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Iridium, ruthenium and rhodium in komatiites: Evidence for iridium alloy saturation

Stephen J. Barnes [a,*], Marco L. Fiorentini [b]

[a] CSIRO Exploration and Mining, Bentley, WA 6102, Australia
[b] Centre for Exploration Targeting, School of Earth and Geographical Sciences, The University of Western Australia, 35 Stirling Highway, Crawley WA 6009, Australia

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ABSTRACT

A large body of new data (over 400 samples) on platinum-group element (PGE) concentrations in Yilgarn Craton komatiites is combined with all available high-quality literature data, to reveal trends in a spectrum of komatiite lithologies ranging from spinifex-textured rocks to pure olivine and olivine–chromite accumulates. The data set is restricted to Carius Tube-isotope dilution analyses, and high-precision nickel sulfide fire-assay-ICP-MS analyses, and we demonstrate good agreement between the two methods. Only S-poor samples are considered, and the data set is filtered to eliminate the effects of addition of cumulus chromite, and addition or segregation of magmatic sulfide liquid.

The residual trends indicate that Ir, Ru and Rh are decoupled from one another and from Pt and Pd. Rhodium behaves more like Pt and Pd, whereas Ru is intermediate between Ir and Rh. Rhodium and Ru both show indications of olivine control with partition coefficients less than unity. The maximum Ir whole-rock content is a roughly linear positive function of MgO, but the minimum is constant, sub-1 ppb and independent of MgO. Ruthenium shows some evidence for limited control by chromite, but anomalous Ru enrichment is also found in some olivine cumulate samples with no evidence for accumulated chromite or sulfide. Neither Rh nor Ir shows evidence for any detectable control by chromite. The distribution of Ir, and to a lesser degree Ru and Rh, cannot be adequately explained by olivine control, and a major influence of an Ir-rich phase is strongly indicated.

The pattern of Ir variance in relation to MgO bears some important similarities to that of Cr. This similarity arises from the fact that both elements are controlled by a temperature-dependent solubility limit: the chromite saturation surface in the case of Cr, and saturation in Ir (or Ir–Os) alloy in the case of Ir. Combining this effect with moderate compatibility in olivine allows us to successfully model the entire range of Ir data. The upper limit of Ir concentration in olivine cumulates, in an exact analogy to that for Cr, is interpreted as the cotectic ratio of olivine to alloy, as determined by the average slope of the tangent to the alloy solubility curve.

Sulfide-undersaturated mantle melts of a wide range of compositions are likely to be Ir alloy saturated. Experimental predictions of very low Ir solubilities in magmas are borne out, with the further implication that true thermodynamic sulfide–silicate liquid partition coefficients, at least for Ir and by inference for the other PGEs, are of the order of 10^7 or even higher.

1. Introduction

The geochemistry of iridium, and the other iridium-group platinum-group elements (IPGEs) Os and Ru, has been enigmatic since the first availability of high-precision ppb-level analyses in the 1970s (Keays and Davidson, 1976; Crocket, 1979; Keays et al., 1981; Keays, 1982). Early data, obtained primarily by neutron activation analysis, established that the IPGEs, and Ir in particular, were fractionated from the remaining PGEs Pt, Pd and Rh (the PPGEs) during igneous processes, and behaved essentially as compatible elements even in the absence of magmatic sulfides (Keays et al., 1981; Barnes et al., 1985; Barnes and Naldrett, 1987). Subsequent detailed studies employing either nickel sulfide fire-assay or Carius Tube isotope dilution pre-concentration techniques followed by ICP-MS, have confirmed the general compatibility of the IPGEs during processes of mantle melting and low pressure crystal fractionation from high-degree olivine-saturated mantle melts such as komatiites and high-Mg basalts (Brugmann et al., 1985; Crocket and MacRae, 1986; Barnes and Naldrett, 1987; Barnes and Picard, 1993; Rehkamper et al., 1999; Puchtel and Humayun, 2000, 2001; Lesher et al., 2001b; Momme et al., 2002, 2003; Maier et al., 2003; Puchtel et al., 2004). Most of these studies have also concluded that the PPGEs behave essentially as incompatible elements in the absence of sulfide liquid, that olivine by itself is incapable of explaining all the variance within the IPGE trends, and that some IPGE-enriched phase other than olivine plays a role in controlling the IPGEs (Puchtel et al., 2004, 2007). This study reports new results, obtained by nickel sulfide fire-assay followed by ICP-MS and also by Carius Tube dissolution followed by isotope dilution ICP-

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* Corresponding author. Tel.: +61 8 6436 8645; fax: +61 8 6436 8586.
E-mail address: steve.barnes@csiro.au (S.J. Barnes).

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MS, on an extensive suite of Munro-type (Al-undepleted) komatiites from the Yilgarn Craton in Western Australia, and combines them with the existing body of high-precision PGE analyses of komatiites in the literature. The sample suite incorporates a range of compositions from fractionated komatiitic basalts through typical spinifex-textured komatiites to very pure olivine adcumulates, with and without cumulus chromite. By analogy with the pattern of variation seen for Cr in relation to MgO in komatiite suites (Barnes, 1998), we argue that the observed distribution of Ir shows a distinctive signal of control by temperature-dependent saturation of komatiite melts with an IPGE-dominated solid phase, probably an Ir-rich alloy, coupled with limited partitioning into olivine. The saturation surface for Ir alloy determines the apparent compatible behaviour of Ir in komatiite liquid compositions, and also the widely variable but distinctively limited pattern of variation in Ir and Ru vs MgO over the whole suite, including olivine-rich cumulates. This conclusion applies to sulfide-bearing komatiite magmas, and hence bears out the applicability of experimental evidence for very low Ir and Ru solubilities in magnesian silicate magmas to sulfide-bearing natural magmas. This in turn provides evidence for extremely high partition coefficients, of the order of 10^7, for Ir between sulfide and silicate melts, based on solubility measurements in S-free systems (O'Neill et al., 1995; Andrews and Brenan, 2002b; Pruseth and Palme, 2004). The conclusions from this study have important implications for the origin of Merensky-type PGE Reefs in layered intrusions, for mantle melting, core formation and for the IPGE budget of the planet.

2. Review of existing geochemical data and experimental results bearing on PGE behaviour in magmas

Detailed interpretation of IPGE trends in komatiites and high-Mg basalts depends on knowledge of partition coefficients (*D*) of these elements into olivine and chromite. A rapidly expanding body of recent data on *D* values and metal solubilities is derived from

a) observed trends of IPGE v.s MgO in komatiite and basalt suites (e.g. Puchtel et al., 2004)
b) experimental measurements e.g. Brenan et al. (2005).

2.1. Partition coefficients—olivine/liquid

Values of the partition coefficient $D_{\mathrm{PGE}}^{\mathrm{olivine/liquid}}$ of between 0.2 and 1.0 for Ir, Ru and Rh were derived from high-precision Carius Tube isotope dilution analyses of komatiites from the Abitibi Greenstone Belt of the Superior Craton in Canada (Puchtel et al., 2004) and from the differentiated komatiitic basalt lava lake (Victoria's Lava Lake) in the Vetreny Belt of the Baltic Shield, Russia (Puchtel and Humayun, 2001). The authors argued that the IPGE trends observed in these systems resulted from the presence of an Os–Ir–Ru-rich phase on the liquidus during the komatiite lava differentiation. Brenan et al. (2005) measured values for $D_{\mathrm{Ir}}^{\mathrm{olivine/liquid}}$ between 0.4 and 2.0, under oxidising conditions (FMQ +2.5), implying dissolution as Ir^{2+}, and presence of Ir as mixture of Ir^{2+} and Ir^{3+} in the melt.

2.2. Partition coefficients—chromite/liquid

Numerous studies have considered the role of spinel, and specifically chromite, in the fractionation of the IPGEs from the PPGEs. Experiments by Righter et al. (2004) obtained very high $D_{\mathrm{IPGE}}^{\mathrm{spin/liq}}$ values—values from 5–22,000 for Ir and values of 76–866 for Ru, with Re, Pt and Au behaving incompatibly in spinel. The highest values were obtained in a Cr-poor spinel. Results were broadly consistent with, but up to an order of magnitude higher than previous experiments by Capobianco and Drake (1990) and Capobianco and Hervig (2004). The data of Righter et al. (2004) imply that spinel could play a significant role in controlling IPGE trends in komatiites. However, experimental oxygen fugacities utilized in the experiments were between the NNO and HM buffer curves to suppress the ubiquitous problem of micro-nugget formation, somewhat higher than the QFM values expected in komatiites (Canil, 1997). The observed inverse relationship between f_{O_2} and *D* would suggest lower values in the natural systems. Absolute levels of PGEs were also very high in the experiments of Righter et al. (2004), raising the question of non-Henry's Law behaviour and positive dependence of *D* on PGE content—this was reported by Capobianco and Hervig (2004), but denied by Righter et al. (2004).

2.3. Experimental data on solubilities of PGEs in silicate melts

Evidence for control by IPGE-enriched magmatic phases implies extremely low solubilities, down to low ppb levels, of the IPGEs under magmatic conditions. Numerous experimental studies support this hypothesis. Brenan et al. (2005) measured Ir solubility in synthetic melts, defined as the concentration of Ir in the silicate melt in equilibrium with pure Ir metal. They found Ir solubility dependent on f_{O_2}, varying log-linearly at 1340 °C from 2.5–5 ppb at FMQ +2.7 to 600 ppb at FMQ +5.4. They also found a maximum solubility of Os of 10 ppb at FMQ +0.6. O'Neill et al. (1995) obtained a solubility limit of around 30 ppb Ir in a haplobasaltic $\mathrm{CaO–MgO–Al_2O_3–SiO_2}$ melt at 1400 °C, for oxygen fugacities between IW and QFM, increasing rapidly for higher f_{O_2}. The constant apparent solubility below QFM implies solution as neutral Ir^0. O'Neill et al. (1995) used this result to derive predicted values for sulfide/silicate partition coefficients as discussed below.

Experimental work by Brenan and Andrews (2001) and Matveev and Ballhaus (2002) suggests that the crystallization of Os–Ir–Ru-rich alloys from basaltic magma may be feasible. Ertel et al. (2006) measured the solubility of Pt in anorthite–diopside eutectic melt from 0.5 to 14 GPa and 1723–2223 K. The authors concluded that “nanonuggets” are part of the stable metal phase and that average–lowest analyses yield meaningful solubility limits. In their study, parameterization of $D^{\mathrm{met/sil}}$ shows that increasing pressure, and to a greater extent increasing temperature, make Pt more lithophile. Borisov and Palme (1995) found evidence for strong f_{O_2} dependence of Ir solubility, decreasing from 430 ppb in air down to 0.3 ppb at $\log f_{\mathrm{O}_2}$ −8 to −12 at 1480 °C, implying a valence of 1. Borisov and Palme (1997) found a corresponding decrease in Pt solubility with decreasing f_{O_2}, implying valence +2. Solubilities range from ~20,000 ppb in pure O_2 to minimum values of ~60 ppb at $\log f_{\mathrm{O}_2}$ −5 and 1400 °C. The only conflicting data come from studies of Amosse and Allibert (1993), who showed the opposite f_{O_2} dependence of Ir solubility, attributing their results to “passivation” of neutral dissolved Ir^0 in the melt by formation of a nano-scale oxide layer. The discrepancy between their results and others has apparently not been resolved.

Solubilities of Ru in sulfide liquids have been shown to be of the order of 1–10%, (Brenan and Andrews, 2001; Andrews and Brenan, 2002a,b), implying that solid laurite and Ru–Ir–Os-rich alloys are only likely to be stable at magmatic temperatures in the absence of sulfide liquid saturation. Solubilities of all the PGEs in sulfide liquids are likely to be at percent levels (Mathez, 1999).

2.4. Empirical evidence for high-temperature PGM saturation

Low solubilities are consistent with observations of laurite and Os–Ir–Ru-rich alloys as inclusions in chromite and ferromagnesian silicates in ophiolites (e.g. Prichard et al., 1981; Economou, 1986; Garuti et al., 1999; Arai et al., 1999), in layered intrusions (Talkington and Lipin, 1986; von Gruenewaldt et al , 1989; Peck and Keays, 1990; Maier et al , 1999; Merkle, 1992), and in tholeiites and ferropicrites (Fiorentini et al., 2004). Conversely, Os–Ir–Ru-rich alloys in chromite or olivine from komatiites have not been previously reported. Fiorentini et al. (2004) argued that the magmatic stability of the Os–Ir–Ru-rich alloys could be temperature dependent, and could therefore vary considerably in a range of magmatic systems. Fiorentini et al. (2004) concluded that the apparent lack of Os–Ir–Ru-rich alloy