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Solubilities of noble metals in Fe-containing silicate melts as derived from experiments in Fe-free systems

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ABSTRACT

The solubilities of noble metals (NM: Ir, Pd, Au, Pt, and Ru) in FeO-free silicate melts are known from recent experimental work. In this paper, calculations are presented that relate solubilities of NM in FeO-free melts to those in FeO-containing melts. The main difference between these two systems is the formation of Fe-NM alloys in FeO-containing melts. At f_{O_2} conditions of the QFM buffer and 1200 °C, binary alloys of Fe with 1 at% Au, 2% Ru, 10% Ir, 17% Pd, and 25% Pt are in thermodynamic equilibrium with a silicate melt with 10 mol% FeO. Thus alloy formation leads to a significant reduction in the solubility of Pt and to a lesser reduction in the solubility of Pd. The effects for Ir and Ru are small, and for Au almost negligible. The reduction in solubilities depends on temperature, oxygen fugacity, and FeO content of the silicate melt. Formation of FePt-alloys would lead to a preferred depletion of Pt in partial melts from the Earth's mantle, which, however, is not observed. One explanation is that mantle melting occurs under very oxidizing conditions (QFM+2). The calculations presented here should be considered a first step toward gaining a better understanding of the behavior of NM during igneous processes.

INTRODUCTION

The group of noble metals (NM) comprises the platinum group elements (PGE: Pd, Pt, Ir, Os, Ru, and Rh) and, in addition, Au and Ag. All NM, probably with the exception of Ag, have very high metal/silicate partition coefficients and are, therefore, commonly termed highly siderophile elements (HSE). The element Re also is considered an HSE. Thus all three terms (NM, PGE, and HSE) include almost the same group of elements and are often used as synonyms. The PGE may be further subdivided into light PGE (Ru, Rh, and Pd) and heavy PGE (Os, Ir, and Pt), or according to Barnes et al. (1985), into the Ir group (IPGE: Ru, Os, and Ir) and the Pd group (PPGE: Rh, Pt, and Pd). In this paper we will concentrate on the behavior of five of these elements: Pd, Au, Ir, Pt, and Ru.

In recent work (Borisov et al. 1994; Borisov and Palme 1995a, 1996, 1997; Borisov and Nachtweyh 1998) solubilities of HSE in silicate melts have been determined at 1 atm total pressure and at a wide range of oxygen fugacities (f_{O_2}). Calculated metal/silicate partition coefficients, extrapolated to the low values of f_{O_2} (IW-2) relevant for terrestrial core formation, were found to be extremely high (10^6–10^{15} at 1350 °C), which suggests that the chondritic HSE signature of the upper mantle cannot be the result of metal/silicate equilibrium, at least at low pressures (Borisov and Palme 1995b).

The data on noble metal solubilities are also important for understanding the NM pattern in the Earth's mantle and the behavior of NM during magmatic processes in the Earth and other planets. How do HSE behave during mantle melting? What is the role of sulfides? How would alloy formation influence the NM pattern? Experiments for NM solubilities have been carried out at f_{O_2} values near QFM; because f_{O_2} values in the upper mantle are assumed to be in that range (Carmichael and Ghiorso 1986; Canil et al. 1994), the results of the solubility experiments can be directly applied to such problems, and there is no need to extrapolate the data beyond the f_{O_2} range used in experiments.

However, there is one important difference between silicate liquids used in experiments and melts in natural systems. All our experiments were made in Fe-free systems (the terms "Fe-free" and "Fe-containing" are used to indicate the presence or absence of FeO in the silicate melt). Experiments with FeO-containing melts are difficult because of the formation of NM-Fe alloys, which would result in differences in solubilities in melts having different FeO contents, even for the same f_{O_2}.

In this paper we will discuss the solubilities of NM in FeO-containing melts, resulting from binary alloy formation (NM-Fe), using known data on activity coefficients in binary NM-Fe systems. The full understanding of the geochemical behavior of PGE in magmatic processes requires, in addition, consideration of complex NM-alloys as well as data on the compatibility of HSE with solid mineral phases (oxides, silicates, and sulfides). In a first step, only the effects of binary NM-Fe alloys are considered, as thermodynamic data on more complex NM and NM-Fe alloys are only poorly known or not known at all. Some of the binary NM-Fe alloys are extremely non-ideal (e.g., PtFe-alloy) and the effects of additional NM on these alloys may be minor. Although there are experimental data on
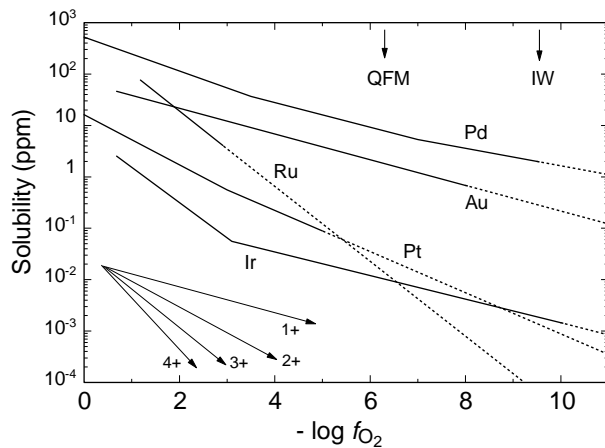
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sulfide/silicate melt partition coefficients in the literature (e.g., Capobianco et al. 1994; Bezmen et al. 1994; Peach et al. 1994; Fleet et al. 1996), we will not consider such equilibria in our calculations, as we are primarily concerned with the behavior of NM in silicate melts in the presence of metal phase.

SOLUBILITIES IN FE-FREE SYSTEMS

We begin with a short summary of the results obtained in Fe-free systems. Most of our experiments were done within a temperature range of 1300–1500 °C with a silicate melt of anorthite-diopside eutectic composition, an FeO-free analogue for a basaltic composition. The solubilities of Pd, Pt, and Ru were determined in equilibrium with pure metals (Borisov et al. 1994; Borisov and Palme 1997; Borisov and Nachtweyh 1998), and the solubilities of pure Au and pure Ir were found by recalculation of the results of experiments with AuPd and $Ir_{10}Pt_{90}$ alloys using known thermodynamic data on Pd-Au and Pt-Ir binaries (Borisov and Palme 1995a, 1996).

For Au, Pd, Pt, and Ru, the temperature dependence of the solubility was taken from the experiments, for Ir no temperature dependence was found within error limits. All data were recalculated to a temperature of 1400 °C and are displayed in Figure 1. Solid lines represent the range of experimentally determined solubilities whereas dashed lines are extrapolations.

All solubilities decrease with decreasing f_{O_2}, implying that NM are dissolved in silicate melts as oxides and not as zero-valence species. For all elements analyzed, the slope of the line relating log of the solubility to $\log f_{O_2}$ is constant at a wide range of f_{O_2}. The following slopes were obtained: for Pd, Au, and Ir ≈ 1/4; for Pt ≈ 1/2; and for Ru ≈ 3/4. This implies (see thermodynamic section below) that Pd^{1+}, Au^{1+}, Ir^{1+}, Pt^{2+}, and Ru^{3+} are the dominant NM-species in silicate melts. Thus, the formal valences of dissolved species are lower than the most stable solid oxides (IrO_2, PdO, PtO_2, or RuO_2) would suggest. At very oxidizing conditions, the slopes for Ir and Pd are higher than 1/4, at reducing conditions the slope for Pd is significantly lower than 1/4. The reasons for the change in slope and the unusually low formal valences are not fully understood (see Borisov et al. 1994, for possible explanations).

Solubilities for various temperatures at QFM, at more oxidizing (QFM+2), and at more reducing (QFM–2) conditions are given in Table 1. For example, absolute values of the solubilities in anorthite-diopside eutectic melts at QFM and 1400 °C are: Ir = 10 ppb, Ru = 14 ppb, Pt = 26 ppb, Au = 2 ppm, and Pd = 7 ppm.

THERMODYNAMIC TREATMENT OF NM-FE ALLOY/ SILICATE MELT EQUILIBRIUM

All metals, including NM, are dissolved as ions in silicate melts. The transition of a neutral NM atom and an Fe atom from an alloy to the silicate melt is thus accompanied by oxidation according to the following equations:

$$\text{NM (alloy)} + (m/4)\cdot O_2 = NMO_{m/2} \text{ (silicate)} \quad (1)$$
$$\text{Fe (alloy)} + 0.5\cdot O_2 = FeO \text{ (silicate)} \quad (2)$$

where m is the valence of the metal ion. The equilibrium constants of reactions 1 and 2 are given by:

$$K_1 = a_{NMO_{m/2}}/[a_{NM}\cdot(f_{O_2})^{m/4}] \quad (3)$$
$$K_2 = a_{FeO}/[a_{Fe}\cdot(f_{O_2})^{0.5}] \quad (4)$$

where a_i are the activities of the relevant components in the alloy or in the silicate melt, respectively.

At constant temperature (K_1 = constant) the log of the NM concentration (C_{NM}) in equilibrium with an alloy is a linear function of $\log f_{O_2}$ and the alloy composition:

$$\log C_{NM} = (m/4)\cdot\log f_{O_2} + \text{const} + \log a_{NM} \quad \textbf{(5)}$$

where const = log ($A\cdot K_1/\gamma_{NMO_{m/2}}$), $\gamma_{NMO_{m/2}}$ is the activity coefficient of the NM-oxide in the silicate, and A is a conversion factor of the mole fraction of the NM-oxide, $X_{NMO_{m/2}}$, to weight fractions C_{NM}, usually given in parts per million or parts per billion. According to this equation, the valence of the metal ion in the melt, m, may be found from the experimentally determined slope of the relationship of log C_{NM} vs. $\log f_{O_2}$. This procedure is only valid if a_{NM}, the activity of the NM in the NM-Fe alloy, is constant (see Eq. 5). If FeO-containing melts are considered, a_{NM} is no longer constant, as higher FeO in the melt reflects higher f_{O_2} and thus leads to lower Fe in the alloy. With this change in alloy composition, a_{NM} will also change. Thus, the formal valence of an HSE in silicate melts can be more easily derived for FeO-free melts.

To simplify further discussion, we will assume that the amount of metal (NM-Fe alloy) is so small that changes in the Fe-content of the alloy will not affect the FeO content of the melt. This is realistic because we are only considering oxygen fugacities significantly more oxidizing than IW, and because NM concentrations in natural melts are in the parts per billion range.
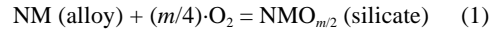

FIGURE 1. Dependence of noble metal solubilities in an anorthite-diopside eutectic melt on oxygen fugacity. All experimental data recalculated to the same temperature of 1400 °C. Solid lines = experimental range, dashed lines = extrapolation. The ideal slopes of the solubility for metal with the valence of 1+, 2+, 3+, and 4+ are shown in the left lower corner.

TABLE 1. Comparison of noble metal solubilities in FeO-free melts, based on experiments in An-Di eutectic melts (QFM+2, QFM, and QFM-2, various temperatures)

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

Note: QFM = quartz-fayalite-magnetite solid buffer (Myers and Eugster 1983).

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Let us now consider how thermodynamic properties of NM-Fe binary alloys affect the NM solubility in silicate melts at different values of f_{O_2}. According to Equation 4, the activity of Fe in the alloy is the following:

$$\log a_{Fe} \text{ (alloy)} = -0.5 \cdot \log f_{O_2} + \log a_{FeO} \text{ (melt)} - \log K_2 \quad (6)$$

For a given melt composition and constant temperature, changes of the Fe activity in the NM-Fe alloy are equivalent to changes in oxygen fugacity,

$$\Delta \log f_{O_2} = -2\Delta \log a_{Fe} \quad (7)$$

Solubilities of NM in FeO-free systems are described by setting $a_{NM} = 1$ in Equation 5:

$$\log C_{NM} \text{ (FeO-free)} = (m/4) \cdot \log f_{O_2} + \text{const} \quad (8)$$

Because all relevant solubility data were obtained in FeO-free systems, we want to relate solubilities in FeO-containing systems to those in FeO-free systems. The difference in NM solubilities between the two systems is, according to Equations 5 and 8:

$$\Delta \log C_{NM} = \log C_{NM} \text{ (FeO-containing melt)} - \log C_{NM} \text{ (FeO-free melt)} = \log a_{NM} \text{ (alloy)}. \quad (9)$$

Thus, the functional dependence of $\log a_{NM}$ (alloy) vs. $\log a_{Fe}$ (alloy) allows the determination of the effect of FeO contents in the melt on the NM solubility at different oxygen fugacities. The relationship of $\log X_{Fe}$ (alloy) vs. $\log a_{Fe}$ (alloy) reflects the affinity of Fe for different NM at different oxygen fugacities. This calculation does not depend on K_1 and K_2, but only on the accuracy of thermodynamic data of NM-Fe binaries. This is important as K_1 values for NM are unknown, and unusually low apparent valences of NM in silicate melts make it impossible to estimate the K_1 values even roughly from solid metal/oxide equilibria. In order to relate the f_{O_2} and a_{Fe} scales, a knowledge of K_2 is required.

Thus, the following procedure has been applied to calculate the NM solubilities in FeO-containing melts:

(1) for given temperature and values of f_{O_2}, the NM solubility in Fe-free melts is calculated using experimentally determined T- and f_{O_2}-dependencies, as discussed above.

(2) for given temperature, f_{O_2}, and FeO content in the melt,

a_{Fe} in a NM-Fe alloy in equilibrium with the silicate melt is calculated from Equation 4. We found it convenient to use the model of Grove (1981) for K_2, where a_{FeO} (melt) = X_{FeO} (melt), although the use of more sophisticated models with constant γ_{FeO} (Holzheid et al. 1997) or even with variable γ_{FeO} (Doyle and Naldrett 1986) in silicate melts may be more accurate.

(3) from the value of a_{Fe} the corresponding a_{NM} in the NM-Fe binary is calculated using thermodynamic data, given in the Appendix.

(4) from the calculated a_{NM} and from C_{NM} (FeO-free melt), values of the solubility of a NM in an Fe-containing melt are calculated using Equation 9.

THE AFFINITY OF FE FOR NOBLE METALS

The thermodynamic approach for calculating the a_{NM} and a_{Fe} in the binary alloys is described in the Appendix.

In Figure 2 we have plotted the mole fraction of Fe in the alloy (X_{Fe}) vs. the log of the activity of Fe in the alloy ($\log a_{Fe}$). Only binary alloys are considered and all data are given for a fixed temperature of 1200 °C. Ideal solid solution (ISS) between Fe and a NM would produce a trend that is shown for comparison in Figure 2 as a solid line. The Au-line is slightly above the ISS-line at $\log a_{Fe} = -0.8$, and slightly below it at
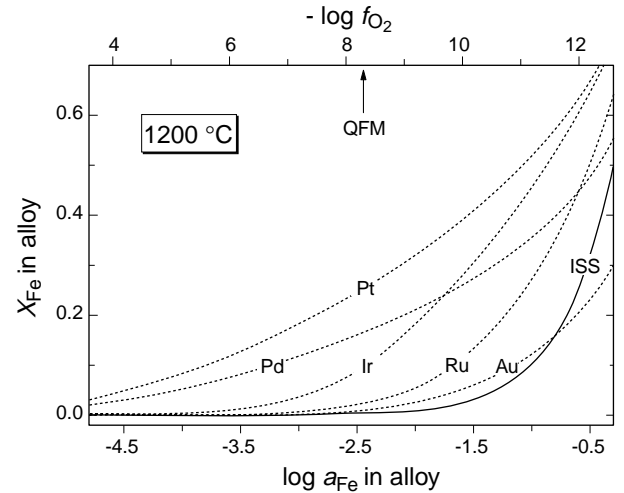
FIGURE 2. Composition of alloys coexisting with FeO-containing melts at 1200 °C (X_{Fe} vs. $\log a_{Fe}$ – plot for AuFe, PdFe, IrFe, RuFe, and PtFe alloys).

higher values of a_{Fe}. This is a consequence of only small deviation of Fe from ideality in Fe-Au alloys. However, in the other alloys, especially in Fe-Pt and Fe-Pd binaries, large negative deviations from ideality are seen for low a_{Fe} values, reflecting the stability of these alloys.

We mentioned above that at fixed temperature and melt composition, variations in log f_{O_2} are equivalent to variations in log a_{Fe} (Eq. 7). A decrease in f_{O_2} will lead to an increase of the activity of Fe and thus to a higher mole fraction of Fe dissolved in the alloy. A log f_{O_2} scale calculated for one particular temperature (1200 °C) and Fe content in the silicate melt (10 mol% FeO) is shown on the top of Figure 2. For example, the f_{O_2} at QFM is equivalent to a log a_{Fe} = –2.44, and the f_{O_2} at IW to log a_{Fe} = –0.72. As a result, we see that at QFM and 1200 °C, Au accepts 1 at% (0.3 wt%) of Fe, Ru = 2 at% (1.2 wt%), Ir = 10 at% (3 wt%), Pd = 17 at% (10 wt%), **{Auth: equal signs okay? Hyphens didn't make sense to me. }** and Pt 25 at% (9 wt%) of Fe in a silicate melt with 10 mol% FeO. Thus Au may be considered as the most noble NM, with the least tendency to accept other common metals such as Fe. Both Pt and Pd will incorporate significant amounts of Fe, even at relatively oxidizing conditions (at QFM+2, about 13 and 9 at%, respectively). The behavior of Ru and Ir is intermediate: at oxidizing conditions they accept only 0.2 and 1.4 at% Fe, whereas at QFM-2 the fraction of Fe will reach about 14 at% in a RuFe-alloy and as much as 32 at% in an IrFe-alloy (see Fig. 2).

From the point of view of the experimental petrologist, Au containers are nearly ideal in preventing Fe loss from natural, FeO-containing melts in experiments at moderately reducing conditions. This fact is, of course, well known. However, because of the low melting point of Au (1064 °C), one has to use Pt-Au alloys (see Biggar 1977 and references therein) or Pd-Au alloys (Kawamoto and Hirose 1994). Biggar (1977) showed that 5 at% Au in the Pt-metal of the container is not sufficient to prevent loss of FeO from silicate melts. Kawamoto and Hirose (1994) demonstrated a significant decrease in Fe loss to AuPd capsules having a high fraction of Au in high-pressure experiments both at wet and dry conditions. It was shown that the Fe loss to $Au_{90}Pd_{10}$ was almost half of that to $Au_{75}Pd_{25}$, which is qualitatively in agreement with our calculations: the higher the Au fraction in Au-Pd alloy, the less Fe should be accepted by such an alloy. From Figure 2 it also follows that Ru and Ir may be useful as a loop material at an f_{O_2} less reducing than QFM. Unfortunately, the brittleness of Ir wires and the absence of commercially available Ru metal in any form other than powder, would make the use of Ir or Ru metals impractical. However, it has been shown recently that Re may be a good alternative to NM both in high-pressure (Herzberg and Zhang 1997) and 1-atm experiments (Borisov and Jones 1999).

The strong affinity of Fe for Pt, on the one hand, and the moderate affinity for Ru, Ir, and Os [thermodynamic properties of Fe-poor, Fe-Os, and Fe-Ru hexagonal closest-packed (HCP) solid solutions are very similar; compare Swartzendruber and Sundman (1983a, 1983b)] on the other hand, are reflected in the very different Fe contents of naturally occurring PtFe and of OsIrRu alloys. For example, Auge and Legendre (1992) reported electron microprobe analyses of PGE minerals in isoferroplatinum nuggets from alluvial deposits of Eastern Madagascar. They showed that tiny OsIrRu alloys contain <0.8 wt% Fe and that these alloys appear to be in thermodynamic equilibrium with the host isoferroplatinum nuggets, containing up to 8 wt% Fe (compare Tables 2 and 3 in Auge and Legendre 1992).

A similar preference of Pt for metallic FeNi is found in meteorites. For example, metal-sulfide-rich grains are commonly found within refractory Ca,Al-rich inclusions in the Allende meteorite. In these metal-sulfide-rich grains, FeNi alloys contain up to 10% Pt and Rh, whereas Os and Ru are concentrated in OsRu nuggets that have only small fractions of Fe. Iridium is distributed equally between OsRu and FeNi alloys. This distribution reflects a decreasing trend of compatibility with FeNi from Pt through Ir to Ru, in accordance with the sequence calculated here. Palladium is absent in these alloys (see Palme et al. 1994 and references therein).

NATURAL MELTS VS. SIMPLIFIED SYNTHETIC LIQUIDS: POSSIBLE EFFECTS ON NM SOLUBILITIES

Iron oxide

In applying the results of these calculations to natural melts we will first assume that, without considering alloy formation, NM solubilities are identical in FeO- (and Fe_2O_3) containing and FeO-free melts, implying the same activity of NM-oxides in both types of melts. This assumption needs some justification. In experiments on the solubility of Ir in silicate melts, Borisov et al. (1992) showed that Ir solubilities in Fe-free and Fe-containing melts (with up to 20 wt% FeO) are identical (at 1350 °C and in air). Capobianco and Hervig (1996) showed that at T = 1300 °C and f_{O_2} = $10^{-2.9}$ atm, the moderate substitution of FeO for MgO in complex silicate melts resulted in only a small increase of Pd solubility. At 10^{-5} atm, however, the solubilities of Pd in Fe-free and Fe-containing melts were found to be similar. In addition, it has been shown by Holzheid et al. (1997) that the activities of NiO and CoO in silicate melts do not depend on the presence or absence of FeO in the melt. Furthermore, O'Neill et al. (1995) argued that FeO and MgO show similar behavior in silicate melts and that both should not have a significant influence on the activity of Ir and other PGE. There is, therefore evidence that the effect of FeO on the solubility of NM in silicate melts is small, thus justifying the approach described above for calculating the effects of NM-Fe alloy formation.

In addition, we also have to consider possible effects of impurities (such as S and C) on NM solubilities. Although S and C are dissolved in natural melts only at the parts per million level, these concentrations are similar to those of the NM; hence S and C might affect the NM speciation in the silicate melt and thus solubility.

Carbon

In principle, we should consider the effects of all carbon species (CO, CO_2, C) soluble in silicate melts on NM solubilities. In our experiments on Pd, Au, and Ir solubilities (Borisov and Palme 1995a, 1996), we used both H_2/CO_2 and CO/CO_2 gas mixtures to define f_{O_2} and we found no difference in the NM behavior, although in experiments with CO/CO_2 gas mix-

tures, the activities of all carbon species in silicate melts must be much higher. Similar tests were made by Holzheid et al. (1994{**Auth: not in ref list? 1994 or 1997, please fix}**) for Ni, Co, and Mo. In high-pressure partitioning experiments, C may affect metal/silicate partitioning of moderately siderophile elements (Jana and Walker 1997a). But C does so primarily indirectly, by alloy formation with metal and by changing the activity in the metal (not silicate) phase. In addition, researchers investigating CO_2 solubilities in silicate melts and/or gas speciation in C-O fluid systems, use a variety of NM in their high-pressure experiments: the outer capsules are made of Pt, and silver oxalate, iridium carbonyl, or platinum dioxide are used as a fluid source, and finally, PdNi/NiO or PdCo/CoO mixtures are commonly used as f_{O_2} sensors (e.g., Pawley et al. 1992; Jakobsson and Oskarsson 1994; Frost and Wood 1997). If C-species interaction with PGE were significant, one would never have obtained any systematic results in such experiments.

Sulfur

The content of S in the Earth's mantle is about 250 ppm (McDonough and Sun 1995). The solubility of S in basaltic melts can, however, reach a few thousand parts per million at high temperatures and low pressures (Mavrogenes and O'Neill 1999). If S serves as a ligand for NM resulting in soluble sulfides, in addition to the NM oxides inferred from the f_{O_2} dependence of the solubilties, then the total NM solubilities may increase dramatically in S-containing natural melts in comparison with synthetic S-free liquids. However, it is more likely that S is dissolved as S^{2-} in an O^{2-} dominated silicate liquid as assumed by O'Neill et al. (1995). In this case, the effect of S on the solubility of NM in silicate melts is negligible, as discussed in detail by O'Neill et al. (1995).

There is one experimental study indicating that the presence of S might increase the Au solubility in silicate melts. Jana and Walker (1997b) investigated the effect of S on partitioning of siderophile elements between liquid metal and liquid silicate at 1500–2200 °C and 10–50 kbar. The authors measured the Au contents in all phases by microprobe analysis and found that, in equilibrium with a metallic phase (mostly Fe-Ni alloy with 3–15 wt% Au), the Au solubility in S-containing silicate melts ranges from 30 to 240 ppm. This is about two orders of magnitude higher than for pure Au solubility in S-free silicate melts at 1 atm total pressure and similar f_{O_2} conditions (see Table 1). Jana and Walter (1997b) concluded that, for some siderophile elements, S species may be more abundant than oxide species in S-containing melts (Jana and Walker 1997b; Dave Walker, personal communication). We cannot completely exclude some effect of S on the Au-solubility, but we can demonstrate that the results obtained by Jana and Walker (1997b) do not provide unambiguous evidence for enhanced Au solubility in S-rich melts. We will show this by discussing an example from a series of experiments made by these authors at 1800 °C and 50 kbar (Jana and Walker 1997b, Table 4). The glass BB317 has a S content of 30 ppm and contains 100 ppm Au. As most of the S atoms are presumably associated with Fe atoms, which are very abundant in the silicate melt (22.4 wt%), there is not much S left to dissolve the Au in the sample, considering that there are only approximately twice

as many S atoms as Au atoms in the melt. If, on the other hand, we assume preferential reaction of S with Au in this silicate melt, we would expect a much higher Au content in S-rich glasses, such as BB294, which contains 4550 ppm S. However, the Au content of this glass is only 180 ppm, less than twice that of BB317, while the S content of BB294 is 150 times higher than that of BB317.

How then can the excess of Au in silicate melts be understood? Most of the experimental glasses of Jana and Walker (1997b) contained tiny metal blebs that the authors believed to be quench phases; therefore they used the raster mode ($30 \, \mu m^2$) of the EMP to analyze the glasses. However, it is not clear that all these metal grains, which contain on average 3.5 wt% Au, are quench products (see a similar discussion in Walker et al. 1993). Simple calculations show that a single metal bleb (as small as 0.1 μm in diameter) per 30 μm^2 raster analysis will give an apparent Au concentration as high as 10 ppm. Our suggestion is supported by the fact that in another experimental series (1500 °C, 10 kbar; Jana and Walker 1997b, Table 2) samples without visible metal blebs contained much lower Au contents, although samples of both series have similar S contents.

Other impurities

There is direct evidence (John Jones, personal communications) that Cl added as KCl to the system does not affect Au partitioning between sulfide and silicate melts. Peach et al. (1994) came to a similar conclusion with respect to Ir. They added NaCl to the system to obtain a Cl concentration of about 1000 ppm and found no distinguishable difference in D^{Ir} (sulfide/silicate). Thus, we conclude that Cl does not affect NM solubilities in basaltic systems.

Other elements such as As, Bi, Ga, and Ge may be expected to react with NM: In earlier work we had suggested that the presence of these elements favors nugget formation in experiments on NM solubility even in synthetic melts (Borisov and Palme 1996). Nevertheless, we believe this to be a purely experimental problem unless one deals with very reducing conditions (Borisov 1999a, 1999b). In this paper, we discuss only moderately reducing conditions (QFM ±2) and assume that such impurities do not affect NM solubilities.

In summary, there is no doubt that major and minor components of natural silicate melts may affect PGE solubilities, but we believe that these effects are small compared with the effects produced by alloy formation. Thus, for a first estimate, we ignore them when applying experimental results to natural processes.

NOBLE METAL SOLUBILITIES IN FE-CONTAINING SILICATE LIQUIDS: STABILITY OF NM-FE ALLOYS IN NATURAL MELTS

In Figure 3, we have displayed the log of the activity of NM in a NM-Fe alloy (log a_{NM}) vs. the activity of Fe in the same alloy (log a_{Fe}). As shown above (Eq. 9), a_{NM} is a measure of the ratio of NM solubilities in an Fe-containing system to NM solubilities in an Fe-free system, while log a_{Fe} is proportional to the log of the oxygen fugacity (Eq. 7). We want to emphasize again that the lower scale on the x-axis is an absolute scale depend-
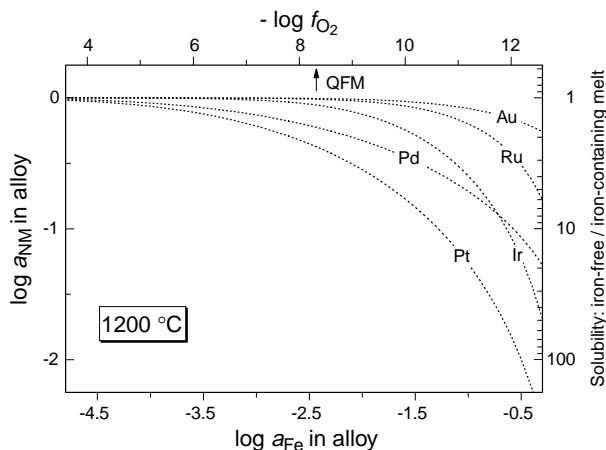
FIGURE 3. Dependence of log a_{NM} vs. log a_{Fe} at 1200 °C for AuFe, PdFe, IrFe, RuFe, and PtFe alloys.

ing only on the accuracy of our models on NM-Fe binaries, whereas the upper scale depends on the assumed FeO-content in the melt and the thermodynamic parameters describing reaction 2. Here we have assumed 10 mol% FeO and the model of Grove (1981) for calculating K_2.

In subsequent discussions we will use a simplified model of the PGE behavior during partial melting and fractional crystallization. The host phases of NM are not specified. At least 20% partial melting is assumed. With this degree of melting, all minor phases, which are potential carriers of PGE in the mantle (e.g., sulfides), are dissolved, excluding, of course, NM-Fe alloys, if they are stable according to our calculations. In addition, we assume that during crystallization of silicate melts, sulfide saturation is never reached. Thus we ignore metal/sulfide and sulfide/melt equilibria. Also, we do not consider fractionation of PGE by differential retention in residual sulfides. Very likely, such processes are not relevant in the Earth's mantle, as recently emphasized by Rehkämper et al. (1999). These and earlier authors (e.g., Ballhaus 1995) invoke formation of PGE alloys or precipitation of PGE metals (Ballhaus 1995) to explain the patterns of PGE in basalts and komatiites. The contents of NM in the Earth's mantle are taken from in McDonough and Sun (1995). In Table 2 we have listed the NM concentrations in CI-meteorites, the primitive upper mantle (PUM), a hypothetical 20% partial melt, and the calculated NM solubilities at one particular temperature (1400 °C).

Gold

According to Figure 3, at around QFM and at more oxidizing conditions, the activity of Au in an AuFe-alloy is nearly unity (log a_{Au} = 1) indicating that the solubility of Au in Fe-containing melts is only slightly lower than in Fe-free melts. Thus, in FeO-free melts, the Au solubility will decrease at QFM and 1200 °C by only 1%. Even at reducing conditions (QFM-2), the Au solubility will decrease by only 10%. Calculations for higher temperatures (1400 °C) give similar results. It is thus justified to use the experimentally determined Au solubility of An-Di eutectic liquids when estimating the Au solubility

in natural melts.

The solubility of Au at 1400 °C and at a log f_{O_2} between QFM+2 and QFM-2 in Fe-containing melts decreases from 5.7 ppm to about 520 ppb (Table 2). The abundance of Au in the Earth's mantle is 1 ppb. Thus, 20% partial melting produces a liquid with 5 ppb of Au, assuming that Au is incompatible with residual mantle phases. This Au concentration is so low that formation of Au-Fe alloys during melt fractionation can be safely excluded.

It is, however, possible that Au is preferentially incorporated into other alloys. Nevertheless, Au as an impurity on a percentage level in other NM alloys, such as PtFe-alloys, is not expected (e.g., Auge and Legendre 1992). Indeed, to be in equilibrium with a primary mantle melt content at 1400 °C and QFM, such alloys should have $a_{Au} \approx 0.003$. Assuming ideal behavior of Au, this activity transforms into an Au content of about 0.3 at% in such alloys. We may expect measurable Au contents in FePt alloys in equilibrium with an Au content of 5–10 ppb in silicate melts only at reducing conditions and at relatively low temperatures where Au solubility is in the range of 100 ppb (see Table 1).

Palladium

A significant decrease of Pd solubility in Fe-containing melts is expected from the calculations. At 1200 °C and QFM, the Pd solubility in FeO-containing melts will decrease by 70% compared to FeO-free melts. The Pd solubility will further decrease with increasingly reducing conditions. At QFM-2, for example, Fe-free melts have 3.2 times more Pd than melts with 10% FeO (Fig. 3). At 1400 °C the effect is lower, but still significant: about 50% at QFM and 2.6 times at QFM-2. Nevertheless, even in Fe-containing melts, the solubility of Pd will be at the parts per million level in all cases (see Table 2). The mantle abundance of Pd is 3.9 ppb and 20% partial melting would produce a liquid with at maximum 20 ppb Pd, which is about 1.5 orders of magnitude below the solubility level. Therefore, FePd alloys are not expected to form in equilibrium with primary mantle melts, similar to what has been found for Au.

Although formation of PdFe alloys are not expected, precipitation of complex Pd-containing alloys (e.g., PtPdFe) cannot be excluded. Indeed, Auge and Legendre (1992) described isoferroplatinum with up to 13 at% Pd.

Iridium and ruthenium

The behavior of Ir and Ru is very different from that of Au and Pd. The corresponding mantle abundances are 3.2 ppb for

TABLE 2. Noble metal content in carbonaceous chondrite (CI), primitive upper mantle (PUM), primary melt (PM) and calculated solubilities in FeO-containing melts (ppb)

NM	CI*	PUM	PM†	Solubilities at 1400 °C		
				QFM+2	QFM	QFM-2
Au	140	1.0	5	5700	1800	520
Pd	550	3.9	20	20900	5100	1420
Ir	455	3.2	16	29	10	2.5
Ru	710	5.0	25	390	14	0.4
Pt	1010	7.1	35	130	13	0.8

* CI and PUM content from McDonough and Sun (1995).
† Primary mantle melt content assuming 20% of partial melting and incompatible behavior of NM.

Ir and 5 ppb for Ru (Table 2). Assuming incompatible behavior, 20% partial melting would produce a liquid with 16 and 25 ppb of Ir and Ru, respectively. These values are higher than the solubility levels even in Fe-free melts (Table 1). In FeO-containing melts, the solubility will further decrease (see Fig. 3 and Table 2). Thus, in the absence of sulfides in residual solids, the Ir and Ru contents of the parent magma are controlled by equilibrium of the melt with metal phases high in Ir and Ru. At high temperatures Ir and Ru form with Fe and other potentially important PGE to form either continuous (Ir-Fe, Ir-Pt, Ir-Rh, Ru-Os) solid solutions, or solid solutions (Ir-Os, Ir-Ru, Ru-Fe, Ru-Pt, Ru-Rh) over a wide compositional range (Savitskii 1984). Thus homogeneous alloys of IrRuOsFe(±Pt,Rh) composition could be expected to be in equilibrium with primary mantle melts.

We should mention that there is evidence that both Ir and Ru may be slightly compatible with olivine. For example, Brügmann et al. (1987) inferred olivine/melt partition coefficients of about 1.8 for Ir, Ru, and Os from a suite of komatiites showing variable degrees of olivine fractionation. However, the role of olivine as a possible PGE carrier has been questioned. For example, Walker et al. (1999) reported analyses for Re and Os in purified olivine and spinel from fresh Gorgona komatiites. They calculated D^{Os} (olivine/melt) to be around 0.084, which differs considerably from the approximately 1.8 estimated by Brügmann et al. (1987) for the same rocks, and especially from the $D^{Os} \geq 20$ reported by Hart and Ravizza (1996) for mafic systems. Walker et al. (1999) concluded that Os is obviously excluded from the olivine structure. As other mineral phases may have lower partition coefficients, the bulk partition coefficients (D*) between olivine-containing residue and partial melt is certainly expected to be below unity. Even for D* = 0.2 (for the batch-melting formula see, for example, Allègre and Minster 1978), 20% partial melting would produce melts with Ir and Ru contents of around 9 and 14 ppb, respectively, which are still similar to their solubility levels in Fe-containing melts (see Table 2). Thus, the slight compatibility of Ir and Ru will not change our conclusion.

With decreasing temperature, both Ir and Ru solubilities decrease. Additionally, incompatibility with crystallizing liquidus silicate minerals will favor formation of Ir- and Ru-rich alloy nuggets. It is possible that these nuggets are too small to settle from the liquid. In this case one would expect other minerals to remove the alloys from the melt, for example, as inclusions (Zhou 1994 and references therein). The net effect would be the same. Finally, wide miscibility gaps assumed in complex PGE systems (see Harris and Cabri 1991 and references therein) may result in decomposition of initially homogeneous alloys during subsequent cooling.

Platinum

The Pt mantle abundance is 7.1 ppb. No experimental data are known about Pt compatibility with residual mantle phases. In a 20% partial melt, we may expect a value of about 7 ppb for slightly compatible behavior (bulk $D^{Pt} = 1$) to 35 ppb Pt for strong incompatibility with mantle minerals. This is within the range of Pt in FeO-free melts at QFM (see Table 1). As Pt has a strong affinity for Fe (see Fig. 2), its solubility in Fe-contain-

ing melts will decrease dramatically (see Fig. 3 and Table 2). In Figure 4 we have drawn isopleths of Pt solubility in silicate melts with 10 mol% FeO. At any condition to the right of the 35 ppb isopleth (assumed in primary melt), a 20% partial melt should be in equilibrium with the relevant FePt alloy. Thus, only at high temperatures and very oxidizing conditions will the primary melt not be saturated with Pt.

During fractional crystallization, if the conditions in the melt change so as to follow the QFM buffer, its cooling will be characterized by precipitation of PtFe alloys with continuously increasing contents of Fe (see discussion below). The proportion of such alloys will be small, but not negligible: for example, 1 m^3 of basaltic melt will produce about 1.7 mm^3 (28 mg) of PtFe alloy during cooling from about 1360 °C (where QFM intersects the 10 ppb isopleth) to 1100 °C (where QFM intersects the 1 ppb isopleth). In Figure 5 we present calculated Fe contents in PtFe alloys in equilibrium with silicate melts containing 10 at% FeO. At QFM and over a wide temperature range, such a melt is in equilibrium with PtFe alloys with 20–30 at% Fe. We want to emphasize that the similarity in composition between magmatic Fe-Pt alloys and Pt_3Fe (isoferroplatinum)
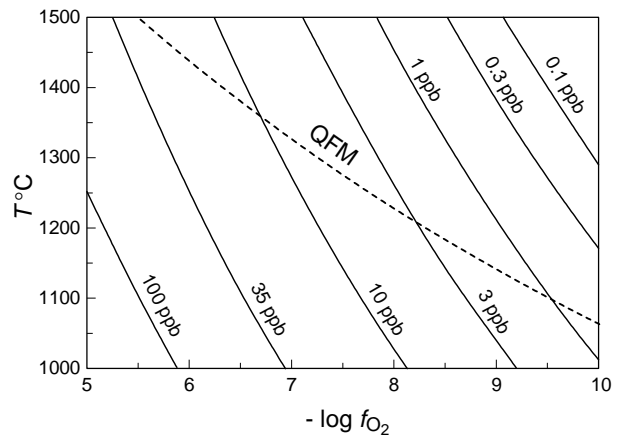

FIGURE 4. Isopleths of Pt solubility (ppm) in Fe-containing melts.
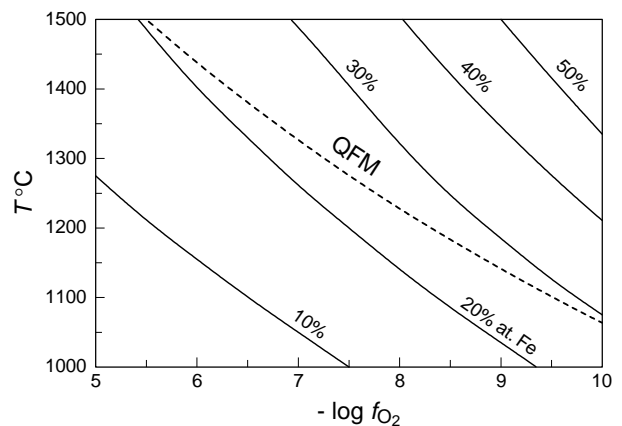

FIGURE 5. Isopleths of Fe content (at%) in PtFe alloys in equilibrium with Fe-containing melts. See text for further explanation.

is a simple consequence of the most-common magmatic redox conditions (close to QFM), average content of FeO in magmatic liquids (about 10 mol%), and the thermodynamic properties of Fe-Pt binary alloys.

There is a tradition in the literature to interpret variations of PtFe alloy composition as resulting from substitutions of either Cu and Ni for Fe and/or other PGE for Pt in the structure of isoferroplatinum (e.g., Cabri and Feather 1975). It is known that a continuous series of solid solutions characterizes the ternary systems Pt-Fe-Cu, Pt-Cu-Ni, Pt-Pd-Ni, and Pd-Fe-Ni at high temperatures (Savitskii 1984). A small fraction of Ni and Cu in solid solution with FePt would simply reflect the low concentrations of these two elements (compared with Fe) in magmatic melts. Additionally, as the solubilities of Cu and Ni are much higher than those of Pt or Ir in silicate melts, major contributions of Cu and Ni to the NM-Fe alloys are not expected. Therefore, minerals such as Pt_3Cu or Pd_3Fe cannot have a magmatic origin.

In summary, in the preceding discussion we have shown that precipitation of PtFe-alloys should be expected during mantle melting. This would lead, as discussed above, to significant depletion of Pt compared with other NM in mantle melts. This result, however, is not found, as demonstrated, for example, in the basalt and komatiite data of Rehkämper et al. (1999). The large difference in the Pd and Pt contents of mantle melts expected from the calculations is not seen in nature. One possibility is that mantle melting occurred under very oxidizing conditions where the effect of PtFe-alloy formation at QFM+2 is negligible, as seen from Table 2. This is the upper limit for upper-mantle oxygen fugacity estimates (Canil et al. 1994). Often, however, more reducing conditions are assumed for mantle melting, in the extreme case Fe-metal saturation (Ballhaus 1995). Another possibility is that PtFe-alloys formed but were removed from the source region, together with the melt and were later oxidzed. However, from the presence of tiny sulfide grains in residual mantle assemblages one may conclude that FePt alloys should also be retained in the residue. In this case, the absence of a negative Pt-anomaly in mantle melts should indicate very oxidizing conditions during formation of mantle melts.

SUMMARY REMARKS

In this paper we have summarized our experimental data on solubilities of Ir, Pd, Au, Pt, and Ru in silicate melts of anorthite-diopside eutectic composition and presented new calculations of solubilities of these elements in FeO-containing melts. We assumed that NM activity coefficients in silicate melts are independent of the Fe oxides content of the melt and calculated NM solubilities in equilibrium with NM-Fe alloys. We have further argued that the presence of minor elements in the melt, such as C and S, on NM-activities does not significantly alter our conclusions. This conclusion, however, requires experimental verification.

The largest effect is calculated for Pt, which has a strong affinity to Fe. Formation of PtFe-alloys will, depending on oxygen fugacity, considerably reduce the Pt solubility in silicate melts and thus lead to fractionation of Pt from Ir and other NM. For Ir and Ru, the decrease in solubility is significant but less pronounced than for Pt, whereas Pd and Au show little effect. The expected depletion of Pt in melts from the mantle is not found, perhaps indicating that mantle melts formed under very oxidizing conditions (QFM + 2).

The approach used here is a first step in considering the effects of alloy formation during partial melting and fractional crystallization. More sophisticated experiments and calculations are required to include more quantitatively the effects alloy formation of more than two metals.

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APPENDIX

Tabulated excess mixing properties of Au-Fe, Pd-Fe, and Ir-Fe binaries are taken from Hultgren et al. (1967 {**Auth: 1973 in ref list? Please fix**}), and fitted to find appropriate interaction parameters applying the formalism of asymmetric solid solution (Thompson 1967):

$$\Delta DG^{ex} = X_{NM} \cdot X_{Fe} \cdot (W^G_{NM} \cdot X_{Fe} + W^G_{Fe} \cdot X_{NM}) \qquad (10)$$

$$\Delta S^{ex} = X_{NM} \cdot X_{Fe} \cdot (W^S_{NM} \cdot X_{Fe} + W^S_{Fe} \cdot X_{NM}) \qquad (11)$$

Where W^G_i and W^S_i are interaction parameters and X_i are the corresponding mole fractions. Appropriate interaction parameters W^H_i were calculated according:

$$W^G_i = W^H_i - T \cdot W^S_i \qquad (12)$$

and are given along with the W^S_i values in Appendix Table 1. Necessary activity coefficients can then be calculated from:

$$RT \cdot \ln \gamma_{NM} = (X_{Fe})^2 \cdot [W^G_{NM} + 2X_{NM} \cdot (W^G_{Fe} - W^G_{NM})] \quad (13)$$

$$RT \cdot \ln \gamma_{Fe} = (X_{NM})^2 \cdot [W^G_{Fe} + 2X_{Fe} \cdot (W^G_{NM} - W^G_{Fe})] \qquad (14)$$

For the Fe-Ru binary, the formalism of regular solid solution was used. The parameter $W^G = -23112$ J from Swarzendruber and Sundman (1983a) was accepted and assumed to be temperature independent.

For the Pt-Fe binary, the Redlich-Kister formulation for the activity coefficients was used:

$$\log \gamma_{Pt} = (X_{Fe})^2 \cdot [B + C \cdot (4X_{Fe} - 3)] \qquad (15)$$

$$\log \gamma_{Fe} = (X_{Pt})^2 \cdot [B + C \cdot (4X_{Fe} - 1)] \qquad (16)$$

where $B = -3.326564$ and $C = 0.221051$ are taken from Heald (1967), who considers this approximation to be valid over the temperature interval 1130–1550 °C . We prefer this model to the approximation of Gudmundsson and Holloway (1993) because the first one was used by Grove (1981) in his calibration of K_2 , which was accepted in this paper for all calculations, including melt/PtFe alloy equilibria.

APPENDIX TABLE 1. Interaction parameters of asymmetric solid solution model for Au-Fe, Pd-Fe, and Ir-Fe binaries at 1200 °C

System Fe-NM	W^H_{Fe} J/mol	W^H_{Fe} J/mol	W^S_{Fe} J/(mol·K)	W^G_{NM} J/mol	W^H_{NM} J/mol	W^S_{NM} J/(mol·K)
Fe-Au	–13871	68757	56.095	29883	63051	22.517
Fe-Pd	–93902	–90388	2.386	–14497	19565	23.124
Fe-Ir	–45581			–65590		

Note: Primary data are taken from Hultgren et al. (1973).