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Melt Percolation, Melt-Rock Reaction and Oxygen Fugacity in Supra-Subduction Zone Mantle and Lower Crust from the Leka Ophiolite Complex, Norway

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Samples of peridotites and pyroxenites from the mantle and lower crustal sections of the Leka Ophiolite Complex (LOC; Norway) are examined to investigate the effects of melt-rock reaction and oxygen fugacity variations in the sub-arc oceanic lithosphere. The LOC is considered to represent supra-subduction zone (SSZ) oceanic lithosphere, but also preserves evidence of pre-SSZ magmatic processes.

Here we combine field and microstructural observations with mineral chemical and structural analyses of different minerals from the major lithologies of the LOC. Wöhlite and websterite bodies in both the mantle and lower crust contain clinopyroxene likely formed at a pre-SSZ stage, characterised by high Al, high Cr, low Mg crystal cores. These clinopyroxenes also exhibit low Al, low Cr, high Mg outer rims and intracrystalline dissolution surfaces, indicative of reactive melt percolation during intrusion and disruption of these lithologies by later, SSZ-related, dunite-forming magmas. Chromian-spinel compositional variations correlate with lithology; dunite-chromite Cr-spinels are characterised by relatively uniform and high TiO$_2$ and Al$_2$O$_3$, indicating formation by melt-rock reaction associated with SSZ processes. Harzburgite Cr-spinel compositions are more variable but preserve a relatively high Al$_2$O$_3$, low TiO$_2$ endmember that may reflect crystallisation in a pre-SSZ oceanic spreading centre setting. An important finding of this study is that the LOC potentially preserves the petrological signature of a transition between oceanic spreading centre processes and subsequent supra-subduction zone magmatism.

Single crystal Cr-spinel Fe$^{3+}$/ΣFe ratios calculated on the basis of stoichiometry (from electron microprobe [EPMA] and crystal structural [X-ray diffraction; XRD] measurements) correlate variably with those calculated by point-source (single crystal) Mössbauer spectroscopy. Average sample EPMA Fe$^{3+}$/ΣFe ratios overestimate or underestimate the Mössbauer-derived values for harzburgites, and always overestimate the Mössbauer Fe$^{3+}$/ΣFe ratios for dunites and chromitites. The highest Fe$^{3+}$/ΣFe ratios, irrespective of method of measurement, are therefore generally associated with dunites and chromitites, and yield calculated log($f_{O_2}$)$_{FMQ}$ values of up to ~+1.8. While this lends support to the formation of the dunites and chromitites during SSZ-related melt percolation in the lower part of the LOC, it also suggests that these melts were not highly oxidised, compared to typical arc basalts ($f_{O_2}$$_{FMQ}$ of +2). This may in turn reflect the early (forearc) stage of subduction zone activity preserved by the LOC and implies that some of the arc tholeiitic and boninitic lava compositions preserved in the upper portion of the ophiolite are not genetically related to the
mantle and lower crustal rocks, against which they exhibit tectonic contacts. Our new data also have implications for the use of ophiolite chromitites as recorders of mantle oxidation state through time; a global comparison suggests that the $\text{Fe}^{3+}/\Sigma \text{Fe}$ signatures of ophiolite chromitites are likely to have more to do with local environmental petrogenetic conditions in sub-arc systems than large length-scale mantle chemical evolution.

INTRODUCTION

The importance of reactive melt flow in the lower oceanic lithosphere has been emphasised by numerous workers (e.g., Quick, 1981; Kelemen et al., 1992; 1995a; 1995b; 1997; Coogan et al., 2000; Lissenberg and Dick, 2008; Collier and Kelemen, 2010; Lissenberg et al., 2013; Lissenberg and McCleod, 2016; Leuthold et al., 2018; Bennett et al., 2019). Although fractional crystallisation has traditionally been considered the dominant driver for magmatic differentiation during mid-ocean ridge basalt (MORB) production (Elthon, 1979; Quick, 1981; Grove et al., 1992; Abily and Ceuleneer, 2013; Coogan and O’Hara, 2015), the possibility of widespread melt-rock reaction in the upper oceanic mantle and lower crust has important implications for interpretations of global MORB compositional variations (e.g., as proxies for mantle source compositions), as well as for understanding the architecture of the lower oceanic crust (Arai and Matsukage, 1996; Dick and Natland, 1996; Lissenberg and Dick, 2008; Lambart et al., 2009; Leuthold et al., 2018). The evidence for reactive melt flow in oceanic samples is present at length-scales spanning several orders of magnitude, including textural, mineral chemical and/or field observations of sub-crystal variation(s) to networks of melt channels and veins that occur over kilometres (e.g., Quick, 1981; Coogan et al., 2000; Lissenberg and McCleod, 2016; Leuthold et al., 2018).

Ophiolites, as fossil sections of the lower part of the oceanic lithosphere, are particularly useful sites for investigating and elucidating the processes of melt-rock interaction (Quick, 1981; Batanova et al., 2011; Renna and Tribuzio, 2011; Sanfilippo et al., 2018). This is because at well-exposed ophiolite localities, lithological and structural relationships between the putative melt channels and host rocks can be observed (e.g., Batanova et al., 2011; Derbyshire et al., 2013). Indeed, seminal work on the Bay of Islands Complex, Newfoundland (Bédard 1993; Bédard and Hébert, 1998; Varfalvy et al., 1996) demonstrated the importance of melt-rock reaction for the evolution of not just the upper mantle portion, but also the lower crustal (gabbroic) portion of that ophiolite. A caveat that comes with using ophiolites as analogues for the oceanic lithosphere is that they may be the product of multiple episodes of melt extraction and percolation: i.e., many ophiolites preserve
evidence suggesting supra-subduction zone (SSZ) processing (Arai et al., 2006; Dilek and Furnes, 2011), which may overprint the effects of magmatism that occurred at a MORB spreading centre.

In addition to the implications of a reactive crustal ‘filter’ for magmatic differentiation and therefore for the eventual chemical composition of the magmas produced, reactive melt flow in the oceanic lithosphere may control other key variables. It is generally accepted that the lavas produced at subduction zones are relatively oxidised (e.g., Osborn, 1959; Carmichael, 1991; Arculus, 1994), but if melt-rock reaction is a key process accompanying melt transport through the sub-arc mantle and lower crust above subduction zones, then what implications does this process have for the redox state of the mantle wedge? Elucidating the oxidation state of the supra-subduction mantle wedge is important, not least because of the multiple valence states that volatile elements (e.g., S, Cl) in slab-derived fluids may be present in, prior to and during the onset of melting of the mantle wedge (e.g., Canil et al., 1994; Parkinson and Arculus, 1999; Lee et al., 2005; Bénard et al., 2018). Oxygen fugacity ($f_{O_2}$) may also control the mobility of redox sensitive base and precious trace metals (e.g., the platinum-group metals [PGE], Au, Cu), thereby controlling the formation of ore deposits in convergent margin settings (e.g., Edmonds et al., 2018; Williams et al., 2018).

Here we aim to constrain the length-scales and effects of reactive melt percolation in the upper mantle and lower oceanic crust by studying ophiolitic rocks from the ~497 Ma Leka Ophiolite Complex (LOC), Norway. An important aspect of this study is to establish whether (reactive) melt percolation in the LOC was associated with variations in $f_{O_2}$ over the length-scales in question (i.e., as manifested by cm to m thick veins and sheets of dunite and chromitite). To carry out this work, we link field observations, petrography, mineral geochemistry and Mössbauer spectroscopic analyses for a set of samples of mantle and lower crustal lithologies. The LOC is an ideal locality to carry out this study. It is superbly exposed, only partly serpentinised and is well-characterised in terms of its petrology and provenance (e.g., Furnes et al., 1988; 1992; Pedersen et al., 1993; Maaløe, 2005, Plümper et al., 2012). Based on its chemical characteristics, age and position in the Norwegian Caledonides, it is broadly considered to represent a SSZ ophiolite. Indeed, the data and observations reported in numerous studies (e.g., Furnes et al., 1988; Maaløe, 2005; O’Driscoll et al., 2015; Carter et al., 2021; Haller et al., in press) show that the LOC preserves abundant evidence for melt percolation in a sub-arc setting and it is primarily this feature that is exploited in the current study.
GEOLOGICAL SETTING

The ~497 Ma Leka Ophiolite Complex (LOC; Nord Trøndelag, Norway; Fig. 1) is one of numerous lower Palaeozoic ophiolites formed during closure of the northern part of the Iapetus Ocean (Dunning and Pedersen, 1988; Furnes et al., 1988, 1992), and formation of the Caledonian-Appalachian orogenic belt. Obduction of the LOC onto the Laurentian margin probably occurred during the Grampian Orogeny (~470 Ma; Titus et al., 2002). Subsequent transference to Baltica occurred during the Scandian Orogeny (~430 Ma), and the LOC presently occurs surrounded by rocks of the Middle (or Lower) Allochthon of the Scandinavian Caledonide nappe pile (Titus et al., 2002). Parts of the LOC, particularly the upper crustal gabbroic and basaltic portions, contain evidence of having been metamorphosed under lower greenschist facies conditions (Furnes et al., 1992). Basaltic lavas and sheeted dykes in the LOC mainly preserve geochemical signatures of arc tholeiitic magmatism (Fig. 1; Furnes et al., 1988; 1992). However, MORB-like magma compositions have also been documented; these have been variably attributed to formation in a marginal (back-arc) basin, distal from the subduction zone (Furnes et al., 1992; Tveit et al., 1993), or an anomalous ridge segment (Prestvik, 1985). The origin of the MORB-like basalts remains obscure because the relationships between the fault-bound blocks that carry the different basalt types (and also between the basalts and the mantle and lower crustal rocks) are uncertain. Some authors have also argued that low temperature alteration of the LOC (including the production of mantle serpentinite and lower crustal rodingites) points to hydration in an open ocean basin environment (Austrheim and Prestvik, 2008; Iyer et al., 2008).

The LOC contains a lithologically heterogeneous suite of mantle rocks. The exposed section below the petrological Moho comprises approximately 65% harzburgite, together with abundant lenses and sheets of dunite and, to a lesser extent, orthopyroxenite, websterite and chromitite. The proportion of non-harzburgitic material increases in the top 200-300 m of the mantle section, i.e., directly below the petrological Moho. The latter boundary, taken here as the contact between residual harzburgite (mantle) and overlying layered dunitic rocks, is locally well-exposed in the LOC, though the mantle section also exhibits fault-bounded contacts against other parts of the ophiolite (Fig. 1). Certain lithologies (chromitites and orthopyroxenites) in the mantle portion of the LOC are suggestive of at least some partial melting and melt/fluid percolation above a subducting slab (O’Driscoll et al. 2015), although constraining the structural setting of ophiolite formation in that context more precisely (e.g., forearc, back-arc, etc) is challenging. Recent work has shown that many of the LOC dunite...
veins, as well as orthopyroxenites and chromitites, lie along a Re-Os isotope errorchron that yields an age of ~485 ±32 Ma (O’Driscoll et al., 2015), consistent with them being the product of SSZ-related melt percolation. However, the latter study also demonstrated that rocks experiencing prior melt depletion and percolation are also present in the LOC; these include veins of websterite whose Re-Os isotope systematics suggest formation during an older (~589 ±15 Ma) melt percolation event and depleted harzburgites with Os isotope model ages >1 Ga. Haller et al. (in press) demonstrated that SSZ-related and older Os isotope heterogeneities most strongly reflect processes that operated at cm-to-m length-scales in the LOC mantle. Plümper et al. (2012) used detailed mineralogical and microstructural evidence to argue for a transient dehydration event in the LOC mantle, though the mechanism and the tectonic setting for this dehydration remain unresolved.

The lower crustal section comprises a rhythmically but locally discontinuously layered, subvertically-dipping dunite-wehrlite/websterite sequence; individual macro-scale layers are on the order of 10-30 m thick. A 3-5 m thick stratiform chromitite occurs in this section, extending laterally for more than 3 km. The lower crustal section of the ophiolite was referred to as a ‘layered series’ by Furnes et al. (1988) and was originally interpreted as a sequence of ultramafic cumulates (Prestvik, 1980). This interpretation was adopted by Maaløe (2005), who suggested that the ‘absence’ of a transition zone in the LOC, as well as ubiquitous serpentinitisation of the ultramafic rocks, indicated formation of the ophiolite at a slow spreading ridge. However, on the basis of abundant field and geochemical evidence for dunite-forming magma intrusions and associated melt-rock reaction, O’Driscoll et al. (2015) suggested that the several hundred metre thick layered series may be equivalent to the Moho transition zones observed in other ophiolite complexes (e.g., the Dunite Transition Zone of the ~90 Ma Oman ophiolite; Boudier and Nicolas, 1995; Abily and Ceuleneer, 2013).

FIELD OBSERVATIONS

Field relationships in the mantle and lower crustal sections of the LOC have been reported in detail by Furnes et al. (1988), Maaløe (2005), Pedersen et al. (1993) and O’Driscoll et al. (2015), and only aspects directly relevant to the current study are described here. Dunite sheets in the mantle section range from millimetre- to metre-scale thicknesses (Fig. 2a). Dunites may exhibit relatively sharp or gradational contacts against the host harzburgite (Fig. 2a). In the latter case, irregularly-shaped volumes of dunite, often containing greater than accessory abundances of Cr-spinel, can occur in the harzburgite (Fig. 2b). Orthopyroxenite, websterite and chromitite bodies are typically 1-30 cm thick. Chromitites are almost
ubiquitously contained within dunite sheets (Fig. 2c). Chromitite bodies in the mantle section rarely exceed 10 cm in thickness and are typically smaller and podiform in nature, compared with those in the lower crustal section. Orthopyroxenite and websterite bodies commonly exhibit evidence for structural deformation. Composite orthopyroxenite-websterite bodies are observed, such as the example in Figure 2d, where an orthopyroxenite lens encloses a websterite core.

Within the lower crustal section, harzburgite is absent and orthopyroxenite is rare compared to its occurrence in the mantle portion of the LOC. Ubiquitously superimposed on the macro-scale rhythmic layering noted above is smaller-scale layering (i.e., 1-30 cm thick) of dunite, chromitite, wehrlite-websterite and clinopyroxenite (Fig. 2e). Rare layered gabbro occurs in the northwestern part of the lower crustal section, with the layering defined by variations in the relative abundances of clinopyroxene and plagioclase. Cross-cutting relationships at the margins of dunite bodies of all sizes suggest that at least some of these dunites are intrusive into an older sequence of dunites, wehrlites and websterites. The layered gabbro described above is also cross-cut by dunite bodies. Centimetre-sized fragments of clinopyroxene-bearing material and individual clinopyroxene crystals are observed close to the margins of (and within) chromitite-bearing dunites (Fig. 2f). Chromitite layers and lenses can be several 100s of cm in thickness and are most developed within the latest generation of intrusive characteristics. More detailed information on sample provenance and lithological characteristics is provided in the Supplementary Information file.

ANALYTICAL TECHNIQUES

Details of the analytical techniques employed are described in the Supplementary Information. In summary, we measured the major and minor element compositions of clinopyroxene and Cr-spinel in the majority of the samples using an electron probe microanalyzer (EPMA). Olivine mineral chemical data, recently reported in Carter et al. (2021) but collected in the same analytical sessions as the clinopyroxene and Cr-spinel data referred to above, are included here for completeness. The compositions of sulfides were measured in a small number of samples. Compositionally zoned clinopyroxene crystals observed in certain clinopyroxene-bearing samples (e.g., LK2, LK35, LK38b[ii]) were analysed by laser ablation-inductively coupled mass spectrometry (LA-ICP-MS), to better evaluate melt-rock reaction processes. Single crystal XRD and point-source Mössbauer analyses of Cr-spinel were carried out to better constrain the variation in Fe$^{3+}$ and Fe$^{2+}$ in suitable samples (see Supplementary Information).
PETROGRAPHIC OBSERVATIONS AND ANALYTICAL RESULTS

Petrography and chemical mapping

Mantle harzburgites

Based on petrographic observations, orthopyroxene pseudomorphs, now bastite, make up ~15 vol.% of harzburgites LK17, LK40 and LK53. In these samples, the pseudomorphs may be composed of domain parallel olivine (DPO), as described by Plümper et al. (2012), with patchy clinopyroxene growths and numerous crystallographically-constrained oxide crystals (Figs. S1a, 3a). The outer margins of some pseudomorphs are lined with oxide crystals (Fig. 3b). Within the pseudomorphs, olivine and clinopyroxene occur with patches of lizardite, at sub-micron to micron length-scales. The oxide crystals in the DPOs span <1-10s μm grainsizes, with those in the larger size range typically exhibiting skeletal morphologies (Fig. 3c). Harzburgites also contain accessory amounts of Cr-spinel, which locally but not typically, has thin rims of ferrian chromite. Rare anhedral (interstitial) clinopyroxene (<1 vol.% ) also occurs in all harzburgites.

Mantle and lower crustal dunites

Chromian-spinel is typically present in greater than accessory abundances in dunites (visual estimates suggest up to 5 vol.%), in particular in the lower crustal dunites (e.g., LK35, LK31; Fig. S1b). In many dunite bodies, Cr-spinel occurs in seams and exhibits a well-developed grain shape-controlled foliation. Aside from olivine, minor (<5 vol.%) clinopyroxene is also present and is intergrown with olivine. Specifically, thin (several 10s of μm) clinopyroxene veinlets cut through olivine crystals, closely associated with fine grained (~1 μm) equant oxide crystals (Fig. 3d). Irregularly-shaped patches of clinopyroxene also locally replace parts of olivine crystals. The clinopyroxene in the veinlets and patches exhibits a granular texture in some instances (Fig. 3d). The isolated clinopyroxene crystals observed within Cr-spinel-bearing-dunite (e.g., LK2; Fig. 2f, S1c) have locally undergone some secondary alteration, and the outer edges of these are sometimes lined with thin seams of chromitite (Fig. S1c). Anhedral blebs of base-metal sulfide are also common in these dunites, in accessory proportions (<1 vol.% ), closely associated with the occurrences of clinopyroxene and/or Cr-spinel crystals. Sulfide blebs attached to Cr-spinel crystals are a common occurrence (Fig. 3e). The sulfide is primarily pentlandite, with secondary millerite and/or heazlewoodite also present.

Clinopyroxene- and Cr-spinel-rich lithologies
Clinopyroxene crystals in the two wehrlite samples (LK24 and LK37) have (oxide) inclusion-rich cores, with overgrown mantles that have a paucity of these inclusions. A similar texture is observed in LK-12-14, an olivine websterite with up to ~40 vol.% clinopyroxene. Chromian-spinel occurs in LOC websterites and wehrlites and exhibits a greater degree of alteration to Fe-rich chromite, manifested by the development of thicker high reflectance sieve-textured/ragged rims on crystals, than other LOC lithologies studied. The massive chromitite LK32 is itself internally layered, with the layering defined by the differences (60-90 vol.%) in the relative abundance of Cr-spinel to interstitial olivine (plus serpentine). Sulfides are only sparsely observed in LK32, and mainly comprise millerite and heazlewoodite.

**The LK38 sample sub-group**

This group of four samples (collected from the outcrop shown in Figure 2e) typify the compositional layering observed in the lower crustal section. In the dunite between the chromitite seams, minor amounts of clinopyroxene are intergrown with the olivine, often near to Cr-spinel crystals. Base metal sulfides are also common, mainly pentlandite, disseminated through the dunite and wehrlite. LK38b(i) contains awaruite (Ni$_2$Fe-Ni$_3$Fe) and native copper (Fig. 3f). LK38b(ii) is a wehrlite layer and contains ~20 vol.% clinopyroxene (Fig. S1d).

Backscatter electron imaging and element mapping reveals that these clinopyroxene crystals are compositionally zoned, as described for other clinopyroxene-rich samples above, with relatively dense cores containing lamellae of fine-grained (<1 μm) oxide grains, and less dense overgrowths. The overgrowths locally enclose relatively coarse-grained (up to ~100 μm in size) subhedral Cr-spinel crystal inclusions. The element maps illustrate that clinopyroxene cores are relatively Al- and Cr-rich, whilst the overgrowths have slightly higher MgO concentrations (Fig. 4a,b). No zoning of olivine occurs. LK38c contains up to ~5 vol.% sulfide, as composite interstitial blebs of pentlandite concentrated into a 1 cm thick layer. O’Driscoll et al. (2015) reported Ni-arsenides from LK38c.

**Mineral chemical and structural data**

The olivine EPMA data from the LOC peridotites and pyroxenites (from Carter et al., 2021) are plotted in Figure S2 and tabulated in Supplementary Tables 2. The EPMA data for clinopyroxene, Cr-spinel and sulfide are reported in Supplementary Tables 2 and plotted in Figures S3, 5 and 6. The Cr-spinel data were corrected for the presence of ferric iron, using the method of Droop (1987). Back-scattered electron maps with associated olivine-
clinopyroxene EPMA analyses are presented in the Supplementary Tables, for selected samples. The clinopyroxene LA-ICP-MS data are reported in Supplementary Table 3 and plotted in Figures 4, 7 and 8. The single crystal structural data are presented in Tables 1, 2 and illustrated in Figure S4. The point-source Mössbauer parameter measurements and two examples of spectra obtained are shown in Table 3 and Figure S5, respectively.

Olivine

As noted in Carter et al. (2021), LOC harzburgites are characterised by olivine with compositions mainly in the range of Fo$_{89-91}$ and NiO contents mostly between 0.3–0.5 wt.% (Ni contents of 1700–3450 μg g$^{-1}$). Olivine in the dunites and wehrlites has a similar though slightly broader range of Fo contents (Fo$_{88-93}$), with lower Ni contents mainly falling between 250–2700 μg g$^{-1}$ (Fig. S2). The interstitial olivine in the chromitite is highly magnesian (~Fo$_{95-98}$) and also exhibits relatively high Ni contents (3000–4000 μg g$^{-1}$).

Clinopyroxene

Clinopyroxene in all the LOC samples studied is close to endmember diopside in composition (Fig. S3a,b; Di$_{>95}$, calculated on the basis of stoichiometry). Clinopyroxene Cr$_2$O$_3$ contents range between less than detection limits (<dl) to 1.7 wt.%; Al$_2$O$_3$ between <dl to 3.9 wt.% and Na$_2$O <dl – 0.7 wt.%. Clinopyroxene TiO$_2$ contents ranging between <dl – 0.25 wt.% for the dunites/wehrlites and <dl – 0.12 wt.% for the harzburgites. Broadly, Al occurs in approximately equal proportions of $^{IV}$Al and $^{VI}$Al in the harzburgites and dunites, with the clinopyroxene-rich lithologies (LK38b, LK37 and LK-12-14) exhibiting a greater proportion (up to 75%) of $^{IV}$Al. High Mg# (Mg/[Mg+Fe$^{2+}$]) clinopyroxenes tend to be those that are associated with reaction-type textures and are present in most lithological types (Fig. 5). Relatively low Mg#, high Al$_2$O$_3$, high Cr# (Cr/[Cr+Al]) clinopyroxene compositions are generally associated with the clinopyroxene-rich samples (e.g., LK37, LK38b(ii) and LK-12-14; Fig. 5a,b). Positive correlations are observed between Cr$_2$O$_3$ and Al$_2$O$_3$ and Cr$_2$O$_3$ and Na$_2$O in most samples, including the harzburgites (Fig. 5). Clinopyroxene-rich samples such as LK37, LK38b(ii) and LK-12-14, and in particular the cores of crystals in those samples, are characterised by the highest Al$_2$O$_3$, Cr$_2$O$_3$ and TiO$_2$ contents (see also Fig. 4b,c). On plots of Na$_2$O versus Cr$_2$O$_3$ and TiO$_2$ versus Na$_2$O, the correlations present relate to lithology, with the dunites (LK38a, LK38b(i), LK38c) exhibiting a trend with a steeper slope than the clinopyroxene-rich samples LK37, LK38b and LK-12-14 (Fig. 5).
The CI chondrite-normalised incompatible trace element abundances for clinopyroxene are shown in Figure 7. In general, clinopyroxene from samples LK2, LK35 and LK38b(ii) are similar, with depletions in many of the most incompatible elements relative to CI chondrite (Fig. 7a). The chondrite-normalised REE patterns for the clinopyroxenes studied are all broadly similar, with LREE contents \(10^{-1}\) less than those of CI chondrite and broadly chondrite-relative MREE and HREE abundances (Fig. 7). No resolvable differences are observed between crystal cores and overgrowths, in terms of absolute REE abundances, except for La, for which the Cr- and Al-poor mantles are slightly enriched. The exception is LK35, for which the slope of the REE pattern is more uniform from sub-chondritic values of the LREE and MREE, to chondrite-like HREE (Fig. 7).

Anhedral compositionally zoned clinopyroxene crystals are typical in websterites and wehrlites in the LOC (e.g., LK2, LK35, LK38b(ii) and LK-12-14). Clinopyroxene crystals in LK35 and LK38b(ii) reveal relatively consistent patterns of major and trace element covariation, as follows. The high-Cr and Al cores of these crystals have relatively low to intermediate La/Sm ratios, and lower Mg# (e.g., 83-84). The overgrowths have lower Cr, moderate to high La/Sm and higher Mg# (e.g., 87-88), and locally-developed thin outermost rims are characterised by relatively low Cr and low La/Sm (Fig. 4c). Some variation in overall La/Sm is also observed from one crystal to the next in LK38b(ii) (Fig. 8a).

The intracrystalline distribution of other incompatible elements in clinopyroxene from LK38b(ii) matches that of the LREE. For example, crystal cores in this sample have low to moderate Zr at high Cr contents, overgrowths have moderate to high Zr at moderate Cr, and outermost rims have low Zr at the lower end of the Cr range (Fig. 8c,d). In the same sample, crystal cores tend to have lower Sc and higher V/Sc than the relatively high Mg# overgrowths, and the outermost rims yield the highest Sc and lowest V/Sc values. There is broad overlap between the different clinopyroxene crystals analysed for Sc, Nd/Yb, Ga and Y contents, and on plots of V versus all of these elements, the V content in clinopyroxene, in particular, distinguishes different subgroups (e.g., Fig. 8e,f). Sample LK35 is similar to LK38b(ii) in Zr versus Cr space, but clinopyroxene from LK2 and LK5 shows relatively low abundances of both elements (Fig. S3c,d). Samples LK2, LK5 and LK35 are distinct from LK38b(ii) on the plot of V/Sc versus Sc, spanning much greater ranges of Sc and/or V/Sc (see Fig. 8e).

Chromian-spinel
The different LOC lithologies are characterised by distinct Cr-spinel compositions (Fig. 6). The harzburgite and LK37 Cr-spinels mainly have relatively low Cr# (~0.4-0.6) and moderate Mg# (0.45-0.6). The dunites have lower Mg# (0.25-0.5) and higher Cr# values (0.6-0.75). The chromitite Cr-spinels have similar Cr# to the dunites (~0.7) and relatively high Mg# (~0.65). Most samples, irrespective of lithology, contain a small number of Fe-Cr-rich Cr-spinels (i.e., with low Mg# values and Cr# approaching unity; see Fig. 6). These analyses correspond to relatively high reflectance rims on some Cr-spinel grains and/or the skeletal oxide crystals associated with the DPOs in the harzburgites. The LOC Cr-spinels also vary in their TiO$_2$ and V$_2$O$_3$ contents, depending on lithology (excluding Cr-spinels with Cr#>0.8). Harzburgite Cr-spinels have relatively low TiO$_2$ (<0.1 wt.%) and high V$_2$O$_3$ (0.19-0.32); wehrlite LK37 Cr-spinel has TiO$_2$ of 0.1-0.2 wt.% and V$_2$O$_3$ of 0.21-0.24 wt.%; and the dunites have TiO$_2$ of 0.2-0.35 wt.% and V$_2$O$_3$ of 0.14-0.23 wt.%. The chromitite (LK32) Cr-spinels have TiO$_2$ of 0.1-0.2 wt.% and V$_2$O$_3$ of 0.08-0.12 wt.%.

The LOC Cr-spinels exhibit a broad negative trend of increasing Mg# with decreasing Cr# (Fig. 6a). Excluding the scatter of ferrian Cr-spinel compositions, the data also broadly fall along a negative trend in TiO$_2$ versus Al$_2$O$_3$ space, with the dunites being characterised by relatively high TiO$_2$-low Cr$_2$O$_3$ compositions and the harzburgites by relatively low TiO$_2$-high Cr$_2$O$_3$ compositions, and with the chromitite and wehrlite LK37 falling in between (Fig. 6b). Excluding the ferrian Cr-spinel compositions (i.e., all corrected Cr-spinel analyses with FeO+Fe$_2$O$_3$ > 40 wt.%), harzburgites and wehrlite Fe$^{3+}$/ΣFe average values range between a minimum of 0.11 ±0.01 to a maximum of 0.13 ±0.01 (LK17 and LK40, respectively; 1σ; Fig. 9a). Treated in the same way, the dunites and chromitites have Fe$^{3+}$/ΣFe average values ranging from 0.21 ±0.01 to 0.33 ±0.02, for LK38a and LK38c, respectively (1σ; Fig. 9a).

The unit cell of the spinel structure can be described as a slightly distorted cubic close-packed (ccp) array of 32 oxygen atoms with 8 cations at tetrahedrally coordinated T sites, and 16 cations at octahedrally coordinated M sites (Hill et al., 1979). The T and M sites lie on special positions with -43m and -3m symmetry, respectively. The only variable geometrical parameters are the unit-cell edge (a) and oxygen coordinates (u, u, u), which are related to the oxygen packing distortion. The ideal ccp structure shows $u = 0.25$. However, the distortion caused by cations with different sizes in the T and M sites means that $u$ has a value of 0.2625 for Cr-bearing spinels when the M-O and T-O bond distances are equal (Hill et al., 1979). The measured cell edges are in the range 8.2813 (4) to 8.3361 (1) Å, while the oxygen positional parameter ($u$), is between 0.26238 (7) and 0.26273 (7) (Fig. S4; Table 1).
Several different procedures may be adopted to determine cation distribution (e.g., Carbonin et al., 1996; Lavina et al., 2002), and satisfactory results can generally be obtained by combining data from single-crystal X-ray structural refinements and electron microprobe analyses, using the procedure described in Lenaz and Schmitz (2017). The obtained cation distributions are listed in Table 2. Major element data were collected by EPMA on the individual Cr-spinels analysed for crystal structural characteristics (i.e., in addition to the other EPMA data collected; see Supplementary Information) and are generally in good agreement with the results reported above (Table 2). The degree of inversion, i.e., the amount of trivalent cations in the T site and vice versa, is in the range 0.010-0.026, signifying a relatively ordered situation. The Fe$_{3+}$/ΣFe is in the range 13-22 according to the cation distribution calculated via EPMA and the structural refinement calculations, for samples LK1, LK30, LK31, LK32, LK35, LK38a and LK52. Values of Fe$_{3+}$/ΣFe calculated for the single Cr-spinel crystals in this way are lower than the bulk rock mean EPMA Fe$_{3+}$/ΣFe values where both methods were applied to the same sample (i.e., LK32 and LK35; see Fig. 9a).

The point-source Mössbauer measurements reveal Fe$_{3+}$/ΣFe ratios in the range 0.101 – 0.183 (i.e., amounts of Fe$_{3+}$ range between 10.1-18.3%). Neither average nor minimum EPMA Fe$_{3+}$/ΣFe values correlate especially well with the Mössbauer values from corresponding samples. Figure 9a illustrates a comparison of Fe$_{3+}$/ΣFe values from the EPMA only and EPMA/structural refinement calculations versus those from Mössbauer measurements, for all relevant samples. In general, Mössbauer Fe$_{3+}$/ΣFe values underestimate those from the EPMA data, though for some harzburgites and a wehrlite (LK17, LK37, LK40), the Mössbauer measurements reveal higher Fe$_{3+}$/ΣFe (Fig. 9a,b). Figure S5 shows examples of $^{57}$Fe Mössbauer spectra obtained from the point-source measurements for those samples with the highest and lowest calculated values of Fe$_{3+}$/ΣFe (LK17 and LK53, respectively).

**DISCUSSION**

**The extent of SSZ overprint on the LOC upper mantle and lower crust**

*State-of-the-art*

There is a bias in the preservation of ophiolites in the geological record such that most known ophiolites have undergone some degree of SSZ processing (Dilek and Furnes, 2014, and references therein). True MORB-type ophiolites are uncommon. Examples may include...
Taitao, Chile (Schulte et al. 2009), parts of the Italian Ligurian Complex (e.g., Tribuzio et al. 2000) and Masirah, Oman (Rollinson, 2017). However, although classifications such as these, based on detailed consideration of magma petrogenesis and tectonic context, are useful, it is also important to remember that individual ophiolite complexes may preserve evidence of episodes of magmatism in differing settings (e.g., Melcher et al., 1997; Schulte et al., 2009; Goodenough et al., 2014; O’Driscoll et al., 2015; Derbyshire et al., 2019).

Metamorphism of the LOC appears to have mainly affected its upper crustal (gabbroic and basaltic) portions (Furnes et al., 1992). Carter et al. (2021) showed that the heavy halogen and noble gas isotope signatures of the mantle and lower crustal rocks are lithologically-controlled, such that the harzburgites preserve signatures similar to typical ocean floor serpentinites whereas the dunites, pyroxenites and chromitites reveal evidence of slab components in their volatile element inventory. On this basis, we do not consider regional metamorphism, which would presumably have resulted in pervasive crustal fluid ingress and circulation, to have played a significant role in mineral chemical variations in the LOC.

Certain characteristics of the LOC have been attributed to formation in an open ocean basin (Prestvik, 1985; Maaløe, 2005), whereas most other workers have recognised that SSZ processes must have played at least some part in its formation (e.g., Furnes et al., 1992; O’Driscoll et al., 2015; Carter et al., 2021). Lithophile trace elements, including the REE, for LOC harzburgites and dunites suggest a pervasive SSZ overprint; for example, all such samples exhibit light REE (LREE) enrichments relative to the middle REE (MREE; O’Driscoll et al., 2015). However, the highly siderophile elements (HSE) and Os isotopes, which are not affected by serpentinisation or late-stage alteration in the same way, reveal distinct processes acting within the ophiolite (O’Driscoll et al., 2015; Haller et al., in press). For example, the relative abundances of the HSE in the LOC harzburgite population are indistinguishable from that of a global compilation of abyssal peridotites, suggesting that for these elements at least, they have been little affected by SSZ processes. In addition, Os isotope model (T_{RD}; see Haller et al. in press for derivation) ages from some LOC harzburgites suggest melt depletion ages of >1 Ga. These are minimum melt depletion age estimates so making links to specific tectonic events on this basis is difficult.

O’Driscoll et al. (2015) reported different errorchron ages for subsets of the dunite, websterite, orthopyroxenite and chromitite sheets. A more recent study on the LOC mantle lithologies demonstrates that HSE and Os isotope heterogeneities present at the cm- to m-
scale are greater than those preserved at the km-scale, suggesting that the drivers for the development of these heterogeneities are a consequence of relatively localised processes (Haller et al. in press). These lines of evidence collectively indicate that, for the LOC: (1) different elemental and isotopic tracers preserve evidence for contrasting melt depletion events even at the scale of individual hand samples, and: (2) peridotites with different petrogenetic histories are juxtaposed (see Supplementary Table 4 for a summary of the evidence for pre-SSZ- and SSZ-related magmatism in the LOC). In this section, we discuss further the mineral chemical and field evidence for a polygenetic origin for the LOC.

Early-formed clinopyroxene-rich lithologies

Given the >600 Ma model ($T_{MA}$) Os isotope ages exhibited by some LOC websterites (O’Driscol et al. 2015), elucidating the timing and mode of formation of the clinopyroxene-rich lithologies in the LOC mantle and lower crust with respect to SSZ processes is an important step in resolving some of the complexities outlined above. On the one hand, the presence of clinopyroxene-rich cumulate in some ophiolites has been attributed to partial melting of lower oceanic crustal gabbros, such that clinopyroxenites and websterites represent gabbros that have undergone partial dissolution by infiltrating melts and subsequent recrystallisation (e.g., Bay of Islands Ophiolite; Bédard, 1991). Alternatively, clinopyroxene-rich cumulate is not an uncommon feature of SSZ ophiolites and may be attributed to a different crystallisation order (olivine $\rightarrow$ clinopyroxene/orthopyroxene $\rightarrow$ plagioclase) to that assumed to form typical MORB compositions (cf. Grove et al., 1992). Clinopyroxene may saturate prior to plagioclase in relatively hydrous basaltic melts at temperatures and pressures typical of the lower oceanic crust, and so in ophiolitic oceanic crust early clinopyroxene could crystallise from SSZ-related hydrous mantle melts (Feig et al., 2006; MacLeod et al., 2013; Yamasaki et al., 2006). However, gabbronorite and wehrlite have also been sampled along active spreading ridges (Arai and Takemoto, 2007; Gillis et al., 2014; Ross and Elthon, 1993) and likely crystallized from nearly anhydrous MORB melts.

In the LOC, clinopyroxene-rich rocks occur both as veins in the mantle section (either parallel or discordant to the mantle fabric) and as sheets and lenses oriented parallel to the main structure of the lower crustal sequence. Although there is some gabbroic rock in the lower crustal section, there is none present in the mantle section, so the assimilation model of Bédard (1991) does not easily apply to the LOC. O’Driscol et al. (2015) suggested that mantle-hosted websterite and certain dunites in the LOC formed during magmatism associated with the opening of the Iapetus Ocean, based on their association along a $^{187}$Re-
Os errorchron of 589 ±15 Ma. The new mineral chemical data presented here lend support to the clinopyroxene-rich rocks representing an early stage of magmatic processing in the LOC. For example, on plots illustrating variations in Mg#, Cr# and some of the minor elements (TiO$_2$, Na$_2$O; Fig. 5), websterites and wehrlites are shown to contain clinopyroxene with relatively high Al$_2$O$_3$, Cr$_2$O$_3$ and TiO$_2$, with many plotting in the field for abyssal peridotites. By contrast, the dunites and harzburgites contain clinopyroxene with compositions that mainly fall into the field for SSZ peridotites. The high Cr-Al clinopyroxene compositions measured here overlap with the compositions of clinopyroxene lamellae in the orthopyroxene-derived DPOs (Fig. 5a), as reported by Plümper et al. (2012), who noted the similarity of these lamellae to those commonly formed by exsolution from orthopyroxene in oceanic harzburgites and suggested a similar origin (see also Cannat et al., 1992).

In general, clinopyroxene from the clinopyroxene-rich LOC lithologies has chondrite-normalised trace element (including REE) patterns resembling those of clinopyroxene from oceanic pyroxenites (e.g., from the Southwest Indian Ridge and the Lena Trough; Dantas et al., 2007, Laukert et al., 2014, respectively; Fig. 7a,b). In addition, we calculated the parental melt REE composition for the high Cr-Al clinopyroxene cores in both LK38b(ii) and LK35, using the partition coefficient predictive model of Wood and Blundy (1997). The resulting patterns are shown on Figure 7b and mainly lie within the concentration range of N-MORB compositions shown by Leuthold et al. (2018; synthesised from the Gale et al. [2013] and Lehnert et al. [2000] databases). Based on these combined lines of evidence, together with the field observations for disruption and assimilation of clinopyroxene-rich lithologies, we suggest that much if not all the clinopyroxene-rich material in the LOC predates SSZ processes and may represent melt percolation and melt-rock reaction beneath an open ocean spreading centre (see below for further detail).

Chromian-spinel as a petrogenetic tracer in the LOC peridotites

Due to its resistance to alteration during the serpentinisation of mantle peridotites, Cr-spinel has found widespread use as a petrogenetic indicator for parental melt composition and conditions of melt extraction in these rocks. On a plot of Cr# versus Mg# (Fig. 6a), the main cluster of LOC dunite data lie between the abyssal peridotite and boninite fields, whereas the harzburgites and wehrlite LK37 fall within the abyssal peridotite field (Fig. 6a). On a plot of TiO$_2$ versus Al$_2$O$_3$ (Fig. 6b), the bulk of the dunites and the chromitite plot in or close to the island arc field, whereas the harzburgite and LK37 Cr-spinels have comparatively high Al$_2$O$_3$ contents, with lower (and variable) TiO$_2$. Figure S4 shows that the crystal structural
characteristics of Cr-spinels from dunite and chromitite are similar to those of other lower Palaeozoic SSZ-related ophiolites. The lowest TiO$_2$ Cr-spinels in samples LK40 and LK53 are probably the closest to residual pre-SSZ upper mantle compositions, supported by their similarity to abyssal peridotite Cr-spinel compositions (Fig. 6a). We applied the algorithms of Rollinson (Rollinson, 2008; adapted from Maurel and Maurel, 1982; Kamenetsky et al., 2001) to the Leka dunites and chromitite to better constrain the compositions of the melts from which they crystallised. There is an implicit assumption in applying these calculations that the Cr-spinels are in equilibrium with their parental melt. This is likely to be an oversimplification given the complex magmatic processes operating to form the rocks described above (e.g., see also El Dien et al., 2019), but the calculations are useful as a first step towards deciphering the tectonic setting in which the chromitites formed. In addition, the dunites and chromitite have relatively uniform Cr-spinel compositions, apart from those very low Al$_2$O$_3$ secondary Fe-Cr-rich Cr-spinels (Fig. 6b). Using those values considered to be representative of primary magmatic compositions, the Leka dunites and chromitite are characterised by parental melt TiO$_2$ and Al$_2$O$_3$ compositions of 0.2-0.4 wt.% and 12-13 wt.%, respectively. These compositions most closely equate to arc tholeiite or boninite-like magmas.

Further insights from (and links to) LOC basaltic lavas

The geochemical characteristics of the exposed sequences of LOC basalts are variable, suggesting the possibility that different magmatic regimes and mantle sources were responsible for their formation (Furnes et al. 1988; 1992). The latter authors reported a preponderance of island arc tholeiite compositions based on the geochemistry of pillow basalts from Madsøya (Fig. 1), matching the predominantly SSZ flavour of the LOC mantle and lower crustal rocks (e.g., O’Driscoll et al., 2015). Furnes et al. (1992) suggested that the MORB-like (and continental arc basalt-like) lavas that also occur (e.g., at Storøya; Fig. 1) are younger, and thus ascribed them to a back-arc setting. However, Furnes et al. (1992) also noted that the field relationships between the different upper crustal components of the LOC are not well-constrained. There is the possibility that the Storøya lavas predate the Madsøya sequence and are linked to the magmatism associated with the putative ~590 Ma event suggested by O’Driscoll et al. (2015). The new information on the clinopyroxene-rich lithologies presented here lends support to the idea that these rocks formed beneath an open ocean spreading centre, especially when considered together with their Re-Os isotope systematics. Further geochemical and isotopic analyses, including dating, of the LOC basalt
sequences therefore represents a worthwhile line of future research and are critical to test the hypothesis that the LOC initially formed at a mid ocean ridge spreading centre, before SSZ processing at ~497 Ma.

**Melt-rock reaction in the mantle and lower crust of the LOC**

**Dunite formation by reactive melt percolation**

Supra-subduction zone-related melt-rock reaction processes may superimpose features resulting from earlier (e.g., oceanic spreading) magmatism in the rocks. Field observations and petrography suggest that melt-rock reaction was widespread and occurred at a range of length-scales in the LOC mantle and lower crustal sections. In particular, the presence of cm-m thick dunite sheets, in many instances with dunitised harzburgite margins, point to this being an important petrogenetic process in the mantle rocks. Mineral chemical evidence supports the idea of dunite formation by reactive percolation. For example, Figure S2 shows that, in general, olivine in the dunites is characterised by lower Ni than that in the harzburgites. Batanova et al. (2011) observed similar behaviour in peridotites in the SSZ-related Voykar Ophiolite, Russia, and attributed this to the production of increasing amounts of olivine during replacement of harzburgite by dunite, thus depleting the melt Ni content (see also Suhr et al., 2003). As discussed below, microstructural and mineral chemical evidence from some of clinopyroxene-rich lithologies in the LOC suggests that melt-rock reaction was important, in this case at the sub-mm length-scale.

In addition, it is now widely accepted in the literature that ophiolitic chromitites, which in the case of the LOC are ubiquitously sheathed in dunite veins, form by reaction of ascending melts with harzburgitic host rock during SSZ processing (e.g., Arai, 1992, 1997; Batanova et al., 2011; Büchel et al., 2002; Derbyshire et al., 2013; González-Jiménez et al., 2011; 2014a, 2014b; Zhou et al., 1996), following the classic work of Kelemen (1990) and Kelemen et al. (1992, 1995a,b). Orthopyroxenite petrogenesis in SSZ ophiolites has also been linked to reactive percolation, in this case of SiO$_2$-rich hydrous melts through the mantle (Kelemen, 1990). Overall, the field relationships suggest the LOC Moho transition zone comprises an older sequence of clinopyroxene-bearing peridotite and gabbro, intruded by numerous dunite sheets, with abundant evidence for incorporation and assimilation of the former into the dunites, at cm-m length-scales. This is also supported by the discordance between mantle fabrics and lower crustal layering across the petrological Moho, taken here as reflecting an intrusive contact (**Fig. 1**). The remainder of this section is concerned with
evaluating the specific lines of clinopyroxene chemical and microstructural evidence for reactive melt percolation in the LOC.

**General LOC clinopyroxene compositional variations**

The clinopyroxene chemical data reveal complex compositional variation and support the occurrence of pervasive melt-rock reaction in many of the mantle and lower crustal samples. As noted above, clinopyroxene compositions in the various LOC peridotites have end-members that span the abyssal to SSZ peridotite fields. A high Al-Cr end-member with relatively low Mg# values is observed in the clinopyroxene-rich lithologies in particular, as well as in relict lamellae in pseudomorphed orthopyroxene crystals in harzburgite (Plümper et al., 2012), whilst dunites and harzburgites have clinopyroxene compositions with a low Al-Cr, high Mg# end-member (Fig. 5). All of the samples have clinopyroxene compositions that range between both of these end-members. Most of the clinopyroxene compositions also lie along a well-defined array with a relatively shallow slope, on a plot of Na$_2$O versus Cr$_2$O$_3$ (Fig. 5d). However, a second group is distinguished by having a steeper slope on this plot, and mainly comprises some of the chromitite-bearing dunites (Fig. 5d). The Mg# values of the second group are high (i.e., mainly >0.96) compared to those of the first, and TiO$_2$ remains comparatively low (<0.1 wt.%). Interstitial clinopyroxene in chromitite-bearing dunite LK38a has the highest Na$_2$O of any measured in this study (up to 0.67 wt.%) and some of the highest Cr$_2$O$_3$ contents (>1.1 wt.%).

The relationships between the components Na+Cr (kosmochlor), Na+Al$^\text{VI}$ (jadeite) and Mg+Ca (diopside) in the LOC clinopyroxenes shows that these variations do not represent ideal (equilibrium) substitutions (Fig. S3b), and point to exchanges involving other elements (Fe and Al). The positive correlations between (refractory) Cr and relatively incompatible Na and Ti suggests that the interstitial melts represented by the clinopyroxene in the dunites did not crystallise from evolved magma compositions. Similar chemical relationships are observed within the wehrlite (LK38b[ii]) zoned clinopyroxene crystals (Fig. 4), with Si+Mg(+Ca)-rich and Al+Cr+Na(+Ti+Fe)-poor rims. Coupled with the textural characteristics of the most Na-rich clinopyroxene measured here (i.e., interstitial character and zoning; Figs. 3, 4), these observations suggest that a disequilibrium (reactive) process was responsible. It is thus suggested that both channelised and porous reactive melt percolation occurred in the LOC during SSZ magmatism, such that the SSZ low Al, low Cr, high Mg# signature is locally preserved in interstitial clinopyroxene in harzburgites and websterite-wehrlite, as well as in demonstrably SSZ-related lithologies such as the dunite
channels. The variation of clinopyroxene compositions preserved in most samples, including within individual crystals in certain samples (Figs. S3, 5), suggests that much if not all of the range of interaction between both endmembers is preserved in them.

*High-Mg clinopyroxene*

Clinopyroxene in the various LOC peridotites is characterised by relatively high Mg# values. Corresponding olivine-clinopyroxene pairs (i.e., mean Mg# values from each sample) suggest that the clinopyroxene and olivine are not in magmatic equilibrium with one another, with the clinopyroxene having consistently higher Mg# values than equilibrium Fe/Mg partitioning would have resulted in (Fig. 10a,b). High Mg# clinopyroxene in the lower oceanic lithosphere can be (1) a function of crystallisation at high pressure (Elthon et al., 1992), (2) subsolidus equilibration of olivine and clinopyroxene (Meyer et al., 1989), or (3) melt-rock reaction (e.g., Bédard et al., 2000; Lissenberg and Dick, 2008; Sanfilippo et al. 2013). The observations that clinopyroxene occurs interstitially (i.e., a late crystallising phase) in many samples and that high average clinopyroxene Mg# values typically occur in samples with the most magnesian olivines make it unlikely that (1) high pressure crystallisation or (2) subsolidus equilibration are responsible. The clinopyroxene crystals with the highest Mg# are those that occur complexly intergrown with olivine in the harzburgites and those that occur as interstitial phases in some of the lower crustal rocks (Fig. 3c,d; see also the back-scattered electron micrographs presented in the Supplementary Tables).

Plümper et al. (2012) reported high-Mg clinopyroxene ‘aggregates’ in their studied harzburgites and referred to these as being hydrothermal in origin, noting that this is a common characteristic of secondary clinopyroxene in meta-peridotites (see also Frost 1975 and Evans 1977). Based on our textural observations, as well as the (intra-sample) compositional variations observed over relatively small length-scales in different LOC lithologies, we concur with the interpretation of Plümper et al. (2012) that the high-Mg clinopyroxene has a metasomatic origin. To be more specific, we suggest that the crystallisation of high Mg# clinopyroxene is a function of fluid-assisted SSZ melt-rock reaction, with consequent olivine dissolution and Mg uptake by clinopyroxene. This is supported by the observation that intergrown olivine-clinopyroxene textures interpreted as having formed by reaction also have the highest Mg# values, relative to sample averages (see maps in Supplementary Tables). It is noteworthy that even the relatively Cr- and Al-rich clinopyroxenes from samples LK-12-14, LK37 and LK38b(ii) have higher Mg# than
predicted by equilibrium partitioning (Fig. 10a). This is possibly because pervasive (diffuse) SSZ-related melt infiltration has reset clinopyroxene Mg# in all samples to some extent.

**Clinopyroxene Cr and Na covariation**

Sympathetically increasing Cr and Na in clinopyroxene is not predicted by established partitioning behaviour, though has been reported from metasomatized mantle xenoliths and orogenic peridotites (Kornprobst et al., 1981). Partition coefficients for Cr between likely basaltic melt compositions and clinopyroxene suggest moderately to strongly compatible behaviour ($D_{Cr}^{cpx/melt}$: 3-36; Dale and Henderson, 1972; Rollinson, 1993; Hart and Dunn, 1993), whilst Na values should be mildly incompatible ($D_{Na}^{cpx/melt}$: 0.1-0.5; e.g., Blundy et al., 1995). Values for $D_{Na}^{cpx/melt}$ in basalt magma exhibit a systematic pressure dependency (increasing with increasing pressure) and have also been suggested to increase with $fO_2$ Blundy et al. (1995). To test whether melt-rock reaction could theoretically produce the observed coupling of Na-Cr in clinopyroxene in certain LOC dunites, and to constrain the conditions under which this occurred, we carried out assimilation-fractional crystallisation (AFC) modelling. As suggested above, fractional crystallisation alone cannot produce the observed correlation between Na and Cr; indeed, the conditions leading to the observed clinopyroxene compositional variations appear to be quite restricted. A scenario involving Cr and Na contents typical of subduction-type parental magmas (i.e., 0.1 and 1-3.5 wt.% respectively, in an arc tholeiite; Schmidt and Jagoutz, 2017), as well as representative concentrations measured in LK38b(i) clinopyroxene here, and assuming a monomineralic (clinopyroxene) assimilant, was modelled. Using reasonable values for $D_{Cr}^{cpx/melt}$ (3.8) and $D_{Na}^{cpx/melt}$ (0.1), and a rate of fractional crystallisation about twice that of assimilation, we see that the AFC crystals produced may exhibit sympathetic covariation in their Na and Cr concentrations, albeit at lower increases in the former with respect to the latter than seen in the LOC data (Fig. S6a). Points of interest to note from this model are that significant fractional crystallisation is required to drive assimilation, although arguably the process of melt throughflow could supply the required heat for dissolution as well. The model is simplistic and it is unlikely that the melt-rock reaction processes envisaged here occurred under equilibrium and/or closed system conditions.

We obtain a better (steeper) correlation in the model by varying $D_{Na}^{cpx/melt}$, through each increment of the model (Fig. S6b), up to a maximum of 0.5. Given the crystallisation of abundant Cr-spinel (i.e., chromitite; LK38a) in proximity, it may not be unreasonable to
consider that $f\text{O}_2$ variation occurred over the lifetime of the LK38b(i) melt channel. Blundy et al. (1995), based on Toplis et al. (1994), emphasised the potential importance of the stabilisation of the acmite ($\text{NaFe}^{3+}\text{Si}_2\text{O}_6$) component in clinopyroxene to increasing $D_{\text{Na}}^{\text{cpx/melt}}$. It is therefore notable that the acmite component increases in some LK38 samples to the maximum observed in the LOC dataset (see Supplementary Tables 2). The AFC model curves in Figure S6 best match the range of clinopyroxene Cr variation at relatively high melt fractions (0.9 – 0.6), lending qualitative support to the idea of open system melt percolation. The array with the steeper slope on the plot of Na$_2$O versus Cr$_2$O$_3$ may represent a temporally or locally distinct generation of melt percolation compared to the main array (Fig. 5d).

**Petrogenesis of complexly zoned clinopyroxene by crystal-melt reaction**

The LA-ICP-MS data for clinopyroxene crystals provide evidence for coupled dissolution-crystallisation episodes, particularly in wehrlite LK38b(ii), although the zoning observed in clinopyroxene in this sample is observed in mantle websterite and clinopyroxene-bearing dunite too. The Al- and Cr-poor second-generation overgrowths are separated from crystal cores by irregular surfaces that are interpreted as dissolution interfaces (Fig. 4b,c). The fact that these overgrowths tend to have relatively slightly elevated La (manifested as high La/Sm; typically >0.25; Fig. 8b), as well as higher Mg#, suggests crystallisation from a compositionally distinct melt to that which crystallised the cores (with typical La/Sm values <0.25). Similar patterns of intracrystalline microstructural and chemical heterogeneity in clinopyroxene oikocrysts to those described above have been reported from layered mafic intrusion (Leuthold et al., 2014) and MORB-related oceanic gabbros (Leuthold et al., 2018) settings, where they have been attributed to reactive percolation of relatively primitive melts in gabbroic rocks, and subsequent crystallisation from the resultant hybrids. A key observation from Leuthold et al. (2014) is that a stepwise depletion in Cr content in clinopyroxene overgrowths (concomitant with depletion in Ti, Al and Na) was due to the increased stability of Cr-spinel following mixing of primitive and evolved melts (see also Irvine, 1977; O’Driscoll et al., 2010; Leuthold et al., 2015); by analogy, we suggest that the process of melt-rock reaction might also produce ‘hybrid’ melts capable of crystallising not just the range of clinopyroxene compositions observed within individual crystals here, but also abundant Cr-spinel, and that this process is recorded by the Cr-Al depletion observed in the clinopyroxene from LK38b(ii). These observations suggest that evidence for melting-assimilation-storage-homogenisation (MASH)-style processes is preserved in the lower
oceanic crust, as also recently proposed by other authors (e.g., Leuthold et al., 2018; Bennett et al., 2019).

Clinopyroxene-Cr-spinel compositional covariation

The composition of Cr-spinel in mantle and lower crustal ultramafic rocks is a function of several controlling factors, including the composition of the parental melt and post-crystallisation equilibration with host silicates (Barnes and Roeder, 2001). Relatively high Cr# values and TiO$_2$ contents for Cr-spinel in the dunites and chromitites suggests that they formed by SSZ-related magmatic processes. This is also supported by microstructural evidence from these samples – for example, dunites (e.g., LK35, LK38a) are characterised by greater abundances (i.e., than surrounding harzburgites) of disseminated euhedral Cr-spinel crystals that define a planar fabric parallel to dunite channel boundaries (Fig. S1b). Vanadium Cr-spinel contents progressively decrease from the harzburgites to the dunites, and further to the chromitite (LK32), suggesting crystallisation from increasingly oxidising melts (Pagé and Barnes, 2009). A plot of average sample clinopyroxene versus Cr-spinel Cr# values highlights that these phases are not in magmatic equilibrium in the sample suite, i.e., no correlation is observed (Fig. 10c). The highest clinopyroxene Cr# values are in the harzburgites, corresponding to the lowest Cr-spinel Cr# values. Relatively low clinopyroxene Cr# values generally correspond to higher Cr-spinel Cr#, apart from LK22 (harzburgite) which is displaced to much higher Cr-spinel Cr# as a result of the predominantly ferrian chromite compositions it contains. We suggest no other singular process can account for the distribution of these data as well as melt percolation and melt-rock reaction. Figure 6 shows that most samples contain the low-Al ferrian Cr-spinel as rims on crystals and as inclusions in DPOs; these are interpreted as a hydrothermal overprint that may be associated with or post-date SSZ processes.

Localised dehydration of the LOC mantle

Domain parallel olivine (DPOs) in LOC harzburgite were interpreted by Plümper et al. (2012) to represent dehydration of bastite-pseudomorphed orthopyroxene. The range of harzburgite-hosted clinopyroxene compositions (high Al, high Cr, low Mg lamellae, low Al, low Cr, high Mg aggregates) described by the latter authors compares well to that observed here. However, we note that clinopyroxene in mantle and lower crustal-hosted wehrlites-websterites has even higher Al and Cr contents (Fig. 6a,b,d). Additionally, low Al, low Cr, high Mg clinopyroxene is observed in most other lithologies of the LOC (Fig. 6a,b),
extending to higher Mg than those compositions reported by Plümper et al. (2012). The latter workers were somewhat equivocal on the nature of the dehydration event responsible for forming the DPOs in their samples. Our observations suggest that DPOs such as that shown in Figure S1a may not be a ubiquitous feature of LOC harzburgites. We note that they are common in samples from close to the Moho, where the abundance of dunite channels and dunitised harzburgite is much higher, compared to samples from the area southwest of Leknes (Fig. 1; not studied here, but refer to O’Driscoll et al., 2015). It is therefore reasonable to suggest that the cause of the dehydration may have been the channelised SSZ-related melt percolation event(s) that formed the dunites, a conclusion supported by a recent halogen and noble gas isotope study of mantle and lower crustal rocks from the LOC (Carter et al., 2021).

Although there is abundant evidence for channelled melt percolation in the LOC mantle (as described above), evidence for significant (porous) melt throughflow in the LOC harzburgites is absent (e.g., from whole rock chemistry, Os isotopes), although minor LREE enrichment in most samples suggests this did occur at a limited scale (O’Driscoll et al. 2015; Haller et al., in press). As an additional line of support, and in agreement with Plümper et al. (2012), we find scant evidence for mobilisation of chemical components in the harzburgites. For example, the formation of a large quantity of ferrian Cr-spinel in the DPOs is not associated with a noticeable increase in bulk rock Cr concentrations, and across all the LOC harzburgites analysed by O’Driscoll et al. (2015) Cr concentrations are identical within uncertainty to typical abyssal peridotite compositions [LOC average of 2523 ±277 μg g⁻¹ [1σ; n= 15], to typical abyssal (harzburgite) peridotite compositions (2532 ±311 [1σ; n=22]; compilation of Day et al., 2017). We therefore suggest that the cryptic dehydration event observed in some LOC harzburgites may have been caused by the thermal effects of proximity to the dunite channels during SSZ-related melt percolation.

Insights into the redox state of the sub-arc mantle from the LOC

Oxygen fugacity in the upper mantle

A common approach to estimating fO₂ variation in upper mantle samples is by geothermobarometry, using the reaction:

\[ 6\text{Fe}_2\text{SiO}_4 \text{ (olivine)} + \text{O}_2 = 3\text{Fe}_2\text{Si}_2\text{O}_6 \text{ (orthopyroxene)} + 2\text{Fe}_3\text{O}_4 \text{ (spinel)} \]

(Mattioli and Wood 1986; O’Neill and Wall 1987; Wood et al., 1990; Ballhaus et al., 1991). This relationship yields values for T, P and fO₂ based on phase equilibria involving minerals...
with variable Fe\(^{2+}/Fe^{3+}\) ratios (i.e., olivine, orthopyroxene and spinel). Of these, accurate
determination of the Fe\(^{3+}/\Sigma Fe\) ratio in spinel is the most essential input variable. However, it
has been established that the approach to quantifying Fe\(^{3+}/\Sigma Fe\) may also be important. Small
to errors in the estimation of this ratio, such as those potentially introduced using electron
microprobe measurements, may produce large errors in the evaluation of mantle parameters
and therefore hamper petrologic interpretations (Wood and Virgo 1989; Sobolev et al., 1999).
These issues arise mainly because of the non-stoichiometry of Fe\(^{3+}\)-rich Cr-spinels, with
implications for the procedure used to calculate Fe\(^{3+}\) from EPMA data. For these reasons,
Mössbauer spectroscopy, or an approach correcting EPMA data using standards analysed by
Mössbauer spectroscopic data (cf. Wood and Virgo 1989), has been considered a more
reliable approach. Here we compare Fe\(^{3+}/\Sigma Fe\) variations from EPMA, single crystal XRD and
Mössbauer and use these and other data to evaluate the redox state of the sub-arc mantle as
represented by the LOC.

\textit{Mössbauer versus EPMA Fe\(^{3+}\) analyses and redox state of the LOC during SSZ processing}

The average EPMA Fe\(^{3+}/\Sigma Fe\) values shown in \textbf{Figure 9a} are filtered to remove ferrian Cr-
spinel compositions, which we consider as likely having formed during dehydration reactions
and/or low temperature metamorphism, on the basis of their microstructural characteristics.
\textbf{Figure 9a} shows that harzburgite Fe\(^{3+}/\Sigma Fe\) values are generally relatively low, compared to
dunite and chromitite Fe\(^{3+}/\Sigma Fe\). Intra-sample variation is fairly limited, but slightly greater in
some dunites than in the harzburgites. The EPMA Fe\(^{3+}/\Sigma Fe\) values do not correlate especially
well with the Mössbauer values from corresponding samples (\textbf{Fig. 9a}). In contrast to other
studies, which have reported that calculations based on EPMA data generally underestimate
the Fe\(^{3+}/\Sigma Fe\) as indicated by Mössbauer analyses (Quintiliani et al., 2006; Adetunji et al.,
2013; Rollinson & Adetunji, 2013, and references therein), our EPMA Fe\(^{3+}/\Sigma Fe\) sample
averages mainly overestimate the corresponding Mössbauer measurement. The data exhibit a
general pattern based on lithology. Harzburgite EPMA Fe\(^{3+}/\Sigma Fe\) ratios may be lower or
higher than the equivalent Mössbauer values, but lie close to the 1:1 line (\textbf{Fig. 9a}). By
contrast, dunite and chromitite EPMA Fe\(^{3+}/\Sigma Fe\) typically extend to higher values than their
associated Mössbauer Fe\(^{3+}/\Sigma Fe\).

No correlation is observed between Cr# and Mössbauer Fe\(^{3+}/\Sigma Fe\) or between Cr# and
the difference between average EPMA and Mössbauer Fe\(^{3+}/\Sigma Fe\) values (cf. Wood and Virgo,
1989; \textbf{Fig. 9b}), suggesting that reconciling the EPMA and Mössbauer values may not be
possible, particularly for the dunite and chromitite samples. We cannot rule out that the stoichiometric calculation from the EPMA data has overestimated the true Fe$^{3+}$/ΣFe ratio in some or most of the individual analyses. However, we suggest that the tendency for the harzburgite Cr-spinels to have relatively low Fe$^{3+}$/ΣFe (as measured by both EPMA and Mössbauer), compared to the dunites, implies a real petrogenetic control. As noted above, other aspects of the mineral chemistry of the harzburgite Cr-spinels suggest that these may be original accessory phases from the residual peridotites (i.e., pre-SSZ processing; Fig. 6b), and these low Fe$^{3+}$/ΣFe values, particularly in samples LK40 and LK53, point to formation in a relatively reduced setting such as an open ocean spreading ridge (Rollinson and Adetunji, 2014). Sample LK53, for which the EPMA and Mössbauer methods return relatively similar Fe$^{3+}$/ΣFe values (0.12 and 0.101, respectively; Fig. 9a), yields log($f$O$_2$)$_{FMQ}$ of ~1.8 using the oxygen barometer of Ballhaus et al. (1991), lending further support to this conclusion. Calculation of oxygen fugacities from the dunites and chromitites in this way is less straightforward, because of the offset between the EPMA and Mössbauer Fe$^{3+}$/ΣFe values. However, using the cation distributions determined from the single-crystal X-ray structural refinements and coupled electron microprobe analyses (cf. Lenaz and Schmitz, 2017), we calculate Fe$^{3+}$/ΣFe of 0.21 and 0.15 for samples LK38a (dunite) and LK32 (chromitite), respectively (see Table 2). These Fe$^{3+}$/ΣFe values yield log($f$O$_2$)$_{FMQ}$ of +1.22 (LK38a) and +1.79 (LK32). The latter $f$O$_2$ estimates suggest relatively oxidising conditions, so are consistent with these lithologies being generated during SSZ processes, as previously suggested by their geochemical characteristics, including Re-Os isotopes (O'Driscoll et al., 2015). It is also worth noting that for LK32, the Mössbauer Fe$^{3+}$/ΣFe value of 0.179 means that the log($f$O$_2$)$_{FMQ}$ of +1.79 is likely an underestimate.

The corresponding temperatures calculated for Mg-Fe$^{2+}$ diffusional closure in LK32 and LK38a are 621 °C and 753 °C, respectively, suggesting a degree of subsolidus chemical equilibration in these rocks, which is a known effect in olivine-Cr-spinel assemblages in mafic-ultramafic rocks in general (Barnes and Roeder, 2001). Based on the significant amount of Cr-spinel in these samples relative to olivine, consideration of the lever rule suggests that the olivine may have become significantly more magnesian whilst the Cr-spinel composition remained relatively constant; e.g., note the olivine Fo contents up to 98 in LK32. The temperatures calculated using the Ballhaus et al. (1991) thermometer are lower than the intracrystalline closure temperatures calculated using the single crystal XRD data, following Princivalle et al. (1999), with LK38a yielding a temperature of 850 °C and LK32 a
temperature of 857 °C (see Table 2). The differences observed in these temperatures are likely due to the crystals for XRD analysis being separated from the interiors of chromitite seams, further from the nearest olivine crystal than the bulk rock average olivine and Cr-spinel compositions used with the Ballhaus et al. (1991) thermometer represent. In other words, most of the olivine analysed in these two samples comes from close to the edges of the respective chromitite seams they contain, and olivine-Cr-spinel subsolidus exchange reactions were likely restricted to short (sub-mm) length-scales. The harzburgite LK53 yields a Mg-Fe\textsuperscript{2+} closure temperature of ~1210 °C using the Ballhaus et al. (1991) thermometer.

**Insights from the V-Sc fO\textsubscript{2} proxy**

The multi-valent nature of V (V\textsuperscript{2+}, V\textsuperscript{3+}, V\textsuperscript{4+}, V\textsuperscript{5+}) means that its concentration in mantle peridotites has been utilised as a proxy for fO\textsubscript{2} conditions during petrogenesis. Vanadium is potentially less susceptible to modification by metasomatism than the Fe\textsuperscript{3+}/Fe\textsuperscript{2+} ratio, and when combined with Sc (or Ga) which are similarly incompatible but not redox sensitive, an indication of oxygen fugacity conditions during melt extraction or melt percolation can be revealed (Lee et al., 2005). In general, V/Sc of residual peridotites should decrease with melt extraction when fO\textsubscript{2} ≥ 1 log unit below FMQ (i.e., <FMQ -1). Under more reducing conditions, V/Sc increases in the residue as V compatibility becomes greater than that of Sc in clinopyroxene and spinel. Plotting the harzburgite whole rock data of O’Driscoll et al. (2015) in the context of the relationships established by Lee et al. (2005), a negatively correlated array spanning fO\textsubscript{2} of <FMQ -2 to ~FMQ (Fig. 11a) is observed, suggesting an evolution toward more oxidising conditions as SSZ melt extraction and/or percolation proceeded. The dunites and websterites/wehrlites are not considered here as these lithologies are interpreted as being wholly the products of melt-rock reaction (cf. Lee et al., 2005). Indeed, Carter et al. (2021) have recently shown that the LOC dunites preserve volatile (halogen and noble gas isotope) element signatures of altered oceanic crust and organic-rich sedimentary pore fluid, strongly suggestive of the transit of subduction zone melts.

Our interpretation of the harzburgite V/Sc trend is in good agreement with inferences drawn for the same samples based on their relationship in V versus Yb space (see O’Driscoll et al., 2015), together with the models of Pearce and Parkinson (1993) and Parkinson and Pearce (1998). Figure 11b shows V/Sc plotted against γOs (calculated percent deviation from a chondritic reference at the time of formation; 497 Ma; data from O’Driscoll et al., 2015) for the LOC harzburgites. The harzburgites with the lowest γOs values, which are also those with the oldest Os isotope model ages (up to ~1 Ga) are generally also those with the
highest V/Sc. This observation supports the idea that SSZ melt extraction from the LOC mantle at ~497 Ma only partially overprinted mantle from which melt had been extracted at an earlier stage, under more reduced conditions.

Information can be retrieved from single crystals as well as bulk rock analyses. Figure 11c shows the bulk rock data in the context of V and Sc contents in clinopyroxene (as well as olivine and Cr-spinel measurements collected in the same analytical sessions). Variations of V/Sc in clinopyroxene from samples LK2, LK5, LK35 and LK38b(ii) suggest the presence of distinct clinopyroxene populations in all of these samples (Fig. S3e). Clinopyroxene in LK38b(ii) appears to exhibit the least scatter, with relatively high V/Sc (>2) and Sc abundances (>90 μg g⁻¹), albeit subtle but consistent differences are even observed between individual crystals in this sample too (Fig. S3f). Crystal rims tend to relatively high Sc contents and low-intermediate values of V/Sc, whereas crystal cores have higher V/Sc and lower Sc abundances. Assuming that V/Sc partitioning between clinopyroxene and silicate melt is relatively insensitive to melt composition, pressure, temperature (e.g., Mallmann and O’Neill, 2009; Li, 2018), these variations may mean that the melt percolation processes responsible for the intracrystalline chemical variations were associated with subtle fO₂ increases during the putative dissolution-crystallisation reactions. Values of V/Sc in samples LK2 and LK35 are generally low (<2) over a wide range of Sc contents (30-110 μg g⁻¹), perhaps consistent with them being clinopyroxene from SSZ-related chromitite-bearing dunite. In LK5, a rare gabbro from the lower crustal portion of the LOC, clinopyroxene cores have V/Sc ranging up to ~5. Based on the field relationships suggesting that this gabbro predates some dunites, it is possible that these clinopyroxenes crystallised from less oxidised, pre-SSZ magmas.

A forearc origin for the LOC

An important result of the new Mössbauer data is that the SSZ upper mantle as represented by the LOC preserves evidence of an evolution towards higher Fe³⁺/ΣFe during formation of the dunites, but at log(fO₂)FMQ of up to ~+1.8 is not highly oxidised overall. By comparison, a suite of chromitites from the Oman ophiolite yielded an average Mössbauer Fe³⁺/ΣFe of 0.357 (range of 0.171-1, ±0.2 [1σ], n=28; Rollinson & Adetunji, 2013). The observations from the LOC lend support to the findings of Parkinson and Arculus (1999), in their study of recent (~zero age) arc peridotites from a range of arc settings, and Mallmann and O’Neill (2009) in an experimental study on V partitioning behaviour. For example, Parkinson and Arculus (1999) suggested that the sub-arc mantle, as represented by their peridotite samples,
was relatively oxidised \( (f_O^2)_{FMQ} \) of +0.3 and +2) compared to oceanic or cratonic mantle, but not compared to the oxidation state of typical arc basalts \( (f_O^2)_{FMQ} \) of +2. To explain the discrepancy, Parkinson and Arculus (1999) postulated that the source was oxidised before melting and that decompression melting, which potentially has the effect of forming magmas with a higher \( f_O^2 \) than that of the source, must have occurred. However, this concept does not easily explain Cr-spinel \( Fe^{3+}/ΣFe \) in the LOC peridotites, which record a stage in the process post source-melting, where the melts are in transit, perhaps to supply surface volcanism.

The Madsøya basalt pillow lavas contain relatively high \( Fe_2O_3 \) contents (>5 wt.%; typical of arc tholeiites; Furnes et al., 1992), so assuming association, some explanation is required for why the ‘fossil’ melt channels studied here don’t preserve a record of throughflow of more oxidised magmas. One possible reason is that the LOC formed in a forearc setting (similar to some of the materials studied by Parkinson and Arculus, 1999) but that it preserves only an early stage (and overprint) of SSZ processing and hence oxidation. This would fit with the evidence presented above for early (pre-SSZ) clinopyroxene and Cr-spinel in the LOC rocks, but also implies that the Madsøya pillow basalts may not have a direct genetic link to the lower crustal and mantle rocks, i.e., they were structurally juxtaposed at a later stage. Such a possibility is permitted by the faulted contacts observed between the Madsøya basalts and other components of the LOC. Arc composition (and hence redox state) may vary significantly at the subduction initiation-forearc stages (Whattam and Stern, 2011), so further progressive oxidation of the LOC mantle and lower crust would be required for them to serve as a source for the highly oxidised basalts typical of mature arcs. In turn this suggests that the LOC (and potentially other lower Palaeozoic ophiolites of the Caledonian orogenic belt e.g., the Shetland Ophiolite Complex) may represent fruitful localities to examine the effects of magmatism and redox variations within a newly developing subduction zone.

**Mantle oxidation state through time**

In addition to placing constraints on the oxidation state of the sub-arc mantle in the lower Palaeozoic Iapetus Ocean lithosphere, our data provide some insight into the utility of ophiolites for estimating mantle oxidation through geological time. Rollinson et al. (2017) compiled Mössbauer data from ophiolite and other chromitites spanning the time 3.8 Ga to 90 Ma and concluded from those data that the oxidation state of the mantle has been relatively constant since the early Archean. In contrast, Stolper and Keller (2018) analysed \( Fe^{3+}/Fe^{2+} \) compositional variations in hydrothermally-altered basalts from a range of ophiolites.
spanning >3.5 Ga to 90 Ma with the aim of establishing the timing of oxygenation of the deep ocean. The latter authors found that between 3.5 Ga and 540 Ma, the ophiolite Fe$^{3+}$/ΣFe record remained relatively constant, but that basalts in ophiolites younger than 540 Ma preserve evidence of increasing degrees of oxidation (Fig. 12). They attributed this to lower Palaeozoic oxygenation of the deep ocean and speculated that increased rates of subduction of these altered and oxidised materials into the mantle in the Phanerozoic were probably responsible for progressive oxidation of this reservoir over the past ~540 Ma. Comparisons of the Rollinson et al. (2017) compilation with the data of Stolper and Keller (2018) are naturally qualitative by virtue of the different techniques used to determine Fe$^{3+}$/ΣFe, but it seems clear from the former study that mantle chromitites do not solely record an increasingly oxidised mantle through time.

The new LOC chromitite data shed further light on these questions, particularly when combined with published Oman and other (Indo Myanmar) chromitite data (Rollinson & Adetunji, 2013; Lenaz et al., 2014a; 2014b). The Fe$^{3+}$/ΣFe values recorded by LOC and some Oman chromitites are the least oxidised of any in this combined dataset measured to date (Fig. 12), suggesting that the oxidation history of the mantle may be more complicated than prior studies suggest. From these comparisons, we suggest here that the Fe$^{3+}$/ΣFe signatures of ophiolite chromitites may have more to do with local environmental petrogenetic conditions of formation in sub-arc systems than large length-scale mantle chemical evolution. This is supported by recent studies of Fe isotopes ($\delta^{56}$Fe) in ophiolite chromitites from Luobosa (Tibet) and Kizildag (southern Turkey), which indicate redox fluctuations within and between different chromitite bodies, even from the same ophiolite (Chen et al., 2015).

However, Mössbauer Fe$^{3+}$/ΣFe data from a much larger sample set of Phanerozoic and pre-Phanerozoic ophiolite chromitites will be required to shed further light on these open questions. In addition, placing stronger field and geochronological constraints on the extent to which the different parts of ophiolites such as Leka are petrogenetically related will enable the Fe$^{3+}$/ΣFe dichotomy between the mantle and upper crustal (i.e., basaltic) portions reported here and more generally (e.g., Parkinson and Arculus, 1999) to be better understood.

CONCLUSIONS

Field observations, microstructural relations and mineral chemical data collectively reveal a rich record of supra-subduction zone-related melt percolation and melt-rock reaction in the
mantle and lower crustal sections of the ~497 Ma Leka Ophiolite Complex. The effects of SSZ-related reactive melt percolation are observed over mm-dm length-scales and involved the formation of dunite, chromitite and orthopyroxenite veins and lenses. The magmatism associated with the latter group of lithologies appears to overprint an earlier (pre-SSZ) suite of rocks including, but not restricted to, wehrlite and websterite bodies. The lower crustal sequence represents a reactive filter comprising pre-SSZ materials intruded by dunite-forming magmas during subduction zone processes. A subset of the harzburgites studied also preserve evidence for pre-SSZ processes (i.e., in their Cr-spinel compositions and calculated \( f_{O_2}^{FMQ} \) of ~1.8). Point-source Mössbauer data from Cr-spinel in dunite and chromitite reveal relatively low Fe\(^{3+}/\Sigma Fe\) ratios (<0.18; i.e., compared to those calculated from EPMA data), and are also low when compared to Mössbauer Fe\(^{3+}/\Sigma Fe\) ratios from other ophiolite chromitites (e.g., Oman; Rollinson & Adetunji, 2013). This suggests that SSZ-related melt percolation did not occur in a particularly oxidised environment and calculated values of \( f_{O_2}^{FMQ} \) are <+1.8, compared to typical arc basalts (\( f_{O_2}^{FMQ} \) of >>+2) such as those preserved in the upper section of the LOC. The LOC basalts may not, therefore, be genetically related to (i.e., sourced from) the oceanic lithosphere represented by the lower portions of the ophiolite. On the basis of these arguments, the LOC mantle and lower crust may have formed at an early stage of subduction zone development, i.e., in a forearc setting. The relatively low values and range of Fe\(^{3+}/\Sigma Fe\) revealed by the LOC Cr-spinel Mössbauer data (Fig. 12) also have implications for the use of ophiolite chromitites as recorders of mantle oxidation state through time, as proposed by some authors (Rollinson et al. 2017). We suggest that the Fe\(^{3+}/\Sigma Fe\) signatures of ophiolite chromitites have more to do with local environmental petrogenetic conditions of formation in sub-arc (and possibly other) systems than large length-scale mantle chemical evolution.

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**Figure 1.** Geological sketch map of the Leka Ophiolite Complex. The mantle section is mainly composed of harzburgite and the lower crustal component mostly comprises layered dunite and wehrlite. The dashed lines in the main map panel represent faulted contacts. The approximate position of the petrological Moho visitor site is shown by the circled ‘M’. This map is modified from Figure 1 of O’Driscoll et al. (2015), itself adapted from Pedersen et al. (1993). The inset on the left is a regional and tectonic map of southwestern Norway and northern Scotland showing the positions of other lower Palaeozoic ophiolites (Karmoy and Unst) relative to Leka. The inset on the bottom right shows a schematic section across the Moho at A-A* on the map. Note the discordance of the lower crustal layering with the Moho, and the distribution of dunite and pyroxenite in the upper mantle portion.

**Figure 2.** Field photographs of features of the mantle and lower crustal lithologies of the LOC. (a) Vertically-oriented dunite channel (light brown), showing diffuse contacts with harzburgite on either side from the LOC mantle section. The full length of the hammer shown for scale is 30 cm. (b) Dunitised harzburgite in the mantle section, wherein irregularly-shaped volumes of dunite occur in and around clots and fragments of harzburgite, the latter including aggregates of orthopyroxene pseudomorphs. The red square delineates an area of dunite containing typically abundant Cr-spinel crystals in this lithology. (c) Chromitite seam encased in dunite envelope in the mantle section. Layers of Cr-spinel-rich dunite and other chromitites occur in the host rocks on either side of the central dunite-chromitite body. The marker pen is 15 cm long. (d) Composite orthopyroxenite (reddish-coloured)-websterite (greenish-coloured) pod, encased in harzburgite, in the mantle section. Top of persons boot for approximate scale. (e) Typical layered outcrop from the lower crustal section and the locality from which the LK38 samples come (red squares show approximate sampling positions). Layering is vertically-oriented. LK38a and LK38b(i) are chromitite seams in dunite, LK38b(ii) is a wehrlite and LK38c is a sulfide-rich dunite. Pen for scale is ~15 cm long. (f) Crystals and glomerocrysts of clinopyroxene (outlined in red squares) incorporated into a diffuse chromitite seam in a lower crustal section dunite. The coin at the top left of the image has a diameter of ~3 cm. Abbreviations used are as follows: Harz = harzburgite; Dun = dunite; Dun-Harz = dunitised harzburgite; Chrmte = chromitite; Opxite = orthopyroxenite; Webs = websterite.

**Figure 3.** Backscattered electron micrographs of mineralogical and microstructural features of interest from various LOC lithologies. Sample labels are shown at the bottom left of all images. (a) Example of DPO texture in mantle harzburgite. The DPO comprises the entire
image below the red line, which delineates the approximate outer margin of the DPO. Note the high abundance of crystallographically-constrained fine-grained Fe-Cr-rich oxides within the DPO. (b) Outer margin of DPO (marked by red line) illustrating the complex olivine-clinopyroxene-serpentine-oxide intergrowth texture within the DPO, and coarse-grained olivine without. (c) Close-up of intergrown olivine (dark-grey), patchy clinopyroxene (light grey) and oxide (white) within a DPO. Note the skeletal morphology of the larger oxide crystals. (d) Coarse-grained olivine in dunite from the lower crustal section. Note the subhedral Cr-spinel (white) at bottom of image, and the thin branching veinlets of clinopyroxene (lighter grey) that cut through the olivine crystal. The three white arrows mark the position of one such veinlet. Although fine-grained oxide crystals are present throughout, there is a propensity for these to be concentrated in the veinlets with the clinopyroxene. (e) Accessory Cr-spinel crystal in sulfide-bearing dunite from the lower crustal section. Note the Fe-rich rim on the Cr-spinel, and the anhedral sulfide bleb attached to the edge of the grain. The sulfide is composite, comprising pentlandite (light grey) and pyrrhotite (darker grey). (f) Anhedral awaruite grain (light grey, centre of image) in chromitite-bearing dunite from the lower crustal section. The small white grains below the awaruite are platinum-group minerals. Abbreviations used are as follows: Ol = olivine; Cpx = clinopyroxene; Crs = Cr-spinel; FeCr = ferrian Cr-spinel; Pn = pentlandite; Py = pyrrhotite; Aw = awaruite; PGM = platinum-group minerals.

**Figure 4.** (a and b) Element maps of clinopyroxene from wehrlite LK38b(ii) acquired by EPMA. (a) Chromium map with the clinopyroxene crystal analysed by LA-ICP-MS shown in the red square and (b) Aluminum map of the area in the red square in (a). Note the compositional zoning in the crystal of interest (darker grey margins) and bright (Fe-Cr-rich) inclusions in the interior high-Al-Cr portion (core) of the crystal (i.e., within the red dashed line). The LA-ICP-MS spots are shown in blue. (c) Chemical profile across zoned clinopyroxene shown in (b). Values of Cr$_2$O$_3$ (filled symbols) show abrupt normal zoning from homogeneous core1 to homogeneous outer mantle (overgrowth) to rim. Core appears relatively enriched in Sm (empty symbols) compared to overgrowth and outer rim, with final strong normal zoning. See Supplementary Table 3 for the plotted data.

**Figure 5.** Clinopyroxene compositional variations in LOC peridotites and pyroxenites. (a) Al$_2$O$_3$ (wt.%) vs. Mg# (Mg/[Mg+Fe$^{2+}$]); (b) Cr# (Cr/[Cr+Al]) vs. Mg#; (c) TiO$_2$ (wt.%) vs. Mg#; (d) Na$_2$O (wt.%) vs. Cr$_2$O$_3$ (wt.%); (e) Na$_2$O (wt.%) vs. Mg#; (f) TiO$_2$ (wt.%) vs. Na$_2$O (wt.%). The fields for abyssal peridotite (grey) and SSZ (orange) clinopyroxene in (a), (b), (c)
and (e) are based on Choi et al. (2008) and references therein. The two fields outlined in red dashed lines on (a) represent the range of high- and low-Al-Cr clinopyroxene compositions from Plümper et al. (2012). The pale versions of symbols represent points measured from a small number of clinopyroxene crystals from those samples.

**Figure 6.** Cr-spinel compositional variations in LOC peridotites and pyroxenites. (a) Cr# vs. Mg#. The fields for boninite and abyssal peridotite Cr-spinel are from Dick and Bullen (1984) and Kepezhinskas et al. (1993). The orange field is the range of peridotite accessory Cr-spinel compositions referred to in Dare et al. (2009). (b) TiO₂ (wt.%) vs. Al₂O₃ (wt.%): In (a) and (b), the compositions of ferrian Cr-spinel rims and inclusions from various samples are shown in a paler version of the symbol/colour for the primary Cr-spinel. The symbols used are otherwise the same as those in previous figures. Abbreviations as before; Wehr = wehrlite.

**Figure 7.** Fields of chondrite-normalised trace element patterns for clinopyroxene crystals measured by LA-ICP-MS (samples LK38b(ii), LK2 and LK5). (a) Incompatible trace element patterns for LOC clinopyroxene together with oceanic pyroxenite clinopyroxene compositions from the Southwest Indian Ridge and the Lena Trough (Dantas et al., 2007, Laukert et al., 2014, respectively). (b) Rare earth element patterns for the LOC clinopyroxenes with those from the oceanic pyroxenites shown in (a), as well as parental melt (labelled PM in key) REE compositions for the high Cr-Al clinopyroxene cores in LK38b(ii) and LK35, calculated using the partition coefficient predictive model of Wood and Blundy (1997). Also shown in (a) and (b) is the bulk rock websterite (LK-12-14) composition of O’Driscoll et al. (2015). The values for CI chondrite used in both panels are from McDonough and Sun (1995).

**Figure 8.** LA-ICP-MS data for clinopyroxene from samples LK38b(ii), LK35, LK2 and LK5. (a, b) La/Sm versus Cr; (c,d) Zr versus Cr; and (e,f) V/Sc versus Sc. For (b), the uncertainty on La/Sm points is smaller than the symbol size. See text for further discussion.

**Figure 9.** (a) EPMA vs. Mössbauer Fe³⁺/ΣFe values and (b) Cr# vs. Mössbauer Fe³⁺/ΣFe for LOC samples. In (a), the EPMA data with uncertainties associated are those Fe³⁺/ΣFe ratios averaged for multiple Cr-spinel measurements from a given sample (at the scale of a single thin section). These data have been filtered for ferrian Cr-spinel compositions as discussed in the text. The uncertainties are 1σ standard deviations. The six EPMA data without
uncertainties shown are those averaged by multiple points on a single crystal – the same crystals in each case as used for the single crystal XRD measurements.

**Figure 10.** (a) Average olivine Fo content versus average clinopyroxene Mg# for LOC samples. Inset shows the area highlighted in green enlarged, with uncertainties on sample averages given as 1 standard deviation. The solid red line illustrates the equilibrium partitioning of Fe and Mg between olivine and clinopyroxene, assuming mineral melt Fe-Mg distribution coefficients of 0.30 and 0.23 for olivine and clinopyroxene, respectively (from Roeder and Emslie, 1970). The dashed lines on either side of the red line represent the uncertainties of 0.02 for each distribution coefficient. (b) Close-up of area highlighted in red in (a). Uncertainties on individual points are 1 standard deviation. (c) Plot of average sample clinopyroxene Cr# versus Cr-spinel Cr# values for LOC samples. The uncertainties shown represent one standard deviation. No correlation is observed, suggesting that these phases are not in magmatic equilibrium. The sample symbols are the same as those used in previous figures.

**Figure 11.** (a) Plot of V/Sc versus Sc (μg g⁻¹) for whole rock LOC harzburgites, with fields shown for dunites, wehrlites and websterites. These data are from O’Driscoll et al. (2015). The isopleths of fO₂ are as calculated by Lee et al. (2005) and illustrate log unit deviations from the fayalite-magnetite-quartz buffer (FMQ). The dunites, wehrlites and websterites (including websterite LK-12-14) are shown for information only; they do not represent residual lithologies so their fO₂ conditions should not be interpreted from this plot. (b) Plot of V/Sc versus γOs (O’Driscoll et al. 2015) for LOC harzburgites. (c) Plot of V/Sc versus Sc (μg g⁻¹) for the bulk rock data of O’Driscoll et al. (2015) with fields of data for the LA-ICP-MS measurements made on clinopyroxene in this study, as well as Cr-spinel and olivine data for these samples (O’Driscoll, B. & Leuthold, J. Unpublished Data). See text for further discussion.

**Figure 12.** Mössbauer Cr-spinel Fe³⁺/ΣFe values from ophiolites of various ages. The Archean Cr-spinel data are from Rollinson et al. (2017). More recent ophiolite Cr-spinel data are from Lenaz et al. (2014a; 2014b) and Rollinson and Adetunji (2013). IM stands for Indo-Myanmar and GOE is Great Oxidation Event. The Mössbauer LOC data of the current study are shown in the red bar. The boxes numbered 1-6 represent Fe³⁺/ΣFe variations in basalts from ophiolites of various ages, after Stolper and Keller (2018). See text for further discussion.
Figure 5

(a) Abyssal peridotite cpx

(b) SSZ peridotite cpx

(c) Mg# (Mg/[Mg+Fe²⁺]) vs. Al₂O₃ (wt. %)

(d) Mg# (Mg/[Mg+Fe²⁺]) vs. Cr# ([Cr]/[Cr+Al])

(e) Mg# (Mg/[Mg+Fe²⁺]) vs. TiO₂ (wt. %)

(f) Mg# (Mg/[Mg+Fe²⁺]) vs. Na₂O (wt. %)

Legend:
- LK17
- LK22
- LK24
- LK35
- LK37
- LK38b(i,ii)
- LK40
- LK-12-14
- LK38c
- LK53

Samples represent various locations and compositions.
**Figure 6**

(a) Cr# [Cr/(Cr+Al)] vs. Mg# [Mg/(Mg+Fe²⁺)]

(b) Cr-spinel TiO₂ (wt.%) vs. Cr-spinel Al₂O₃ (wt.%)

- High-K/Calk Alkaline
- MORB
- Tholeiite
- Island Arc
- Boninite
- Det lim on TiO₂ ~0.03 wt.%
Figure 9

(a) EMPA Fe$^{3+}$/Fe$_{tot}$ ratio vs. Mossbauer Fe$^{3+}$/Fe$_{tot}$ ratio

(b) Mossbauer Fe$^{3+}$/Fe$_{tot}$ ratio vs. Cr-spinel Cr#

Key

- **EPMA**
  - LK17 (Harz)
  - LK40 (Harz)
  - LK53 (Harz)
  - LK35 (Dun)
  - LK38a (Dun)
  - LK38c (Dun)

- **XRD+EPMA**
  - LK1 (Dun)
  - LK30 (Dun)
  - LK31 (Dun)
  - LK35 (Dun)
  - LK52 (Chmte)
  - LK32 (Chmte)
Table 1: Results of structure refinement $a_0$: cell parameter (Å); $u$: oxygen positional parameter; T-O and M-O: tetrahedral and octahedral bond lengths (Å), respectively; m.a.n.T and M: mean atomic number; U(M), U(T), U(O): displacement parameters for M site, T site and O; N. Refl.: number of unique reflections; R1 all (%), wR2 (%), GooF as defined in Sheldrick (2008). Space Group: Fd-3m. Origin fixed at $-3m$. Z=8. Reciprocal space range: $-19 \leq h \leq 19$; $0 \leq k \leq 19$; $0 \leq l \leq 19$. Estimated standard deviations in brackets. Abbreviations as follows: Dun, dunite; Chrmte, chromitite.

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Table 2. Chemical analyses and cation distribution. Mean chemical analyses (10-20 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 Mössbauer analyses, electron microprobe and structural refinement. Cr#: Cr/(Cr+Al); Mg#: Mg/(Mg+Fe$^{2+}$); Fe#: Fe$^{3+}$/(Fe$^{3+}$+Al+Cr); 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 exchange closure temperatures (T °C) were calculated using the thermometer of Princivalle et al. (1999). The thermometer is based on cation order-disorder processes in the T and M sites. *As a consequence of loss of the single crystal used for structural refinement for this sample, we used the average of 26 crystals analysed in LK38a to calculate cation distribution. Abbreviations as follows: Dun, dunite; Chrmte, chromitite.

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Table 3. Mössbauer parameters and $(\text{Fe}^{3+}/\sum\text{Fe})$ from point-source Mössbauer spectroscopic measurements for LOC Cr-spinels. $\delta$: centroid shift (mm/s); $\Delta E_Q$: quadrupole splitting (mm/s); $\Gamma$: full width at half maximum (mm/s). Abbreviations as follows: Harz, harzburgite; Dun, dunite; Wehr, wehrlite; Chrmte; chromitite.

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