107	54-133
Phase	Fo	Ol	Ol	Fa	Opx	Opx	Cpx	Cpx	Cpx	Pl	Pl	Svt
SiO_2	41.91	34.50	31.82	29.28	51.77	57.97	50.59	41.42	36.90	43.83	44.61	43.56
TiO_2	n.d.	0.04	0.05	0.11	0.39	n.d.	0.60	1.87	0.59	0.23	0.40	n.d.
Al_2O_3	0.00	0.02	0.02	0.02	1.55	0.58	2.08	11.47	13.04	34.96	28.79	35.32
Fe_2O_3*	–	–	–	–	–	–	–	–	17.42	–	–	–
Cr_2O_3	n.d.	0.00	0.01	0.00	0.19	n.d.	0.02	0.02	0.02	n.d.	0.01	n.d.
FeO**	1.03	44.13	53.48	66.63	21.36	1.32	13.17	13.91	–	0.87	4.19	0.02
MnO	0.11	n.d.	1.18	1.80	n.d.	0.40	0.36	0.22	n.d.	0.03	0.06	0.00
MgO	55.52	19.95	9.20	0.83	19.12	37.74	12.30	6.01	7.70	0.07	1.74	0.02
CaO	0.47	0.93	3.69	1.40	4.69	1.26	21.03	24.88	24.19	19.05	18.90	19.24
Na_2O	0.03	0.05	0.03	0.05	0.04	0.00	0.06	0.03	0.03	0.14	0.28	0.24
K_2O	0.00	n.d.	0.04	0.01	n.d.	0.01	0.00	0.02	n.d.	0.07	0.68	0.01
Total	99.07	99.62	99.52	100.13	99.11	99.28	100.21	99.85	99.89	99.25	99.66	98.41
			O = 4				O = 6			O = 8		O=8
Si	1.00	1.01	1.00	0.98	1.96	1.99	1.92	1.62	1.43	2.04	2.04	2.04
Ti	n.d.	0.00	0.00	0.00	0.01	n.d.	0.02	0.06	0.02	0.01	0.01	n.d.
Al	0.00	0.00	0.00	0.00	0.07	0.02	0.09	0.53	0.60	1.95	1.55	1.95
Fe^{3+}	–	–	–	–	–	–	–	–	0.51	–	–	–
Cr	n.d.	0.00	0.00	0.00	0.01	n.d.	0.00	0.00	0.00	n.d.	0.00	n.d.
Fe^{2+}	0.02	1.08	1.40	1.86	0.68	0.04	0.42	0.46	–	0.03	0.16	0.00
Mn	0.00	n.d.	0.03	0.05	n.d.	0.01	0.01	0.01	n.d.	0.00	0.00	0.00
Mg	1.97	0.87	0.43	0.05	1.08	1.90	0.70	0.35	0.44	0.00	0.12	0.00
Ca	0.01	0.03	0.14	0.05	0.19	0.04	0.86	1.04	1.01	0.96	1.04	0.96
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.02	0.04
K	0.00	n.d.	0.00	0.00	n.d	0.00	0.00	0.00	n.d.	0.00	0.04	0.00

cluded that, due to unusual Fe^{3+} distribution, this pyroxene should be called subsilic ferrian aluminian diopside.

Nevertheless, it should be noted that the physico-chemical conditions change drastically even on the scale of microvolumes in the heaps. Thus, there is an equal probability of finding disordered clinopyroxenes (Subsilic ferrian aluminan diopsides) as well as ordered esseneites in the object under consideration. On the whole, in the absence of direct data on the site occupancies, this mineral can be determined as a Fe^{3+},Al-rich Ca-clinopyroxene.

The occurrence of various Fe-bearing pyroxenes is appreciably governed by the redox conditions of their formation. Orthopyroxene, stable under reducing conditions, decomposes with the formation of magnetite as f_{O2} increases (Kalugin *et al.*, 1991). This reaction can be observed in cordierite nodules from the heaps of the Chelyabinsk coal basin. Oxygen fugacities approaching the hematite-magnetite buffer (P = 1 bar) are required to stabilize this unusual Fe^{3+}-rich clinopyroxene (Cosca & Peacor, 1987).

Feldspars. At least four different feldspars have been identified in the burned heaps. These are sanidine and three polymorphic modifications of $CaAl_2Si_2O_8$ which are triclinic (anorthite), orthorhombic (svyatoslavite) and hexagonal (dmisteinbergite). The last two minerals are new species (Chesnokov *et al.*, 1989, 1990). The new minerals and their names were officially recognized by the Commission on New Minerals and Mineral Names, IMA (Jambor & Grew, 1991; Jambor & Vanko, 1992).

Anorthite is the rock-forming mineral of basalt-like rocks and cordierite nodules (Table 2, 3). It occurs as 0.1–1 mm long polysynthetically twinned tabular grains. In the cavities, it forms platy crystals (Fig. 1). Anorthite is widespread in silicate crusts surrounding the fragments of petrified wood in the "black blocks" (Chesnokov & Tsherbakova, 1991). All examined plagioclases are anorthites (An = 90–95), but differ in having high contents of iron oxides, which attain 4 wt.%.

Svyatoslavite and dmisteinbergite are found on the walls of cracks in the fragments of woody coal from the "black blocks". It is associated with anorthite, troilite, kogenite, chondrodite, fluorphlogopite, fayalite, sphene and graphite. The physical characteristics of svyatoslavite and dmisteinbergite are close to those of orthorhombic and hexagonal synthetic phases of $CaO \cdot Al_2O_3 \cdot 2SiO_2$ (Davis & Tuttle, 1952).

Table 3 (cont.).

Rock	3	2	2	4	2	2	3	3	3	2	2	4
Sample	54-133	55-29	45-3	42-B1	55-27	55E-27	54-171	54-171	54-157	55-22	55-22	54-2
Phase	Dmt	Crd	Crd	Crd	Crd	Crd	Osm	Osm	Osm	Mul	Mul	Wo
SiO_2	43.89	51.20	48.46	45.48	49.69	46.32	61.52	60.49	60.57	23.18	33.79	52.78
TiO_2	n.d.	n.d.	n.d.	0.24	n.d.	n.d.	0.27	0.12	0.00	0.23	0.29	n.d.
Al_2O_3	35.39	33.22	33.10	35.46	33.67	31.78	25.12	25.37	24.84	71.66	61.89	0.04
Fe_2O_3*	–	–	–	–	–	–	–	–	–	5.64	4.64	–
Cr_2O_3	n.d.	n.d.	n.d.	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	0.03	0.02	n.d.
FeO**	0.01	1.38	5.62	7.65	6.35	15.34	1.94	3.36	2.10	–	–	1.24
MnO	0.00	0.46	0.42	0.15	0.34	0.71	0.22	0.24	0.29	0.03	0.00	0.68
MgO	0.01	12.89	10.45	8.58	9.81	4.13	7.07	6.28	6.92	0.18	0.30	0.43
CaO	19.29	0.07	0.17	0.05	0.08	0.04	0.04	0.04	0.05	n.d.	n.d.	44.79
Na_2O	0.32	0.04	0.18	0.15	0.04	0.02	0.37	0.30	0.39	n.d.	n.d.	0.03
K_2O	0.03	0.27	0.75	1.75	0.00	0.00	3.81	3.45	3.90	n.d.	n.d.	0.01
Total	98.94	99.53	99.15	99.57	99.98	98.34	100.36	99.65	99.06	100.95	100.93	100.00
	O=8			O = 18				O = 30		$C^{\dagger} = 6$		O = 9
Si	2.05	5.06	4.93	4.69	4.99	4.95	10.08	10.03	10.08	1.24	1.83	3.06
Ti	n.d.	n.d.	n.d.	0.02	n.d.	n.d.	0.03	0.02	0.00	0.01	0.01	n.d.
Al	1.95	3.87	3.97	4.31	3.99	4.00	4.85	4.96	4.87	4.51	3.95	0.00
Fe^{3+}	–	–	–	–	–	–	–	–	–	0.23	0.19	–
Cr	n.d.	n.d.	n.d.	0.00	n.d.	n.d.	n.d.	n.d.	n.d.	0.00	0.00	n.d.
Fe^{2+}	0.00	0.11	0.48	0.66	0.53	1.37	0.27	0.47	0.29	–	–	0.06
Mn	0.00	0.04	0.04	0.01	0.03	0.06	0.03	0.03	0.04	0.00	0.00	0.03
Mg	0.00	1.90	1.58	1.32	1.47	0.66	1.73	1.55	1.72	0.01	0.02	0.03
Ca	0.97	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	n.d.	n.d.	2.76
Na	0.03	0.01	0.04	0.03	0.01	0.00	0.12	0.10	0.13	n.d.	n.d.	0.00
K	0.00	0.03	0.10	0.23	0.00	0.00	0.80	0.73	0.83	n.d.	n.d.	0.00

Note: Rocks: 1– basalt-like paralava; 2– cordierite nodules; 3– "black block" rocks; 4– clinker. Fo– forsterite; Ol– olivine; Fa– fayalite; Opx– orthopyroxene; Cpx– clinopyroxene; Pl– plagioclase; Svt– svyatoslavite; Dmt– dmishteinbergite; Crd– cordierite; Osm– osumilite; Mul– mullite; Wo– wollastonite. n.d. = not determined.

* total Fe as Fe_2O_3. ** total Fe as FeO. † mullite formula was calculated on the basis of 6 cations.

Svyatoslavite is present as small (0.5–0.8 mm) colourless crystals (Fig. 2). The mineral is biaxial negative, $\alpha = 1.552(2)$; $\beta = 1.578(2)$; $\gamma = 1.581(2)$. $-2V_{calc} = 37.08°$ **Z** = a, **Y** = b, **X** = c. The chemical composition corresponds to pure $CaAl_2Si_2O_8$ (Table 3). Space group is $P2_12_12$. Cell dimensions (Å): $a_0 = 8.232(5)$; $b_0 = 8.606(10)$; $c_0 = 4.852(5)$.

Dmisteinbergite occurs as hexagonal plates (Fig. 3). Uniaxial positive, $\varepsilon = 1.580$; $\omega = 1.575$. Chemical composition corresponds to $CaAl_2Si_2O_8$ (Table 3). Space group is *P6/mmm*. Cell dimensions (Å): $a_0 = 5.122(5)$; $c_0 = 14.781(5)$.

Sanidine was established by X-ray methods as a member of osumilite-bearing associations from the "black blocks".

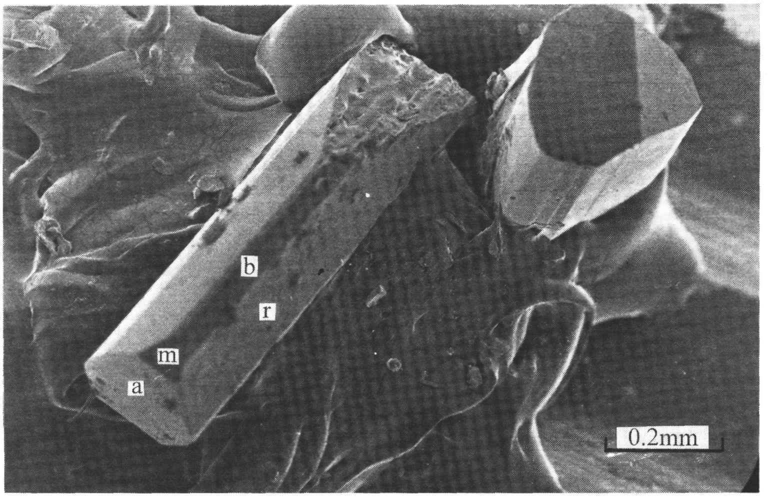

Fig. 2. Habit of svyatoslavite crystals: a {100}, b {010}, m {110}, r {011}. Sample 54-133.

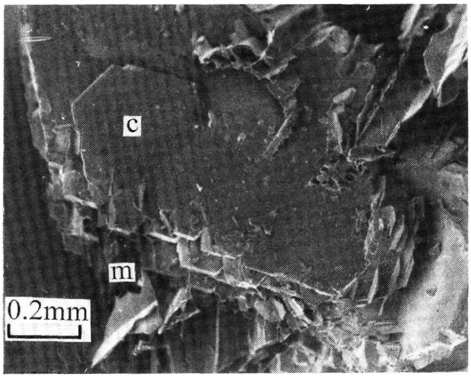

Fig. 3. Typical tabular split crystals of dmisteinbergite (sample 54-133). Crystal habit: c {001}, m {10$\bar{1}$0}.

A peculiar feature of the examined pyrometamorphic rocks is the absence of intermediate Na-Ca plagioclases and the rare occurrence of potassium feldspars, typical of paralavas from other regions (Cosca *et al.*., 1989; Kalugin *et al.*, 1991). The most probable reasons for anorthite formation are the intense burn-out of Na at earlier stages of annealing and the high content of Al in initial sedimentary rocks.

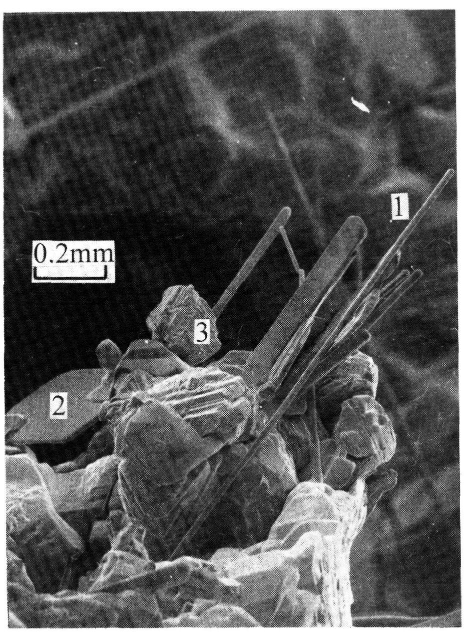

Fig. 4. Cavity in cordierite nodule, encrusted by flattened crystals of mullite (1), anorthite plates (2) and magnetite octahedra (3). Sample 55E-27.

Mullite is a widespread rock-forming mineral of pyrometamorphic rocks. It forms well-developed crystals of various habits. In the cavities of basalt-like paralavas, we observed transparent crystals of leucite and needles of mullite. In the cordierite nodules, there are thin flexible and elastic needles of mullite (Fig. 4). Subparallel and sheaf-like aggregates of mullite are present in samples with osumilite in "black block".

Mullites from cordierite nodules are non-uniform in chemical composition. The eight examined samples of mullite can be subdivided into two groups: a) with Al_2O_3 = 67–72 wt.%, SiO_2 = 23–25 wt.%; b) Al_2O_3 = 61–63 wt.%, SiO_2 = 32–34 wt.%. In all cases, the Fe_2O_3 content is rather high, *i.e.* 4.0–5.5 wt.%. The first group of analyses is close to 3 : 2 mullite. The second group can be assigned to aluminous sillimanite, or, taking into account the high content of Fe^{3+}, to a solid solution between sillimanite and mullite.

Wollastonite – β-$Ca_3Si_3O_9$ (triclinic) is a rock-forming mineral in the "black blocks". It forms white needles on the surfaces of annealed mudstone fragments and enters into the composition of anorthite-wollastonite-clinopyroxene crusts from cherry clinker. Microprobe analyses indicate that it is nearly pure $Ca_3Si_3O_9$.

K-Mg-osumilite is found here in pyrometamorphic rocks for the first time. It occurs as flattened hexagonal prisms in the cracks of the "black blocks" (Fig. 5). The mineral is intimately associated with mullite, graphite, iron carbides – Fe_3C, FeC_4(?) – and natural iron ± cordierite, sanidine, quartz). Crystals are colourless and transparent. Osumilite is uniaxial positive (ε = 1.544; ω = 1.536). Cell dimensions: a = 10.106(4) Å, c = 14.329(7) Å, V = 1267.5(10) Å^3 (for sample 54–157).

The examined crystals belong to K-Mg species (Table 3). Compared with osumilites from the other rock types, the mineral samples from burned heaps are characterized by a much higher concentration of Al = 4.8–4.9 cations pfu and lower contents of (Mg+Fe+Mn) = 2.05 cations pfu. Thus, the osumilites from pyrometamorphic rocks are close to the stoichiometric synthetic compound $KMg_2Al_3[Al_2Si_{10}O_{30}]$.

In accordance with the experimental data, under conditions of low water pressure and low fugacity of oxygen at T > 900°C, the fields of stability of osumilite-bearing parageneses are extended compared with the cordierite-bearing parageneses (Audibert *et al.*, 1995). The favourable physico-chemical conditions for K-Mg-osumilite formation are thought to occur just in the "black blocks".

Cordierite is a rock-forming mineral in the red zones of the heaps, in the annealed mudstones of "black blocks", and also in crystalline nodules.

In thin section, cordierite nodules consist of a mixture of cordierite, anorthite, tridymite, mullite, rare plates of biotite, iron oxides and pseudobrookite. In gas vesicles, cordierite occurs as pseudohexagonal prisms 0.1–1 mm in size (Fig. 6).

The cordierite crystals are strongly pleochroic (O = γ) violet; E (= α): colourless). All the grains examined are optically negative. The crystals from the gas vesicles occur as simple trillings; while grains from the groundmass are complex polysynthetic twins.

F-values for cordierites vary from 5.2 to 70.6 %, where F = (Fe+Mn)/(Fe+Mn+Mg)$\times$ 100 %. Grains from various nodules occurring in the same block of cake (1–1.5 m^3 in size) show a range of F-values from 30 to 70%. At the same time, in separate nodules (samples 0.5–3 cm in size), variations of F-values of cordierites do not exceed the change in F within a unit grain and amount to less than 9%.

An uncommon relation of the impurities of K, Ca and Na is a characteristic property of the investigated cordierites. Cordierite crystals from nodules are characterized by variations of the K_2O content from 0.00 to 0.75 wt.%, CaO contents from 0.04 to 0.17 wt.% and Na_2O contents from 0.02 to 0.18 wt.%. Cordierites with the highest concentrations of K_2O (1.75 wt.%) are found in the annealed mudstones (Table 3, sample 42-B1). They occur as hexagonal crystals (5–40 µm) within an acid K-rich glass matrix. This is a good reason to suppose that the introduction of K into cordierite structure is achieved at high temperatures, under dry, very low-pressure conditions. Under these conditions, some artificial anthropogenic materials and natural pyrometamorphic rocks can be formed, as well as some types of volcanic rocks (Lotova & Nigmatulina, 1989; Schreyer *et al.*, 1990).

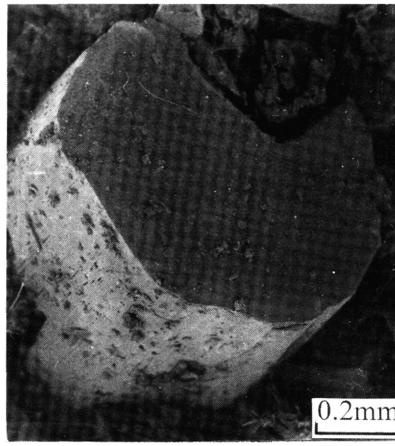

Fig. 5. Morphology of short-prismatic crystal of osumilite: basal face {0001}, the first-order hexagonal prism {10$\bar{1}$0} and second-order prism {11$\bar{2}$0}. Sample 54-157.

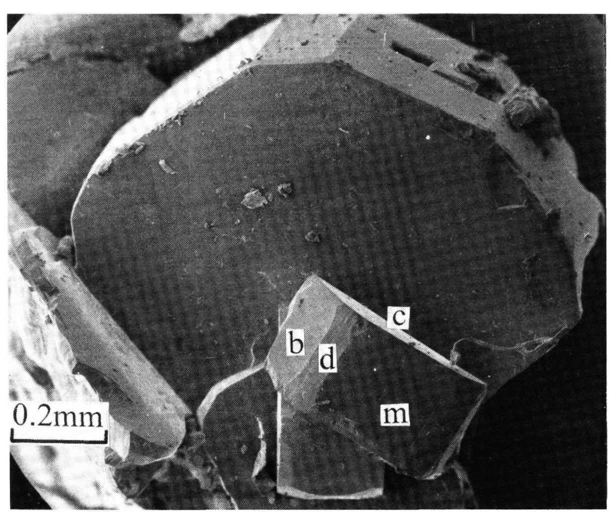

Fig. 6. Short-prismatic crystals of cordierite from a cavity in cordierite nodule. Growth forms: b {010}, c {001}, m {110} and d {130}. Sample 55E-27.

XRD patterns indicate the presence of the different structural modifications of cordierite. The examined grains from the nodules are related to the orthorhombic modification (Δ = 0.250–0.280 ±0.005). Most of cordierites from annealed mudstones from red clinker are characterized by considerably lower values of Δ = 0.10 – 0.23 (±0.01). Cordierite samples from annealed mudstones of the "black blocks" are close to indialite (Δ = 0.0–0.15). In accordance with the experimental data of Redfern *et al.* (1989), «maximum orthorhombic» K-cordierites have a significantly lower Δ index in comparison with Δ = 0.25 K-free Mg-cordierite. Inasmuch as all cordierites from annealed mudstones are K-rich, the low values of their distortion indices appear explicable.

Discussion

The formation of mineral assemblages in pyrometamorphic rocks is mainly governed by three factors: chemical composition of the substratum, the annealing temperature and gas atmosphere composition. The rocks in question may also be distinguished according to the prevailing mechanisms of mass transfer to the reaction zone: redistribution of components in the rock with the participation of an intergranular fluid, gas transport reactions, or migration in the melt.

The annealing process of silicate rocks results in the decomposition of clay minerals to the point of an amorphous state and the crystallization of new phases from an amorphous matrix. Under oxidizing annealing conditions, the quartz-mica assemblage of yellow "mudstones" is replaced by the Qtz+Mul+Hc association of pink "mudstones", and then gives way to refractory cherry clinker: Trd (Qtz, Crs) + Mul + Crd (±Hem).

With the process of mudstone annealing there is no active fractionation of Si, Al, Mg, Ti or Mn. Nevertheless, the redistribution of Fe (its transport by gas jets and re-deposition in the form of hematite) and the burn-out of sodium apparently took place in this case as well.

During the annealing of carbonaceous mudstones, this assemblage is supplemented with anorthite and wollastonite. It is not inconceivable that, under such conditions, Ca can be partially removed (as a result of the carbonate dissociation reaction). The presence of hematite, pseudobrookite and Fe^{3+},Al-rich Ca-clinopyroxene is an indicator of the extreme oxidizing conditions of the formation of red and cherry clinker (Parodi *et al.*, 1989; Foit *et al.*, 1987; Kabalov *et al.*, 1997). Due to the initial high porosity of waste masses and the branching system of gas venting during the annealing process, practically all spoil-heaps are well aerated, so the majority of new mineral assemblages represent annealing products formed under oxidizing conditions.

Only a minor part of the waste sedimentary rocks was subjected to reducing annealing. This is especially true as regards the so-called "black blocks". Annealing under reducing conditions implies a radical change of the phase composition of pyrometamorphic rocks. Such distinctions can be established for the products of annealing of the same mudstones that already contain cordierite, quartz, sanidine and osumilite assemblage (Table 2).

Mineral crystallization from the gas phase is by far the most interesting feature of mineral formation in the pyrometamorphic system. This phenomenon was noted for all the rock types, but the most pronounced and varied gas-transport synthesis was achieved in the "black blocks". The black carbon mass and cracks in the annealed rocks contain abundant perfect crystals of pure oxides, sulphides, silicates and carbides. Chesnokov & Tsherbakova (1991) have pointed out an interesting feature of the mineralogy of the "black blocks" – the formation of ferrous minerals (fayalite, monosulphides and carbides of iron, as well as native iron as the product of carbide decomposition), minerals rich in Mg (norbergite, chondrodite, fluorphlogopite, spinel, forsterite, K-Mg-osumilite and periclase), or Ca (various polymorphic modifications of $CaAl_2Si_2O_8$, wollastonite, sphene), and the lack of phases of intermediate composition (Fe-Mg, Mg-Ca, Ca-Fe solid solutions) in these parts of the spoil-heaps.

We suggest that a decisive control on the process of Ca, Mg and Fe separation and the formation of their minerals is exerted by the type of complex metal compounds containing S, C, and H, that are responsible for gas transport. It has been experimentally established that practically all crystals of Ca and Mg silicates synthesized under hydrogen atmosphere conditions did not contain admixtures of Fe, which occur in the form of separate phases, including native metal (Putilin *et al.*, 1992). It is possible that, in a gas atmosphere of complex composition, along with native metals, sulphides and carbides of iron would be crystallized, as one can observed in the object under consideration.

The examined basalt-like rocks are close in chemical and mineral composition to paralavas from East Kazakhstan (Kalugin *et al.*, 1991), which were generated as a result of the melting of a combination of mudstones, siderite concretions and carbonaceous clays during the natural pyrometamorphism of coal-bearing sediments. Physico-chemical calculations carried out by Kalugin *et al.* (1991) showed that the mineral composition of the paralavas had been significantly influenced by the oxygen regime. Based on these previous results and judging from the mineral assemblaged of the studied basalt-like rocks, we conclude that the rocks were formed under reducing conditions. As shown from our experiments on the melting of paralava samples from the study area, the temperature of initial melting can be estimated at 1000°C.

We may consider cordierite nodules as the products of partial local melting of the same lithology (siderite concretions + mudstone + carbonaceous mudstone), but under more oxidizing annealing conditions. This last suggestion is confirmed by the widespread occurrence of hematite, pseudobrookite, and Fe^{3+},Al-rich Ca-clinopyroxene. Nevertheless, the formation of cordierite nodules cannot be restricted solely to the phenomenon of melt crystallization. Here, too, the interaction of melt with refractory high-alumina products of mudstone annealing proceeded actively with gas-transport reactions. This is revealed by reaction zones at the contacts of the nodules and enclosed mudstone xenoliths, the proximity of cordierite nodules to channels of gas jets, and the abundance of cavities and pores in the nodules.

Thus, the essential factors responsible for the mineralogical variety of anthropogenic pyrometamorphic rocks are high temperature of combustion (up to 1000–1200°C), high temperature gradients, chemical heterogeneity of the initial waste mass, an aggressive gaseous medium (O_2 – from atmosphere; S, F, Cl – from coals and waste rocks), high porosity and permeability of the spoil-heap materials, and intense gas circulation.

The pyrometamorphism phenomenon in anthropogenic annealed rocks is significantly different from natural metamorphic processes in displaying relatively active redistribution of a number of components within the waste mass (Fe, Ca, F) and the removal of other elements (Na, S, C) away from the heaps. This gives us the possibility of studying the migration capacity of elements on the micro- as well as on the macro-scale and to estimate the ecological impacts of changes in atmospheric composition in coal-mining regions.

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