

## Kinetic isotope effect of C in siderite growth at 298.15 K.

CLANCY JIANG<sup>1</sup>, ITAY HALEVY<sup>2</sup>, NICHOLAS TOSCA<sup>1</sup>

<sup>1</sup>Dept. of Earth Sciences, University of Oxford, Oxford, UK.

<sup>2</sup>Earth & Planetary Sciences, Weizmann Institute of Science, Israel.

$\delta^{13}\text{C}$  value measured on ancient sedimentary rocks and sediments is extensively used in the interpretation of paleoenvironmental conditions and geobiological processes. However, we don't understand how kinetic fractionation might influence siderite  $\delta^{13}\text{C}$ , especially given that siderite precipitation may occur under relatively high supersaturation (in light of solubility difference between siderite and calcite).

Isotopic studies on siderite associated with late Archaean banded iron formations (~2.5Ga, Hamersley Basin, Australia, and Transvaal Craton, South Africa) show some negative  $\delta^{13}\text{C}$  values, which coupled with  $\delta^{56}\text{Fe}$  values, have been considered as a support for an important role of dissimilatory iron reduction (DIR) in the genesis of iron formations [1,2]. Our recent contribution [3] discussed that the texturally and petrographically syndepositional and/or early diagenetic siderite exhibits  $\delta^{13}\text{C}$  fractionation range between 0 and -8‰. This  $\delta^{13}\text{C}_{\text{Sid}}$  range can be interpreted in three ways: (1) precipitation from hydrothermal-seawater mixing fluid with a mixed isotopic composition between the mantle and seawater [3], (2) vital isotope effect including dissimilatory iron reduction, and (3) kinetic isotope fractionation associated with abiotic precipitation.

This study presents an experimental investigation on the abiotic growth kinetics of siderite at surface conditions, delineates the rate-saturation relationship by adopting a chemical affinity-based kinetic model [4], and describes the associated kinetic isotope effect of carbon. The following conclusions are reached: (1) transport-controlled siderite growth operates in solution saturation ( $\Omega$ ) up to 400 with respect to siderite equilibrium, (2) solubility considerations and new growth rate data support the conclusion that several geological occurrences of siderite (e.g., banded iron formations) may reflect an origin from highly-supersaturated solutions, and (3) kinetic isotope effects accompanying abiotic siderite growth from highly-supersaturated solutions result in  $\delta^{13}\text{C}_{\text{Sid}}$  down to -10‰. The kinetic isotope effects we describe here raise the possibility that abiotic growth may have contributed to the formation of at least some  $^{13}\text{C}$ -depleted siderite identified from the geological record.

[1] C. M. Johnson et al. 2008. *GCA*, 72.1 pp. 151–169.

[2] A. Heimann et al. 2010. *EPSL*, 294.1-2, pp. 8–18.

[3] C. Jiang and N. Tosca. 2019. *EPSL*, 506, pp. 231–242.

[4] C. Jiang and N. Tosca. 2020. *GCA*, in press.