

Crystallization of platinum-group minerals from silicate melts: Evidence from Cr-spinel-hosted inclusions in volcanic rocks

Vadim S. Kamenetsky^{1*}, Jung-Woo Park^{2,3}, James E. Mungall⁴, Evgeny V. Pushkarev⁵, Alexei V. Ivanov⁶, Maya B. Kamenetsky¹, and Gregory M. Yaxley²

¹School of Physical Sciences, University of Tasmania, Hobart, TAS 7001, Australia

²Research School of Earth Sciences, Australian National University, Canberra, ACT 2601, Australia

³School of Earth and Environmental Sciences & Research Institute of Oceanography, Seoul National University, Seoul 151-742, South Korea

⁴Department of Earth Sciences, University of Toronto, Toronto, Ontario M5S 3B1, Canada

⁵Institute of Geology and Geochemistry, Ural Branch of the Russian Academy of Science, Ekaterinburg 620075, Russia

⁶Institute of the Earth's Crust, Siberian Branch of the Russian Academy of Sciences, Irkutsk 664033, Russia

ABSTRACT

The formation of platinum-group minerals (PGM) during magma differentiation has been suggested to be an important process in primitive magma evolution, but decisive textural evidence is difficult to obtain because PGM tend to be very small and very rare. We have investigated Cr-spinel phenocrysts from two oxidized magmas (Siberian meimechite and Vanuatu [Ambae Island] arc picrite) and one reduced magma (Uralian [Russia] ankaramite) for PGM inclusions and their platinum-group element (PGE) contents. We observed Os-Ir and Pt-Fe alloys entrapped as inclusions in Cr-spinel in all three suites of lava. The alloys may occur in association with PGE-bearing sulfides and co-trapped silicate melt. Cr-spinel crystals also contain measurable amounts of Os, Ir, Ru, and Rh, which are at concentrations 2×–100× higher than mantle values. Thermodynamic models indicate that the arc picrite and ankaramite melts were probably both saturated with the observed PGM phases, whereas the Os-Ir alloy grain observed in the meimechite is not in equilibrium with the “bulk” melt. Our results demonstrate that PGM (alloys and sulfides) occur as liquidus phases in primitive (unfractionated) melts at high temperature and at a variety of redox conditions, and that Cr-spinel is a significant host of PGE, either in the crystal structure or as PGM inclusions.

INTRODUCTION

The distribution of the platinum-group elements (PGE) in mantle-derived magmas is controlled by their extremely chalcophile and siderophile behavior. Alloys of the PGE with Fe or with each other show sharply increasing solubility in silicate melts as both temperature and oxygen fugacity (f_{O_2}) increase (e.g., Amossé et al., 1990; Borisov and Palme, 1997; Ertel et al., 1999; Laurenz et al., 2013; Mungall and Brennan, 2014). These phases, as well as other platinum-group minerals (PGM) such as laurite, are highly soluble in sulfide liquid (e.g., Brennan and Andrews, 2001; Mungall and Brennan, 2014). As a result, occurrence of PGM as potential phenocryst phases in magmas is extremely sensitive to f_{O_2} both directly via their solubility in silicate melt and indirectly because of the instability of sulfide melt at high f_{O_2} . PGM have been widely reported in layered mafic intrusions and ultramafic members of ophiolites and Ural-Alaskan complexes, and to a lesser extent in mantle peridotites. In all occurrences, the PGM have a marked spatial association with accumulations of Cr-spinel (i.e., chromitites); indeed, a Web of Science (<https://login.webofknowledge.com>) search on Pt and chromite turns up 559 research articles since 1969. PGM relationships with Cr-spinel were considered in a number of empirical and experimental studies. At high f_{O_2} , the iridium-group elements (IPGE) and Rh are incorporated into Cr-spinel in solid solution, but they may exsolve upon cooling (e.g., Brennan et al., 2012; Fiorentini et al., 2004; Locmelis et al.,

2011; Pagé et al., 2012; Park et al., 2012). Conversely, PGM may form at the liquidus and be entrapped by growing Cr-spinel, a process possibly aided by slight depression of f_{O_2} in diffusive boundary layers surrounding growing spinel crystals (e.g., Amossé et al., 1990; Augé et al., 2005; Barnes and Fiorentini, 2008; Fiorentini et al., 2004). Most observations of PGM inclusions in Cr-spinel are related to either deep-seated intrusive rocks that experienced sub-solidus recrystallization or peridotitic mantle restites that are not only metamorphic in nature, but usually hydrothermally altered. Apart from Pt-Fe alloy inclusions in Cr-spinel phenocrysts briefly described from the Ambae volcano, Vanuatu (Park et al., 2012), there have been no other direct observations of magmatic PGM in rapidly cooled volcanic rocks. This paper reports new findings of unambiguously magmatic PGM in Cr-spinel phenocrysts in three volcanic suites from different geodynamic environments and explores the factors potentially responsible for PGM saturation.

SAMPLE DESCRIPTION AND PREPARATION

The three sample sets employed in this study are olivine-clinopyroxene-phyric volcanic rocks with abundant microphenocrysts of Cr-spinel. The Siberian meimechite dike, representing the Permian-Triassic large igneous province (Meimecha River, near Lenkos-Haya Mountain), is an incompatible element-rich continental picrite produced by very low degrees of melting of refertilized mantle at high ambient f_{O_2} (Arndt et al., 1995; Sobolev et al., 2009) with high, unfractionated PGE abundances (Mungall et al., 2006). The two other lava samples, a Devonian ankaramite from the Main Uralian fault, Russia, (Spadea et al., 2002), and picrite from the active Ambae volcano, Vanuatu (Eggins, 1993), represent primitive island-arc magmas. The Uralian ankaramite, found in the serpentinite mélange (30 km northwest of Uchaly), is characterized by exceptionally low contents of Al_2O_3 , TiO_2 , Na_2O , and incompatible trace elements, consistent with an origin by remelting of previously melt-depleted peridotite. The Ambae arc picrite belongs to a low-Ti suite with moderate enrichment in the rare earth elements and highly fractionated PGE contents (Park et al., 2012). All of the samples have high CaO/ Al_2O_3 (1.05 in arc picrite to 2.54 in ankaramite; Table DR1 in the GSA Data Repository¹), compared to common mantle-derived melts (<0.8) and high-Cr# compositions of Cr-spinel.

The Cr-spinel from the meimechite and arc picrite samples is among the most oxidized worldwide, in contrast to the moderately reduced ankaramite Cr-spinel (Fig. 1; Table DR4). Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) analyses of PGE in Cr-spinel

¹GSA Data Repository item 2015303, methods (LA-ICPMS analysis of PGE in Cr-spinel and standards), Tables DR1–DR3 (full analytical results and modeling) and Figures DR1 (element maps of PGM inclusions) and DR2 (normalized PGE compositions of Cr-spinel and rocks), is available online at www.geosociety.org/pubs/ft2015.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

*E-mail: Dima.Kamenetsky@utas.edu.au

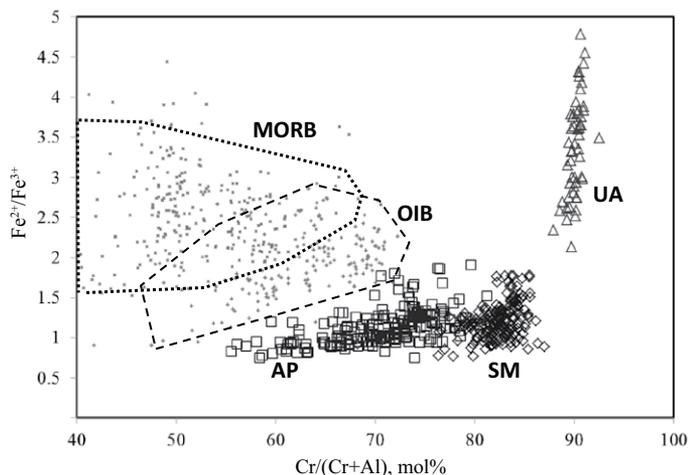


Figure 1. Compositional features of Cr-spinel from Siberian meimechite (SM), Ambae picrite (Vanuatu [Ambae Island]; AP), and Uralian ankaramite (Russia; UA). Compositions of Cr-spinel (after Kamenetsky et al., 2001) from mid-oceanic ridge basalts (MORB) and ocean island basalts (OIB) are plotted for comparison.

were performed using the established instrumentation and technique (Park et al., 2012; see methods in the Data Repository).

Several hundred Cr-spinel grains (0.2–0.5 mm) were hand-picked from each crushed sample and mounted in epoxy resin. Due to Cr-spinel opacity, a search and semiquantitative analysis of PGM were performed on sequentially exposed and polished grain surfaces using scanning electron microscopes with energy dispersive X-ray spectrometers (FEI Quanta 600 and Hitachi SU-70, University of Tasmania, Australia). Although the sequential grinding technique allowed examination of numerous surfaces (up to 50 in larger grains) at ~10 μm intervals, many PGM grains were likely polished away because of their small size (<5 μm).

PGM INCLUSIONS AND PGE IN Cr-SPINEL PHENOCRYSTS

In the meimechite chromite concentrate (Figs. 2A and 2B; Fig. DR1A in the Data Repository) we located only a single ~5 μm euhedral grain of Os-Ir-Ru alloy ($\text{Os}_{0.53}\text{Ir}_{0.37}\text{Ru}_{0.10}$) with a thin rim enriched in Fe and Ni and depleted in PGE [wt%, (Fe + Ni)/PGE = 0.38; Fe/Ni = 1.66]. Three PGM inclusions recorded in the arc picrite sample are Pt-Fe alloys (~Pt_{0.83}Fe_{0.17}) containing minor Ir, Os, and Rh (Park et al., 2012). The largest (~7 μm) euhedral inclusion contains an ~2.5- μm -long inclusion of Os (with minor Ir) (Figs. 2C and 2D; Fig. DR1B). Five PGM inclusions in Cr-spinel phenocrysts from the ankaramite sample are 2–5 μm Pt-Fe alloys (~Pt_{0.6}Fe_{0.4}; Figs. 2E–2G). They contain variable amounts of Ni, Cu, and Rh (up to 15 at% total). Their shapes are perfectly euhedral (Figs. 2E and 2F). One euhedral inclusion has two protuberances of the same composition, extending at a right angle to each other (Fig. 2G). These offshoots, observed under the surface of host Cr-spinel, have a length comparable with the size of the inclusion. Other types of PGE-bearing phases hosted by the ankaramite Cr-spinel phenocrysts are sub-micrometer in size and represented by Ru-Os sulfide [(Ru_{0.67}Os_{0.33})S₂, possibly laurite-erlichmanite solid solution] intergrown with Rh-Ni-Fe sulfide (Ni_{0.8}Rh_{0.12}Fe_{0.08})S; both are attached to the Pt-Fe alloy inclusion and complement the crystal habit of the latter (Fig. 2F). Additionally a Fe-Ni alloy with ~10 wt% Pt is found as two equant-shaped blebs inside the Cu-Fe-Ni sulfide [compositions vary between Cu₂FeS₂ and Cu(Fe,Ni)₂S₂] inclusion (Fig. 2H; Fig. DR1C). Submicrometer-sized PGM, invisible in the optical microscope, are recorded during the LA-ICP-MS analyses of Cr-spinel in all samples. For example, nine co-incident spikes of Pt, Ir, Os, and Rh in time-resolved spectra were recorded in five out of 87 analyzed Cr-spinel grains in the arc picrite sample (Park et al., 2012). The PGE spikes in the ankaramite (Pt)

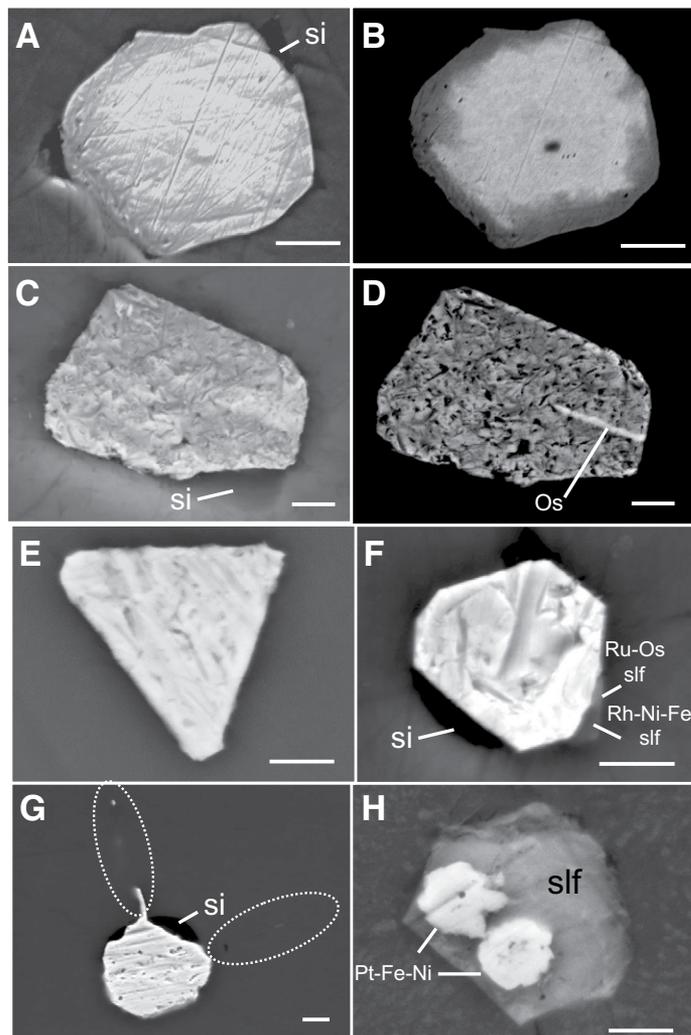


Figure 2. Electron microscope images of platinum group element (PGE)-bearing inclusions in Cr-spinel phenocrysts from Siberian meimechite (A, B), Ambae picrite (Vanuatu [Ambae Island]; C, D), and Uralian ankaramite (Russia; E–H). Note coexisting silicate (si) and sulfide (slf) phases and protuberances of Pt-Fe alloy (circled in G). Details of compositions are given in text and in Figure DR1 (see footnote 1). Images are made using secondary electrons (A, C) and back-scattered electrons (B, D, E–H). Scale bar is 1 μm .

and meimechite (Pt and Pt-Ir) samples also represent micro-inclusions of PGM. The PGM inclusions in all studied samples are co-entrapped with silicate phases (Figs. 2A, 2C, 2F, and 2G) that are too small for analysis, but can be distinguished by characteristic Si and Ca signals on the energy dispersive spectroscopy (EDS) element maps (Fig. DR1) that may represent co-entrapped melt. Several polyphase PGM and silicate-bearing inclusions have the negative crystal shape of the host Cr-spinel (Figs. 2C and 2G), suggesting origins as melt inclusions.

Cr-spinel grains from all samples contain measurable amounts of IPGE and Ru (Table DR3; Fig. DR3) with uniformly high count rates in time-resolved LA-ICP-MS spectra apart from occasional and easily recognized spikes, which we attribute to nano-scale nuggets of PGM, whereas Pt and Pd contents are below the 2 ppb detection limit. Osmium, Ir, and Ru are enriched in the meimechite Cr-spinel, whereas their Rh concentration is about a factor of five lower than those of Cr-spinel from the arc picrite and ankaramite (Table DR3; Fig. DR3). The concentrations of Os, Ir, and Ru in the ankaramite Cr-spinel are approximately a factor of 5–10 lower than those of the arc picrite and meimechite.

DISCUSSION

The occurrences of alloys of Pt-Fe and Os-Ir detected in this study as visible grains and micronuggets included in the Cr-spinel phenocrysts from volcanic rocks in continental and subduction-related settings suggest that PGM occurred as primary magmatic phases at liquidus temperatures, estimated from mineral and rock compositions, ranging from 1100 °C for arc picrite (Eggins, 1993) to >1400 °C for meimechite (Sobolev et al., 2009). Direct crystallization of PGM from the melt is consistent with the results of several experimental studies reviewed by Finnigan et al. (2008). Moreover, entrapment of PGM by liquidus Cr-spinel appears to support the model of slightly reduced conditions at the melt–Cr-spinel interface, promoting saturation in PGE (e.g., Finnigan et al., 2008) and a related hypothesis of “physical affinity between chromite and PGM” (Augé et al., 2005, p. 730).

The hypothesis that the observed PGM could have been stable under magmatic conditions is amenable to testing by quantitative estimation of their solubilities in silicate melt under the conditions of crystallization of the host chromite grains (Table DR4). We estimate the f_{O_2} at which the observed Pt-Fe alloys would coexist with the magmas at their inferred liquidus temperatures, using the activity-composition model of Kessel et al. (2001), compared with estimates done using olivine-spinel oxygen geothermobarometry for those samples containing olivine (Ballhaus et al., 1991) (Table DR4). Alloy solubilities were estimated by calculating solubilities of pure metals (e.g., Borisov and Palme, 1997; Ertel et al., 1999; Mungall and Brenan, 2014) corrected for the activity of Pt in Pt-Fe alloy (Kessel et al., 2001) or Ir in Os-Ir-Ru alloy (assuming ideal mixing in lieu of a multicomponent solution model for these complex compositions) and corrected for the presumed existence of metal-sulfur complexes in the silicate melt (Mungall and Brenan, 2014).

Several key points emerge from this exercise. The meimechite and the arc picrite both appear to have existed at high f_{O_2} well above the range of stability of sulfide liquid due to oxidation of sulfide to sulfate (e.g., Jugo et al., 2010). Consequently the enhancement of PGE solubility as metal-sulfide complexes must have been negligible, and their solubilities can be assessed solely in terms of oxide species solubilities. On the other hand, the alloy observed in the ankaramite has far higher Fe/Pt than that in the arc picrite. The high Fe/Pt requires alloy precipitation at much lower f_{O_2} , close to the fayalite-magnetite-quartz (FMQ) oxygen buffer. To constrain sulfur fugacity (f_{S_2}), we note that the presence of laurite-erlichmanite solid solution co-entrapped with Pt-Fe alloy within chromite in the ankaramite (Fig. 2F) implies that f_{S_2} was close to or equal to that required to stabilize sulfide liquid (Brenan and Andrews, 2001); however, if any more than an infinitesimal quantity of sulfide liquid had been present, then the PGE would have been concentrated within the sulfide liquid rather than as discrete PGM (e.g., Mungall and Brenan, 2014). Hence we assume that f_{S_2} was either buffered by reaction with sulfide melt or just slightly below the saturated value.

The concentrations of Pt in both the arc picrite and the ankaramite are fully consistent with the occurrence of the observed Pt-Fe alloys as stable phases at the inferred f_{O_2} and f_{S_2} (Table DR4). The models of alloy solubility are constructed using sparse experimental data and hence are rather imprecise. If the estimated solubility falls within a factor of two of the measured whole-rock concentration, we consider it plausible that the magma was alloy saturated. If the difference between estimated solubility and whole-rock concentration exceeds an order of magnitude, we think it unlikely that the magma was alloy saturated. Although the models do not prove that these two magmas were saturated with the Pt-Fe alloy, they certainly support that proposition. On the other hand, the measured concentration of Ir in the ankaramite is 150× higher than its estimated solubility in the absence of metal-sulfur complexes, whereas the estimated Ir solubility at the chosen value of f_{S_2} is much higher. We have no *a priori* knowledge of f_{S_2} , but the choice of an f_{S_2} within plausible limits would produce an estimated Ir solubility matching the ob-

served concentration. Thus, we conclude that the observations are consistent with the occurrence of the Ir alloy as a magmatic phase, although this cannot be tested definitively.

Only one grain of alloy was observed in all of the chromite grains examined from the Siberian meimechite; this is not surprising in light of the very high estimated alloy solubilities for both Pt and Ir at the f_{O_2} implied by olivine-spinel equilibrium. In order to achieve saturation with Ir alloy, the magma would have to be reduced to f_{O_2} one log unit above the FMQ buffer (Table DR4). Under this condition, it would remain far undersaturated with Pt-Fe alloy, but an Os-Ir-Ru alloy might be expected to form at the observed concentration of Ir.

As a further check on the inferred redox conditions, we compared our measured PGE concentrations in chromite with their concentrations in the host rocks. We observed enrichments of Ru and Ir in chromite/bulk rock of 50–140 and 8–55, respectively. These elements show somewhat higher compatibility in the meimechite than in the ankaramite, which is expected in light of the higher proportion of $Fe^{3+}/(Fe^{3+} + Cr^{3+})$ in the more oxidized meimechite (Brenan et al., 2012). A single grain of Os-Ir alloy found in the meimechite suggests that it crystallized under more reducing conditions than those recorded by the olivine-spinel pairs. The PGE-poor rim surrounding this grain (Fig. 2B) may represent an incomplete re-equilibration of the alloy with the ambient conditions in the host magma.

A chemical signature of PGE-rich phases entrapped in magmatic Cr-spinel, namely Os-Ir (meimechite) and Pt-Fe (ankaramite and arc picrite), corresponds to the bulk compositions of the host rocks (Table DR1; Fig. DR3) and is reflected on a large scale in PGM deposits related to regional intrusive bodies. In the case of Siberian meimechites, it is the spatially and temporally associated Guli pluton (Vasil'ev and Gora, 2014), known for being the source of Os and Os-Ir placer deposits (Okrugin, 1998), whereas the ankaramite magma is considered parental to the platiniferous peridotite-pyroxenite complexes in the Urals (Krause et al., 2007).

CONCLUSIONS AND IMPLICATIONS

We have documented the PGE alloy phases present as mineral inclusions in magmatic chromite crystals from arc picrite, subduction-related ankaramite, and possibly within-plate alkali picrite (i.e., meimechite). In the two subduction-related suites we demonstrated that the concentrations of PGE in the magmas are approximately equal to the expected solubilities of the observed alloy phases, lending strong support to the notion that these magmas crystallized alloys as liquidus phases. On the other hand, the meimechite from Siberia would be strongly alloy undersaturated under the conditions at which chromite crystallized; hence, the single observed alloy grain in this sample could be interpreted as being derived from a reduced component of a pooled magma. However, the chromite from the meimechite has very high concentrations of IPGE apparently contained in solid solution, in accordance with the expected compatibility of IPGE at high f_{O_2} . Cr-spinel is not only a collector of early magmatic PGM (e.g., Hiemstra, 1979), but also a significant depository of PGE, both in the crystal structure and in nanosized inclusions, in amounts exceeding those in the model chondrite mantle (McDonough and Sun, 1995) by 2×–100× times. We conclude that strongly compatible behavior of PGE at early stages of melt crystallization (e.g., Fiorentini et al., 2004; Locmelis et al., 2011; Pagé et al., 2012; Park et al., 2012) may result in their ultimate storage in magmatic cumulates and related PGE depletion of remaining magmas, depending on the shape of the alloy saturation surface in pressure-temperature-composition space (e.g., Barnes and Fiorentini, 2008). This conclusion may lead to revisiting partitioning of PGE between the source mantle and primary melts, followed by constraints on more incompatible behavior of PGE during partial melting, the intragroup fractionation, and related impact on current modeling of the Re-Os systematics and geochronology.

ACKNOWLEDGMENTS

We thank B.G. Pokrovsky for donating the meimechite sample. Thorough reviews by Steve Barnes, Reid Keays, and Sarah Jane Barnes helped to improve the manuscript. The study was supported by the Australian Research Council (Discovery grants DP1092823 and DP130100257).

REFERENCES CITED

- Amossé, J., Allibert, M., Fischer, W., and Piboule, M., 1990, Experimental study of the solubility of platinum and iridium in basic silicate melts: Implications for the differentiation of platinum-group elements during magmatic processes: *Chemical Geology*, v. 81, p. 45–53, doi:10.1016/0009-2541(90)90038-9.
- Arndt, N., Lehnert, K., and Vasil'ev, Y., 1995, Meimechites: Highly magnesian lithosphere-contaminated alkaline magmas from deep subcontinental mantle: *Lithos*, v. 34, p. 41–59, doi:10.1016/0024-4937(95)90009-8.
- Augé, T., Genna, A., Legendre, O., Ivanov, K.S., and Volchenko, Y.A., 2005, Primary platinum mineralization in the Nizhny Tagil and Kachkanar Ultramafic Complexes, Urals, Russia: A genetic model for PGE concentration in chromite-rich zones: *Economic Geology and the Bulletin of the Society of Economic Geologists*, v. 100, p. 707–732, doi:10.2113/gsecongeo.100.4.707.
- Ballhaus, C., Berry, R.F., and Green, D.H., 1991, High pressure experimental calibration of the olivine-orthopyroxene-spinel oxygen geobarometer: Implications for the oxidation state of the upper mantle: *Contributions to Mineralogy and Petrology*, v. 107, p. 27–40, doi:10.1007/BF00311183.
- Barnes, S.J., and Fiorentini, M.L., 2008, Iridium, ruthenium and rhodium in komatiites: Evidence for iridium alloy saturation: *Chemical Geology*, v. 257, p. 44–58, doi:10.1016/j.chemgeo.2008.08.015.
- Borisov, A., and Palme, H., 1997, Experimental determination of the solubility of platinum in silicate melts: *Geochimica et Cosmochimica Acta*, v. 61, p. 4349–4357, doi:10.1016/S0016-7037(97)00268-8.
- Brenan, J.M., and Andrews, D., 2001, High-temperature stability of laurite and Ru-Os-Ir alloy and their role in PGE fractionation in mafic magmas: *Canadian Mineralogist*, v. 39, p. 341–360, doi:10.2113/gscanmin.39.2.341.
- Brenan, J.M., Finnigan, C.F., McDonough, W.F., and Homolova, V., 2012, Experimental constraints on the partitioning of Ru, Rh, Ir, Pt and Pd between chromite and silicate melt: The importance of ferric iron: *Chemical Geology*, v. 302, p. 16–32, doi:10.1016/j.chemgeo.2011.05.015.
- Eggins, S.M., 1993, Origin and differentiation of picritic arc magmas, Ambae (Aoba), Vanuatu: *Contributions to Mineralogy and Petrology*, v. 114, p. 79–100, doi:10.1007/BF00307867.
- Ertel, W., O'Neill, H.S., Sylvester, P.J., and Dingwell, D.B., 1999, Solubilities of Pt and Rh in a haplobasaltic silicate melt at 1300 °C: *Geochimica et Cosmochimica Acta*, v. 63, p. 2439–2449, doi:10.1016/S0016-7037(99)00136-2.
- Finnigan, C.S., Brenan, J.M., Mungall, J.E., and McDonough, W.F., 2008, Experiments and models bearing on the role of chromite as a collector of platinum group minerals by local reduction: *Journal of Petrology*, v. 49, p. 1647–1665, doi:10.1093/ptrology/egn041.
- Fiorentini, M.L., Stone, W.E., Beresford, S.W., and Barley, M.E., 2004, Platinum-group element alloy inclusions in chromites from Archaean mafic-ultramafic units: Evidence from the Abitibi and the Agnew-Wiluna Greenstone Belts: *Mineralogy and Petrology*, v. 82, p. 341–355, doi:10.1007/s00710-004-0044-6.
- Hiemstra, S.A., 1979, The role of collectors in the formation of the platinum deposits in the Bushveld complex: *Canadian Mineralogist*, v. 17, p. 469–482.
- Jugo, P.J., Wilke, M., and Botcharnikov, R.E., 2010, Sulfur K-edge XANES analysis of natural and synthetic basaltic glasses: Implications for S speciation and S content as function of oxygen fugacity: *Geochimica et Cosmochimica Acta*, v. 74, p. 5926–5938, doi:10.1016/j.gca.2010.07.022.
- Kamenetsky, V.S., Crawford, A.J., and Meffre, S., 2001, Factors controlling chemistry of magmatic spinel: An empirical study of associated olivine, Cr-spinel and melt inclusions from primitive rocks: *Journal of Petrology*, v. 42, p. 655–671, doi:10.1093/ptrology/42.4.655.
- Kessel, R., Beckett, J.R., and Stolper, E.M., 2001, Thermodynamic properties of the Pt-Fe system: *The American Mineralogist*, v. 86, p. 1003–1014.
- Krause, J., Brugmann, G.E., and Pushkarev, E.V., 2007, Accessory and rock forming minerals monitoring the evolution of zoned mafic-ultramafic complexes in the Central Ural Mountains: *Lithos*, v. 95, p. 19–42, doi:10.1016/j.lithos.2006.07.018.
- Laurenz, V., Fonseca, R.O.C., Ballhaus, C., Jochum, K.P., Heuser, A., and Sylvester, P.J., 2013, The solubility of palladium and ruthenium in picritic melts: 2. The effect of sulfur: *Geochimica et Cosmochimica Acta*, v. 108, p. 172–183, doi:10.1016/j.gca.2013.01.013.
- Locmelis, M., Pearson, N.J., Barnes, S.J., and Fiorentini, M.L., 2011, Ruthenium in komatiitic chromite: *Geochimica et Cosmochimica Acta*, v. 75, p. 3645–3661, doi:10.1016/j.gca.2011.03.041.
- McDonough, W.F., and Sun, S.-s., 1995, The composition of the Earth: *Chemical Geology*, v. 120, p. 223–253, doi:10.1016/0009-2541(94)00140-4.
- Mungall, J.E., and Brenan, J.M., 2014, Partitioning of platinum-group elements and Au between sulfide liquid and basalt and the origins of mantle-crust fractionation of the chalcophile elements: *Geochimica et Cosmochimica Acta*, v. 125, p. 265–289, doi:10.1016/j.gca.2013.10.002.
- Mungall, J.E., Hanley, J.J., Arndt, N.T., and Debedelievre, A., 2006, Evidence from meimechites and other low-degree mantle melts for redox controls on mantle-crust fractionation of platinum-group elements: *Proceedings of the National Academy of Sciences of the United States of America*, v. 103, p. 12,695–12,700, doi:10.1073/pnas.0600878103.
- Okrugin, A.V., 1998, Mineralogy, types, and origin of the platinum-bearing placer deposits of the Siberian Platform: *International Geology Review*, v. 40, p. 677–687, doi:10.1080/00206819809465231.
- Pagé, P., Barnes, S.J., Bedard, J.H., and Zientek, M.L., 2012, In situ determination of Os, Ir, and Ru in chromites formed from komatiite, tholeiite and boninite magmas: Implications for chromite control of Os, Ir and Ru during partial melting and crystal fractionation: *Chemical Geology*, v. 302, p. 3–15, doi:10.1016/j.chemgeo.2011.06.006.
- Park, J.W., Campbell, I.H., and Eggins, S.M., 2012, Enrichment of Rh, Ru, Ir and Os in Cr spinels from oxidized magmas: Evidence from the Ambae volcano, Vanuatu: *Geochimica et Cosmochimica Acta*, v. 78, p. 28–50, doi:10.1016/j.gca.2011.11.018.
- Sobolev, A.V., Sobolev, S.V., Kuzmin, D.V., Malitch, K.N., and Petrunin, A.G., 2009, Siberian meimechites: Origin and relation to flood basalts and kimberlites: *Russian Geology and Geophysics*, v. 50, p. 999–1033, doi:10.1016/j.rgg.2009.11.002.
- Spadea, P., D'Antonio, M., Kosarev, A., Gorozhanina, Y., and Brown, D., 2002, Arc-continent collision in the Southern Urals: Petrogenetic aspects of the forearc-arc complexes, *in* Brown, D., et al., eds., *Mountain Building in the Uralides: Pangea to the Present: American Geophysical Union Geophysical Monograph 132*, p. 101–134, doi:10.1029/132GM07.
- Vasil'ev, Y.R., and Gora, M.P., 2014, Meimechite-picrite associations in Siberia, Primorye, and Kamchatka (comparative analysis and petrogenesis): *Russian Geology and Geophysics*, v. 55, p. 959–970, doi:10.1016/j.rgg.2014.07.004.

Manuscript received 10 June 2015

Revised manuscript received 4 August 2015

Manuscript accepted 7 August 2015

Printed in USA