

Diversity of platinum-group element mineralization styles in the North Atlantic Igneous Province: new evidence from Rum, UK

M. R. POWER*, D. PIRRIE & J. C. Ø. ANDERSEN

Camborne School of Mines, University of Exeter, Redruth TR15 3SE, UK

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Abstract – Two generations of sulphide-hosted platinum-group element mineralization occur in the West Sgaorishal ultramafic plug, Rum. Disseminated Cu and Ni sulphides around the margin of the plug host a restricted platinum-group mineral assemblage that is dominated by Pd bismutho-tellurides and sperrylite (PtAs_2) with subordinate electrum (AuAg), froodite (PdBi_2) and unidentified Pt–Bi–Te phases. Later sulphide-rich dykes cross-cut the plug and host an assemblage dominated by Pd bismutho-tellurides, sperrylite and locally very abundant paolovite (Pd_2Sn). Whole rock combined platinum-group element + Au concentrations are proportional to the sulphide abundance with slightly elevated values in disseminated sulphide lithologies (> 400 ppb) and very high values (> 2000 ppb) in the sulphide-rich dykes. Both generations have relatively flat chondrite-normalized plots indicating a primitive magmatic source. Negative $\delta^{34}\text{S}$ values (-9.2 to -18.3 ‰) indicate that the disseminated mineralization is due to contamination probably derived from Jurassic sedimentary rocks leading to sulphur saturation and collection of platinum-group elements. The sulphide-rich dykes must have entrained a platinum-group element-rich sulphide liquid collected from a much larger volume of magma. The presence of platinum-group elements and sulphide-rich dykes with $\delta^{34}\text{S}$ values between -10.8 and -15.0 ‰ indicates that parts of the Rum Layered Suite became sulphur saturated through magmatic contamination. It appears likely that platinum-group element mineralization styles within the southern North Atlantic Igneous Province are diverse and may be present in a wider variety of mineralogical associations than previously recognized.

Keywords: Rum, platinum-group element, mineralization.

1. Introduction

Widespread Palaeogene magmatism in the North Atlantic Igneous Province was initiated in response to the arrival and decompression melting of the Icelandic plume head beneath eastern Greenland (White, 1988; White & McKenzie, 1989). This resulted in the formation of extensive volcanic terranes on Baffin Island, West and East Greenland, the Faeroes, the Vøring and Rockall plateaus, and on the British Isles. In particular, dense dyke swarms, voluminous flood basalts and numerous central intrusive complexes are well exposed along the east coast of Greenland and along the northwestern seaboard of the British Isles (Fig. 1). Elevated platinum-group element (PGE) concentrations are a common feature of the North Atlantic Igneous Province (Andersen, Power & Momme, 2002) and can be ascribed to a combination of decompression melting of fertile mantle and plume-related elemental enrichment. Consequently, PGE mineralization is a common feature of many of the central intrusive complexes (Table 1).

In eastern Greenland, diverse PGE mineralization has been documented from five intrusions (Table 1). All of the occurrences are strongly associated with small amounts of interstitial disseminated sulphides and

appear to be related to sulphide-saturation during different magmatic differentiation processes (Andersen, Power & Momme, 2002). For example, platinum-group minerals (PGM) are associated with stratabound disseminated Cu–Fe sulphides in the Skaergaard Intrusion (Bird *et al.* 1991; Andersen *et al.* 1998) and the Kap Edvard Holm Complex (Bird *et al.* 1995; Arnason & Bird, 2000), along the lower contact of a transgressive ultramafic intrusion in the Kruuse Fjord Complex (Arnason *et al.* 1997) and in the marginal zones of the Nordre Aputitêq Intrusion and the Miki Fjord Macrodyke (J. G. Arnason, unpub. Ph.D. thesis, Stanford Univ. 1995). In contrast, in the southern North Atlantic Igneous Province, PGE mineralization has only previously been identified in association with ultramafic-hosted chromitites in the central intrusive complexes of Rum (Butcher *et al.* 1999; Power *et al.* 2000a) and Mull and Skye (Pirrie *et al.* 2000) (Table 1). However, on Rum, disseminated sulphides occur around the margin of the West Sgaorishal plug external to the main Rum intrusive centre (Wadsworth, 1994), together with previously undocumented cross-cutting sulphide-rich dykes. Neither has previously been examined for the presence of PGE mineralization.

Not only does this paper document chromite-poor, PGE-rich disseminated sulphide mineralization within a plug external to the main intrusive centre, but it also documents for the first time in the North Atlantic

* Author for correspondence: M.Power@csm.ex.ac.uk

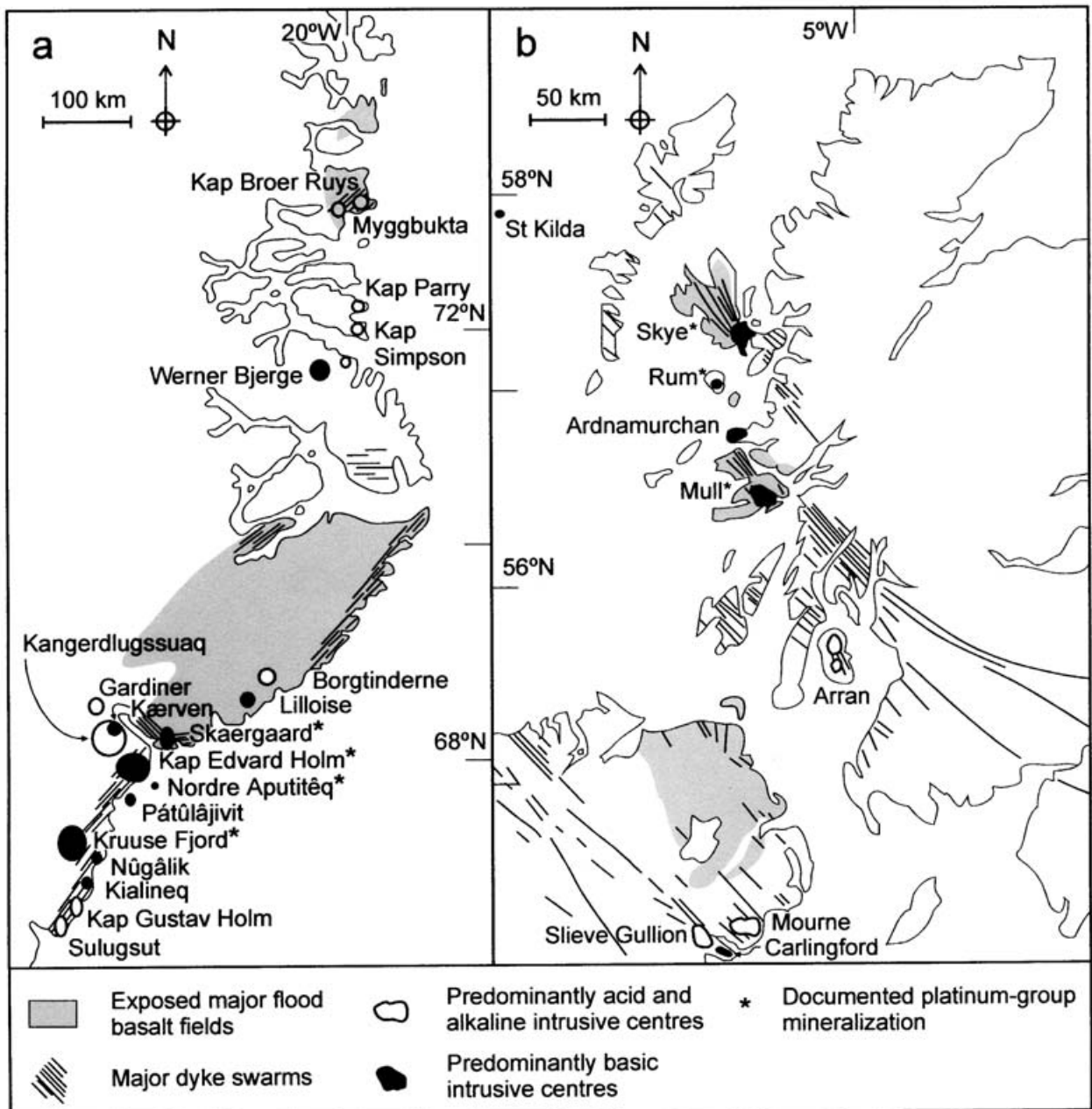


Figure 1. Simplified map showing the location of major intrusive centres within (a) East Greenland and (b) the southern North Atlantic Igneous Province. The Miki Fjord Macrodyke which lies immediately to the east of the Skaergaard intrusion has been omitted for clarity.

Igneous Province, substantial PGE mineralization associated with late-stage sulphide-rich dykes. This work indicates that the range of PGE mineralization styles associated with the North Atlantic Igneous Province is exceptionally diverse and highlights the potential for magmatic sulphide deposits in the area.

2. Geological setting

Central intrusive complexes of the southern expression of the North Atlantic Igneous Province are represented by several major acid and basic intrusive centres ex-

posed along the northwestern flanks of the British Isles extending from St Kilda in the north to Carlingford in the south (Fig. 1), although an isolated offshoot is found as far south as Lundy Island in the Bristol Channel. Many of these intrusive centres host layered mafic-ultramafic intrusions such as those on the islands of Rum, Mull, Skye and on the Ardnamurchan Peninsula, all of which represent the crystalline products of dynamic, open-system magma chambers. However, due to the complex magmatic history of these centres and the current erosion levels, typically only fragments of the ultramafic lithologies are exposed. On Skye, the

Table 1. Summary of documented platinum-group mineralization occurrences within the North Atlantic Igneous Province

Intrusion	Association	Common phases
<i>British Isles</i>		
Rum Central Complex (Butcher <i>et al.</i> 1999; Power <i>et al.</i> 2000a)	Chromitite with finely disseminated Cu and Ni sulphides	Laurite, irarsite, braggite, kotulskite, michenerite, moncheite, electrum, hongshiite, etc.
Ben Buie, Mull (Pirrie <i>et al.</i> 2000)	Chromitite (sulphide-poor)	Laurite, irarsite, sperrylite, Pd–Bi–Sb, Pd–Bi–Te, etc.
Peridotite Series, Skye (Pirrie <i>et al.</i> 2000)	Chromitite (largely sulphide-poor)	Laurite, sperrylite, ruarsite, Pd–Bi–Te, etc.
<i>Greenland</i>		
Skaergaard (Bird <i>et al.</i> 1991; Andersen <i>et al.</i> 1998)	First appearance of disseminated Cu sulphides	(Cu,Fe)(Pd,Au,Pt) alloys, electrum, atokite, zvyagintsevite, hongshiite, kotulskite, etc.
Kap Edvard Holm Complex (Bird <i>et al.</i> 1995; Arnason & Bird 2000)	Stratabound layer within gabbroic cumulates; disseminated Cu-Fe sulphides	Gold, Pt alloys, sperrylite, cooperite and moncheite
Kruuse Fjord Complex (Arnason <i>et al.</i> 1997)	Lower contact of transgressive ultramafic intrusion; disseminated Cu and Ni sulphides	Sperrylite, kotulskite, moncheite, gold, hollingworthite, platarsite, etc.
Nordre Aputitêq (J. G. Arnason, unpub. Ph.D. thesis, Stanford Univ. 1995)	Gabbroic pegmatites; interstitial Cu, Ni sulphides and transgressive sulphide-bearing veins	Gold, kotulskite, telluropalladinite, keithconnite and sperrylite
Miki Fjord Macrodyke (J. G. Arnason, unpub. Ph.D. thesis, Stanford Univ. 1995)	Margin of intrusion; disseminated Cu, Fe sulphides	PGE-bearing sulphides, kotulskite, atokite and stibiopalladinite

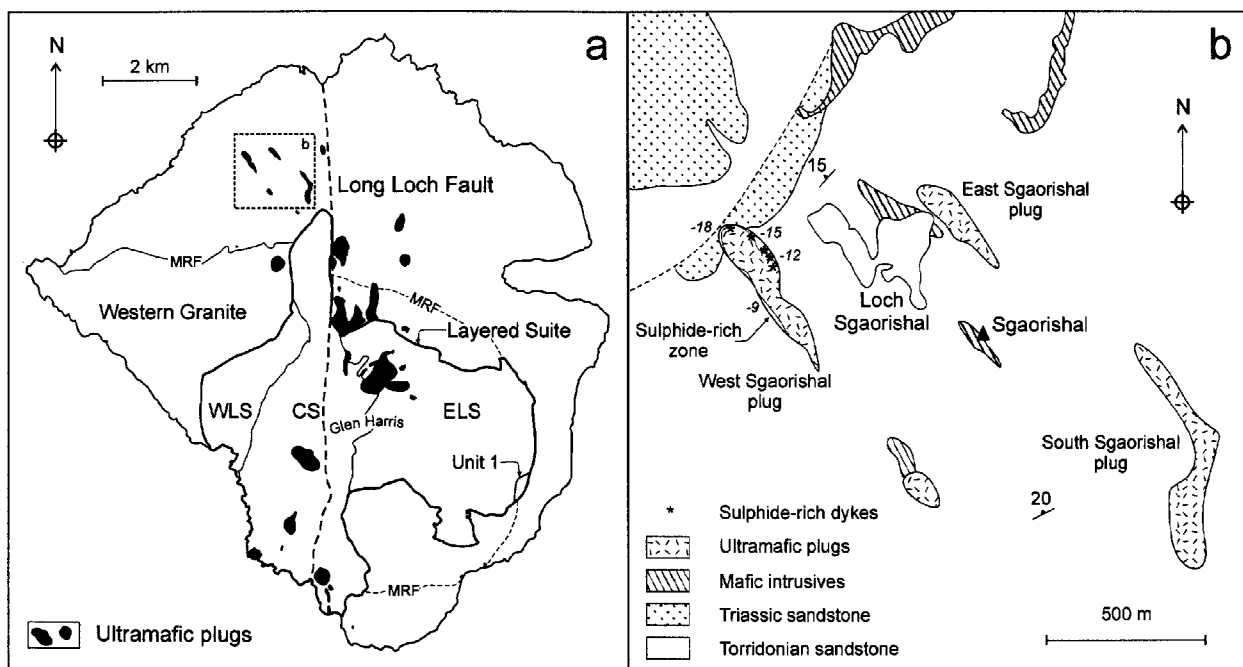


Figure 2. (a) Map showing the distribution of the major lithostratigraphic units within the Rum Layered Suite (late-stage gabbroic intrusions have been omitted for clarity). WLS – Western Layered Series, CS – Central Series, ELS – Eastern Layered Series, MRF – Main Ring Fault. (b) Simplified geological map of the Sgaorishal plugs and surrounding area. The numbers in italics are summarized $\delta^{34}\text{S}$ values (in ‰) for the disseminated sulphide mineralization.

Peridotite Series is largely cut out by later gabbroic intrusions (e.g. Claydon & Bell, 1992), whilst on Mull, ultramafic lithologies have only been documented in the Ben Buie gabbro (W. M. Lobjoit, unpub. Ph.D. thesis, Univ. Manchester, 1957). It is only on Rum that extensive ultramafic lithologies are well exposed.

2.a. The Rum Layered Suite

The Layered Suite of Rum is an area of largely undeformed and unaltered mafic and ultramafic lithologies

intruded into predominantly Torridonian Supergroup sediments overlain by a now largely eroded succession of Mesozoic sediments (e.g. Smith, 1985; Emeleus, 1997). It comprises three main divisions: the broadly contemporaneous Eastern and Western Layered series separated by the younger, discordant Central Series (Fig. 2). All divisions exhibit igneous layering on a variety of scales. Modal layering is very well developed in the Eastern Layered Series with 16 sequentially numbered megacyclic units (with Unit 1 at the base), each comprising olivine cumulates passing

upwards into plagioclase cumulates (e.g. Volker & Upton, 1990; Emeleus *et al.* 1996). Thin (< 5 mm) chromitite laminae are commonly developed at the base of megacyclic units and more rarely within the ultramafic lithologies of individual units (e.g. Power *et al.* 2000b). Within the Western Layered Series, layering is defined by grain size variation with coarse harrisitic olivine cumulates interleaved with fine-grained, equigranular dunites; plagioclase cumulates are absent. Thin (< 2 mm) chromitite laminae and seams are common but rarely occur at lithological boundaries. Modal layering is also well developed in parts of the Central Series, but numerous broad N–S-trending igneous breccia zones that contain a wide variety of locally derived igneous clasts obscure the lithological and stratigraphical relationships. More substantial (rarely > 100 mm) chromitites are present sporadically throughout the Central Series both as clasts within the breccia zones and as laminae concordant with igneous layering.

Sulphides are present in small amounts throughout the Rum Layered Suite, but are only abundant in the lowermost unit of the Eastern Layered Series (Unit 1), where sulphide concentrations locally reach 3 modal percent (Faithfull, 1985). Here the sulphides are disseminated and locally large blebs up to 1 cm across occur at the boundary between peridotite and overlying leucotroctolite; sulphur concentrations average 1917 ppm (Hulbert *et al.* 1992). Sulphur isotope data ($\delta^{34}\text{S} = -14.8$ to -0.9%) indicate that the sulphides formed by contamination with ^{32}S -rich ($\delta^{34}\text{S} = -15.8\%$) Mesozoic sediments and carbonates leading to sulphide oversaturation of the magma (Hulbert *et al.* 1992). Assimilation of the Torridonian Supergroup sediments was discounted on the basis of their relatively high (-2.9%) $\delta^{34}\text{S}$ ratios (Hulbert *et al.* 1992). Further up in the Eastern Layered Series, the sulphides are far less abundant (typically less than 0.5%), and occur mostly as small grains (< 100 μm) disseminated within the chromitite laminae. Sulphur concentrations average 185 ppm from Unit 10 and 136 ppm from Unit 14 whilst sulphur isotope ratios indicate that little contamination has occurred (Hulbert *et al.* 1992). The sulphides display complex assemblages that appear to be related to late- to post-magmatic oxidation (Power *et al.* 2000a). Primary minerals are chalcopyrite and pentlandite with minor pyrrhotite; alteration products include bornite, digenite, chalcocite, native Cu, magnetite and Fe-hydroxides (Dunham & Wilkinson, 1985; Power *et al.* 2000a).

Numerous late-stage mafic and ultramafic plugs cut both the Layered Suite (predominantly the Eastern Layered Series and Central Series) and the surrounding country rocks (e.g. R. M. Forster, unpub. Ph.D. thesis, Univ. Durham, 1980; Wadsworth, 1994) (Fig. 2). Wadsworth (1994) noted that the plugs occur in three distinct situations: within the Layered Suite (intra-series plugs), as elongate bodies extending from the

northern margin of the Layered Suite (tongues), and as bodies within the surrounding country rocks (satellitic plugs). The satellitic plugs are particularly prevalent in northwest Rum (Fig. 2) where they have steeply dipping margins and are arranged in a roughly radial pattern focused on Glen Harris (e.g. Dunham & Emeleus, 1967). Modal layering is developed within a number of the ultramafic plugs, but rather than the cumulus mineralogy (typically olivine) varying, the modal proportion of intercumulus clinopyroxene and plagioclase changes (matrix banding: Dunham, 1965). This texture has been attributed to oscillatory crystallization of intercumulus melt close to the pyroxene–plagioclase cotectic (Dunham, 1965) during particularly tranquil magmatic conditions (Wadsworth, 1994). Sedimentary rocks up to 6 m from an ultramafic satellitic plug 200 m in diameter are extensively bleached and contain paramorphs of tridymite indicating that melting of the sediments reached 70 volume percent (Holness, 1999). This relatively small aureole combined with the presence of matrix banding suggests that the ultramafic plugs represent blind intrusions and that the peridotite was injected as a crystal mush close to its solidus, probably crystallizing within four years (Wadsworth, 1994; Holness, 1999). In contrast, small gabbroic plugs (50 m in diameter) with theoretically lower solidus temperatures have significantly larger (up to 16 m) aureoles in which partial melting reached 95 volume percent, suggesting that they represent longer-lived feeder conduits (Holness, 1999).

2.b. Platinum-group element mineralization

Previous work in the southern North Atlantic Igneous Province has largely concentrated on documenting PGE mineralization associated with chromitites within the ultramafic lithologies of the Rum, Mull and Skye igneous centres (e.g. Butcher *et al.* 1999; Pirrie *et al.* 2000). By far the most abundant and diverse PGE mineralization documented occurs throughout the Rum Layered Suite and in particular, the Eastern Layered Series (e.g. Power *et al.* 2000a). Discrete PGM occur as small grains (predominantly < 10 μm) spatially associated with sulphides. Most of the PGM occur at grain boundaries rather than enclosed within the sulphides; a few grains occur enclosed within silicates or chrome-spinel (Power *et al.* 2000a). The PGM assemblage varies with stratigraphic height with Pt- and Pd-bismuthotellurides, gold and electrum dominating the Unit 5–6 chromitite, laurite (RuS_2), Pt- and Pd-Fe alloys and sulphides at the Unit 7–8 chromitite, whilst Pt- and Pd-arsenides and bismuthotellurides are the principal phases within the Unit 11–12 chromitite (Power *et al.* 2000a). Positively identified phases include kotulskite (PdTe), laurite, irarsite (IrAsS), sperrylite (PtAs_2), michenerite (PdBiTe), moncheite (PtTe_2) and braggite ((Pt,Pd)S), amongst a host of others (Butcher *et al.* 1999; Power *et al.* 2000a). Similar

mineralization styles are present within the Western Layered Series and Central Series, albeit with a more limited diversity. Laurite and irarsite are common in the Western Layered Series whilst Pd–Cu alloys and Pt–Fe alloys are locally abundant within the Central Series chromitites (Power & Andersen, 2001). Whole rock total precious metal contents (PGE+Au) exceed 2500 ppb within the chromitites of the Eastern Layered Series (Power *et al.* 2000a), whilst the sulphide-rich zone within Unit 1 of the Eastern Layered Series has slightly elevated precious metal concentrations (232 ppb; Hulbert *et al.* 1992) although no discrete PGM have been identified (Power *et al.* 2000a).

Chromitites are only sporadically developed within the Ben Buie intrusion on Mull and host a relatively restricted PGM assemblage (Pirrie *et al.* 2000). The PGM typically occur either as euhedral phases (commonly laurite) within chrome-spinel grains or as clusters of minute inclusions (< 2 µm) within intercumulus plagioclase and clinopyroxene. PGM include sperrylite, laurite, irarsite, froodite (PdBi₂) and unidentified Pd–Bi–Te and Pd–Bi–Sb phases. Well-developed chromitites occur within the Peridotite Series of Skye but host a restricted PGM assemblage dominated by laurite (typically enclosed in chrome-spinel) with subordinate sperrylite, ruarsite (RuAsS), Pt–Rh–Fe alloy and Pd arsenides commonly occurring at silicate, sulphide and chrome-spinel grain boundaries (Pirrie *et al.* 2000). Total PGE+Au values are mildly enriched within the Ben Buie chromitites with values of up to 189 ppb whilst values of up to 508 ppb have been reported from the Peridotite Series chromitites (Prout *et al.* 2002).

3. The Sgaorishal plugs

Three elongate plugs intrude Torridonian Supergroup sandstones and locally Triassic sandstones (with well-developed calcretes) on the flanks of Sgaorishal (Fig. 2). Of these, the largest and best-exposed is the West Sgaorishal plug which crops out over an elliptical area approximately 500 × 100 m to the west of Loch Sgaorishal (Fig. 2). The plug shows some of the best-developed matrix banding of all of the satellitic plugs (Wadsworth, 1994) and comprises cumulus olivine with varying proportions of intercumulus plagioclase and clinopyroxene. Chrome-spinel is disseminated throughout but, in common with the other ultramafic plugs, chromitites are absent. Disseminated sulphides are abundant (up to 5 modal percent) in an irregular zone that locally exceeds 5 m in width and broadly follows the margin of the plug (Fig. 2b). Within this zone olivine and clinopyroxene are notably more Fe-rich (Wadsworth, 1994). Although this sulphide-rich marginal zone is poorly exposed, the sulphides appear to be more abundant towards the contact with the surrounding sediments. In addition, at least five thin (< 200 mm wide), deeply weathered gabbro

dykes trending approximately NW–SE cut the plug and contain abundant sulphides (> 40 modal percent sulphide). The dykes appear to thin towards the centre of the intrusion but due to the intense weathering of the sulphides are only well-exposed in the craggy outcrops at the margin of the plug. Cross-cutting relationships are obscured by the poor exposure of the contact zone and no sulphide-bearing dykes have been identified intruding the (poorly exposed) country rock. No sulphide-rich zones or dykes have been identified in either the South or East Sgaorishal plugs.

No definitive age relationships have been determined for any of the Sgaorishal plugs despite the presence of cross-cutting dykes. Numerous xenoliths (up to 100 mm in diameter) of coarse gabbro are exposed at the southern margin of the South Sgaorishal plug, and zones of what appear to be partially resorbed gabbroic xenoliths occur throughout, indicating that the plugs post-date at least parts of the Layered Suite. The similarity to some of the intra-series plugs (that clearly cross-cut the Eastern Layered Series and Central Series) suggests that the Sgaorishal plugs represent late-stage manifestations of the Layered Suite magmatic activity (cf. Wadsworth, 1994; Emeleus, 1997).

4. Analytical techniques

A suite of 30 samples was collected from the West Sgaorishal plug, all of which were examined optically under both reflected and transmitted light microscopy to determine the sulphide and silicate mineralogy. Reported mineral abundances are estimated modal percentages. PGM were located using a JEOL 840 scanning electron microscope (SEM) fitted with a Links System (Oxford Instruments) AN10000 energy dispersive spectrometer (EDS) operating with an accelerating voltage of 20 kV and a beam current of 3 nA. A lower beam current (0.6 nA) with a count time of 100 seconds was used to obtain quantitative chemical analyses of the larger PGM. Five samples (> 500 grams each) were analysed by Activation Laboratories Ltd, Canada for whole rock PGE by Ni-sulphide fire assay with an INAA finish. Furthermore, prepared metal sulphides from twelve samples were analysed for sulphur isotopic composition using a Micromass Isoprime continuous flow mass spectrometer in the School of Earth Sciences, University of Leeds. All data are reported in standard delta notation relative to the V-CDT standard. Estimated accuracy and precision, from analysis of run standards and international reference materials, is better than 0.3 per mil (‰).

5. Mineralogy and petrology

The overall mineralogy of the West Sgaorishal plug is relatively uniform and comprises cumulus olivine (typically 75 %) and chrome-spinel (less than 1 %) with variable proportions of intercumulus plagioclase,

clinopyroxene and subordinate biotite defining the matrix banding. Slight alteration and hydration of the silicate phases (typically along fractures) has resulted in a secondary assemblage including chlorite, serpentine, sericite and rare calcite. Within the zones rich in disseminated sulphides, approximately equal proportions of intercumulus chalcocopyrite, pyrrhotite and pentlandite (both as discrete grains and as flames within pyrrhotite) are locally abundant and comprise up to 5 % of the rock. Sulphide grain sizes range from small blebs (< 20 µm) through to large (> 5 mm) polyphase aggregates. Many of the larger sulphide aggregates partially enclose cumulus olivine and chrome-spinel (Fig. 3a). Alteration of the sulphides is not significant although Fe oxides locally rim pentlandite and pyrrhotite whilst chalcocite locally rims chalcopyrite.

The sulphide-rich dykes are characterized by an interlocking fabric of plagioclase (30 %), clinopyroxene (30 %) and sulphides (40 %); olivine and chrome-spinel are absent. Plagioclase commonly has an alteration rim of clay minerals (probably picking out zoning) and is extensively Fe stained and fractured (especially in weathered samples) whilst clinopyroxene is largely unaltered. The sulphide assemblage is dominated by pyrrhotite (65 %) with lesser quantities of chalcocopyrite (30 %) and subordinate pentlandite (5 %). Pentlandite occurs primarily as flames within pyrrhotite; discrete grains are relatively rare. Alteration of pyrrhotite and pentlandite is very pronounced in weathered samples and results in an assemblage of Fe oxides and hydroxides whereas chalcocopyrite is largely unaltered although magnetite and covellite are locally developed along fractures.

In addition to the pyrrhotite-rich dykes, one dyke contains numerous elongate blebs of chalcocopyrite (with minor pentlandite) typically 50 × 10 mm that occur within a heavily bleached and altered zone aligned along the centre of the dyke. Within this altered zone, silicates are largely replaced by clay minerals, chlorite, tremolite and quartz but the original grain boundaries are preserved. In addition, rare vugs are infilled with zeolites (thomsonite and yugawaralite have been tentatively identified by X-ray diffraction) and quartz. No veining or major fractures are present and the chalcocopyrite clearly pre-dates zeolite crystallization. Localized surface weathering and oxidization of the chalcocopyrite has resulted in an assemblage of bornite, chalcocite, covellite with rare Cu-sulphates. The main body of the dyke is largely unaltered and comprises plagioclase (65 %), clinopyroxene (30 %) and disseminated sulphides (5 %). The sulphides are dominated by chalcocopyrite and pentlandite whilst pyrrhotite is rare.

Galena is common within all lithologies and occurs as small (typically < 20 µm) blebs enclosed within, or closely spatially associated with, larger sulphide grains. Other phases include small (< 5 µm) grains

of native Ag and unidentified Bi- and Pb-tellurides; in some cases the latter contain small quantities of Pd. Within the chalcocopyrite-rich dyke, a very varied accessory mineralogy is present and includes abundant galena and Ag telluride (?hessite) with lesser quantities of native Ag, cinnabar (HgS), CdS and a Ni-Bi phase.

6. Platinum-group mineralogy and petrology

Discrete PGM are present in all of the samples analysed and more than 300 individual PGM grains have been identified.

6.a. Disseminated sulphide mineralization

Within the disseminated sulphide mineralization, the majority of PGM occur as discrete monomineralic grains that are either wholly enclosed within sulphides (55 % of observed PGM) or are at sulphide-silicate grain boundaries (22 %), and 23 % occur solely in association with silicates. Relict PGM are present within altered sulphides (now Fe oxides and hydroxides) and in association with alteration rims around silicates. Indeed, a thin serpentine-filled fracture dissects one PGM (Fig. 3b). In rare cases, PGM also occur as elongate grains roughly parallel to cleavage within chlorite after biotite (Fig. 3c) suggesting that at least some of the PGM are associated with late-stage hydrous processes.

The platinum-group mineralogy is dominated by Pt- and Pd-bearing phases and in comparison to the chromite-hosted mineralization of the Layered Suite (e.g. Power *et al.* 2000a) is quite restricted. Pd tellurides and bismutho-tellurides such as kotulskite are common as is sperrylite; together these phases comprise 80 % of the observed PGM. Other, less common phases include froodite (PdBi₂), electrum and unidentified Pt-Bi-Te and Pd-Sb-Te phases (e.g. Fig. 3d, e). No Os-, Ir- or Ru-bearing phases have been located. A wide range of grain sizes is present with an approximately log-normal distribution ranging from the smallest detectable (nominally 0.2 µm) through to grains in excess of 10 µm although more than half of the grains are less than 2 µm in size. Most PGM occur as anhedral blebs, whereas sperrylite commonly occurs as thin rims and chains (typically 1–2 µm wide) at, or close to, the margins of larger sulphides and can exceed 50 µm in length (Fig. 3f).

The overall abundance of the PGM appears to correlate with the sulphide abundance and, other than the general increase in the abundance of sulphides towards the margin of the plug, there does not appear to be any concentration of PGM towards the contact.

6.b. Dyke-hosted sulphide mineralization

Despite the abundance of sulphides within the pyrrhotite-rich dykes, in most cases, PGM are relatively rare (typically only two or three grains in a 2 × 4 cm

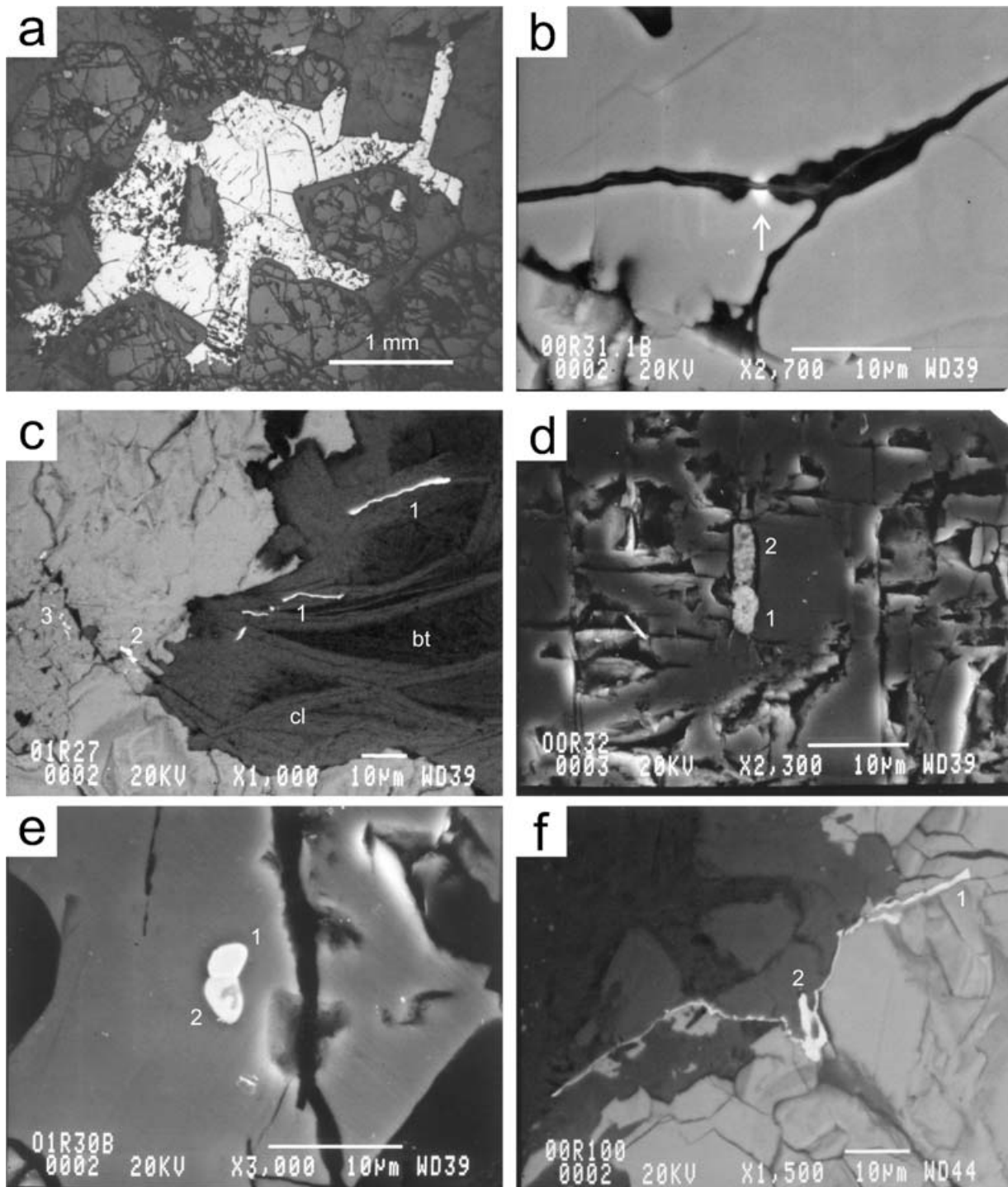


Figure 3. Scanning electron micrographs (unless otherwise stated) of the disseminated sulphide mineralization. (a) Reflected light photomicrograph of an intercumulus polyphase (chalcopyrite and pyrrhotite) sulphide grain surrounding euhedral olivine (now partially serpentinized). (b) Fractured Pd–Bi–Te grain (arrowed) within pyrrhotite. Fracture is infilled with serpentine. (c) Cluster of PGM including Pt–Pd–Bi–Te (1) in chlorite (cl) after biotite (bt), Pd–Te (2) and sperrylite (3) both enclosed within chalcopyrite. Taken in backscatter electron mode. (d) Pd–Bi–Te phase (1) with native Te (2) both enclosed within chalcopyrite. (e) Froodite (PdBi_2) (1) with a Pt–Bi–Te phase (2) enclosed in chalcopyrite. (f) Sperrylite (PtAs_2) (1) partially rimming the edge of a pentlandite grain with a Pd–Bi–Te grain in the centre (2).

polished section). The PGM assemblage is also restricted and comprises sperrylite, Pd tellurides and bismutho-tellurides (probably kotulskite) and unidentified Pd–Ag–Bi–Te phases, all of which occur as small

(typically $< 5 \mu\text{m}$) anhedral blebs enclosed within sulphide grains. Rare composite grains where several intergrown but discrete PGM occur within a single grain are also present (Fig. 4a).

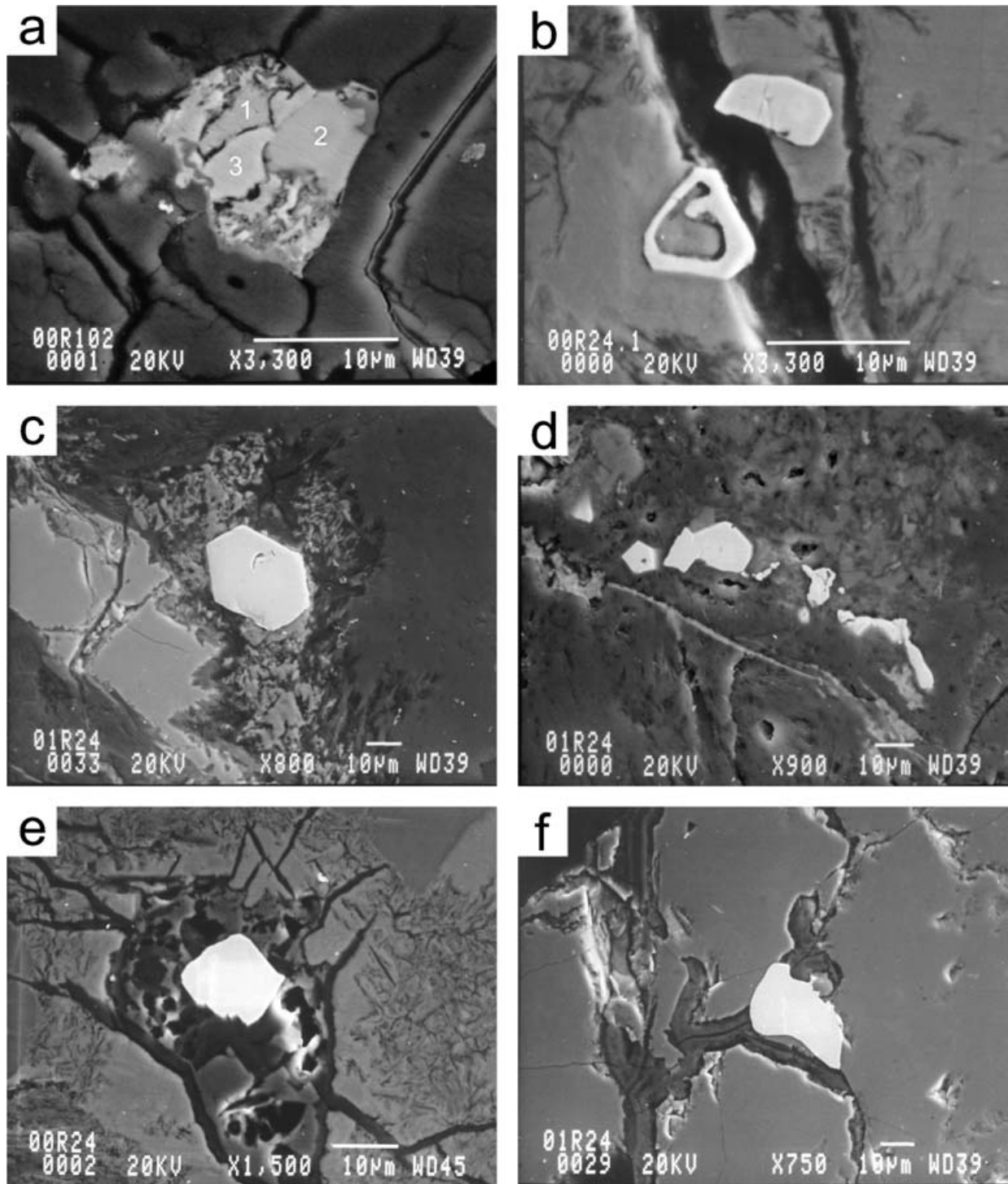


Figure 4. Scanning electron micrographs of the sulphide-rich dyke-hosted mineralization. (a) Composite PGM within pentlandite containing an unidentified Pd–Ag–Te phase (1), kotulskite (2) and froodite (3). (b) Euhedral and euhedral skeletal paolovite grains within chalcopyrite. (c) Large euhedral sperrylite grain within plagioclase and altered pyrrhotite. (d) Cluster of sperrylite grains within quartz and Fe oxides. (e) Large paolovite grain within Cu-sulphates (dark mineral) and covellite (mid-grey mineral). (f) Large grain of electrum at altered grain boundary between pentlandite and chalcopyrite.

In contrast, the chalcopyrite-rich dykes host substantial PGE mineralization that is largely concentrated within the chalcopyrite-rich blebs. Not only are the PGM very abundant (> 100 in a single polished section), they are also exceptionally large in comparison

to all the other PGM occurrences throughout the southern North Atlantic Igneous Province (cf. Power *et al.* 2000a; Pirrie *et al.* 2000). The PGM vary from < 1 μm through to > 40 μm with approximately 36% of PGM grains greater than 5 μm in size. The mineral

assemblage is dominated by paolovite (Pd₂Sn) (30 % of grains), Pd bismutho-tellurides such as keithconnite (Pd_{3-x}Te), telluropalladinite (Pd₉Te₄) and kotulskite (50 % of grains) with subordinate sperrylite, froodite, Pd–Ag–Bi–Te phases and electrum (Table 2); native Ag is locally very abundant. The vast majority of PGM grains (particularly Pd bismutho-tellurides and electrum) occur as rounded anhedral blebs enclosed within chalcopyrite and pentlandite. However, the larger grains of paolovite and sperrylite are commonly subhedral or euhedral (Fig. 4b, c, d). Paolovite almost exclusively occurs within chalcopyrite, bornite or covellite, although several grains are located near fractures and are surrounded by a thin weathering rim of Cu sulphates (Fig. 4e). A relatively small proportion (< 10 %) of the PGM occur enclosed within silicates such as quartz and chlorite whilst several relict PGM phases occur within the alteration rims of sulphide phases (Fig. 4f); in some cases they are even altered themselves. Furthermore, a small cluster of electrum and native Au grains occur within a late-stage fracture suggesting that, in common with the disseminated sulphide mineralization, PGE mineralization was a protracted process.

7. Whole rock PGE concentrations

Five ~500 g samples (three of disseminated mineralization and two pyrrhotite-rich dykes) were submitted for whole rock precious metal analyses by nickel sulphide fire assay with an INAA finish. Due to the small sample size, the chalcopyrite-rich dyke was not analysed. The whole-rock PGE analyses are presented in Table 3.

Samples of the disseminated sulphide mineralization have slightly elevated PGE concentrations (ΣPGE+Au 254 to 407 ppb) whilst the dyke-hosted pyrrhotite-rich mineralization is substantially more enriched with respect to PGE (ΣPGE+Au 1541 to 2175 ppb). The absolute PGE concentrations are considered to be largely dependent on the sulphide content of the sample with higher sulphide contents giving higher overall values. Relative (chondrite-normalized) PGE concentrations for both mineralization styles have remarkably similar profiles and both show weakly positive slopes (Fig. 5). In comparison to primitive mantle, Ir, Os, Ru (the IPGE; cf. Barnes, Naldrett & Gorton, 1985) content of the disseminated sulphide mineralization is only mildly enriched whilst Pt, Pd, Rh (the PPGE; cf. Barnes, Naldrett & Gorton, 1985) contents are significantly enriched (especially Pd). The sulphide-rich mineralization shows strong enrichment of all the PGE with respect to primitive mantle with extremely enriched Pd values exceeding 1000 ppb. Overall, the weak positive slopes indicate that only slight fractionation of the PGE has occurred. Indeed, the degree of fractionation is less than that observed within the Eastern Layered Series (Fig. 5) and indicates that the primary magma formed by partial melting

Table 2. Selected platinum-group mineral analyses

	Pd	Pt	Au	Bi	Te	Ag	Pb	Sn	As	Cu	Ni	Fe	Total	Formula
1	61.96	—	—	—	—	—	—	34.20	—	2.62	< 0.10	0.40	99.18	(Pd _{1.9} Cu _{0.14} Fe _{0.02})Σ _{2.06} Sn _{0.94}
2	61.46	—	—	—	—	—	—	36.94	—	0.60	< 0.10	0.43	99.43	(Pd _{1.91} Cu _{0.03} Fe _{0.03})Σ _{1.97} Sn _{1.03}
3	61.41	—	—	—	—	—	—	34.68	—	2.83	< 0.10	0.74	99.66	(Pd _{1.87} Cu _{0.14} Fe _{0.04})Σ _{2.05} Sn _{0.95}
4	—	54.92	—	—	—	—	—	—	43.41	0.89	0.15	0.10	99.47	(Pt _{0.96} Cu _{0.05} Ni _{0.01} Fe _{0.01})Σ _{1.02} As _{1.98}
5	—	54.91	—	—	—	—	—	—	44.10	0.37	0.11	0.45	99.94	(Pt _{0.95} Cu _{0.02} Ni _{0.01} Fe _{0.03})Σ _{1.01} As _{1.99}
6	31.28	—	—	21.14	40.13	—	—	—	—	2.26	3.13	1.71	99.65	(Pd _{0.71} Cu _{0.09} Ni _{0.13} Fe _{0.07})Σ _{1.00} (Te _{0.76} Bi _{0.24})Σ _{1.00}
7	—	—	75.95	—	—	23.53	—	—	—	0.87	n.d.	< 0.25	100.35	Au _{0.63} Ag _{0.35} Cu _{0.02}
8	—	—	74.62	—	—	24.54	—	—	—	n.d.	0.78	0.37	100.31	Au _{0.61} Ag _{0.36} Ni _{0.02} Fe _{0.01}
9	21.62	—	—	76.23	—	—	—	—	—	2.14	—	< 0.25	100.00	(Pd _{1.0} Cu _{0.17} Σ _{1.18} Bi _{1.82}
10	9.48	12.80	—	6.15	61.65	—	—	—	—	0.49	8.62	1.32	100.51	(Pd _{0.32} Pt _{0.22} Cu _{0.03} Ni _{0.52} Fe _{0.08})Σ _{1.18} (Te _{1.71} Bi _{0.10})Σ _{1.82}
11	17.74	—	—	15.50	48.29	9.49	—	—	—	1.12	7.04	1.05	100.23	(Pd _{0.58} Cu _{0.06} Ni _{0.42} Fe _{0.06})Σ _{1.12} (Te _{1.31} Bi _{0.26} Ag _{0.31})Σ _{1.88}
12	8.76	—	—	< 0.50	31.28	—	53.76	—	—	5.10	< 0.10	1.46	100.36	(Pd _{0.36} Ni _{0.35} Fe _{0.11})Σ _{0.82} (Te _{1.06} Pb _{1.12})Σ _{2.18}

— = not analysed. In all cases S was not detected except in sample 9 where chalcopyrite fluorescence was corrected for and analysis recalculated to 100 %. Analyses 1–3: paolovite (Pd₂Sn), 4 and 5: sperrylite (PtAs₂), 6: kotulskite (PdTe), 7 and 8: electrum (AuAg alloy), 9: froodite (PdBi₂), 10–12: ?merenskyite (PdTe₂).

Table 3. Whole rock PGE + Au concentrations for the disseminated sulphide (marked by an asterisk) and pyrrhotite-rich dyke hosted platinum-group element mineralization (all data in ppb)

Sample no.	Os	Ir	Ru	Rh	Pt	Pd	Au	Total
00R99*	12	6.3	10	6.5	49	170	20	274
00R101*	11	5.9	14	6	44	159	14	254
00R105*	22	5.2	10	28	77	215	50	407
00R102	240	98	210	128	398	1070	31	2175
00R104	96	42	77	34	292	978	22	1541
ELS (max)	110	100	140	47	1550	1290	820	2618
ELS (min)	13	19	29	7	232	60	33	502

Data for the chromitite-hosted platinum-group element mineralization of the Eastern Layered Series (from Power *et al.* 2000a) are shown for comparison.

without residual sulphides from a primitive mantle source, and that there was little chromite fractionation.

Notably, within the Eastern Layered Series, there is a very strong correlation between the observed PGM abundance and the total precious metal concentration and also the PGM assemblage and relative abundance of the individual PGE (Power *et al.* 2000a). However,

whilst this is broadly the case for the disseminated sulphide mineralization, neither the total precious metal concentrations nor the relative PGE concentrations are reflected in the PGM abundance or assemblage within the pyrrhotite-rich dykes suggesting that a significant proportion of the PGE must be contained in solid solution within the sulphides.

8. Sulphur isotopes

The sulphur isotope data are presented in Table 4. All of the disseminated sulphide samples have large negative values ranging from -18.3‰ to -9.2‰ that are much lower than those expected in magmatic sulphides (typically 0‰ to -2‰ ; e.g. Hoefs, 1997). These low values suggest that the magma must either have undergone extreme fractionation (for which there is little evidence) or the magma has been contaminated with strongly bacterially reduced sulphur (e.g. Hoefs, 1997). Notably, the disseminated mineralization has sulphur isotope values that are increasingly negative towards the Triassic lithologies exposed at

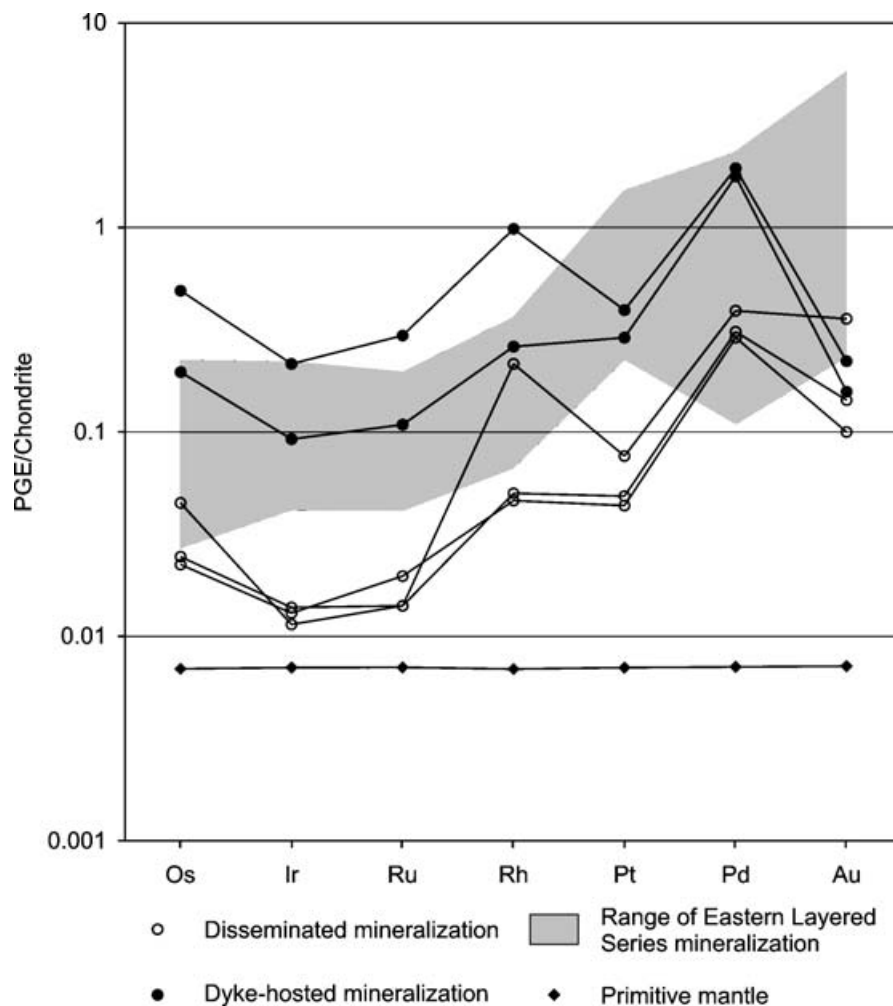


Figure 5. Spider diagram of selected samples of disseminated sulphide mineralization and dyke-hosted sulphide mineralization. All data normalized using the values of McDonough and Sun (1995). Primitive mantle values (McDonough & Sun, 1995) and data for the Eastern Layered Series (Power *et al.* 2000a) are provided for comparison.

Table 4. Summary of sulphur isotope data for sulphide-bearing samples

Sample	Mineralization type	Mineralogy	$\delta^{34}\text{S}$ (‰)
00R102	Dyke	Pyrrhotite	-13.2
01R26	Dyke	Pyrrhotite	-14.7
00R104	Dyke	Pyrrhotite	-15.0
01R24	Dyke	Chalcopyrite	-10.8
99R31	Disseminated	Mixed pyrrhotite, chalcopyrite and pentlandite	-15.4
99R33	Disseminated		-11.8
00R99A	Disseminated		-12.4
00R99B	Disseminated		-11.8
00R105	Disseminated		-18.0
01R23	Disseminated		-12.9
01R27	Disseminated		-18.3
01R29	Disseminated		-9.2

the northwest margin of the intrusion (Fig. 2b). The sulphide-rich dykes have similarly negative sulphur isotope ratios ($\delta^{34}\text{S} = -15.0$ to -10.8 ‰) that are also indicative of significant contamination with a reduced sulphur source.

9. Discussion

During the last 15 years, extensive exploration and research has established the North Atlantic Igneous Province as one of the most extensive and diverse PGE provinces in Europe and probably the world. Although mostly subeconomic, the numerous occurrences in eastern Greenland (e.g. Arnason *et al.* 1997; Andersen *et al.* 1998) and western Scotland (e.g. Butcher *et al.* 1999; Pirrie *et al.* 2000) appear to have formed in response to the regional tectonic and magmatic framework established by the Icelandic mantle plume (Andersen, Power & Momme, 2002). High concentrations of PGE and sulphur-undersaturated fractionation in the primary magmas are the most significant aspects for the PGE potential in the province, and in eastern Greenland sulphur saturation appears to be the dominant control on the PGE distribution. Although there could be differences between the setting and magma source regions (as indicated by the more chromite-rich, calcic cumulates which are dominant in Scotland), there is no obvious reason why widespread sulphide-related PGE deposits could not have also formed within the Scottish central intrusive complexes.

Previously reported chromitite-hosted PGE mineralization in western Scotland has been attributed to magma mixing and consequent PGE concentration (e.g. Pirrie *et al.* 2000; Power *et al.* 2000a). However, as there is no evidence for magma mixing in the West Sgaorishal plug, the mechanisms for sulphide saturation and PGE concentration must be different.

A hydrothermal source can be largely discounted on the basis of the petrography and whole rock PGE concentrations. The modal composition of the West Sgaorishal plug and its cumulate textures suggest that it was intruded as a crystal-rich magma (e.g. Wadsworth, 1994). Many of the sulphides show clear

poikilitic intercumulus textures that have not been destroyed by later overgrowths, indicating that a sulphide liquid was an integral component of the magma. PGM typically occur within or next to these poikilitic sulphides suggesting that both the sulphide and PGE concentration mechanisms were coeval. Furthermore, within hydrothermal systems, PPGE and Au are typically more mobile than IPGE and the resulting mineralization is characterized by significant enrichment of the PPGE, whereas magmatic systems tend to have a more uniform chondrite normalized PGE content (e.g. Barnes, Naldrett & Gorton, 1985). Thus, the elevated IPGE content in comparison to primitive mantle values, coupled with the relatively flat chondrite normalized PGE content of the disseminated sulphide lithologies, indicates that hydrothermal activity was not a significant mineralization process within the West Sgaorishal plug.

Similar PGE-bearing disseminated sulphide mineralization has been reported from the North Atlantic Igneous Province within marginal zone settings in the Miki Fjord Macrodyke and the Nordre Aputitêq Intrusion on East Greenland (J. G. Arnason, unpub. Ph.D. thesis, Stanford Univ. 1995; Andersen, Power & Momme, 2002) and indeed Unit 1 of the Eastern Layered Series (Hulbert *et al.* 1992). In these places they were attributed to wall-rock contamination and possibly volatile enrichment (cf. J. G. Arnason, unpub. Ph.D. thesis, Stanford Univ. 1995; Andersen, Power & Momme, 2002; Hulbert *et al.* 1992). The partial melting observed in the contact aureole (cf. Holness, 1999), coupled with the evolved olivine and clinopyroxene compositions within the sulphide-rich zone (Wadsworth, 1994), indicates that assimilation and sulphur contamination may have contributed significantly to the sulphur saturation in the West Sgaorishal plug, but there is no direct evidence such as sedimentary xenoliths to prove this. Furthermore, as the Torridonian Supergroup sediments typically have $\delta^{34}\text{S}$ values of -2.9 ‰ (Hulbert *et al.* 1992), a more ^{32}S -rich source is required. A decrease in $\delta^{34}\text{S}$ towards the Triassic lithologies to the northwest of the intrusions suggests that they may be the sulphur source, but although small quantities of chalcopyrite are present close to the faulted northern margin of the Triassic (Emeleus, pers. comm. 2003), sulphides are rare. In addition, calcretes are well developed (and baryte cements are present elsewhere in the Hebridean province: McKeevor, 1992) and are indicative of formation in an arid continental setting. As such, the sediments would be expected to yield strongly positive $\delta^{34}\text{S}$ values (e.g. Hoefs, 1997). Hence, it is unlikely that the Triassic lithologies are the source of the sulphur contamination. Similar (albeit PGM-poor) disseminated sulphide mineralization within Unit 1 of the Eastern Layered Series was attributed to sulphur contamination derived from ^{32}S -rich Jurassic lithologies (Hulbert *et al.* 1992). Hence, the most

plausible source of sulphur contamination is a Jurassic succession that has been entirely eroded from the area around the Sgaorishal plug (cf. Hulbert *et al.* 1992).

The occurrence of a small number of PGM within late-stage hydrous phases such as biotite and chlorite and the presence of chains of sperrylite at, or near, sulphide grain boundaries suggests that late-stage hydromagmatic processes may also have been locally significant. However, the preservation of euhedral olivine grains outlined by poikilitic sulphides indicates that little or no sulphide mineralization occurred during or after the serpentinization event. This is in accord with the observation that late-stage serpentine-filled fractures cut PGM grains (e.g. Fig. 3b). The presence of PGM within late-stage intercumulus phases has also been documented from Mull (Pirrie *et al.* 2000) and attributed to PGE-enriched fluids during the very latest stages of magma crystallization; this model is consistent with the hydrous silicate-hosted mineralization documented here. Hence, the disseminated sulphide and associated PGE mineralization is interpreted to be largely magmatic in origin although PGE mineralization associated with late-stage hydromagmatic fluids also occurred.

In contrast, the sulphide-rich dykes are too thin to cause significant partial melting of the sediments. Similarly, the sulphide content is too high for the sulphides to have been dissolved within the magma. Hence, assimilation of sedimentary material by the intruding magma cannot reasonably be proposed to account for the oversaturation of the magma with respect to sulphur. Again, a hydrothermal origin can largely be discounted on the basis of sulphide textures together with the shallow positive slopes of the chondrite-normalized plots and the strong enrichment of IPGE in comparison to primitive mantle concentrations. Thus, the magma reservoir must have contained a PGE-rich immiscible sulphide liquid prior to the emplacement of the dykes. As PGE are very efficiently removed by sulphide liquids, the presence of late-stage PGE-enriched sulphides within the dykes implies that the parental magma cannot have been sulphur saturated at any point before dyke intrusion. In addition, the relatively high IPGE content indicates that the parental magma is unlikely to have crystallized substantial chromite as this results in the crystallization of IPGE-rich phases and a corresponding depletion of IPGE within the residual liquid (Barnes, Naldrett & Gorton, 1985). Therefore, the parental magma chamber must have become very sulphur-rich but remained sulphur-undersaturated until the time of tapping and dyke intrusion. The low sulphur isotope ratios (-15.0 to -10.8 ‰) indicate that the most plausible mechanism to account for the sulphur saturation of the parental magma chamber is contamination by sedimentary, bacterially reduced sulphur. Magma mixing (cf. Power *et al.* 2000a) and magmatic fractionation (cf. Andersen

et al. 1998; Prendergast, 2000) can be discounted, as primary magmatic $\delta^{34}\text{S}$ values are typically around 0 ‰ (e.g. Hoefs, 1997). Again, a more ^{32}S -rich source than the Torridonian Supergroup sediments is required and given the substantial sulphide content of the dyke-hosted mineralization, a significantly sulphur-enriched source is also required. One possible sulphur source is the pyrite-rich Lower Jurassic shales that are entrained within the marginal rift zone at the southeastern margin of the Layered Suite (Smith, 1985). These are likely to have overlain much of the area prior to being intruded by the magmas of the Rum Complex (cf. Smith, 1985).

The presence of vugs (now filled with zeolites and quartz) within the chalcopyrite-rich dykes suggests that a volatile-rich component was present, but the mineral textures suggest that the volatiles were entrained within the magma and are therefore probably hydromagmatic in origin. The large negative sulphur isotope values of both the pyrrhotite-rich and chalcopyrite-rich dykes indicates that they are genetically related and that the chalcopyrite-rich dykes represent a late-stage, volatile-rich event.

Despite the uncertainty over their origin, the major implication of this study is that, in order to produce such PGE- and sulphur-enriched dykes, a much larger PGE- and sulphur-rich parental body must have existed. The location of the PGE- and sulphide-rich parental magma chamber is unclear and could either be largely eroded away or currently unexposed. Because of their high density, the mechanisms for moving sulphide liquids upwards must involve very high flow velocities. However, no brecciation is observed and it seems more likely that the sulphide liquid leached sideways (outwards) or downwards into the host rocks (cf. Sudbury; Grant & Bite, 1984). As suggested by Dunham & Emeleus (1967), the satellitic plugs and dykes represent a radial system centred on Glen Harris. As such, they indicate that radial fracturing occurred in response to overpressuring in the Layered Suite, possibly analogous to the sulphide- and PGE-rich offset dykes at Sudbury (Grant & Bite, 1984). It seems reasonable that the parental magma chamber was located within the Layered Suite (possibly in the region of Glen Harris) and that the sulphide-rich dykes were largely intruded outwards during radial fracturing. This is in accord with the sulphur isotope data that suggest that the parental magma chamber was probably contaminated by ^{32}S -rich sediments and therefore may have been intruded (at least partially) into overlying Jurassic sediments. Although this requires significant erosion to have taken place after intrusion, material derived from the Layered Suite is present within early Tertiary sediments underlying the lavas of northwestern Rum (Emeleus, 1985). These sediments were deposited very soon after crystallization of the Layered Suite and it has been estimated that more than a kilometre of material was eroded from the Layered Suite within a few million years (Emeleus,

1985). This also concurs with data that indicate that approximately 500 m of cover have been eroded from the flanks of the intrusion (Holness, 1999; 2002). It is therefore probable that the parental magma chamber is now largely eroded away. Similarly, many other sulphide-rich dykes may be present across Rum but will be largely obscured due to preferential weathering and erosion. Hence, strongly PGE-enriched dykes may be far more widespread than previously thought, both in association with the Rum Layered Suite and other intrusive centres throughout the North Atlantic Igneous Province. These occurrences are in accord with the regional geochemical prediction by Andersen, Power & Momme (2002) that the region may host orthomagmatic sulphide-PGE deposits.

10. Conclusions

Widespread platinum-group element mineralization has been documented from a wide variety of geological settings throughout the North Atlantic Igneous Province. The data presented here indicates that PGE mineralization is present in association with both disseminated magmatic sulphides and late-stage sulphide-rich dykes within the West Sgaorishal plug, Rum. The disseminated sulphide mineralization is attributed to sulphur contamination derived from a sedimentary reduced sulphur source causing localized sulphur saturation of the magma. The resulting sulphide liquid scavenged and concentrated the PGE. The sulphide-rich dykes are attributed to sulphur contamination and saturation with attendant PGE concentration within a parental magma chamber prior to dyke intrusion. Textural evidence suggests that the majority of the PGM are magmatic in origin; a mild late-stage hydromagmatic or hydrothermal overprint is also recognized.

The presence of substantial PGE mineralization within late-stage dykes external to the main intrusive centre on Rum suggests not only that a larger PGE- and sulphide-rich parental magma chamber existed, but also that many more PGE-enriched dykes may be present but are poorly exposed. This study therefore highlights the potential for orthomagmatic sulphide-PGE deposits within the southern North Atlantic Igneous Province and indicates that PGE mineralization may be far more diverse and more widespread throughout the North Atlantic Igneous Province than previously recognized.

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