Oldhamite (CaS) is a rare mineral only observed naturally in enstatite meteorites (chondrites and achondrites). It has never been observed on terrestrial samples, nor in other meteorite groups. However, under the conditions of 1.5 GPa, 1240 °C and 0.5 GPa, 1050 °C, with the oxygen fugacity is in the range of ΔFMQ−2 to ΔFMQ−0.2 (the log(\(f_O^2\)) value determined relative to the buffering equilibrium \(3Fe_2SiO_4 + O_2 = 2Fe_3O_4 + 3SiO_2\); we denote this value ΔFMQ), the oldhamite (CaS) was found during the melts reaction between the pyrrhotite-pentlandite-bearing orthopyroxenite and CaCO₃. We name this the two-melt mechanism. It is reasonable to infer that the formation of CaS can occur at the interface between the asthenosphere and the oceanic lithosphere under the mid-ocean ridge and during the process of mantle plume intruding into the lithosphere in Earth. CaS is very easy to combine with oxygen to form CaSO₄, which probably is the reason why it has never been found in geological samples from Earth. We speculate that part of the anhydrite and gypsum in the black smokers of mid-ocean ridges are related to the oxidation of CaS in the underlying mantle. The Siberian mantle plume can generate CaS when it intruded into the lithosphere. The C and CO in the mantle plume lava with low oxygen fugacity can also react with gypsum in the crust to generate CaS and CO₂. When the magma cools, CaS can be oxidized to form CaSO₄. During the formation and oxidation of 1 molecule of CaS, 1 molecule of CO₂ can be produced, and a half to two moles of O₂ will be fixed by CaSO₄. This mechanism perhaps is a reason for the reduction of oxygen content in the atmosphere at the Permian-Triassic boundary. The existence of the intermediary product CaS was one of the factors to promote the mass extinction most severe biotic crisis in the past 500 million years at the Permian-Triassic boundary.
The oxygen-poor signature of EM may suggest they formed in the center of a solar system nebula, within the orbit of Mercury. It is widely accepted that the oldhamite formed in a reduced environment. For example, oldhamite could be a predominant component of the Mercury surface. However, the formation process of oldhamites in EM is still under dispute. There are currently three main views regarding this issue.

Some researchers held the view that CaS is the product of the condensation of nebula gas. Laboratory smoke experiments show that pure CaS and a solid solution of CaS and CaO [Ca(S,O)] are condensed from vapor phase calcium, sulfur, and oxygen with the O/S atomic ratio of <2 and between 2 and 10, respectively. This is the direct evidence for the nebular gas origin. Moreover, thermodynamic calculations under highly reducing conditions in the nebular show that oldhamite is REE-enriched and the predicted REE patterns are similar to those observed in EM. Besides, according to first-principles calculations, oldhamite is easier to be enriched in light Ca isotopes in equilibrium compared to the other solid minerals, but the condensed Ca-bearing minerals from nebular gas are enriched in heavy Ca isotopes relative to the residual gaseous Ca. Natural oldhamites in EM are isotopically heavier than coexisting silicate materials, indicating that EM oldhamites should have been formed during solar nebular gas condensation. However, sulfur isotope data did not support the nebula gas origin. The correlation between $\Delta^{33}S$ and $\Delta^{36}S$ of some EM does not show the trends of photochemistry in the solar nebula with $\Delta^{36}S = -2.98\Delta^{33}S$ and cosmic-ray spallation during presolar nebula with $\Delta^{36}S = 8\Delta^{33}S$.

Some scholars believed that the oldhamite in EM was igneous origin. Textural evidence for igneous origin includes apparent primary igneous grain boundaries between oldhamite and forsterite, and the presence of round, droplet-like Mn-Fe-Mg-Cr-Na sulfide inclusions within oldhamite which appear to represent an immiscible sulfide liquid. However, the most represented REE pattern of oldhamite in EM is characterized by both slight to large positive Eu and Yb anomalies and is enriched in light REEs relative to heavy REEs. But experimental petrology studies have shown that the Ca-rich sulfide liquid is enriched in the heavy REEs at 1250°C and oxygen fugacity of log$f(O_2)$ = −1.14. The REE fractionation between the Ca-rich sulfide liquid and the silicate liquid (D value) is extreme, with $D(Lu) = 60*D(La)$ at 1200°C. This finding is at odds with the igneous origin.

The latest view about the genesis of CaS in EM is the thermal metamorphism of calcite. The main evidence is that: Ca(OH)$_2$, CaS, and pentlandite outward ring structures were found in meteorites. Thus, these researchers insist that CaCO$_3$ thermally decomposed into CaO, and CaO reacted with the sulfur ion to form the CaS.

During the reaction of between the pyrrhotite-pentlandite-bearing orthopyroxenite and CaCO$_3$ in graphite-lined Au$_{75}$Pd$_{25}$ capsule (Fig. 1a), under the conditions of 1.5 GPa, 1240°C and 0.5 GPa, 1050°C, oldhamites were observed at the
central reaction area (Figs. 1b and 1c). That is, the oldhamite could be formed during the interaction of carbonate melt and sulfide-bearing silicate melt at suitable P-T-fO₂ conditions. Here, we name this formation process the two-melt mechanism. Former researchers thought that the oxygen fugacity was the key factor for the formation of oldhamite in EM¹,²,⁵. For the CaCO₃ contamination experiments in the graphite-lined Au₇₅Pd₂₅ capsule, the oxygen fugacity of the central reaction melt (Figs. 1b and 2) is FMQ−2.2≤fO₂<FMQ−0.2 (please see Figure S2 in the Method), which is higher than the oxygen fugacity IW−3 of EM. The two-melt mechanism extends the range of oxygen fugacity for CaS formation. In the absence of calcium carbonate, the magmas produced by the partial melting of the orthopyroxenite under two temperature and pressure conditions are similar in composition, and both are high-magnesium basalt magmas (SiO₂ = 54.5–54.9 wt.%, MgO = 9.54–10.19 wt.%, please see Method part and Supplementary Table 3). Basaltic melts (laves) are common in mid-ocean ridges and large igneous provinces. These P-T-fO₂ experimental conditions of CaS formation are easily achieved inside the Earth. We speculate that the two-melt mechanism can occur in the process of carbonate melt metasomatism in mantle or the intrusive of mantle-derived magma into the lithosphere or crust. Some kinds of sulfide occurred around the CaS, and the bubbles are always around the CaS (Fig. 1b and Fig. 2). Therefore, the most probable route for the CaS formation is: CaCO₃(melt) = CaO (melt) + CO₂(gas), CaO (melt) + FeS (melt) =  CaS (melt) + FeO (melt). To date, CaS has never been found in natural samples on Earth, probably due to the ΔH₂⁹⁸K of the reaction CaS(solid) + 2O₂ = CaSO₄(solid) is −960.9 kJ/mol¹⁶. That is, CaS reacts particularly readily with oxygen to form calcium sulfate. In this way (named reaction process 1), one molecule of CO₂ is produced accompanied by two molecules of O₂ disappeared from the atmosphere.
a) 

Au$_{15}$Pd$_{25}$

c) Bubble

b) Opx with disseminated Pb and Pn

Marginal reaction area

Central reaction area

Marginal reaction area

b) Opx with disseminated Pb and Pn

Marginal reaction area

Central reaction area

Marginal reaction area
Fig. 1. The state and location of CaS (oldhamite) generated in the two-melt mechanism. a. Reaction chamber for the contamination experiments between the Po-Pn-bearing orthopyroxenite and CaCO₃; b. General view of scanning electron microscope image after contamination experiment No. C1 under 0.5 GPa and 1050°C; c. Drop-shaped CaS is produced in the inner part of the central reaction area, and the bright white mineral disseminated in Figures b and c is Fe-Ni sulfide. Opx = orthopyroxenite, Po = pyrrhotite, Pn = pentlandite, and Od = oldhamite.

Opx = orthopyroxene, Cpx = clinopyroxene, Po = pyrrhotite, Pn = pentlandite, and Od = oldhamite.

Fig. 2. Reaction zoning of the two-melt mechanism.

The possible existence of CaS in mantle inclusions

There are sulfates including anhydrite inclusions in kyanite of crust-type eclogites or diamond in dolomitic marble in the Dabie-Sulu ultra-high pressure metamorphic belt. The peak metamorphic pressure for the eclogite and the dolomitic marble is 3.0−4.5 GPa and 4.3−6.0 GPa, respectively. Experimental petrology results show that when the oxygen fugacity is smaller than FMQ−1, there is almost no S⁶⁺ in the melt under \( f_{\text{O}_2} < \text{FMQ}−1 \). Under the metamorphic conditions of 4.3−6.0 GPa, the upper limit of the oxygen fugacity for diamond formation is FMQ−2. Thus, it is nearly impossible that sulfate exist under such low oxygen fugacity. A reasonable explanation is that the primary inclusion component was CaS, and then oxidation
occurred during the ascending and denudation process to form anhydrite, or newly formed sulfate ions were combined with other ions to form new sulfates.

**The link between CaS and anhydrite in black smoker of middle ocean ridge**

Generally, the oxygen fugacity of the Earth’s mantle gradually decreases with depth\(^{22,23}\). For the mantle below the mid-ocean ridge, at a depth of about 160–170 km, the transformation from diamond to graphite would occur when the oxygen fugacity is above \(\Delta F_{\text{FMQ}} - 2\)^{24,25}. Redox melting \([\text{C(graphite)} + 2\text{Fe}_2\text{O}_3(\text{melt}) + \text{O}_2^{-}(\text{melt}) = 4\text{FeO} + \text{CO}_3^{2-} \text{(both in the melt)}]\)^{26,27} would occur mainly at the depth of 120–150 km\(^{25}\). The carbonate melt produced by the redox melting will ascend as a flux to the overlying mantle and will react with the mantle silicates to stabilize a carbonated silicate melt\(^{28}\). At about 60 km depth, the carbonate melt will evolve towards a silicate melt composition\(^{25}\). Middle ocean ridge basalt (MORB), at the top location of the silicate melt, is characterized by a redox state of \(\Delta F_{\text{FMQ}} - 0.42 \pm 0.43\)^{29}. From the diamond-to-graphite interface to the location of MORB, the oxygen fugacity range is consistent with the formation conditions of CaS, and there are a large number of carbonate melts, silicate melts, and sulfide. Thus, it is reasonable to speculate that if the sulfide liquid is properly aggregated, the formation of CaS is possible (Fig. 3).

Large amounts of anhydrite (\(\text{CaSO}_4\)) and gypsum (\(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}\)) exist in black smoker at middle ocean ridge (BSMOR)\(^{30-32}\) (Fig. 3), which is considered to be derived from seawater as the most \(\delta^{34}\text{S}_{\text{VCDT}}\) value of these sulfates are nearly as same to that of modern seawater\(^{33,34}\). The \(\delta^{34}\text{S}_{\text{VCDT}}\) of modern seawater sulfate is 21.24‰\(^{35}\). However, the \(\delta^{34}\text{S}_{\text{VCDT}}\) value of anhydrite gradually shrinks from seawater’s value 20 ± 1‰ to a value of 3.4‰, and the \(^{87}\text{Sr}/^{86}\text{Sr}\) values of anhydrite decrease downward from seawater’s value 0.7088 to a value of MORB 0.7029 in a 1.8 km depth drillhole for the ocean-ridge black smoker systems\(^{36,37}\). This is no doubt that the S and Sr source from the MORB beneath the black smoker is attributed to the anhydrite. The \(\delta^{34}\text{S}_{\text{VCDT}}\) value 3.4‰ is much lower than that of modern seawater, which is considered to be the oxidation of low-\(\delta^{34}\text{S}\) sulfide to sulfate during the fluid extractions in the basalt basement\(^{38}\). CaS is more easily be oxidized than the other sulfide, due to the \(\Delta H_{298 \text{ K}}\) for the reaction \(\text{CaS(solid)} + 2\text{O}_2 = \text{CaSO}_4(\text{solid})\) is \(-960.9\) kJ/mol\(^{16}\) (Fig. 3). As the CaS can exist in the mantle region under the mid-ocean ridge, the deep CaS perhaps is an important source for the anhydrite and gypsum in BSMOR.
The possible existence area and evolution trend of CaS beneath the mid-ocean ridge. The reference sources of the important interface in the figure are as follows. The limit thickness of the ocean lithosphere is about 90–95 km\(^3\). At 160–170 km depth, the transformation from diamond to graphite would occur when the oxygen fugacity is above \(\Delta\text{FMQ} = 2^{24,25}\). At the depth of 150 ± 50 km\(^2\), redox melting \([\text{C(graphite)} + 2\text{Fe}_2\text{O}_3(\text{melt}) + \text{O}_2^- (\text{melt}) = 4\text{FeO} + \text{CO}_3^{2-} \text{(both in the melt)}]\)\(^{26,27}\) would happen. This ‘redox melting’ process would occur over a depth interval of 30 km, over which 30 p.p.m. of carbon in the mantle source would be oxidized\(^{25}\). Therefore, some carbonate melts occur through this reduction of Fe\(^{3+}\) in silicate phases\(^{25}\). The ascending carbonate melt will act as a flux to the overlying mantle and will react with the mantle silicates to stabilize a carbonated silicate melt\(^{28}\). At about 60 km depth, the carbonate melt will evolve towards a silicate melt composition\(^{25}\). The oxygen fugacity value of MORB is about \(\Delta\text{FMQ} = 0.42 \pm 0.43\)\(^{29}\).

The role of CaS in the Permian-Triassic boundary mass extinction

The Permian-Triassic boundary (PTB) mass extinction was the most severe biotic crisis in the past 500 million years\(^{40,41}\). The eruption of Siberian large igneous province (LIP) was considered to be the major cause of this extinction\(^{42,43}\). Contact metamorphism around intrusions in dolomite, evaporate, coal, or organic-rich shale generates large quantities of greenhouse and toxic gases (\(\text{CO}_2, \text{CH}_4, \text{SO}_2\)), which subsequently vent to the atmosphere and cause global warming and mass extinctions\(^{44}\). Global warming records were widespread found\(^{45,46}\). The atmospheric \(\text{CO}_2\) concentration at PTB is estimated to be \((3314 \pm 1097)\) ppmv, which is \((12 \pm 4)\) times that of the current atmosphere. This is more than double the Permian average\(^{47}\). Meanwhile, the atmospheric oxygen shows a very sharp drop from 30% to 15% (volume fraction) at the PTB\(^{48}\). As the magnitude of \(\text{CO}_2\) increase is much smaller than that of \(\text{O}_2\) decrease, the decrease of atmospheric \(\text{O}_2\) content cannot be solely
explained by the increase of CO\textsubscript{2} content. The seawater absorption cannot explain the large reduction in O\textsubscript{2}, because the oxygen content in the ocean is also decreasing, and the ocean is in an anoxic environment\textsuperscript{49-52}. The abundant emergence of anoxygenic photosynthesis at PTB could reduce atmospheric O\textsubscript{2} supply\textsuperscript{50}. Besides, O\textsubscript{2} perhaps was pinned down by other reservoirs. A direct way to consume oxygen is N\textsubscript{2} + O\textsubscript{2} = 2NO\textsubscript{2}, which has been observed in hot lava flows to fix atmospheric nitrogen at their surface\textsuperscript{53}. At 1200 and 1400 K (a good approximation of the surface temperature of an advancing lava flow\textsuperscript{53}), the molar fraction of NO generated by this mechanism in volcanic gases has been calculated to be 2×10\textsuperscript{-4} and 6×10\textsuperscript{-4}, respectively\textsuperscript{54}. With such low values, it is difficult to say that this mechanism is the single or major cause of the decrease in O\textsubscript{2}. There are large amounts of anhydrite and gypsum layers or anhydrite-containing rocks in or around the Siberian LIP, and the visible thickness of the anhydrite layer could reach 25 m\textsuperscript{55}. Most scholars held the view that anhydrite contamination occurred promoting the formation of the world’s largest Noril’sk Cu-Ni deposit\textsuperscript{42,56}. Carbon contamination is widespread in Siberian LIP\textsuperscript{56}, reducing the oxygen fugacity of magma, and even native Fe appears\textsuperscript{57}, which only occurs when the oxygen fugacity is less than FMQ–5\textsuperscript{58}. Significant quantities of CH\textsubscript{4}, CO, CO\textsubscript{2}, and SO\textsubscript{2} were released during the assimilation of carbonaceous sediments\textsuperscript{58,59}. When CaSO\textsubscript{4} encounters such a reducing gas, S can not exist in hexavalent. In modern industry, the reaction of C and CaSO\textsubscript{4} (CaSO\textsubscript{4} + 2C = CaS + 2CO\textsubscript{2}) in the temperature range of 750–1080°C is a method of producing CaS\textsuperscript{60}. Under the condition that CO, N\textsubscript{2}, and CO\textsubscript{2} are mixed as reducing agents, through the reaction CaSO\textsubscript{4} + 4CO = CaS + 4CO\textsubscript{2}, at 650°C, the generation efficiency of CaS is 95%\textsuperscript{61}. These two reactions probably happen at Siberian LIP (Fig. 4). When the lava is cooled, the generated CaS can combine with O\textsubscript{2} again to form CaSO\textsubscript{4}. In this process (named reaction process 2), one CO\textsubscript{2} molecule is produced accompanied by one or a half molecules O\textsubscript{2} disappeared from the atmosphere.

Terina ultramafic lamprophyres were considered to be the result of Siberian mantle plume, which are derived from carbonate-rich mantle beneath the Siberian lithosphere with an oxygen fugacity of about FMQ–1 at 6 GPa\textsuperscript{62}. Anhydrite was found in olivine which is considered to be formed at the asthenosphere-lithosphere boundary. Hexavalent sulfur is difficult to exist under this oxygen fugacity condition, anhydrite most likely originally existed in the form of CaS at the asthenosphere-lithosphere interface during Siberian mantle plume activity (Fig. 4).

The Noril’sk traps are dominated by low magnesium (MgO < 7 wt. %) tholeiitic basalts and contain minor olivine basalts and picrites (MgO could reach 24 wt. %)\textsuperscript{63}. This composition is roughly similar to the composition of the initial melt formed by the partial melting of orthopyroxenite in this research (Supplementary Table 3). There are abundant coal-petroleum-bearing carbonate and sandstone in or around the Siberian LIP. The average oxygen fugacity of primary melts of Gudchikhinsky Formation on the surface in the Noril’sk region is FMQ–1.5\textsuperscript{63}. Magmatic anhydrite was found in some intrusions\textsuperscript{64}. The CaS formation by two-melt mechanism (reaction
process 1, Fig. 4) probably existed at the stage magma chamber and the shallow crust (Fig. 4).

For the reaction process 1 and 2, one CO₂ molecule is produced accompanied by two molecules and a half to one molecule of O₂ will be fixed by CaSO₄, respectively. To simplify the calculation, we assume that the production of one molecule of CO₂ is accompanied by the consumption of one molecule of O₂ during the entire process of CaS formation and oxidation. 170 ×10¹² tonnes CO₂ was thought to be produced during the activity of Siberian mantle plume⁴². Thus, the maximum O₂ fixed by CaSO₄ can be 123 ×10¹² tonnes. We assume that the air mass in the Late Permian is the same as in modern times with a value of 5.1480 ×10¹⁵ tons⁶⁵, and the volume ratio of N₂ and O₂ is 70:30. In this way, the 7.1% mass fraction of the total oxygen content in Late Permian can be fixed by CaSO₄. Due to part of CO₂ production was not being related to CaS, the above calculation process, the effect of CaS on oxygen consumption may be exaggerated. But CaS played a role in reducing the oxygen content which promoted the PTB mass extinction.

![Fig. 4. Schematic diagram of the possible location of CaS in the magma system of the Siberian igneous province. The oxygen fugacity of the origin magma of Terina ultramafic lamprophyres is FMQ−1⁶². The average oxygen fugacity of primary melts of Gudchikhinsky Formation in the Noril’sk region is FMQ−1.5 (2.5 orders of magnitude below the Ni–NiO buffer)⁶³.](image)

**Platinum group elements aggregation effect of CaS**

For the graphite-lined Au₇₅Pd₂₅ capsule, under the condition of 1.5 GPa and 1240℃,
if the duration time is longer than 1.5 hours in melt experiment, Pd will enter the melt. During experiment No. 3 (P = 1.5 GPa, T = 1240°C, duration time = 4 h), a CaS-dominated sulfide liquid enriched with Pd was detected by the electron probe energy spectrometry analysis. The mass fraction (wt. %) of Ca, Co, Ni, S, and Pd is 21.49, 0.19, 11.92, 29.99, and 36.27, respectively. Therefore, the CaS melt can also enrich platinum group elements (PGEs). There are sulfates in the carbonate inclusions of Dali Lake discovered in the Central Asian Orogenic Belt, and the content of PGEs in the carbonate inclusions is more than 1,000 times that of sedimentary carbonates.

Due to the distribution coefficient between sulfides and silicates (D_{Sul/Sil}) ranging from $4 \times 10^5$ to $2-3 \times 10^6$ for PGEs, the high PGEs content is explained by the ingress of mantle sulfides. The presence of sulfates was considered to be the recycling of sedimentary carbonates during oceanic crust subduction, which can improve the oxygen fugacity of the lithospheric mantle and promote the oxidation of sulfides in the mantle. However, the above explanation contradicts the existence of Si-dominated super-reduced minerals in the carbonate inclusions, including SiC, TiC, natural metals (Si, Fe, Ni), and silicides (Fe$_3$Si, and Fe$_3$Si$_7$). Sulfate cannot coexist with these super-reduced minerals under this low oxygen fugacity. The alternative explanation for the occurrence of highly reducing minerals, sulfates, and high platinum group element content in the mantle carbonate inclusion is that reducing sulfides such as CaS generated in the carbonate melt during the metasomatism of the mantle, which promoted the enrichment of platinum group elements, during the process of rising to the surface, reducing sulfides such as CaS are oxidized to form sulfates.

The mediating role of CaS in rare earth elements enrichment in Earth

Isotopic similarities between the Earth and enstatite meteorites are remarkable. Primitive earth was considered to be constructed mainly by enstatite meteorites. Among these meteorites, oldhamite grains display REE enrichments (10–100 times the REE abundance of CI carbonaceous chondrites), indicating that oldhamite could be the most important primary source for rare earth elements deposits on Earth. During the laboratory melts experiment, the presence of Ca-rich sulfide liquid can cause the enrichment of heavy rare earth in itself and the enrichment of light rare earth in the silicate melts. Sulfate, which can be formed by the oxidation of CaS, is an important or even dominant anionic ligand in the ore-forming fluids of many REE deposits. Thus, CaS may play an intermediary role in the formation of rare earth elements ore deposits on Earth.
Methods

Mineral composition and chemical composition of start materials
The orthopyroxenite samples were collected at a depth of 259 meters from the drillcore ZK11E05 in the Xiarihamu giant Ni ore deposit in the Qinghai-Tibet Plateau (Fig. S1). The composition of the orthopyroxenite samples was listed in Supplementary Table 1.

Fig. S1. Orthopyroxenite at the depth of 259 m from the drillcore ZK11E05 in the Xiarihamu giant Ni ore deposit in the Qinghai-Tibet Plateau.

The orthopyroxenite is composed of 85% orthopyroxene, 5–7% clinopyroxene, and minor plagioclase and sulfides (Fig. S2-a). The orthopyroxene in the rock is approximately 0.4 to 1.5 mm in diameter (Fig. S2-a). The sulfides are located mainly in the interstitial space between orthopyroxene grains. The sulfides are mainly pyrrhotite and pentlandite (Fig. S2-b). The composition of the orthopyroxene was shown in Supplementary Table 2.
Calcium carbonate with a purity of 99.99% from the Alfa Aesar company was used in this study.

**Whole-rock major-element analysis**

This sample was crushed in steel jaws to −10 mesh powder, and ~200 g of this fraction was then ground to ~200 mesh powder using a tungsten carbide ring mill. Whole-rock Cu and Ni contents of samples were measured via inductively coupled plasma atomic emission spectroscopy (ICP-AES), with lower limits of detection of ~0.01 wt. %, at ALS Chemex (Guangzhou) Co. Ltd. Whole-rock S contents were measured using a gravimetric method and IR absorption (IR08) by the infrared sensor at 1,350°C with a lower limit of detection of ~0.01 wt. %. The analytical precision was ±8% of the amount present for S and ±3% for Ni and Cu. The other major element concentrations were determined using X-ray fluorescence (XRF) and a PANalytical Axios XRF instrument at ALS Chemex (Guangzhou) Co. Ltd. The result
is presented in Supplementary Table 1.

High pressure and temperature experiments
Experiments at 0.5 and 1.5 GPa were conducted at 1050 and 1240℃, respectively, using a multi-anvil apparatus at the University of Nevada, Las Vegas. We used semi-sintered MgO octahedra with 14 mm edge length as pressure media. The pressure was calibrated at room temperature using the cubic PbS to orthorhombic PbS transformation at 2.5 GPa73, Bi II-III at 2.7 GPa74, and Bi III-V at 7.7 GPa75. The furnace assembly consisted of a graphite furnace sleeve with moly electrodes at the ends, a zirconia outer sleeve, and MgO inner pieces. Sample powder was packed in a graphite crucible (3 mm height, outer diameter = 2.7 mm, inner diameter = 2mm) placed in an Au75Pd25 outer capsule with outer diameter of 3 mm. The assembled octahedra, furnace parts, and sample capsule were stored in a vacuum oven overnight at 260 ℃ before an experiment. The contamination experiments No. C1, No. C2, and No. C3 between the pyrrhotite-pentlandite orthopyroxenite (PPO) and CaCO3 were performed at 0.5 GPa and 1050℃ with a duration time of 1.2 h, at 1.5 GPa and 1240℃ with a duration time of 1.2 h, and at 1.5 GPa and 1240 with a duration time of 4h, respectively. The mass of PPO and CaCO3 in each experiment was 70–79 mg and 16–18 mg, respectively. Before the contamination experiments, partial melting experiments of PPO powders at two P-T conditions (P = 0.5 GPa, T = 1050℃ for experiment No. P1; P = 1.5 GPa, T = 1240℃ for experiment No. P2) with a duration time of 1.2 h. Type C thermocouple is used to measure temperature. The silicate components of the melts produced by the partial melting of PPO are all high-magnesium basalt. The results are shown in Supplementary Table 3.

Mineral and melts compositions analysis
Mineral compositions were determined using an electron microprobe at Chang'an University. The analytical conditions included energy of 15 kV, a beam current of 20 nA, a beam diameter of 1–5 µm, and a peak-counting time of 20 s. The standard materials used in the analysis were as follows: albite, K-feldspar, hematite, forsterite, xenotime, pyrophanite, corundum, wollastonite, Cr-spinel, kyanite, pyrophanite, metallic nickel, metallic cobalt, metallic gold, metallic palladium, and metal zinc, respectively. The lower limit of detection for all of the elements was 0.01%. The analytical relative error was ±2%. The typical composition of oldhamite was listed in Supplementary Table 4. The results of silicate minerals and melt compositions in different reaction areas of contamination No. C1 are listed in Supplementary Table 5.

X-ray Photoelectron Spectroscopy analysis
X-ray photoelectron spectroscopy measurements were conducted using ESCALAB 220i-XL XPS (Thermo Scientific, UK) at Zhejiang University. Monochromated Al Kα
X-rays at 1486.6 eV was used. The target voltage and target current are 15 kV and 10 mA, respectively. The vacuum chamber pressure is less than $2 \times 10^{-6}$ Pa, and the X-ray spot diameter was 650 μm. The pass energy was 30 eV, and the measurement step was 0.1 eV. C peak standard is 284.8 eV. Data analysis was carried out using XPSPEAK4.1 software and Origin software version 2018. The XPS results are presented in Supplementary Table 6. According to the Handbook of X-ray Photoelectron Spectroscopy, the binding energy of $S^{2-}$, $S^{4+}$, and $S^{6+}$ ranges from 160.3 to 164.0 eV, from 165.5 to 168.0 eV, and from 168.2 to 171.0 eV, respectively. Therefore, we believe that the three main peaks 163.2, 167.9, and 168.5 eV in this test result are caused by $S^{2-}$, $S^{4+}$, and $S^{6+}$, respectively (Fig. S3). Some sulfites were detected by electron microprobe, and the composition of sulfite was shown in Supplementary Table 7. This supports that the 167.9 eV is caused by $S^{4+}$. After the data is smoothed, Gaussian fitting is performed on the peak shape, and the ratio of peak area represents the mole ratio (Fig. S3). In this way, we got the $S^{6+}/S^{2-}$ ratio with a value of 0.004.

![Fig. S3. S$_{2p}$ X-ray photoelectron spectroscopy of the melts in the inter part of the central reaction area.](image)

**Oxygen fugacity determination of inter part of the central reaction area**

Oxygen fugacity in graphite-lined Pt or Pt$_{95}$Rh$_{05}$ capsule is about QFM−2.2. For
the experiment in this research, adding CO₂ from decarbonation can greatly increase the \( f_{O_2} \) value of melt \(^{79-81}\). Thus, it is reasonable that the lower limit of the oxygen fugacity of the melt formed by the reaction between the CaCO₃ and orthopyroxenite in the graphite-lined Au₇₅Pd₂₅ capsule is QFM−2.2. The \( S^{6+}/S^{2−} \) ratio of melts determined by the XPS method in Experiment No. C1 (\( T = 1050^\circ \text{C}, P = 0.5 \text{ GPa} \)) is 0.004. The oxygen fugacity could be calculated by the formula \( S^{6+}/\Sigma S = 1/(1+10^{(2.1-2\Delta \text{FMQ})}) \) \(^{82}\), and the FMQ value is determined by Formula 1 \(^{83}\).

\[
\log f_{O_2}(\text{FMQ}) = 82.75 + 0.00484 T - 30681/T - 24.45 \log(T) + 0.094 P/T - 0.000002 P, \tag{1}
\]
where \( P \) is in the bar and \( T \) is in K.

In this way, the oxygen fugacity of inter part of the central reaction area is FMQ−0.2. As the sulfur could be oxidized during sample preparation after quench, such as cutting and polishing process, it is reasonable that FMQ−0.2 is the upper limit of the actual oxygen fugacity of the melt. Therefore, the oxygen fugacity of inter part of central reaction area is FMQ−2.2 < \( f_{O_2} \) < FMQ−0.2.

1. Larimer, J. W. & Buseck, P. R. Equilibration temperatures in enstatite chondrites. *Geochimica Et Cosmochimica Acta* **38**, 471-477 (1974).
2. Brett, R. & Sato, M. Intrinsic oxygen fugacity measurements on seven chondrites, a pallasite, and a tektite and the redox state of meteorite parent bodies. *Geochimica Et Cosmochimica Acta* **48**, 111-120 (1984).
3. Kallenbach, R. et al. in *Solar System History from Isotopic Signatures of Volatile Elements* (eds R Kallenbach et al.) 413-422 (Springer Science & Business Media).
4. Bennett, C. J. et al. Investigating potential sources of Mercury's exospheric Calcium: Photon-stimulated desorption of Calcium Sulfide. *Journal of Geophysical Research: Planets* **121**, 137-146 (2016).
5. Yokoyama, K., Kimura, Y. & Kaito, C. Experiments on condensation of calcium sulfide grains to demarcate environments for the formation of enstatite chondrites. *ACS Earth and Space Chemistry* **1**, 601-607 (2017).
6. Larimer, J. W. & Ganapathy, R. The trace element chemistry of CaS in enstatite chondrites and some implications regarding its origin. *Earth and Planetary Science Letters* **84**, 123-134 (1987).
7. Lodders, K. & Fegley Jr, B. Lanthanide and actinide chemistry at high C/O ratios in the solar nebula. *Earth and Planetary Science Letters* **117**, 125-145 (1993).
8. Huang, F., Zhou, C., Wang, W., Kang, J. & Wu, Z. First-principles calculations of equilibrium Ca isotope fractionation: Implications for oldhamite formation and evolution of lunar magma ocean. *Earth and Planetary Science Letters* **510**, 153-160 (2019).
9. Zhou, C. *Theoretical calculations of the equilibrium Ca isotope fractionation factors* Master Degree thesis, University of Science and Technology of China, (2019).
10. Chakraborty, S., Jackson, T. L., Ahmed, M. & Thiemens, M. H. Sulfur isotopic fractionation in vacuum UV photodissociation of hydrogen sulfide and its potential relevance to meteorite analysis. *Proceedings of the National Academy of Sciences* **110**, 17650-17655 (2013).
11 Farquhar, J., Jackson, T. L. & Thiemens, M. H. A 33S enrichment in ureilite meteorites: evidence for a nebular sulfur component. *Geochimica Et Cosmochimica Acta* **64**, 1819-1825 (2000).

12 Wheelock, M. M., Keil, K., Floss, C., Taylor, G. & Crozaz, G. REE geochemistry of oldhamite-dominated clasts from the Norton County aubrite: igneous origin of oldhamite. *Geochimica Et Cosmochimica Acta* **58**, 449-458 (1994).

13 Gannoun, A., Boyet, M., El Goresy, A. & Devouard, B. REE and actinide microdistribution in Sahara 97072 and AlHA77295 EH3 chondrites: A combined cosmochemical and petrologic investigation. *Geochimica Et Cosmochimica Acta* **75**, 3269-3289 (2011).

14 Jones, J. & Boynton, W. in *Lunar and planetary science conference*. 353-354.

15 Haberle, C. W. & Garvie, L. A. Extraterrestrial formation of oldhamite and portlandite through thermal metamorphism of calcite in the Sutter's Mill carbonaceous chondrite. *American Mineralogist* **102**, 2415-2421 (2017).

16 Yrjas, P., Hupa, M. & Iisa, K. Pressurized stabilization of desulfurization residues from gasification processes. *Energy Fuels* **10**, 1189-1195 (1996).

17 Hwang, S.-L. *et al.* Crust-derived potassic fluid in metamorphic microdiamond. *Earth and Planetary Science Letters* **231**, 295-306 (2005).

18 Zhang, Z.-M. *et al.* Fluids in deeply subducted continental crust: petrology, mineral chemistry and fluid inclusion of UHP metamorphic veins from the Sulu orogen, eastern China. *Geochimica Et Cosmochimica Acta* **72**, 3200-3228 (2008).

19 Jugo, P. J., Luth, R. W. & Richards, J. P. Experimental data on the speciation of sulfur as a function of oxygen fugacity in basaltic melts. *Geochimica Et Cosmochimica Acta* **69**, 497-503 (2005).

20 Stachel, T. & Luth, R. Diamond formation—Where, when and how? *Lithos* **220**, 200-220 (2015).

21 Stagno, V., Frost, D., McCammon, C., Mohseni, H. & Fei, Y. The oxygen fugacity at which graphite or diamond forms from carbonate-bearing melts in eclogitic rocks. *Contributions to Mineralogy and Petrology* **169**, 16 (2015).

22 Campbell, A. J. *et al.* High pressure effects on the iron–iron oxide and nickel–nickel oxide oxygen fugacity buffers. *Earth and Planetary Science Letters* **286**, 556-564 (2009).

23 Rohrbach, A. & Schmidt, M. W. Redox freezing and melting in the Earth’s deep mantle resulting from carbon–iron redox coupling. *Nature* **472**, 209-212 (2011).

24 Stagno, V. & Frost, D. J. Carbon speciation in the asthenosphere: Experimental measurements of the redox conditions at which carbonate-bearing melts coexist with graphite or diamond in peridotite assemblages. *Earth and Planetary Science Letters* **300**, 72-84 (2010).

25 Stagno, V., Ojwang, D. O., McCammon, C. A. & Frost, D. J. The oxidation state of the mantle and the extraction of carbon from Earth’s interior. *Nature* **493**, 84-88 (2013).

26 Frost, D. J. & McCammon, C. A. The redox state of Earth’s mantle. *Annu. Rev. Earth Planet. Sci.* **36**, 389-420 (2008).

27 Kadik, A. Evolution of Earth’s redox state during upwelling of carbon-bearing mantle. *Phys. Earth Planet. Inter.* **100**, 157-166 (1997).

28 Dasgupta, R. & Hirschmann, M. M. The deep carbon cycle and melting in Earth’s interior. *Earth and Planetary Science Letters* **298**, 1-13 (2010).

29 Bézos, A. & Humler, E. The Fe**3+**/Fe ratios of MORB glasses and their implications for mantle melting. *Geochimica Et Cosmochimica Acta* **69**, 711-725 (2005).
| Number | Reference                                                                                              |
|--------|--------------------------------------------------------------------------------------------------------|
| 30     | Amini, M. et al. Calcium isotope ($\delta^{44/40}$Ca) fractionation along hydrothermal pathways, Logatchev field (Mid-Atlantic Ridge, 14° 45′ N). *Geochimica Et Cosmochimica Acta* **72**, 4107-4122 (2008). |
| 31     | Goodfellow, W. D. & Franklin, J. M. Geology, mineralogy, and chemistry of sediment-hosted clastic massive sulfides in shallow cores, Middle Valley, northern Juan de Fuca Ridge. *Economic Geology* **88**, 2037-2068 (1993). |
| 32     | Humphris, S. E. et al. The internal structure of an active sea-floor massive sulphide deposit. *Nature* **377**, 713-716 (1995). |
| 33     | Spiess, F. N. et al. East Pacific Rise: hot springs and geophysical experiments. *Science* **207**, 1421-1433 (1980). |
| 34     | Styrt, M. et al. The mineralogy and the isotopic composition of sulfur in hydrothermal sulfide/sulfate deposits on the East Pacific Rise, 21°N latitude. *Earth and Planetary Science Letters* **53**, 382-390 (1981). |
| 35     | Tostevin, R. et al. Multiple sulfur isotope constraints on the modern sulfur cycle. *Earth & Planetary Science Letters* **396**, 14-21 (2014). |
| 36     | Teagle, D. A., Alt, J. C. & Halliday, A. N. Tracing the chemical evolution of fluids during hydrothermal recharge: Constraints from anhydrite recovered in ODP Hole 504B. *Earth and Planetary Science Letters* **155**, 167-182 (1998). |
| 37     | Teagle, D. A., Bickle, M. J. & Alt, J. C. Recharge flux to ocean-ridge black smoker systems: a geochemical estimate from ODP Hole 504B. *Earth and Planetary Science Letters* **210**, 81-89 (2003). |
| 38     | Alt, J. C., Zuleger, E. & Erzinger, J. in *Proceedings of the Ocean Drilling Program, Scientific Results*. 155-166 (Citeseer). |
| 39     | Stein, C. A. & Stein, S. A model for the global variation in oceanic depth and heat flow with lithospheric age. *Nature* **359**, 123-129 (1992). |
| 40     | Xie, S., Pancost, R. D., Yin, H., Wang, H. & Evershed, R. P. Two episodes of microbial change coupled with Permo/Triassic faunal mass extinction. *Nature* **434**, 494-497 (2005). |
| 41     | Yin, H., Xie, S., Luo, G., Algeo, T. J. & Zhang, K. Two episodes of environmental change at the Permian–Triassic boundary of the GSSP section Meishan. *Earth Sci. Rev.* **115**, 163-172 (2012). |
| 42     | Sobolev, S. V. et al. Linking mantle plumes, large igneous provinces and environmental catastrophes. *Nature* **477**, 312-316 (2011). |
| 43     | Burgess, S. D., Bowring, S. & Shen, S.-z. High-precision timeline for Earth’s most severe extinction. *Proceedings of the National Academy of Sciences* **111**, 3316-3321 (2014). |
| 44     | Ganino, C. & Arndt, N. T. Climate changes caused by degassing of sediments during the emplacement of large igneous provinces. *Geology* **37**, 323-326 (2009). |
| 45     | Penn, J. L., Deutsch, C., Payne, J. L. & Sperling, E. A. Temperature-dependent hypoxia explains biogeography and severity of end-Permain marine mass extinction. *Science* **362** (2018). |
| 46     | Sun, Y. et al. Lethally hot temperatures during the Early Triassic greenhouse. *Science* **338**, 366-370 (2012). |
| 47     | Retallack, G. J. A 300-million-year record of atmospheric carbon dioxide from fossil plant cuticles. *Nature* **411**, 287-290 (2001). |
| 48     | Berner, R. A. GEOCARBSULF: a combined model for Phanerozoic atmospheric $O_2$ and $CO_2$. *Geochimica Et Cosmochimica Acta* **70**, 5653-5664 (2006). |
| 49     | Isozaki, Y. Permo-Triassic boundary superanoxia and stratified superocean: records from lost |
deep sea. Science **276**, 235-238 (1997).

50 Grice, K. *et al.* Photic zone euxinia during the Permian-Triassic superanoxic event. Science **307**, 706-709 (2005).

51 Clarkson, M. *et al.* Ocean acidification and the Permo-Triassic mass extinction. Science **348**, 229-232 (2015).

52 Shen, Y. *et al.* Multiple S-isotopic evidence for episodic shoaling of anoxic water during Late Permian mass extinction. *Nature Communications* **2**, 1-5 (2011).

53 Huebert, B. *et al.* Volcano fixes nitrogen into plant-available forms. Biogeochemistry **47**, 111-118 (1999).

54 Mather, T. *et al.* Nitric acid from volcanoes. Earth and Planetary Science Letters **218**, 17-30 (2004).

55 Ryabov, V., Shevko, A. Y. & Gora, M. *Trap magmatism and ore formation in the Siberian Noril’sk region.* Vol. 2 (Springer, 2014).

56 Lacono-Marziano, G., Ferraina, C., Gaillard, F., Carlo, I. D. & Arndt, N. T. Assimilation of sulfate and carbonaceous rocks: experimental study, thermodynamic modeling and application to the Noril’sk-Talnakh region (Russia). *Ore Geology Reviews* **90**, 399-413 (2017).

57 Ryabov, V. & Lapkovsky, A. Native iron (–platinum) ores from the Siberian Platform trap intrusions. Aust. J. Earth Sci. **57**, 707-736 (2010).

58 Pernet-Fisher, J. F., Day, J. M., Howarth, G. H., Ryabov, V. V. & Taylor, L. A. Atmospheric outgassing and native-iron formation during carbonaceous sediment–basalt melt interactions. *Earth and Planetary Science Letters* **460**, 201-212 (2017).

59 Lacono-Marziano, G. *et al.* Extremely reducing conditions reached during basaltic intrusion in organic matter-bearing sediments. *Earth and Planetary Science Letters* **357**, 319-326 (2012).

60 Van der Merwe, E., Strydom, C. & Potgieter, J. Thermogravimetric analysis of the reaction between carbon and CaSO₄·2H₂O, gypsum and phosphogypsum in an inert atmosphere. *Thermochem. Acta* **340**, 431-437 (1999).

61 Li, H. & Zhuang, Y. Catalytic reduction of calcium sulfate to calcium sulfide by carbon monoxide. Ind. Eng. Chem. Res. **38**, 3333-3337 (1999).

62 Prokopyev, I., Starikova, A., Doroshkevich, A., Nugumanova, Y. & Potapov, V. Petrogenesis of ultramafic lamprophyres from the Terina complex (Chadobets upland, Russia): Mineralogy and melt inclusion composition. *Minerals* **10**, 419 (2020).

63 Sobolev, A. V., Krivolutskaya, N. A. & Kuzmin, D. Petrology of the parental melts and mantle sources of Siberian trap magmatism. *Petrology* **17**, 253-286 (2009).

64 Li, C., Ripley, E. M., Naldrett, A. J., Schmitt, A. K. & Moore, C. H. Magmatic anhydrite-sulfide assemblages in the plumbing system of the Siberian Traps. *Geology* **37**, 259-262 (2009).

65 Trenberth, K. E. & Smith, L. The mass of the atmosphere: A constraint on global analyses. *J. Clim.* **18**, 864-875 (2005).

66 He, D., Liu, Y., Moynier, F., Foley, S. F. & Chen, C. Platinum group element mobilization in the mantle enhanced by recycled sedimentary carbonate. *Earth and Planetary Science Letters* **541**, 116262 (2020).

67 Mungall, J. E. & Brenan, J. M. Partitioning of platinum-group elements and Au between sulfide liquid and basalt and the origins of mantle-crust fractionation of the chalcophile elements. *Geochimica Et Cosmochimica Acta* **125**, 265-289 (2014).

68 He, D. *et al.* SiC-dominated ultra-reduced mineral assemblage in carbonatitic xenoliths from...
the Dalihu basalt, Inner Mongolia, China. *American Mineralogist* **102**, 312-320 (2017).

69 Defouilloy, C., Cartigny, P., Assayag, N., Moynier, F. & Barrat, J.-A. High-precision sulfur isotope composition of enstatite meteorites and implications of the formation and evolution of their parent bodies. *Geochimica Et Cosmochimica Acta* **172**, 393-409 (2016).

70 Hou, W., Ouyang, Z. Y., Xie, H. S. & Hu, G. X. Petrological Model for Condensation Process of Solar Nebula: (III) Nebular Condensation in Terrestrial Planet Region and Estimation of Earth's Primitive Composition. *Acta Petrologica Sinica* **12**, 471-477 (1996).

71 Wan, Y., Wang, X., Chou, I.-M. & Li, X. Role of sulfate in the transport and enrichment of REE in hydrothermal systems. *Earth and Planetary Science Letters* **569**, 117068 (2021).

72 Migdisov, A. A. & Williams-Jones, A. A spectrophotometric study of Nd (III), Sm (III) and Er (III) complexion in sulfate-bearing solutions at elevated temperatures. *Geochimica Et Cosmochimica Acta* **72**, 5291-5303 (2008).

73 Zhou, X. et al. New exploration on phase transition and structure of PbS under high pressure and temperature. *Journal of Applied Physics* **113**, 043509 (2013).

74 Bundy, P. Phase diagram of Bismuth to 130 000 kg/cm², 500°C. *Physical Review* **110**, 314 (1958).

75 Aoki, K., Fujiwara, S. & Kusakabe, M. Stability of the bcc structure of bismuth at high pressure. *J. Phys. Soc. Jpn.* **51**, 3826-3830 (1982).

76 Moulder, J. F., Stickle, W. F., Sobol, P. E. & Bomben, K. D. Handbook of X-ray photoelectron spectroscopy. *Perkin-Elmer, USA*, 261 (1992).

77 Médard, E., Mccammon, C. A., Barr, J. A. & Grove, T. L. Oxygen fugacity, temperature reproducibility, and H₂O contents of nominally anhydrous piston-cylinder experiments using graphite capsules. *American Mineralogist* **93**, 1838-1844 (2008).

78 Li, Y. & Audéat, A. Partitioning of V, Mn, Co, Ni, Cu, Zn, As, Mo, Ag, Sn, Sb, W, Au, Pb, and Bi between sulfide phases and hydrous basanite melt at upper mantle conditions. *Earth and Planetary Science Letters* **355**, 327-340 (2012).

79 Frezzotti, M., Selverstone, J., Sharp, Z. & Compagnoni, R. Carbonate dissolution during subduction revealed by diamond-bearing rocks from the Alps. *Nat. Geosci.* **4**, 703-706 (2011).

80 Wenzel, T., Baumgartner, L. P., Brügmann, G. E., Konnikov, E. G. & Klslov, E. Partial melting and assimilation of dolomitic xenoliths by mafic magma: the loko-Dovyren intrusion (North Balkal Region, Russia). *Journal of Petrology* **43**, 2049-2074 (2002).

81 Mungall, J. E. Roasting the mantle: Slab melting and the genesis of major Au and Au-rich Cu deposits. *Geology* **30**, 915-918 (2002).

82 Jugo, P. J., Wilke, M. & Botcharnikov, R. E. Sulfur K-edge XANES analysis of natural and synthetic basaltic glasses: Implications for S speciation and S content as function of oxygen fugacity. *Geochimica Et Cosmochimica Acta* **74**, 5926-5938 (2010).

83 O'Neill, H. S. Quartz-fayalite-iron and quartz-fayalite-magnetite equilibria and the free energy of formation of fayalite (Fe₂SiO₄) and magnetite (Fe₃O₄). *American Mineralogist* **72**, 67-75 (1987).