

Mineralization of Atmospheric CO₂ Under Conditions of Isotopic Disequilibrium: Implications for Fingerprinting CO₂ Sequestration in Ultramafic Mine Tailings

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Mineralization of CO₂ in ultramafic mine tailings can occur on a scale that is significant relative to the greenhouse gas emissions of a mine. Consequently, some active mining operations may be able to take advantage of C mineralization within their tailings to offset part of their greenhouse gas emissions. The secondary Mg-carbonate mineral, hydromagnesite [Mg₅(CO₃)₄(OH)₂·4H₂O], which forms in tailings at the Mount Keith Nickel Mine, Western Australia, is a safe and durable trap for C and its presence may represent substantial disposal of atmospheric CO₂ at this site.

Traditionally, light stable isotopes of C and O have been used to fingerprint the source of these elements in carbonate minerals. However, stable isotope data for hydromagnesite from Mount Keith fail to unambiguously fingerprint the source of CO₂ within this mineral. We have used analogue experiments to assess the fractionation of stable C isotopes during precipitation of dypingite [Mg₅(CO₃)₄(OH)₂·5H₂O] from an evaporative, saline system with only one significant source of C: the atmosphere. These conditions were chosen to replicate those under which the structurally and chemically related mineral, hydromagnesite, precipitates at Mount Keith.

The results of our experiments demonstrate precipitation of dypingite out of C isotopic equilibrium with the laboratory atmosphere. A kinetic fractionation of C isotopes is observed during diffusion of gaseous CO₂ into these high-pH, saline systems. This kinetic effect produces a DIC pool and carbonate mineral precipitates that are significantly depleted in ¹³C relative to predictions made assuming equilibrium exchange of C between the atmosphere and DIC. We have obtained an equilibrium isotopic fractionation factor for exchange of C between dypingite and DIC: $10^3 \ln \alpha_{\text{dypingite-DIC}} = (3.8 \pm 1.2)\%$. Our results provide a compelling explanation for the depleted, ambiguous stable C isotope data for Mount Keith hydromagnesite. Furthermore, they suggest that equilibrium fractionation factors fail to describe the $\delta^{13}\text{C}$ signature of DIC in mine process water, even when the only significant source of C is the atmosphere. Our work at Mount Keith suggests that radiogenic ¹⁴C is the most robust mechanism for assessing sequestration of atmospheric C in mine tailings.

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