

# Crystallization and Stability of Noble Metal Alloys in the Magmatic Process

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**Abstract**—The possibility of existence of noble metal–iron alloys in the magmatic process was estimated on the basis of experimental investigations of noble metal solubility in silicate melts and thermodynamic modeling. It was shown that Fe–Pt and Ir–Ru–Os alloys must be stable in magmatic melts. In contrast, Au-rich alloys cannot be stable in magmatic melts under any conditions. It was shown that the noble metals are incompatible in mineral phases and the bulk analyses of minerals with high contents of platinum-group elements (PGE) that have been reported in the literature can be explained by the contamination of the mineral phases by microinclusions of noble metal alloys. Under certain conditions (low oxygen fugacity and a high concentration of As, Bi, or Sb in the melt), PGE can form liquid compounds with these trace elements, which should facilitate their mobilization by high-temperature fluids.

## INTRODUCTION

The geochemistry of platinum group elements (PGE), as well as the geochemistry of other minor and trace elements, is controlled to a considerable extent by their ability to enter the crystal lattice of rock-forming minerals. Whether the noble metals, whose abundances in the mantle are only 1–7 ppb (McDonough and Sun, 1995), must be completely dissolved in typical minerals of basaltic magmatism (olivine, pyroxenes, plagioclase, and spinel) or they can form their own phases (and if they do, which phases) is the key question of PGE geochemistry.

Furthermore, it is evident that the origin of large and giant deposits of noble metals must be somehow connected with their dissolution, transportation, and redeposition by magmatic melts and/or hydrothermal solutions. Therefore, understanding of the principles of noble metal solubility in magmatic melts and, as a consequence, inferences on the stability or instability of PGE alloys in magmatic rocks can have a significant influence on the development of models for the transportation and deposition of noble metals.

This paper focuses on the behavior of six elements: Pd, Au, Ir, Pt, Ru, and Os.

Two decades ago, Barnes *et al.* (1985) considered the geochemistry of PGE and suggested that the different solubilities of PGE can be responsible for their fractionation in the magmatic process, but these authors also pointed out the lack of experimental data.

A number of experimental studies have been published during the past 10–15 years on the solubility of noble metals in silicate melts (Borisov *et al.*, 1994,

2004; Borisov and Palme, 1995, 1996, 1997, 2000; Borisov and Nachtweyh, 1998; Ertel *et al.*, 1999; Borisov and Walker, 2000; Borisov, 2001; Fortenfant *et al.*, 2003). These studies have been aimed primarily at understanding the behavior of these elements during the accretion and differentiation of the Earth and terrestrial planets.

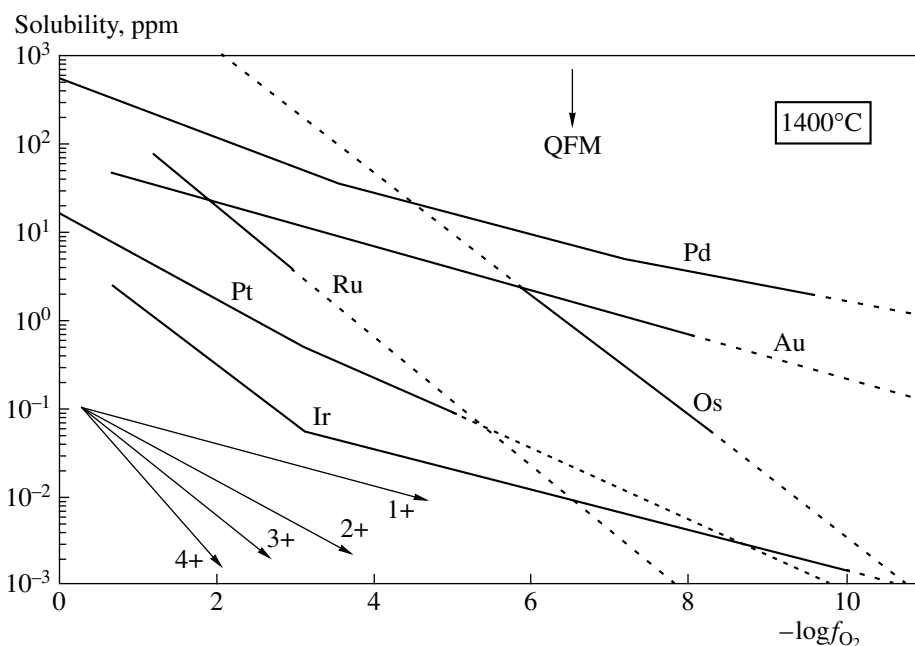
However, the obtained solubility data can also provide insight into the geochemistry of noble metals in the magmatic process. This paper is restricted to low-sulfur melts. In sulfide-bearing magmas, sulfides control the behavior of noble metals because of the high partition coefficients of these elements between sulfide and silicate melt (Bezmen *et al.*, 1994).

## A REVIEW OF EXPERIMENTAL DATA ON NOBLE METAL SOLUBILITY IN A MODEL ANORTHITE–DIOPSIDE MELT

Most experiments on the solubility of noble metals were conducted at 1300–1500°C using an iron-free basalt analog melt of eutectic composition in the anorthite–diopside system. The experimental data for all the metals were recalculated to the same temperature of 1400°C (Fig. 1).

The solubilities of all the metals decrease with decreasing oxygen fugacity, which implies that the noble metals are dissolved in the melts in the ionic rather than the zero-valence form. For each particular metal, the slope ( $k$ ) of the dependency of the logarithm of solubility on  $\log f_{\text{O}_2}$  is constant over a wide range of oxygen fugacity:  $k \approx 1/4$  for Pd, Au, and Ir;  $k \approx 1/2$  for Pt; and  $k \approx 3/4$  for Ru and Os. This implies that  $\text{Pd}^{1+}$ ,  $\text{Au}^{1+}$ ,  $\text{Ir}^{1+}$ ,  $\text{Pt}^{2+}$ ,  $\text{Ru}^{3+}$ , and  $\text{Os}^{3+}$  are the predominant cat-

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**Fig. 1.** Comparison of the solubility of noble metals in *Di-An* melt at 1400°C. Data for alloys were recalculated to pure metals. Experimental intervals and extrapolations are shown by solid and dashed lines, respectively. Ideal slopes for the solubility of metals in various valence states are shown at the lower left.

ions of noble metals in silicate melts. Thus, the apparent valence of the cations is lower than could be expected from the valences of corresponding metals in stable solid oxides:  $\text{IrO}_2$ ,  $\text{PdO}$ ,  $\text{PtO}_2$ ,  $\text{RuO}_2$ , and  $\text{OsO}_2$ . Under very oxidizing conditions, the values of  $k$  for Ir and Pd solubility are higher than 1/4; under reducing conditions,  $k$  for Pd solubility is lower than 1/4. Possible reasons for such a behavior of palladium were discussed by Borisov *et al.* (1994).

The table shows numerical solubility values for various temperatures and three levels of redox conditions: under  $f_{\text{O}_2}$  corresponding to the quartz–fayalite–magnetite buffer (QFM), as well as somewhat more oxidizing (QFM + 2) and more reducing (QFM – 2) conditions. For instance, the following solubility values were obtained at QFM and 1400°C: 10 ppb Ir, 14 ppb Ru, 26 ppb Pt, from 280 ppb to 1.2 ppm Os (depending on the model of Os activity in Ni–Os alloys), 2 ppm Au, and 7 ppm Pd.

#### EQUILIBRIA OF IRON-BEARING MELTS WITH NOBLE METAL–IRON ALLOYS

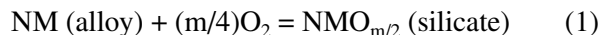
Since the experimental results obtained in model iron-free systems must be applied to natural iron-bearing melts, the possible influence of major oxides, primarily FeO, on the solubility of metals in melt is evaluated.

The experimental data (Borisov and Palme, 1997, 2000; Borisov *et al.*, 2004) have shown that the major and minor components of natural magmatic melts exert an influence on the solubility of noble metals, but this

effect is small compared with those of temperature and, especially, oxygen fugacity. As a first approximation, this influence can be ignored in applying our experimental results to natural processes.

The only component of natural melts that cannot be ignored is iron oxide. Many PGE show a strong affinity for iron. The existence of pure PGE in natural basalts is therefore impossible, and the incorporation of iron in PGE must inevitably decrease the solubility of these elements in equilibrium melts.

The thermodynamics of equilibria between iron-bearing melts and noble metal–iron alloys (NM–Fe) was discussed in detail by Borisov and Palme (2000), and only the main points are presented here. This equilibrium can be described by the reactions



and



If the solubility of a noble metal in iron-free melt ( $C_{\text{NM}}$ ) and its activity in the alloy equilibrated with the iron-bearing melt ( $a_{\text{NM}}$ ) are known, the following expression holds:

$$\begin{aligned} C_{\text{NM}} (\text{Fe-bearing melt}) \\ = a_{\text{NM}}(\text{alloy}) \times C_{\text{NM}}(\text{iron-free melt}). \end{aligned} \quad (3)$$

Thus, the solubility of a noble metal in iron-bearing melt can be calculated in the following manner:

Comparison of noble metal solubilities in the eutectic melt of the anorthite–diopside system

T, °C			1200	1250	1300	1350	1400	1450	1500
QFM + 2	Au	ppm	0.4	1	2	5	6	7	8
	Pd		3	6	9	15	23	34	51
	Os		–	–	–	–	229	–	–
	Ir	ppb	10	14	18	23	29	37	45
	Ru		28	57	114	216	390	700	1370
	Pt		40	59	85	120	160	220	610
QFM	Au	ppm	0.1	0.3	0.7	1.5	1.8	2.1	2.5
	Pd		1.6	2.4	3.5	5	7	10	13
	Os		–	–	–	–	1.2	–	–
	Ir	ppb	4	5	6	8	10	13	16
	Ru		1	2	4	7	14	24	48
	Pt		6	9	13	19	26	35	97
QFM – 2	Au	ppm	0.04	0.1	0.2	0.5	0.6	0.7	0.8
	Pd		0.7	1.1	1.6	2	3	4	6
	Os		–	–	–	–	0.05	–	–
	Ir	ppb	1.2	1.6	2.2	2.8	3.5	4.4	5.4
	Ru		0.03	0.07	0.1	0.3	0.5	0.8	1.7
	Pt		1.0	1.5	2.1	3.0	4.1	5.5	15

Note: QFM is the solid-phase quartz–fayalite–magnetite buffer (Myers and Eugster, 1983); the solubility of pure Os was calculated assuming an ideal behavior of Os in an experimental Ni–Os alloy.

(1) for the given temperature and  $f_{O_2}$ , the solubility of the NM in iron-free melt is calculated using the experimentally established  $T$  and  $f_{O_2}$  dependences;

(2) for the given temperature,  $f_{O_2}$ , and FeO concentration in the melt, the activity of iron in the equilibrium NM–Fe alloy ( $a_{Fe}$ ) is calculated using the available thermodynamic data for the constant of reaction (2) and the activity of iron oxide in the melt;

(3) using the calculated  $a_{Fe}$ , the corresponding  $a_{NM}$  value is determined using various sources of thermodynamic data for binary NM–Fe alloys, for instance (Hultgren *et al.*, 1973);

(4) given the calculated  $a_{NM}$  and  $C_{NM}$  values for iron-free melt,  $C_{NM}$  in the target iron-bearing melt is calculated from Eq. (3).

Thermodynamic data relevant to binary NM–Fe systems; the affinity of various noble metals for iron; the influence of the transition from iron-free melts to iron-bearing ones on the solubility of Au, Pd, Ir, Ru, and Pt; and the stability of noble metal alloys in magmatic melts were discussed in detail by Borisov and Palme (2000).

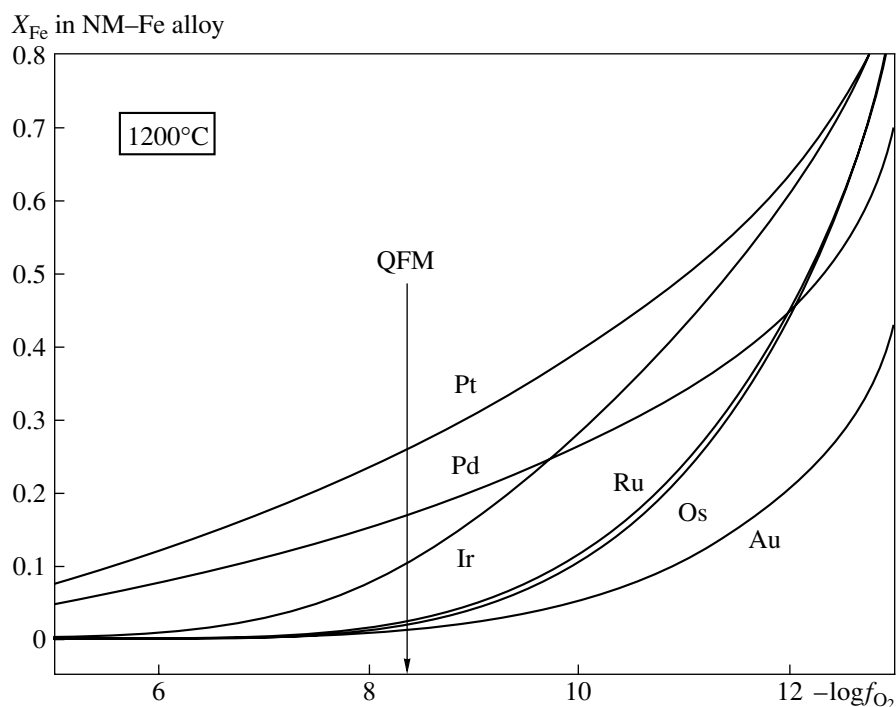
*The affinity of noble metals for iron is very variable* (Fig. 2). As can be seen from this figure, at QFM and 1200°C, metallic Au must accommodate 1 at % Fe (0.3 wt %) from a basaltic melt containing 10 mol % FeO; Ru and Os, about 2 at % Fe (1.2 and 0.6 wt %,

respectively); Ir, 10 at % Fe (3 wt %); Pd, 17 at % Fe (10 wt %); and Pt, 25 at % Fe (9 wt %).

Thus, gold is the only “true” noble metal, absorbing only a very minor portion of iron from the melt over a wide range of oxygen fugacity. Both platinum and palladium absorb considerable amounts of iron from the melt even under oxidizing conditions (about 13 and 9 at %, respectively, at QFM + 2). The behavior of Ru, Os, and Ir is transitional: under oxidizing conditions, they absorb only 0.2 (Os and Ru) and 1.4 at % Fe (Ir), whereas, at QFM – 2, the fraction of iron can be as high as 13–14 at % in Fe–Os and Fe–Ru alloys and even 32 at % in Fe–Ir alloys.

The high affinity of iron for platinum, on the one hand, and the moderate affinity of iron for ruthenium, iridium, and osmium, on the other hand, are reflected in very different iron contents in natural Pt–Fe and Os–Ir–Ru alloys. For instance, Auge and Legendre (1992) presented electron microprobe analyses of PGE minerals in isoferroplatinum nuggets from the alluvium deposits of Eastern Madagascar. Tiny inclusions of Os–Ir–Ru alloys with less than 0.8 wt % Fe were probably in equilibrium with the host isoferroplatinum grains, containing up to 8 wt % Fe (Tables 2 and 3 in (Auge and Legendre, 1992)).

*The solubility of noble metals in iron-bearing melts* is always lower than that determined in experiments with iron-free melts (Eq. (3)), and the difference increases with increasing affinity of iron for the noble



**Fig. 2.** Affinity of noble metals for iron. Concentrations of Fe in NM-Fe alloys in equilibrium with a silicate melt containing 10 mol % FeO.

metal. For instance, the affinity of iron for gold is negligible, and the difference is so small that experimental results obtained for iron-free melts can be directly applied to natural melts without significant errors. In contrast, the difference between the solubilities of platinum and palladium in iron-bearing and iron-free melts is very large.

Figure 3 shows the solubility of platinum, which shows the maximum affinity for iron among the metals considered here. The calculations were performed for a constant temperature of 1400°C. It is evident that, under oxidizing conditions, when only a minor fraction of Fe is incorporated in Pt-Fe alloy in equilibrium with a melt with a certain iron content (10 mol % FeO in the case considered), the difference between platinum solubility in iron-free and iron-bearing melts is insignificant. In contrast, under reducing conditions, the accommodation of considerable amounts of iron in platinum strongly depresses the activity of Pt in the resulting alloy, which must lead to significantly lower Pt solubility in iron-bearing melts compared with iron-free liquids.

#### STABILITY OF NOBLE METAL ALLOYS IN MAGMATIC PROCESSES

In the following discussion, a simplified model will be used for the behavior of noble metals during partial melting.

(1) We do not specify in which phases PGE occur in the mantle. These may be sulfides or native metals. The

bulk concentrations of noble metals in upper mantle rocks are taken from McDonough and Sun (1995).

(2) We consider a 20% melting of the mantle material and assume that such a degree of melting is sufficient for the complete melting of the phases that host the noble metals in the mantle.

(3) It is suggested that all the noble metals are incompatible in the major mantle minerals, i.e.,  $D^{NM}(\text{mineral/melt}) < 1$ . It will be shown below that this is the case.

Now, the possible concentrations of noble metals in primary melts can be compared with the solubility data in order to establish whether particular alloys are stable or not.

**Gold.** According to the calculations, the solubility of Au in iron-bearing melts at 1400°C and  $f_{O_2}$  between QFM + 2 and QFM - 2 decreases from 5.7 ppm to 520 ppb. The abundance of Au in mantle rocks is about 1 ppb, and 20% partial melting will produce liquids containing only 5 ppb Au. This estimate is several orders of magnitude lower than the Au solubility. Consequently, the formation and stability of Au-Fe alloys in the mantle process can be completely excluded.

**Palladium.** A considerable decrease in Pd solubility in iron-bearing natural magmas compared with iron-free model melts can be expected (for instance, by 70% at 1200°C and QFM). The solubility can be further depressed by a decrease in oxygen fugacity. The abundance of Pd in the mantle is about 3.9 ppb; i.e., 20%

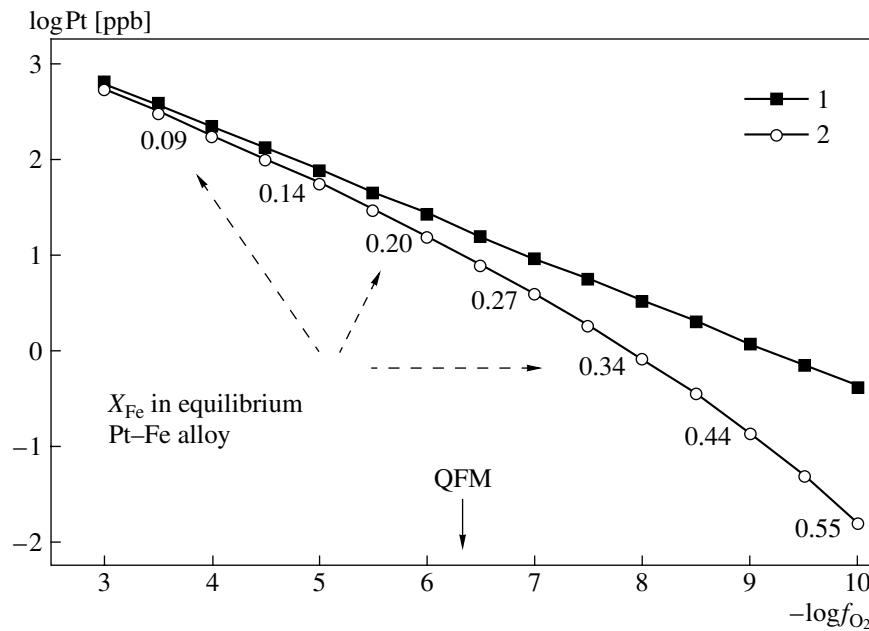


Fig. 3. Comparison of Pt solubility in (1) iron-free and (2) iron-bearing melts with 10 mol % FeO at 1400°C.

partial melting generates a melt with no more than 20 ppb Pd, which is lower than the Pd solubility by about one and a half orders of magnitude. Consequently, the occurrence of Fe–Pd alloys in magmatic melts is also hardly possible.

On the other hand, the precipitation of complex Pd-bearing alloys (e.g., Pt–Pd–Fe) cannot be ruled out. Indeed, Auge and Legendre (1992) reported isoferroplatinum with up to 13 at % Pd.

*Iridium, ruthenium, and osmium.* The behavior of these PGE is fundamentally different from that of gold and palladium. Their abundances in the mantle are 3.2 ppb Ir, 5 ppb Ru, and 3.4 ppb Os. The melt produced by 20% mantle melting must contain 16 ppb Ir, 25 ppb Ru, and 17 ppb Os.

The contents of Ir and Ru are higher than their solubilities even in iron-free melts. The situation with Os is somewhat more complicated because the solubility experiments were performed with Ni–Os alloys rather than with pure Os. Using various solid solution models (Borisov and Walker, 2000), solubilities from 0.3 to 1.2 ppm were obtained for QFM and from 12 to 50 ppb for QFM – 2. If the fraction of Os in the complex alloy is not high, the solubility in equilibrium magmatic melts is additionally decreased by at least an order of magnitude. Thus, it can be concluded that complex Ir–Ru–Os–Fe alloys must be stable in primary magmatic melts because the calculated concentrations of Ir, Ru, and Os in these melts are higher than their solubilities.

The solubilities of Ir and Ru decrease with decreasing temperature (Borisov and Palme, 1995; Borisov and Nachtweyh, 1998). Furthermore, the incompatibility of Ir, Ru, and Os in the crystallizing silicate phases is also

favorable for the crystallization of these metal alloys. They may be too small to settle independently in magma chambers. However, it is reasonable to expect that they will be captured as inclusions in crystallizing minerals (olivine, spinel, etc.).

*Platinum.* The abundance of Pt in the mantle is 7.1 ppb; i.e., primary melts must contain about 35 ppb Pt. This value is comparable with the Pt solubility in iron-free melts at QFM. Since platinum shows the maximum affinity for iron among the PGE, significant Fe incorporation into platinum is inevitable in equilibrium with basaltic melts. This factor must additionally depress the solubility of platinum, which will certainly be lower than 35 ppb. Thus, Fe–Pt alloys must be stable in primary melts.

The solubility of platinum as a function of temperature and oxygen fugacity is well known (Borisov and Palme, 1997). This allows us to evaluate its behavior during crystallization of magmatic melts. Figure 4 shows isopleths of Pt solubility in iron-bearing melts. If oxygen fugacity remains at the level of the QFM buffer equilibrium with decreasing temperature, a decrease in Pt solubility, i.e., crystallization of Pt–Fe alloys, is inevitable. For instance, about 1.7 mm<sup>3</sup> (28 mg) of Pt–Fe alloy will crystallize in 1 m<sup>3</sup> of basaltic melt during cooling from 1360°C (where the QFM curve intersects the 10 ppb isopleth) to 1100°C (where the QFM curve intersects the 1 ppb isopleth).

*Reasons for misinterpretation of PGE behavior.* It is obvious that the very small amounts and minute sizes of crystallizing PGE alloys are not favorable for their independent settling in magma chambers. On the other hand, PGE nuggets can serve as growth centers for sil-

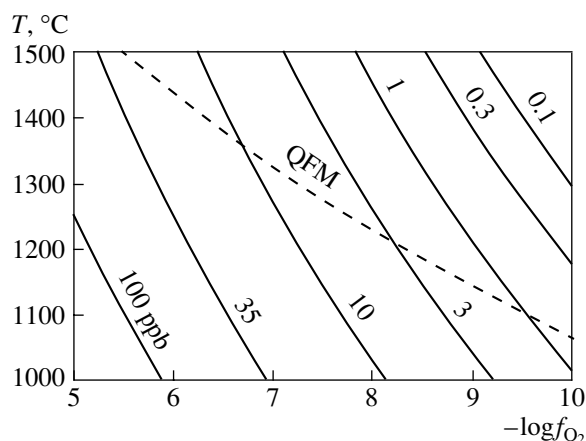


Fig. 4. Isopleths of Pt solubility (ppb) in iron-bearing melts.

icates and oxides (olivine, chromite, etc.). If an investigation of PGE geochemistry in igneous rocks is not accompanied by an analysis of the forms of PGE occurrence in minerals, false conclusions on the compatibility of PGE in minerals are inevitable.

For instance, Brüggmann *et al.* (1987) measured the bulk concentrations of Ir, Ru, and Os in the komatiites of Gorgona Island and observed a correlation between these elements and MgO content. Since MgO variations in komatiites are mainly related to the abundance of olivine in the rocks, these authors used a very simple

numerical model and calculated the partition coefficients of Ir, Ru, and Os between olivine and melt as 1.8. Figure 5 shows the concentrations of PGE in the Gorgona komatiites. It can be seen that the correlation of Ir, Os, and Ru with MgO is described by a line in the three-dimensional space. In other words, the concentrations of PGE in these komatiites can be explained by their contamination to a varying degree with complex alloys with approximately constant proportions of Ru, Ir, and Os. Subsequently, Walker *et al.* (1999) measured Re and Os contents in pure olivines from the same komatiites and obtained a  $D^{Os}$  (olivine/melt) value of only 0.084, which demonstrated the incompatibility of PGE in olivine.

*Other forms of noble metal occurrence in igneous rocks.* It should be noted that iron-rich Fe–Pt and iron-poor Ir–Ru–Os phases are not the only possible natural PGE alloys. Under very reducing conditions (not expected in terrestrial magmatism but possible, for instance, in a solar nebula), the noble metals can react with silica with the formation of silicides, which was shown by Borisov (1999b) by the example of palladium. In terrestrial magmatic systems, alloys of platinum or palladium with aggressive trace elements in melts, such as As, Sb, Bi, et al. cannot be excluded (Borisov, 1999a). The lower the oxygen fugacity and the higher the concentration of these trace elements, the more possible the formation of such compounds in

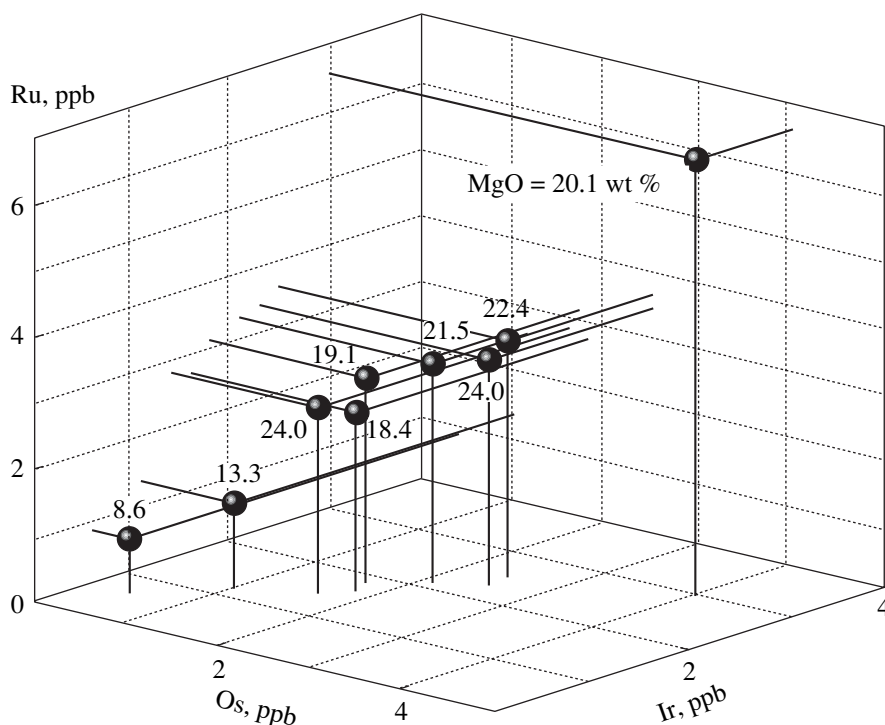
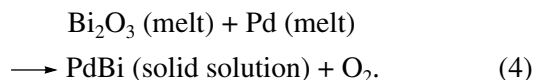


Fig. 5. Concentrations of Ir, Os, and Ru in the komatiites of Gorgona Island (Brüggmann *et al.*, 1987). Numbers near the points denote the MgO contents of the rocks, wt %.

accordance with the reaction (with Bi and Pd as an example)



Pt and Pd can form low-temperature eutectics with these trace elements. For instance, the eutectic nearest to Pd in the Bi–Pd system (60 at % Pd) has a temperature of 577°C, and the lowest temperature eutectic in this system lies at a palladium content of 6 at % and 256°C (Elliott, 1985). It is evident that, if such compounds form in nature, the mobilization of PGE by high-temperature fluids and/or hydrothermal solutions must be more efficient compared with the case where PGE are incorporated as solid solutions in the lattice of rock-forming minerals.

#### ACKNOWLEDGMENTS

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