

Oldhamite: a new link in upper mantle for C–O–S–Ca cycles and an indicator for planetary habitability

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To date, oldhamite (CaS) has not been reported to occur in mantle rock, and it is extremely rare in crustal rocks. However, we found the formation of oldhamite through the reaction between sulfide-bearing orthopyroxenite and molten CaCO₃ at upper mantle and lower crust conditions. Oldhamite is easily oxidized to CaSO₄ or hydrolyzed to produce calcium hydroxide. The low oxygen fugacity of magma, the extremely low oxygen content of the atmosphere, and the lack of a large amount of liquid water on the planets' surface are necessary for the widespread existence of oldhamite on the surface of a planet; otherwise, anhydrite or gypsum will exist in large quantities. This study points out that oldhamite may exist in the mantle beneath the mid-ocean ridge, and it may be the precursor of some calcium sulfate in black smokers. Additionally, oldhamites may have been a contributing factor to the early Earth's atmospheric hypoxia environment, and the transient existence of oldhamites during the interaction between reducing sulfur-bearing magma and carbonate could have had an impact on the changes in atmospheric composition during the Permian-Triassic Boundary.

The article [1] defines two oxygen fugacity buffers: one at CaS–CaO–S equilibrium (OLS oxygen fugacity meter) and can be calculated through the following Eq. (1), and the other at CaS–CaSO₄ equilibrium (OA oxygen fugacity meter), and can be calculated through Eq. (2):

$$\lg f_{O_2} = -21.1162 + 3.65342 \times 10^7/T^3 - 6205.07/T^2 + (-16237.94 - 0.11450P)/T + 0.43722 \times 10^{-3}T + 11.13544 \lg T + \lg f_{S_2} \quad (1)$$

$$\lg f_{O_2} = 2.19144 + 1.09305 \times 10^{-4}T - 25137/T - 1551.42/T^2 + 1.5305 \times 10^7/T^3 + 0.04777P/T + 2.7838 \lg T \quad (2)$$

The unit of *P* is bar, and *T* is in K, and results are shown in Fig. 1 at 0.5 GPa. For example, at 0.5 GPa/1320 K, OA = FMQ + 2.21; OLS = FMQ – 0.52. These two equations determine the oxygen fugacities at S^{2–}/S⁰ equilibrium and S^{2–}/S⁶⁺ equilibrium, respectively, providing important references for the study of planetary sulfur cycle and mineral deposits.

References:
[1] Liu, Chou, Chen, Wu, Li, Bagas, Ren, Liu, Mei, Wang, 2023. National Science Review 10, nwad159.

