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Gorbachev N.S., Kostyuk A.V., Nekrasov A.N., Gorbachev P.N., Sultanov D.M. Melting and phase relations in the basalt-FeS-Fe-C system at P= 4 GPa, T= 1400°C: Re behavior at FeS-FeC liquation of a Fe-S-C melt. UDC: 550.4.02

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Abstract. During partial melting of the graphite-saturated Fe–S–C system with the addition of trace elements at P = 4 GPa, T=1400°C, the liquid phases are represented by immiscible Fe–S (Ms) and Fe–C (Mc) melts, which give Fe-sulfide matrix with inclusions of Fe-C globules coexisting with relics of the original Re and multiphase microcrystalline restite. Re is predominantly concentrated in the mc melt, with $DMc/Ms \sim 10$. At a Re concentration of Mc > 11 wt.%, saturation of the Mc melt of Re is observed with precipitation of the Fe-Re phase containing up to 25 wt.% Re. The relics of the original rhenium in the Ms melt of Fe-Re composition coexist with the Fe phase formed as a result of the reduction of Fe^{-2} Ms by rhenium during the red-ox reaction according to the scheme: FeS (Ms) + Re = Fe + ReS (Ms) or ^{+2}Fe (Ms) + 2e = ^{0}Fe (Mc), ^{0}Re (Mc) − 2e = ^{+2}Re (Ms). Fractionation of Re relative to Os is observed when distributed between Mc-Ms melts with distribution coefficients Kd Re/Os (Mc-Ms) $\sim$ 9. This effect will lead to a shift in the Re/Os ratio and the Re-Os system of isotopes based on the β-decay of ^{187}Re up to ^{187}Os in environments with Mc-Ms layering.

Keywords: metal, sulfide, silicate, liquation, experiment, distribution of Re

Melting and phase relationships in the basalt–FeS–Fe–C system are of interest in connection with the problems of early differentiation of cosmic bodies, the phase composition of meteorites, as well as magmatic iron–sulfide deposits, since in the presence of carbon the sulfide melt separates into Fe – metallic (Mc) and Fe–sulfide (Ms) melts, immiscible with silicate ones. Previously, based on models of homogeneous accretion of the Earth and impact melting of its matter, the early differentiation of the Earth's matter with the formation of the Fe core and silicate mantle was associated with the separation of metallic iron melts from the silicate melt (Sorokhtin, Ushakov, 1991; Halliday, Wood, 2009). However, it turned out that during the separation of the metal component during the formation of the core, the content of high-siderophile elements (HSE) in the mantle is significantly higher than it should be, based on the equilibrium of the silicate melt with the Fe-metal during its separation (Li, Agee, 1996).

Meanwhile, based on the chondrite composition of the primary matter of cosmic bodies, similar in composition to carbonaceous chondrites, containing up to 15 wt.% Fe-FeS (Mc Donougf, Sun, 1995), the triple Fe-S-C system with immiscibility between Mc and Ms melts.

Phase relationships and distribution of trace elements in the Fe-S-C system are also of interest in connection with the problems of the genesis of magmatic sulfide deposits in the Norilsk region. The possibility of the existence of FeC-FeS liquation during their formation follows from the peculiarities of the geological setting (Gorbachev et al., 2021). When emplaced, the hypabyssal ore-bearing intrusions of the Norilsk region broke through a thick, up to 15 km, platform cover, many of whose rocks are enriched not only in sulfur, but also in carbon (carbonaceous matter, oil and gas bearing horizons). If assimilation by melts of ore-bearing intrusions of sulfur from the rocks of the platform cover is possible, which is confirmed by the isotope composition of sulfur in sulfides (δS^{34} + 8-12‰), then carbon assimilation is quite possible, and as a result, FeC-FeS segregation of sulfide melt during carbon contamination.

The paper considers some features of the phase relationships and behavior of rhenium, osmium and platinum in the basalt-FeS-Fe-C system at 4 GPa, 1400°C.

The experiments were carried out at the IEM RAS on an anvil-and-hole setup according to the multiampoule quenching technique (Gorbachev, 1990). The temperature was measured with a Pt30Rh/Pt6/Rh thermocouple, and the pressure at high temperatures was calibrated using the quartz–coesite equilibrium. The accuracy of temperature and pressure determination is estimated at ± 10ºC and ± 1 kbar (Litvin, 1991). The initial sample consisted of silicate (glass of magnesian basalt) and ore (pyrrhotite - 58 wt.%, Fe - 36 wt.%, carbon black - 6 wt.%) fractions in a ratio of 1:2 with the addition of metallic Re, Os and Pt.

The quenched sample consisted of silicate and ore parts. The silicate part is consist of products of partial melting of magnesian basalt, represented by restite Grt-Cpx composition and silicate glass of ferrobasalt composition in the form of intergranular melts between Grt and Cpx and massive precipitates among sulfides during the injection of silicate melt. Garnet alm_{60}–pyr_{20}–$gros_{20}$ composition $X_{Mg} = 0.42$, $X_{Ca} = 0.23$, contains ≤ 1 wt % TiO_2 and Cr_2O_3. Clinopyroxene of diopside-hedenbergite composition $(Ca_{0,6}Mg_{0,5}Fe_{0,4})(Al_{0,3}Na_{0,1})Si_2O_6$ coexists with a silicate melt of ferrobasalt composition.

Table 1. Compositions of coexisting sulfide phases in the ore part of the sample

Phase	S	Fe	Ni	Co	Re	Os	Pt
Microcrystalline restite matrix							
1	27.04 ± 1.04	71.67 ± 1.22	0.43 ± 0.14	0.77 ± 0.11	-	0.77 ± 0.41	0.67 ± 0.38
2	33.97 ± 2.75	62.51 ± 3.03	0.22 ± 0.12	-	-	-	-
3	-	88.01 ± 1.61	-	-	8.88 ± 1.49	-	-
4	-	32.57 ± 4.59	0.13 ± 0.06	-	65.92 ± 4.69	1.80 ± 0.37	-
5	-	86.19 ± 1.35	0.39 ± 0.25	-	11.58 ± 2.26	-	-
Massive sulfides							
6	26.68 ± 0.56	72.18 ± 0.80	0.40 ± 0.12	0.80 ± 0.18	0.79 ± 0.45	0.36 ± 0.06	0.63 ± 0.10
7	10.80 ± 3.69	88.34 ± 3.38	0.49 ± 0.08	-	0.47 ± 0.21	≤ 0.17	0.17 ± 0.04
8	1.45 ± 0.49	88.18 ± 1.69	0.37 ± 0.15	1.28 ± 0.16	9.96 ± 1.49	0.54 ± 0.16	0.39 ± 0.22
9	0.89 ± 0.08	84.74 ± 1.44	0.47 ± 0.12	-	11.60 ± 1.48	1.92 ± 0.54	0.65 ± 0.10
10	0.10 ± 0.06	71.69 ± 0.83	0.29 ± 0.13	-	27.25 ± 0.76	0.96 ± 0.35	≤ 0.10
11	1.01 0.63	90.34 ± 1.20	0.39 ± 0.08	-	8.01 ± 1.20	0.31 ± 0.07	≤ 0.10
Rhenium relics in massive sulfides							
12	-	32.57 ± 4.59	0.13 ± 0.06	-	65.92 ± 4.69	1.80 ± 0.37	-
13	1.42 ± 0.85	88.73 ± 1.69	0.36 ± 0.20	-	8.86 ± 1.99	-	-

Note: Microcrystalline restite matrix: 1 – bulk composition; 2 - sulfides; 3 – Fe-metal phase; 4 - relics of rhenium; 5 – Fe-metal phase at contact with rhenium relics. Massive sulfides: 6 – bulk composition; 7 – quenching metal phase; 8 – bulk composition of Fe-metal globules without inclusions; 9 – bulk composition of Fe-metal globules with rhenium phase inclusions; 10 – rhenium phase inclusions in Fe-metal globules; 11 – matrix of Fe-metal globules with rhenium phase inclusions. Rhenium relics in massive sulfides: 12 – rhenium relics; 13 – Fe-metal phase at contact with rhenium relics.
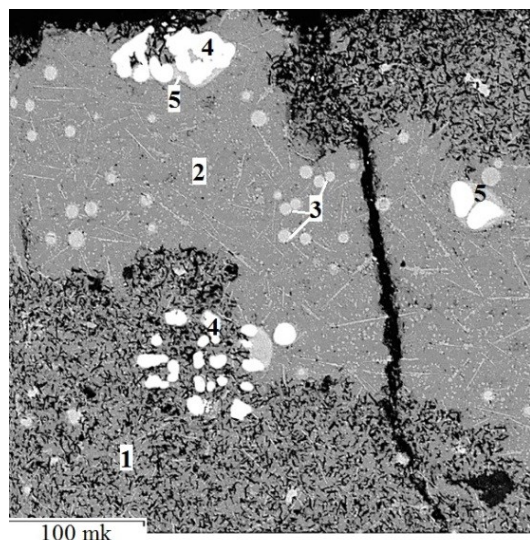
Fig. 1. BSE micrograph of the ore part of the quenched sample, characterizing the phase relationships: 1) microcrystalline matrix, 2) massive sulfides, 3) Fe-metal globules, 4) rhenium relics, 5) Fe-Re phase at contact with rhenium relics.

The "mineral chaos" of the microcrystalline matrix consists of a mixture of micron-sized particles of a sulfide, metallic composition, with inclusions of relics of rhenium in association with the Fe-metal phase. Bulk composition: Fe - 72 wt.% and S - 27 wt.%, content of Ni, Co, Re, Os, Pt 0.4–0.8 wt.%.

The matrix of massive sulfides contains inclusions of globules of the Fe-metal phase, single-phase, without inclusions and polyphase, with

inclusions of the Fe-Re phase, as well as relics of rhenium in contact with the Fe-metal phase. Its composition, taking into account the hardening phases, corresponding to the composition of the sulfide melt, is characterized by an excess sulfur content relative to troilite, low (0.4–0.8 wt.%) contents of each of the ore elements Ni, Co, Re, Os, Pt.

Table 2. Compositions of Mc and Ms melts, ratios and distribution coefficients of Re/Os and Pt/Os between them.

	Mc	Ms	D $^{Mc/Ms}$
Fe	88,18	72,18	1,22
Ni	0,37	0,4	0,92
Re	9,96	0,79	12,64
Os	0,54	0,36	1,51
Pt	0,39	0,63	0,62
S	1,45	26,68	0,05
Co	1,28	0,80	1,60
Re/Os	18,44	2,2	8,37 (Kd)
Pt/Os	0,72	1,77	0,41 (Kd)

Fe-metal globules are the products of quenching of the Fe-metal melt (Mc), immiscible with the sulfide (Ms) melt, formed during separation (liquation) of the C-containing sulfide melt.

Single-phase Fe-metal globules, corresponding to the composition of the Fe-metal melt coexisting with the sulfide melt, are characterized by high contents of Fe (87–89 wt.%), Re (8–11 wt.%), contain up to 1.3 wt.% Co, about 0.3–0.6 wt.% Ni, Os, Pt.

Polyphase, rhenium-saturated Fe-metal globules, with inclusions of the Fe-Re phase, composition 72 wt.% Fe, 27 wt.% Re, up to 1 wt.% Os, below the detection limit of Pt. The solubility of rhenium in the Ms melt, corresponding to saturation, is more than 10.0 ± 1.5 and less than 11.6 ± 1.5 wt.%, the carbon content, determined by adding the sum of the analysis to 100 wt.%, is about 4 wt.%.

Relics of rhenium occur in a microcrystalline matrix and massive sulfides and are characterized by wide variations in the contents of Re (61–69 wt.%) and Fe (28–36 wt.%), contain up to 2 wt.% Os, below the detection limit of Pt. The Fe metal phase at the contact with rhenium relics contains 86–90 wt.% Fe and 7–10 wt.% Re. The close paragenesis of rhenium relics with metallic Fe in the sulfide matrix is due to redox reactions between the sulfide melt and metallic rhenium with the reduction of the $^{+2}$Fe ion of the sulfide melt to a metallic one: $^{+2}$Fe (Ms) + $2e = ^{0}$Fe (Mc) and the oxidation of metallic rhenium: ^{0}Re (Ms) - $2e = ^{+2}$Re (Ms) to 2 or 4 valence ion.

A sensitive indicator of the processes of accretion of terrestrial planets and the formation of their metallic cores is the distribution of Fe, Co, Ni, Re, Os, Pt between Mc and Ms melts. The fact is that Re, Os, Pt are both strongly siderophile and strongly chalcophile elements, since in the associations silicate (Sil) - Mc melts or Sil - Ms melts, these elements are effectively concentrated in both Mc and Ms melts with separation factors D Mc/Sil and D Ms/Sil reaching 3 or more orders of magnitude (Liu and Fleet, 2001; Bezmen N.I. et al., 1994). In addition, the Mc and Ms distributions of Re, Os, Pt are of interest given the genetic significance of the ^{187}Re/^{187}Os and ^{190}Pt/^{186}Os isotope ratios based on the β-decay of ^{187}Re to ^{187}Os and the α-decay of ^{190}Pt to ^{186}Os during the early differentiation of cosmic bodies and meteorites. According to the same parameters, Fe, Co, Ni are both moderately siderophile and moderately chalcophile elements with D Mc/Sil and D Ms/Sil on the order of $n \cdot 10^2$ (Rajamani and Naldrett, 1978). Explonation of the behavior of these elements during Mc and Ms liquation of a sulfide melt is of interest for understanding the geochemistry of the Mc-Ms liquation in the Fe-S-C system and assessing the chalcophile and siderophile properties of these elements.

Table 2 shows the representative compositions of Mc and Ms melts, separation coefficients of ore elements, and distribution coefficients of Re/Os and Pt/Os between Mc and Ms melts.

In the Re-Os association, rhenium is a more siderophilic element, D Mc/Ms = 12.64 than osmium, D Mc/Ms = 1.51. High values of D (Mc/Ms) Re with respect to D (Mc/Ms) Os and high values of the distribution coefficient Kd (Mc/Ms) Re/Os (8.37) indicate effective fractionation of Re relative to Os during Mc-Ms separation sulfide melt due to the redistribution of Re into the Fe-metal phase. This effect will lead to a decrease in the Re/Os and ^{187}Re/^{187}Os ratios in the coexisting sulfide melt.

In the Pt-Os association, osmium is a siderophile element in terms of the separation coefficients Kd (Mc/Ms) Os and Pt (1.51 and 0.62, respectively), while Pt is a chalcophile element.

Considering the close separation coefficients of Re, Os, and Pt between the silicate, Mc, and Ms melts, it is obvious that their relative concentrations in the silicate melt will be the same in the coexisting Mc and Ms melts.

Co and Ni, according to the same parameters as Re, Os, Pt, are both moderately siderophile and moderately chalcophile elements with D Mc/Sil and D Ms/Sil on the order of $n \cdot 10^2$. The distribution of Co and Ni between Mc and Ms melts is similar to the distribution of Pt and Os. Based on D (Mc / Ms) Co (1.60) and Ni (0.92), the siderophile element is Co,

and the chalcophile element is Ni. However, the values of D (Ms/Ms) for both Co and Ni close to 1 indicate the absence of effective fractionation of Co and Ni in the distribution between Ms and Ms melts in settings with metal sulfide separation in the basalt–Fe–S–C system.

Thus, the behavior of Re, Co, Ni, Os, and Pt during metal-sulfide separation of sulfide melt in the basalt–FeS–Fe–C system is different. Close to 1 D Mc/Ms Co, Ni, Os, and Pt indicate the absence of their noticeable fractionation in the distribution between Mc and Ms melts. At the same time, high values of D Mc/Ms Re indicate efficient fractionation of Re due to redistribution into the Mc melt. Fractionation of Re during metal-sulfide liquation in the basalt–Fe–S–C system will lead to a change in the Re/Os and $^{187}Re/^{187}Os$ ratios in the coexisting silicate, Fe-metal, and Fe-sulfide melts. Minor variations in Pt/Os and $^{190}Pt/^{186}Os$ ratios in coexisting Mc, Ms and Sil melts, indicating the absence of effective fractionation of Os and Pt in the distribution between Mc, Ms and Sil melts and will not significantly change the Pt/Os and $^{190}Pt/^{186}Os$ ratios between coexisting silicate, metallic, and sulfide melts in environments with metal-sulfide liquation.

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Iskrina A.V.[1,2], Bobrov A.V.[1,2,3], Spivak A.V.[2], Kuzmin A.V.[4], Chariton S.[5], Fedotenko T.[6] Dubrovinsky L.S.[7] Postspinel phases at the conditions of the Earth's transition zone and lower mantle. UDC: 549.02

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Abstract. Spinel is a widespread mineral, however, the area of its stability is limited, and at great depths there is a transformation into the so-called post-spinel phases. Phases with structures of calcium ferrite (CF), calcium titanate (CT) and marokite are considered as the main candidates for the role of post-spinel phases. Natural post-spinel phases have a complex composition. Structures with a "marokite" channel can include various cations, e.g. Cr, Al, Mg, Fe, Ca, Ti, Fe, Na, while forming solid solutions. High-pressure post-spinel phases have been found as inclusions in diamonds, meteorites, and impact craters. Experimental studies have determined the conditions of formation, the boundaries of phase transitions and changes in the physical properties of post-spinel phases in various chemical systems over a wide range of pressures and temperatures. In this study we report on natural and experimental post-spinel phases of various structures, their solid solutions and stability areas.

Keywords: post-spinel phases, transition zone, lower mantle, structure, "marokite" channel, phase relations

Spinel is a widespread mineral found in various geological environments. Most spinels decompose to oxides at high pressure (Reid and Ringwood, 1969) or undergo structural phase transitions. Phases with structures of calcium ferrite (CF), calcium titanate (CT) and marokite are considered as the main candidates for the role of post-spinel phases (Decker and Kasper, 1957, Rogge et al., 1998, Giesber et al., 2001). The structures with a centered *Cmcm* (*Bbmm*) and primitive *Pnma* (*Pmcn*), *Pbcm* (*Pmab*) cells are distinguished within this family of topologically related structures with a "marokite" channel formed by six octahedra.

Unfortunately, at present, post-spinel phases, their properties, and the ability to form the series of