



Research Paper

Sulfide-scale insights into platinum-group element behavior during carbonate mantle metasomatism and evolution of Spitsbergen lithospheric mantle



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ARTICLE INFO

Article history:

Received 9 June 2015

Accepted 29 November 2015

Available online 17 December 2015

Keywords:

PGE

Re–Os isotope

Peridotite

Sulfide

Spitsbergen

ABSTRACT

We report combined Re–Os isotope and highly siderophile element data for whole-rock and whole-sulfide grains from Spitsbergen peridotites. The Os–Ir contents in whole-rocks are elevated compared to those of the primitive mantle, but the Pt–Pd–Re contents are depleted, reflecting refractory monosulfide solid solution (Mss) control during mantle melting. There are two general types of sulfide documented in global mantle samples: primary residual Mss with subchondritic Pd/Ir ratios and secondary metasomatic sulfides with suprachondritic Pd/Ir ratios. Most Spitsbergen sulfides have elevated Ir contents, and belong to the residual group. Most but not all Spitsbergen sulfides, however, are unusual in that they show a fractionation of Os (and Ru) from Ir which cannot be reconciled with a simple partial melting process. The Os (+ Ru) fractionation from Ir is most notable in a sample containing mantle-derived carbonate-bearing pockets. Infiltration of carbonate-rich S-undersaturated melt into the Spitsbergen lithospheric mantle may result in the formation of localized S-rich liquid by dissolving residual Mss. Such melt compositions may promote laurite crystallization before Mss, causing the combined depletion of Os + Ru relative to Ir in later-formed Mss. The Re-depletion model ages of residual sulfide grains from Spitsbergen peridotites coincide with crustal ages determined for Spitsbergen, indicating coupled mantle–crust evolution, and furthermore, they coincide with the previously proposed major peaks of pulsed crustal formation periods in Earth at ca. 2.7, 1.9 and 1.2 Ga.

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1. Introduction

Most radiogenic isotope systems (Rb–Sr, Sm–Nd and U–Th–Pb) are based on elements which behave moderately to highly incompatibly during mantle melting, and are highly susceptible to perturbation by metasomatism within the mantle. For the Re–Os isotopic system, Re is moderately incompatible and Os is compatible during mantle melting. Therefore, the Re–Os system has been extensively used for dating mantle melt extraction events (Carlson et al., 2005; Pearson et al., 1995; Reisberg and Lorand, 1995; Shirey and Walker, 1998; Walker et al., 1989).

Platinum-group elements (PGE: Os, Ir, Ru, Rh, Pt, and Pd) and Re, encompassing the Re–Os isotope system, can provide important information for petrogenetic processes in peridotites, such as mantle melting and melt–rock interaction (e.g., Lorand et al., 2013). The budget of PGE in mantle rocks is typically dominated by Fe–Ni–Cu sulfides (base metal sulfide; BMS) and, in particular, monosulfide solid solution (Mss), which is a typical BMS in mantle rocks (e.g., Alard et al., 2000; Lorand and Alard, 2001; Lorand et al., 2008, 2010). Olivine may accommodate

divalent Ir and possibly Ru, substituting for base metals in its octahedral sites (Brenan et al., 2005; Mungall and Brenan, 2014). However, the sulfide–silicate melt partition coefficients for Ir and Ru are three orders of magnitude higher than the olivine–silicate melt coefficient (Bockrath et al., 2004; Brenan et al., 2005; Mungall and Brenan, 2014). Osmium, Ir, Ru and Rh may substitute for trivalent cations in Cr-spinel at high oxygen fugacity ($f_{O_2} = (FMQ) + 2.5 \log \text{ units}$, where FMQ is fayalite–magnetite–quartz) (Capobianco and Drake, 1990; Park et al., 2012; Righter et al., 2004), which is, however, greater than those estimated for the asthenosphere and majority of continental spinel peridotite xenoliths (FMQ + 1 to FMQ – 2 log units; Ballhaus et al., 1991; Frost and McCammon, 2008; Wood and Virgo, 1989). Meanwhile, micro-metric alloy could be a main PGE host in highly refractory BMS-free mantle peridotites (Luguet et al., 2007; Mungall and Brenan, 2014).

The Svalbard archipelago is located on the northwestern-most edge of the Eurasian Plate, near the Gakkel Ridge and Knipovich Ridge in the Arctic and North Atlantic Ocean, respectively (Fig. 1a). Quaternary alkali volcanic activity is found at three centers (Sverrefjell, Sigurdffjell and Halvdanpiggen) in the Bockfjorden area of northwestern Spitsbergen, Svalbard (Fig. 1b). The volcanic lavas contain abundant xenoliths: mainly peridotite and mafic to intermediate granulites (Amundsen, 1987; Amundsen et al., 1987; Choi et al., 2010; Griffin et al., 2012; Ionov

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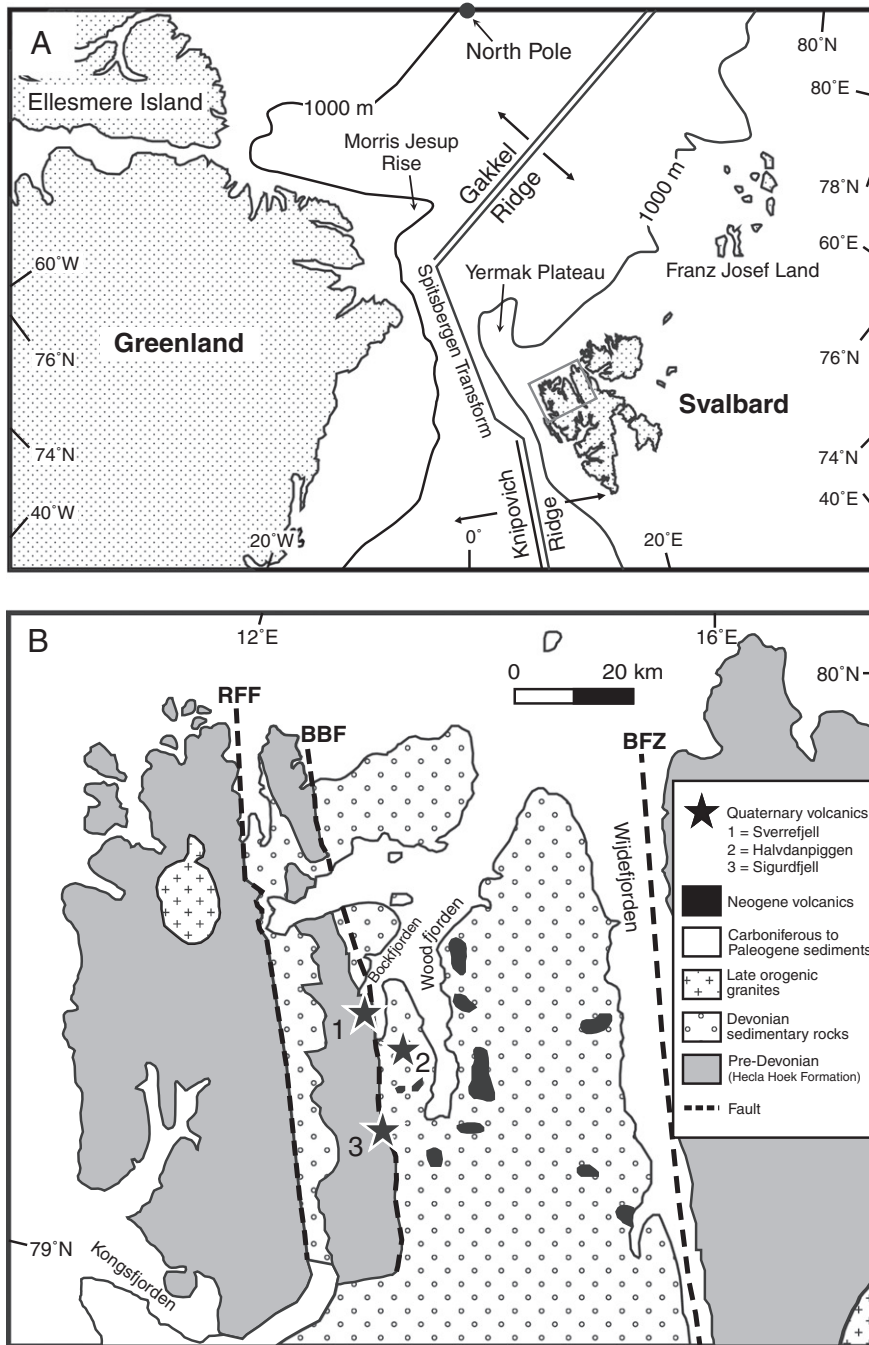


Fig. 1. (A) Location of Svalbard, and (B) simplified geological map of NW Spitsbergen (after Choi et al., 2010). BBF = Breibogen–Bockfjorden Fault; BFZ = Billefjorden fault zone; RFF = Raudfjorden fault.

et al., 1996, 2002). The xenoliths are up to 15 cm in diameter. Spinel lherzolite is the dominant mantle lithology, and some Spitsbergen peridotites contain mantle-derived carbonate-bearing pockets (Amundsen, 1987; Ionov et al., 1996). The carbonates range from dolomite to Mg-bearing calcite (Ionov et al., 1996).

Mantle metasomatism refers to mineralogical and/or compositional modification of primordial mantle rocks due to infiltration of secondary melts/fluids such as silicate melts (Dawson, 1984; Harte, 1983), carbonatite melts (Ionov et al., 1996) and C–O–S–H-bearing fluids (Alard et al., 2011). Two distinctive types of metasomatism have been invoked to explain the overprinted characteristics observed. Modal metasomatism (Harte, 1983) results in secondary mineral formation, such as hydrous or carbonate phases. Cryptic metasomatism (Dawson, 1984) may result in compositional enrichments without any visible

mineral or textural changes. Previous studies (e.g., Amundsen, 1987; Choi et al., 2010; Griffin et al., 2012; Ionov et al., 1996, 2002) show petrological and geochemical evidence for metasomatic overprinting in Spitsbergen peridotites. In fact, multiple episodes of metasomatism have been documented, such as Sr-enrichment and the formation of hydrous phases (e.g., amphibole, phlogopite) with/without apatite, and also including carbonate metasomatism (Ionov et al., 1996, 2002). The secondary events were more severe in the Sigurdjell and Halvdanpiggen than the Sverrefjell peridotites, probably due to independent evolutionary history of the lithospheric mantle beneath both areas (Griffin et al., 2012).

Previous work (Choi et al., 2010; Griffin et al., 2012) tried to constrain the age of lithospheric mantle stabilization, using the Re–Os isotopic system applied to whole-rocks and in-situ analysis of sulfides in the

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