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Kinetic isotope effect in siderite growth; an abiotic origin for depleted $\delta^{13}C$-siderite in banded iron formations.

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The widespread occurrence of siderite ($FeCO_3$) at the Earth's surface has been frequently cited as a proxy for palaeoenvironmental reconstruction. Isotopic studies on siderite associated with late Archaean banded iron formations show some negative $\delta^{13}C$ values, which coupled with $\delta^{56}Fe$ values, have been considered as a support for an important role of dissimilatory iron reduction (DIR) in the genesis of iron formation.

Facies-specific analysis show that texturally and petrographically syndepositional and/or early diagenetic microsparitic (<10μm in diameter) siderite exhibits $\delta^{13}C$ range between -3 and -7‰ [1], [2]. This potentially primary $\delta^{13}C$-siderite range can be interpreted in three ways: (A) DIR coupled with partial oxidation of organic carbon (<-25‰) [1], (B) precipitation from hydrothermal-seawater mixing fluid with mantle-derived carbon (~-6.5‰; [2]), and (C) kinetic isotope effect (KIE) associated with crystal growth.

This study presents isotopic analyses of abiotic siderite growth experiments from a wide range of solution saturation at room temperature. With a complete set of kinetic data [3], KIE of carbon during siderite growth is simulated with a modified surface kinetic fractionation model [4] to obtain Monte Carlo-optimised values of equilibrium and kinetic fractionation factors, and delineate KIE as a function of growth rate and solution saturation.

These constraints allow us to assess the origins of depleted $\delta^{13}C$ in microsparitic siderite in iron formations. The current knowledge of seawater chemistry during the Archaean-Palaeoproterozoic transition suggests a moderate level of supersaturation (**Ω** up to 30), which would have induced KIE of C by -4 ‰ in fluid-buffered early diagenetic siderite growth from the percolating deepwater. Consider the pulsed deposition of iron-rich sediments caused by intense hydrothermal activities (source of Fe), crystal growth-induced KIE from deepwater with an elevated supersaturation and/or a mantle-influence $\delta^{13}C$-DIC provides a straightforward, abiotic explanation for the $\delta^{13}C$-siderite range in banded iron formations.

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