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Calibration and validation of cerium-in-apatite oxybarometer: Applications to Earth and planetary materials

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Oxygen fugacity (fO_2) is a fundamental parameter governing volatile cycling, metal speciation and transport, and thermochemical evolution of Earth and other planets. However, quantifying fO_2 remains particularly challenging in both highly reduced and strongly oxidized systems because existing oxybarometers often saturate and become unstable under such conditions. Herein, we report a new cerium-in-apatite oxybarometer based on spectroscopically determined Ce^{4+}/Ce^{3+} values in apatite from a suite of magmatic-hydrothermal rocks and meteorites of well-established fO_2 values. In particular, combined analyses of Ce L_3-edge X-ray absorption near-edge structure (XANES) and Ce 3*d* X-ray photoelectron spectroscopy (XPS) reveal that Ce^{4+} persists in highly reduced Martian and chondrite meteorites, overturning the long-standing assumption that cerium occurs exclusively in the Ce^{3+} state under such conditions. Moreover, our results demonstrate that the Ce^{4+}/Ce^{3+} values in apatite does not approach saturation in a wide oxygen fugacity range from FMQ-3.0 to at least FMQ+3.0. Therefore, the Ce-in-apatite oxybarometer retains its sensitivity across this redox range and complements its S-in-apatite counterpart, which exhibits nonlinear and saturating behavior near the FMQ buffer. By providing a high-precision and high-resolution window into the "redox blind spots" of early planetary evolution, the Ce-in-apatite oxybarometer enables reconstruction of the redox evolution of terrestrial magmatic-hydrothermal systems and other planetary processes, offering a unified framework for cross-planetary redox correlations.