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The influence of chromite on osmium, iridium, ruthenium and rhodium distribution during early magmatic processes

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ABSTRACT

Chromite-rich plutonic rocks are enriched in Os, Ir, Ru (IPGE) and Rh which is usually attributed to the presence of micron-size inclusions of platinum-group minerals. It is also known that volcanic rocks show positive correlations between Cr and IPGE and Rh with the most primitive lavas (olivine + chromite phyric) being enriched in these elements compared to the more fractionated lavas suggesting that chromite phenocrysts somehow influence and concentrate the IPGE and Rh. Previous results from in situ analysis of chromite phenocrysts from komatiites and from oxidized arc lavas showed that they contain IPGE and Rh in their structure. Our new results confirm these previous observations and show that the enrichment is a common phenomenon observed in volcanic rocks from several geological settings including MORB, boninite, komatiite, picrite and Hawaiian tholeiite. In contrast, in situ analysis of plutonic chromites show that they contain low concentrations of IPGE and Rh. Mass balance calculations indicate that chromite phenocrysts from volcanic samples are not the major hosts of Os, Ir and Rh accounting for <40%, <25% and <30% of the whole rock budgets, respectively, but they account for ≥30% of the whole rock Ru budget. As in the case of volcanic chromites, plutonic chromites do not have a great influence on Os, Ir and Rh whole rock budget in accounting for <25%, in contrast with volcanic chromites, plutonic chromites account for ≤10% of the whole rock Ru budget. These new results show that chromite from rapidly cooled environments can act as the main Ru-carrier phase but has a minor role in hosting Os, Ir and Rh. Overall, plutonic chromite has a minor role in hosting IPGE and Rh. Chromites from Bushveld ultramafic sills have also been analyzed. They show IPGE and Rh enrichments comparable to chromites from plume related magmas (komatiite and picrite) whereas chromites from Bushveld chromitites show low IPGE and Rh concentrations like other chromitite samples despite the fact that they crystallized from magmas of similar composition. This clearly indicates a change in Os, Ir, Ru and Rh behavior between rapidly cooled and slowly cooled environments.
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1. Introduction

Until recently our understanding of the role of chromite in the fractionation of Os, Ir, Ru, Rh, Pt and Pd (PGE) was essentially indirect and based on the correlations between whole rock Cr and whole rock PGE (Pagé et al., 2012, and references therein). Chromite-rich rocks from many environments (layered intrusions, Uralian–Alaskan type complexes, ophiolites) are enriched in Os, Ir, Ru (IPGE) and Rh, relative to the magmas from which they crystallize, as example the LG1 to LG4 chromitites of the Bushveld Complex (Naldrett et al., 2009), the chromitites of the Kytlym Complex, Northern Urals (Zaccarini et al., 2011), and the chromitites of Shetland Ophiolite (Prichard and Lord, 1993). In situ analysis of chromite from plutonic rocks shows that they contain insufficient IPGE and Rh to account for the whole rock IPGE and Rh budget (Pagé et al., 2012; Park et al., 2012). Chromites from plutonic rocks commonly contain small (1–10 μm) grains of laurite [Ru,±Os,±Ir]S_2 and/or Ru–Os–Ir-rich alloys, both of which are visible using scanning electron microscopy and as peaks on time resolved analysis spectrum of laser ablation analysis (Fig. 6b of Pagé et al., 2012). Their presence has led to the idea that the enrichment of IPGE in the chromitites is due to entrapment of these phases in chromite during their crystallization and growth (Hiemstra, 1979; Legendre and Augé, 1986). In a series of experiments Finnigan et al. (2008) demonstrated that platinum-group minerals (PGM) can crystallize due to a local decrease in oxygen fugacity in the boundary layer of a crystallizing chromite.

Variations in whole rock concentrations of IPGE and Rh in volcanic rocks show a complimentary behavior to the plutonic rocks, with the most primitive lavas being enriched in these elements (Barnes and Picard, 1993; Arguin et al., submitted for publication). Despite the presence of IPGE minerals (IPGM) in chromitites from plutonic rocks the possibility that the IPGE partition into spinel and olivine has also been investigated with some experimental work supporting the partition of IPGE and Rh into spinels and olivine (Capobianco and Drake, 1990; Righter et al., 2004; Brenan et al., 2003, 2005, 2012). Mineral separates from ferropicrites, tholeiitic basalts, komatiitic basalts, and komatiitic flow from the Abitibi Greenstone Belt, Superior Craton, and the Vetreny

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Belt, Baltic Craton have been analyzed for IPGE and Rh (Puchtel and Humayun, 2001; Stone and Crocket, 2003; Puchtel et al., 2004). These results showed that the chromite concentrates are systematically enriched in IPGE relative to the whole rock; however these studies could not answer the question of whether the IPGE and Rh are present in the chromite lattice or as PGM inclusions in the chromite. In situ analyses of chromite phenocrysts from komatiites from Australia and Canada by Locmelis et al. (2011), Pagé et al. (2012) and Méric et al. (2012) found that Ru is present in the chromites. Pagé et al. (2012) also report the presence of Os and Ir from the komatiite chromites and in situ analysis of chromite phenocrysts from oxidized arc lavas (the Ambae Volcano in the Vanuatu Island Arc) also show enrichment in IPGE and Rh (Park et al., 2012). The distribution of IPGE and Rh in the chromites is homogeneous (at least on the scale of ~0.2 μm) thus Locmelis et al. (2011), Pagé et al. (2012) and Park et al. (2012) all concluded that the IPGE and Rh are present in the chromite in solid solution (Wijbrans et al., 2015).

These observations raise questions: 1) How common is the enrichment in IPGE and Rh in chromites from volcanic rocks? Whereas there are numerous studies of the phases hosting PGE in chromites from plutonic settings there are very few studies for chromites from volcanic rocks, thus we do not know whether the presence of IPGE and Rh in chromite phenocrysts is a common phenomenon. 2) If the IPGE and Rh partition into chromite in volcanic settings then why are they present as PGM in plutonic settings? In order to investigate these questions we have determined the platinum-group element content of chromite phenocrysts in volcanic rocks and of chromites from plutonic rocks from a number of different settings. Finally we have determined the IPGE and Rh contents of chromites from the marginal sills of the Bushveld (B-1-UM) and compare these with IPGE and Rh content of chromites from chromitite layers within the intrusion.

These new results combined with mass balance calculations show that IPGE and Rh partition into chromite phenocrysts from many settings, with empirical apparent partition coefficients in the 10 to 100 range. When the chromite phenocrysts data are combined with whole rock analyses we find that Ru is mostly hosted by chromite whereas in addition to chromite other phases are required to host most of Os, Ir and Rh. In contrast and as it has been found in previous studies of plutonic rocks, chromite only hosts a minor amount of the IPGE and Rh and IPGE and Rh enrichments in these rocks also need the presence of other phases. The IPGE and Rh contents of the chromites from the Bushveld sills and the chromites from the Bushveld chromitite are surprisingly different. The IPGE and Rh contents of chromites from the marginal sills contain significant amounts of IPGE and Rh and the IPGE and Rh contents and ratios resemble chromite phenocrysts from plume related volcanic rocks. In contrast the chromites from chromitites within the Bushveld contain very little IPGE and Rh and resemble chromite from other plutonic rocks. The contrast observed between volcanic and plutonic chromites leads us to suggest that the laurite inclusions commonly observed in plutonic chromite form by subsolidus processes.

2. Methodology

2.1. Samples selection

The sample set used for this study includes some samples that have already been analyzed and presented by Pagé et al. (2012), but have now been re-analyzed with new equipment which has lower detection levels, and some new samples. Together these samples include rocks derived from magmas formed from different degrees of partial melting (komatiite to N-MORB) (Fig. 1) and different

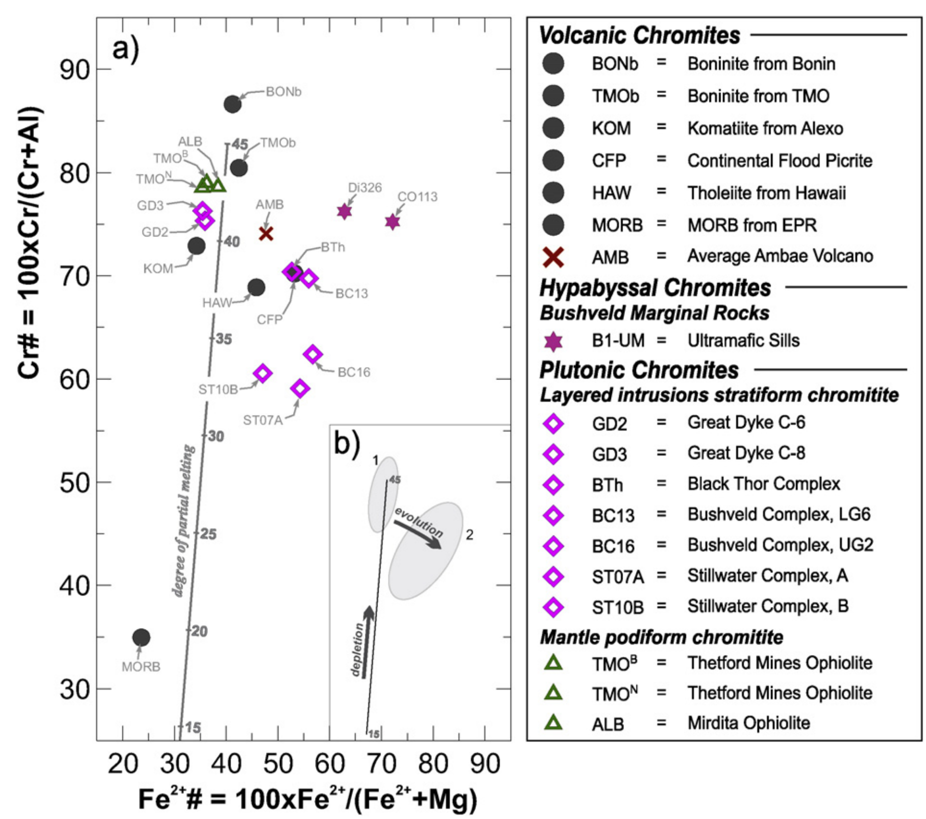

Fig. 1. (a) Cr# versus Fe^{2+}# for chromite from studied samples including chromite phenocrysts from volcanic rocks, chromite from Bushveld marginal sills and chromite from chromitites from layered intrusions and from ophiolitic mantle. The degree of partial melting scale is from Pagé et al. (2008) based on batch melting experiments from Hirose and Kawamoto (1995). (b) The inset shows the two groups of chromite, group 1 has low Fe^{2+}# (<42.5) and group 2 has high Fe^{2+}# (>45.8), see text for more details.

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