

# The crystal structures of synthetic Re- and PGE-bearing magnesioferrite spinels: Implications for impacts, accretion and the mantle.

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**Abstract.** Re- and PGE-bearing magnesioferrite spinels were synthesized at oxidizing conditions between 0.1 MPa and 5.0 GPa, and 1150 to 1600 °C in equilibrium with Re- or PGE-bearing metals and/or oxides. Electron microprobe analysis and single crystal X-ray diffraction techniques were employed to determine the composition, crystal structures and site occupancies, indicating that the magnesioferrite structure can accommodate wt% levels of Re and the platinum group elements (PGE) at oxidized conditions. These results suggest that magnesioferrite spinels found in K-T boundary samples worldwide could be an important host phase for the Ir, Ru, Os, Re, and Rh anomalies found in the boundary layer. Higher Ru/Ir values in Pacific magnesioferrite-bearing samples may be a reflection of higher condensation temperatures of the oxides. The distribution of PGE's in mantle and magmatic rocks may depend on the stability of spinel-structure oxides, especially those with a high magnesioferrite component. Finally, magnetite-rich meteorite fusion crusts may hold PGEs in oxidized form.

## 1. Introduction

Oxides that have the spinel crystal structure are common in nature—they often form solid solutions of chromites ((Fe,Mg)Cr<sub>2</sub>O<sub>4</sub>), magnetite (FeFe<sub>2</sub>O<sub>4</sub>), magnesioferrite (MgFe<sub>2</sub>O<sub>4</sub>), spinel (MgAl<sub>2</sub>O<sub>4</sub>), and hercynite (FeAl<sub>2</sub>O<sub>4</sub>). Under oxidizing conditions, the magnesioferrite component is significant in many spinels. In particular, magnesioferrite is found in the cosmic spherules present in Cretaceous-Tertiary boundary samples (e.g., Smit and Kyte, 1984; Kyte and Smit, 1986, Kyte and Bostwick, 1995) and is known to be a significant component of mantle and magmatic spinels (e.g., Haggerty, 1992) and spinels in meteorite fusion crusts (Genge and Grady, 1999). Some experimental work suggests that PGE can be accommodated in the spinel structure (e.g., MgRh<sup>3+</sup><sub>2</sub>O<sub>4</sub> - Capobianco, 1993; Nell and O'Neill, 1997 or Mg<sub>2</sub>Ru<sup>4+</sup>O<sub>4</sub> - Dulac, 1969), and analyses of K-T boundary magnesioferrites and natural chromite-rich material yield high concentrations of PGEs (Bohor et al., 1986/87; Montanari et al., 1983; Smit and Hertogen, 1980; Walker et al., 1996), yet a comprehensive study of PGE compatibility in spinel structures has not been undertaken. A study of PGE compatibility in spinels has been initiated with specific emphasis on magnesioferrites.

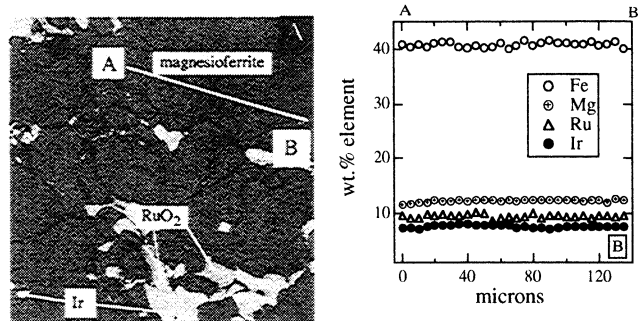
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Paper number 2000GL012184.  
0094-8276/01/2000GL012184\$05.00

## 2. Experimental and analytical methods

Magnesioferrite (synthesized as described in O'Neill et al., 1992) and either ReO<sub>2</sub>, IrO<sub>2</sub>, Rh<sub>2</sub>O<sub>3</sub>, PtO<sub>2</sub>, Os or RuO<sub>2</sub> were welded into AuPd alloy ( $\leq 1400$  °C) or Pt ( $> 1400$  °C) capsules (due to the volatility of most of these oxides), and equilibrated at 0.1 MPa, 1.0 or 5.0 GPa. A summary of the experimental conditions and analytical results is presented in Table 1. Iridium and Ru were paired together to look for variations in Ru/Ir with temperature and/or pressure (see discussion below), and in order to avoid overlapping peaks during later electron microprobe analysis (i.e., Ir, Re and Os have overlapping lines). The 0.1 MPa experiments were conducted in a Deltech vertical resistance furnace, and those at higher pressures in piston cylinder and multi-anvil apparatus, calibrated at pressure and temperature as described by Righter et al. (1997) and Righter and Drake (2000), respectively. Experiments at 1.0 GPa were run for as long as 48 hrs before shutting off power; these long runs were done to ensure equilibrium and growth of large crystals suitable for single crystal X-ray diffraction work. Multi-anvil runs were heated for 3-4 hours at 1400 °C and 5.0 GPa. Quenched run products were analyzed with an SX50 electron microprobe, using AuPd, Re, Os, PtRh, Ru, and Ir metals, MgO, and fayalite as standards, and a PAP correction procedure (Pouchou and Pichoir, 1991). Oxygen fugacity in many of the runs was high - for instance those with Ir and IrO<sub>2</sub> present buffered oxygen fugacity at logfO<sub>2</sub> values close to air (O'Neill and Nell, 1997; Figure 1a). In general the 0.1 MPa runs show evidence for disequilibrium or incomplete reaction (e.g., analyses for run 87 in Table 1). Higher-pressure experiments produced homogeneous and large ( $> 100$  micron) crystals (Figure 1b).

In order to determine site occupancies, selected crystals from high-pressure runs 111, 115, 116, and 117 were chosen for single-crystal X-ray diffraction experiments. The peaks shapes were sharp,  $\sim 0.1^\circ$  full-width at half-height, demonstrating that the samples were well equilibrated. Cell and positional parameters were refined, as well as site occupancies that were constrained to match the microprobe data. Results of X-ray diffraction experiments (using a Picker 4-circle diffractometer with Mo radiation) and the refined structural formulae are summarized in Table 2. The resulting tetrahedral bond lengths match those obtained by O'Neill et al. (1992) for magnesioferrite with the same tetrahedral site occupancies, demonstrating the quality of the refined data. The results of these experiments show that magnesioferrite can easily accommodate PGEs into the octahedral site of its structure (e.g., up to 25% Re; Table 1).

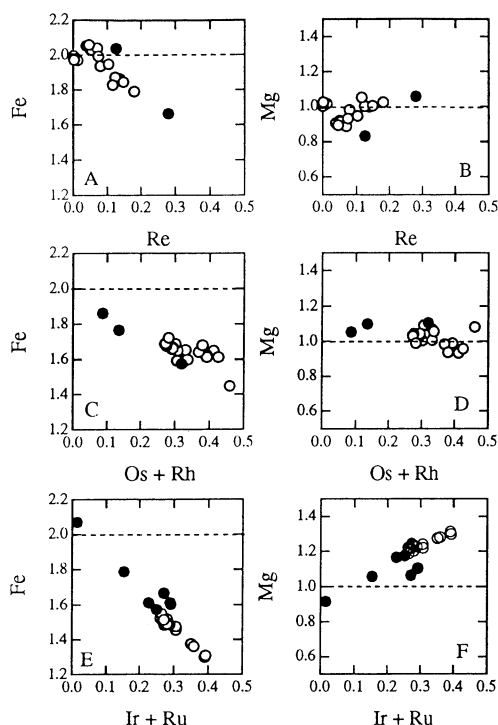


**Figure 1.** A) Back scattered electron (BSE) image of products from run 110 (1.0 GPa; 1600 °C) with RuO<sub>2</sub>- and IrO<sub>2</sub>-bearing magnesian ferrite (dark grey), Ir (bright white) and (Ru, Ir)O<sub>2</sub> (intermediate grey). B) profile of Fe, Mg, Ir and Ru across traverse A-B in sample 110 (Figure 1A). The flat profiles, as well as the very sharp X-ray diffraction peaks obtained in the single crystal work, are an indication that equilibrium was attained in these experiments.

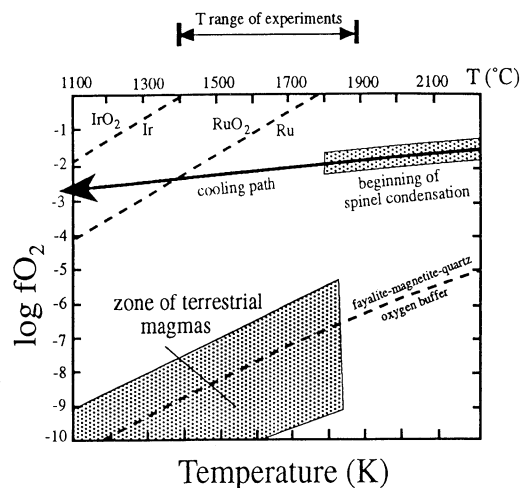
### 3. Discussion

#### 3.1 Substitution mechanisms

The extent to which specific PGE's will substitute on the octahedral site will depend upon the relative stabilities of the fully-substituted PGE end members, as well as the valences of the various PGE's under oxidized conditions. For instance,



**Figure 2.** A,B: Correlation between Re and Fe for data from runs 31, 32, 37, 38, 108 and 111. Note the relatively constant molar Mg in Fig. 2B with substantial variation in Re. C,D: Correlation between (Os+Rh) and Fe for data from runs 87, 94, 106 and 117. Note also the relatively constant Mg in Fig. 2D with variation in (Os+Rh). E,F: Correlation between (Ir+Ru) and Fe for data from runs 30, 93, 105, 107, 109, 110, 113, 114 and 115. Open symbols are 0.1 MPa runs, closed symbols represent high-pressure runs, and all elements are normalized to 3 cations.



**Figure 3.** Oxygen fugacity vs. temperature diagram illustrating the cooling path of an impact-generated vapor, the condensation temperature of magnesian ferrite spinel (both from Ebel and Grossman, 1999), the stability relations of Ru-RuO<sub>2</sub> and Ir-IrO<sub>2</sub> (from O'Neill and Nell, 1997), and the temperature range of experiments in this study. Pure Ru or Ir will not be stable either in an impact generated vapor cloud, or in the terrestrial mantle. These stability fields are relevant to the extent that as a gas cools from high temperatures (e.g., 2000 °C) Ru will become more stable in the oxidized form before Ir. The phases in which they are likely to be hosted in oxidized form are magnesian ferrite spinels, not pure oxides or silicate melts (see text for more discussion).

the covariation of Re and Fe at constant Mg (Figure 2A,B), suggests that an equilibrium such as  $2\text{Re} + \text{MgFe}_2\text{O}_4 + \text{O}_2 = 2\text{FeO} + \text{MgRe}_2\text{O}_4$  is sustained in these runs. This would be consistent with a valence of 3+ for Re, as is found in experimental work on Re solubility in silicate melt at the high oxygen pressures of this study (e.g., Walter et al., 2000). However, the stoichiometric and structural constraints (above) indicate that Re could be substituting as 2+. Osmium and Rh are also involved in a 1:1 substitution for Fe (Fig. 2C,D), again with constant Mg. Equilibria such as  $2\text{Os} + \text{MgFe}_2\text{O}_4 + \text{O}_2 = 2\text{FeO} + \text{MgOs}_2\text{O}_4$ , or  $2\text{Rh} + \text{MgFe}_2\text{O}_4 + \text{O}_2 = 2\text{FeO} + \text{MgRh}_2\text{O}_4$  may be operating, consistent with the presence of excess (Mg,Fe)O in many of the runs. This would require a valence of 3+ for both Os and Rh, as also demonstrated in solubility studies of Os and Rh in silicate melt under oxidized conditions (e.g., Walter et al., 2000). On the other hand, charge balance and stoichiometric constraints from the structural formula indicate  $\text{Rh}^{4+}$  and  $\text{Os}^{3+}$ . Finally, for both Ru and Ir, the end member spinel components are likely to be  $\text{Mg}_2\text{RuO}_4$  and  $\text{Mg}_2\text{IrO}_4$  (e.g., Krutzsch and Kemmler-Sack, 1983; Dulac, 1969), involving quadrivalent cations, as indicated by negative correlations with Fe and positive correlations with Mg (Fig. 2E,F). Again, however, charge balance and stoichiometry constraints indicate substitution as  $\text{Ir}^{4+}$  and  $\text{Ru}^{3+}$ . Additional work on PGE-bearing spinels is required to resolve these discrepancies regarding the specific end members and valence states that are possible for each kind of spinel.

#### 3.2 K-T boundary spherules

These new results have immediate applications to K-T boundary samples, which are enriched not only in Ir (Alvarez

**Table 1.** Experimental conditions and representative oxide analyses\*

run	T °C	Pressure	hrs.	Fe <sub>2</sub> O <sub>3</sub>	MgO	Re <sub>2</sub> O <sub>3</sub>	Os <sub>2</sub> O <sub>3</sub>	Total
<b>Re</b>								
31	1162	0.1 Mpa	120	64.11(63)	17.47(16)	17.02(68)	-	98.60
32	1162	0.1 Mpa	120	69.60(66)	5.98(12)	3.32(33)	-	98.26
37	1150	0.1 Mpa	168	72.49(69)	17.77(18)	10.19(66)	-	100.44
38	1150	0.1 Mpa	168	67.59(67)	18.27(18)	13.17(65)	-	99.03
39	1120	0.1 Mpa	168	77.79(72)	21.44(20)	0.47(19)	-	99.69
40	1180	0.1 Mpa	144	76.28(70)	18.93(19)	3.84(39)	-	99.05
108	1300	1.0 Gpa	19	55.55(56)	17.79(18)	24.72(74)	-	98.06
111	1400	1.0 Gpa	42	67.38(67)	14.85(16)	15.44(75)	-	97.79
116	1400	1.0 Gpa	48	77.60 (71)	14.24 (16)	6.40 (51)	-	98.40
89	1400	5.0 Gpa	4	43.75(20)	9.57(12)	42.10(42)	5.08(46)	100.05
<b>Rh, Os</b>								
						Rh <sub>2</sub> O <sub>3</sub>	Os <sub>2</sub> O <sub>3</sub>	
82	1154	0.1 Mpa	72	66.92(66)	22.42(20)	0.49(10)	9.33(33)	99.20
87	1153	0.1 Mpa	72	58.64(70)	19.57(18)	18.03(17)	2.77(28)	99.48
“	0.1 Mpa	“	“	48.56(73)	18.37(18)	26.68(25)	6.41(51)	100.02
106	1300	1.0 Gpa	25.5	72.09 (68)	20.57(20)	3.87(15)	2.58(26)	99.11
117	1400	1.0 Gpa	48	66.90 (62)	19.41 (18)	5.81(21)	5.43 (52)	97.56
94	1400	5.0 Gpa	4	55.80(67)	19.75(19)	11.07(18)	11.72(39)	100.44
<b>Ru, Ir</b>								
						RuO <sub>2</sub>	IrO <sub>2</sub>	
30	1150	0.1 Mpa	120	57.04(68)	22.85(20)	10.97(33)	9.15(46)	100.00
105	1300	1.0 Gpa	25	60.03(72)	21.97(20)	9.36(29)	8.33(58)	99.69
107	1400	1.0 Gpa	8.5	59.51(71)	20.51(20)	15.05(38)	4.75(48)	99.82
109	1500	1.0 Gpa	18	56.88(75)	21.62(20)	10.25(32)	9.67(60)	98.41
110	1600	1.0 Gpa	4	58.31(76)	20.30(19)	12.44(34)	8.84(57)	99.88
113	1400	1.0 Gpa	24	79.59(72)	17.79(18)	0.92(18)	0.04(02)	98.39
114	1400	1.0 Gpa	24	67.83(67)	20.25(19)	8.84(29)	1.56(26)	98.48
115	1400	1.0 Gpa	48	59.63(72)	19.47(18)	14.66(35)	3.77(40)	97.52
93	1400	5.0 Gpa	4	66.71(66)	21.89(20)	10.05(33)	2.03(32)	100.96

¥ total includes 19.30 NiO for run 32, 0.49 IrO<sub>2</sub> for run 82, and 2.10 PtO for run 94.

\*oxides were calculated with valences expected under oxidized conditions: Os<sup>3+</sup>, Re<sup>3+</sup>, Rh<sup>3+</sup>, Ir<sup>3+</sup>, Ru<sup>4+</sup>, Pt<sup>2+</sup> and Pd<sup>1+</sup>. It is noteworthy that only small amounts of Pd entered the oxides in the experiments using AuPd capsules. This is consistent with the low valence for Pd of 1+ (Borisov and Palme, 1996), and the finding of incompatibility of Pd in spinels (Capobianco and Drake, 1990). No Pt was detected in any runs except 94. Also present in run products were Re-oxides, OsRh metal and Rh<sub>2</sub>O<sub>3</sub>, and Ir and (Ir,Ru)O<sub>2</sub>. Numbers in parentheses represent 1σ error based on counting statistics.

et al., 1980) but also many other highly siderophile elements such as Re, Rh, and Os (Smit and Kyte, 1984). The suggestion that Ir may be hosted by magnesioferrite (Bohor et al., 1986/87) is supported fully by the experimental data presented here. If the spherules condensed out of an impact vapor cloud, then another possible host phase is the silicate melt. However, the solubility of PGE's into a silicate melt is relatively low. For instance, the solubility of Re, Os, Ru, Ir and Rh in air, are ~1 wt%, 1000 ppm, 800 ppm, 8 ppm, and 10 ppm, respectively (Walter et al., 2000). When coupled with the results of this study (also oxidized conditions), it is clear that the partition coefficients of these five elements between magnesioferrite spinel and silicate melt will be very high, at least > 25 for Re, but with values as high as 1000 to 10<sup>6</sup> for the others. Phases such as olivine and pyroxene, also present in some K-T spherules, do not make good hosts for the PGE's either (e.g., Righter et al., 2000).

The elevated Ru/Ir ratios in K-T samples from the Pacific (noted by Evans et al., 1995) may be understood in terms of slightly higher condensation temperatures. Magnesioferrite-rich spinels, nearly identical in composition to those found in K-T spherules, will condense from impact generated vapors at temperatures of approximately 1600 -1800 °C (Ebel and Grossman, 1999, and Figure 3). Because a<sub>RuO2</sub> will be higher than a<sub>IrO2</sub> with decreasing temperature, early higher temperature spinel condensates are likely to be enriched in RuO<sub>2</sub> over IrO<sub>2</sub> (Figure 3). Higher temperatures for the Pacific spinels were also previously suggested based on compositional differences from other K-T spinels (Kyte and Bostwick, 1995). Perhaps the distribution of higher temperature K-T spinel can provide information about the impact angle and/or direction of the K-T impactor (e.g. oblique impacts; Pierazzo and Melosh, 1999).

### 3.3 Mantle and magmatic spinels

The distribution of PGE's in mantle and magmatic materials is usually controlled by sulfides. However, in some environments such as oxidized or deep conditions, sulfide is not stable, and oxides may be a significant host phase for the PGE's. The activity of Fe<sup>3+</sup>/Fe<sup>2+</sup> and thus of magnesioferrite in mantle and magmatic spinels is strongly dependent upon oxygen fugacity. The range of oxygen fugacity recorded in mantle-derived material is large, and parts of the mantle are very oxidized (e.g., Carmichael, 1991). Between FMQ+4 and FMQ (FMQ = fayalite-magnetite-quartz oxygen buffer), there is a significant amount of ferric iron present (e.g., 0.3 to 0.4 Fe<sup>3+</sup>/Fe<sup>total</sup>; McGuire et al., 1991). As a result, spinels in such an environment, where sulfide may not be stable, could be significant host phases for Re, Os, Ir, Ru and Rh. While it is

**Table 2.** Results of single crystal X-ray diffraction.

run	a (Å)	V (Å <sup>3</sup> )	u	r-factor	n	R(MO) (Å)	R(TO) (Å)	formula
111	8.4158(2)	596.06(4)	0.2563(5)	2.4 %	226	2.052(4)	1.914(3)	(Fe <sub>.612(8)</sub> Mg <sub>.305</sub> Re <sub>.083</sub> ) <sub>2</sub> (Fe <sub>.756</sub> Mg <sub>.244</sub> )O <sub>4</sub>
116	8.4055(2)	593.86(4)	0.2570(2)	1.2 %	226	2.044(2)	1.922(1)	(Fe <sub>.680(4)</sub> Mg <sub>.282</sub> Re <sub>.038</sub> ) <sub>2</sub> (Fe <sub>.784</sub> Mg <sub>.216</sub> )O <sub>4</sub>
115	8.4034(3)	593.42(7)	0.2567(1)	1.5 %	215	2.046(1)	1.9162(7)	(Fe <sub>.447(3)</sub> Mg <sub>.417</sub> Ru <sub>.115</sub> Ir <sub>.021</sub> ) <sub>2</sub> (Fe <sub>.771</sub> Mg <sub>.229</sub> )O <sub>4</sub>
117	8.3955(3)	591.75(6)	0.2568(3)	1.6 %	231	2.043(3)	1.917(2)	(Fe <sub>.488(4)</sub> Mg <sub>.435</sub> Rh <sub>.050</sub> Os <sub>.028</sub> ) <sub>2</sub> (Fe <sub>.831</sub> Mg <sub>.169</sub> )O <sub>4</sub>

- Magnesioferrite starting material, a = 8.3912(6) Å and V = 590.8(1) Å<sup>3</sup>.
- a is the length of the unit cell, V is unit cell volume.
- The tetrahedral cation is at [1/8,1/8,1/8], the octahedral cation is at [1/2,1/2,1/2] and the oxygen is at [u,u,u].
- n is the number of unique reflections used in the refinement.
- R(MO) and R(TO) are the octahedral and tetrahedral bond lengths for each structure.

clear that our oxidizing laboratory conditions do not duplicate the natural mantle environment, our conditions were necessary to produce high concentrations of Re and the PGE's to enable detection by electron microprobe analysis. Furthermore, our runs at high pressure (5.0 GPa) and temperature (1400 °C) indicate that Re, Ir, Ru, Os and Rh continue to be compatible in ferrite spinels at these deep mantle conditions. Because olivine goes through a transition to spinel structure within the mantle (e.g., fayalite at 5.75 GPa; Yagi et al., 1987) it is possible that silicate spinels (Hazen, 1993) may be significant hosts for PGE in the deep mantle, again where sulfide is not likely to be stable. Such a large reservoir could host a significant fraction of the deep mantle PGE and thus warrants further study.

### 3.4 Accretion and meteorite fusion crust

Finally, fusion crusts on meteorites form when their surfaces are heated during entry into Earth's atmosphere. Because this is an oxidizing environment, magnetite- and magnesioferrite-rich spinels are found in meteorite fusion crusts (Genge and Grady, 1999). Chondritic meteorites contain large concentrations of PGE's, and so these oxides will be host phases for the PGE's within fusion crusts. This will undoubtedly have implications for the efficiency of accretion of *oxidized* PGE's over Earth history.

**Acknowledgments.** Discussions with C. Capobianco, M.J. Drake, and J. Chesley are greatly appreciated. The journal reviews of D. Ebel and an anonymous reviewer clarified the presentation. T. Teska and K. Domanik provided assistance on the electron microprobe. This work is supported by NSF grants EAR-9706024, EAR-0074036 and EAR-9903104.

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(Received August 8, 2000; revised October 25, 2000; accepted November 1, 2000.)