

Stable isotope compositions of Cadmium in stony meteorites

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Variations of elemental abundances in primitive meteorites and bulk planets are largely controlled by volatility. Moderately volatile elements (VE) (e.g. Na, K and Zn) are distinguished from highly VE (e.g. Cd, Tl) by their condensation temperatures, which are above or below that of FeS, respectively. In some chondrite classes, highly VE and moderately VE with condensation temperatures below ~700K are depleted to a similar extent, e.g. they maintained CI chondrite-like Zn/Cd ratios. This co-depletion is due to the main process of VE depletion that is possibly caused by incomplete condensation or chondrule formation. For other chondrite classes, the highly VE are either further depleted or occasionally enriched by (probably) secondary processes.

Cd isotopes were measured by MC-ICPMS for a range of stony meteorites and terrestrial samples. Clear evidence for Cd isotope fractionation on earth was only found for a tektite sample. In contrast, the Cd isotope variations in meteorites exceed the external analytical precision by more than a factor of 50. This indicates that Cd isotopes are suitable and selective tracers of evaporation/condensation processes.

Carbonaceous and enstatite chondrites (CC and EC) with CI-like Zn/Cd ratios have terrestrial isotope compositions (CI, CM2, CR2, C2 ungr., CV3_{ox.}, EH4). Hence, the first-order VE depletion trend did not lead to the fractionation of Cd isotopes. CC, EC and ordinary chondrites (OC) with Zn/Cd different from CI chondrites typically show Cd isotope fractionation. Some CC and EC (CO3, CV3_{red.}, EL3, 6 & 7) show Cd depletion and a heavy Cd isotope signature, both consistent with evaporation. While Zn abundances in OC are very uniform, Cd abundances are highly variable. Metamorphosed OC have very low Cd concentrations, whereas unequilibrated OC display both, depletions and enrichments of Cd relative to Zn, and heavy as well as light Cd isotope compositions. This may be due to volatilisation of Cd from OC material, possibly during accretion or thermal metamorphism, and recondensation in the colder, un-equilibrated parts of the respective parent body.

Many highly shocked or brecciated chondrites do not show isotope fractionation, indicating that these processes did not cause Cd isotope fractionation. Thermal meta-morphism, accretion and perhaps nebular processes may have caused the Cd redistribution and isotope fractionation.

Cd isotope data for Earth, Mars and the HED parent body are similar to most CC and EH4. Thus, the formation and differentiation of planetary bodies did not produce large-scale stable isotope fractionation of Cd.

The hydrothermal geochemistry of tungsten in granitoid environments: Solubilities of ferberite and scheelite as a function of T, P, pH and salinity.

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The majority of tungsten deposits are spatially associated with granitoid plutons. In this study we focus on W deposits in siliceous, carbonate-free rocks. The primary W minerals in granitoid-related W deposits hosted in siliceous rocks (e.g., Mount Pleasant, Ohtani, Panasqueira) are wolframite and scheelite. These minerals were deposited mostly between 200 and 500 °C, and 200 and 1500 bars, from fluids with salinities typically less than 15 wt. % NaCl equivalent (but up to 55 wt. %). The predominant dissolved component is NaCl. X_{CO_2} values vary, but typically range from 0 to 0.1. The ore-forming fluid was moderately acidic with oxygen fugacities between those of the QFM and HM buffers.

Solubilities of scheelite and ferberite in NaCl-HCl-H₂O solutions were calculated at 200 to 600°C, 500 to 1000 bars, pH from 3 to 6 and m_{NaCl} from 0.1 to 5.0 moles/kg H₂O. The calculations take account of the species H⁺, OH⁻, Na⁺, Cl⁻, NaCl⁰, HCl⁰, NaOH⁰, H₂WO₄⁰, HWO₄⁻, WO₄²⁻, Fe²⁺, FeCl⁺, FeCl₂⁰, FeOH⁺, FeO⁰, HFeO₂⁻, Ca²⁺, CaCl⁺, CaCl₂⁰, CaOH⁺, NaHWO₄⁰, and NaWO₄⁻.

Our calculations indicate that: (1) hundreds to thousands of ppm of W as simple tungstate species are possible in equilibrium with scheelite and ferberite; (2) W-chloride, -fluoride, or -carbonate complexes, or more exotic species, are not required to transport sufficient W to form an ore deposit; (3) W concentrations in equilibrium with scheelite and ferberite increase strongly with increasing temperature, increasing NaCl concentration and decreasing pH, but are weakly dependent on pressure; (4) the Ca/Fe ratio of a solution in equilibrium with scheelite and ferberite decreases strongly with increasing temperature; (5) simple cooling of a solution with a constant Ca/Fe ratio cannot result in the replacement of ferberite by scheelite; (6) late-stage replacement of ferberite by scheelite requires an increase in the Ca/Fe ratio concomitant with cooling.

Experimental data not used in parameterizing our model generally agree with the results of calculations performed using our thermodynamic database within an order of magnitude. However, significant uncertainty remains in several parameters (e.g., the solubility products of scheelite and ferberite). Carefully conceived, executed, controlled and interpreted experiments are required to provide accurate measurements of these parameters and hence reduce the uncertainty.