Re–Os isotopic constraints on the genesis and evolution of the Dergamish and Ivanovka Cu (Co, Au) massive sulphide deposits, south Urals, Russia

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Abstract

Rhenium and osmium elemental and isotopic data have been obtained for the two mafic–ultramafic hosted volcanogenic massive sulphide (VMS) deposits of Dergamish and Ivanovka from the south Urals. The associated ophiolitic blocks belong to the Main Uralian Fault (MUF) melange zone considered to represent obducted early Palaeozoic oceanic crust. Despite their close geographical proximity, the two ore bodies are morphologically, mineralogically and isotopically quite different. Sulphides from Ivanovka possess higher Ni and Os and lower Re and Cu relative to those from Dergamish.

The Re and Os isotope data for Dergamish define a best-fit line corresponding to a Late Devonian age of 366 ± 2 Ma (2σ) with an MSWD of 4.6. This age is some 40 My younger than the inferred Silurian crystallisation age of the associated mafic–ultramafic rocks, but in good agreement with the previously published Rb–Sr and Ar–Ar ages of 360–380 Ma corresponding to the high-pressure metamorphic age of the adjacent Maksyutov metamorphic complex. These data suggest that Re–Os systematics of the Dergamish sulphide deposit were reset, either by diffusion or recrystallisation, during high-pressure metamorphism or subsequent cooling.

The preservation of unradiogenic Os isotopic ratios in some of the Ivanovka samples and the near chondritic initial Os isotopic composition obtained for the Dergamish samples indicates that most of the Os in the massive sulphides was ultimately derived from the mantle. The corresponding tectonic setting equates to an area with submarine high-level mantle rocks. In contrast, sulphides from Ivanovka have experienced continued re-equilibration and have been modified by post-depositional processes at least some of which occurred relatively recently.
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1. Introduction

Understanding ore formation and resolving the age of mineralisation have been important objectives in the study of metallogenesis. Previous isotopic studies have usually been confined to lithophile elements

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such as Rb–Sr, Sm–Nd and U–Th–Pb in rocks related to the ore deposits, in order to constrain the mineralization ages. With the exception of Pb–Pb, all these isotopic systems yield only indirect information on the metallic ores because they are hosted by the silicate rocks.

The Re–Os system is based on the decay of ^{187}Re to ^{187}Os by beta emission ($\lambda_{187\,Re}$ decay constant of 1.666×10^{-11} year^{-1}; Smoliar and Walker, 1996), and provides a powerful geochemical tool for investigating base metal deposits. Because of their siderophile and chalcophile nature, Re and Os are incorporated directly into sulphide phases, and therefore the Re–Os system can be used to directly constrain the source of metals and the age of an ore body.

Large Re/Os fractionation has been observed in sulphide ore deposits from various tectonic settings (Brügmann et al., 1998; McCandless and Ruiz, 1993; Ruiz et al., 1997; Freydier et al., 1997; Mathur et al., 2000). During mantle melting, Os behaves as a compatible element and is preferentially retained in the residue, while Re is moderately incompatible and is preferentially incorporated into melts (Allègre and Luck, 1980; Shirey and Walker, 1998). Consequently, oceanic basalts and other crustal rocks are characterized by higher Re/Os ratios than their mantle source and tend to develop highly radiogenic Os isotopic ratios with time. Whether metals found in ore deposits are of mantle or crustal origin is a fundamental question in ore metallogenesis. Initial Os isotope ratios obtained from isochrons can constrain the nature of sources involved in ore genesis. Another application is the use of the Re–Os system as a chronometer using molybdenite, which is remarkably robust, often surviving intense deformation and high-grade thermal metamorphism (Stein et al., 1998). In the last decade, most Re–Os studies of ore minerals have been performed on magmatic sulphides associated with mafic igneous complexes. Due to their elevated Os concentration relative to crustal hydrothermal ores, the Re–Os isotopic system could be used as viable petrogenetic tracer (Foster et al., 1996).

Recently, new analytical techniques developed by Birck et al. (1997) have allowed precise measurements of Os at a few tens of parts per trillion (ppt, 10^{-12} g/g) levels, enabling the analysis of more common sulphides ores. This study uses the same analytical techniques to obtain precise age and isotopic information for sulphide ores from two mafic–ultramafic bodies in the Urals.

Although the study of the Uralian Orogen has been active during last decade, few radiometric studies have been performed on mafic–ultramafic complexes from this area (Edwards and Wasserburg, 1985; Fershtater et al., 1997). The data presented here report direct Re–Os investigation of volcanogenic massive sulphide (VMS) ore deposits from south Urals and are compared with the available radiometric and stratigraphic age of mafic and ultramafic complexes.

2. Geological setting

The Urals form a linear orogenic belt extending for 2500 km from south to north and result from the Late Paleozoic collision of the east European Platform with a Siberian–Kazakhian microplate assemblage (Alvarez-Marron et al., 2000; Brown and Spadea, 1999). The Uralides consist of a large Paleozoic mountain belt developed during the period of 500–230 Ma (Matte et al., 1993; Puchkov, 1997). It is widely accepted that their formation was due to the closure of a Paleozoic ocean by subduction, continent–island arc collision and finally continent–continent collision (Puchkov, 1997).

The Main Uralian Fault (MUF) is a suture zone from 1 to 20 km wide, which separates the East Europe platform from the Ural fold belt (Fig. 1). It is interpreted as the relic of an eastward dipping Palaeozoic subduction zone (Zaykov, 1991). The MUF is composed of fragments of early Paleozoic ophiolites, comprising basalts, minor bodies of gabbro and diabase, and serpentinite sheets. (Prokin and Buslaev, 1999). A wide development of mafic and ultramafic rocks has led to the formation of numerous ore deposits in middle Paleozoic. There are about 100 massive sulphide deposits in the Urals (Prokin et al., 1998).

The Uralian VMS deposits have been subdivided by Russian authors into four types (Cyprus-, Urals-, Baimak- and Besshi-type) according to their geological association, mineralogy and their original position in the oceanic environment (Prokin et al., 1998). The Cyprus-type deposits are hosted within dominantly tholeiitic basaltic volcanic sequences and the ores are
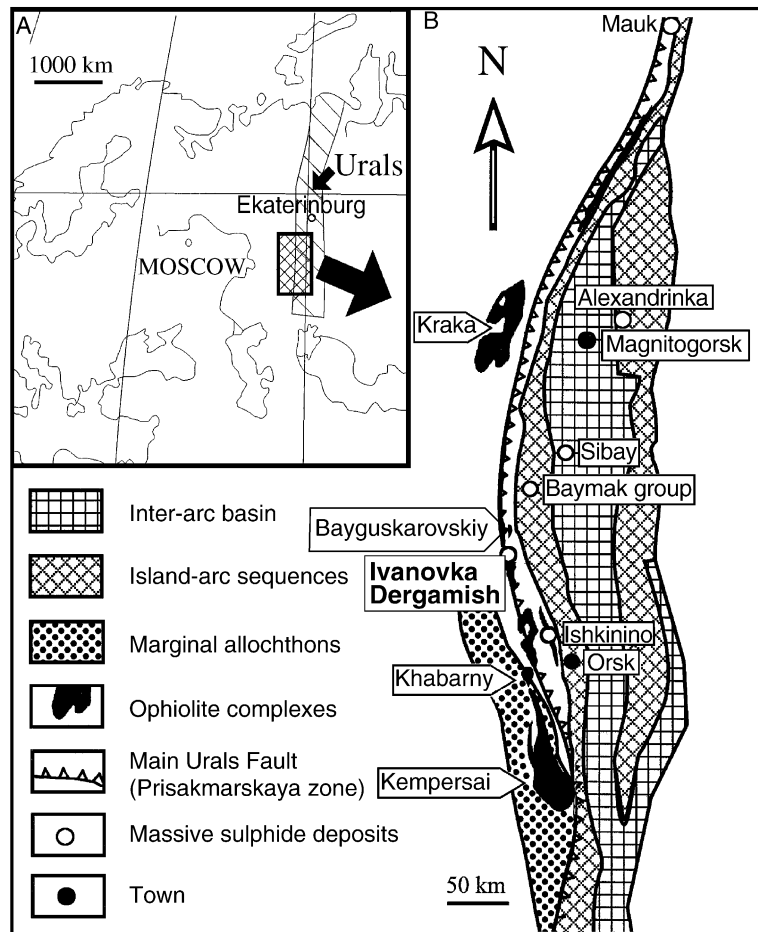
Fig. 1. Key structural elements of the South Urals Paleozoic island arc–inter-arc sequences (after Zaykov, 1991) showing the ophiolite complexes (after Kontar and Libarova, 1997) and major massive sulphides deposits.

dominated by pyrite and chalcopyrite with subsidiary sphalerite. Many of these deposits are linked to ophiolite sequences (Zaykov et al., 2000) and are preserved in Ordovician to Devonian sequences.

Massive sulphide deposits belonging to Cyprus type are represented by about 40 occurrences. They are all situated within Prisakmarskaya zone (west of the magnitogorsk island-arc suture) in the immediate hanging wall of the east-dipping Main Uralian fault. The main deposits (Ivanovka, Dergamish, and Ishkinino) have been worked since the beginning of the 20th century.

The Ivanovka and Dergamish deposits belong to the Bayguskarovskiy ophiolite complex of Sakmar-

sko–Khalilovsky group (Buchkovsky, 1970). These ophiolite complexes form a 250-km-long and 1–5-km-wide meridian belt between the Kraka and Kempersay ophiolite complexes (see Fig. 1) and separate the metamorphic belt of Ural–Tau zone (in the West) from the volcano-sedimentary rocks of the Magnitogorsk island-arc zone (in the East). The complex is composed of serpentinite derived from harzburgite and dunite (Buchkovsky, 1970; Dmitrenko, 1994; Savelieva et al., 1997), which are typical of the depleted oceanic mantle sequence. Thick basaltic formations (including pillow lavas) have also been observed, and both units are cut by a gabbroic intrusion. The distinctive association of these deposits
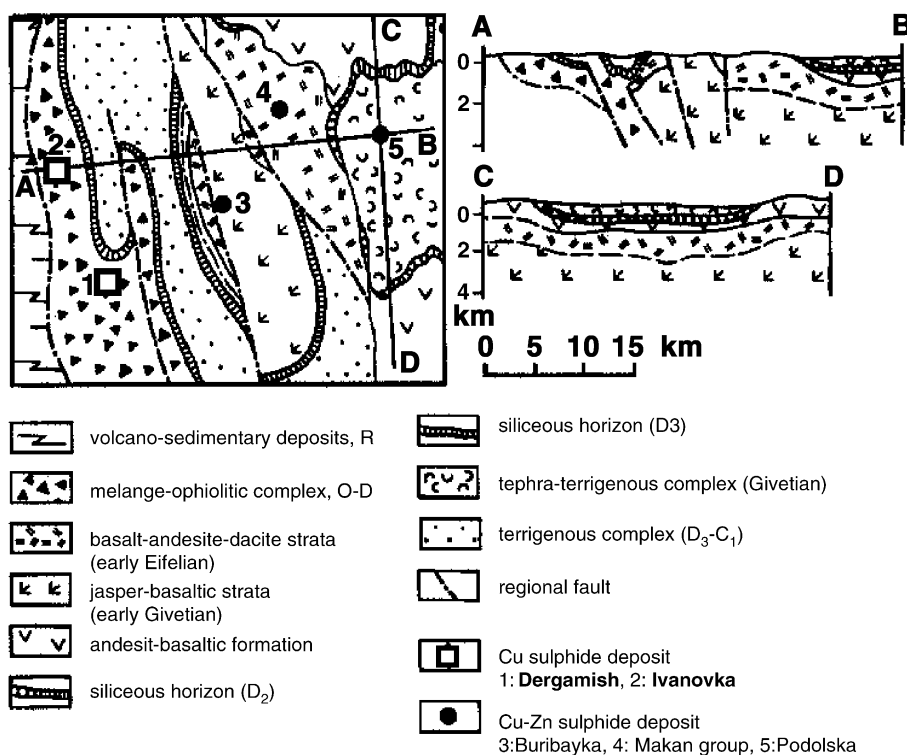
Fig. 2. Simplified geological map of the formations surrounding the studied sulphide deposits.

with Silurian serpentinites and tholeiitic basalts points to a tectonic setting similar to some Mid-Atlantic Ridge hydrothemal fields (Murphy and Meyer, 1998) (Fig. 2).

3. Ivanovka and Dergamish ore bodies

A set of samples recovered from drilling conducted as part of a joint project between BRGM (France) and Bashkyrgeologia (Russia) has been investigated in this study. This study focuses on materials sampled during 1999 from Ivanovka (drillhole 2T) and Dergamish (drillhole D1).

The Dergamish ore body is restricted to a horizon of serpentinitic breccia in the Baygusarovskiy ophiolite complex. The general structure of the ore field is synclinal, as highlighted by a series of Upper Devonian siliceous rocks occurring over the ore-bearing deposit. The sulphide body has a lenticular form, dipping 15–20° north, and varying in thickness from 6 to 40 m. Interlayers and clasts of altered serpentinitic breccia are found in the ore body.

Three general types of ores are represented by:

(i) Massive ore with colloform and brecciated structure, composed of chalcopyrite (3–4%), carbonate (10%), melnikovite (10–15%), marcasite (10–15%) and pyrite (40–50%). Marcasite and pyrite occassionally replace pyrrhotite.

(ii) Streaky-disseminated hematite–magnetite mineralization with chlorite developed between serpentinitic clasts in the breccia of the lower wall of the deposit.

(iii) Streaky-disseminated cubanite-pyrrhotitic ore which is located in the foot wall close to the massive ore body (stockwork zone). Magnetite, chromite, ilmenite, cobaltite, chalco-pyrrhotite and arseno-pyrite are also found as minor phases. This type of ore is analogous to some of the mineralisation that occurs at Ivanovka.

Colloform sulphides in the mound-like top section of the Dergamish deposit were probably exposed to the seafloor surface and have been partially destroyed, with a clastic sulphide facies formation showing evidence of graded bedding.

The deposit is rich in cobalt. The cobalt is present in the ore as cobaltite and as an isomorphic admixture in pyrite. The massive sulphide ores exhibit low Ni contents falling below that of the ore-bearing serpentinite (0.2–0.3%).

The Ivanovka ore deposit consists of several east-dipping lenses and layers (15 to 50°E) located at the contact between ultramafic rocks and Silurian basaltic formations. Acid volcanic rocks are absent (Zakharov and Zakharova, 1975; Kontar and Libarova, 1997). Generally, the ore forms massive lenses that are hosted either in the altered serpentinite or chlorite rocks after mafic lithologies and also in the gabbro or at the contact between the serpentinite and the overlying basalt. In rare cases, the ore lenses are totally enclosed within basalt. Branching veins and stockworks are also observed.

In the lithologies of drillhole Ivanovka 2T, the mafic–ultramafic sequence shows hydrothermal alteration to talc–carbonate–Mg saponite (after ultramafic rocks) and chlorite (after mafic rocks). Mafic rocks dominate the basal section (from 130 m downwards) of the drillhole. The sulphide mineralisation is enriched in Ni, Co, Cu and locally Au. The main mineralisation is in the form of coarse-granular pyrrhotite (75–80 vol.%) with interstitial chalcopyrite. Ore textures vary from massive to disseminated, irregularly distributed pyrite–chalcopyrite–pyrrhotite and chalcopyrite–pyrrhotite aggregates. Ores hosted in serpentinites contain elevated amount of pentlandite.

4. Analytical procedure

Fresh fragments from each sample were granulated in an agate mortar. In most case for the ores studied here, only sulphides were handpicked on the basis of their optical characteristics. The selected minerals were then powdered in agate. Re and Os concentrations and the Os isotopic composition were determined by negative thermal ionisation mass spectrometry (NTIMS) on a Finnigan MAT 262 at IPG-Paris (Creaser et al., 1991; Völkening et al., 1991).

The detailed analytical procedure has been described elsewhere (Birck et al., 1997). Approximately 0.15–0.30 g of each sample was used for the analyses and was spiked using a mixed ^{190}Os–^{185}Re spike and then dissolved with HBr+HF in a Teflon bomb at 145 °C. This step was followed by oxidation of Os to OsO_4 in a nitric acid solution containing chromium trioxide in order to ensure the spike/sample isotopic homogenisation. Finally, Os was extracted in liquid bromine and purified by microdistillation. The supernate was reduced by ethanol and Re was extracted and purified by liquid/liquid extraction with iso-amylic alcohol and 2 N HNO_3.

Total procedural blanks for Os during the course of this study were 0.030 ± 0.015 pg/g ($n=8$). The $^{187}Os/^{188}Os$ value of the blank ranged between 0.178 and 0.488 with a mean value of 0.282. The Re blank ranged between 1 and 6 pg/g with a mean value of 3.4 pg/g. Since total blank for both Re and Os were run as part of each batch of dissolutions, the appropriate blank correction for each batch was applied.

5. Results

Isotopic and elemental data are shown in Table 1. Rhenium and Os concentrations for massive sulphides from Dergamish ore body range from 7.23 to 41.21 ppb and from 0.06 to 0.6 ppb, respectively. Both Re and Os distributions are similar to those found in ores from the Iberian pyrite belt (Mathur et al., 1999), but the Re/Os ratios are much higher than those observed in the J-M Reef sulphides of the Stillwater Complex (Lambert et al., 1994). The large range in Re concentrations in the Dergamish sulphides is comparable to the Re range observed in both hydrothermal sulphides from TAG (Ravizza et al., 1996; Brügmann et al., 1998) and Noril'sk mineralised systems (Walker et al., 1994). This large range is up to two orders of magnitude higher than generally observed in other crustal rocks or in oceanic basalts.

Massive sulphides from Ivanovka are distinctive compared with those from Dergamish in that they are

Table 1
Re–Os elemental and isotopic data of Dergamish and Ivanovka sulphides

Sample[a]	Mineralogy[b]	Cu[c] (wt.%)	S[c] (wt.%)	Co[c] (ppm)	Ni[c] (ppm)	Au[c] (ppm)	$^{187}Os/^{188}Os$[d]	^{188}Os (ppt)	Os (ppt)	$^{187}Re/^{188}Os$[e]	Re (ppb)	T_{MA}[f] (Ma)	Os_{com}[g] (ppt)	Re/Os_{com}
Dergamish														
D21	Serpentinite						7.878 ± 0.039	0.317	4.86	482.8	0.260	964.3	2.393	108.6
D45.1	Chlorite-rock						1.054 ± 0.003	2.862	24.47	208.3	0.969	267.6	21.80	44.43
D45.8	Py	0.19	2.67	270	530	0.13	5.276 ± 0.025	8.622	109.9	865.7	11.98	357.2	65.28	183.6
D46.3	Cpy–Py	4.27	37.97	74	140	5.07	3.129 ± 0.012	10.03	106.4	503.0	8.126	358.4	76.17	106.7
D46.3[h]	Cpy–Py						4.574 ± 0.008	5.760	69.41	723.5	6.679	369.1	43.66	153.0
D47.5	Py–Cpy	2.65	38.86	1570	130	4.67	7.059 ± 0.026	7.184	104.3	1120	12.93	371.5	54.26	238.3
D50.7	Po–Py–Carb	1.40	33.41	58	85	0.53	19.67 ± 0.29	7.575	205.1	3221	39.09	364.3	56.20	695.6
D50.7[h]	Po–Py–Carb						14.19 ± 0.68	10.56	228.3	2357	39.87	358.2	78.97	504.9
D50.7[h]	Po–Py–Carb						4.062 ± 0.005	20.89	241.1				158.4	
D56.7	Mc–Py	1.15	32.86	2070	280	1.28	1.090 ± 0.004	69.98	600.7	158.7	17.82	364.9	533.0	33.43
D59	Mc–Py	1.86	33.95	1460	140	1.28	16.82 ± 0.07	2.780	67.36	2719	12.14	368.5	20.71	586.0
D59[h]	Mc–Py						20.31 ± 0.11	2.232	61.83				16.54	
D59.7	Mc–Py	1.86	33.95	1460	140	1.28	19.53 ± 0.07	8.070	217.3	3189	41.21	365.2	59.88	688.3
D62.5	Mc–Py	0.67	40.61	570	55	0.65	15.72 ± 0.03	3.821	88.42	2570	15.75	364.3	28.51	552.5
D67	Mc–Py	1.05	37.43	1040	45	0.44	6.649 ± 0.024	23.13	326.5	1065	39.46	367.7	174.8	225.7
D67[h]	Mc–Py						15.83 ± 0.06	9.773	227.1	2568	40.17	367.0	72.90	551.1
D70	Mc–Py	1.45	34.72	1940	90	0.35	48.68 ± 0.15	1.445	80.82	7970	18.48	365.7	10.27	1799
D70[h]	Mc–Py						46.45 ± 0.28	1.521	81.71	7597	18.53	366.0	10.85	1707
D71.7	Py	1.71	36.41	1870	75	0.67	14.78 ± 0.04	8.355	185.5	2398	32.09	366.8	62.41	514.2
D75	Py–Mc	1.15	20.79	1670	260	0.16	1.147 ± 0.003	25.79	222.8	173.6	7.231	353.2	196.4	36.82
D75[h]	Py–Mc						2.580 ± 0.018	7.752	78.04				58.92	
Ivanovka														
Iv2	Chlorite-rock						0.3887 ± 0.0021	2.586	20.39	73.79	0.305	213.6	19.72	15.48
Iv272.6	Cpy–Po						0.2977 ± 0.0009	2.332	18.18	329.7	1.230	31.02	17.78	69.17
Iv36	Serpentinite						0.3334 ± 0.0006	8.187	64.12	53.56	0.701	232.5	62.42	11.24
Iv80.5	Po–Py (Cpy)	0.64	31.62	550	1880	0.18	0.1332 ± 0.0004	322.7	2463	2.00	1.031	212.7	2461	0.42
Iv84	Po–Cpy (Py)	1.48	19.75	430	1260	5.36	1.537 ± 0.008	0.378	3.41	304.6	0.184	278.1	2.879	64.02
Iv100.1	Po–Py–Cpy	0.14	20.41	230	1060	0.04	0.1192 ± 0.0005	161.4	1230	4.70	1.214	1097[i]	1230	0.99
Iv110.5	Car–Tc alter serp						0.1197 ± 0.0008	95.45	727.2	2.55	0.389	1032[i]	727.2	0.53
Iv123.5	Po–Py	0.14	16.43	220	1310	0.29	0.2542 ± 0.0027	2.559	19.84	266.2	1.089	28.61	19.51	55.83
Iv126.5	Po	0.10	17.81	140	1450	0.40	0.1332 ± 0.0004	87.48	667.7	43.57	6.096	7.95	667.2	9.14
Iv127.7	Cpy–Po	0.18	26.52	170	1320	1.27	0.1249 ± 0.0003	307.5	2344	3.49	1.715	346.9[i]	2344	0.73
Iv130.5	Chlorite-rock						0.3754 ± 0.0014	8.315	65.46	133.2	1.771	112.1	63.39	27.94
Iv148	Cpy–Po (Py, Co)	0.82	33.76	500	1510	3.73	0.2327 ± 0.0009	7.366	56.95	187.4	2.208	33.76	56.17	39.32
Iv148[h]	Cpy–Po (Py, Co)	0.82	33.76	500	1510	3.73	0.1634 ± 0.0060	11.49	88.02	94.79	1.742	22.84	87.60	19.88
Iv154	Cpy–Po (Co)	0.44	27.64	300	1640	0.65	0.1267 ± 0.0006	220.1	1678	2.92	1.029	106.3[i]	1678	0.61

enriched in Os and lower in Re, with concentrations varying between 0.02 and 2.46 ppb and between 0.18 and 6.1 ppb, respectively. In both cases, there are no relationships between the Re and Os abundances and depth of sampling or with the type of mineralisation. Comparison of the sulphide chemistries shows that the Dergamish mineralisation is enriched in Re and Cu and depleted in Os and Ni with respect to the Ivanovka (Fig. 3; Table 1). The relatively high concentrations of Ni (1060–1880 ppm) in the Ivanovka sulphides are similar to the range observed in Ishkinino massive sulphide deposit from south Ural (Wipfler et al., 1999). In the Ni vs. Re or Os space, both deposits are distinct from each other (Fig. 3). This illustrates that, in spite of the close geographical proximity of the two ore deposits, the fluids or magmas involved in these mineralisations, or else their post crystallisation history, must have been different. The Au contents are highly variable in the investigated samples and range from 0.04 and 5.36 ppm and show the same range in both of the studied bodies. This range is similar to the range observed in the Ishkinino massive sulphide deposit (Wipfler et al., 1999). No correlation is observed between Au with Re or with Os content. In contrast, there is a general positive correlation between Au and Cu for the Ivanovka and Dergamish deposits.

The ultramafic country rocks in both cases are generally serpentinised and metasomatised. The Os and Re concentrations vary between 0.004 and 0.73 ppb and from 0.26 to 1.77 ppb, respectively. The Os range is significantly lower than for typical ultramafic rocks found in ophiolites (1–4 ppb).

The Dergamish sulphides show a large range for both $^{187}Re/^{188}Os$ and $^{187}Os/^{188}Os$, 158 to 7970 and from 1.09 to 48.7, respectively. All Dergamish sulphides analysed in this study plot on a linear array in the isochron diagram (Fig. 4a), suggesting a common age and an isotopically homogeneous source. According to the best-fit calculation, a precise age of 366 ± 2 Ma and initial Os of 0.127 ± 0.049 (MSWD = 4.6) can be defined (2σ error). When we exclude the disseminated sulphide samples from the regression (i.e. D45.8 and D75), the precision of the initial ratio and MSWD is slightly improved (MSWD = 2.4). Replicate measurements of the same sulphide powders repeated through both chemistry and mass spectrometry show heterogeneous distribution of both their Re and Os contents but their isotopic ratios plot close to the same line defined by the isochron. Samples enriched in pyrrhotite and pyrite have Re and Os concentrations and $^{187}Os/^{188}Os$ ratios within the ranges of the samples enriched in marcassite and pyrite. This large range indicates that crystallographic constraints on the distribution of Re and Os cannot be discerned in the samples studied here.

The whole-rock isochron demonstrates that the Re–Os isotopic system in these samples has remained closed for 365 Ma, suggesting that continued tectonic processes in the area did not significantly affect the Re–Os geochemistry of most of the analysed samples.

In contrast to the Dergamish samples, $^{187}Os/^{188}Os$ for the Ivanovka samples show a less radiogenic, and limited, range varying from 0.119 to 1.537 despite a wide variation of $^{187}Re/^{188}Os$ from 2 to 330. The unradiogenic Os isotopic compositions are similar to those of harzburgites from Uralian Myndyak ophiolite (A. Gannoun, unpublished data) and to depleted peridotites from orogenic massifs (Shirey and Walker, 1998). The unradiogenic signature is observed in both the sulphide ore (i.e. sample Iv100.1, Po–Py–Chp)

Notes to Table 1:

[a] All numbers following samples reflect depths (m) of drill cores.

[b] Abbreviations represent the order of the dominate phase in the sample analysed: Cpy = chalcopyrite; Mc = marcasite; Py = pyrite; Car = carbonate; Po = pyrrhotite; Co = cobaltite; Tc = Talc.

[c] Determined by XRF.

[d] All errors are $2\sigma_m$, $^{187}Os/^{188}Os$ ratio are normalized to $^{192}Os/^{188}Os = 3.08271$ (Luck and Allègre, 1983) and corrected using measured $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios of 0.002047 and 0.00037, respectively. IPG-Paris 100 pg internal standard yields 0.17396 ± 19 ($n = 10$), 10 pg yields 0.1742 ± 6 ($n = 14$).

[e] $^{187}Re/^{188}Os$ ratio determined to a precision of $\pm 1\%$.

[f] Model age are calculated assuming an single stage differentiation and using $^{187}Os/^{188}Os_{PM} = 0.1275$, $^{187}Re/^{188}Os_{PM} = 0.4243$ (Shirey and Walker, 1998) and $\lambda_{Re} = 1.666 \ 10^{-11}$ year^{-1} (Smoliar and Walker, 1996).

[g] Common Os is calculated excluding radiogenic Os (^{187}Os) results from decay of ^{187}Re after the formation age.

[h] Replicate measurements of the same whole-rock powder repeated through both chemistry and mass spectrometry.
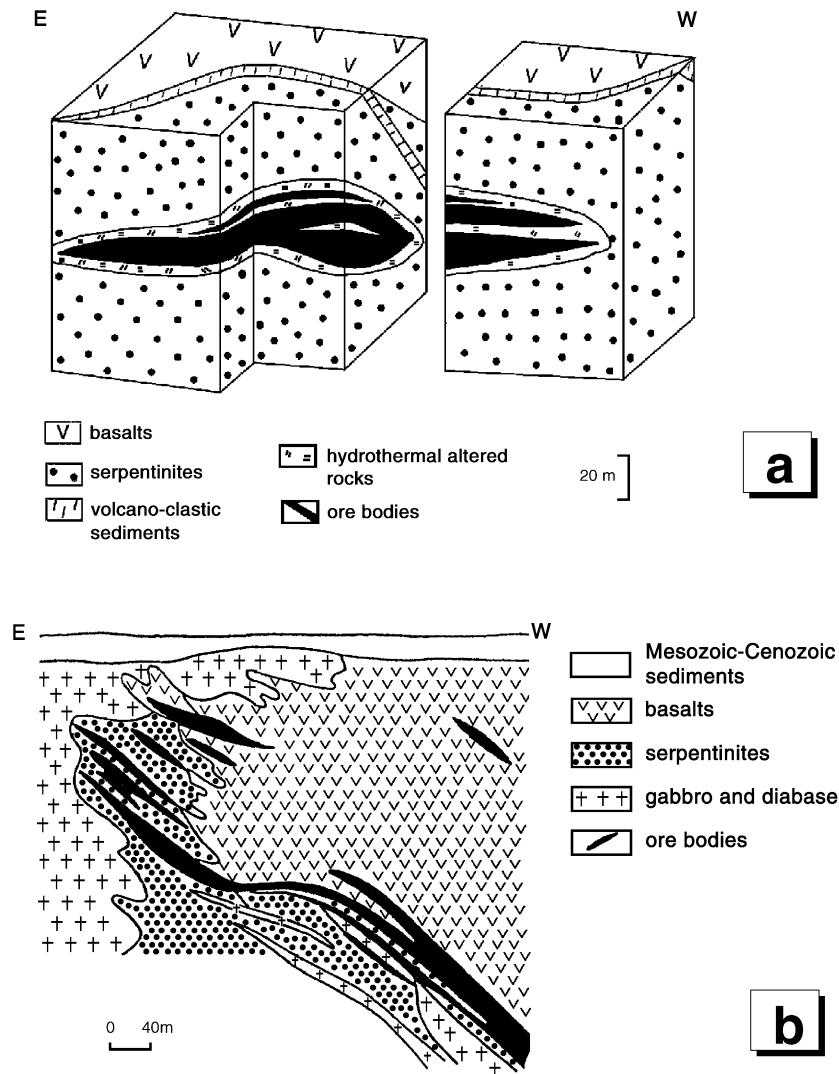
[i] Corresponding to Re-depletion age.

Fig. 3. (a) Schematic blok diagram of Dergamish ore deposit (after Ismagilov, 1962); (b) Cross-section through the Ivanovka ore deposit (modified after Kontar and Libarova, 1997).

and the host rock (sample Iv110.5, carbonate–talc altered serpentinite) and are similar within error to the isochron-based initial $^{187}Os/^{188}Os$ for the Dergamish sulphides (0.117 ± 0.046). No clear correlation was observed in the $^{187}Re-^{187}Os$ isochron diagram suggesting that the mineralised assemblages must have evolved as an isotopically open system or from initially heterogeneous source. Radiogenic osmium (^{187}Os) calculated for each sample using the isochron age constitute a large proportion of the

total osmium and ranges between 11% and 87%. This distribution differs from the Ivanovka's samples in which the radiogenic osmium is less than 10% of the total Os.

The calculated model ages (T_{MA}) range from 8 to 280 Ma and are significantly younger than the Late Devonian age obtained for the Dergamish sulphides. If one precludes the silicate samples and one sulphide sample characterized by low Os and Re contents, then the data suggest an age of 32 My, which is much
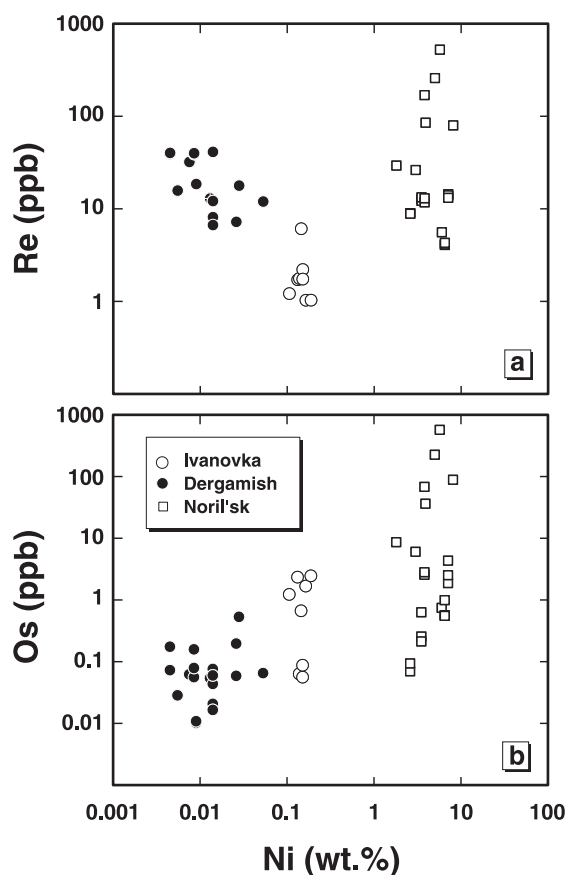
Fig. 4. Re and Os concentrations versus Ni contents for the massive sulphides samples from Dergamish and Ivanovka. Sulphides data from Noril'sk are included for comparison (Walker et al., 1994).

younger than any documented metamorphic or tectonic events in the area.

6. Discussion

6.1. Dergamish age relationship and geodynamical evolution

The Dergamish sulphides are cogenetic but show a large Re/Os fractionation. The large uncertainty of the $^{187}Os/^{188}Os$ intercept is exacerbated by the elevated values in both Re/Os and $^{187}Os/^{188}Os$ and the lack of less radiogenic samples ($^{187}Os/^{188}Os$ less than 1.08 and $^{187}Re/^{188}Os$ less than 158) with which to precisely constrain the initial ratio. The ^{187}Re–^{187}Os age

for all sulphides is robust, because the large range in the $^{187}Re/^{188}Os$ ratios (from 158 to 8000) allows for rapid growth of ^{187}Os and thus, possible isotope inhomogeneities at the 0.05 level in the fluid that deposited the sulphides are insignificant.

Geochronological studies of several ophiolites from the southern Urals show older ages. Sm–Nd mineral isochron age of studied mafic–ultramafic rocks from the Kempersai massif (Edwards and Wasserburg, 1985; Melcher et al., 1999) are all within a range of 394–427 Ma. These ages correspond either to magmatic crystallisation or the time of equilibration of the Sm–Nd system, and are consistent with a period of extension within the Sakmara zone of the Uralian ocean. Similar ages are found in many other ophiolite complexes within the Western Urals along the MUF (Edwards and Wasserburg, 1985; Sharma et al., 1995). However, other authors (Fershtater et al., 1997) have attributed a middle Ordovician (460–480 Ma) age to the formation of ophiolites and consider the above isotopic ages to be due to resetting of the isotopic systems during the early Devonian (395–410 Ma). Melcher et al. (1999) have also obtained younger ages for veins and pods post-dating crystallisation of massive chromitite of Kempersai. Pargasitic amphiboles give $^{40}Ar/^{39}Ar$ stepwise heating ages of 365 to 385 Ma. This age is similar to the 379 Ma Rb–Sr mineral isochron obtained for a pyroxenite vein in the western part of the massif. These authors concluded that the Kempersai massif was pervasively metasomatised by large volumes of fluid and melt derived from a subducted slab (large chromite ore bodies were formed in this second stage). Additionally, the HP-LT metamorphism (blueschists and eclogites), well exposed along the Sakmara river (Maksyutov complex) to the west of the MUF, has been dated by ^{40}Ar–^{39}Ar in phengites at about 370–380 Ma (Matte et al., 1993; Beane and Connelly, 2000).

Direct corroborating evidence for the same Uralian high-pressure metamorphism has been recorded by the Rb–Sr mineral systematics in nine eclogites from the gneissic unit #1 of the Maksyutov complex. These give concordant internal isochron ages with an average age of 375 ± 2 Ma (Glodny et al., 2002). Consequently, if the Dergamish sulphide ores are contemporaneous with the Silurian–lower Devonian stage of ophiolite crystallisation, the Late Devonian age yielded by the Re–Os is ∼40 Ma younger than

expected from radiometric crystallisation ages and 10–20 Ma younger than the peak HP metamorphism stage. The interval of 10–20 Ma is the estimated time elapsed between eclogite-facies metamorphism and the retrogression event at blueshist to greenschist facies conditions (Matte et al., 1993; Beane and Connelly, 2000; Glodny et al., 2002). This stage of metamorphism is most likely responsible for the high temperature pyrrhotite (As–Ni–Co) mineralogical

assemblage. Thermometric data for Co- and Ni-bearing mineral assemblages favour this latter hypothesis. These deposits subsequently underwent deformation and metamorphism. Experimental study of the diffusion of Os in pyrrhotite and pyrite (Brenan et al., 2000), show the relative low closure temperature which are considerably lower than for Sr in apatite but similar to those calculated for Ar retention in biotite. These results suggest that both
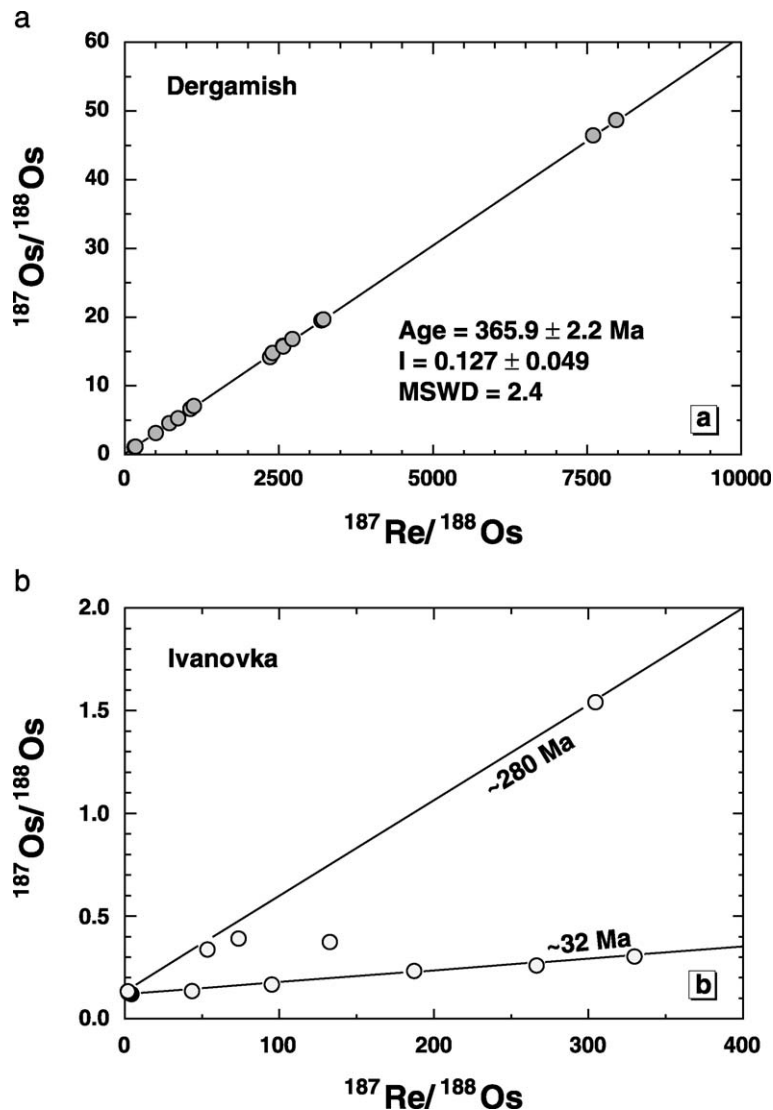

Fig. 5. (a) Re–Os isochron diagram for Dergamish sulphides; errors are smaller than symbols; the two serpentinites are excluded from the regression. (b) Re–Os isotopic evolution diagram for Ivanovka sulphides.

minerals are susceptible to open system exchange in the presence of post depositional stage hydrothermal fluids.

Even though the Dergamish sulphides were re-equilibrated 40 Ma after their deposition on the seafloor, their initial $^{187}Os/^{188}Os$ close to the mantle value suggests that the fluid that promoted reequilibration contained little crustally derived Os. Within 40 Ma, a sulphide with a $^{187}Re/^{188}Os$ of 2500 would be characterized by a $^{187}Os/^{188}Os$ of 1.8, which is far more radiogenic than the initial reported above. A similarly radiogenic $^{187}Os/^{188}Os$ would be found for the mafic rocks associated with the Dergamish deposits. For example, mafic rocks associated with MUF-related Mindyak and Nurali ophiolites have high Re/Os and radiogenic $^{187}Os/^{188}Os$ (A. Gannoun, unpublished data). Thus, the Dergamish VMS deposit most likely re-equilibrated with a fluid that contained Os derived from peridotites but not from crustal rocks.

6.2. Distribution of Re and Os and preservation of unradiogenic initial osmium isotopic composition within the Ivanovka deposit

The ore isotopic data from Ivanovka present a more complex case than Dergamish in that considerable redistribution of Re and Os must have occurred some time after 366 My. Data from Ivanovka would appear to indicate that fluids are isotopically heterogeneous during deposition and chemically distinct from those that generated the Dergamish massive sulphides. However, if the silicate rocks and sample Iv84 (which has a very low Os content and is thus more prone to contamination) are excluded, then the remaining massive sulphides define a line with a 32 Ma age and an intercept of approximately 0.12. This initial $^{187}Os/^{188}Os$ ratio is consistent with a mantle-derived Os signature and is similar to that found for Dergamish. Sulphides with unradiogenic $^{187}Os/^{188}Os$ are characterised by high
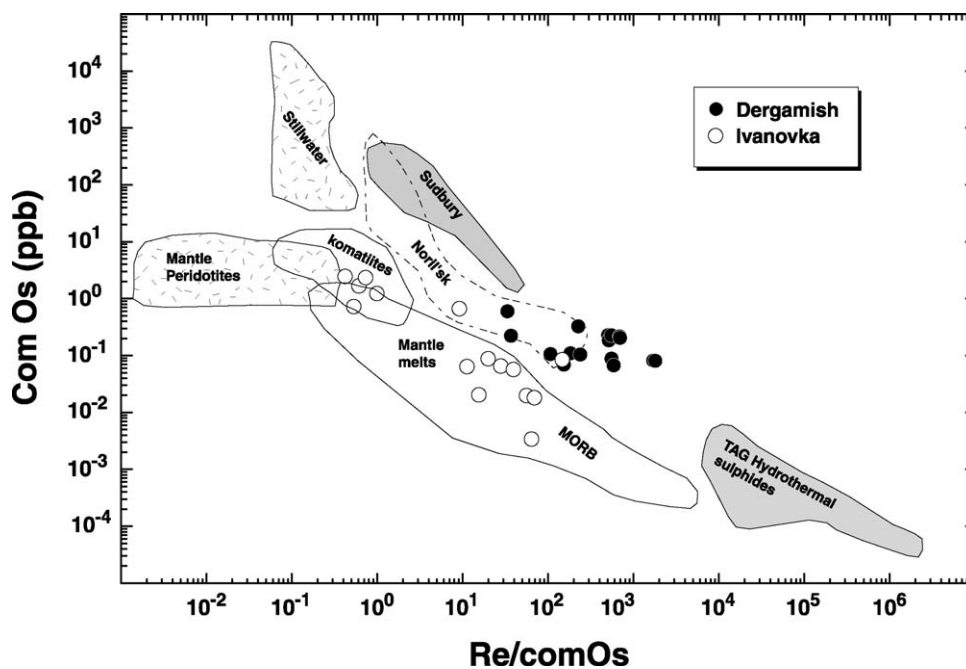

Fig. 6. Plot of common Os (ppb) against Re/Os ratio for the Dergamish and Ivanovka massive with mafic and ultramafic rocks and some mineralised provinces. Stillwater data are from Lambert et al. (1994). Field of TAG hydrothermal sulphides is from Brügmann et al. (1998) and field of Noril'sk sulphides is from Walker et al. (1994). MORB, OIB and Komatiites fields are from references compiled in Shirey and Walker (1998).

common Os concentrations (>1 ppb) and plot close to the field of komatiite lavas in the common Os vs. Re/Os diagram (Fig. 5).

Sulphides (Iv272.6, Iv123) characterised by relatively unradiogenic Os isotope compositions but with high $^{187}Re/^{188}Os$ ratios (than the chondritic mantle ratio of ~ 0.43) attest to recent Re addition or Os loss (Fig. 6). In contrast, serpentinite Iv36 and the chlorite-bearing rock (Iv84) possess both high Re/Os ratios and radiogenic Os isotope compositions, which might indicate that they also experienced old (T_{MA} ~ 280 Ma) fluid metasomatism (see Fig. 6). The most radiogenic sulphide ($^{187}Os/^{188}Os$ ~ 1.5) has probably re-equilibrated with a fluid around that time with a mantle derived-fluid. The Ivanovka ores belong to the same ophiolite as Dergamish, but their multistage mineralisation history differs radically from Dergamish.

The hydrothermal–metasomatic hypothesis for the origin of Ivanovka deposit (Buchkovsky, 1970; Zakharov and Zakharova, 1975) is based on the presence of relics of the host rocks in the ore and on the dependence of the ore composition on the type of host rock (mafic or ultramafic). This model is supported by the increase in Re content in the mafic basal section of the ore field dominated by mafic-derivative chlorite bearing rocks (up to − 126 m in depth) and by the recent model ages obtained for the samples from this basal part (~ 32 Ma). The flat slope of the errorchron reflects the very young age of these sulphide samples or a recent addition of Re. This young age for the massive ores suggests that a recent event has disturbed the Re–Os systematics of the Ivanovka deposit, which could be related to a mobilization of Re in oxidized fluids.

Superficially, the ore texture and the mineral assemblage (pyrrhotite, chromite, pentlendite) bears some similarities with magmatic sulphide ores formed as a result of sulphide immiscibility in silicate magma such as in Noril'sk (Walker et al., 1994). Immiscible sulphides are very efficient collectors of the ore metals or PGE such as Re and Os. However, in the case of Ivanovka, the low Re content suggests a different process.

The appearance of pyrrhotite ore is the result of the increase of temperature and changes in the chemical potentials of O_2, S_2 and CO_2 and overall suggests more reducing conditions than at Dergamish. In these conditions, pyrrhotite and chalcopyrite formed rather than pyrite. It is possible that the lower Re contents in the Ivanovka sulphides compared with the Dergamish sulphides also reflect a lower Re mobilization in the hydrothermal fluids because of more reducing conditions.

The mantle origin of Ivanovka ores are supported principally by the preservation of unradiogenic Os isotopes ratios (samples with $^{187}Os/^{188}Os$ between 0.119 and 0.127) and by the mean Pb isotope compositions of the ores (Ershov and Prokin, 1992; Tessalina, unpublished data) indistinguishable from depleted upper mantle values (17.24 and 15.42 for $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$, respectively).

The ubiquitous traces of chromite in the high-temperature metasomatic ores can be considered as refractory vestiges of the former magmatic assemblage in the metasomatised ultramafic host-rock. At Ivanovka, the significant Ni-enrichment in massive ore is possibly related to a long-lived interaction between hydrothermal fluids and ultramafic host rock in the sub-seafloor environment. A similar sub-seafloor ore deposition has been described on the sediment-covered Escanaba Trough, Southern Gorda Ridge (Zierenberg et al., 1993).

7. Summary

The study of two ores deposits from the MUF suture zone, south Urals, shows that the Re–Os geochronology of sulphide mineralisation can, in some cases, provide reliable age estimates regardless of the complexity of the post-deposition history in the area. The initial Os isotopic ratio for the Dergamish deposit and the preservation of unradiogenic $^{187}Os/^{188}Os$ in some Ivanovka ores suggest a dominantly mantle origin for the PGE found in the ore minerals.

If these sulphide deposits are contemporaneous with the Silurian crystallisation age of mafic–ultramafic rocks, then the Late Devonian Re–Os age is ~ 40 Ma younger than their actual formation and is probably due to a resetting of Re–Os during metamorphism associated with arc-continent collision. This event is also 10–20 Ma younger than the peak

of HP metamorphism. This interval could be the time elapsed between eclogite-facies metamorphism and the retrogression event at blueschist to greenschist facies conditions found to the west of the MUF at Maksyutov complex.

The situation is more complex in the Ivanovka deposit. Ore texture, mineral compositions, elemental (Re, Os, Ni, Co) and isotopic data show that the fluids or magmas involved in ore genesis differ from those of Dergamish. Ivanovka sulphides are most likely the result of multiple-stage fluid and metasomatic interactions, some of which occurred relatively recently.

Appendix A. Simplified mineral description for Dergamish and Ivanovka sulphides

Sample	Description
Dergamish	
D45.8	Disseminated pyrite in chlorite-rich rock.
D46.3	Abundant traces of disseminated chalcopyrite and pyrite in chlorite-rock after gabbro.
D47.5	Chalcopyrite–pyrite fine-grained clastic ore with porous dark grey matrix (pyrite + carbonate).
D50.7	Pyrrhotite–pyrite massive fine-grained ore with shell-like fractures and "shade" of sulphide beds. Talc–carbonate veinlets of up to 3 cm wide and with rare sulphide dissemination cut the ore.
D56.7	Marcasite–pyrite fine to coarse-grained brecciated ore with talc–carbonate matrix.
D59	Coarse-grained ore of marcasite–pyrite clasts (up to 10–20 cm).
D59.7	Idem
D62.5	Idem
D67	Idem
D70	Idem
D71.7	Fine to medium grained clastic ore of pyrite in greenish-gray talc–carbonate cement.
D75	Pyrite–marcasite fine-grained ore with fine chalcopyrite–carbonate–magnetite veinlets.
Ivanovka	
Iv80.5	Pyrrhotite crystals (55%) with pyrite and marcasite inclusions. Chalcopyrite–cubanite lamellae aggregates (2%) occur between pyrrothite crystals. The matrix is composed of chlorite.
Iv84	The matrix consists of chlorite and Mg-saponite–talc aggregate with abundant rutile lamellas. Ore mineralization is presented by abundant pyrrhotite (50%), with magnetite and rare chalcopyrite.
Iv100.1	Fine- to coarse-grained pyrrhotite crystals contain pyrite inclusions. Chalcopyrite (3–5%) occurs in a gangue and between pyrrhotite grains.
Iv123.5	Disseminated pyrrhotite (80%) and pyrite (20%) in chlorite-rock.
Iv126.5	Coarse-grained tabular pyrrhotite crystals. Chalcopyrite, marcasite and pyrite inclusions together with fine fiamme-like pentlandite inclusions occurs in the pyrrhotite matrix.
Iv127.7	Massive chalcopyrite–pyrrhotite ore with numerous inclusions of cobaltite. The gangue is composed by chlorite, Mg-saponite, quartz and carbonate.
Iv148	Massive chalcopyrite–pyrrhotite ore with pyrite inclusions. The rare cobaltite crystals, rounded Co-pyrite and fine fiamme-like Co-pentlandite inclusions occurs in pyrrhotite.
Iv154	Massive chalcopyrite–pyrrhotite ores with rare fragments of cobaltite crystals, fine fiamme-like pentlandite and small Co-pyrite inclusions.
Iv272.6	Chalcopyrite(5–10%)–pyrrhotite (3–7%) ores with cobaltite inclusions (up to 0.05 mm) in both minerals. Mackinawite inclusions in chalcopyrite and fine fiamme-like pentlandite in pyrrhotite.

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