Physicochemical Parameters of Magmatic and Hydrothermal Processes at the Yaman-Kasy Massive Sulfide Deposit, the Southern Urals

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Abstract—Melt and fluid inclusions in minerals have been studied and physicochemical parameters of magmatic processes and hydrothermal systems estimated at the Yaman-Kasy copper massive sulfide deposit in the southern Urals. It was established that relatively low-temperature (910-945°C) rhyodacitic melts belonging to the tholeiitic series and containing 2.7–5.2 wt % water participated in the formation of the igneous complexes that host the Yaman-Kasy deposit. As follows from ion microprobe results, these silicic magmas had a primitive character. In the distribution of trace elements, including REE, the rhyodacites are closer to basaltic rather than silicic volcanic rocks, and they are distinguished in this respect from the igneous rocks from other massive sulfide deposits of the Urals and the Rudny Altai. Two types of solutions actively took part in the formation of hydrothermal systems: (1) solutions with a moderate salinity (5-10 wt % dissolved salts) and (2) solutions with a low salinity (a value close to that of seawater or even lower). Concentrated fluids with more than 11.5 wt % dissolved salts were much less abundant. Hydrothermal solutions heated to 130–160, 160–270, or occasionally 280–310°C predominated in ore formation. The sequence of mineral-forming processes at the Yaman-Kasy deposit is demonstrated. Mineral assemblages were formed with an inversion of the parameters characterizing ore-forming solutions. An increase in the temperature and salinity of solutions at the early stages was followed by a decrease at the final stages. The evolution of the hydrothermal system at the Yaman-Kasy deposit has much in common with the parameters of black smokers in the present-day Pacific backarc basins.

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INTRODUCTION

The formation of copper massive sulfide deposits in the southern Urals is closely related to the evolution of bimodal rhyolite-basalt volcanic complexes. The study of these complexes is important not only in regard to the spatial association with orebodies but also because these magmatic systems serve as a source of ore components. However, the secondary alteration of igneous rocks substantially hinders the consideration and reconstruction of the primary parameters of magmatic systems. The study of melt inclusions in minerals provides a way out of this situation. Being incorporated into the matrix of host minerals, they retain direct primary information on melts that existed in the geological past. The study of these microinclusions is extremely laborand time-consuming, especially as concerns inclusions in minerals from silicic rocks. Therefore, the publications on melt inclusions in quartz from silicic rocks that belong to igneous complexes at massive sulfide deposits are not numerous (Karpukhina et al., 1998; Naumov et al., 1999; Lapukhov et al., 2001; Simonov et al.,

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2002b). Unfortunately, these publications do not bear information on contents of ore components in melts. Recently, we were successful in detecting elevated copper concentrations in melt inclusions in quartz phenocrysts from porphyry rocks at massive sulfide deposits of the Rudny Altai (Simonov et al., 2004, 2005).

The estimation of the temperature characterizing crystallization of massive sulfide ore remains an important problem. Mineral and isotopic thermometers are widely applied for this purpose, but comparison with data based on fluid inclusions indicates that the parameters calculated from compositions of coexisting sulfides are often insufficient for reliable assessment of the temperature corresponding to the mineral formation (Bortnikov, 1993; Bortnikov et al., 1990, 1995). As has been shown by long-term studies of ore deposits, fluid inclusions in minerals of ore assemblages are very helpful for elucidation of the parameters of hydrothermal ore-forming processes. This approach is particularly important for comparison of ancient massive sulfide deposits with present-day black smokers, whose physicochemical conditions are established not only by direct measurements from manned submersibles but

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Fig. 1. (a) Location of the Yaman-Kasy deposit (star) in the southern Urals and (b) sketch map of open pit at this deposit, after Zaykov et al. (1995). (1) Basaltic andesite and basalt; (2) zone of quartz–sericite alteration of the rhyolitic–dacitic dome; (3) rhyodacitic and dacitic lava, lava clastite, and hyaloclastite; (4) basaltic lava and volcanomictic clastic rocks with interlayers of dark gray and lilac siltstones; (5) copper–zinc massive sulfide lode; (6) sulfide biostrome; (7) units of iron oxide deposits; (8) faults; (9) open pit contour.

also by analysis of fluid inclusions (Nehlig, 1991; Naumov et al., 1991; Binns et al., 1993; Herzig et al., 1993; Simonov et al., 1997, 2002a; Graupner et al., 2001; Bortnikov et al., 2004; Vanko et al., 2004). While carrying out a comparative analysis of the results obtained at the Yaman-Kasy deposit, we involved data on modern ore occurrences most similar in their geological and geodynamic characteristics to the massive sulfide deposits of the Uralian type.

The Yaman-Kasy copper massive sulfide deposit (Fig. 1) attracts considerable attention because the composition of ore, host sediments, and mineralized vent fauna allows this ore lode to be compared with modern black smokers. The deposit is located in Orenburg oblast 5 km southwest of the town of Mednogorsk and 1 km north of the railway station of Blyava. The deposit occurs in the Sakmara Zone and is hosted in the Silurian rhyolite-basalt complex. The main ore-bearing structural feature of the district is the Utyagul-Blyava Trough, where four deposits—Yaman-Kasy, Razumovsky, Komsomol'sky, and Blyava-are localized in the eastern wall. The narrow (1-5 km) tract that hosts these deposits is composed largely of rhyolite; dacite; and, to a lesser extent, andesite and basalt of the Blyava Complex (Zaykov et al., 1995). The section of the ore-bearing tract differs from the sections of island-arc ore fields by the absence of basaltic andesites. In chemical composition, the Blyava rhyolite-basalt complex is a rock association transitional between the marginal-sea tholeiitic and island-arc calc-alkaline series (Seravkin and Rodicheva, 1990). Basalts are distinguished by low TiO₂ and K₂O contents (0.8 and 0.5–0.7 wt %, respectively). Rhyolites and dacites belong to the sodic type; their geochemical signatures are close to those of the backarc basaltic series (Simonov et al., 2001) and thus support the idea of formation of the igneous complexes at the Yaman-Kasy and Blyava massive sulfide deposits in an ancient marginal sea (Maslennikov and Zaykov, 1998; Zaykov, 2006).

According to the results of exploration and mining works, the lenticular ore lode at the Yaman-Kasy deposit dips westward at angles of 30°-60° conformably with the bedding of the host rocks and is considered to have been a sulfide mound originally (Zaykov et al., 1995; Maslennikov and Zaykov, 1998; Maslennikov, 1999). The massive chalcopyrite-pyrite ore of the mound core contains numerous remains of mineralized fauna similar to the organisms that inhabit present-day black smokers. Relics of autochthonous sealed paleohydrothermal sulfide chimneys are located near the colonies of bottom organisms. The chimneys are comparable in their structure with hydrothermal sulfide chimneys of black smokers (Maslennikov et al., 1997; Herrington et al., 1998). A pyrite lens isometric in plan view that underlies a sulfide mound composed of sphalerite-chalcopyrite ore marks the ore-forming conduit. Subore dacite has been transformed into quartz– sericite metasomatic rock with numerous chalcopyrite– pyrite veinlets. Residual breccia that consists of sphalerite–pyrite and chalcopyrite–pyrite blocks occurs in the thickest ore layers. Indications of cracking and halmyrolysis of colloform and massive ores are observed. Biomorphic ore is a prominent feature of the deposit. The mineralized fauna is represented by vestimentiferans, polychaetes, monoplacophorans, gastropods, and inarticulate brachiopods.

Pyrite, sphalerite, and chalcopyrite are the major ore minerals; marcasite, galena, würtzite, and barite are less abundant. Altaite, hessite, sylvanite, coloradoite, tellurobismuthite, covellite, bornite, fahlore, isocubanite, native tellurium, and native gold are rare minerals (Maslennikov et al., 1997). Chalcopyrite–pyrite and chalcopyrite–sphalerite–pyrite assemblages dominate in the central portion of the ore lode; sphalerite–pyrite, barite–sphalerite, quartz–pyrite, galena–sphalerite, sphalerite–chalcopyrite–pyrite, and hematite–covellite–pyrite– chalcopyrite assemblages are localized near the roof and at the flanks of the lode.

The geological data indicate that orebodies did not undergo substantial tectonic rearrangement, destruction, or displacement, so that the history of the deposit is related to one uninterrupted event.

Despite the opinion that most massive sulfide deposits in the Urals are affected by metamorphism (Yarosh, 1972), the Yaman-Kasy deposit has remained in an unmetamorphosed state (Shadlun, 1991; Zaykov et al., 1995; Herrington et al., 1998). All fine attributes of modern black smokers and colloform pyrite have been left intact at this deposit. As follows from the occurrence of marcasite, the temperature of ore deposition did not exceed 200–240°C (Maslennikov, 2006).

The samples of rocks and ores from igneous complexes and ore-bearing hydrothermal assemblages of the Yaman-Kasy deposit were collected during fieldwork. In processing the sample collection, the main attention was paid to the analysis of melt and fluid inclusions in minerals in order to ascertain parameters of magmatic and hydrothermal systems. Melt inclusions were studied in a high-temperature heating chamber with an inert medium (Sobolev and Slutsky, 1984). The high-temperature experiments with inclusions were carried out taking into account the results obtained by Sobolev (1997) and Sobolev and Danyushevsky (1994) and on the basis of our own experience (Simonov, 1993). The compositions of homogenized melt inclusions were determined with a Camebax Micro microprobe at the Institute of Geology and Mineralogy, Siberian Division, Russian Academy of Sciences (RAS), in Novosibirsk. The trace elements, ore elements, H₂O, and F in melt inclusions were determined with an IMS-4f ion microprobe at the Institute of Microelectronics, RAS, in Yaroslavl using the technique described by Sobolev (1996). Fluid inclusions were studied with thermometric and cryometric methods (Borisenko, 1977; Ermakov and Dolgov, 1979; Roedder, 1984) using cryogenic chambers and heating stages of original design (Simonov, 1993). To obtain the most reliable information, 50–100 fluid inclusions were analyzed in each sample. All experiments with melt and fluid inclusions were performed at the Institute of Geology and Mineralogy.

MELT INCLUSIONS

Primary melt inclusions $10-75 \ \mu$ m in size are uniformly distributed in quartz crystals from rhyolite at the Yaman-Kasy deposit. The inclusions are commonly rounded, often with hexagonal faceting. As a rule, they contain a large number of tiny brownish crystalline phases associated with large gas bubbles. Inclusions filled with light glass are less frequent. The most reliable results of high-temperature experiments were obtained for sample C-14v-99. Having been placed on a heating stage, the inclusions homogenized completely at 910–945°C. This temperature is substantially lower than that established for melt inclusions in quartz from silicic igneous rocks at the Siberian massive sulfide deposits (Simonov et al., 1999, 2000, 2005).

In chemical composition, the studied melt inclusions in quartz from rhyolite of the Yaman-Kasy deposit (Table 1) belong to the family of low-alkali rhyodacites and rhyolites and fall into the field of the tholeitic series in FeO/(MgO–SiO₂) coordinates. The inclusions contain no more than 0.9 wt % K₂O, are characterized by a low K₂O/Na₂O ratio, and correspond to the boundary between the K–Na and Na series. The alkalinity and Fe and Al contents drop with increasing silica, whereas the FeO/MgO ratio increases in the same direction (Fig. 2).

The silicic melts at the Yaman-Kasy deposit are much less alkaline and are enriched in Fe and depleted in K relative to the magmas of the Verkhneural'sk ore district in the southern Urals and of the Rudny Altai, which pertain to the tholeiitic K–Na series, with a distinct decrease in Fe and Al contents against increasing SiO₂ (Figs. 2c, 2d). The diminishing Al content testifies to plagioclase fractionation.

In proportions of major chemical elements, the silicic melts from the Yaman-Kasy deposit are close to those at the Kyzyl-Tashtyg deposit in eastern Tuva. Since the latter was formed in a backarc basin (Simonov et al., 1999), this similarity is an additional argument in favor of the formation of the Yaman-Kasy deposit in a marginal-sea setting. At the same time, the silicic melts from the Yaman-Kasy deposit differ from the melts of the Verkhneural'sk ore district, formed in an island-arc setting (Zaykov et al., 1995; Maslennikov and Zaykov, 1998; Zaykov, 2006).

As was established with the ion microprobe (Table 2), the silicic melt inclusions at the Yaman-Kasy deposit contain 2.7-5.2 wt % H₂O. Similar water concentrations were determined in quartz-hosted inclusions from

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No.	Sample/analysis	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P_2O_5	Cl	Total	$T_{\rm hom}, ^{\circ}{\rm C}$
1	S-14v-99/1	76.54	0.21	10.15	2.75	0.10	0.16	1.98	2.46	0.78	0.04	0.18	95.35	935
2	S-14v-99/1	75.90	0.19	9.51	2.64	0.08	0.16	1.92	2.83	0.77	0.04	0.17	94.21	935
3	S-14v-99/1	76.45	0.13	9.87	2.62	0.09	0.14	1.97	2.22	0.77	0.07	0.15	94.48	935
4	S-14v-99/2	76.36	0.16	10.07	2.67	0.07	0.14	1.97	2.45	0.75	0.07	0.17	94.88	935
5	S-14v-99/2	76.75	0.15	9.92	2.65	0.09	0.12	1.94	2.48	0.74	0.05	0.16	95.06	935
6	S-14v-99/2*	75.95	0.17	10.31	2.65	0.12	0.13	2.10	2.67	0.74	0.08	0.18	95.09	935
7	S-14v-99/3	71.83	0.24	12.20	3.22	0.09	0.19	2.53	2.58	0.87	0.08	0.22	94.05	940
8	S-14v-99/3	71.72	0.21	12.00	3.17	0.11	0.18	2.54	2.76	0.86	0.06	0.19	93.79	940
9	S-14v-99/3*	71.81	0.20	12.23	3.19	0.12	0.21	2.60	2.68	0.91	0.06	0.19	94.20	940
10	S-14v-99/4	75.60	0.20	10.35	2.68	0.10	0.15	2.14	2.44	0.74	0.08	0.19	94.47	945
11	S-14v-99/4	76.28	0.21	10.13	2.79	0.09	0.13	2.12	2.53	0.81	0.07	0.17	95.33	945
12	S-14v-99/4*	75.69	0.19	10.83	2.63	0.10	0.12	2.14	2.32	0.85	0.07	0.18	95.12	945
13	S-14v-99/5	78.82	0.20	9.77	2.37	0.07	0.10	1.76	2.52	0.78	0.05	0.16	96.61	910
14	S-14v-99/5	79.65	0.13	9.34	2.28	0.07	0.11	1.65	2.39	0.80	0.05	0.16	96.63	910
15	S-14v-99/5	79.41	0.16	9.47	2.31	0.09	0.11	1.70	2.19	0.82	0.06	0.18	96.49	910
16	S-14v-99/6	74.52	0.25	10.91	2.89	0.09	0.14	2.36	2.21	0.79	0.06	0.20	94.41	930
17	S-14v-99/6	75.76	0.20	10.57	3.02	0.08	0.18	2.43	0.60	0.75	0.07	0.19	93.85	930
18	S-14v-99/6*	74.80	0.22	10.93	2.99	0.10	0.17	2.34	1.19	0.76	0.08	0.16	93.73	930

Table 1. Representative analyses of homogenized melt inclusions in quartz from rhyolite at the Yaman-Kasy deposit, wt %

* Inclusions where trace elements, water, and fluorine were determined with an ion microprobe.

the massive sulfide deposits of the Verkhneural'sk ore district in the southern Urals (Naumov et al., 1999) and of the Rudny Altai (Simonov et al., 2005). The melts from the Yaman-Kasy deposit are depleted in trace elements relative to island-arc silicic volcanics and resemble basalts in this respect. In particular, the Y/Zr ratio in melt inclusions virtually coincides with this ratio in basalt from the deposit. The chondrite-normalized REE patterns of melt inclusions from the Yaman-Kasy deposit are markedly different from those characterizing rhyolites of the Kuril-Kamchatka island arc (Fig. 3). However, the REE patterns of melts from both localities have some features in common. In particular, they reveal a distinct Eu minimum as a result of plagioclase fractionation. At the same time, the REE patterns of melt inclusions from the Verkhneural'sk ore district are close to the Yaman-Kasy patterns but are devoid of an Eu minimum. The melt inclusions from the Yubileiny deposit in the Rudny Altai have an Eu minimum but sharply differ in high LREE contents, typical of island-arc silicic melts (Fig. 3).

The spidergrams of trace elements in melt inclusions from the Yaman-Kasy deposit are close to those from backarc basins in distribution of La, Ce, Sr, Nd, and Sm contents normalized to the primitive mantle; a maximum of mobile incompatible elements (K); lower Zr, Ti, Y, and Yb contents; and a distinct Ti minimum. In trace element geochemistry, the melt inclusions are close to tholeiitic plagiogranites, which are regarded as derivatives of mantle tholeiitic melts (Tauson, 1977). The concentrations of ore components in melt inclusions were determined with the ion microprobe. The Cu contents are not very high (31–74 ppm) and are comparable with the average Cu content in silicic rocks. However, our recent studies of melt inclusions (Simonov et al., 2005) have shown that silicic melts from massive sulfide deposits may be much richer in copper, up to a few thousands of parts per million.

FLUID INCLUSIONS

To elucidate physicochemical parameters of the hydrothermal processes responsible for the formation of the Yaman-Kasy deposit, samples of ores and rhyolites were investigated. The ore assemblages containing minerals with fluid inclusions are represented by fragments of sulfide chimneys and mineralized fauna.

Sulfide chimneys, 10 cm in diameter and with an outer pyrite shell, have well-developed inner channels commonly filled with sphalerite and quartz with marcasite inclusions. Sporadic goldfieldite, bornite, covellite, and digenite grains were identified in quartz.

Chalcopyrite–pyrite–marcasite–sphalerite chimneys, 2 cm in diameter, are the most diverse in minerals. The outer shell of the chimneys is commonly composed of pyrite–marcasite aggregates. The percentage of marcasite and quartz and then of sphalerite and chalcopyrite increases inward. Relict marcasite, galena, and tennatite incorporated into sphalerite and quartz occur on the inner side of the chimney shell in addition to euhedral



Fig. 2. (a) $Na_2O + K_2O$, (b) FeO/MgO, (c) Al_2O_3 , and (d) FeO versus SiO_2 , wt %, in homogenized melt inclusions in quartz from rhyolite at the Yaman-Kasy deposit, after data of the authors and Naumov et al. (1999). (1, 2) Melt inclusions in quartz from porphyries at the (1) Yaman-Kasy deposit and (2) Verkhneural'sk ore district in the southern Urals. (I) Field of melt inclusions in quartz from porphyries at the Yubileiny massive sulfide deposit in the Rudny Altai; (T) tholeiitic series; (CA) calc-alkaline series.

pyrite. The chalcopyrite crust of this chimney is thinner than in other chimneys. The first layer is distinctly delineated and consists of fine-grained chalcopyrite with marcasite inclusions, pyrite and sphalerite crystals, and various accessory minerals. Some chimneys enriched in sphalerite contain abundant disseminations of native gold in association with galena, euhedral pyrite, and Te oxides. The axial holes of chimneys are occasionally filled with quartz or barite.

The mineralized fauna is represented largely by vestimentiferans and alvinellids. The worm-shaped fragments collected at the Yaman-Kasy deposit are subdivided into three groups by diameter of tubes: 2–4 cm, 1–1.5 cm, and 1–4 mm. Each group of tubes is distinguished by specific morphological features that allow their comparison with present-day tubicolous worms. The results of the study of large tubicolous worms turned out to be new for paleontology and paleoecology. The tubular casts show a fundamental similarity with vestimentiferans that inhabit the hydrothermal oases of active black smokers (Little et al., 1996). At present, the large mineralized tubicolous worms are referred to Vestimentifera. The length of some fragments reaches 0.5 m. The tubes are cylindrical or flattened and most of them are surrounded by a bacterial shell. The inner portion of the tubes is encrusted with drusy aggregates of pyrite, marcasite, or sphalerite or filled with a sulfide sand. Some tubes are filled with quartz or barite crystals.

The small tubicolous worms of alvinellid type are tubes rounded in section, 0.8–4 mm in diameter and as long as 75 mm. Most of the tubes have a zonal mineral filling, concentrically bedded from the outer wall to the inner part and composed of fine-grained pyrite; crystalline drusy pyrite; and sphalerite, barite, or quartz.

Fluid inclusions were studied in quartz of a (marcasite-pyrite)-chalcopyrite-sphalerite-quartz chimney (sample Y-K-86) and in barite of a galena-bearing marcasite-chalcopyrite-(sphalerite-barite) chimney (sample 98-5-23).

As concerns the mineralized fauna, fluid inclusions were studied in most detail in quartz and barite of sample Ya-554-3 (alvinellids replaced with sulfides, barite, and quartz); in quartz of sample Y-K-I-vest (a vestimentiferan with a pyrite shell and quartz filling); and in bar-

Element	1	2	3	4	5	6	7	8	9
Li	0.92	1.83	1.65	3.06	0.55	0.42	0.36	0.28	0.66
Be	0.52	0.38	0.58	0.29	0.01	0.54	0.52	0.41	0.29
В	17.14	14.77	20.01	24.04	14.41	18.58	18.15	12.77	10.22
Th	n.a.	0.83	n.a.	0.81	0.79	n.a.	n.a.	n.a.	0.81
Sr	84.9	117.1	104.3	106.3	110.6	97.0	100.4	60.2	100.1
V	3.60	5.68	4.82	5.21	3.95	4.17	4.46	1.77	4.11
La	3.76	5.60	4.81	4.90	5.35	4.57	4.72	2.81	4.79
Ce	10.21	13.71	12.49	12.86	14.15	11.91	12.44	7.38	12.78
Nd	6.39	8.95	7.99	7.76	9.13	7.52	7.71	4.48	7.79
Sm	1.99	2.59	2.30	2.29	2.80	2.37	2.17	1.37	2.24
Eu	0.24	0.57	0.34	0.54	0.80	0.29	0.44	0.32	0.55
Gd	n.a.	2.13	n.a.	2.37	3.59	n.a.	n.a.	n.a.	2.35
Dy	2.50	3.29	2.86	2.91	3.66	2.83	3.18	1.74	2.77
Er	1.56	2.95	2.19	2.37	2.78	2.25	2.39	1.43	2.57
Yb	1.94	3.09	2.08	2.88	3.31	2.18	2.24	1.34	2.58
Y	17.1	22.4	19.8	19.2	22.2	19.5	19.4	12.0	19.7
Zr	46.8	62.1	52.5	54.6	64.3	53.3	55.9	32.9	55.4
Nb	n.a.	2.23	n.a.	1.70	2.07	n.a.	n.a.	n.a.	1.89
Cu	"	42.1	"	73.6	42.6	"	"	"	30.4
Pb	"	1.71	"	1.71	2.10	"	"	"	4.30
Hf	"	2.60	"	2.27	2.64	"	"	"	2.10
Та	"	0.49	"	0.45	0.48	"	"	"	0.43
H ₂ O	3.83	2.67	4.84	5.24	2.98	4.71	3.47	2.93	1.94
F	n.a.	0.05	n.a.	0.05	0.02	n.a.	n.a.	n.a.	0.02

Table 2. Trace element (ppm) and water and fluorine contents (wt %) in homogenized melt inclusions in quartz from rhyolite at the Yaman-Kasy deposit

Note: (1-9) Melt inclusions (sample/specimen numbers): (1, 2) S-14v-99/2, (3, 4) S-14v-99/3, (5-7) S-14v-99/4, (8, 9) S-14v-99/6.

ite of sample V-1 (vestimentiferans replaced with sulfides and barite).

Fluid inclusions were also studied in quartz phenocrysts from quartz porphyry where melt inclusions underwent investigation (sample S-14V-99).

The fluid inclusions in quartz of a sulfide chimney are 3–12 µm in diameter and uniformly distributed throughout the mineral grain. Numerous, commonly rounded, primary and pseudosecondary inclusions often make up bands and zones. Study in a cryogenic chamber showed that the contents of two-phase inclusions freeze at $-(35-47)^{\circ}$ C. The eutectic temperature varies from -20 to -28°C. A MgCl₂ admixture most likely occurs in solution in addition to NaCl. Most of the last tiny crystals disappear in solution within a temperature range from -0.4 to -4.6°C; a narrow interval of -7.9 to -9.2°C is also recorded. Two groups of inclusions with salinities of 0.6–7.9 and 11.5–12.7 wt % are distinguished, respectively. Three intervals of homogenization temperatures are recorded: 115–123, 128–152, and 163–185°C.

The fluid inclusions in barite of a sulfide chimney are 3-15 µm in diameter and uniformly distributed throughout the mineral grain. Numerous primary and pseudosecondary inclusions often make up bands and zones. The inclusions are rounded with elements of faceting and are often irregularly angular in shape. In outer appearance, they resemble the fluid inclusions in barite from hydrothermal sulfide mounds of the present-day Woodlark and Manus backarc basins in the Pacific Ocean. Study in a cryogenic chamber showed that the contents of two-phase inclusions freeze at -(40-50)°C. The eutectic temperature varies from -28to -31°C. A MgCl₂ admixture most likely occurs in solution in addition to NaCl. Most of the last tiny crystals disappear in solution within a temperature range from -4 to -7° C. Four ranges of melting temperatures of the last tiny crystals are recorded (°C): above -1.5, -(2-4), -(4-7), and -(7-11). Four groups of inclusions with salinities of <2, 3-6, 6-10, and 10-14 wt % are distinguished, respectively. The inclusions pertaining to the two middle groups are obviously predominant. The main group of inclusions has a homogenization



Fig. 3. Chondrite-normalized REE patterns of homogenized melt inclusions in quartz from rhyolite at the Yaman-Kasy deposit, after data of the authors, Kuz'min (1985), and Naumov et al. (1999). (1–3) Melt inclusions in quartz from (1, 2) porphyries at the (1) Yaman-Kasy deposit and (2) Verkhneural'sk ore district in the southern Urals and (3) ore-bearing porphyries at the Yubileiny massive sulfide deposit in the Rudny Altai; (4) rhyolite from the Kuril–Kamchatka island arc. Chondrite compositions were taken from Boynton (1984).

temperature within the range $140-200^{\circ}$ C. A group with a higher homogenization temperature (200-250°C) overlaps the temperature range of inclusions in anhydrite from the Manus Basin. In addition to the two prevalent temperature ranges, a low-temperature interval (110-130°C) and a high-temperature interval (280-300°C) are characteristic of barite from the Yaman-Kasy chimneys. Each temperature group is distinguished by a specific salinity. The lowest salinity (0.9 wt %) is inherent to the low-temperature inclusions (110-130°C); the two medium-temperature groups (140-200 and 200-250°C) fit the salinity range of 3.5– 13.8 wt %; and the high-temperature group is characterized by high salt contents, from 9.4 to 12.6 wt %.

The fluid inclusions in quartz from mineralized fauna are $3-16 \ \mu m$ in size and arranged as bands or chains and occasionally uniformly occupy particular volumes of crystal. The inclusions, most likely, pseudo-secondary, are flat and demonstrate negative faces.

Study in a cryogenic chamber has shown that the filling of two-phase inclusions freezes at $-(35-45)^{\circ}$ C. The eutectic temperature varies from -30 to -32° C, -28 to -30° C, and -22.5 to -23.5° C; i.e., a MgCl₂ or KCl admixture occurs in solution in addition to NaCl. Most of the last tiny crystals disappear in solution within a temperature range from -4 to -7° C. Three ranges of melting temperature of the last tiny crystals are recorded: -(0.8-2.2), -(2.9-5.3), and $-(6.4-8.5)^{\circ}$ C. In some inclusions, the last crystals dissolve at -13.5° C. Several groups of inclusions with salinity of

1.2–4.5, 5.3–8.1, 11.6–12.0, and up to 16.9 wt % are distinguished, respectively. Three intervals of homogenization temperatures are recognized: 102–139, 140–175, and 178–196°C.

The fluid inclusions in barite from mineralized fauna, $3-15 \,\mu\text{m}$ in size, are located uniformly throughout the crystal and are often faceted to some extent. Study in a cryogenic chamber showed that the inclusions freeze at $-(35-45)^{\circ}$ C. The eutectic temperature varies from -21.5 to -24.5° C; NaCl with a KCl admixture dominates in the solution. Judging from the low melting temperature of the last crystals (from -1.1 to -3.2° C), the salinity of inclusions is not high (1.6–5.0 wt %). According to the thermometric data, two groups of inclusions with homogenization temperatures at 112-168 and $183-267^{\circ}$ C are distinguished. Higher values up to 272° C are established occasionally.

The fluid inclusions in quartz from rhyolite (3–9 μ m in size) are localized near the melt inclusions mentioned above. They are localized along sealed fractures; isolated inclusions are also observed. Study in a cryogenic chamber showed that the contents of two-phase inclusions freeze at –(37–53)°C. The eutectic temperature varies from –24 to –31°C. At least two components, KCl and MgCl₂, occur in solution in addition to NaCl. Most of the last tiny crystals disappear within the temperature range from –11 to –2°C. The salinity covers the range from 3 to 15 wt % NaCl equiv. The thermometric study showed that the homogenization temperature is within the range from 130 to 290°C, which



Fig. 4. Bar chart of salt concentrations (C, wt %) in fluid inclusions in minerals at the Yaman-Kasy deposit, after data of the authors and Simonov et al. (2002a). (1) Inclusions in barite; (2) inclusions in quartz. The solid line depicts data on fluid inclusions in minerals from hydrothermal mounds in the Manus Basin. The dashed line depicts data on fluid inclusions in quartz phenocrysts from porphyries at the Yaman-Kasy deposit. SW is the seawater salinity.

comprises four temperature intervals: 110–130, 130– 180, 180–220, and 220–250°C; measurements also yielded sporadic values in the range 260–290°C.

The analysis of fluid inclusions shows the complex character of the hydrothermal system that acted to create the Yaman-Kasy deposit. Representative data on fluid inclusions occurring both in barite and in quartz testify to several types of hydrothermal ore-forming solutions. By contents of salts, the inclusions in barite are subdivided into three groups with salinity <6, 6.0-11.5, and >11.5 wt %. Approximately the same intervals of salinity (<5, 5–9, and >11.5 wt %) were established from the data on fluid inclusions in quartz (Fig. 4). The mean salinity range of inclusions in quartz virtually coincides with the values for fluid inclusions in barite and anhydrite from black smokers in the Manus backarc basin (5-8 wt %, Fig. 4) and is close to the data for inclusions in minerals of hydrothermal assemblages from other basins: 3-7 wt % (Bortnikov et al., 2004) and 3.4-5.8 wt % (Binns et al., 1993) in the Woodlark Basin and 5.0-6.2 wt % in the Lau Basin (Herzig et al., 1993; Graupner et al., 2001). At the same time, the inclusions in barite from the Yaman-Kasy deposit have a higher salinity (Fig. 4). In general, the wide range of salinity established for inclusions in minerals from the Yaman-Kasy deposit (from <5 to >11.5 wt % or higher) is consistent with recent data on the Manus Basin, where the variation in salinity reaches 7.3 wt % or even considerably more (Vanko et al., 2004), and with the range of fluid inclusion salinity of 2–15 wt % in minerals from the Kuroko-type ore in the JADE hydrothermal field of the Central Okinawa Trough (Luders et al., 2001).

Three types of solutions may be distinguished at the Yaman-Kasy deposit from the homogenization temperatures of fluid inclusions. The inclusions from barite are homogenized at 110–140; 140–250; and, less frequently, 260–290°C (Fig. 5). The medium-temperature group, which coincides with inclusions from the Manus Basin, is obviously prevalent. The fluid inclusions in quartz from ore samples are characterized by more limited temperature intervals at 110–135 and 135–210°C, with a distinct prevalence of the low-temperature (110– 135°C) characteristics (Fig. 5). The fluid inclusions in quartz phenocrysts also demonstrate a rather complex thermal regime with a wide variation of homogenization temperatures from 110 to 250°C.

It was established that two intervals of homogenization temperatures—(1) below 135–140 and (2) 140– 250°C—are predominant in fluid inclusions captured by barite and quartz of sulfide ore at the Yaman-Kasy deposit. These data virtually coincide with the maxima constrained by fluid inclusions in minerals from hydro-



Fig. 5. Bar chart of homogenization temperatures (T_{hom} , °C) of fluid inclusions in minerals at the Yaman-Kasy deposit. See Fig. 4 for legend.

thermal assemblages in the Manus Basin (160–210 and 220–270°C).

The groups of inclusions with different salinity (Fig. 4) are distinguished by relationships between salinity and homogenization temperature (Figs. 6, 7). In each group, the inclusions in barite reveal elevated homogenization temperature and salinity relative to the inclusions in quartz. Furthermore, a positive correlation between temperature and salinity is inherent to inclusions in barite; in other words, these inclusions become less concentrated with falling temperature (Fig. 6). Inclusions in quartz do not display such a correlation (Fig. 7). The fluid inclusions in quartz phenocrysts cover a wide field that overlaps most of the data points related to the other two groups of inclusions with elevated salt concentrations. This indicates that the hydrothermal fluids affected the igneous rocks most intensely during the ore formation.

The most general parameters of the hydrothermal solutions responsible for the ore formation at the Yaman-Kasy deposit were presented above on the basis of data obtained from the study of fluid inclusions. These parameters have much in common with those of ore-forming systems acting at the bottom of the present-day oceanic basins. At the same time, it is known that submarine sulfide mounds evolve with an inversion of the temperature regime. A progressive initial stage with increasing temperature is followed by a final stage of decreasing temperature (Bortnikov, 1995; Bogdanov and Sagalevich, 2002; Maslennikov, 2006).

This specific feature of sulfide deposit formation was emphasized by Pisutha-Arnold and Ohmoto (1983) on the basis of fluid inclusion study. Using the geological and mineralogical information available to us, we made an attempt to arrange the obtained data on fluid inclusions in chronological order.

As follows from the geological data, the Yaman-Kasy deposit and associated igneous rocks were formed under submarine conditions. Quartz phenocrysts were affected by heated seawater immediately after their crystallization from rhyolitic melt. This process inevitably left marks in fluid inclusions that bear information on the initial, probably premineral, stage of the evolution of the hydrothermal system. The subsequent ore-forming process was recorded in fluid inclusions in minerals from sulfide chimneys and mineralized fauna.

The chimneys were formed at the earliest stage of the sulfide mound growth at the Yaman-Kasy deposit. The growth of a typical sulfide chimney began with formation of a primary opal or anhydrite (?) shell that enveloped the hydrothermal stream. Afterward, the chimney surface was overgrown by colloform pyrite or sphalerite, while the conduit walls were encrusted with chalcopyrite. With an increase in temperature in the innermost portion of the chimney shell, these minerals were replaced with a quartz–sphalerite–chalcopyrite– pyrite aggregate. At the retrograde stage, the walls of the axial conduit were overgrown by pyrite, marcasite, sphalerite, quartz (opal), and barite.



Fig. 6. Salt concentrations (*C*, wt %) in fluid inclusions in barite versus their homogenization temperatures (T_{hom} , °C), after data of the authors and Simonov et al. (2002a). (1–3) Groups of inclusions with different salt concentrations. (I) Field of inclusions in quartz phenocrysts from porphyries at the Yaman-Kasy deposit; (II) field of inclusions in minerals from hydrothermal mounds of the Manus Basin. SW is the seawater salinity.



Fig. 7. Salt concentrations (*C*, wt %) in fluid inclusions in quartz versus their homogenization temperatures (T_{hom} , °C). See Fig. 6 for legend.

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The replacement of fauna with ore minerals at the Yaman-Kasy deposit was a complex process. The overgrowth of organic remains with colloform pyrite occurred contemporaneously with growth of sulfide chimneys. Mineralized fragments occasionally fell into a chimney. The faunal remains were filled with quartz somewhat earlier than with barite. Barite crystallized in vestimentiferans when a chimney was displaced toward the flank of the deposit.

On the basis of the geological and mineralogical data discussed above, an approximate sequence of crystallization and transformation of the minerals containing fluid inclusions may be outlined. Most likely, the fluid inclusions in quartz phenocrysts of rhyolite were formed first, at the premineral stage. After that, quartz was formed at the progressive stage of the sulfide chimney growth, giving way to the crystallization of barite at the retrograde stage. Barite in the mineralized fauna was the last mineral to crystallize at the deposit. The position of quartz in the mineralized fauna still remains uncertain. This quartz is suggested to have crystallized simultaneously with the quartz in sulfide chimneys, as supported by similar parameters of fluid inclusions.

Thus, four consecutive stages of the mineral formation at the Yaman-Kasy deposit may be distinguished from the analysis of fluid inclusions (Fig. 8): (I) premineral solutions (inclusions in quartz phenocrysts of rhyolite); (II-IV) ore-forming stages: (II) inclusions in quartz from sulfide chimneys and mineralized fauna, (III) inclusions in barite from sulfide chimneys, and (IV) inclusions in barite from mineralized fauna. As can be clearly seen from Fig. 8, the ore mineral assemblages were formed with inversion of the parameters of ore-forming solutions. The salinity and temperature of solutions increased from stage II to stage III, while, on passing to the final stage (IV), these parameters dropped. This sequence is basically similar to the sequence established from fluid inclusions at Kurokotype sulfide deposits (Pisutha-Arnold and Ohmoto, 1983). The premineral solutions (I) are distinguished by elevated salinity and by an interval of elevated temperature in comparison with the initial stage (II) of the ore-forming system proper. A sequence of relatively high-temperature intervals repeats almost completely the general trend with inversion during the ore-forming stages (II-IV) (Fig. 8). Thus, two fluids heated to different temperatures acted at the Yaman-Kasy deposit simultaneously (Fig. 8).

The formation of hydrothermal solutions with elevated temperature and salinity at the premineral stage testifies to the effect of fluid derived from melt. This possibility is in line with high (up to 5%) water contents detected in melt inclusions from quartz phenocrysts in silicic volcanics. Magmatic fluid hardly participated in the ore-forming process at its initial stage (II), when low-temperature and low-salinity solutions dominated. At the same time, barite in sulfide chimneys, which partly crystallized at elevated parameters, might have been affected by magmatic fluid. Low-temperature solutions with low contents of dissolved salts (actually, heated seawater) circulated at the final stage. Thus, a contribution from magmatic fluids is suggested at the premineral stage and at the peak of the progressive development of the mineral-forming system. Seawater served as the hydrothermal solution background at the initial and final stages of the ore-forming process. The possible effect of magmatic fluids at the peak of ore deposition is supported by the results of fluid inclusion studies in quartz from porphyries at the massive sulfide deposits of the Rudny Altai (Simonov et al., 2005). The pre- and postmineral silicic melts there were waterdeficient (0.19-0.77 and 0.94-1.84 wt % H₂O, respectively), whereas the ore-bearing magmas were relatively enriched in water (1.56–4.30 wt % H₂O). In other words, fluid was accumulated in the ore-bearing magmatic melts.

To establish the real crystallization temperatures, a correction for pressure was introduced into homogenization temperatures. The possible pressure in paleohydrothermal systems was estimated taking into account the formation of the Yaman-Kasy deposit in an ancient backarc basin similar to the present-day Manus, Woodlark, and Lau basins in the western Pacific (Maslennikov and Zaykov, 1998; Simonov et al., 2001). In particular, the depth of the Manus Basin in the vicinity of the Vienna Woods hydrothermal field is about 2500 m (Bortnikov and Lisitsyn, 1995) and the corresponding minimal pressure in the ore-forming systems should be ~250 bars. A similar pressure was quite possible for hydrothermal activity at the Yaman-Kasy deposit because, according to geological data, the depth of the basin where this deposit was formed was 2000-3000 m (Zaykov et al., 2002). Thus, taking into account a correction for a pressure of 250 bars, the temperature of hydrothermal solutions at this deposit was 130–160, 160-270, and 280-310°C. The high-temperature intervals correspond to the temperature regime of black smokers on the bottom of present-day basins (Hydrothermal Systems..., 1993; Bortnikov et al., 2004); are consistent with temperatures of homogenization of fluid inclusions in minerals from the hydrothermal mounds in the Manus backarc basin, estimated at 242-285°C (Simonov et al., 2002a); and coincide with the results of direct measurements of the temperature of ore-forming fluid at the vent of an active chimney on the bottom of the Manus Basin (275°C) (Lisitsyn et al., 1992). A wider temperature range of 150-385°C recently obtained from the study of fluid inclusions (Vanko et al., 2004) overlaps completely our results for the Yaman-Kasy deposit. These results are consistent with information on fluid inclusions in minerals from present-day hydrothermal systems in other backarc basins (200-300°C in the Lau Basin (Herzig et al., 1993) and 203-316°C (Bortnikov et al., 2004) and



Fig. 8. The evolution of parameters of hydrothermal solutions established from fluid inclusions at the Yaman-Kasy deposit. (1) Data on fluid inclusions in quartz; (2) data on fluid inclusions in barite. Consecutive stages: (I) premineral solutions (fluid inclusions in quartz phenocrysts from rhyolite); (II–IV) ore-forming stages: (II) inclusions in quartz from sulfide chimneys and mineralized fauna, (III) inclusions in barite from sulfide chimneys, (IV) inclusions in barite from mineralized fauna.

184–244°C (Binns et al., 1993) in the Woodlark Basin) and the results of direct temperature measurements of hydrothermal solutions on the bottom of the Woodlark Basin (270–350°C) performed with aid of the Mir manned submersibles (Gordeev, 1992). Comparison with the results of a study of fluid inclusions in minerals from the Kuroko-type ores in the JADE hydrothermal field in the Central Okinawa Trough that yielded 270–360°C (Luders et al., 2001) has shown that the maximal temperature intervals for the Yaman-Kasy deposit are somewhat lower but nevertheless close to the aforementioned estimates. These intervals also fit data on

fluid inclusions in minerals from altered basalts in the vicinity of the Kuroko deposit that documented hydrothermal activity at 230–280°C (Shikazono et al., 1995).

The presence of several temperature intervals in hydrothermal systems at the Yaman-Kasy deposit is in agreement with data on the Manus Basin, where the early mineral assemblages were formed at a temperature above 240°C and the late assemblages, at a lower temperature (Shadlun et al., 1992). Our results are also consistent with the estimates of 200–300°C obtained for the ore formation at the Yaman-Kasy deposit by Shadlun (1991) and Maslennikov et al. (1997).

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