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# The phase system Fe-Ir-S at 1100, 1000 and 800°C

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## ABSTRACT

Phase relations in the dry condensed Fe-Ir-S system were determined at 1100, 1000 and 800°C. Orientational runs were performed at 500°C. Between 1100 and 800°C, the system comprises five sulphides and an uninterrupted field of γ(Fe,Ir). $Fe_{1-x}S$ dissolves 5.8 at.% Ir at 1100°C, 3.4 at.% Ir at 1000°C and 1.0 at.% Ir at 800°C. The solubility of Fe in $Ir_2S_3$, $IrS_2$ and $IrS_{\sim 3}$ increases with decreasing temperature, reaching 2.5 at.% in the latter two sulphides at 800°C. Thiospinel '$FeIr_2S_4$' is non-stoichiometric, from $Fe_{22.3}Ir_{19.8}S_{58.0}$ to $Fe_{18.9}Ir_{23.1}S_{58.0}$, depending on $a_S$ and $a_{Fe}$ i.e. on a phase association. Thiospinel is absent at 800 and 500°C.

**KEYWORDS:** platinum group elements, iridium, phase system iron-iridium-sulphur.

## Introduction

IN connection with the considerable recent interest in the platinum-group deposits with low sulphur contents (Johan, 1995; Johan *et al.*, 1989, 1990) we investigated the potential role of Ir alloys and sulphides as geothermometers for these associations. Our results for the ternary system Fe-Ir-S are reported in the present paper, the low-S portions of the system Fe-Pt-Ir-S will be described in a subsequent publication.

## Previous research

The Ir-Fe system was studied by Raub *et al.* (1964) and summarized by Kubaschewski (1982) and by Swatzendruber (1984). At 1100 and 1000°C continuous γ(Fe,Ir) solid solution exists; at 800°C the situation is complicated by the appearance of α-Fe with up to 3 at.% Ir. Below 625°C, a broad field of hexagonal ε-(Fe,Ir) appears, centred on ~33 at.% Ir and flanked by broad solubility gaps towards the α and γ phases.

The Ir-S system between 880 and 1073°C was investigated by Biltz *et al.* (1937) who found $Ir_2S_3$, $IrS_2$ and $Ir_3S_8$ (the latter with a composition range of 72.1–72.7 at.% S). Wöhler *et al.* (1933) also quote IrS, stable below 750°C in $N_2$ atmosphere. Hulliger (1964) determined the complex structure of orthorhombic $IrS_2$, confirming that Ir is trivalent in this phase. Rietveld refinement of this structure was presented by Jobic *et al.* (1990). The eutectic equilibrium liquid-Ir-$Ir_2S_3$ was found by Fishman *et al.* (1992) to lie at 2000±100°C, and at ~12 wt.% S. In the Fe-Ir-S system, the only published reference appears to be that on the preparation of thiospinel $FeIr_2S_4$ by Hulliger (1968). The mineralogy of iridium is usually characterized by Pt-Ir and Ir-Os alloys, together with cubic irarsite (Ir,Ru,Rh,Pd)AsS and monoclinic iridarsenite $(Ir,Ru,Pt,Os)As_2$. Several sulphides of Ir have been described, either from Cu-rich associations or from those with ferroplatinum. Unnamed $(Ir,Ru,Pt,Os)S_2$ was described by Toma and Murphy (1977). Cubic xingzhongite (Yu *et al.*, 1974) is $(Ir_{0.43}Cu_{0.28}Rh_{0.13}Fe_{0.08}Pd_{0.07}Pt_{0.04}Os_{0.03})_{\Sigma=1.06}S_{0.94}$, i.e. $Me_{16.9}S_{15}$, potentially close to the phase $Ir_{17}S_{15}$ proposed in the present study. Kashinite $(Ir,Rh)_2S_3$ (orthorhombic, isotypic with $Ir_2S_3$ and $Rh_2S_3$) has been found in several deposits (Begizov *et al.*, 1985; Slansky *et al.*, 1991; Augé and Legendre, 1992; Cabri *et al.*, 1996). Inaglyite $PbCu_3(Ir,Pt)_8S_{16}$ and cuproiridsite $(Cu,Fe)(Ir,Pt,Rh)_2S_4$ were described by Rudashevskii *et al.*

(1984,1985). At present, cuproiridsite is known from a number of deposits (Cabri *et al.*, 1996). Analyses of a potential Fe-Ir thiospinel were published by Dmitrenko (1994).

## Experimental

One hundred and thirteen 100 mg charges were weighed out from pure chemicals (Fe rod, Johnson-Matthey Ltd., 15–20 ppm metallic impurities; Ir powder, Johnson-Matthey Ltd., 99.995% (metal basis), and elemental sulphur, Fluka puriss., 99.999%). Annealing times in evacuated silica glass tubes were 2 to 5 weeks, with one homogenization. Quenched charges were examined texturally and by microprobe analyses. Composition estimates in the following sections are averages of multiple microprobe measurements, each with a narrow analytical spread. The Fe-*K*α, S-*K*α and Ir-*L*α analytical lines were used, with $CuFeS_2$ and Ir metal as standards. Further experimental details can be found in Makovicky and Karup-Møller (1993) and subsequent publications. Microprobe results from all experimental runs (Table 1) have been deposited; copies are available from the Principal Editor on request.

### *Phase relations at 1100°C*

At this temperature, four binary sulphides, one ternary thiospinel, two sulphide melts, and Fe-Ir alloys are present in the condensed dry Fe-Ir-S system (Fig. 1). Five ternary and five binary

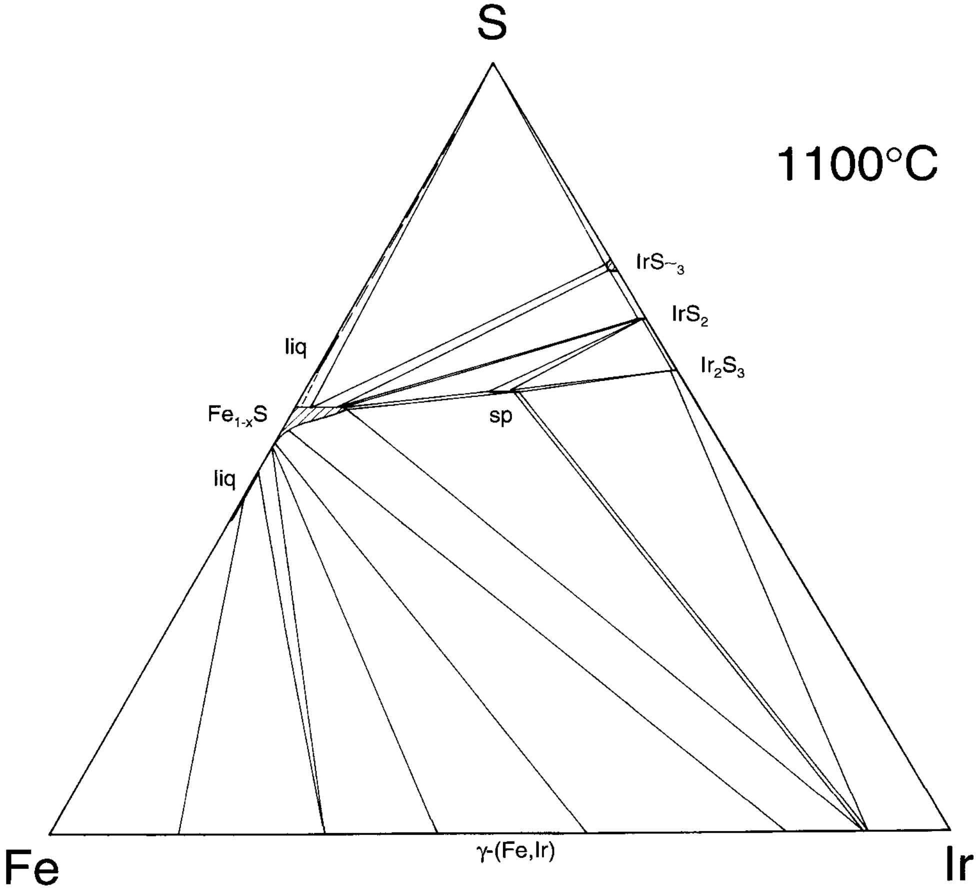

FIG. 1. The condensed phase system Fe-Ir-S at 1100°C.

associations involving $Fe_{1-x}S$ dominate the system. The Fe-rich sulphide melt shows the composition range 43.7–46.5 at.% S; Ir solubility is <0.05 at.% (in most cases no Ir was detected). The range of alloys associated with these changes in the melt composition is 85.9–72.6 (or even 69.4) at.% Fe, with no S detected. Alloys richer in Fe than 85.9 at.% Fe associate with melts with ~43.7 at.% S. On the other end of the melt range, in association with Ir-free pyrrhotite and alloy (69.4 at.% Fe), the melt contains no more than 0.03 at.% Ir.

For the two-phase field alloy-pyrrhotite (po), the following pairs are typical:

$Fe_{49.9}Ir_{0.02}S_{50.1}$-$Fe_{57.0}Ir_{43.0}$
$Fe_{49.4}Ir_{0.02}S_{50.6}$-$Fe_{40.6}Ir_{59.4}$
$Fe_{47.0}Ir_{0.6}S_{52.4}$-$Fe_{18.3}Ir_{81.7}$,

followed by the three-phase association po($Fe_{38.7}Ir_{5.8}S_{55.5}$)-thiospinel ($Fe_{19.3}Ir_{22.9}S_{57.8}$)-alloy ($Fe_{9.7}Ir_{90.3}$).

The thiospinel (sp) is involved in further three-phase associations:

(a) sp ($Fe_{18.9}Ir_{23.1}S_{58.0}$)-alloy ($Fe_{9.2}Ir_{90.8}$)-$Ir_2S_3$ ($\leqslant$0.4 at.% Fe)

(b) sp($Fe_{20.1}Ir_{22.5}S_{57.3}$)-$Ir_2S_3$ (0.5 at.% Fe)-$IrS_2$, and

(c) sp ($Fe_{22.3}Ir_{20.5}S_{57.2}$)-$IrS_2$ (~0.5 at.% Fe)-po ($Fe_{39.7}Ir_{5.8}S_{54.5}$)

There exist two ternary associations at elevated S contents:

(a) po ($Fe_{39.7}Ir_{4.8}S_{55.5}$)-$IrS_2$ ($\leqslant$0.8 at.% Fe)-$IrS_{\sim 3}$ ($Ir_{26.2}Fe_{0.8}S_{73.0}$) and,

(b) po ($Fe_{43.3}Ir_{1.8}S_{54.9}$)-$IrS_{\sim 3}$ (0.6 at.% Fe)-elemental S.

The S contents of reliable individual analyses of $IrS_{\sim 3}$ lie between 73.0–74.3 at.% S (average is 73.6 at.% S). This range is broader than for $IrS_2$ or $Ir_2S_3$ and suggests the possibillity of a variable Me/S ratio in this compound.

### *Phase relations at 1000°C*

At this temperature, the Fe-Ir-S system (Fig. 2) has the same topology as at 1100°C. The Fe-rich sulphide melt centred on the composition $Fe_{56.1}Ir_{0.02}S_{43.9}$ associates with alloy $Fe_{93.3}Ir_{6.7}$ and troilite $Fe_{50.0}Ir_{<0.01}S_{50.0}$. It is the only case where the alloy is present as small, well developed crystals; elsewhere it is present as pseudormorphs of the very fine-grained Ir reagent. In spite of this, all alloy compositions are well equilibrated, giving narrow composition ranges.

Typical composition pairs for the binary association $Fe_{1-x}$ S-alloy are as follows:

$Fe_{50.3}Ir_{0.02}S_{49.7}$-$Fe_{89.4}Ir_{10.6}$
$Fe_{50.2}Ir_{0.02}S_{49.8}$-$Fe_{83.8}Ir_{16.2}$
$Fe_{49.9}Ir_{0.02}S_{50.1}$-$Fe_{77.5}Ir_{22.5}$
$Fe_{48.7}Ir_{0.04}S_{51.3}$-$Fe_{50.5}Ir_{49.5}$
$Fe_{48.4}Ir_{0.06}S_{51.6}$-$Fe_{34.2}Ir_{65.8}$
$Fe_{46.6}Ir_{0.74}S_{52.7}$-$Fe_{17.3}Ir_{82.7}$

and, finally, the three-phase association

po ($Fe_{43.0}Ir_{3.4}S_{53.6}$)-alloy $Fe_{11.2}Ir_{88.7}$-thiospinel ($Fe_{19.7}Ir_{23.2}S_{57.1}$ ).

Thiospinel $Fe_{19.3}Ir_{22.5}S_{58.2}$ is involved in yet another ternary association with alloy $Fe_{10.6}Ir_{89.4}$ and $Ir_2S_3$ (0.3–0.4 at.% Fe).

Associations with medium S contents involve $Fe_{1-x}S$ with the highest Ir contents:

(a)$Fe_{1-x}S$ ($Fe_{41.4}Ir_{3.4}S_{55.2}$)-thiospinel ($Fe_{22.3}Ir_{19.8}S_{58.0}$)-$IrS_2$ ($Fe_{2.5}Ir_{30.7}S_{66.9}$).

and

(b)$Fe_{1-x}S$ ($Fe_{42.2}Ir_{2.6}S_{55.3}$)-$IrS_2$ ($Fe_{0.9}Ir_{31.8}S_{67.3}$)-$IrS_{\sim 3}$ ($Fe_{0.7}Ir_{>28.7}S_{<70.5}$)

At high S contents, the broad two-phase association po-$IrS_{\sim 3}$ is followed by the ternary $Fe_{1-x}S$ ($Fe_{42.6}Ir_{2.0}S_{55.4}$)-$IrS_{\sim 3}$ ($Fe_{0.5}Ir_{25.1}S_{74.4}$)-sulphur and binary $Fe_{1-x}S$-S.

### *Phase relations at 800°C*

Phase relations are simplified because of the disappearance of the thiospinel and the sulphide liquid. All three-phase associations involve $Fe_{1-x}S$ (Fig. 3).

The alloy participates in the three-phase association $Fe_{1-x}S$ ($Fe_{46.3}Ir_{0.87}S_{52.8}$)-alloy ($Fe_{12.0}Ir_{88.0}$)-$Ir_2S_3$ ($Fe_{1.0}Ir_{41.8}S_{57.2}$). At lower S fugacities, it is replaced by the binary association $Fe_{1-x}$ S-alloy with typical pairs

$Fe_{49.3}Ir_{0.04}S_{50.7}$-$Fe_{83.5}Ir_{16.5}$
$Fe_{49.2}Ir_{0.14}S_{50.7}$-$Fe_{65.5}Ir_{34.4}$
$Fe_{48.5}Ir_{0.07}S_{51.5}$-$Fe_{35.4}Ir_{64.6}$

In the two-phase association alloy-$Ir_2S_3$, about 6 at.% Fe in the alloy associate with approximately 0.3 at. % Fe in $Ir_2S_3$.

The ternary associations with moderate-to-high S contents are:

(a)$Fe_{1-x}S$($Fe_{44.9}Ir_{0.9}S_{54.2}$)-$Ir_2S_3$(0.3 at.% Fe)-$IrS_2$(2.4 at.% Fe)

(b)$Fe_{1-x}S$($Fe_{44.3}Ir_{1.0}S_{54.7}$)-$IrS_2$ ($Fe_{0.4}Ir_{32.6}S_{67.0}$)-$IrS_{\sim 3}$($Fe_{0.6}Ir_{26.9}S_{72.5}$)

(c)$Fe_{1-x}S$($Fe_{44.9}Ir_{0.2}S_{54.9}$)-$IrS_{\sim 3}$(~$Fe_{2.5}Ir_{24.7}S_{72.8}$)-sulphur.

### *Note on phase relations at 500°C*

The reactivity of Ir in the Fe-Ir-S system at 500°C is so low that even total annealing of 5 weeks did

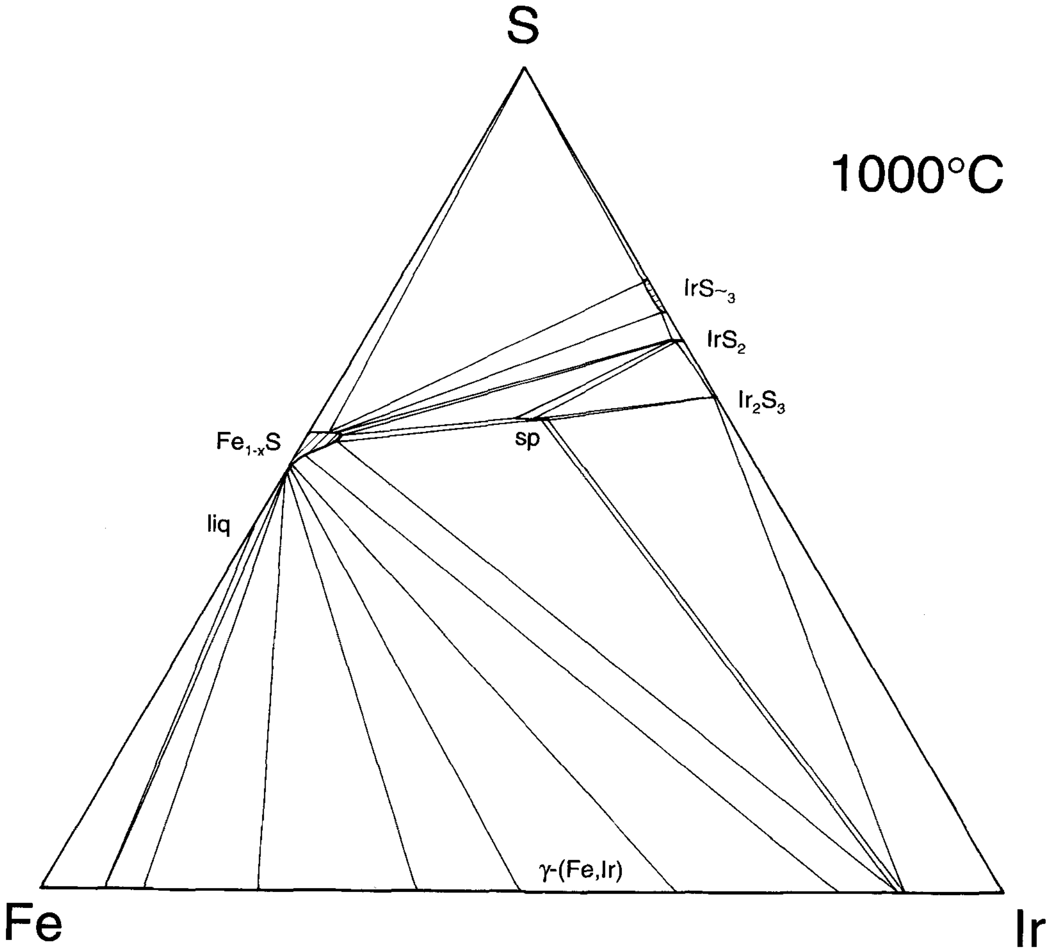

FIG. 2. The condensed phase system Fe-Ir-S at 1000°C.

not produce charges with grain size sufficient for reliable microprobe analyses. The following tentative suggestions can be made: (a) Pyrite appears to dominate all medium-to-high sulphur associations; suggestions for the presence of $Ir_2S_3$ and $IrS_2$ exist. (b) There are very strong indications for the stability of $Ir_{17}S_{15}$ in the association pyrite (with Ir present systematically at the level of 0.1–0.2 at.%)-$Ir_{17}S_{15}$ (0.2–0.5 at.% Fe)-alloy ($\ll$1 at.% Fe). (c) There is an indication of a three-phase assemblage, pyrite (~0.15 at.% Ir)-$Fe_{1-x}S$ ($\leqslant$0.2 at.% Ir)-alloy (~1.6 at.% Fe).

The $Fe_{1-x}S$-alloy assemblage has been proven for the alloy compositions with 19 to 47 at.% Fe, with scattered data to 90 at.% Fe. It involves po with at most trace amounts of Ir.

## Composition ranges

The solubility of Ir in $Fe_{1-x}S$ depends on S fugacity. At all investigated temperatures it is practically nil for stoichiometric FeS and increases towards S-rich associations. At 1100°C it culminates at 5.8 at.% Ir for the association $Fe_{1-x}S$-thiospinel-$IrS_2$; at 1000°C it culminates at 3.4 at.% S for the same association. At 800°C it culminates for the association $Fe_{1-x}S$-$IrS_2$-$IrS_{\sim 3}$ as 1.0 at.% Ir. The solubility of Fe in iridium sulphides is given in Table 2.

The composition range of the thiospinel '$FeIr_2S_4$' deserves special attention. At 1100 and 1000°C, the only examined temperatures at which it was detected, it does not assume the stoichio-

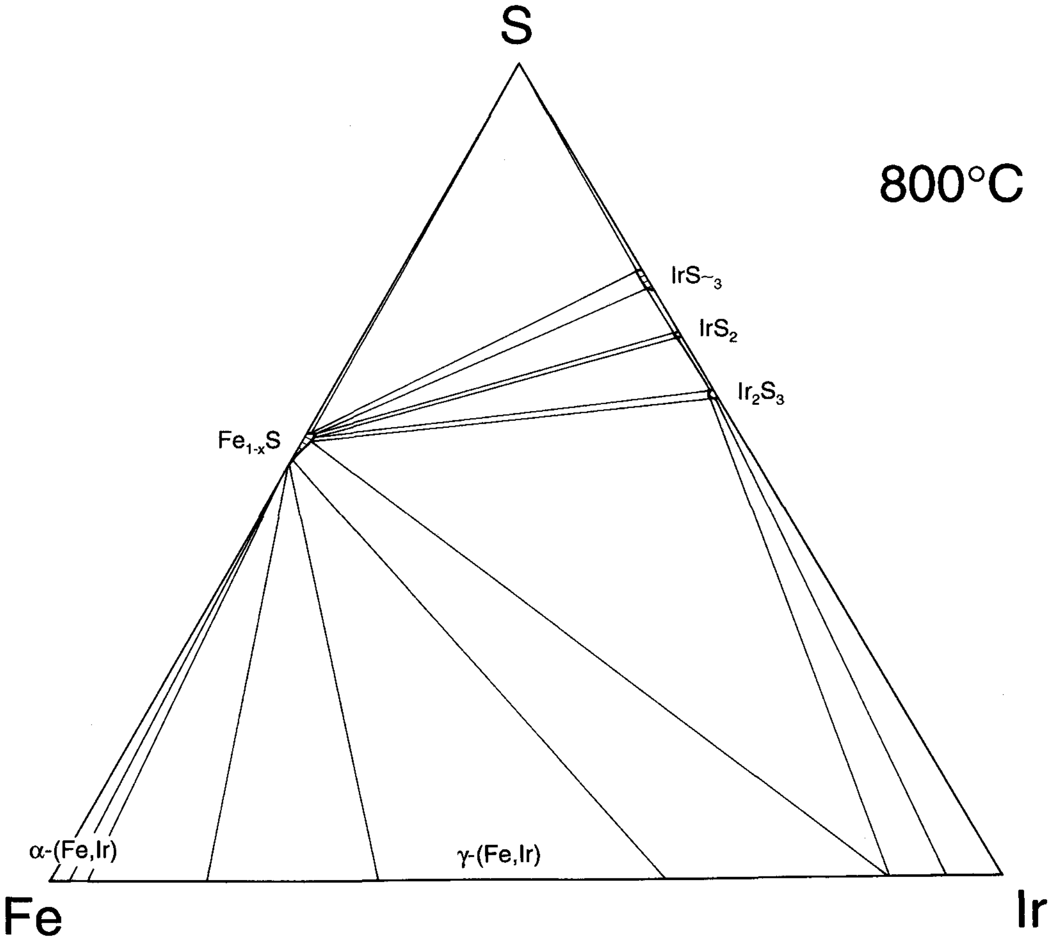

FIG. 3. The condensed phase system Fe-Ir-S at 800°C.

metric composition $FeIr_2S_4$ ($Fe_{14.3}Ir_{28.6}S_{57.1}$). At 1100 and 1000°C [the 1000°C values are in square brackets] for S- and Fe-poor assemblages the Fe/Ir ratio is 0.818 [0.858] instead of the theoretical ratio of 0.5; for S-poor, Fe-rich associations which involve $Fe_{1-x}S$ it is 0.843 [0.848] but for the 'S-rich' association with $Fe_{1-x}S$ and $IrS_2$ it is 1.088 [1.125]. The Fe-poor, S-rich association spinel-$Ir_2S_3$-$IrS_2$ has this ratio equal to 0.893 at 1100°C. The first case mentioned above can be expressed as containing 17.3 [19.3] % of the $Fe_3S_4$ end-member, the rest being the pure ideal $FeIr_2S_4$ end-member. The percentage of iron thiospinel ('greigite') end-member in the Fe-Ir thiospinel from the other above mentioned associations is 18.6 [18.8] mol.% and 28.2 [29.4] mol.%, respectively, the last case mentioned being 20.8 mol.% $Fe_3S_4$. These results were confirmed by the runs in the Fe-Ir-Pt-S system, where similar composition ranges, with maximum 2.2 at.% Pt were observed (Makovicky and Karup-Møller, in prep.).

TABLE 2. Solubility limits for minor elements (at. %)

| Phase | Temperature | | |
|---|---|---|---|
| | 1100°C | 1000°C | 800°C |
| $Fe_{1-x}S$ | 5.8 Ir | 3.4 Ir | 1.0 Ir |
| $Ir_2S_3$ | 0.5 Fe | 0.3–0.4 Fe | 1.0 Fe |
| $IrS_2$ | ≤0.8 Fe | 2.5 Fe | 2.4 Fe |
| $IrS_{\sim 3}$ | 0.8 Fe | 0.7 Fe | 2.5 Fe |

The closest natural analogue to '$FeIr_2S_4$' was reported by Dmitrenko (1994) from the lherzolite Tamvatney massif, Koryak Mountains, E. Siberia. The analysed thiospinels gave compositions $(Fe_{12.1}Cu_{5.5})(Ir_{12.8}Rh_{2.6}Pt_{1.1}Ni_{8.1})S_{58.0}$ (the 'Fe/PGE' ratio equal to 0.72), $(Fe_{6.7}Cu_{6.5})(Ir_{19.0}Rh_{1.7}Pt_{3.6}Os_{0.2}Ni_{3.3})S_{58.8}$ (ratio equal to 0.48), and $(Cu_{13.0}Fe_{0.3})(Pt_{12.4}Ir_{7.3}Rh_{6.8}Os_{0.2})S_{59.3}$ (ratio of 0.49), i.e. from cuprian-nickeloan '$FeIr_2S_4$' to ferroan cuproiridsite and Ir-Rh malanite. Small grain size prevented closer investigation of these phases which occur associated with laurite, irarsite, (Ru,Os,Fe) and pentlandite.

The phase $IrS_{\sim 3}$ represented analytical problems at all temperatures. Conservative estimates of its S range were accepted.

Microprobe estimation of the composition of sulphur rich melt at 1100°C yields reliable results only for the Fe/Ir ratio. In order to check the effects of sulphur escape during retrograde boiling, a series of charges was prepared without Ir with 56, 57, 58 and 70 at.% S and annealed at 1100°C. The S microprobe estimates obtained were those for S in pyrrhotite, increasing from 53.6 to 54.2 at.% over the charge series. Thus, the microprobe data on M/S ratios from charges with S-rich melts which underwent sulphur boil-off are unreliable and we have to rely upon the published values of ~60 to 65 at.% S in the Fe-S melt. No measurable extension of this melt into the Ir-Fe-S ternary was observed.

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