

Chromium-spinel, sulphide and PGM chemistry in podiform chromitites of the Shetland Ophiolite Complex (Scotland): implications for deciphering chromitite petrogenesis and late stage alteration

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The upper mantle portion of the ~492 Ma Shetland Ophiolite Complex (SOC; Isle of Unst, Scotland) contains abundant compositionally heterogeneous podiform chromitite deposits (> 60 % vol. Cr-spinel) enclosed in elongate dunite lenses close to the petrological Moho. Pervasive serpentinisation of the mantle sequence has altered the primary silicate mineral assemblage to serpentine (lizardite with minor chrysotile and antigorite) and has reduced primary magmatic sulphides (pentlandite [(Ni, Fe)₉S₈]) to heazlewoodite [Ni₃S₂] and millerite [NiS]. Despite the extensive serpentinisation of the mantle sequence, the mineral chemistry and crystal structure of Cr-spinel crystals provide valuable insights into complex mantle melting processes that have occurred and late-stage alteration. Alteration of Cr-spinel in the SOC chromitites is usually restricted to thin Fe-rich alteration rims (ferritchromit) at the crystal margins, except in chromitites from the Cliff locality where ferritchromit alteration can form > 50 % of the Cr-spinel crystals.

The Cliff chromitites are located < 200 m from the Burra Firth Lineament, a structure that is believed to have excised the ophiolite sole thrust. Unusually for ophiolite chromitites, the Cliff samples contain elevated concentrations of Pt and Pd-based minerals (253 ppm Pt + Pd) and strongly positive patterns on platinum-group element abundance diagrams, previously attributed to metasomatic overprinting of the primary platinum-group element (PGE) distribution. Sperrylite grains [PtAs₂], the dominant Pt-bearing phase, are closely associated with extensively altered Cr-spinel crystals either situated in, or touching ferritchromit alteration rims. The thick ferritchromit rims also contain abundant rounded Ni-arsenide grains (maucherite [Ni₁₁As₈]), a mineral not as common elsewhere in the SOC. Importantly, the intracrystalline equilibration temperatures of these Cr-spinels record anomalously high temperatures (1067-1260°C) probably artificial, caused by secondary Mg²⁺ and Al³⁺ re-ordering between the T and M sites at ~ 500°C, temperatures that closely correspond with ferritchromit formation. Furthermore, ferritchromit formation temperatures (~500°C) overlap both maucherite and sperrylite formation temperatures (400-700°C and 300°C, respectively) implying contemporaneous formation under oxidising conditions post-serpentinisation.

The PGE-rich chromitites from Cliff therefore preserve evidence for a post-serpentinisation oxidation event associated with the introduction of an As-rich fluid along the Burra Firth Lineament. Arsenic activity is strongly controlled by Fe³⁺ under oxidising conditions resulting in the close association of As-based minerals (sperrylite) and Fe³⁺-rich mineral phases (ferritchromit). The limited abundance of Ni-sulphides (pentlandite and heazlewoodite) and prevalence of Ni-arsenide (maucherite) in the Cliff chromitites, in contrast to other SOC chromitites, suggests localised substitution of S for As, conditions which have apparently promoted the significant dissolution and mobilisation of Pt and Pd.