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Abstract: Podiform chromitites from the Ballantrae Ophiolite Complex (BOC), NW Scotland, are examined to investigate their petrogenesis and elucidate the nature of melt percolation in the supra-subduction zone oceanic mantle more generally. The mantle portion of the BOC comprises two petrologically distinct serpentinite belts, whose differences have previously been attributed to contrasting degrees of melt extraction. Chromitite occurs in each of the northern and southern serpentinite belts, at Pinbain Bridge and Poundland Burn, respectively. Field relationships suggest that chromitites were formed by melt-rock reaction in channel-like conduits in the upper mantle. Chromitite Cr-spinel compositions from the two localities show marked differences to one another, with the Pinbain Bridge chromitite Cr-spinels being characterised by relatively high Cr# [Cr/(Cr+Al); 0.62-0.65] and lower abundances of certain trace elements (e.g., Ti, Ga, V), whereas the Poundland Burn chromitite Cr-spinels exhibit relatively low Cr# (0.44-0.46) and higher concentrations of these trace elements. The contrasting Cr-spinel compositions are used to estimate parental magma compositions for the chromitites; the Pinbain Bridge chromitites crystallised from magmas resembling arc tholeiites whereas MORB-like magmas were involved in formation of the Poundland Burn chromitites. While it is possible that this dichotomy points to early derivation of the BOC at a MORB spreading centre, with subsequent processing in a supra-subduction zone, we suggest that the differences reflect melt extraction from different parts of an evolving subduction zone, such that the MORB-like magmas were generated in a back-arc setting. This interpretation finds support in the Ti/Fe3# versus Ga/Fe3# systematics of peridotite-hosted accessory Cr-spinel that we present here, as well as previously published trace element data and geochronological constraints on the basalt lava sequences associated with the BOC, which collectively favour formation of the Poundland Burn chromitites in subduction zone mantle.

Data will be made available on request

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Dr Andrew Kerr,
Editorial Board,
Lithos

February 27th 2019

Re: Submission of manuscript for review in Lithos

Dear Dr Kerr,

I am submitting this cover letter on behalf of a past PhD student (co-author, Dr LJ Derbyshire), to accompany a manuscript entitled '**Chromitite petrogenesis in the mantle section of the Ballantrae Ophiolite Complex (Scotland)**'. I would be grateful if you would consider the article for publication in *Lithos*. This work has not been submitted to, accepted by, or published in any other journal.

The manuscript presents the results of a study carried out on chromitites of the lower Palaeozoic Ballantrae Ophiolite Complex (BOC), with the specific aim of using chromitite Cr-spinel compositions to elucidate the nature of melt percolation in the BOC upper mantle. Mantle Cr-spinels are relatively resistant to post-magmatic alteration (e.g., serpentinisation) so have been applied as petrogenetic indicators of their parental melt composition and degree of partial mantle melting in a variety of tectonic settings. We find that two distinct populations of chromitite are present in the BOC, mirroring previous observations that have suggested the two serpentinite belts in which the chromitites occur have experienced different melt depletion histories. The chromitite Cr-spinel compositional differences are manifest in major and trace element mineral chemistry, as well as crystal structural characteristics. Broadly speaking, the presence of the bimodal chromitite Cr-spinel compositions in the BOC permits two models for their formation. The first is a two-stage melting process that requires processing of the BOC mantle in different tectonic settings (i.e., at a mid-ocean ridge spreading centre and subsequently in a supra-subduction zone). The second explanation envisages all of the melt percolation occurring above (or associated with) an evolving subduction zone, where the population of chromitite Cr-spinels that record a lower degree of partial melting may have formed in a back-arc setting. We favour the latter scenario, for reasons that we outline in the text.

In addition to providing new insights into the petrogenesis of one of the classic UK ophiolites, we believe that our multi-technique approach to characterising chromitite Cr-spinel compositions will be of relevance to future ophiolite studies that focus on mantle petrology and subduction zone dynamics. For these reasons, we feel that this study will be of interest to the broad petrology- and mineralogy-based readership of Lithos.

I have taken the liberty of suggesting several referees in the dedicated section of the online submission pages, for their expertise in various aspects of ophiolite petrology, including the Ballantrae ophiolite, upper mantle processes, as well as chromitite petrogenesis, all of which are covered in this paper.

If you require any further details or information, please do not hesitate to contact me.

Yours sincerely (on behalf of all authors),

(**Brian O'Driscoll**)

Chromitite petrogenesis in the mantle section of the Ballantrae Ophiolite Complex (Scotland)

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Highlights:

- Chromitite in the Ballantrae ophiolite formed by channelized melt-rock reaction
- Significant compositional differences in chromitites from the Ballantrae ophiolite
- Calculated chromitite parental melts approximate both MORB-like and arc magmas
- Ballantrae chromitites formed during melt extraction in an evolving subduction zone

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1. Introduction

The harzburgitic mantle sections of some supra-subduction ophiolites preserve a rich petrological and geochemical record of melt percolation and melt-rock reaction (e.g., Boudier and Nicolas, 1995; Bédard and Hébert, 1998; Piccardo et al. 2007; Rampone et al. 2008; Batanova et al., 2011; Derbyshire et al. 2013; O'Driscoll et al., 2015). The harzburgite typically hosts veins and sheets of dunite, pyroxenite and chromitite (>60 vol.% Cr-spinel) that point to a predominance of channelized, rather than porous, melt percolation in the mantle wedge (e.g., Maaløe, 2005; Batanova et al., 2011). Considerable complexity has been documented in the field relations and other characteristics of these 'fossil' upper mantle melt conduit systems, leading to interpretations invoking multiple generations of melt extraction. For example, O'Driscoll et al. (2015) employed Os isotopes and highly siderophile element abundances to argue that chromitites and orthopyroxenites in the ~497 Ma Leka Ophiolite Complex (Norway) formed during subduction-related melt percolation as the Iapetus Ocean closed, but that the websterites there may have formed ~80 Ma earlier, during Iapetus opening. Compositional variation in Cr-spinel in mantle peridotites and chromitites has also been utilised to elucidate a range of conditions of partial melting and melt

percolation in the oceanic mantle, even within the same ophiolite. Cr-spinel is relatively resistant to low temperature alteration during the serpentinisation of mantle peridotites, facilitating its widespread use as a petrogenetic fingerprinting tool, with applications in estimating the Cr-spinel parental melt composition and degree of partial mantle melting. In a study that showed how Cr-spinel chemistry could be used to decipher multiple melt extraction events, Melcher et al. (1997) reported two populations of chromitites in the Kempirsai ophiolite (Kazakhstan), one with high Cr# [Cr/(Cr+Al)] Cr-spinel and one with relatively low Cr# Cr-spinel. The low Cr# chromitites were attributed to low degree partial melting and melt percolation beneath an oceanic spreading centre (i.e., mid-ocean ridge; MOR), whilst the high Cr# chromitites were attributed to the comparatively high degrees of partial melting and fluxing of hydrous melts through a mantle wedge above a subduction zone (supra-subduction zone; SSZ). Thus, the mantle portion of the Kempirsai ophiolite was suggested to preserve evidence of ocean opening and closing, over a period of ≥50 My.

An increasing number of studies in recent years have recognised that podiform chromitites form by processes of melt percolation and consequent melt-rock reaction in the upper mantle (see Arai and Miura 2016 for a review). Podiform chromitites that preserve a bimodal distribution of Cr# compositions have been recorded in the mantle sections of other ophiolites, including the Semail Ophiolite (Oman; Ahmed and Arai, 2002; Rollinson, 2008), the Mayarí-Cristal Ophiolite (Cuba; González-Jiménez *et al*., 2011), the Muğla Ophiolite (Turkey; Uysal et al., 2009) and the Luobusa Ophiolite (Tibet; Zhou *et al*., 1996). Zhou and Robinson (1997), Ahmed and Arai (2002), Uysal et al. (2009) and Xiong et al. (2017) all invoke a model similar to that proposed by Melcher et al. (1997), whereby relatively low degrees of (anhydrous) partial melting at a MOR was followed by higher degrees of (hydrous) partial melting in a SSZ setting, forming Al- and Cr-rich chromitites, respectively. However, an alternative model proposes chromitite Cr-spinel compositions are temporally controlled by the progressive release of fluids, water and/or melt from the subducting slab during subduction zone development, forming increasingly Cr-rich chromitites over time (Zhou

et al., 1996; Arai, 1997; Büchl *et al.*, 2004; Rollinson, 2008; González-Jiménez *et al.*, 2011; Whattam and Stern, 2011).

The Ballantrae Ophiolite Complex (BOC; Scotland) is a potentially useful locality to examine the extent to which the supra-subduction mantle wedge records evidence of multiple episodes of melt percolation. Firstly, geochemical studies of the lava sequences and poorly-exposed sheeted dykes have revealed broad spectrums of REE trends, ranging from LREE-enriched to LREE-depleted patterns (e.g., Wilkinson and Cann, 1974; Jones, 1977; Lewis and Bloxam, 1977; Thirlwall and Bluck, 1984; Smellie and Stone, 1992, 2001; Smellie *et al.*, 1995; Oliver and McAlpine, 1998). This led to extensive debate about the tectonic provenance of the BOC; proposed settings involve melt generation in an island arc with a back-arc basin, a MOR, a volcanic arc and the involvement of a mantle plume in the formation of the ophiolite (Wilkinson and Cann, 1974; Jones, 1977; Lewis and Bloxam, 1977; Thirlwall and Bluck, 1984; Oliver and McAlpine, 1998; Smellie and Stone, 2001). In addition, it has been suggested that the mantle portion of the BOC has been processed in different tectonic settings (Stone, 2014). In particular, the two broad serpentinite belts that comprise the BOC mantle have different petrological characteristics and sparse data published on the podiform chromitites hosted in each suggests significant differences in chromitite Cr-spinel Cr# exist (**Fig. 1**; Stone and Smellie, 1988; Stone, 2014). In this study, we present detailed new petrological and mineral chemical observations on the chromitites from the BOC. Our principal aims are to investigate the petrogenesis of chromitite in the BOC, elucidate the implications of chromitite formation for melt percolation in the palaeo-oceanic mantle preserved by the BOC, and to better constrain the conditions and setting(s) of partial mantle melting responsible for melt generation.

2. Geological setting

A thorough review of the different lithological components of the BOC and their contact relationships with each other has recently been published by Stone (2014). The BOC is exposed

over an area of ~75 km^2 between Girvan and Ballantrae in south-west Ayrshire, Scotland (**Fig. 1**; Bonney, 1878; Church and Gayer, 1973; Stone and Smellie, 1988). The ophiolite was obducted onto the Laurentian margin during the closure of the Iapetus Ocean (i.e., the Grampian Orogeny; Church and Gayer, 1973; Bluck et al., 1980; Oliver et al., 2002; Power and Pirrie, 2004). Obduction is dated at 478 ±8 Ma, by K-Ar dating of amphibolite in the ophiolite sole (Bluck et al., 1980). The complex is bound to the south by the Stinchar Valley Fault and unconformably overlain to the north by younger Llanvirn Barr and Caradoc-Ashgill Ardmillian Group sediments (Stone and Smellie, 1988; **Fig. 1**). Early work by Peach and Horne (1899), Pringle (1935), Bailey and McCallien (1952, 1957) and Church and Gayer (1973) attempted to explain the structural complexity of the BOC by invoking folding of the lava sequence, serpentinite intrusion and an anticlinal structure for the complex. Jones (1977) suggested that the BOC consists of a series of folded thrust sheets based on the lava sequence having uniform dips and strikes within each volcanic block, two compositionally distinct serpentinite belts and the observation that all lithological units appear to be fault-bounded.

The mantle portion of the BOC comprises variably serpentinised harzburgite and dunite which crop out in two broad NE-SW trending belts (**Fig. 1**; Stone and Smellie, 1988). The northern serpentinite belt is dominantly formed of harzburgite with lherzolite and minor pyroxenite (Jelínek et al., 1980, 1984; Stone and Smellie, 1988). It is metasomatised and preserves a strong tectonic fabric. By contrast, the southern serpentinite belt comprises harzburgite with dunite, wehrlite and minor troctolite (Stone and Smellie, 1988). The southern serpentinite is less metasomatised and locally exhibits a weak tectonic fabric. Chromitite has been documented in key localities in each of the serpentinite belts, at Pinbain Bridge and at Poundland Burn (**Fig.1**; Stone and Smellie, 1988) and these are the localities that concern the present study. It has been suggested that their lithological characteristics reflect formation of the southern serpentinite belt at a shallower depth than the northern belt (Stone, 2014 and references therein). A cumulate dunite sequence (i.e., a Moho transition zone; Boudier and Nicolas, 1995) has not been clearly distinguished in the BOC. The main masses of gabbro crop out at Millenderdale and from Byne Hill to Grey Hill (**Fig. 1**). The

Millenderdale gabbros have been dated by K-Ar on amphibole, yielding an age of 487 ±8 Ma, and trondhjemite at Byne Hill has revealed a U-Pb zircon age of 483 ±4 Ma (Bluck et al., 1980). These gabbros exhibit intrusive relationships with their host rocks (Stone, 2014). The sheeted dyke complex in the BOC is represented at Duniewick Fort near Knockdolian, and possible poorly-developed elsewhere, e.g., at Millenderdale (**Fig. 1**; Oliver and McAlpine, 1998; Oliver et al., 2002). The basalt lava sequences are exposed to the north of the northern serpentinite belt (Pinbain, Slockenray, Brandy Craig), between the serpentinite belts (Knockormal Hill, Moak Hill, Knockdaw Hill) and to the south of the southern serpentinite belt (Mains Hill, Craig Hill, Bargain Hill; **Fig. 1**).

3. Field observations at Poundland Burn and Pinbain Bridge

In the northern serpentinite belt at Pinbain Bridge, a sliver of structurally-fragmented and serpentinised harzburgite crops out in a sea cliff. The harzburgite contains small (0.2-0.5 cm; **Fig. 2a**) brown orthopyroxene pseudomorphs and abundant serpentinite (chrysotile) veining (~5 cm thick). A pervasively serpentinised, 4-5 m thick dunite lens occurs in the harzburgite and constitutes a broadly east-west trending zone that hosts poorly-defined lensoid chromitite bodies. The chromitite seams are characterised by variation in Cr-spinel abundance (from 60-95 vol.% Cr-spinel). Cr-spinel-rich dunites (containing 20-40 vol.% Cr-spinel) are also observed. The chromitite seams exhibit a range of thicknesses (from 5 cm to 0.5 mm). The northern margin of the chromitite band is marked by a brecciated fault zone that separates the chromitite from serpentinised harzburgite. Both harzburgite and dunite are commonly cross-cut by abundant ~5 cm thick fibrous chrysotile veins.

The chromitites and Cr-spinel-bearing peridotites at Poundland Burn in the southern serpentinite belt are enclosed in dunite lenses that are interlayered with harzburgite. Harzburgite is easily distinguished from dunite by the presence of randomly-oriented, brown orthopyroxene crystals (<0.5-1 cm in size), the majority of which have been pseudomorphed by bastite. Chromitites and Cr-spinel-bearing peridotites at Poundland Burn exhibit a range of textures,

including well-developed nodular and anti-nodular varieties (**Figs. 2b,c**). Nodular-textured chromitite is characterised by 0.2-1.5 cm diameter sub-rounded, spheroidal to ellipsoidal Cr-spinel nodules in a serpentinised dunite groundmass (**Fig. 2b**). Where the nodules are ellipsoidal, several examples exhibit weak local alignments, but most are massive-textured. Variation in nodule packing is observed. The large (>1 cm) nodules are loosely-packed with the dunite groundmass clearly distinguishable between individual nodules. However, as the Cr-spinel nodules decrease in size (from >1 to 0.2 cm), they exhibit closer-packing and a consequent decrease in groundmass proportion (i.e., from ~50 vol.% to ~25 vol.%). Smaller nodules do not tend to exhibit ellipsoidal morphologies to the same extent as the larger ones. Nodules tend to be locally very well sorted, in a given chromitite pod. However, size grading of Cr-spinel nodules from large (~1 cm) to small (<0.2 cm) is observed, with the largest nodules usually in the centres of the pods. Anti-nodular chromitite is also observed, formed of a dense Cr-spinel network enclosing small (<1 cm) spheroidal or ellipsoidal volumes of serpentinised dunite (**Fig. 2c**). The Cr- spinel crystals that form the network range from <1-0.5 mm in size. Between the different nodular and anti-nodular chromitite seams, the serpentinised dunites contain varying proportions of Cr-spinel as disseminated seams, clusters and accessory Cr-spinel crystals. For example, rounded and elongate Cr-spinel clusters of <20 crystals in dunite are formed from Cr-spinel crystals ranging from <0.2-0.5 mm in size. Small Cr-spinel stringers (<5 cm long) and thin (<1 cm) seams are also present in the dunite units. The dunites transition to harzburgite gradationally (i.e., the boundaries between lithologies are not sharply defined) and often contain abundant magnetite veining. Harzburgite rarely contains Cr-spinel; if present, the Cr-spinel crystals occur in accessory proportions and are <0.2 cm in size.

4. Sample selection and analytical techniques

4.1 Sample selection

Sample selection was dictated to some extent by the poor degree of exposure and alteration of the BOC rocks. Only chromitites (Samples BA-10-03, BA-10-04) were analysed in detail from Pinbain

Bridge, due to the high degrees of weathering and alteration of the peridotites there. Sample BA-10-03 is from a ~5 cm thick chromitite pod located towards the centre of the dunite lens at Pinbain Bridge, whereas BA-10-04 is from a thinner (~0.5 cm) close to the dunite-harzburgite contact. The Poundland Burn samples were collected at a poorly exposed outcrop at the head of Poundland Burn; samples of nodular chromitite (BA-10-06, BA-10-07), anti-nodular chromitite (BA-10-10), Cr-spinel-rich dunite (BA-10-13) and dunite with accessory Cr-spinel (BA-10-11, BA-10-12) were selected for further analyses. Samples BA-10-06 and BA-10-07 are nodular-textured chromitite, sampled ~2 m away from one another (along strike, in the centre of the same seam). Sample BA-10-10 is an anti-nodular chromitite sampled ~20 m away across strike from the nodular-textured chromitite that yielded BA-10-06 and BA-10-07. The relationships between BA-10-06/BA-10-07 and BA-10-10 are obscured by vegetative cover. Sample BA-10-13 was collected at the margin of the nodular-textured seam, and is a Cr-spinel rich dunite with a texture somewhat resembling that of anti-nodular chromitite, but with a greater proportion of silicate present. BA-10-11 and BA-10-12 are dunites from the envelope containing the main nodular-textured seam, and contain only accessory amounts of Cr-spinel.

4.2 Mineral chemistry by electron microprobe

A JEOL JXA-8900RL electron microprobe at the University of Göttingen (Germany) was employed to make backscatter electron micrographs and analyse the Cr-spinel/sulfide compositions from the two target chromitite localities. Analyses were conducted on both Cr-spinel crystal cores and sieve-textured alteration rims to enable compositions of both to be studied. Cr-spinel mineral chemical data were obtained using a 20.0 kV acceleration voltage, a 20 nA beam current and a 5 μm beam diameter with a 15 s peak count and 5 s background count for Mg, Al, Cr, Fe, Si and Mn and a 30 s peak count and 15 s background count for V, Ti, Ni and Zn. The standards were MgO, Al_2O_3, Cr_2O_3, TiO_2, NiO, V (synthetic), hematite for Fe, wollastonite for Si, rhodonite for Mn and gahnite for Zn. Ferric iron was calculated from the FeO content assuming perfect stoichiometry according to the method of Droop (1987). Sulphide grains situated in Cr-spinel alteration rims or adjacent to

Cr-spinel crystals in the serpentinised groundmass were measured quantitatively using a 20.0 kV accelerating voltage, a 20 nA beam current and a 10 μm beam diameter. Larger sulphide grains (≥10 μm) were analysed with a 5 μm beam diameter. For sulphides, peak and background count times were 15 s and 5 s, respectively, for S, Fe and Zn, 30 s and 15 s peak and background, respectively, for As, Cu, Ni, Pb, Sb, and Co and 60 s and 30 s peak and background, respectively, for Se and Te. Standards used were ZnS, AsGa, galena, gahnite and pure elements Te, Cu, Ni, Se, Sb, Fe and Co. Most sulphides were smaller than ~10 μm, so some were also analysed by EDS.

4.3 LA-ICP-MS trace elements

In situ trace element analysis was carried out by LA-ICP-MS at IGG-CNR, Pavia (Italy), using an Elan DRC-e quadrupole mass spectrometer coupled with a Q-switched Nd-YAG laser source (Quantel Brilliant). Sample ablation was carried out with a laser beam of 266 nm wavelength and a 60 μm spot size. Helium was used as carrier gas and mixed with Ar downstream of the ablation cell. NIST SRM 610 was used as external standard, while the Al content determined by EMPA was used as the internal standard. Precision and accuracy were assessed from repeated analyses of the BCR-2g and NIST SRM 612 standards, resulting in better than ±10% for concentrations at ppm levels. The LA-ICP-MS analysis was designed for the complete elemental characterisation of the spinels. It involved the concomitant acquisition of the signals of nearly 60 masses, encompassing major elements, REE, LILE, HFSE, Actinides, and most of the transitional elements relevant for the geochemical investigations. Detection limits were typically in the range of 100-500 ppb for Sc, 10-100 ppb for Sr, Zr, Ba, Gd and Pb, 1-10 ppb for Y, Nb, La, Ce, Nd, Sm, Eu, Dy, Er, Yb, Hf and Ta, and usually <1 ppb for Pr, Th and U. Further information about the analytical methods and data statistics employed is reported in Miller et al. (2012).

The electron microprobe Cr-spinel analyses carried out to reduce the LA-ICP-MS data were performed on a CAMECA-CAMEBAX microprobe at IGG-CNR (Istituto di Geoscienze e Georisorse-Consiglio Nazionale delle Ricerche), Padua, operating at 15 kV and 15 nA. A 20 s

counting time was used for both peak and total background. Synthetic $MgCr_2O_4$ and $FeCr_2O_4$ spinels (Lenaz et al. 2004a) were used for Mg, Cr and Fe determination, Al_2O_3 for Al, $MnTiO_3$ for Ti, and Mn, NiO for Ni and sphalerite for Zn. The raw data were reduced by a PAP-type correction software provided by CAMECA.

4.4 Single crystal X-ray diffraction

The combination of crystal structural parameters and mineral compositional data offers a potentially powerful way to evaluate Cr-spinel petrogenesis when combined with conventional mineral compositional microprobe data (cf. Lenaz et al., 2007). Eight representative Cr-spinel crystals (two from Pinbain Bridge and six from Poundland Burn) were separated from the BOC samples and analysed for their crystal structural characteristics using a KUMA-KM4 diffractometer (University of Trieste, Italy), using MoKα radiation and a monochromatised graphite crystal. Twenty-four equivalent reflections (12 8 4) or (8 4 4) were used depending on the size of the Cr-spinel crystal. Structural refinements were calculated using the SHELX-97 programme (Sheldrick, 1997) using the Fo^2_{hkl} in the *Fd-3m* space group. After X-ray data collection, the same crystals used for X-ray data collection were mounted on glass slides, polished and carbon coated for electron microprobe analyses on a CAMECA-CAMEBAX microprobe at IGG-CNR (Istituto di Geoscienze e Georisorse-Consiglio Nazionale delle Ricerche) (Padua), using the procedures and standards utilised for the Padua electron microprobe analyses described in the previous section. T and M site cation distribution was calculated using the method described in Carbonin et al. (1996) and Lavina et al. (2002). The Cr-spinel compositions obtained for crystal structural analysis at the Padova electron microprobe are consistent with the Cr-spinel compositions analysed at the University of Göttingen (Germany). Intracrystalline closure temperatures for the BOC Cr-spinel crystals were calculated using the Princivalle et al. (1999) thermometer to provide insight into compositional changes occurring during Cr-spinel crystallisation and to determine their thermal history.

5. Results

5.1 Petrographic observations

The Cr-spinel contained in the Pinbain Bridge massive-textured chromitite seams consists of subhedral to euhedral crystals that range from 50-600 μm in size. The crystals are often highly-fractured and locally display alteration to Fe-rich thin rims around their edges, manifested by their relatively bright appearance under back-scattered electrons (**Fig. 3a**). Fine-grained magnetite is locally associated with these rims. In some instances, the rims are developed up to ~2 μm thick. Towards the centres of seams, Cr-spinel crystals occur as massive aggregates with poorly defined crystal boundaries. Locally, where euhedral (polygonal) crystals occur within seams, they exhibit apparent (2D) dihedral angles of ~120˚ at Cr-spinel three-grain junctions, suggesting solid-state textural equilibration. The chromitite seam groundmass predominantly comprises mesh-textured serpentine pseudomorphs after olivine. Small (5-10 μm) irregularly-shaped sulphide grains occur in the serpentine groundmass and/or touching the altered rims at the edges of Cr-spinel crystals. More rarely, larger sulphide grains (>10 μm) are also observed, typically touching or close to Cr-spinel crystal edges. Fractures that cut through larger (100-200 μm) Cr-spinels (i.e., at the centres of seams) contain abundant small (<20 μm) Cr-spinel fragments (**Fig. 3b**). The majority of fractures that cut through Cr-spinel crystals are not associated with alteration of the Cr-spinel, suggesting they formed later, possibly in relation to the adjacent fault.

The Pinbain Bridge dunites hosting the chromitites are completely serpentinised, but rare olivine pseudomorphs are present. The harzburgites are also extensively serpentinised (~85-90 vol.%) but contain rare orthopyroxene pseudomorphs and accessory Cr-spinel (<1 %). Relict olivine crystal outlines are also observed in the harzburgite, ranging in size from 0.3-0.6 mm. The pseudomorphed orthopyroxene crystals, ranging between 200-700 μm in size, are replaced by bastite. Cr-spinel crystals (40-200 μm in size) are anhedral and sparsely distributed throughout the fine-grained serpentine groundmass. The groundmass exhibits a mesh texture and often contains

293 thin, discontinuous veins of calcite and/or serpentine. The serpentine veins are composite, pointing
294 towards repeated serpentinisation events.
295 The sub-rounded to elliptical chromitite nodules in the Poundland Burn chromitite seams
296 locally display very thin and discontinuous Fe-rich alteration rims, though most nodules do not
297 exhibit this feature at all (**Fig. 4**). Those nodules with the thickest alteration rims have irregular (i.e.,
298 non-rounded) nodule edges. The alteration of Cr-spinel is confined to the chromitite seam edges and
299 is almost absent from the centres of chromitite seams. A small proportion of the Cr-spinel nodules
300 have cores that contain silicate inclusions (mostly serpentine). A typical feature of the interiors of
301 Cr-spinel nodules is the presence of cuspate-shaped areas filled with serpentine (**Figs. 3c, 4**),
302 whereas the outer parts of nodules comprise massive Cr-spinel. Where two nodules are in contact,
303 one may exhibit a concavity at its margin to accommodate the other, suggesting indentation. All of
304 the nodules are moderately to heavily fractured. Cr-spinel crystals in finer grained nodular-textured
305 seams also contain silicate inclusions (**Figs. 3c, 4a,c**). The fractures that cut through the Cr-spinel in
306 the seams may or may not be associated with alteration of the Cr-spinel. The groundmass hosting
307 the nodules consists of aggregates of fine-grained serpentine. Anti-nodular chromitite textures form
308 a network of small (<100 μm) Cr-spinel crystals that surround (<1 mm diameter) rounded spheroids
309 of serpentinised dunite. The Poundland Burn chromitites contain limited amounts of sulphides in
310 the serpentinised groundmass, typically close to Cr-spinel alteration rims, or in Cr-spinel crystal
311 fractures.
312 The Poundland Burn mantle peridotites comprise variably serpentinised harzburgite and
313 dunite. Harzburgite contains large (<1 mm in size), randomly orientated, partially pseudomorphed
314 orthopyroxene crystals. Where pseudomorphed, the orthopyroxene comprises bastite, mostly at the
315 crystal edges and along cleavage planes (**Fig. 3d**). Olivine pseudomorphs, ranging from 0.2-1 mm
316 in size, contain relict olivine domains partially replaced by a finer grained serpentine rim. The
317 serpentinised groundmass has a reticulate texture, and rare, small (<20 μm) euhedral Cr-spinel
318 crystals occur in the groundmass. The dunites contain euhedral to anhedral Cr-spinel crystals in

small clusters and stringers of crystals, ranging from 50-400 μm in size (**Fig. 3e**). The abundance of Cr-spinel in dunite is variable but generally higher than in harzburgite samples. Olivine pseudomorphs are typically less than 1 mm in size and are surrounded by thin magnetite veins. Isolated Cr- spinel crystals in dunite commonly have thicker Fe-rich rims than those in the chromitites (**Fig. 3f**). Infrequently, Cr-spinel crystals contain rounded silicate inclusions in their cores, usually adjacent to fractures; this occurs in Cr-spinel crystals of all sizes, although it is generally found in larger Cr-spinels (**Fig. 3f**).

5.2 Cr-spinel and sulphide major element compositions

The electron microprobe analyses of the BOC chromitites (both fresh Cr-spinel cores and sieve-textured rims, as well as sulfides) are tabulated in the electronic supplement (*Table S1*). Generally, there is a marked bimodality in Cr-spinel composition between the two chromitite localities (**Fig. 5**). Poundland Burn chromitite Cr-spinels have relatively low Cr# (0.44-0.46), similar Mg# ([Mg/(Fe^{2+}+Mg)]; 0.52-0.77) values, and higher TiO_2 contents (0.21-0.27 wt.%) compared to the Pinbain Bridge chromitites overall (**Figs. 5a, 5b**). The Pinbain Bridge chromitites have moderately high Cr# (0.62-0.65), variable Mg# (0.54-0.70) and relatively low TiO_2 contents (0.08-0.12 wt.%). In particular, the nodular-textured chromitites analysed from Poundland Burn have a range of Cr# (0.44-0.45), Mg# (0.70-0.77) and TiO_2 (0.22-0.26 wt.%) that is distinct from the Pinbain Bridge chromitites. On plots of Cr# versus Mg# and TiO_2 versus Cr# (**Fig. 5**), the Poundland Burn Cr-spinel compositions mainly fall within the abyssal peridotite or MORB fields, and the Pinbain Bridge Cr-spinels (with higher Cr# and lower TiO_2) lie closer to (but mostly not within) the boninite field. Traverses across individual nodules in the Poundland Burn chromitite reveal that they are extremely homogenous with respect to their Cr, Al, Fe and Ti (**Fig. 4**) concentrations. Accessory Cr-spinels from Poundland Burn dunites exhibit more variable Cr# and Mg# values (0.42-0.49, 0.52-0.68, respectively) and TiO_2 contents (0.21-0.36 wt.%) than the chromitite Cr-spinels (Figs. 5. The discontinuous sieve-textured alteration rims on the Pinbain Bridge Cr-spinels

record moderate depletion in Mg^{2+} and Al^{3+} and enrichment in Cr^{3+} and Fe^{3+} at the crystal edges, so yield values toward the higher Cr# and TiO_2, and lower Mg# end of the ranges quoted above. Thin, highly discontinuous relatively Fe-rich rims on the Cr-spinels in the Poundland Burn dunites have Cr#: 0.37-0.47 and TiO_2: 0.19-0.39 wt.%, values similar to the Fe-rich rims in the Poundland Burn chromitite Cr-spinels (Cr#: 0.38-0.54; TiO_2: 0.17-0.29 wt.%).

The BOC chromitites contain only sparse base-metal sulphides (and platinum-group minerals; PGM). Where present, these grains are very small (~5 μm) situated either in Cr-spinel crystal cores or in the serpentinised groundmass. Three small (<3 μm) Ni-Fe-S grains were identified by EDS in the serpentinised groundmass adjacent to Cr-spinel crystals in the Pinbain Bridge chromitite. One small (<2 μm) irarsite ([Ir,Ru,Rh,Pt]AsS) grain was documented at Pinbain Bridge. The nodular-textured chromitite from Poundland Burn contains several small sulphide grains (~10 μm) large enough for quantitative analysis. Five such sulphides were identified as heazlewoodite (Ni_3S_2) with minor Fe impurities (<1 wt. %) and one as millerite (NiS). Other small (<5 μm) sulphides identified by EDS in the Poundland Burn chromitites include Ni-S and Ni-Fe-S grains. No PGM were analysed from any of the Poundland Burn chromitites or associated dunites.

5.3 Cr-spinel trace element abundances

All of the LA-ICP-MS data are tabulated in the electronic supplement (*Table S2*), and only those elements with particular bearing on the petrogenetic interpretation are reported below. The trace element compositional variations in the BOC chromitites mirror the major element bimodality described above. For example, the Pinbain Bridge chromitite Cr-spinels have Sc contents that range from 5.1-6.6 ppm (n=7), V from 715-865 ppm, Mn from 1265-1654 ppm, Co from 218-243 ppm and Ga from 36-43 ppm. The Poundland Burn nodular chromitite Cr-spinels have Sc contents that range from 3-5 ppm (n=8), V from 889-929 ppm, Mn from 1156-1361 ppm, Co from 223-264 ppm and Ga from 54-60 ppm. By contrast, accessory Cr-spinel in dunite from Poundland Burn has Sc contents that range from 1.3-6.2 ppm (n=6), V from 1033-1214 ppm, Mn from 1586-3071 ppm, Co

from 358-474 ppm and Ga from 47.6-61.7 ppm. The relationships of Ga, V and Co with Cr# are shown in **Figures 6a, 6b** and **6c**, with the fields of trace element compositions of other (unpublished) UK ophiolite Cr-spinels shown for comparison. A well-developed positive correlation is noted between Ga and Cr#, in particular (**Fig. 6a**), when considered in light of the data from other ophiolites. Values for Cu, Ni and Zn are not as easily distinguished between the different Cr-spinel groups as the aforementioned elements, though a notable positive correlation is observed between Cu/Zn versus Cu/Ni for the whole population (**Fig. 6d**), probably reflecting a sulfide control on these elements.

We have plotted the BOC Cr-spinel compositions on the spidergram of Pagé and Barnes (2009), which displays a range of important major and trace elements normalised to MORB (**Fig. 7**). The Poundland Burn Cr-spinels are similar to MORB with respect to their Ga, Ti, Ni, Zn and V abundances. They are relatively enriched in Co and Mn, and depleted in Sc, compared to MORB. In contrast, the Pinbain Bridge Cr-spinels are mildly depleted in Ga and Ni, and particularly in Ti, compared to MORB. They have similar abundances of Zn, V and Sc, and are enriched in Co and Mn, relative to MORB. Compared to boninite, BOC Cr-spinels are relatively enriched in Ga, Ti and Ni, similar in terms of Zn, Co and Mn abundances, and quite depleted with respect to V and Sc.

5.4 Crystal structural measurements

Cr-spinel crystals from Poundland Burn chromitites and Cr-spinel-bearing dunites have notably different cell edge lengths (a_0) and oxygen positional parameters (*u*) compared to the Cr-spinels in the Pinbain Bridge chromitites (*Table 1,* **Fig. 8**). It is worth highlighting that in spinel, the anions form a nearly cubic close-packed array, parallel to (111) planes, and the cations fill part of the tetrahedral (T) and octahedral (M) interstices available in the framework. Movement of the oxygen atom along the cube diagonal [111] causes the oxygen layers in the spinel structure to be slightly puckered so that variations in *u* correspond to displacements of the oxygens along the cube diagonal, and reflect adjustments to the relative effective radii of cations in the tetrahedral and

octahedral sites. An increase in *u* corresponds to an enlargement of the tetrahedral coordination polyhedra and a compensating decrease in the octahedra (Lindlsey, 1976). The Poundland Burn chromitite Cr-spinels display minimal variation in their a_0 and *u* values (8.2204-8.2285 Å and 0.2630-0.2634, respectively; **Fig. 8a**). Accessory Cr-spinel from Poundland Burn dunites displays longer cell edge lengths (a_0: 8.2456-8.2528 Å) and *u* values consistent with the other Poundland Burn chromitites (*u*: 0.2630-0.2631). Cr- spinel crystals from the Pinbain Bridge chromitites display the longest cell edge lengths (a_0: 8.2704- 8.2740 Å) and lowest *u* values (*u*: 0.2625). It is interesting to note that the Cr-spinels from Poundland Burn show the lowest cell edge lengths and the highest oxygen positional parameters among the different ophiolitic Cr-spinels analysed via X-ray single crystal diffraction (Shetland, a_0:8.26-8.31 Å; *u*: 0.2623-0.2631, Derbyshire et al., 2013; Oman, a_0: 8.24-8.29 Å; *u*: 0.2608-0.2629, Lenaz et al. 2014a; Albania, a_0: 8.27-8.31 Å; *u*: 0.2616-0.2627, Bosi et al., 2004; India, a_0: 8.28-8.30 Å; *u*: 0.2619-0.2623, Lenaz et al., 2014b).

6. Discussion

6.1 Petrogenesis of nodular-textured and anti-nodular-textured chromitite in the BOC

Podiform chromitite has been documented from the mantle portions of numerous SSZ ophiolite complexes (Dick and Bullen, 1984; Arai, 1992; Melcher et al., 1997; Barnes and Roeder, 2001; Rollinson, 2008; Pagé and Barnes, 2009; Uysal et al., 2009; González-Jiménez et al., 2010, 2011; O'Driscoll et al. 2012a; Derbyshire et al., 2013; Arai and Miura, 2016). By contrast, ophiolites that do not have a SSZ provenance do not appear to ubiquitously develop chromitite (e.g., the Lizard, UK; Taitao, Chile; see also Rollinson and Adetunji (2013) and Arai and Miura (2015) for recent discussion), suggesting that perhaps melt percolation in the supra-subduction mantle wedge is particularly conducive to their formation. The recognition that chromitite typically occurs within dunite envelopes in SSZ settings has led to widespread acceptance of melt-rock interaction mechanisms as fundamental processes for chromitite petrogenesis (Arai, 1992; 1997; Arai and Yurimoto, 1994; Zhou et al., 1996; Batanova et al., 2011; González-Jiménez et al., 2011;

Derbyshire et al., 2013; González-Jiménez et al., 2014a, 2014b; Arai and Miura, 2016), following the classic work of Kelemen et al. (1990) and Kelemen et al. (1992; 1995). Field observations on the BOC chromitites therefore also implicate melt-rock interaction, in 'channels' of focused melt flow, as the key petrogenetic mechanism. This is because chromitite bodies in the BOC are ubiquitously hosted in dunite envelopes. Where visible (e.g., at Poundland Burn), harzburgite-dunite contacts are clearly defined and relatively sharp, although gradational boundaries are also present. Dunite lenses at Pinbain Bridge and Poundland Burn invariably contain more Cr-spinel than the host harzburgite. The abundance of Cr-spinel in dunite ranges from sparse clusters and stringers oriented parallel to the dunite-harzburgite contacts, to chromitite *sensu stricto*.

Nodular-textured chromitite is not ubiquitous in ophiolitic mantle, but has been documented in a number of cases worldwide including the Luobusa Ophiolite (Tibet; Zhou et al., 1996, 2001), the Kempirsai Massif (Kazakhstan; Melcher et al., 1997), the Troodos Ophiolite (Cyprus; Greenbaum, 1977) and the Semail Ophiolite (Oman; Ahmed and Arai, 2002; Rollinson and Adetunji, 2013; Zagrtdenov et al., 2018). Published nodular Cr-spinel analyses have been shown to display intermediate to high Cr# (0.60-0.86; Bilgrami, 1969; Greenbaum, 1977; Ahmed, 1982; Orberger et al., 1995; Vuollo et al., 1995; Zhou et al., 1996; Melcher et al., 1997; Ahmed and Arai, 2002; Morishita et al., 2006; Pagé and Barnes, 2009), considerably higher than those in the BOC (Cr#: ~0.45). The formation of nodular-textured chromitite is not well understood, although most workers have implicated physical processes (Arai and Miura, 2016), e.g., the coalescence of nodules in turbulent melt flow (Lago et al., 1982), magma mixing in melt flow conduits (Ballhaus, 1998) and melt-rock interaction (Zhou et al., 2001). Ballhaus (1998) showed that nodular chromitite can form by the mingling of compositionally distinct melts in melt conduits. In his experiments, Ballhaus produced nodular chromitite remarkably similar to natural examples and his model proposes that each Cr-spinel nodule forms from incomplete mixing of a silica-poor melt (from deeper in the mantle) with a more siliceous melt (produced from melting of the harzburgite host). Matveev and Ballhaus (2002) expanded the work of Ballhaus (1998) to consider the effect of water

449 on the formation of nodular chromitite, showing that the crystal-fluid and crystal-melt interfacial
450 energies provide a control on Cr-spinel nodule formation. The Matveev and Ballhaus (2002) model
451 proposes that fluid exsolved from a water-rich melt forms small bubbles that nucleate around
452 dispersed Cr-spinel microphenocrysts contained within the melt. Due to the density contrast and
453 differences in surface tension between the fluid bubbles and the melt, the Cr-spinel bearing fluid
454 bubbles rise up the magma conduit and coalesce with other fluid bubbles to form a larger 'fluid
455 pool' (Matveev and Ballhaus, 2002). In a more recent and novel X-ray microtomographic study,
456 Prichard et al. (2015) reported that chromite nodules from the Troodos Ophiolite comprised a single
457 skeletal crystal in their centres, surrounded by an outer mantle of polycrystalline chromite. The
458 skeletal crystal at the nodule core crystallised from a chromite oversaturated melt, and Prichard et
459 al. (2015) attributed the rounded smooth outer surfaces of nodules to dissolution by a chromite
460 undersaturated melt. One of the main implications of the Prichard et al. (2015) Troodos study is that
461 the random growth-by-accumulation of chromite nodules in fluid bubbles within a turbulently-
462 flowing melt, as per the Matveev and Ballhaus model, is not necessary.
463 In the BOC, the nodular chromitites are found in close proximity to anti-nodular textured
464 chromitite. The Cr-spinel in anti-nodular-textured chromitite has an almost identical composition
465 (Cr#: 0.44-0.46) to that of the adjacent nodular-textured chromitite. The *in situ* growth model of
466 Prichard et al. (2015) does not easily account for the common existence of anti-nodular chromitite.
467 However, the BOC nodules do exhibit some textural similarities with the Troodos examples, in that
468 silicate commonly occupies cuspate-shaped areas within the interiors of nodules (**Figs. 4**), and the
469 outer mantles of nodules comprise massive-textured Cr-spinel. Rollinson and Adetunji (2013) also
470 described this texture in a nodule from Maqsad, in the Oman Ophiolite (see their Figure 7), so it
471 would seem that it is a common feature of nodular-textured chromitite. However, the BOC nodules
472 have also undergone fracturing and deformation, obscuring some of the primary microstructure and
473 making it difficult to positively identify skeletal intergrowths at the centres of nodules (if they
474 exist). The relative compositional homogeneity of the nodular and anti-nodular chromitites

combined with the lack of internal elemental zonation in individual nodules (**Fig. 4**) means that chemical evidence is not preserved for a process of magma mixing, as proposed by Ballhaus (1998). If magma mixing caused chromitite formation, then the mixing process must fortuitously have resulted in hybrid melts capable of crystallising Cr-spinel of very similar composition, despite the very different physical appearance of the nodular and anti-nodular textured chromitites. It has been noted by other studies that different chromitite textures may grade into each other, from massive textures in the centre of the chromitite pod through nodular Cr-spinel to anti-nodular and disseminated textures at the chromitite pod margin (Ahmed, 1982; Zhou et al., 1996, 2001; González-Jiménez et al., 2009, 2010; Marchesi et al., 2010; Borisova et al., 2012), suggesting a complex fluid dynamic regime. Unfortunately, a lack of exposure of the precise contact between the anti-nodular and nodular chromitites at Poundland Burn means that direct observation of the nature of the relationship between both is not possible. The nodular-textured chromitites at Poundland Burn rarely display any preferred alignment of nodules. However, indentation of nodules by one another is observed, pointing toward a degree of deformation in the conduit whilst the nodules were semi-crystalline.

In summary, the balance of evidence suggests that the Poundland Burn nodular chromitites formed in a conduit by melt-rock interaction, followed by a degree of flow (perhaps gravity-driven) sorting of the Cr-spinel nodules to explain the evidence for localised ductile deformation. We have not been able to verify the presence of skeletal crystals at the Cr-spinel nodule cores (cf. Prichard et al. 2015), which would point to an oversaturation event in the melt conduit. The key observation that there are cuspate areas of silicate minerals within most BOC Cr-spinel nodules (**Figs. 3c, 4**) may be significant and a future research direction for the Poundland Burn chromitites will be to carry out X-ray microtomography experiments and establish whether these cuspate areas are the 3D manifestations of skeletal structure in nodule interiors. The observation that size-grading of nodules occurs within individual pods of the Poundland Burn chromitites, may lend support to the Zhou et al. (2001) and Matveev and Ballhaus (2002) models of turbulent flow in melt channels. In this

scenario, the size range of the BOC Cr-spinel nodules (<0.2 mm to >1 cm) might be controlled by a primary physical process such as 'snowballing' (cf. Zhou et al., 2001). The interaction of two immiscible liquids of differing viscosities promotes turbulent flow due to the dispersion of the more vicious liquid in the less vicious fluid (Joseph et al., 1984a, 1984b; Lemenand et al., 2003; Abarzhi, 2010; Abarzhi et al. 2005). The contrast between the densities and viscosities of the ascending (H_2O-rich) basaltic melt (lower density and viscosity) and the siliceous melt produced from orthopyroxene dissolution in the harzburgitic host rock (higher density and viscosity) increases the Rayleigh-Taylor instability, promoting favourable conditions for turbulent flow (Huppert and Sparks, 1985; Ballhaus, 1998; Gerya and Yuen, 2003; Herbert et al., 2009; Hack and Thompson, 2011). The largest (~1 cm) Cr-spinel nodules form in the centre of the melt channel where the flow is most turbulent, the melt flux is greatest and the availability of Cr is highest. The turbulent flow in the centre of the melt channel promotes the 'snowballing' of the developing Cr-spinel nodules, facilitating the formation of larger nodules. With increasing proximity to the channel boundary, the flow regime is more laminar, the melt flux and availability of Cr is lower, limiting the ability of the Cr-spinel nodule to 'snowball' and thus restricting the size of the nodules.

The observation of grading of Cr-spinel nodules from large (~1 cm) to small (<0.2 mm) in the Poundland Burn nodular chromitite bands can therefore be interpreted as preserving a portion of the melt channel, from the channel margin to the channel centre. As noted above, a potentially important observation that is not explained by the model above is the similar chemical composition of the nodular and anti-nodular chromitite Cr-spinels. This issue could be accounted for if magma mixing is efficient and if chromitites all formed part of the same melt channel system. The abundance of small Cr-spinel crystals surrounding the silicate nodules in the anti-nodular chromitite might suggest high Cr-spinel nucleation rates and slower crystal growth, resulting from part of the melt channel with a lower melt flux. The BOC nodular- and anti-nodular-textured chromitites have similar *u* values (0.2629-0.2634), indicating they experienced the same crystallisation and cooling history, lending indirect support to this idea.

6.2 Petrogenetic conditions and signatures of melt percolation in the BOC mantle

The compositional variation of Cr-spinel in ophiolite mantle sections has been shown to be a rich source of information on parental melt composition and the conditions of petrogenesis (cf. Dick and Bullen, 1984; Barnes and Roeder, 2001; Rollinson, 2008). In the BOC, the effects of late-stage alteration on Cr-spinel composition are relatively easy to diagnose in terms of physical appearance of crystals and compositional variation (e.g., intra-crystal fracturing, Fe-rich rims). Similarly, accessory Cr-spinels from dunites and harzburgites are not considered to retain evidence of parental melt evolution. These crystals have probably extensively reequilibrated with the dominant surrounding silicate, as shown by their higher intracrystalline closure temperatures (see below). Therefore, only those Cr-spinels considered to be free from such alteration and modification are considered in the following discussion. The distinct bimodality of Cr-spinel compositions observed between the two BOC localities is different to the continuous compositional trends observed from many SSZ ophiolite chromitites (Troodos Ophiolite, Büchl et al., 2004; Semail Ophiolite, Rollinson, 2005; and the Shetland Ophiolite Complex, Derbyshire et al., 2013), but has been documented from others as noted previously. No intermediate Cr-spinel compositions have been found in the BOC, between the relatively aluminous Cr-spinels in the Poundland Burn chromitites (Cr#: 0.44-0.46) and the Cr-rich Cr-spinels in the Pinbain Bridge chromitites (Cr#: 0.62-0.65), suggesting that these two localities reflect melt percolation under different upper mantle environmental conditions. This point is also well illustrated by consideration of where the Cr-spinel populations from Pinbain Bridge and Poundland Burn group relative to one another on of Cr# versus Mg# and TiO_2 versus Al_2O_3 diagrams (**Fig. 5**). The Poundland Burn Cr-spinels plot in the MORB (abyssal peridotite) field in both instances, whereas the Pinbain Bridge Cr-spinels plot in or towards the island arc/boninite fields (**Fig. 5**).

The major element compositional differences between the Poundland Burn and Pinbain Bridge chromitites are also borne out in the trace element data. The Cr-spinels in the Pinbain Bridge chromitites have lower Al_2O_3, Ga, Ti and Ni, and generally higher Sc and Cr_2O_3, than the

554 Poundland Burn chromitite Cr-spinels (**Fig. 7**). The Pinbain Bridge chromitites therefore bear more
555 resemblance to boninite Cr-spinels than the Poundland Burn chromitite Cr-spinels. Dare et al.
556 (2009) introduced the Ti/Fe^3# versus Ga/Fe^3# diagram as a means of discriminating the tectonic
557 setting and petrogenesis of Cr-spinels in mantle peridotites (**Fig. 9a**). Gallium is an interesting
558 element for fingerprinting Cr-spinel petrogenesis because it occurs as a trivalent cation, so is
559 unlikely to change during cooling and subsolidus processes, and is not known to be redox
560 dependent, like Fe^{3+} (Dare et al., 2009). The diagram is principally for use with accessory Cr-
561 spinels and there are limitations in its application to Cr-spinels from podiform chromitite, because
562 of the important down-temperature control that host silicate plays in the chemical equilibration of
563 Cr-spinel that is reduced or absent in chromitite. However, our dataset includes measurements of
564 accessory dunite-hosted Cr-spinel from Poundland Burn (Samples BA-10-11, BA-10-12), that fall
565 within the 'peridotite field' of Dare et al. (2009) on the Cr# versus Mg# diagram (**Fig. 5a**), and it is
566 interesting to note that these spinels fall across the MOR- and SSZ-reacted field on the Ti/Fe^3#
567 versus Ga/Fe^3# diagram (**Fig. 9a**). The BOC chromitite analyses are included on the diagram for
568 reference, but as noted by Dare et al. (2009), the fields they fall in may or may not reflect the
569 petrogenetic conditions of formation. A field encompassing accessory Cr-spinels from the Lizard
570 Ophiolite is included on **Figure 9a**, and points to a MORB setting for their crystallisation, in line
571 with existing interpretations for that ophiolite (O'Driscoll et al., 2012b; Derbyshire, 2014).
572 The Cr-spinel crystal lattice can accommodate the substitution of cations (with different
573 valences and ionic radii) and cation vacancies in the T and M sites (Lavina et al., 2002; Lenaz et al.,
574 2004a, 2006; Juhin et al., 2007; Bosi et al., 2010; Fregola et al., 2011). Substitution of different
575 cations forces the Cr-spinel crystal lattice to deform to accommodate the new cation by lattice
576 relaxation and/or tilting of the cation sites (Juhin et al., 2007; Bosi et al., 2010; Hålenius et al.,
577 2011). The spinel structure is non-convergent, displaying no change to the lattice symmetry
578 between an ordered and disordered spinel (Harrison et al., 1999; Harrison and Putnis, 1999;
579 Andreozzi et al., 2000; Nestola et al., 2007). The strong preference of Cr^{3+} for the M site can restrict

580 the exchange of Mg and Al between the T and M sites (Lenaz et al., 2004b, 2010, 2012), resulting
581 in a more ordered spinel structure (degree of inversion (x): 0 for ordered spinel, x: 1 for disordered
582 spinel; Andreozzi et al., 2000; Nestola et al., 2007). Sack and Ghiorso (1991) showed that a
583 completely random cation distribution between the T and M sites has an inversion value 'x': 2/3.
584 The low inversion values determined for the BOC Cr-spinels (x: 0.14-0.21) using the Andreozzi et
585 al. (2000) equation shows that they have a largely ordered cation distribution. The presence of large
586 trivalent cations in the M site (e.g., Fe^{3+}, Cr^{3+}) modifies the octahedral angle and shared edge
587 resulting in a lengthening of the T-O bond (Lavina et al., 2002). Lenaz et al. (2012) suggested that if
588 the T-O bond is longer than the M-O bond, it indicates that a large cation is situated in the T site
589 (e.g. Fe^{2+}). Octahedral distortion in Cr-spinel structure can be determined using the Bosi et al.
590 (2010) equation: $<\lambda_M> = 1.741 – 1.301(M\text{-}O/T\text{-}O) + 0.571(M\text{-}O/T\text{-}O)^2$ with a non-distorted
591 octahedron having $<\lambda_M>$: 1. All of the BOC Cr-spinels display some distortion of the octahedron
592 ($<\lambda_M>$: 1.010-1.013), overlapping with other ophiolite Cr-spinels ($<\lambda_M>$: 1.010-1.012; Bosi et al.,
593 2004; **Fig. 8a**). The octahedral distortion in the Cr-spinel lattice directly affects the crystal stability
594 in relation to changing parental melt composition, temperature and pressure (Bosi *et al.*, 2010). The
595 Cr-spinel crystals from the Cr-rich Pinbain Bridge chromitites (Cr#: 0.62-0.65) have long cell edge
596 lengths (*Table 1*), T-O bonds longer than their M-O bonds, distortion of the octahedral site and
597 structural inversion (a_0: 8.2704-8.2740; T-O: 1.969-1.970; M-O: 1.964-1.9696; $<\lambda_M>$: 1.010-1.011;
598 x: 0.20-0.21) that is associated with a relatively ordered Cr-spinel structure resulting from the high
599 abundance of Cr^{3+} restricting cation exchange between the T and M sites. The Al-rich Poundland
600 Burn Cr-spinels (Cr#: 0.44-0.46) have shorter cell edge lengths, lower structural inversion and
601 comparable octahedral site distortion than the Pinbain Bridge Cr-spinels (a_0: 8.2204-8.528; x: 0.14-
602 0.18; $<\lambda_M>$: 1.012-1.013; *Table 1*). The T-O bond lengths in the Poundland Burn Cr-spinels
603 correspond with Mg^{2+} being ordered in the T site (T-O bond length for Mg^{2+}: 1.965 Å, T-O bond
604 length for Fe^{2+}: 1.997 Å; Lenaz et al., 2004a). The distortion to the octahedral site in the Poundland
605 Burn Cr-spinel crystals ($<\lambda_M>$: 1.012-1.013) may not result from distortion in the tetrahedral site

606 (Bosi et al., 2010), but may be attributed to varying the extent of Al^{3+} substitution for Cr^{3+} and Fe^{3+}
607 in the M site. Therefore, the structural differences between the Cr-spinels from each locality may be
608 a function of either compositional variation of the parental melt (controlling cation distribution by
609 the availability and preference of Cr^{3+} for the M site; Princivalle et al., 1989; Lenaz et al., 2004b,
610 2010, 2012), or the rate of cooling (slow cooling facilitates cation ordering between the T and M
611 sites; Princivalle et al., 1989; Uchida et al., 2005; Lenaz et al., 2012), or a combination of both
612 factors.
613 Crystal structural analysis of Cr-spinels can provide insights into their thermal history by
614 utilising *u* values, cation ordering and by determining intracrystalline closure temperatures
615 (Princivalle et al., 1999; Uchida et al., 2005; Lenaz et al., 2010; 2011; 2012). Intracrystalline
616 closure temperatures calculated for the BOC Cr-spinels plot away from values previously calculated
617 for Shetland Ophiolite Complex and Albanian Ophiolite Cr-spinels (Derbyshire et al., 2013 and
618 Bosi et al., 2004, respectively). The Cr-spinels from the Pinbain Bridge chromitites record closure
619 temperatures of 793-853°C. The Poundland Burn nodular-textured and anti-nodular-textured
620 chromitites reveal crystal closure temperatures of 623-708°C and 591°C, respectively. The
621 Poundland Burn massive-textured chromitite yields a closure temperature of 630°C, falling within
622 the nodular chromitite temperature range. Accessory Cr-spinel in dunite from Poundland Burn
623 yields the highest range of closure temperatures (724-789°C); this is considered to be the result of
624 secondary ordering and/or exchange of Al and Mg cations between Cr-spinel and other mineral
625 phases (e.g., olivine; Lenaz et al., 2011; 2012). Small *u* values (<0.2625), cation disorder between
626 the T and M sites and higher intracrystalline closure temperatures are considered to indicate rapid
627 cooling (Princivalle et al., 1989; Della Giusta et al., 1996; Lenaz et al., 2012). Crystal structural
628 analysis of the BOC chromitites shows that all display a limited range in *u* vales (0.2625-0.2634), a
629 relatively ordered structure (x: 0.14-0.21) and moderate intracrystalline closure temperatures (591-
630 853°C). The *u* parameter may also be controlled by changes in the bulk chemistry of the Cr-spinel
631 crystal (specifically Cr^{3+}; Lenaz et al., 2007, 2010, 2011). The consistent Cr content (0.81-0.86

apfu) over the restricted *u* value range (*u*: 0.2629-0.2634) of the Poundland Burn Cr-spinels indicates that changes in bulk composition have not affected the *u* parameter. Instead, the *u* values are considered to reflect the rapid cooling of the chromitites. The correlation between lowest *u* values and highest Cr content (*u*: 0.2526-0.2625; Cr#: 0.62-0.65; **Fig. 8,** *Table 1*) in the Pinbain Bridge Cr-spinels may result from changes to the bulk chemistry of the parental melt (increased Cr^{3+}) rather than from the rate of cooling.

We applied the algorithms of Rollinson (2008; adapted from Maurel and Maurel, 1982; Kamenetsky et al., 2001) to calculate the chromitite parental melt Al_2O_3 and TiO_2 compositions. For the Poundland Burn chromitites (that have relatively low Cr# values), the following expressions were applied:

$$Al_2O_3\text{-}melt = 7.1518 \times Al_2O_3\text{-}spinel^{0.2387}$$

$$TiO_2\text{-}melt = 1.5907 \times TiO_2 spinel^{0.6322}$$

For the Pinbain Bridge chromitites, of likely arc affinity, the following equations were used:

$$Al_2O_3\text{-}melt = 5.2181 \times ln(Al_2O_3\text{-}spinel) - 1.0505$$

$$TiO_2\text{-}melt = 1.0963 \times TiO_2 spinel^{0.7863}$$

The calculations were only carried out for fresh Cr-spinel cores analysed from each of the BOC chromitite localities, and reveal evidence of two compositionally distinct parental melts (**Fig. 9b**). The Pinbain Bridge parental melt is calculated to have had 13-14 wt. % Al_2O_3 and low TiO_2 contents (~0.2 wt. %), a composition similar to that of a boninitic melt (10.0-14.4 wt. % Al_2O_3; Maurel and Maurel, 1982; Kamenetsky et al., 2001; Pagé and Barnes, 2009; Uysal et al., 2009; Derbyshire et al., 2013). The Poundland Burn chromitites (including nodular-textured chromitite) yield higher Al_2O_3 (16-17 wt. %) and TiO_2 contents (0.55-0.75 wt. %) than the Pinbain Bridge chromitites indicating a MORB-like parental melt (MORB-like melt: >16 wt. % Al_2O_3). The calculations suggest the parental melts of the accessory Cr-spinels from the Poundland Burn dunites contained 15-16 wt. % Al_2O_3 and 0.3-0.5 wt. % TiO_2. Overall, the Poundland Burn chromitite and Cr-spinel bearing dunite parental melts plot within the MORB field whereas the Pinbain Bridge

chromitite parental melts fall between the SSZ and MORB fields, suggesting formation of the latter by slightly lower degrees of partial melting than required for melts in the arc field. The presence of rare I-PGE grains (laurite [RuS_2], erlichmannite [OsS_2], irarsite [IrAsS] and Ir-Os-Ru alloys; Power and Pirrie, 2004) in the Pinbain Bridge chromitites and the apparent absence of PGM in the Poundland Burn chromitites provides supporting evidence for higher degrees of partial mantle melting reflected in the Pinbain Bridge Cr-spinel chemical compositions (cf. Prichard et al., 1996; Melcher et al., 1997; Ahmed and Arai, 2002; Büchl et al., 2004; González-Jiménez et al., 2011).

6.3 Insights into the formation and tectonic setting of the BOC

The tectonic provenance of the BOC has been the subject of protracted debate (e.g., Wilkinson and Cann, 1974; Jones, 1977; Lewis and Bloxam, 1977; Thirlwall and Bluck, 1984; Stone and Smellie, 1988; Smellie and Stone, 1992, 2001; Smellie et al., 1995; Oliver and McAlpine, 1998; Stone, 2014). There are multiple reasons for this, amongst the most important are the lack of good inland exposure, the structurally fragmented nature of the complex and the contrasting trace element chemistry from the different basalt lava sequences. The BOC basalt lavas have trace element compositions ranging from MORB-like (LREE-depleted; Central Balcreuchan Group 3) to island arc tholeiite-like (LREE-enriched with a negative Nb + Ta anomaly; Central Balcreuchan Group 2, Southern Balcreuchan Group 1, Southern Balcreuchan Group 2), with two further lava blocks interpreted as exhibiting ‘within-plate’ signatures (LREE-enriched with high REE concentrations; Northern Balcreuchan Group and Central Balcreuchan Group 1) (Wilkinson and Cann, 1974; Jones, 1977; Thirlwall and Bluck, 1984; Smellie and Stone, 2001). In addition, boninite signatures have been documented from the Games Loup lava sequence (Stone, 2014). Previously proposed tectonic settings for the BOC have therefore included within-plate (mantle plume-related; Wilkinson and Cann, 1974), a mid-ocean ridge (Jones, 1977) and an island arc associated with a back-arc basin (Bluck et al., 1980; Thirlwall and Bluck, 1984; Smellie and Stone, 1992, 2001; Smellie et al., 1995; Oliver and McAlpine, 1998; Armstrong et al., 1999). There has been a broad general consensus

amongst many previous studies that the compositional disparity between the different lava blocks and gabbro units, the presence of arc-derived sediments situated beneath the lavas near Pinbain Hill (Smellie and Stone, 1992; Armstrong et al., 1999) and the MORB-like chemistry of the sheeted dyke complex (Oliver and McAlpine, 1998) point to an island arc setting with an associated back-arc basin prior to obduction of the BOC onto the Laurentian margin (Bluck et al., 1980; Thirlwall and Bluck, 1984; Smellie and Stone, 1992, 2001; Oliver and McAlpine, 1998; Armstrong et al., 1999). The formation of the back-arc basin supposedly resulted from the rifting of the Grampian arc, with the ophiolite representing the oceanward portion of the rifted arc and the back-arc basin (cf. Smellie and Stone, 1992, 2001). However, other workers have suggested alternating obduction/accretion events with basin filling and volcanism (Bluck, 1990; 2002).

The mantle portions of the BOC, as represented by the northern and southern serpentinite belts, are lithologically and chemically distinct from one another and therefore also contribute to the difficulty in invoking a single tectonic environment of formation for the BOC. The northern serpentinite contains a lithological assemblage and other characteristics consistent with it representing more depleted oceanic mantle than that preserved in the southern serpentinite belt (Stone, 2014). The Cr-spinel data reported here serve to further highlight the distinction between the two serpentinite belts. Indeed, the Cr# of chromitite Cr-spinel can be used to estimate the degree of partial mantle melting in each serpentinite (after Hellebrand et al., 2001; Chapter 2). The relationship put forward in Hellebrand et al. (2001) is:

$$F = 10\ln(Cr\#) + 24$$

where F is the degree of partial mantle melting. The equation is derived from the correlation of HREE (specifically Dy, Er and Yb) in clinopyroxene with the Cr# of Cr-spinel and is calibrated for Cr-spinels with Cr#: 0.10-0.60, a range which covers the majority of abyssal Cr-spinel compositions. Voigt and von der Handt (2011) determined that for Cr-spinels with Cr#: >0.60, the equation underestimates the degree of mantle partial melting. The Poundland Burn chromitites and Cr-spinel-bearing dunites yield a range of F of 14-16% partial melting, with the dunites consistently

giving 1% higher (~16%) degrees of partial melting than the chromitites (14-15%). The Pinbain Bridge chromitites reveal values in the range 19-20% but as noted above this is likely to be an underestimate as these Cr-spinels have typical Cr# values in the range 0.62-0.65. Notwithstanding this uncertainty, the comparatively lower degree of partial melting calculated from the Poundland Burn chromitites lends support to the notion that these formed in less refractory mantle than the Pinbain Bridge chromitites.

Broadly speaking, the presence of the bimodal chromitite compositions in the BOC permits at least two models for their formation. The first is a two-stage melting process that requires processing of the BOC mantle in different tectonic settings (i.e., MOR and SSZ; cf., Melcher et al., 1997; Ahmed and Arai, 2002; Uysal et al., 2009). The second explanation envisages all of the melt percolation occurring above (or associated with) a developing subduction zone. In the latter case, it is possible that low Cr# chromitite could develop with incipient fore-arc (low degree) partial melting, with progression to higher Cr# chromitite as hydrous fluxing of the mantle wedge developed properly, analogous to the 'subduction initiation' geochemical evolution of ophiolite lava sequences proposed by Whattam and Stern (2011). Another option is that the low Cr# chromitite reflects melt percolation in the mantle below a back-arc spreading centre, simulating MORB-like melt depletion, which would necessarily be coeval with or postdate the high Cr# chromitite formation. Although imprecise, the chronological information available for the BOC points to the latter as being the more likely scenario. This is because the available geochronology (see Stone 2014 for a summary) points to a significant temporal overlap between the arc and 'within-plate' lava sequences in the BOC. Whether fore-arc or back-arc, the characteristics of the Poundland Burn peridotite Cr-spinels on the Ti/Fe^{3}# versus Ga/Fe^{3}# diagram of Dare et al. (2009; **Fig. 9a**) also support a subduction-related environment of formation for the dunite (and therefore the chromitite) channels, rather than a MORB setting.

One of the lines of support for melt generation in a back-arc setting comes from the presence of LREE-enriched lavas with high Zr/Nb, low Zr/Y ratios and high REE concentrations (Northern

736 Balcreuchan Group at Pinbain, Slockenray, Brandy Craig and the Central Balcreuchan Group at
737 Bennane Head). The Northern Balcreuchan Group and Central Balcreuchan Group 1 lavas display
738 enrichment in the HFSE and REE and do not exhibit a negative Nb + Ta anomaly (Thirlwall and
739 Bluck, 1984; Smellie and Stone, 2001). Interestingly, the apparent absence of a Nb depletion
740 signature in some arc lavas and tuffs from the Aeolian arc (southern Italy), the Aegean arc (Greece)
741 and in western Ireland as observed, for example, by Clift and Blusztajn (1999) and Draut and Clift
742 (2001), has been attributed to the slowing and termination of subduction. The LREE-enriched
743 Northern Balcreuchan Group and Central Balcreuchan Group 1 lavas might therefore represent late-
744 stage melts formed during the slowing and eventual termination of the southward subduction before
745 the subduction polarity reversal after the accretion of the Grampian arc (Dewey and Ryan, 1990;
746 Ryan and Dewey, 1991; Oliver et al., 2002; Strachan et al., 2002; Dewey, 2005; MacDonald and
747 Fettes, 2006). The slowing of subduction would restrict the amount of fluid available for fluxing the
748 mantle wedge thus lowering the degree of partial melting. The resulting melt would be enriched in
749 LILE, HFSE and LREE, but would also generate chromitite with lower Cr#, offering a plausible
750 scenario for the petrogenesis of the Poundland Burn chromitites forming in the mantle beneath a
751 back-arc spreading centre.
752
753 **7. Summary and Conclusions**
754 Although obscured to a degree by late-stage faulting and secondary alteration (serpentinisation), the
755 Ballantrae Ophiolite Complex preserves evidence for melt extraction and percolation in a SSZ
756 environment. The Pinbain Bridge and Poundland Burn chromitites formed by melt-rock reaction in
757 channel-like conduits in the upper mantle. Although the formation of nodular-textured chromitite in
758 ophiolitic mantle is generally not well understood (Arai and Miura, 2016), the BOC examples have
759 textural and lithological similarities to those reported from other ophiolites (including Oman and
760 Troodos). This suggests a common mechanism of formation and, looking forward, new constraints
761 on their petrogenesis may result from the application of the X-ray microtomography technique of
762 Prichard et al. (2015) to test for an origin by *in situ* crystallisation. The petrological differences

previously documented between the northern and southern serpentinite limbs of the BOC are reflected in the chemical compositions of chromitite Cr-spinel from each.

The presence of high-Cr# (Pinbain Bridge) and low Cr# (Poundland Burn) chromitites suggests that either the Ballantrae mantle section preserves evidence for melt extraction at both a MOR and in a SSZ setting, or the contrasting chromitite compositions reflect progressice changes in the compositions of the parental melts (and hence the style of melt extraction) in a complex subduction zone setting. Our combined datasets and observations suggest that the latter scenario is more likely, and the trace element characteristics of accessory Cr-spinel formed in dunite at Poundland Burn (i.e., illustrated in **Fig. 9a**) serve to support this inference. Given the diversity of basalt compositions associated with the BOC (cf. Stone, 2014), the contrasting signatures preserved in the chromitites provide a useful dimension to aiding interpretation of the environment of formation of the ophiolite, as well as highlighting more generally the utility of mantle-hosted chromitites as for finger-printing melt percolation and melt-rock reaction.

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Figure Captions

Figure 1. Geological sketch map of the Ballantrae Ophiolite Complex, Scotland, showing the major lithological units and the locations of the Pinbain Bridge and Poundland Burn chromitite bodies. The sketch map is adapted from those in Stone (2014). The inset is a regional map of Scotland showing the regional location of the BOC in Ayrshire (red square).

Figure 2. (a) Field photograph illustrating typical harzburgite texture at Pinbain Bridge. (b) Nodular chromitite at Poundland Burn; the nodules are up to 1 cm in diameter and are hosted in a serpentinised dunite matrix. (c) Anti-nodular chromitite in close proximity to (b). The silicate nodules comprise serpentinite and are <1 cm in size, with a groundmass network of fine-grained Cr-spinel crystals. Pen-tip is shown for scale in (a) – (c).

Figure 3. (a-b) Backscattered electron micrographs of chromitite textures from Pinbain Bridge. Note the thin discontinuous Fe-rich (bright) rim on the grey Cr-spinel crystal in (a) and the fracture and associated brittle deformation in chromitite in (b). In (a) and (b), the black-coloured groundmass is predominantly serpentinite. (c) Thin section scan of BA-10-06 nodular-textured chromitite. The cuspate-shaped areas infilled with silicate in nodule centres (located within the red outline in one nodule) and relatively massive outer nodule mantles are described in the text. (d) Plane polarised light photomicrograph of orthopyroxene pseudomorph in a serpentinised harzburgite from Poundland Burn, in which bastite is partly replacing orthopyroxene. (e) Plane polarised light photomicrograph of Poundland Burn dunite – note the elongate stringer of Cr-spinel crystals (black) in the bottom-right of the image, as well as other isolated Cr-spinel crystals elsewhere in the serpentinised olivine groundmass. (f) Backscattered electron micrograph of accessory Cr-spinel from Poundland Burn dunite, with relatively thick Fe-rich rim and abundant silicate inclusions.

Figure 4. Panels illustrate the internal structure and chemical composition of a single Cr-spinel nodule from Poundland Burn (Sample BA-10-06). (a) Thin section scan showing the location (red square) of the nodule featured in (b) and (c). (b) Mineral chemical transect of the nodule, showing the relative homogeneity in Mg#, Cr# and TiO_2 from one side to the other. The transect represents 40 individual spot points, from X-Y, taken at equal spacings apart on the traverse shown in (c), but avoiding inclusions and fractures. (c) Stitched backscattered electron micrographs, showing the internal structure of an individual nodule and the position of the electron microprobe traverse shown in (b).

Figure 5. Plots of (a) Cr# versus Mg# and (b) TiO_2 versus Cr# discriminate the tectonic setting (and parental melt composition) of the Ballantrae Cr-spinels. In (a), the two solid black outline ellipses delineate the range of Pinbain Bridge and Poundland Burn chromitite compositions. The fields for boninite and abyssal peridotite are taken from Dick and Bullen (1984) and Kepezhinskas et al. (1993). The green field is the range of peridotite accessory Cr-spinel compositions referred to in Dare et al. (2009); it is important to note that the Ballantrae chromitite Cr-spinels fall outside of the outer limits of this field. In (b), the fields for MORB/boninite and layered intrusions, ophiolites and komatiites, come from Hunt et al. (2012) and references therein.

Figure 6. Trace element characteristics of the Ballantrae Cr-spinels. (a) V versus Cr#, (b) Co versus Cr#, (c) Ga versus Cr# and (d) Cu/Zn versus Cu/Ni. The symbols are the same as in **Figure 5**. Ranges of trace element compositions for the Lizard, Shetland and Corrycharmaig are shown for comparison (B O'Driscoll; unpublished data). The MORB and two boninite compositions come from Pagé and Barnes (2009). The symbols are the same as for **Figure 5**, unless otherwise specified. In (d), the R^2 values were calculated by least squares regression in Microsoft Excel.

Figure 7. Spidergram showing the major and trace element characteristics of the Ballantrae Cr-spinels, relative to two boninite compositions, and normalised to MORB. The boninite and MORB compositions are taken from Pagé and Barnes (2009). Abbreviations as follows: TMO, Thetford Mines Ophiolite; EPR, East Pacific Rise. See text for further discussion.

Figure 8. (a) Crystal structural analysis plot displaying cell edge length (a_0) against oxygen positional parameter (*u*). The majority of the Ballantrae Cr-spinels have low a_0 and higher *u* values than the Shetland Ophiolite Complex Cr-spinels (orange field) from Derbyshire et al. (2013). (b) Cr-spinel crystal structural plot displaying Cr# versus oxygen positional parameter (*u*). The Pinbain Bridge Cr-spinels have higher Cr contents and correspondingly smaller *u* values whilst the Poundland Burn Cr-spinels display relatively consistent Cr contents across a small range in *u* (0.2629-0.2634). The symbols are the same as for **Figure 5**, unless otherwise specified.

Figure 9. (a) The Ti/Fe^{3}# versus Ga/Fe^{3}# diagram of Dare et al. (2009), illustrating that the Ballantrae Cr-spinels, in particular those from the Poundland Burn dunites, have compositions spanning the boundary between MOR-reacted and SSZ-reacted compositions (though mainly in the latter). Chromitite compositions are plotted too for reference but these are probably unreliable for the reasons outlined in Dare et al. (2009). The ranges of compositions of Shetland, Lizard and Corrycharmaig Cr-spinels are also shown for comparison, and it is notable that the Lizard Cr-spinels in particular, which are an accessory phase in dunite, plot in the MOR-reacted field, consistent with published interpretations of the Lizard as a MORB-type ophiolite (O'Driscoll et al. 2012b). (b) Calculated TiO_2 versus Al_2O_3 for the Ballantrae Cr-spinel parental melts. See text for further discussion. The values for MORB and boninite, as well as the various boninite fields, come from Pagé and Barnes (2009). The grey-shaded boninite and MORB fields come from Rollinson (2008). The symbols are the same as for **Figure 5**, unless otherwise specified.

Sample	BA-10-03	BA-10-04	BA-10-06	BA-10-07	BA-10-10	BA-10-11	BA-10-12	BA-10-13
a_0	8.27043 (9)	8.2740 (4)	8.2206 (3)	8.2204 (3)	8.2205 (1)	8.2456 (4)	8.2528 (3)	8.2285 (5)
u	0.2625 (1)	0.2627 (1)	0.2630 (1)	0.2630 (1)	0.2631 (1)	0.2631 (1)	0.2629 (1)	0.2634 (2)
MgO	14.5 (2)	15.2 (2)	16.8 (3)	16.8 (3)	16.7 (2)	13.5 (3)	13.3 (2)	15.6 (3)
Al_2O_3	18.3 (2)	19.9 (4)	30.9 (4)	30.9 (2)	30.7 (4)	27.0 (5)	26.3 (5)	29.0 (1)
TiO_2	0.12 (2)	0.11 (1)	0.26 (1)	0.24 (2)	0.28 (2)	0.25 (2)	0.26 (2)	0.24 (2)
Cr_2O_3	50.4 (2)	49.3 (3)	37.4 (3)	37.5 (4)	37.6 (3)	34.3 (4)	33.7 (6)	36.8 (5)
MnO	0.21 (3)	0.21 (4)	0.18 (3)	0.18 (3)	0.19 (3)	0.25 (2)	0.24 (3)	0.19 (3)
FeO_{tot}	16.1 (2)	14.8 (1)	14.0 (2)	13.9 (2)	14.2 (1)	23.5 (7)	25.1 (4)	17.4 (2)
NiO	0.10 (3)	0.17 (4)	0.20 (1)	0.18 (4)	0.18 (4)	0.20 (3)	0.24 (2)	0.18 (3)
ZnO*	0.07 (2)		0.07 (2)		0.05 (2)	0.14 (3)	0.17 (3)	
Sum	99.84	99.74	99.84	99.65	99.88	99.25	99.27	99.41
FeO	12.6 (2)	11.6 (1)	11.0 (2)	11.1 (2)	11.3 (1)	15.2 (7)	15.4 (4)	12.6 (2)
Fe_2O_3	3.96	3.61	3.33	3.13	3.21	9.25	10.8	5.36
Sum	100.24	100.10	100.17	99.96	100.20	100.18	100.35	99.95
T site								
Mg	0.639 (7)	0.672 (8)	0.683 (9)	0.66 (1)	0.663 (8)	0.55 (1)	0.540 (9)	0.639 (9)
Al	0.027 (1)	0.026 (2)	0.029 (2)	0.042 (2)	0.028 (2)	0.025 (2)	0.032 (2)	0.015 (1)
Mn	0.006 (1)	0.006 (1)	0.004 (1)	0.004 (1)	0.005 (1)	0.006 (1)	0.006 (1)	0.005 (1)
Fe^{2+}	0.295 (4)	0.297 (4)	0.242 (4)	0.263 (5)	0.267 (4)	0.38 (1)	0.379 (9)	0.311 (5)
Fe^{3+}	0.032 (4)		0.040 (6)	0.034 (7)	0.036 (5)	0.040 (7)	0.040 (4)	0.030 (4)
Zn	0.002 (1)		0.002 (1)		0.001 (1)	0.003 (1)	0.004 (1)	
M site								
Mg	0.028 (2)	0.027 (2)	0.044 (2)	0.070 (4)	0.058 (2)	0.057 (4)	0.059 (3)	0.042 (2)
Al	0.643 (6)	0.68 (1)	1.03 (1)	1.020 (8)	1.030 (9)	0.94 (1)	0.91 (1)	0.998 (7)
Ti	0.003 (1)	0.003 (1)	0.006 (1)	0.005 (1)	0.006 (1)	0.006 (1)	0.006 (1)	0.005 (1)
Cr	1.234 (6)	1.195 (9)	0.858 (8)	0.862 (9)	0.861 (7)	0.81 (1)	0.81 (1)	0.861 (9)
Fe^{2+}	0.028 (1)	0.002 (1)	0.024 (1)	0.006 (1)	0.007 (1)	0.007 (2)	0.013 (2)	
Fe^{3+}	0.061 (5)	0.086 (8)	0.031 (6)	0.033 (7)	0.034 (5)	0.17 (1)	0.20 (1)	0.089 (7)
Ni	0.003 (1)	0.004 (1)	0.005 (1)	0.004 (1)	0.004 (1)	0.005 (1)	0.006 (1)	0.004 (1)
F(X)	0.23	0.27	0.09	0.05	0.14	0.21	0.05	0.20
T°C	853	793	623	708	630	724	789	591

Table 1. Cell parameters, chemical analyses and cation distribution of Cr-spinels analysed by X-ray single crystal diffraction. Mean chemical analyses (up to 15 spot analyses for each crystal) and cation distribution in T and M site of the analyzed Cr-spinels on the basis of four oxygen atoms per formula unit. Fe^{3+} from stoichiometry. a_0: cell parameter (Å); *u*: oxygen positional parameter;. F(x): minimization factor, which takes into account the mean of square differences between calculated and observed parameters, divided by their standard deviations. Estimated standard deviations are in brackets. Intracrystalline closure temperature calculated by using the Princivalle et al (1999) thermometer. *Zinc distribution is not reported when the standard deviation on chemistry is higher than the half of the mean value.

Figure 1

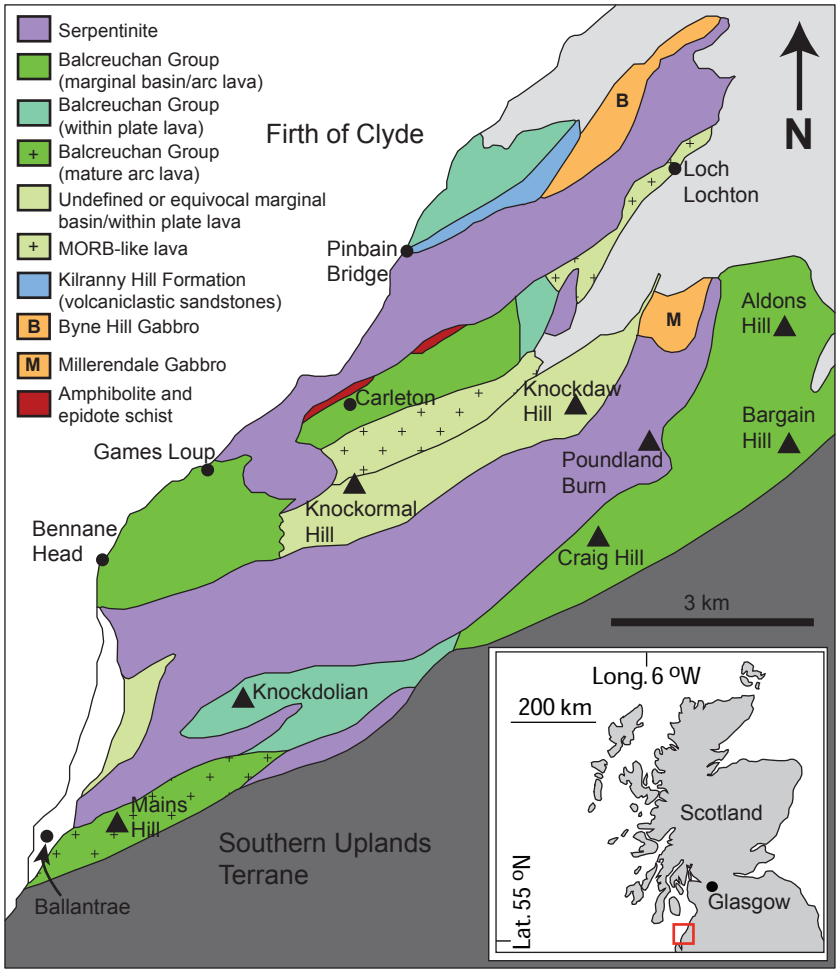

Serpentinite
Balcreuchan Group (marginal basin/arc lava)
Balcreuchan Group (within plate lava)
Balcreuchan Group (mature arc lava)
Undefined or equivocal marginal basin/within plate lava
MORB-like lava
Kilranny Hill Formation (volcaniclastic sandstones)
Byne Hill Gabbro
Millerendale Gabbro
Amphibolite and epidote schist
Firth of Clyde
N
B
M
Loch Lochton
Pinbain Bridge
Aldons Hill
Carleton
Knockdaw Hill
Bargain Hill
Games Loup
Poundland Burn
Knockormal Hill
Bennane Head
Craig Hill
3 km
Knockdolian
Mains Hill
Southern Uplands Terrane
Ballantrae
Long. 6 °W
200 km
Scotland
Lat. 55 °N
Glasgow

Figure 2

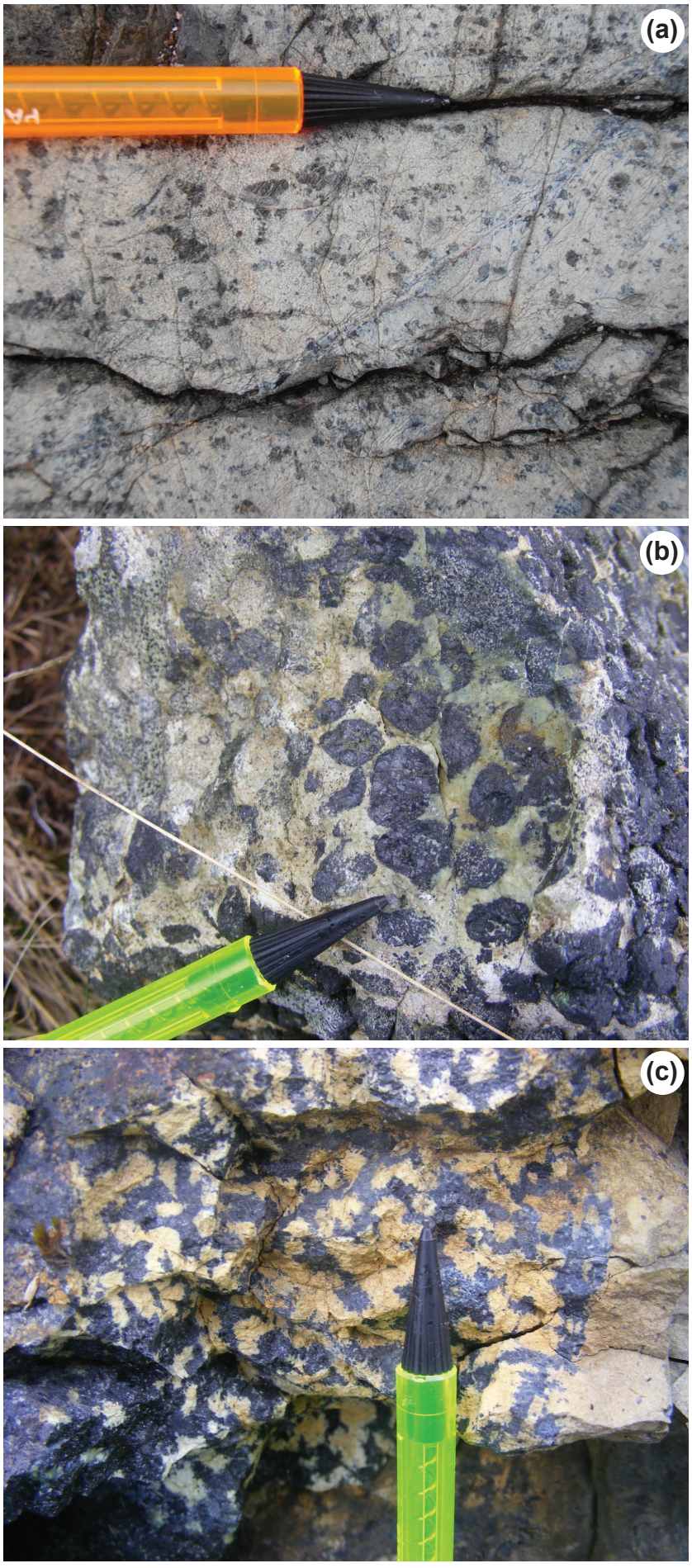


Figure 3

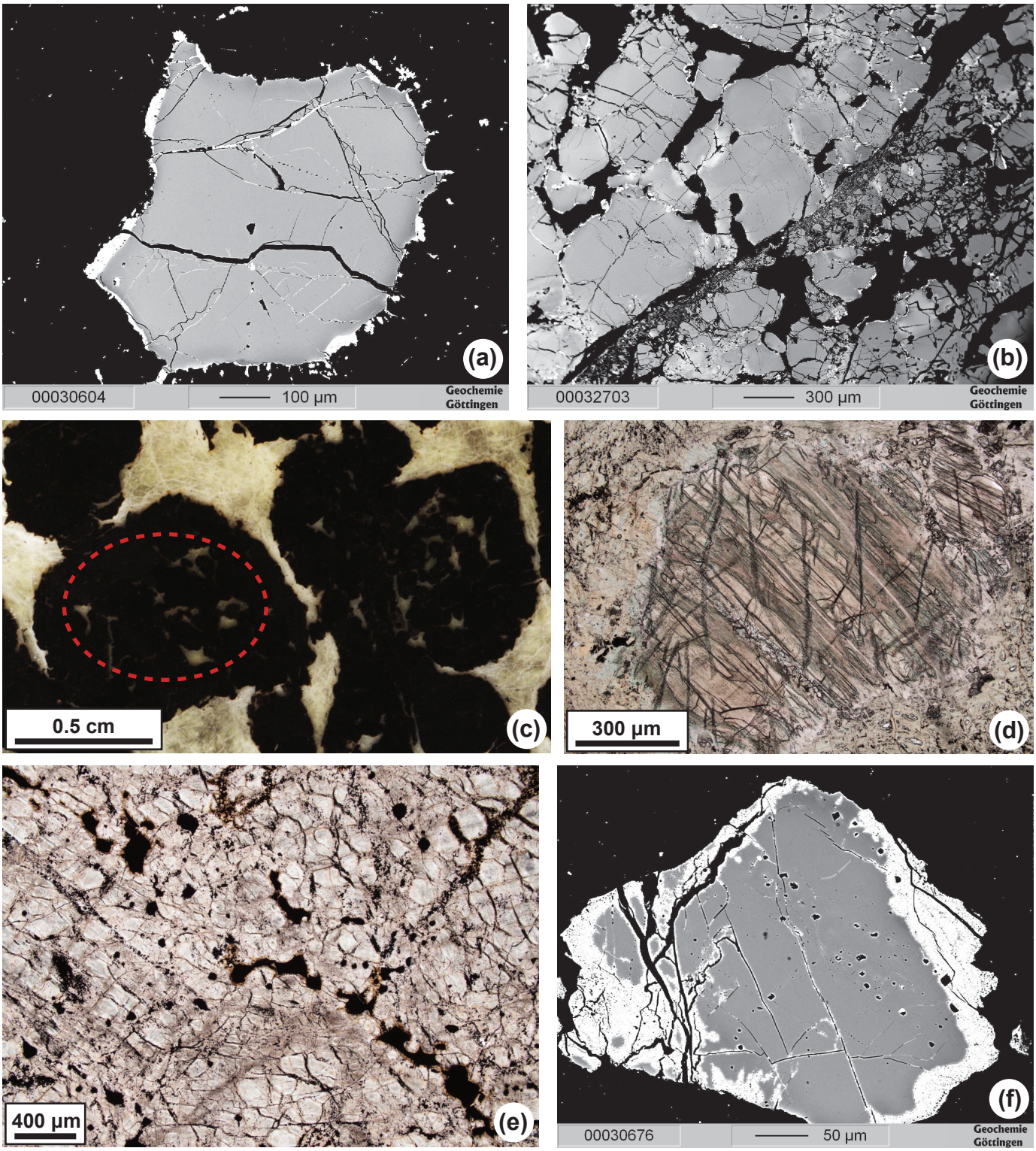
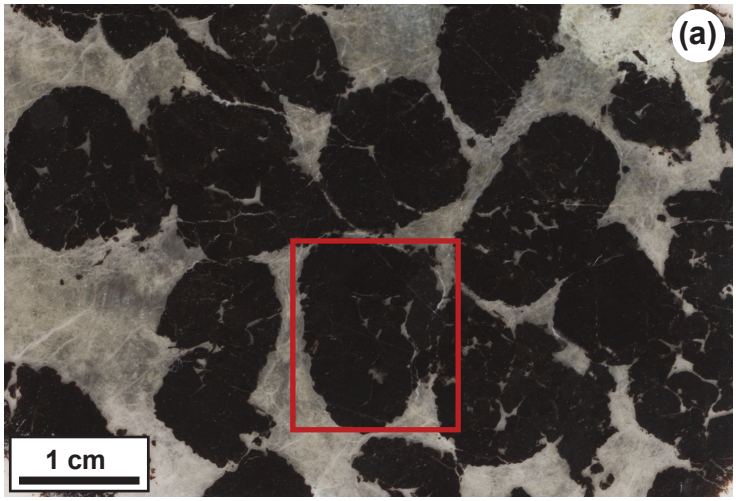
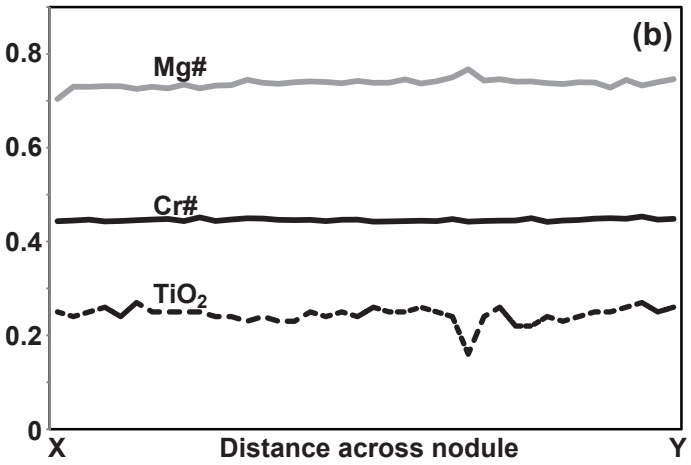

(a)
00030604
100 µm
Geochemie Göttingen
(b)
00032703
300 µm
Geochemie Göttingen
0.5 cm
(c)
300 µm
(d)
400 µm
(e)
(f)
00030676
50 µm
Geochemie Göttingen

Figure 4


(a)
1 cm


(b)
0.8
0.6
0.4
0.2
0
Mg#
Cr#
TiO2
X
Distance across nodule
Y

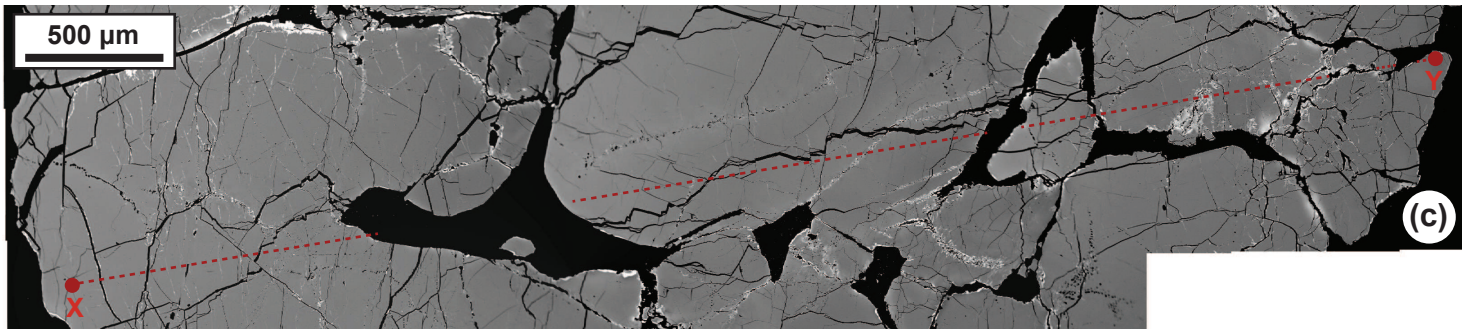

500 µm
X
Y
(c)

Figure 5

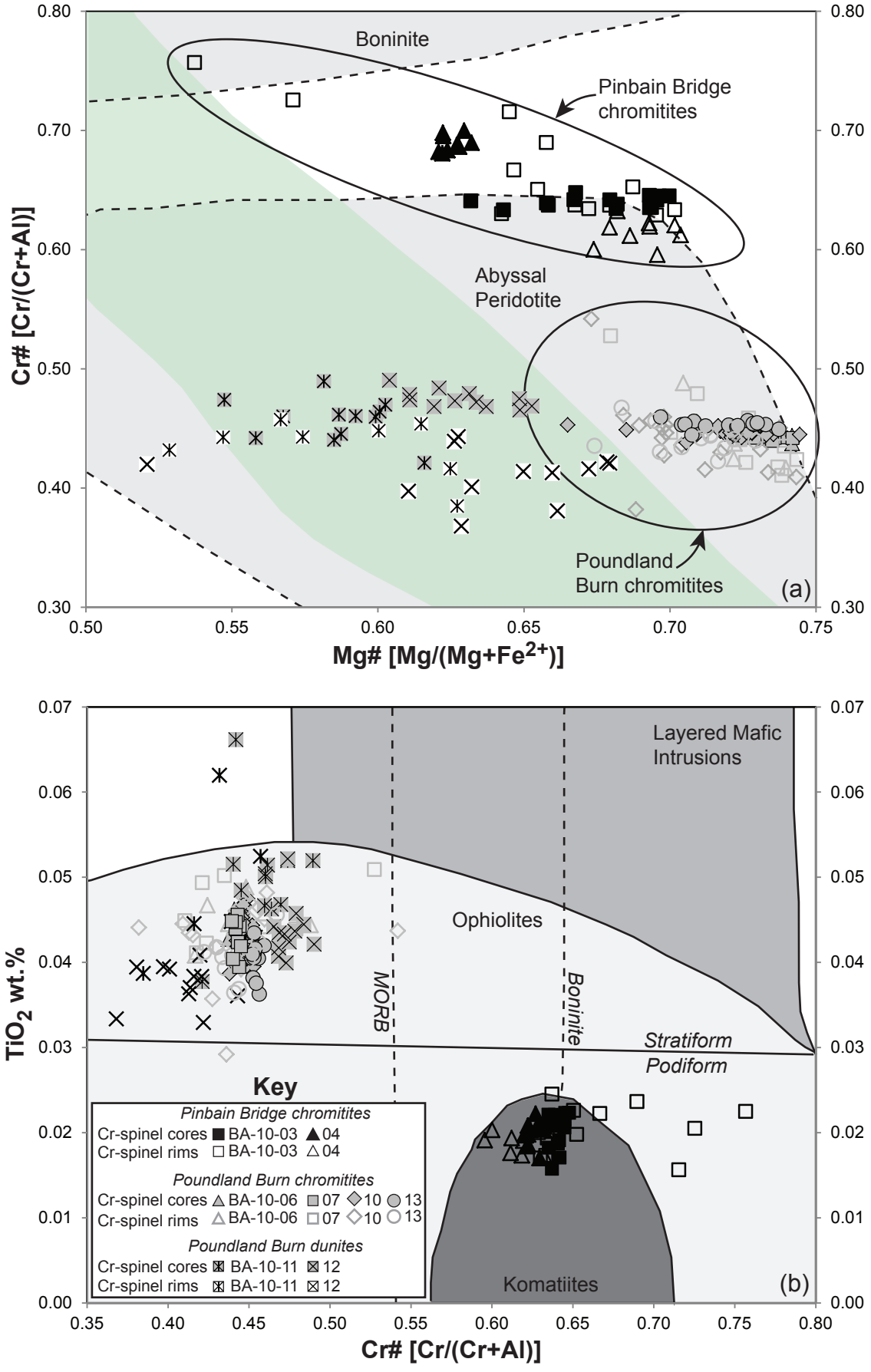

Boninite
Pinbain Bridge chromitites
Abyssal Peridotite
Poundland Burn chromitites
(a)
Cr# [Cr/(Cr+Al)]
Mg# [Mg/(Mg+Fe2+)]
Layered Mafic Intrusions
Ophiolites
MORB
Boninite
Stratiform
Podiform
Komatiites
(b)
TiO2 wt.%
Cr# [Cr/(Cr+Al)]
Key
Pinbain Bridge chromitites
Cr-spinel cores ■ BA-10-03 ▲ 04
Cr-spinel rims □ BA-10-03 △ 04
Poundland Burn chromitites
Cr-spinel cores △ BA-10-06 ▩ 07 ◇ 10 ◯ 13
Cr-spinel rims △ BA-10-06 □ 07 ◇ 10 ◯ 13
Poundland Burn dunites
Cr-spinel cores ⊠ BA-10-11 ⊠ 12
Cr-spinel rims ⊠ BA-10-11 ⊠ 12

Figure 6

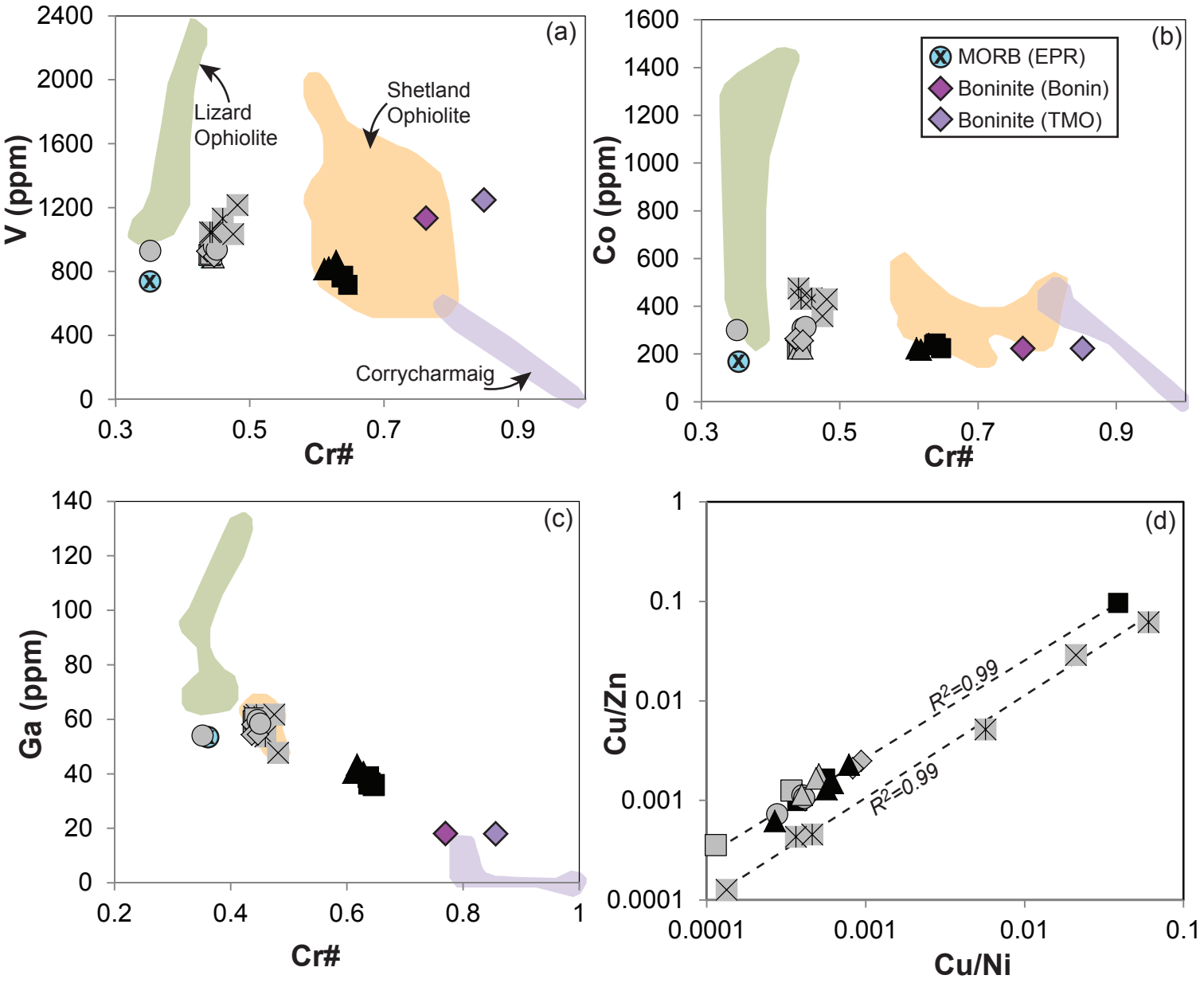

(a)
V (ppm)
Cr#
Lizard Ophiolite
Shetland Ophiolite
Corrycharmaig
(b)
Co (ppm)
Cr#
MORB (EPR)
Boninite (Bonin)
Boninite (TMO)
(c)
Ga (ppm)
Cr#
(d)
Cu/Zn
Cu/Ni
R²=0.99
R²=0.99

Figure 7

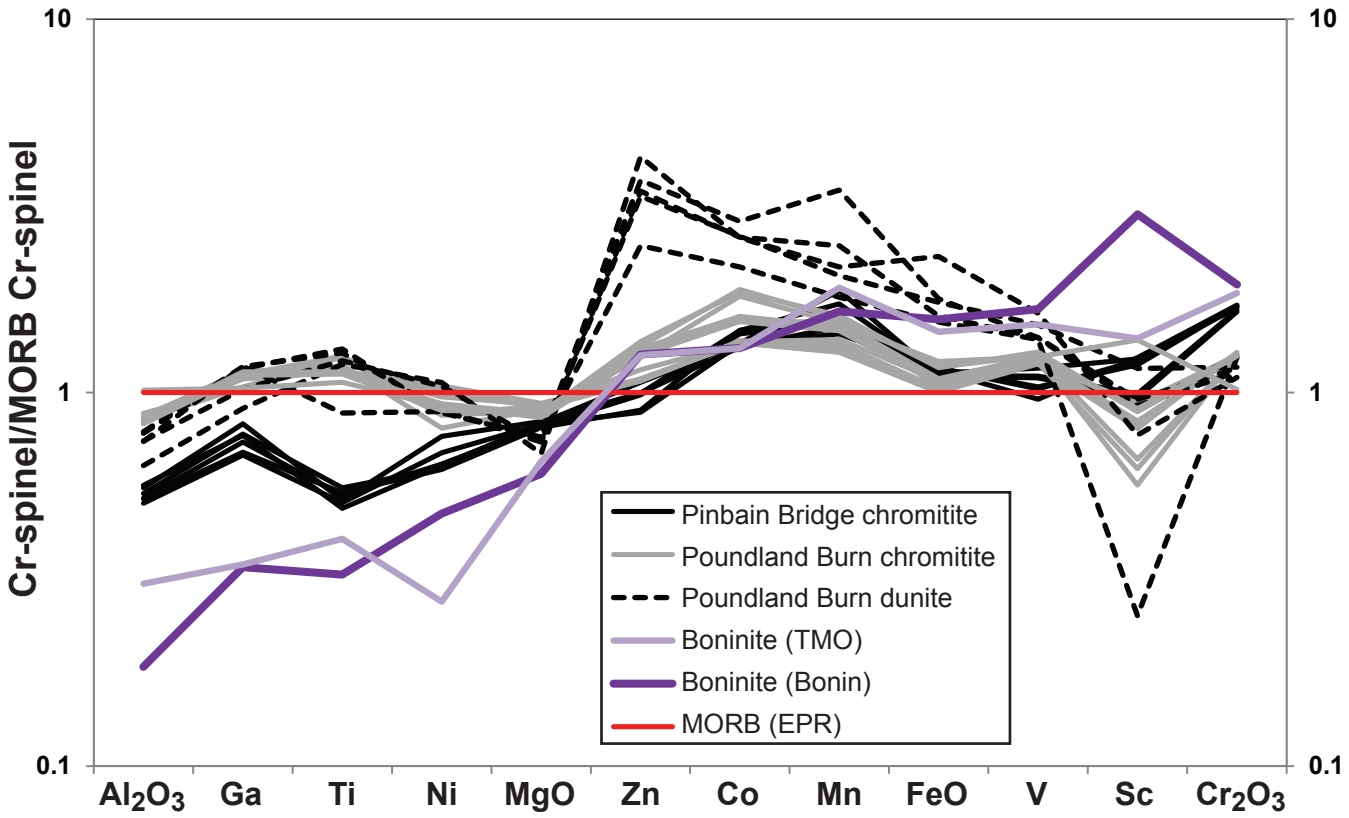

10
1
0.1
Cr-spinel/MORB Cr-spinel
Al2O3
Ga
Ti
Ni
MgO
Zn
Co
Mn
FeO
V
Sc
Cr2O3
Pinbain Bridge chromitite
Poundland Burn chromitite
Poundland Burn dunite
Boninite (TMO)
Boninite (Bonin)
MORB (EPR)

Figure 8

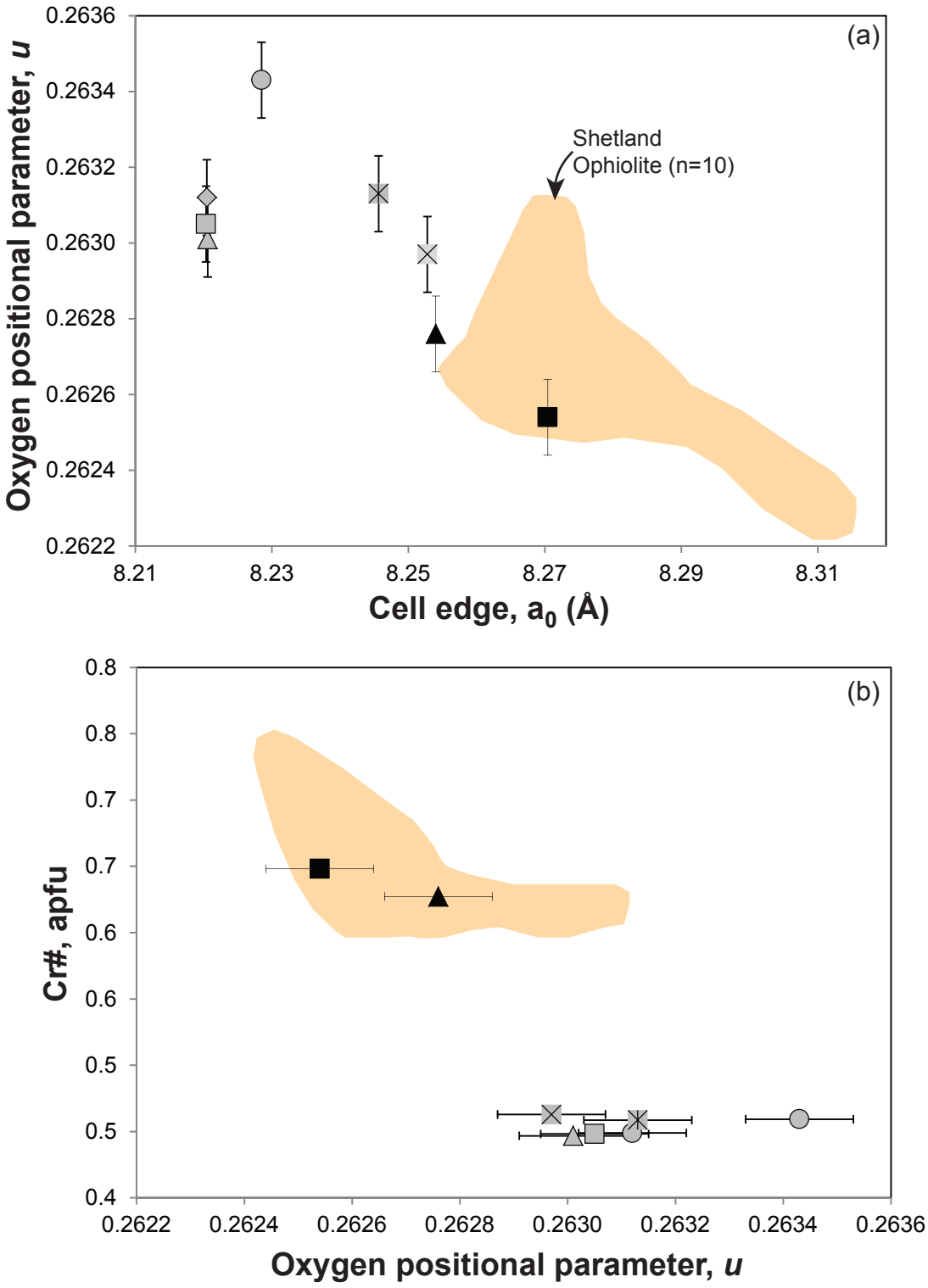
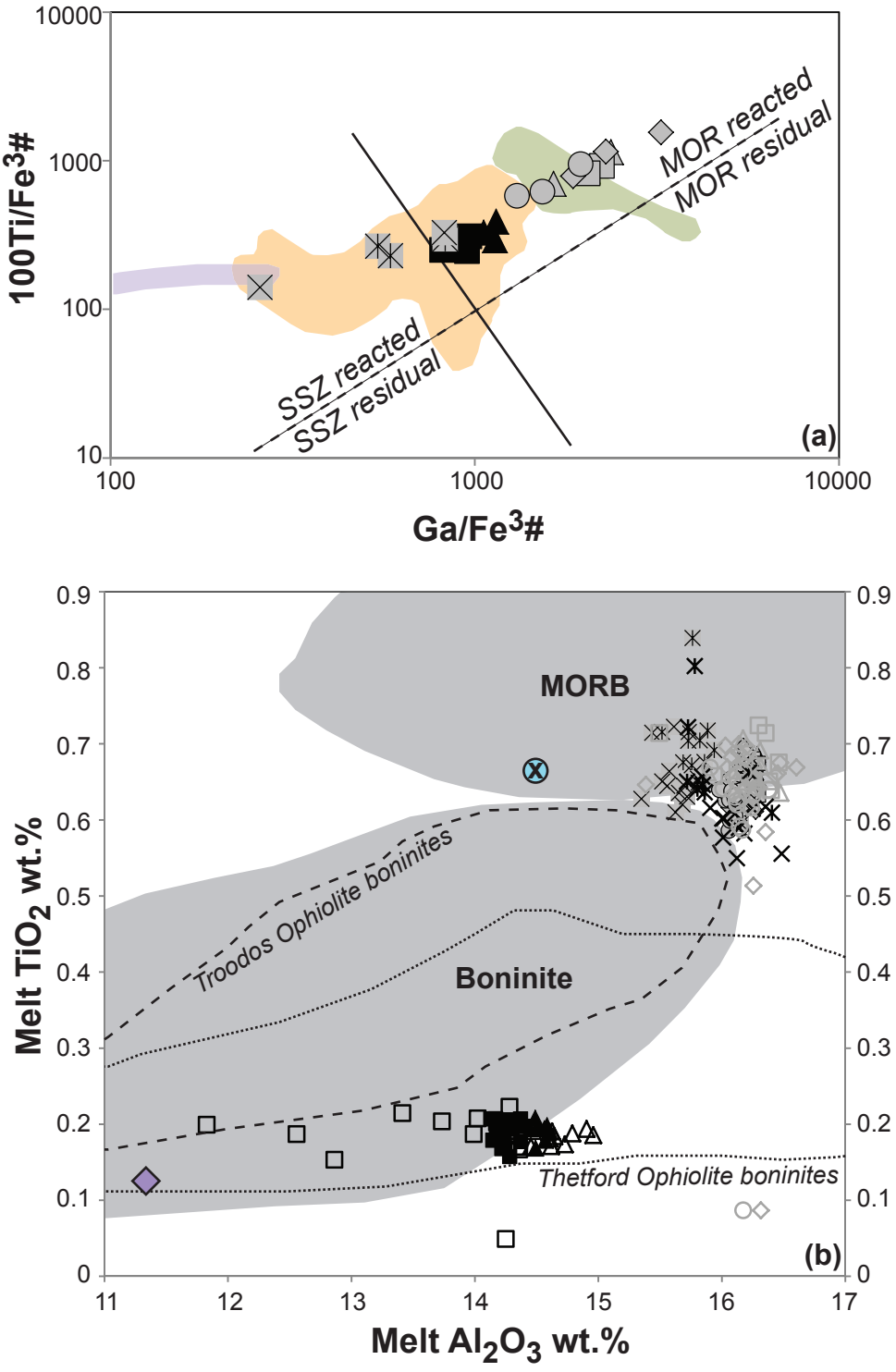

(a)
Shetland
Ophiolite (n=10)
Oxygen positional parameter, u
Cell edge, a0 (Å)
0.2636
0.2634
0.2632
0.2630
0.2628
0.2626
0.2624
0.2622
8.21
8.23
8.25
8.27
8.29
8.31
(b)
Cr#, apfu
Oxygen positional parameter, u
0.8
0.8
0.7
0.7
0.6
0.6
0.5
0.5
0.4
0.2622
0.2624
0.2626
0.2628
0.2630
0.2632
0.2634
0.2636

Figure 9


10000
1000
100
10
100Ti/Fe3#
100
1000
10000
Ga/Fe3#
MOR reacted
MOR residual
SSZ reacted
SSZ residual
(a)
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Melt TiO2 wt.%
MORB
Troodos Ophiolite boninites
Boninite
Thetford Ophiolite boninites
(b)
11
12
13
14
15
16
17
Melt Al2O3 wt.%

Supplementary Tables S1,S2

Click here to download Background dataset for online publication only: Supplementary Tables S1,S2.xls