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Incipient carbonate melting drives precious metal and sulfur mobilisation in the mantle

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Abstract
We present results from high-pressure, high-temperature experiments that generate incipient carbonate melts at mantle conditions (~90km depth and temperatures between 900 - 1050°C). We show that these melts can effectively sequester sulfur, in its oxidised form of sulfate, platinum group elements, and first-row transition metals from mantle lithologies of peridotite and pyroxenite. These primitive oxidised melts may be effective agents to dissolve, redistribute and concentrate sulfur as well as chalcophile metals within the mantle, and from the mantle to shallower regions within the Earth, where localised dynamic physio-chemical processes can lead to ore genesis at various crustal depths. It is proposed that these carbonate-sulfur rich melts may be more widespread than previously thought, and may play a first order role in the metallogenic enhancement of localised and predictable lithospheric domains.

Introduction
The mobilisation and anomalous concentration of chalcophile, siderophile and first-row transition (FRTEs) elements into discrete mantle domains has been intimately linked to the behaviour and mobility of sulfur, which is known to complex with base and precious metals into a variety of compounds1–3. Much attention has therefore been directed towards understanding the solubility, saturation, and speciation of sulfur, as well as the partitioning behaviour of chalcophile, siderophile and first-row transition elements into primitive melts 4–7. Specifically, most work has concentrated on basaltic
compositions, which represent relatively large degrees of partial melting of their mantle sources, whereas the behaviour of sulfur and metals in the presence of incipient melts is still very much poorly known.

The S solubility in melts is strongly controlled by $fO_2$: at reduced conditions sulfur is present as sulfide, whereas sulfate is the soluble species under oxidised conditions. It has been demonstrated that the solubility of sulfur increases by an order of magnitude under oxidised conditions when sulfate is stable. Therefore, melts which are highly oxidised should incorporate higher concentrations of sulfur. Furthermore, in the absence of sulfide, chalcophile and siderophile elements will partition preferentially into the melt. Primitive oxidised melts are therefore expected to be effective agents to dissolve, redistribute and concentrate sulfur as well as chalcophile metals within the mantle and from the mantle to shallower regions within the Earth, where localised dynamic physio-chemical processes can lead to ore genesis at various crustal depths.

Incipient melts (<5% partial melting) may be locally generated in the mantle due to a significant reduction in the solidus temperature associated with the presence of small amounts of volatile components such as H$_2$O and CO$_2$. They exist over a large temperature interval (~300°C) and are one of the most effective metasomatising agents in the deep Earth. Incipient melts generated from partial melting of volatile-bearing peridotite are carbonate-rich as long as conditions are sufficiently oxidising, which are expected at depths of 200 km or less in the mantle. The carbonate-rich incipient melts gradually change their composition with increasing degrees of partial melting ranging from carbonatites with typically <10 wt% SiO$_2$ and >40 wt% CO$_2$ to carbonated silicate melts with >25 wt% SiO$_2$ and <25 wt% CO$_2$. We use the term carbonate melts hereafter to encompass this full geochemical diversity of carbonatite-like incipient melts, which are thought to be responsible for widespread metasomatism within the sub-continental lithospheric mantle (SCLM). Mantle xenoliths which sample the SCLM often show evidence of carbonate metasomatism, and may contain sulfides associated with carbonate minerals suggesting a common association between S and carbon (C). However, no experimental evidence has ever been produced to support the inferences from natural occurrences.
Incipient melts are unlikely to ever reach the surface unmodified but may be responsible for the (re)enrichment of the SCLM and the lower crust in chalcophile and siderophile elements, such as sulfur (S), nickel (Ni), copper (Cu) and the platinum group elements (PGEs). The role of oxidised incipient melts in mobilising sulfur, chalcophile and siderophile elements from the mantle has not been experimentally investigated, despite growing evidence from natural samples that conditions to liberate and concentrate S are favoured during the earliest stages of mantle melting. Here, we present new high-pressure, high-temperature experiments in combination with high-precision nano-scale analysis to demonstrate that carbonate melts are effective transport agents for S, PGEs and FRTEs during the initial stages of mantle melting.

Results

High-pressure experiments

Near-solidus melting experiments were conducted on two natural mantle compositions, a biotite pyroxenite from western Uganda and a fertile spinel lherzolite from Lake Nyos, Cameroon. Both compositions were doped with small amounts of H₂O (1.5 and 1 wt%), CO₂ (3 and 2.5 wt%), S (0.8 and 0.5 wt%) and PGEs (800 and 500 ppm), respectively (full experimental details in Methods). Experiments were performed in Pt-lined double chambered graphite capsules at temperatures between 750 and 1050°C, and pressures of 2.5 GPa generated using a rapid quenching piston cylinder. The double chambered capsules allowed for both compositions to be run simultaneously in the same experiment ensuring that both compositions were subject to the same pressure, temperature conditions. Incipient melts coexist with olivine (Olv), orthopyroxene (Opx), clinopyroxene (Cpx), spinel (Sp), and clinohumite (Ch) within the peridotite, and phlogopite (Phl), ilmenite (Ilm), Cpx, and Olv within the pyroxenite. The stable carbonate phase for both rock compositions at sub-solidus and near-solidus conditions at 2.5 GPa is dolomite. The initial melts for both compositions are carbonatites (1.91 – 2.30 SiO₂, 32.33 - 42.61 CaO wt%; supplementary information), which occur as poorly quenched mats segregated towards one end of the experimental capsule (Figures 1-2), as is typical for these low viscosity highly mobile melts.
Carbonatite melts exploit grain boundaries to travel rapidly within a solid silicate rock network infiltrating by a dissolution-precipitation mechanism, which allows for effective and efficient exchange of trace and incompatible elements between the mantle reservoir and percolating melt. The infiltration of carbonatites through the silicate rock and their relationship to chalcophile and siderophile elements was further investigated here on a single high-pressure experiment (M21-107) at a nano- and micro-scale using transmission electron microscopy (TEM), synchrotron sulfur x-ray absorption near edge spectroscopy (S-XANES) and Photo-induced Force Microscopy (PiFM). Two electron-transparent foils of ~100 nm thickness were cut from experimental charge M21-107 (2.5 GPa and 1050°C): foil locations were selected along grain boundaries where evidence for melt percolation and sulfide droplets could be recognised from scanning electron microscope (SEM) images. Although the carbonatite melts could not be seen in SEM-micrographs along these grain boundaries, evidence of melt infiltration was visible by an increase in the forsterite content \( X_{\text{Fo}} \) of olivine grains along grain boundaries. Olivine will re-equilibrate with coexisting melt to match the Mg-Fe ratios of the liquid, in this case the Fe-poor carbonate melts result in the growth of Mg-rich olivine rims highlighted by the increased forsterite content. Synchrotron S-XANES was conducted at the Advanced Photon Source, Argonne National Laboratory, USA, on beamline 13-ID-E; full analytical details are provided in Methods. Further nano-scale analysis was conducted using PiFM, which combines atomic force microscopy with infrared spectroscopy, allowing for the collection of FTIR maps at a sub-micron scale. PiFM maps were collected across grain boundaries which had been affected by melt infiltration. These novel techniques are used here for the first time to investigate incipient carbonatite melt migration in high-pressure experiments.

Coexistence of sulfur and carbonatite melts
TEM images of the peridotite sample reveal the presence of ca. 1µm sulfide blebs surrounded by a matrix of clinohumite, with a thin veneer of quenched carbonatite liquid at the interface between sulfide and clinohumite. The clinohumite displays dislocations close to the sulfide blebs, suggesting that space had to be generated for the sulfide blebs within the silicate network when they quenched from
Figure 1. Back-scattered electron micrographs of experimental sample M21-107 (2.5GPa, 1050°C – peridotite), at different magnifications. (a) Overview of experimental charge. The carbonate melt is pooled at the top right and displays typical quench structure with sub-micron scale quench crystals in a fine-grained network. A clinohumite rim (dark grey) surrounds the residual peridotite highlighting the widespread activity of the melt throughout the experiment. (b) Magnified view of the orange box in (a): tiny droplets of sulfide are visible along grain boundaries which have been affected by the presence of melt. Clinohumite (Ch) is interpreted to have formed due to a reaction between olivine (Olv) grains and the percolating melt. (c) Shows the location of the FIB-lamella which was extracted for TEM-analysis. This location is also highlighted by the white box in (a).
Figure 2. Electron-backscattered micrographs of M21-107 (2.5GPa, 1050°C – pyroxenite), at varying magnifications. (a) Low-magnification overview, carbonated melts occur along the edges of the experimental charge and are rimmed by olivine (Olv), which has grown as an incongruent melting product as phlogopite began to melt. Clinopyroxene (Cpx), ilmenite (Ilm) and phlogopite (Phl) are present throughout the charge. The yellow box highlights the position of the FIB-lamella used for TEM analysis. (b) Magnified view of the carbonated melt quench structure encroaching onto the olivine grains. The quenched phases consist of fluorite, brucite and calcite (identified using TEM-EDS).
the carbonatite liquid, inducing strain in the clinohumite crystals (Fig 3a). Quenched carbonatite liquid also surrounds sulfide blebs in the pyroxenite sample, where a larger volume of melt was recovered around them (Fig. 3c-d). The crystallised quenched components of the carbonatite liquid are visible in STEM images (Fig. 3c) and TEM-EDS (Fig. 3d).

The low-volume quenched carbonatite liquid in the pyroxenite and peridotite samples occurs below and around the sulfide blebs, with no clear exposure to the polished 2D surface used in SEM imaging (Fig. 3b, d). The melts exist along the grain boundaries of silicate minerals, as revealed by high concentrations of Ca in a thin coating surrounding the sulfide blebs identified using TEM-EDS analysis (Fig. 3b, d). The calcium cannot be attributed to the surrounding silicate minerals as the sulfide bleb within the peridotite was located between olivine and clinohumite, neither of which contain significant concentrations of Ca. Also, TEM-EDS of the clinohumite showed no appreciable Ca. Strong depletions of Si and Mg in the olivine and clinohumite adjacent to the carbonatite veneer also testify to this being a separate phase from the silicate mineral network.

The sulfide bleb within the pyroxenite sample was located at the interface of two olivine grains that had grown as incongruent melting products of pyroxenite, a reaction that is well documented throughout the literature in both natural samples and experiments. The volume of melt recovered in the pyroxenite is appreciably higher than in the peridotite sample, and the typical quenched structure of carbonatite melts is clearly visible at the nano-scale (Fig. 3d). Upon cooling, carbonatites quench into multiple micron-sized phases. Four distinct quenched phases were identified with TEM-EDS in the carbonatite that formed from incipient melting of the pyroxenite sample: calcite (CaCO$_3$), calcium fluoride (CaF$_2$), brucite (Mg(OH)$_2$) and graphite (C), as shown in Fig. 3c-d.

The tiny sulfide blebs (<1 µm) are common along grain boundaries in both peridotite and pyroxenite experiments where melt-present interfaces are visible in the SEM images (Figs. 1-2). There is no evidence to suggest that any sulfide melts were interconnected along grain boundaries, as discrete blebs occur tens of microns apart. This regular dispersion of micro-scale sulfide blebs is commonly attributed to dissolved sulfur in melts, which quench out of experimental melts to form tiny sulfide droplets as
Figure 3. Transmission electron micrograph of M21-107, peridotite (a) and Scanning transmission electron micrograph of M21-107, pyroxenite (c). Compositional maps (b) and (d) were determined using TEM-energy dispersive spectroscopy. (a) TEM image of the peridotite lamella (see Figure 1a and c for location) showing sulfides in cross sectional view. The TEM image highlights high-density inclusions within both sulfide blebs. These sulfides occur along an olivine-clinohumite grain boundary and dislocations induced by quenching of the sulfide blebs are highlighted by the white arrows. A low-density rim surrounds both sulfides and was identified as carbonated melt by TEM-EDS (b). (b) TEM-EDS of the same sulfide blebs: a thin veneer of carbonated melt (green) surrounds both sulfides. (c) High-angle annular dark field scanning transmission electron micrograph of the pyroxenite lamellae (see Figure 2a). The STEM image shows two sulfide blebs with inner high-density inclusions surrounded by quenched carbonate melt. Graphite is also present in this quenched melt-sulfide complex (dark red in (d)). (d) TEM-EDS of the pyroxenite lamellae in (c) using the same colours in (b) and (d). The pyroxenite lamella recovered a larger volume of melt surrounding the sulfide blebs: brucite, graphite and fluorite were identified in addition to calcite as quenched products of carbonate melt. The graphite within the carbonate melt is a result of the oxidation of sulfides to sulfate in exchange for the reduction of carbon dioxide to graphite.
seen in Fig. 4.5,10,30. Sulfide melts typically require at least 5 vol% of sulfide liquid to interconnect within a four-phase peridotite matrix.31 As it is unlikely that any sulfide liquids would have reached this interconnectivity threshold in the experiments presented here, their presence along grain boundaries implies physical mobilisation coupled to the extremely mobile carbonatite liquids, which are able to interconnect at melt volumes of just 0.3%.27

**PGEs, FRTEs and sulfur**

STEM analysis of the sulfide blebs revealed the presence of high-density cores, which were chemically analysed using TEM-EDS and found to be inclusions of platinum group metals (PGMs). The PGM inclusion within the peridotite hosted sulfide bleb consists of Pt, Re, Ru and Ir (Fig. 4), whilst the sulfide bleb in the pyroxenite is rich in Pt and Rh (Fig. 5, Supp. Table 7).

PGEs are known to strongly partition into sulfides and refractory metal alloys during melting of silicate mantle rocks. However, the partitioning behaviour of PGEs during low-degree melting to produce carbonatite melts has not been determined, and neither have $D_{PGE}^{sulfide/carbonatite}$ coefficients. LA-ICP-MS in-situ analyses of the pooled carbonatite melts segregated to one end of the experimental charge confirmed the presence of elevated PGE concentrations in carbonatite liquids, which were also free of sulfide droplets. LA-ICP-MS proved to be advantageous over EDS to circumvent the challenge of interpreting spectral overlaps, allowing easy detection of all PGEs in the ablated melt pockets.

The experiments presented here were not designed to determine $D_{PGE}^{sulfide/carbonatite}$ coefficients, but results attest to: (1) the mobilisation of PGEs in carbonatite liquids and (2) the preferential partitioning of PGEs into sulfides in the presence of carbonatite melts (Figs. 4 and 5). Texturally the sulfide blebs appear to have quenched from a liquid, as evidenced by strain and dislocations induced in the surrounding silicate minerals (Fig. 3) and by the variation of the sulfide compositions between the peridotite and pyroxenite assemblages. The sulfides in the peridotite sample are Fe-Ni-sulfide (Fig. 4), whilst those present in the pyroxenite sample are Fe-Rh-sulfide. The sulfides in both mantle compositions have sequestered first-row transition elements (FRTEs) requiring diffusion of FRTEs from the silicate mineral network to the sulfides. As
Figure 4. TEM micrograph of M21-107 - peridotite and TEM-EDS maps (b-f) highlighting PGE association with sulfide blebs. (a) High-angle annular dark field image of the left sulfide bleb from Figure 3a. The PGE-rich high-density inclusion is visible as the bright white area contained within the sulfide. (b)-(f) Quantitative EDS maps of the sulfide bleb showing the distribution of sulfur (b), platinum (c), iridium (d), iron (e) and nickel (f). There is no detectable sulfur within the PGE-inclusion (cf. Supp. table 7).
Figure 5. TEM-EDS maps of the sulfide blebs within the pyroxenite lamella (Figure 3c). Two distinct Fe-PGE rich inclusions are contained within the sulfide. Compositions of the PGE inclusion on the left are provided in Supp. table 7.
Figure 6. First-row transition element compositions determined by LA-ICP-MS of olivine and neighbouring clinohumite either side of the TEM-lamella (Figure 1c). Carbonate melts make their way through silicate rocks by a dissolution and precipitation mechanism, evidenced by the transport of Ni, Cu, Co and Fe from the silicate minerals to the melt. Typically, carbonate melts do not preferentially include first-row transition elements. However, their strong depletions in clinohumite suggest that sulfate-rich carbonate melts are responsible for this preferential partitioning. The depletion of Fe within the clinohumite is balanced by increased Mg concentrations (a), testifying to the exchange of elements with a percolating melt. The black arrows in a-c highlight the effect of passing melt on the olivine-clinohumite pairs.
Sulfides are typically immobile; this uptake of FRTEs was assisted by the carbonate melts that percolated along grain boundaries of silicate minerals, such as olivine, exchanging Mg and Ca cations for Fe, Cu, and Co. Additional LA-ICP-MS measurements on the peridotitic olivine and neighbouring clinohumite confirmed the removal of Fe, Cu and Co from the mantle olivine into the carbonate liquids (Fig. 6). Carbonate melts typically do not remobilise FRTEs, but are generally associated with metasomatism and localised enrichments in incompatible elements. However, more recently elevated PGE contents have been reported in carbonatites, which also contain abundant quenched sulfides.

**Sulfur speciation in carbonatite liquids**

We analysed the segregated carbonatite melts using synchrotron S-XANES to determine sulfur speciation and constrain oxygen fugacity (\(fO_2\)) of the experimental carbonatite melts. Multiple S – XANES spot analyses were taken across the quenched carbonatites (Fig. 7); following normalisation and peak fitting, S-XANES spectra indicated that the majority of sulfur present within the analysed regions was sulfate (\(\sum S = 0.92\)), and oxygen fugacity was determined at \(\Delta FMQ + 1.25\) using Jugo et al.‘s (2010) experimentally calibrated model.

The mobilisation of sulfur is intrinsically linked to its oxidation state, with sulfides (S\(^{2-}\)) reaching saturation in basaltic melts at ~1200 ppm, whereas sulfur solubility increases to ~1.2 wt% under oxidised conditions in which sulfate (S\(^{6+}\)) is the dominant species. The transition of sulfide to sulfate in basaltic melts occurs in a restricted \(fO_2\) space between \(\Delta FMQ -1\) to +2 at pressures of 1.5 GPa. Similar constraints on carbonatites are not yet available, but recent work investigating sulfur concentration at sulfide saturation in carbosilicate melts at pressures greater than 2.5 GPa have yielded sulfur concentrations of ~800-3000 ppm. Sulfur concentrations within our experimental melts were 600 – 1000 ppm in the peridotite and 800 – 900 ppm in the pyroxenite, suggesting that the carbonatites generated here had not reached sulfide saturation.

In addition to S-XANES, PiFM maps were acquired at infrared wavenumbers known to correspond to the \(v_3\) stretching vibration of aqueous sulfate anions (SO\(_4^{2-}\)) at 1100 cm\(^{-1}\) (Fig. 8). The PiFM maps highlight multiple nanometre-sized sulfate particles...
Figure 7. Synchrotron micro-XRF map of M21-107 peridotite and accompanying Sulfur-XANES spectrum. (a) The synchrotron micro-XRF map highlights compositional variations across the sample. Sulfur (red) is concentrated along grain boundaries and within the carbonatite melt pool. The clinohumite rim also shows strong depletions in iron. (b) Sulfur-XANES spectrum of the carbonatite, taken from the white square in (a). Most of the sulfur within the carbonatite is present as oxidised sulfate ($S^{6+}$).
Figure 8. Photo-induced Force Microscope (PiFM) map of M21-107-pyroxenite at different magnifications. (a) PiFM map acquired at the sulfate peak (1100 cm\(^{-1}\) wavenumber): the bright gold regions correspond to sulfate, which is predominately found along grain boundaries between silicate minerals. (b) PiFM map of the red box in (a) combining spectra for olivine (green), mica (blue - phlogopite) and red (sulfate). (c) A high-magnification PiFM map of the red box in (b): here, interstitial carbonatite melt (black) is identified in addition to olivine, mica and sulfate. The sulfate peaks correspond to aqueous sulfate anions dissolved in the carbonatite melt.
Along grain boundaries, which we interpret were present as anions within the melt as the $v_3$ band splits into several spectral features when the sulfate anion is present within a solid-state medium such as a mineral. The distortion of sulfate polyhedra by the incorporation of cations (such as Ca$^{2+}$ and Ba$^{2+}$) also results in the appearance of $v_1$ stretches (1000 cm$^{-1}$). The lack of splitting or additional peaks suggests there was no solid-state bonding of cations to the sulfate anions within the melts. Both the S-XANES (Fig. 7b) and PiFM maps (Fig. 8) testify to the presence of sulfur predominately as dissolved sulfate anions in the melt, which would have required oxidised conditions ($\Delta$FMQ > 1) to persist throughout the duration of the experiments.

Discussion

The association of sulfur with carbon is well documented in mantle xenoliths and in diamond-hosted inclusions, but the processes which lead to their co-occurrence both in mantle derived melts and at the Earth’s surface are poorly understood. Both carbon and sulfur are found in vanishingly small concentrations (~100 and 200 ppm, respectively) in the bulk silicate Earth, and are highly incompatible in silicates, which represent the main rock forming minerals of our planet. However, both elements form major volatile species degassing from the planet’s interior through volcanism, and concurrently occur within economically significant ore deposits linking the deep carbon and sulfur cycles with lithosphere-atmosphere-biosphere systems. Despite the apparent overabundance of both sulfur and carbon within Earth’s surface reservoirs, the mobilisation and concentration of sulfur and metals from the Earth’s mantle to the surface is problematic.

Mantle melting under anhydrous conditions begins at temperatures above the melting point of monosulfide solid solution sulfides (MSS at 2.5Gpa, 1200 – 1230°C), which are the main host of sulfur within the upper mantle. Despite MSS being molten at the onset of mantle melting, sulfides remain immobile until they dissolve into the surrounding silicate melts up to the sulfur concentration at sulfide saturation threshold (SCSS), which is ~1200ppm in basalts. Basalts represent less than 15% partial melting of their mantle source, and typically do not exhaust the mantle of MSS, restricting the concentration of metals that can be liberated from the mantle to well below that required to generate economically viable ore deposits.
However, the mantle is not anhydrous and volatile components from the surface including H$_2$O and CO$_2$ have been effectively recycled back into the mantle throughout the geological evolution of our planet $^{48}$ and are known to significantly depress the solidus at low concentrations (950°C at 2.5GPa)$^{13}$ in localised domains of the mantle. This depressed solidus may be close to, or below, the stability limit for solid MSS, with recent work placing the MSS melting point at 975 - 1000°C at 2.5GPa $^{41}$. The experiments presented here were run at conditions close to this reported solidus of MSS $^{41}$: therefore, molten sulfide may have been present at the onset of melting. Whether the sulfides were molten or solid at the conditions at which carbonatite melts were generated in our experiments is not important, as the ubiquitous presence of sulfate along grain boundaries and in pooled carbonatite melts demonstrates the extreme mobility of sulfur under oxidised conditions.

Our experiments demonstrate that under sufficiently oxidised conditions ($\geq \Delta$FMQ+1.25) sulfur preferentially dissolves as sulfate in the carbonate melts. The oxidation of sulfide to sulfate is balanced by a reduction of CO$_2$ from the melts to graphite (Fig. 3d). The migrating melts are extremely mobile and become enriched in S, PGEs and FRTEs (Fig. 6), transporting them rapidly away from the residual mantle source and potentially concentrating them in localised domains of the overlying continental crust.

Carbonatite melts can only exist under oxidised conditions in the Earth’s mantle, where carbonate redox melting may occur, which is equivalent to $\Delta$FMQ $\geq +1$, at depths of 3 GPa (~90 km)$^{17}$ at the solidus for CO$_2$ and H$_2$O bearing peridotite $^{13}$. At more reduced conditions than $\Delta$FMQ + 1 and/or depths greater than 7 GPa, carbonate-rich melts do not exist because carbon is stable as graphite or diamond and remains stable until these reduced forms of carbon are oxidised to carbonates $^{17}$. This prerequisite of oxidised conditions to generate carbonatite melts is achieved close to the well-defined and sharp transition from sulfide to sulfate ($\Delta$FMQ $> +1)^{8,9}$, which can only be attained in specific geodynamic settings. As long as there is sufficient CO$_2$ to counterbalance the oxidation of sulfide to sulfate, during melting sulfate anions will become enriched in carbonatite melts as demonstrated here (Figures 7 - 8).

Previous experimental work on the partitioning of trace elements (but not PGEs) between sulfate and silicate melts had demonstrated that trace elements prefer sulfate
This partitioning behaviour may also be responsible for the uptake of PGEs and FRTEs into the carbonate melts along with sulfate. Carbonatites and silicate melts have differing melt structures, which may lead to differences in the partitioning of PGEs and FRTEs. Silicate melts are anionic liquids with Si-O tetrahedra, typically requiring cations in tetrahedral coordination to charge compensate the system. This crystallographic structure limits the abundance of $X^{2+}$ cations that can be incorporated into the silicate liquid structure, with $X^{3+}$ cations preferentially partitioned into silicate melts. Conversely, carbonatites are ionic liquids consisting of carbonate $\text{CO}_3^{2-}$ molecules, and – unlike silicate melts – they are considered to be structureless. This lack of structure results in the inability of carbonatites to polymerise, allowing transition metals to bond with carbonate ions by donating outer electrons. This results in increased solubility of FRTEs into carbonatites compared to silicate melts. However, the behaviour of sulfates in carbonatites warrants further detailed investigations.

The carbonate melts generated within our experiments represent low degree, low volume melts, which are unlikely to reach the surface of the planet. However, they exist in the mantle over an enormous pressure-temperature range. Due to their low viscosities, carbonatites and carbonate silicate melts are incredibly efficient metasomatising agents, which are able to rapidly redistribute and locally concentrate elements such as S, PGEs and FRTEs (Fig. 6). In view of these unique properties and their persistence to low temperatures, we propose a new mechanism by which sulfur, PGEs and FRTEs can be 1) mobilised in the mantle through the generation of carbonatite melts, and 2) concentrated into metasomatised regions of the mantle, creating fertile domains that may play a first order control on the genesis of mineralised regions.

These processes are summarised in Figure 9: in the deep mantle at depths of <200 km (6.5 GPa), small volumes of carbonate melt are generated when the solidus of carbon- and water-bearing peridotite and pyroxenite is exceeded (~1100°C at 6.5 GPa). These low volume oxidised carbonatite melts are extremely mobile, and assist in the oxidation of mantle sulfides to sulfates, which readily dissolve in the carbonate melts along with PGEs and FRTEs. As the melts migrate to shallower depths the oxidation processes continue and further S, PGEs and FRTEs are extracted from the adjacent wall-rocks until either the sulfur concentration at anhydrite
Figure 9. Schematic diagram of melting processes in the lithospheric mantle. (a) Incipient melts are likely widespread throughout the lithospheric mantle where small amounts of CO$_2$ and H$_2$O significantly depress the solidus of peridotite and pyroxenite to temperatures of ~950°C at 2.5 GPa. The first formed melts are carbonatitic in composition, provided oxidised conditions persist. The lithospheric mantle is oxidised enough at depths less than 200 km and carbon is stable as carbonates in preference to its reduced form of diamond or graphite. (b) The oxidised carbonatite melt can interconnect at tiny volumes and, as documented here, oxidise mantle sulfide to sulfate, thereby increasing their sulfur carrying capacity. This effectively mobilises sulfur from its mantle reservoir to shallower depths within the Earth. The addition of sulfate anions to the melt likely causes a chemical potential gradient and first-row transition elements (Cu, Fe, Ni and Co) partition strongly from olivine into the sulfate-carbonatite melt, along with PGEs. These highly mobile low-degree melts quickly leave their mantle sources and rise towards the crust, where they will react and metasomatise the deep lower crust, enriching it with precious elements that are essential for ore genesis.
saturation (SCAS) is reached within the carbonatites – this concentration is currently unconstrained – or the percolating carbonatites freeze or are exhausted by reacting with overlying mantle or crustal rocks, resulting in the formation of metasomatised domains. Since the migrating melts also contain H$_2$O, the metasomatised products are commonly enriched in hydrous phases, which facilitate subsequent re-melting and remobilisation owing to the lowered melting temperatures of the hydrous assemblages \textsuperscript{21}. Evidence for this is seen in mantle xenoliths, where sulfides commonly occur together with hydrous and Ti-oxide minerals \textsuperscript{52,55}, and regions where the lithospheric mantle outcrops \textsuperscript{56}.

These metasomatised domains can be thought of as primed regions within the mantle with higher concentrations of S, PGEs and FRTEs relative to surrounding mantle lithologies, which require only a small heat anomaly or lithospheric thinning to remelt before interacting with the crust \textsuperscript{57}. This final reheating and melting event can potentially lead to supersaturation of S in the resultant alkaline ultramafic melts.

This type of re-enrichment process telescopes metals from an extensive depth range into a more restricted depth window at higher levels of the mantle \textsuperscript{58}. It has been used extensively to argue for the generation of volatile-rich melts such as kimberlites, ultramafic lamprophyres, and lamproites \textsuperscript{29,59}. These alkaline-ultramafic melts commonly occur in close proximity to S-rich ore deposits in continental settings \textsuperscript{60}. Their spatial and temporal co-occurrence is consistent with a complex two-stage melting of an oxidised mantle lithology where incipient melts pre-fertilise discrete domains of the source with elevated PGEs and incompatible trace elements, which can be subsequently entrained by larger volumes of melts that can accumulate metal-rich sulfides at various crustal levels \textsuperscript{19}. A scenario to illustrate this process may have generated mineralisation associated with the Siberian picrites \textsuperscript{61}, which have elevated PGE and Au contents, and higher concentrations of sulfur than would be expected if these metals were only present in sulfide in these melts. Mungall et al. (2016) interpreted the Siberian picrites as having attained their elevated PGE contents by low degrees of partial melting (2.6\%) from a mantle source at oxidised conditions (FMQ +2).

Carbonates, and therefore CO$_2$ have a greater oxidising potential than ferric iron-bearing phases, if CO$_2$ is available in excess such as in carbonatites \textsuperscript{33,62,63}. The
reduction of CO\textsubscript{2} in association with the oxidation of sulfur results in the release of the metal cargo held within mantle sulfides and transfers it to the mobile carbonatite melts. This mechanism of sulfur removal from the mantle may operate only locally within previously metasomatised regions of the mantle. However, continued episodic fluxing of low volume carbonatites, which are probably more widespread in the mantle than previously thought, would remove the requirement for large degrees of partial melting to exhaust mantle sulfides and generate metal-rich primitive melts. A corollary of this hypothesis is that metallogenically fertile regions of the mantle may be identified in areas that were previously deemed as non-prospective.

**Methods**

Two natural mantle xenoliths were chosen as end members for peridotite and pyroxenite starting lithologies. A fresh spinel lherzolite from Lake Nyos was chosen as the representative end member for a peridotite and a mica pyroxenite from Uganda. Compositions for both starting materials are provided in Supplementary Table 1. Both compositions were doped with small amounts of volatiles, S and PGE’s; CO\textsubscript{2} was added as carbonates of siderite (FeCO\textsubscript{3}) and magnesite (MgCO\textsubscript{3}) to maintain the Mg:Fe ratios present within the natural rocks; H\textsubscript{2}O as brucite (Mg(OH)\textsubscript{2}); S as pyrite (FeS\textsubscript{2}) and PGE’s as nitric acid solutions. The rock powders were initially dried at 250°C to liberate adsorbed water, before PGE’s in solution were added further drying overnight at 750°C to liberate the nitric acid before finally adding the volatile components and sulfur.

All experiments were conducted at the high-pressure laboratory at Macquarie University using a rapid quenching end-loaded piston cylinder apparatus with a ½” natural CaF\textsubscript{2} assembly \textsuperscript{24}. The powdered starting materials were loaded into dual chambered graphite capsules, and single wrapped in 25µm thick platinum foil. Temperature was monitored with Type B Pt\textsubscript{30}Rh\textsubscript{70}-Pt\textsubscript{5}Rh\textsubscript{94} thermocouples and pressure calibrations were conducted using the quartz-coesite transition \textsuperscript{64} and the albite = jadeite + quartz reaction \textsuperscript{65}. All experimental charges were brought to the desired pressure first then heated to the target temperature in 20 minutes. Experiments were kept at high-pressure and high-temperature for 24 hours to ensure equilibrium had been reached, subsequently power was cut to the furnace and the
experiments quenched to room temperature in under 10 seconds. Experimental run conditions and results are detailed in Supplementary Table 2.

Upon recovery of the experimental charges, the capsules were embedded directly into epoxy resin before polishing with baby oil or ethanol in a water-free environment to minimise loss of carbonates or carbonatite melts. Experimental charges were polished to a ¼ micrometre finish using diamond and silicate carbide laps.

**Analytical details**

All samples were initially imaged at Macquarie University using an FEI-Field Emission Scanning Electron Microscope (FE-SEM) operating at 15 kV and a working distance of 10 mm. Following imaging, chemical compositions for the carbonated melts and minerals recovered from experiments were determined using quantitative energy dispersive spectroscopy (EDS) on a Zeiss EVO SEM fitted with an Oxford Instruments large area Quant-EDS detector operating at 20 kV, calibrated to a beam current of 10\(\mu\)A, and a working distance of 12 mm. To ensure accurate compositions, electron microprobe standards were analysed before each SEM session to ensure EDS measurements were within 2% of reported compositions. The compositions of melts and minerals recovered from high-pressure experiments in presented in Supplementary Tables 3 and 4. Carbonatite melts are extremely heterogeneous and quench into multiple micron-size crystals large areas of melt were analysed via quantitative-EDS mapping and compositions were determined from these large, homogenised areas.

Trace-element and platinum group element compositions of clinohumite, olivine and carbonatites were determined using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at Macquarie GeoAnalytical (MQGA) housed at Macquarie University. Trace element analyses were performed using a Teledyne Photon-Machine Excite Excimer (193 nm) Analyte laser ablation system equipped with a HelEx II active 2-Volume cell, coupled to an Agilent 8900 ICP-MS system. The ICP-MS was optimised for sensitivity whilst ablating NIST SRM 610 in line scan mode 4. Ablation spot sizes were 50 microns, ablating at 5 Hz with a laser energy of 7 J cm\(^{-2}\). Detection limits were improved by mixing 5 mL min\(^{-1}\) of molecular hydrogen gas into the laser carrier gas\(^{66}\). Data were acquired by taking a background measurement for 120 s, signal for 60 s, and finishing with a 20 s washout time between each analysis.
The NIST SRM 610 reference material was used as the primary reference material (Georem preferred values 2022) and USGS BHVO-2G– was also included as a secondary standard. Unknowns were measured in blocks of 6 and were bracketed by analyses of standards. An average of two analysis points were collected for each phase per experiment. Data were processed using GLITTER data reduction software. SiO$_2$ and CaO values determined by Quant-EDS were used as internal standard values for silicate mineral and carbonatite melt analyses, respectively. Concentrations of platinum group elements within carbonated melts are presented in Supplementary Table 5.

Two electron transparent foils were prepared by focussed ion bean (FIB) milling using a FEI Helios Nanolab G3 CX DualBeam FIB/SEM for transmission electron microscopy (TEM) at the Centre for Microscopy, Characterisation and Analysis at the University of Western Australia.

TEM foils were prepared first by protecting the sample surface with the deposition of amorphous carbon strips which were 12 $\mu$m long, 2 $\mu$m wide and 1.5 $\mu$m thick. The locations of TEM foils were chosen along grain boundaries where small sulfide blebs could be seen along a melt-pathway in back-scattered electron mode. One foil was cut from the peridotite composition and the second from the pyroxenite. Following the deposition of the protective carbon strip, material either side was removed by a gallium ion beam operating at 30 kV and a beam current of 21 nA. This resulted in troughs either side of the strip which were 30 $\mu$m deep trenches, the sample was cleaned and thinned with lower ion beam currents (9.3 nA). An in situ micromanipulator was attached to the sample using a Pt weld whilst the remaining edges of the sample were milled away to create a U-shape cut to liberate the sample. The micromanipulator was used to lift-out the sample and transfer it to a copper TEM sample holder, two additional platinum welds were used to secure the thinned sample to the copper grid. The micromanipulator was freed from the sample and the sample thinned to ~100 nm at beam currents varying from 2.5 nA to 0.43 nA, a final cleaning of the surface was conducted at 5 kV and 15 pA.

Bright field TEM imaging, High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) imaging, and element mapping were carried out using a FEI Titan G2 80-200 TEM/STEM with ChemiSTEM Technology operating at
200 kV. In a bright field image, heavy element features are dark. In the equivalent
HAADF-STEM image, heavy element features appear bright. The element maps were
obtained by energy dispersive X-ray spectroscopy (EDS) using the Super-X detector
on the Titan with a probe size ~1 nm and a probe current of ~0.3 nA. The EDS spectra
and elemental maps were processed using the ESPRIT 2 (Bruker Corporation)
software. Spectral maps, and quantitative EDS spectra of sulfides in the TEM foils is
presented in Supplementary Tables 6 and 7.

Sulfur speciation of the carbonatite melts in experiment M21-107 was determined
using synchrotron sulfur x-ray absorption near edge spectroscopy (S-XANES) at the
Advanced Photon Source (APS) on beamline 13-IDE. S-XANES measurements were
collected in fluorescence mode using a Si [1 1 1] monochromator crystal. The sample
was placed into a He atmosphere to reduce interaction of the photon beam with the
surrounding atmosphere. Peak positions were calibrated by measuring gypsum which
provided a S$^{6+}$ peak position at 2481.82 eV. Multiple measurements were collected
using a 2 x 2 $\mu$m beam diameter and a beam intensity of 2.4 x 10$^{10}$ photons/s. Sulfur
K-edge spectra were collected by scanning between the 2447 – 2533 eV energy
range, spectra were collected at 1.5 eV steps between 2447 - 2460, 0.1 eV between
2460 – 2486 eV and 1.5 eV steps between 2486 – 2533 eV. A dwell time of 2 seconds
per step was used and 3 analyses per sample were obtained.
Synchrotron S-XANES causes photo-reduction of S$^{6+}$ to S$^{4+}$, as has been
demonstrated elsewhere \cite{34}. The growth of sulfite was observed in some of the
analyses collected as part of this analysis cycle, the sulfite contribution was small and
corrected back to S$^{6+}$ using the correction method outlined in Lerner et al. (2021).
All of the S-XANES spectra were normalised and fitted using XAS viewer within the
Larch software package \cite{68}. The protocol for fitting normalised spectra was based on
the approach outlined in Lerner et al., (2021), 6 Gaussian peaks and an error step
function for background were simultaneously fitted to the entire energy range
measured (2447 – 2533 eV), with bounds for peak width, amplitude and centre guided
by the determination of Lerner et al. (2021). Fitted spectra are presented in
Supplementary Figures 1-2. Following peak fitting, S$^{6+}/\Sigma S$ ratios were determined and
oxygen fugacity was calculated based on the experimentally constrained calibration of Jugo et al., (2010).

Photo-induced Force Microscopy (PiFM) was conducted at the Research School of Earth Sciences at the Australian National University, Canberra to investigate the distribution of sulfate within sample M21-107. PiFM is a phase analytical technique that combines the simultaneous acquisition of AFM and characteristic molecular compound information with a spatial resolution of ~5 nm, i.e., an infrared spectrometer on the nanoscale. The acquisition of the absorption features utilises IR lasers that are both tuneable with respect to wavenumber and pulse repetition rates that illuminate the sample just below the metal-coated AFM tip. The sample’s molecules absorb different wavelengths of the laser according to their composition, which is recorded by the sharp cantilever tip as it is being pulled towards the sample by the induced attractive forces. For sample M21-107 the surface was excited by using a mid-IR-range ‘quantum cascade laser’ module (QCL, Block Engineering LLC) consisting of four serially connected gap-free QCLs to sweep across the 800 to 1800 cm\(^{-1}\) range. Absorption features have been identified at 940 cm\(^{-1}\), 1000 cm\(^{-1}\), 1100 cm\(^{-1}\), and 1400 cm\(^{-1}\), which correspond to those found in olivine, (phlogopite)-mica, sulfate, and carbonate, respectively (John Wiley & Sons, Inc. SpectraBase).

Author contributions

I.S.E. and S.F.F. lead the conceptualisation of the research project. I.S.E conducted the experiments, analysis, interpretation of results and wrote the original manuscript draft. S.F.F. assisted in interpretation of results, manuscript writing and revisions. M.S. conducted the TEM analysis, assisted in interpretation of results and manuscript revisions. M.F.F. conducted the PiFM analysis and assisted in interpretation of results. S.S.S. helped with high-pressure experiments and interpretation of the data, and manuscript revisions. L.R.G. assisted with LA-ICP-MS analysis, interpretation of data and interpretation of S-XANES data, in addition to revisions to the manuscript. M.L.F. assisted in interpretation of the results, manuscript writing and revisions.
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Supplementary Files

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- Supplementarydata.pdf