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Compositionally heterogeneous podiform chromitite in the Shetland Ophiolite Complex (Scotland): Implications for chromitite petrogenesis and late-stage alteration in the upper mantle portion of a supra-subduction zone ophiolite

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ABSTRACT

The mantle sequence of the ~492 Ma Shetland Ophiolite Complex (SOC; Scotland) contains abundant compositionally heterogeneous podiform chromitite bodies enclosed in elongate dunite lenses in the vicinity of the petrological Moho. Chromitite petrogenesis and late-stage alteration events recorded in these seams are examined here using petrography, mineral chemistry and crystal structural data. The resistant nature of Cr-spinel to serpentinisation and other late-stage alteration means that primary igneous compositions are preserved in unaltered crystal cores. Chromitite mineralogy and texture from five sampled localities at The Viels, Hagdale, Harold's Grave, Nikka Vord and Cliff reveal significant inter-pod chemical heterogeneity. The Cr-spinel mineral chemistry is consistent with supra-subduction zone melt extraction from the SOC peridotites. The occurrence of chromitite seams in the centres of the dunite lenses combined with variable Cr-spinel compositions at different chromitite seam localities supports a model of chromitite formation from spatially (and temporally?) fluctuating amounts of melt–rock interaction through channelised and/or porous melt flow.

Pervasive serpentinisation of the SOC has led to the almost complete replacement of the primary (mantle) silicate mineral assemblages with serpentine (lizardite with minor chrysotile and antigorite). Magmatic sulphide (e.g., pentlandite) in dunite and chromitite is locally converted to reduced Ni-sulphide varieties (e.g., heazlewoodite and millerite). A post-serpentinisation (prograde) oxidisation event is recorded in the extensively altered Cliff chromitite seams in the west of the studied area, where chromitite Cr-spinel is extensively altered to ferritchromit. The ferritchromit may comprise >50% of the volume of the Cliff Cr-spinels and contain appreciable quantities of 1–2 μm inclusions of sperrylite ($PtAs_2$) and Ni-arsenide, signifying the coeval formation of these minerals with ferritchromit at temperatures of up to ~500 °C. The SOC chromitite Cr-spinels thus not only preserve key insights into the complex melting processes occurring in the upper mantle wedge but can also be utilised to construct a comprehensive alteration history of the lower mantle portions of such supra-subduction zone ophiolites.

1. Introduction

The resistant nature of Cr-spinel to low temperature alteration during the serpentinisation of mantle peridotites has historically led to its widespread application as a petrogenetic indicator for parental melt composition and degree of partial mantle melting in a variety of tectonic settings (Arai, 1992, 1997; Barnes and Roeder, 2001; Dare et al., 2009; Dick and Bullen, 1984; González-Jiménez et al., 2011; Hanghøj et al., 2010; Hellebrand et al., 2001; Irvine, 1965, 1967; Melcher et al., 1997; Mellini et al., 2005; Mukherjee et al., 2010; Pagé and Barnes, 2009; Power et al., 2000; Voigt and von der Handt, 2011). One of the most well-known occurrences of Cr-spinel in mantle lithologies is podiform chromitite (>60 vol.% Cr-spinel; Hunt et al., 2011; O'Driscoll et al., 2010, 2012a,b), which typically occurs in the upper mantle sections of mid-ocean ridge (MOR) and supra-subduction zone (SSZ) ophiolites (see Uysal et al., 2009 for a recent review). In this study, we employ the term petrological Moho to describe a major structure in the Shetland Ophiolite Complex (SOC; Scotland) immediately above and below which most of the podiform chromitites are found (cf. Flinn, 1996, 2001). The petrological Moho demarcates the transition from harzburgite to dunite at the base of the Moho transition zone (O'Driscoll et al., 2012a; Pagé and Barnes, 2009; Zhou et al., 2005) and is distinct from the Moho as defined seismically in many other ophiolites, i.e., at the base of the gabbro unit (Ahmed and Arai, 2003; Alexander and Harper, 1992; Arai, 1997; Boudier and Nicolas, 1995; Hanghøj et al., 2010; Rollinson, 2008).

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The origin of podiform chromitite remains provocative and uncertain. Models involving the blending of a primitive melt and a more SiO_2-rich melt (Arai and Yurimoto, 1994; Ballhaus, 1998; Irvine, 1977; Matveev and Ballhaus, 2002; Uysal et al., 2009; Zhou et al., 1994) and melt–rock interaction (Arai, 1997; Kelemen et al., 1992, 1995; Melcher et al., 1997; Uysal et al., 2009) have been proposed. It has been established that podiform chromitite Cr-spinel composition can reflect formation in different tectonic regimes, e.g., MOR (Cr# [Cr/(Cr + Al)]: <0.60); Abe, 2011; Arai and Matsukage, 1998; Dick and Bullen, 1984; and SSZ settings (Cr#: >0.60; Arai and Yurimoto, 1994; Dick and Bullen, 1984; González-Jiménez et al., 2011; Whattam and Stern, 2011; Zhou et al., 1996). However, podiform chromitites are a particularly common feature of SSZ ophiolites (cf. Lago et al., 1982). In such settings, associated with high degrees of fluid-assisted partial mantle melting, chromitite seams have been attributed to melt–rock reaction in channels of focussed melt flow (Arai, 1997; Arai and Yurimoto, 1994; Batanova et al., 2011; Büchl et al., 2004; González-Jiménez et al., 2011). One aspect of podiform chromitite petrogenesis that makes them of special interest is their almost ubiquitous enrichment in platinum-group elements (PGE; Os, Ir, Ru, Rh, Pd, and Pt; Marchesi et al., 2010; Prichard et al., 1996; Uysal et al., 2009). The PGE are typically sited in platinum-group minerals (PGM) and alloy phases (Ahmed and Arai, 2002, 2003; Marchesi et al., 2010; Uysal et al., 2009); most workers seem to find little evidence that the PGE are incorporated into the Cr-spinel lattice during crystallisation, although there may be exceptions (cf. Brenan et al., 2011). Mobilisation and subsequent enrichment of PGE in podiform chromitites is also considered to be associated with the large quantities of melt that migrate through the oceanic mantle during SSZ zone melting (González-Jiménez et al., 2011; Melcher et al., 1997; Prichard et al., 1996).

The mantle portion of the SOC contains abundant podiform chromitites (Flinn and Oglethorpe, 2005; Prichard and Lord, 1993), typically encased in dunite lenses and concentrated directly above and below the petrological Moho. The SOC is a particularly valuable location to study podiform chromitite petrogenesis and PGE-enrichment as the mantle peridotites have apparently undergone minimal tectonic deformation and are superbly well exposed. Certain localities in the SOC are also known to contain exceptionally high concentrations of the PGE (O'Driscoll et al., 2012a; Prichard and Lord, 1993). One of these localities, Cliff (Fig. 1), has previously attracted attention in the published ophiolite literature as its PGE budget is different to that of most other ophiolite podiform chromitites. Specifically, Cliff chromitites are substantially enriched in the Platinum-PGE (P-PGE; Pt, Pd, and Rh) relative to the Iridium-PGE (I-PGE; Os, Ir, and Ru) (O'Driscoll et al., 2012a; Prichard and Lord, 1993). In this study, we select five chromitite localities situated in close (~500 m) proximity to the petrological Moho, including Cliff, to carry out a detailed study of the scales of mineralogical and compositional inter-seam heterogeneity. Sulphide and PGM populations at each locality are also studied, so that insight can be gained into the formation and subsequent evolution of these minerals in podiform chromitites in this upper mantle section. The SOC chromitites apparently preserve evidence of primary magmatic heterogeneity, subsequently overprinted by two metamorphic alteration events. The first of these events pervasively serpentinised the mantle silicate mineral assemblages, predominantly to lizardite. The second was a prograde oxidation event, the effects of which are primarily restricted to the Cliff locality and which may reflect movements on the tectonic structure that excised the ophiolite sole thrust, the Burra Firth Lineament (Cutts et al., 2011).

2. Geological setting

The SOC was obducted as part of a regional SSZ ophiolite suite associated with the collision between a nascent oceanic island arc and the Laurentian margin in the Early–Mid Ordovician (Chew et al., 2010; Woodcock and Strachan, 2000). This event is considered to be related to closure of the Iapetus Ocean and is referred to as the Grampian Orogeny (cf. Chew et al., 2010; Cutts et al., 2011). A zircon U–Pb crystallisation age from a plagiogranite vein cutting the upper portion of the SOC gives a minimum age of 492 ± 3 Ma (Spray and Dunning, 1991). The SOC preserves a partially complete ophiolite sequence (Flinn, 2001; Prichard et al., 1994) principally outcropping on the eastern side of Unst and to a lesser degree on Fetlar (Fig. 1). Ophiolite obduction occurred in two stages; the lower nappe was obducted first onto Proterozoic Dalradian Supergroup schists and gneiss basement during Grampian orogenesis at 470 Ma (Chew et al., 2010; Flinn, 2001; Flinn and Oglethorpe, 2005; Flinn et al., 1991; Spray, 1988). Flinn and Oglethorpe (2005) and Flinn (2007) suggested that emplacement of the upper nappe occurred much later, during thrusting associated with the Scandian Orogeny at ~425 Ma. Flinn (1996, 2001) suggested that obduction occurred 'cold' (<500 °C), based on the relative abundance of antigorite serpentine within a 100 m wide linear zone along the trace of the Burra Firth Lineament. The latter structure marks the western extent of the ophiolite complex and is probably not the ophiolite sole thrust, but a younger basal contact formed during a later tectonic event (Cutts et al., 2011; Flinn, 2001; Flinn and Oglethorpe, 2005). The latter authors suggested that approximately 10 km of the ophiolite crustal section is missing, based on the apparent dichotomy in metamorphic grade between the low grade rocks associated with the ophiolite and the higher P–T conditions recorded in the footwall metasediments (i.e., ~10 kbar and 775 °C).

The upper and lower nappes are pervasively serpentinised (Flinn and Oglethorpe, 2005). The lower nappe contains a 7 km thick, stratigraphically continuous portion of the ophiolite sequence including mantle harzburgites, dunites and wehrlites, crustal gabbros and a poorly-developed ('pseudo'-) sheeted dyke complex (Flinn, 2001; Flinn and Oglethorpe, 2005; Prichard and Lord, 1993; Spray and Dunning, 1991). Wehrlite occurs as xenoliths and lenses, between 1 m and 1 km in length, scattered throughout the upper section of the mantle dunite sequence and also extending into the layered gabbros in a broadly NE–SW trend (Fig. 1; Flinn, 2001; Flinn and Oglethorpe, 2005). The scattered distribution of the wehrlites has been attributed to late stage disruption by dunite intrusions into a continuous wehrlite layer in the mantle (Flinn, 1996). The mantle section comprises harzburgite interlayered with broadly east–west trending elongate dunite lenses, the frequency of which increases towards the petrological Moho (Flinn, 1985). Dunite lenses often contain laterally discontinuous podiform chromitite seams in close proximity to the petrological Moho (Flinn, 1985, 2001). The chromitite seams are commonly concentrated in the centre of the dunite lenses (Prichard, 1985). Folded chromitite seams have been attributed to dunite deformation before it was fully crystalline (e.g., Flinn, 1996).

The Shetland chromitite seams commonly contain Ni-sulphides, predominantly pentlandite [$(Ni,Fe)_9S_8$], heazlewoodite [Ni_3S_2] and millerite [NiS] (Prichard et al., 1994). The chromitite seams from Cliff (Fig. 1) contain abundant Ni-arsenides in addition to sulphides. Arsenides previously identified at Cliff include maucherite [$Ni_{11}As_8$] and orcelite [Ni_5As_2] (Prichard et al., 1994). Platinum-group minerals previously documented from the SOC include laurite [$(Ru,Os)S_2$], PGM of the irarsite-hollingworthite series [(Ir,Ru,Rh,Pt)AsS] together with sperrylite [$PtAs_2$] (Prichard and Tarkian, 1988). At Cliff, laurite is the only Ru-bearing PGM observed in the fresh Cr-spinel crystal cores, whilst Os-poor laurite is concentrated in sieve-textured alteration rims (Tarkian and Prichard, 1987). Platinum- and Pd-based PGM such as sperrylite, genkinite [$(Pt,Pd)_4Sb_3$] and stibiopalladinite [Pd_5Sb_2] dominantly occur at the edges of Cr-spinel crystals (Prichard and Tarkian, 1988; Prichard et al., 1994).

3. Field observations

The area of interest stretches from the eastern shore of Loch Cliff in the east to The Viels [HP 64212 10812] on the east coast of Unst