CaS: a key medium for Ca-S-C-O cycles in Earth

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Oldhamite (CaS) is a rare mineral only observed naturally in enstatite meteorites. No papers reported the existence of CaS in terrestrial samples, nor in other meteorite groups. However, in experiments at 1.5 GPa, 1510 K and 0.5 GPa, 1320 K, when the $\log f_{O_2}$ is lower than $-10.57$ (FMQ−0.52), CaS was produced in this study by a two-melt mechanism involving the reaction between molten pyrrhotite-pentlandite-bearing orthopyroxenite and molten CaCO$_3$. CaS combines very easily with oxygen to form CaSO$_4$ or be hydrolyzed to form calcium hydroxide, which likely explains why it has never been found in geological samples from Earth. We speculate that part of the anhydrite and gypsum in black smokers along mid-ocean ridges are related to the oxidation of CaS in the underlying mantle. The Siberian mantle plume perhaps had generated CaS when it intruded into the lithosphere.

Enstatite meteorites (EMs), which are the most reduced, undifferentiated extraterrestrial materials and are the only rock type in which oldhamite (CaS) occurs, likely experienced an oxygen fugacity well below IW−2.7 (IW = iron-wüstite)

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buffering equilibrium, in \( \log(f_{O_2}) \). The oxygen-poor signature of EMs suggests that they formed near the center of the solar system nebula, i.e., within the orbit of Mercury. It is widely accepted that CaS formed in a reduced environment. For example, CaS could be a major component of Mercury’s surface. However, the formation process of CaS in EMs remains under dispute. There are currently two main views regarding this issue.

Some researchers hold the view that CaS is a product of condensation of the nebula gas. Laboratory smoke experiments demonstrate that pure CaS and a solid solution of CaS and CaO [Ca(S,O)] condense from vapor phase calcium, sulfur, and oxygen with the O/S atomic ratio of <2 and between 2 and 10, respectively. This evidence directly supports a nebular gas origin. Furthermore, according to first-principles calculations, at equilibrium oldhamite is more easily enriched in light Ca isotopes than the other solid minerals; in contrast, 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 the condensation of solar nebular gas. However, sulfur isotope data do not support the nebula gas origin. The correlation between \( \Delta^{33}S \) and \( \Delta^{36}S \) of some EMs does not follow the trends of photochemistry in the solar nebula with \( \Delta^{36}S = -2.98\Delta^{33}S \) and of cosmic-ray spallation during presolar nebula with \( \Delta^{36}S = 8\Delta^{33}S \).

Some scholars argue that the oldhamite in EMs is of igneous origin. Textural evidence 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\(^8\). However, the most representative rare earth elements (REE) pattern of oldhamite in EMs is characterized by slight to large positive Eu and Yb anomalies and enrichment in light REEs relative to heavy REEs\(^9\). Nevertheless, experimental petrology studies have shown that the Ca-rich sulfide liquid is enriched in the heavy REEs at 1523 K and oxygen fugacity of \(\log f_O^2 = -17\)\(^{10}\). The REE fractionation between the Ca-rich sulfide liquid and the silicate liquid (D value) is extreme, with \(D(Lu) = 60 \times D(La)\) at 1473 K\(^{10}\). This finding is at odds with an igneous origin.

In current study, after reaction between pyrrhotite-pentlandite-bearing orthopyroxenite (PPO) and CaCO\(_3\) in a graphite-lined Au\(_{75}\)Pd\(_{25}\) capsule (Fig. 1a), at 1.5 GPa, 1510 K and 0.5 GPa, 1320 K, oldhamites were observed at the central reaction zone in recovered samples (Figs. 1b, 1c, and S3). That is, oldhamite appears to have formed during interaction of carbonate melt and sulfide-bearing silicate melt at suitable \(P-T-f_O^2\) conditions. Here, we name this formation process the two-melt mechanism. In the absence of calcium carbonate, the magmas produced by the partial melting of orthopyroxenite under two \(P-T\) conditions are similar in composition, and both are high-magnesium basaltic magmas (\(\text{SiO}_2 = 54.5–54.9\ \text{wt.\%}, \text{MgO} = 9.54–10.19\ \text{wt.\%}; \text{Methods section and Supplementary Table 3}\)). Basaltic melts are common at mid-ocean ridges and large igneous provinces. Oxygen fugacity in graphite-lined noble metal capsule is about FMQ–2.2\(^{11}\) (FMQ = buffer equilibrium \(3\text{Fe}_2\text{SiO}_4 + \text{O}_2 = 2\text{Fe}_3\text{O}_4 + 3\text{SiO}_2\)). These \(P-T-f_O^2\) experimental conditions for CaS
formation are easily achieved inside the Earth. We speculate that the two-melt mechanism can occur during carbonate melt metasomatism in mantle or the intrusive of mantle-derived magma into the lithosphere. The outward ring structure in the order of Ca(OH)$_2$, CaS, and pentlandite were found in meteorites$^{12}$. Thus, these researchers propose that CaCO$_3$ thermally decomposed into CaO, and CaO reacted with the sulfur ion to form CaS$^{12}$. In this study, some sulfides occurred around CaS, and bubbles are always present close to CaS (Fig. 1b and Fig. S3). Therefore, the most probable route for the CaS formation is: CaCO$_3$ (melt) = CaO (melt) + CO$_2$ (gas), CaO (melt) + FeS (melt) = CaS (solid) + FeO (melt).
Fig. 1. State and location of CaS generated by 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 at 0.5 GPa and 1320 K; average composition of Cpx, Opx, and melts at different reaction zone were listed in Supplementary Table 5. c. Drop-shaped CaS in the inner part of the central reaction zone and disseminated Fe-Ni sulfide (bright white). Opx = orthopyroxenite, Po = pyrrhotite, Pn = pentlandite, and Od = oldhamite.

To date, no papers reported the existence of CaS in natural terrestrial samples, probably due to the following reactions occurred:

\[
\text{CaS (s) + 1/2O}_2 (\text{g}) = \text{CaO (s) + S}_2 (\text{g}) \quad (\Delta H_{298 \text{ K}} = -31.9 \text{ kJ/mol}), \quad (1)
\]

\[
\text{CaS (s) + 2O}_2 (\text{g}) = \text{CaSO}_4 (\text{s}) \quad (\Delta H_{298 \text{ K}} = -959.5 \text{ kJ/mol}), \quad (2)
\]

\[
\text{CaO (s) + H}_2\text{O (l)} = \text{Ca(OH)}_2 (\text{s}) \quad (\Delta H_{298 \text{ K}} = -109.2 \text{ kJ/mol}), \quad (3)
\]

\[
\text{CaS (s) + 2H}_2\text{O (l)} = \text{Ca(OH)}_2 (\text{s}) + \text{H}_2\text{S (g)} \quad (\Delta H_{298 \text{ K}} = -290 \text{ kJ/mol}), \quad (4)
\]

\[
\text{CaS (s) + 2O}_2 (\text{g} + 2\text{H}_2\text{O (l)} = \text{CaSO}_4 \cdot 2\text{H}_2\text{O (s)} \quad (\Delta H_{298 \text{ K}} = -838.5 \text{ kJ/mol})^{13}. \quad (5)
\]

That is, CaS reacts particularly readily with oxygen to form calcium sulfate. Moreover, in the presence of H₂O, CaS can be hydrolyzed to form calcium hydroxide. Thus, whether the CaS generated by magmatism in planet can be preserved on the surface of a planet is considered to be related to at least three factors (1) the oxygen fugacity of the magma; (2) the oxygen content in the atmosphere; (3) the H₂O content of the planet surface.
The oxygen fugacity at the oldhamite–anhydrite equilibrium (CaS (s) + 2O2 (g) = CaSO4 (s), named OA buffer) and the oldhamite–lime equilibrium (CaS (s) + 1/2O2 (g) = CaO (s) + S2 (g), named OL buffer) can be determined by the formula 6 and 7, respectively (Method section):

\[
\log f_o^2 = 2.19144 + 1.09305 \times 10^{-4} T - 25137/T - 1551.42/T^2 + 1.5305 \times 10^7/T^3 + 0.04777P/T + 2.7838\log T, \quad (6)
\]

\[
\log f_o^2 = -21.1162 + 3.65342 \times 10^7/T^3 - 6205.07/T^2 + (-16237.94 - 0.11450P)/T + 0.43722 \times 10^{-3}T + 11.13544\log T + \log f_s^2, \quad (7)
\]

where \( P \) is in bar, \( T \) is in K.

Fig. 2. Representative oxygen fugacity vs. temperature curves typically used in geochemistry, including IW (Fe + ½O2 = FeO), OL (CaS (s) + ½O2 (g) = CaO (s) + S2
CaS is stable when the $\log f_{O_2}$ is below OL buffer and wound never exists if the $\log f_{O_2}$ is above OA buffer. At 0.5 GPa and 1320 K, OA = FMQ + 2.21 ($\log f_{O_2} = -7.83$) and OL = FMQ − 0.52 ($\log f_{O_2} = -10.57$) (Fig. 2). The $\log f_{O_2}$ value of Mercury’s surface magma ranges from IW −2.93 to IW−10.5 ($\log f_{O_2} = -13.2$ to −21.7) at 1600−1700 K (Fig. 2), and the $\log f_{O_2}$ value of Mercury’s atmosphere is −14.7. These values are much lower than the OL buffer (Fig. 2), and no H$_2$O was found in the atmosphere and the surface of Mercury, which probably are the reasons why CaS could be preserved on Mercury. Although $\log f_{O_2}$ of Martian magma is significantly lower than OL, due to the existence of H$_2$O on Mars and the high $\log f_{O_2}$ value (−4.32) of the Martian atmosphere (Fig. 2), which is significantly higher than OA, no CaS but some sulfate has been found on Mars. The average $\log f_{O_2}$ of arc basalt, ocean island magma, and most basalt related to mantle plume on Earth is FMQ + 0.96, FMQ + 0.82, and FMQ + 0.1, respectively $^{20}$, which is higher than OL. Moreover, the $\log f_{O_2}$ value $-0.67$ of Earth
atmosphere is much higher than OA (Fig. 2), and H$_2$O widely exist on Earth’s crust. The above environments are difficult for the preservation of CaS in Earth samples. However, we believe that CaS can exist in the interior of the Earth and that CaS can exist transiently in certain Earth surface environments.

**The possible existence of CaS in mantle inclusions**

Native Fe, native Ni, and numerous anhydrite inclusions were identified in diamonds from the Juina Area, Brazil$^{21}$. Anhydrite has been reported as inclusions in kyanite from crustal-type eclogites from the Dabie-Sulu ultra-high pressure metamorphic belt, where diamond exists$^{22,23}$. When oxygen fugacity is lower than FMQ−1, there is almost no S$^{6+}$ in the melt$^{24}$. The upper limit of the oxygen fugacity for diamond formation in mantle is FMQ−1.5$^{25}$. Thus, it is nearly impossible that sulfate exists during the diamond formation process. A reasonable explanation is that the primary inclusion component was CaS. CaS could react with the O$_2$ to form anhydrite during the ascending and exhumation of the host rocks.

**The possible transient presence of CaS in the Siberian large igneous province**

The Siberian large igneous province (SLIP) at the Permian-Triassic boundary (PTB) is dominated by low magnesium (MgO < 7 wt. %) tholeiitic basalts and contains minor olivine basalts and picrites$^{26}$. 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). The average lg$f_{O_2}$ of magma erupting at and around the mantle plumes of Hawaii, Erebus, Iceland, and the Canary Islands is FMQ
+ 0.1$^{20}$. However, the Siberian mantle plume is characterized by much lower oxygen fugacity. The average oxygen fugacity of primary melts of Gudchikhinsky Formation on the surface in the SLIP is FMQ$^{-1.5}$$^{26}$. Abundant coal- and petroleum-bearing carbonates occur in or around the SLIP. Carbon contamination is widespread in SLIP$^{27}$, reducing the oxygen fugacity of magma so much that even native Fe appears$^{28}$, which only occurs if the oxygen fugacity is less than FMQ$^{-4.5}$ (Fig. 2). Magmatic anhydrites have been found in some intrusions in the SLIP$^{29}$. It is hard to think anhydrite could exist under the oxygen fugacity range from FMQ$^{-1.5}$ to FMQ$^{-4.5}$ (Fig. 2). Thus, it is reasonable that the CaS formation via the two-melt mechanism likely occurred in the SLIP.

Moreover, large quantities of anhydrite and gypsum layers or anhydrite-containing rocks exist in or around the SLIP with the visible thickness of some anhydrite layers reaching 25 m on surface$^{30}$. Most scholars hold the view that anhydrite contamination promoted the formation of the world’s largest magmatic Cu-Ni deposit$^{27,31}$. When CaSO$_4$ encounters such a reducing magma with lg$^{f_{O_2}}$ value from FMQ$^{-1.5}$ to FMQ$^{-4.5}$, hexavalent S can no longer exist. In the modern industry, CaS is produced by the reaction of C and CaSO$_4$ (CaSO$_4$ + 2C = CaS + 2CO$_2$) in the temperature range of 1023–1353 K$^{32}$. Under the condition that CO, N$_2$, and CO$_2$ are mixed as reducing agents, through the reaction CaSO$_4$ + 4CO = CaS + 4CO$_2$, at 923 K, the generation efficiency of CaS is 95%$^{33}$. These two reactions likely proceeded during the interaction between the carbon-contaminated Siberian magma with lg$^{f_{O_2}}$ value from FMQ$^{-1.5}$ to FMQ$^{-4.5}$ and the surrounding anhydrite rocks in SLIP.
When the lava was cooled, the generated CaS combined with O₂ again to form CaSO₄. In this process, one CO₂ molecule is produced with one or one half O₂ molecule removed from the atmosphere. The transient presence of CaS may have played a role in increasing CO₂ content and decreasing the O₂ content in the atmosphere at PTB.

**The link between CaS and anhydrite in black smokers**

In the mantle below a mid-ocean ridge, at a depth of about 160–170 km, diamond would transform to graphite if the oxygen fugacity is above FMQ–2³⁴,³⁵ (Fig. 3). Redox melting \[ \text{C(graphite) + } 2\text{Fe}_2\text{O}_3(\text{melt}) + \text{O}_2^-(\text{melt}) = 4\text{FeO} + \text{CO}_3^{2-} \text{(both in the melt)} \] occurs mainly at a depth of 120–150 km³⁵. The carbonate melt produced by redox melting will ascend as a flux into the overlying mantle and react with mantle silicates to stabilize a carbonated silicate melt³⁷ (Fig. 3). At a depth of about 60 km, the carbonate melt evolves towards a silicate melt composition³⁵. The mid-ocean ridge basalt (MORB), at the top location of the silicate melt, is characterized by a redox state of FMQ–0.4¹³⁸ (Fig. 3). Most of the part from the diamond-to-graphite interface to the location of MORB is the CaS stable area (below OL), and carbonate melt and basaltic melts are common. Thus, it is reasonable to speculate that the formation of CaS is possible (Fig. 3). Large amounts of anhydrite and gypsum exist in black smokers along mid-ocean ridges (BSMOR)³⁹ (Fig. 3), which is considered to be derived from seawater as the \( \delta^{34}\text{S}_{\text{CDT}} \) values of these sulfates are nearly the same to that of modern seawater⁴⁰. The \( \delta^{34}\text{S}_{\text{CDT}} \) of modern seawater sulfate is 21.24‰⁴¹. However, the \( \delta^{34}\text{S}_{\text{CDT}} \) value of anhydrite gradually decreases from the seawater’s 20
± 1‰ to 3.4‰, and \(^{87}\text{Sr}/^{86}\text{Sr}\) value of anhydrite decrease downward from the seawater value of 0.7088 to a MORB value of 0.7029 in a 1.8 km deep drillhole for the ocean-ridge black smoker systems\(^{42,43}\). The S and Sr sources from the MORB beneath the black smoker are attributed to the anhydrite. The \(\delta^{34}\text{S}_{\text{CDT}}\) value of 3.4‰ is much lower than that of modern seawater which is considered to result from the oxidation of low-\(\delta^{34}\text{S}\) sulfide to sulfate during the fluid extractions in the basalt basement\(^{44}\). CaS is easily oxidized, due to the large negative \(\Delta H_{298K}\) for the reactions 2 and 5. As CaS can exist in the mantle region beneath a mid-ocean ridge, CaS perhaps is a source for the anhydrite and gypsum in BSMOR (Fig. 3).

Fig. 3. Possible area for existence and evolution of CaS beneath a mid-ocean ridge. At a depth of 160−170 km, the transformation from diamond to graphite occurs if the oxygen fugacity is above FMQ−2\(^{35}\). At a depth of 150 ± 50 km\(^{35}\), ‘redox melting’ \([\text{C(graphite)} + 2\text{Fe}_2\text{O}_3(\text{melt}) + \text{O}^{2-}(\text{melt}) = 4\text{FeO} + \text{CO}_3^{2-} \text{(both in the melt)}]\)\(^{36}\) takes place over a depth interval of 30 km, over which 30 ppm of carbon in the mantle
source is oxidized\textsuperscript{35}. The ascending carbonate melt acts as a flux to the overlying mantle and reacts with the mantle silicates to stabilize a carbonated silicate melt\textsuperscript{37}. At a depth of 60 km, the carbonate melt evolves toward a silicate melt composition\textsuperscript{35}.

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