Evidence of sub-arc mantle oxidation by sulphur and carbon

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Abstract

The oxygen fugacity (fO2) of the Earth’s mantle at subduction zones exerts a primary control on the genesis of mineral deposits in the overlying magmatic arcs and on speciation of volcanic gases emitted into the atmosphere. However, the processes governing mantle fO2 such as the introduction of oxidised material by subduction are still unresolved. Here, we present evidence for the reduction of oxidised fluid-borne sulphur and carbon during alteration of depleted mantle by slab fluids at ultra-high pressure in the Bardane peridotite (Western Gneiss Region, Norway). Elevated ferric iron in metasomatic garnet, determined using synchrotron X-ray absorption near edge structure (XANES) spectroscopy, indicates that this process drove oxidation of the silicate assemblage. Our finding indicates that subduction oxidises the Earth’s mantle by cycling of sulphur and carbon.

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Letter

Plate tectonics drives recycling of surface material into the Earth’s interior, introducing hydrated and oxidised oceanic lithosphere into the mantle at subduction zones (Wood et al., 1990; Evans, 2012). Fluids liberated during dehydration of subducted crust trigger partial melting of the overlying mantle leading to the formation of volcanic arcs, dominated by oxidised rocks (Ballhaus, 1993; Kelley and Cottrell, 2009). Correlation between oxidation of arc lavas and addition of slab material by aqueous fluids to their mantle source has been quantitatively established (Kelley and Cottrell, 2009; Brounce et al., 2014), indicating that slab fluids are somehow responsible for the observed oxidation. However, although calculations suggest that fluid-borne oxidised sulphur may be important (Evans and Tomkins, 2011), the process has not been resolved with physical evidence. Determination of redox processes associated with fluid–mantle interaction cannot be indisputably resolved by studying the product of the arc system (i.e. arc lavas); it is best approached by examining rocks from the deep portion of mantle wedge close to the slab–mantle interface that have been altered by slab fluids, which are preserved as orogenic peridotites.

The Western Gneiss Region of Norway hosts several orogenic peridotite bodies that represent a portion of transition zone mantle that upwelled, melted (Stage M1) and accreted to cratonic lithosphere (Stage M2; Spengler et al., 2006). Subsequently, during the Caledonian orogeny, fluids derived from subducting slab locally promoted metasomatism (Stage M3), as recorded by the Bardane peridotite on Fjortoft island (Brueckner et al., 2002; Van Roermund et al., 2002; Scambelluri et al., 2008). Other portions have not been infiltrated by slab fluids and preserve the original mantle assemblage (M1-M2), exemplified by the Ugelvik peridotite on the island of Otrøy (Brueckner et al., 2002; Spengler et al., 2006). Although there is debate on the origin of metasomatism at Bardane, the trace element and isotopic signature of the metasomatic assemblage are comparable to the effects of typical subduction zone fluids sensu lato (cf. Brueckner et al., 2002; Scambelluri et al., 2008). The Bardane peridotite represents the best-known analogue for the study of fluid-related redox processes at sub-arc depth.

Previous studies at Bardane focused on a megacrystic garnet–websterite lens (e.g., Brueckner et al., 2002) and showed that interaction between slab fluids and depleted mantle generated metasomatic orthopyroxene, clinopyroxene, spinel, diamond (Van Roermund et al., 2002) and majoritic garnet, which indicate peak conditions of ~6.5 GPa and 800–1000 °C (M3-3 stage; Scambelluri et al., 2008). Multi-phase solid inclusions (MSI) are hosted in M3 minerals and are thought to have crystallised from slab fluids that permeated the peridotite and contain phlogopite, spinel, amphibole, dolomite, monazite, magnesite, graphite and diamond (Van Roermund et al., 2002; Malaspina et al., 2010).

We found a new occurrence of majoritic garnet as megacrysts in the Bardane peridotite coexisting with clinopyroxene, orthopyroxene, phlogopite and spinel hosted in harzburgitic domains (Fig. 1a). The garnet megacrysts contain sparse exsolved clinopyroxene and orthopyroxene needles (Fig. 1b) with similar size, abundance and distribution to the exsolution previously reported for M3 garnet (Scambelluri et al., 2008). MSI are abundant in the garnet (Fig. 3c). In addition to the previously reported mineralogy (Van Roermund et al., 2002; Malaspina et al., 2010) we found MSI containing phlogopite with barite (BaSO4; Figs. 2a, S-1) or magnesite (MgCO3), and phosphate minerals (apatite and monazite; Fig. 2b), as well as various multi-silicate inclusions. Single mineral inclusions of pentlandite (Fig. 2c) and graphite (Fig. 2d) also occur. Because of the similarity in mineralogy to that previously reported, this new-found metasomatic assemblage is considered to be equivalent to the M3-3 stage of Scambelluri et al. (2008).
The Ugelvik peridotite records stages M1 and M2 but has not been affected by later metasomatism (Brueckner et al., 2002; Spengler et al., 2006). Compositional mapping of UGL01 garnet, a garnet megacryst from harzburgitic domain in the Ugelvik peridotite, shows an absence of hydrous minerals or MSI (Fig. 3a). An excess of Si indicates a majoritic component in UGL01 garnet (Table S-1), implying an equilibration pressure of ~7.6 GPa (Supplementary Information).
To investigate whether slab-derived fluids promoted oxidation of depleted mantle through metasomatism at Bardane we measured Fe\(^{3+}/\text{Fe}_{\text{tot}}\) in garnet from Bardane and Ugelvik using XANES spectroscopy (Supplementary Information). Our results show that the metasomatic garnet from Bardane has higher Fe\(^{3+}/\text{Fe}_{\text{tot}}\) compared to the primary garnet from Ugelvik, despite having formed at lower pressure (Fig. 3b; Table S-1; cf. Luth et al., 1990). Fe\(^{3+}/\text{Fe}_{\text{tot}}\) is a proxy for oxidation state such that an increase in Fe\(^{3+}/\text{Fe}_{\text{tot}}\) indicates more oxidising conditions (Berry et al., 2010). Oxygen fugacity (f\(_O_2\)) for UGL01 (7.6 GPa; 1572°C), calculated using the Miller et al. (2016) calibration, ranges from Δlog FMQ -6.36 to -4.75, and for BDN03 (6.3 GPa; 1000°C) from Δlog FMQ -3.47 to -3.16 (Fig. 4; Table S-1; Supplementary Information). It should be noted here that mantle f\(_O_2\) is not buffered by FMQ, but varies relative to FMQ as a function of pressure via Fe\(^{3+}-\text{Fe}^{2+}\) exchange between olivine, orthopyroxene and garnet (e.g. Miller et al., 2016). Figure 4 shows that the metasomatised sample from Bardane, BDN03, has a higher f\(_O_2\) compared to a model depleted mantle (Supplementary Information). This relative oxidation implies that metasomatic fluids introduced oxidised species into the harzburgite (cf. Van Roermund et al., 2002; Scambelluri et al., 2008).

Since the MSI are considered to have precipitated from fluids that permeated the peridotite (Van Roermund et al., 2002; Scambelluri et al., 2008), the presence of carbonate and sulphate imply the introduction of oxidised sulphur and carbon during metasomatism. Furthermore, the presence of minerals with reduced sulphur and carbon enclosed in the garnet require that some of the oxidised sulphur and carbon has been reduced to S\(_2^-\) and C\(^0\). At present, there are no experimental data on sulphur speciation at the pressure and temperature recorded by the Bardane peridotite; however, oxidation can be achieved by reduction of any oxidised sulphur species (e.g. SO\(_2^-\), HSO\(_4^-\) or a polysulphide such as S\(_3^-\)) because all require addition of electrons to be reduced to S\(_2^-\) to form sulphide, as shown by Reaction 1 in the case of sulphate, and Reaction 2 for S\(_3^-\). Carbon in aqueous fluids at elevated f\(_O_2\) and neutral pH is predicted to be predominantly present as CO\(_2\) (Sverjensky et al., 2014) and its reduction to form diamond/graphite is illustrated in Reaction 3. Reduction of oxidised sulphur and carbon to sulphide and graphite require the addition of electrons (Reactions 1, 2 and 3), which must come from other multivalent elements in harzburgite minerals, most likely iron. Metasomatism involving these redox equilibria results in net oxidation of the silicate assemblage by conversion of ferrous iron to ferric iron in newly formed metasomatic minerals such as garnet (Reaction 4).

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\begin{align*}
\text{Reaction 1:} & \quad \text{S}^{6+} + 8\text{e}^- = \text{S}^2^- \quad \text{(sulphide/liquid)} \\
\text{Reaction 2:} & \quad \text{S}_3^- + 5\text{e}^- = 3\text{S}^2^- \quad \text{(sulphide/liquid)} \\
\text{Reaction 3:} & \quad \text{C}^{4+} + 4\text{e}^- = \text{C}^0 \quad \text{(diamond)} \\
\text{Reaction 4:} & \quad \text{Fe}^{2+} \quad \text{(slab/orthopyroxene)} = \text{Fe}^{3+} \quad \text{(garnet)} + 1\text{e}^- 
\end{align*}
\]

The role of carbon as an oxidant at subduction zones has previously been disregarded because the f\(_O_2\) of the sub-arc mantle was considered to be above the graphite–carbonate buffer; however, the f\(_O_2\) of the sub-arc mantle has been inferred from spinel-bearing xenoliths (cf. Evans and Tomkins, 2011) sampling only the shallower portion of the wedge. Geophysical investigations have shown that the depth of the slab–mantle interface below volcanic arcs and the depth of melting lies largely in the garnet stability field (e.g. Syracuse and Abers, 2006). Accordingly, the portion of mantle wedge that can be directly oxidised by slab fluids, i.e. between the slab and the locus of melting, is mainly confined to the garnet stability field. Figure 4 shows that the f\(_O_2\) of depleted garnet-bearing mantle is within the stability field of elemental carbon, delineated by the EMOD/G line (Luth, 1993) for the entire range of depths relevant to direct alteration by slab fluids (Supplementary Information). This implies that CO\(_2\) introduced by slab fluids in the deeper mantle wedge will be reduced to graphite/diamond during fluid-mantle interaction (Reaction 3), promoting oxidation of ferrous iron (Reaction 4).
Further oxidation can be achieved by reduction of oxidised sulphur, which can increase $f_O_2$ above the EMODG curve up to the sulphide–sulphate oxygen buffer ($\approx$FMQ +2; Mungall, 2002; Jugo et al., 2010). BDN03 and other natural samples from the mantle wedge that have been metasomatised by slab fluids display $f_O_2$ values higher than the depleted mantle curve estimated here (Malspina et al., 2009, 2010) (Fig. 4). The majority of these samples lie in the elemental carbon field, meaning that, contrary to previous suggestions (e.g., Evans and Tomkins, 2011), oxidation of the mantle wedge can be achieved by $C^4+$ reduction alone. However, some samples plot on the right side of the EMOD/G curve, implying that sulphur reduction must have taken place in these cases.

The clear difference in barite content between UGL01 and BDN03 (cf. Figs. S-1, S-2) indicates that the oxidising fluid was also barium-rich. This observation is consistent with the positive correlation between Ba enrichment and oxidation state seen in arc basalts (e.g., Brounce et al., 2014), and combined, these observations hint that barite precipitation may have been tied to the oxidation process. Although barite stability has not been investigated experimentally at high pressure and temperature, Ba$^{2+}$ is immobile in the presence of $SO_4^{2-}$ at upper crustal conditions, whereas modestly oxidised conditions allow its mobility (more reduced than 1 log unit $f_O_2$ below the pyrite–haematite and haematite–magnetite buffers; Hanor, 2000). In the sub-arc mantle, the polysulphide ion, $S_{5-}$, may be dominant at moderate $f_O_2$ conditions (Pokrovski and Dubessy, 2015); the lack of sulphate in solution would allow Ba mobility in typical slab fluids. We suggest that equilibration between $S_{5-}$ and the mantle during metasomatism would allow introduction of Ba via moderately oxidised fluid and formation of both sulphides and barite whilst oxidising Fe$^{2+}$ to Fe$^{3+}$ in the silicate assemblage, as illustrated by Reaction 5:

$$\begin{align*} CaAl_2SiO_4 + 7Fe^{2+}SiO_3 + 3MgSO_4 + 2S_{5-} + Ba^{2+} &
\rightarrow CaFe^{2+}SiO_3 + Mg_3Al_2SiO_4 + 7FeSiO_3 + 5FeS + BaSO_4 \\
\text{garnet} &\quad \text{olivine} \\
\text{fluid} &\quad \text{orthopyroxene} \\
\text{barite} &\quad \text{orthopyroxene–sulphide} \\
\text{garnet} &\quad \text{barite} \\
\end{align*}$$

Reaction 5

In this redox equilibrium, Reaction 2 is incorporated to modify the garnet–olivine–orthopyroxene $f_O_2$ buffer defined by Luth et al. (1990), which controls the oxygen fugacity of the garnet-bearing mantle. A comparison between the oxygen fugacity of the Bardane metasomatic assemblage and that of depleted mantle (Fig. 4) shows that Reaction 5 is a feasible mechanism for oxidising the sub-arc mantle. Given that sulphur and carbon are the major redox-sensitive elements in aqueous slab fluids (Evans, 2012), the extent of oxidation achievable by mantle metasomatism is likely to be limited to the sulphide–sulphate transition.

Oxidation of the lower mantle wedge by $CO_2$ reduction is supported by the C isotope signature of cratonic diamonds, many of which formed during the Archean (Smart et al., 2016), implying that this oxidative process has been ongoing for billions of years. In contrast, $S$-driven oxidation may have become predominant during the Phanerozoic (Evans and Tomkins, 2011). Therefore, $C$ may have been more important for long-term redox cycling through arcs, although limiting the magnitude of Precambrian mantle oxidation.

Formation of sulphide through reduction of oxidised sulphur provides a sink for chalcophile elements such as Cu and Au, which can be carried in slab fluids. Prolonged metasomatism of the sub-arc mantle by slab fluids would thus form hydrated, oxidised and metal-enriched domains. Because sulphur is an order of magnitude more soluble in oxidised basaltic magma (Jugo et al., 2010) melting of these domains generates $H_2O$-rich and oxidised magma enriched in sulphur and metals. These are characteristics necessary for formation of magmatic-hydrothermal ore deposits at arcs, such as porphyry Cu–Au (Mungall, 2002).

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**Additional Information**

**Supplementary Information** accompanies this letter at www.geochemicalperspectivesletters.org/article1713

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**References**


