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## Kinetic and thermodynamic controls of divalent metals isotope composition in carbonate: Experimental investigations and applications

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### Abstract

The very contrasting steric and electronic properties of divalent metals (i.e. Ba, Ca, Mg, Sr, Zn, Cu, Cd, Mn, Co, Ni) dramatically affect the reactivity of their aqueous ions in solution and their partitioning between fluids and minerals including calcium carbonates. In this study we show that these contrasting properties result in very distinct kinetic and thermodynamic behaviors of their isotopic fractionation between aqueous fluids and carbonate minerals. For example, because of steric effects, the light isotopes of Ca, Mg, Sr, and Ba, are enriched in precipitated calcite but the extent of Mg isotopes fractionation decreases with increasing calcite growth rate whereas that of Ca, Sr and Ba increases with calcite growth rate. The distinct behavior of Mg stems from the reduced lability of water molecules in its coordination sphere compared to Ca, Ba and Sr. In contrast, the heavy isotopes of Zn (and probably Cu, Cd, Ni) are slightly enriched in precipitated calcite in accord with the great affinity of these metals for the solid (partition coefficient  $K_D > 1$ ), and the extent of their fractionation decreases with increasing calcite growth rates. Moreover, transition metals, especially Cu which is affected by the Jahn-Teller effect, exhibit a strong affinity for  $RO^-$  ligands and thus a marked dependence of their equilibrium isotope distribution among aqueous fluids and calcite on solution pH,  $\Sigma CO_2(aq)$  and the presence of aqueous inorganic and organic ligands. These observations provide new insights into the mechanisms controlling the incorporation of divalent metals into calcite as well as new tools to reconstruct paleo-environmental conditions from their isotope composition recorded in carbonate sediments.

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### 1. Introduction

Isotope exchange reactions between calcium carbonates and seawater are the basis for paleo-reconstructions including determination of past temperature, atmospheric CO<sub>2</sub>, and ocean pH from oxygen, carbon and boron isotopes, respectively. Despite the success of these proxies, the isotope composition of divalent trace metals in calcium carbonates has, surprisingly, attracted fairly little attention. Nevertheless, the isotopic compositions of these metals look to be promising paleo-proxies because, notwithstanding their distinct steric and electronic properties, divalent metals substitute into the octahedral calcium site within the calcite structure. Moreover, as the equilibrium and kinetic partition of these elements between calcite and its co-existing aqueous fluid exhibit very contrasting behaviours, it can be expected that their isotope composition in calcite exhibits distinct trends. Towards the creation of new and robust paleo-proxy tools, we have performed a series of experimental studies to investigate how crystal growth rates, and fluid pH and speciation impact the isotopic composition of divalent metals incorporated in the calcite lattice. To generate unambiguous experimental data, calcite growth experiments have been performed over large pH and pCO<sub>2</sub> ranges using mixed flow reactors which operate at constant steady-state conditions including constant Me<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> concentrations, pH, saturation state and precipitation rate.

### 2. Results and discussion

a) *Crystals growth rate* appears to have contrasting impacts on the isotopic fractionation of divalent metals. For example, it can be seen on Fig. 1a that the extent of Mg isotope fractionation between calcite and aqueous solution

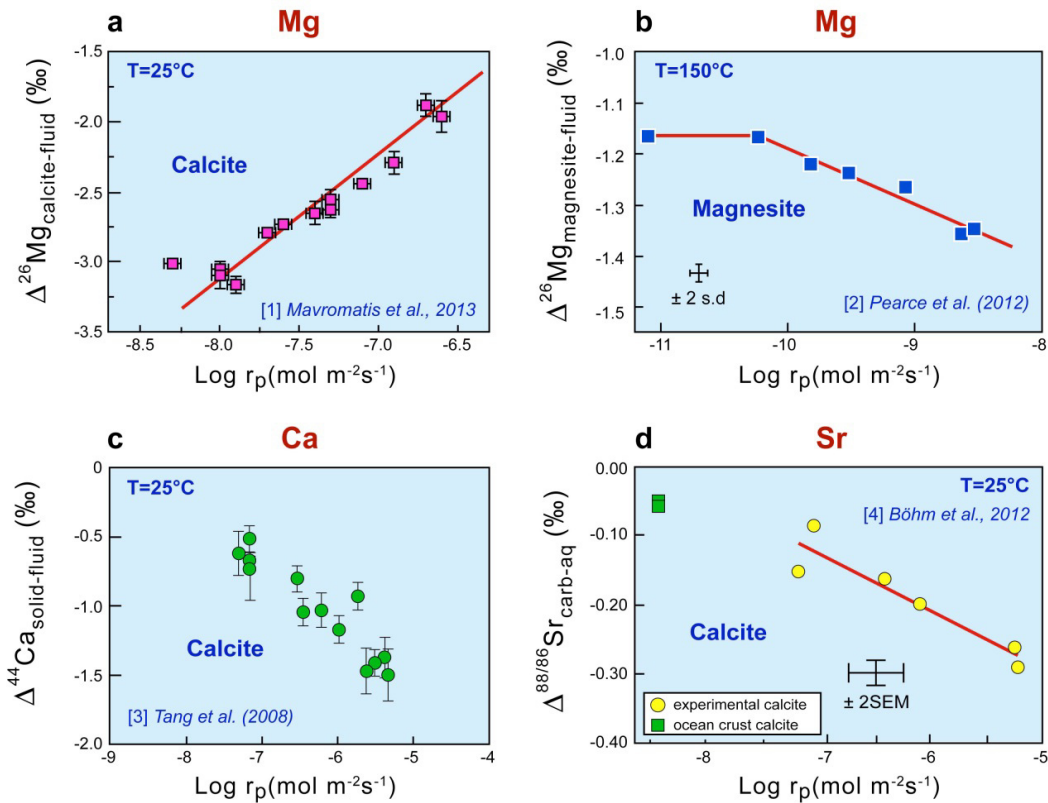


Fig. 1 (see caption below)

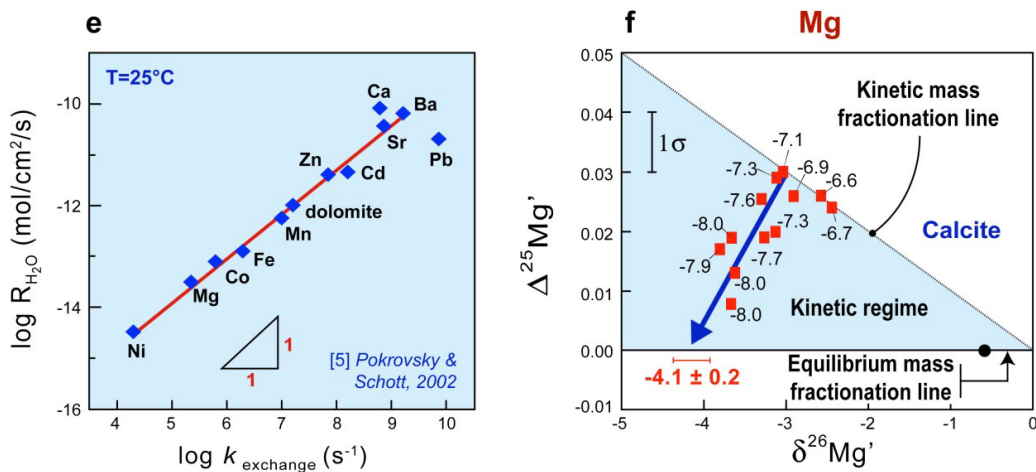


Fig. 1. Kinetic isotopic fractionation of alkaline earth metals between carbonate minerals and solution. a)  $\Delta^{26}\text{Mg}_{\text{calcite-fluid}}$  as a function of calcite growth rate [1]; b)  $\Delta^{26}\text{Mg}_{\text{magnesite-fluid}}$  as a function of magnesite growth rate [2]; c)  $\Delta^{40}\text{Ca}_{\text{calcite-fluid}}$  as a function of calcite growth rate [3]; d)  $\Delta^{88/86}\text{Sr}_{\text{calcite-fluid}}$  as a function of calcite growth rate [4]; e) Dissolution of  $\text{Me}^{2+}$ -carbonates at 25°C ( $I = 0.01 \text{ M}$ ,  $5 < \text{pH} < 8$ ) as a function of the rate of exchange water molecules in the metal aquo ion coordination sphere [5]; f) Mg isotopes fractionation between calcite and solution (data from [1]) plotted in a 3-isotope space. The blue arrow indicates the average  $\delta^{26}\text{Mg}'$  value calculated from the extrapolation of experimental data, yielding  $\Delta^{26}\text{Mg}_{\text{calcite-fluid}}(\text{equil}) = -3.5 \text{ ‰}$  at 25°C. The numbers next to the symbols indicate the logarithm of calcite growth rate.

( $\Delta^{26}\text{Mg}$  exceeds  $-3 \text{ ‰}$ , with the solid enriched in light Mg) is strongly influenced by the calcite growth rate (by near 2 ‰). But the most striking feature of Mg isotopes behaviour is the decrease of fractionation with increasing growth rate which contrasts with that observed for Mg in magnesite (Fig. 1b), Ca in calcite (Fig. 1c), Sr in calcite (Fig. 1d), and Ba in calcite. The distinct behavior of Mg, which stems from the reduced lability of water molecules in its coordination sphere compared to Ca, Ba, or Sr, (Fig 1e), provides new insight on carbonate growth controlling mechanisms. Zn co-precipitated with calcite is enriched in heavy Zn which is consistent with the high compatibility of transition metals for calcite lattice ( $K_D > 1$ ) and results in a decrease in its isotopic fractionation with increasing growth rate.

The kinetic isotope fractionation of a divalent metal impurity like Mg can be quantified using three isotope diagrams (Fig. 1f) which allow the precise determination of equilibrium fractionation factors and provides a new tool to quantify the growth rates of calcite precipitated in the deep past. Such tools also provide insight into the saturation state of the fluids present when the calcite precipitated. The degree to which such signals are preserved over geological timeframes is, however, currently under debate [2, 6] as the Mg isotopic composition of magnesite, and the Ca and O isotopic composition of calcite have been observed to change dramatically over week to month timeframes when in contact with fluids having a bulk composition in equilibrium with the co-existing carbonate.

b) *Electrons in d-orbitals of transition metals* like Zn, Cu or Ni lead to ligand stabilization energy (LSE) and thus to the formation of stronger complexes of these metals with oxygen donors ligands compared to alkaline-earth metals like Sr, Ca or Mg (Fig 2a). It follows that the equilibrium distribution and isotopic composition of these metals in calcite will depend strongly on pH and the concentrations of aqueous inorganic and organic ligands present in solution. For example, the isotope fractionation between aqueous Zn(II) and Zn co-precipitated with calcite at fixed pH, saturation state and  $\text{pCO}_2$  ( $0 \text{ ‰} \leq \Delta^{66}\text{Zn}_{\text{calcite-fluid}} \leq 0.4 \text{ ‰}$ ) is consistent with the incorporation of  $\text{Zn}^{2+}$  in the solid lattice and thus is controlled by the isotopic composition of  $\text{Zn}^{2+}$ , as deduced from Zn aqueous speciation and the values of the partition functions  $\beta$  of Zn aqueous species present in solution reported by Fujii et al. [7]. Consequently, the Zn isotope composition of Zn sedimentary carbonates is a potential paleo pH and  $\text{pCO}_2$  proxy in marine environments. In contrast, Cu may be an accurate probe of biotic processes; as shown on Figure 2a,  $\text{Cu}^{2+}$

forms stronger complexes with organic acids than other divalent metals because of the tetragonal distortion of the  $\text{Cu}^{2+}$  aquo ion by the Jahn-Teller effect. The  $\text{Cu}^{2+}$  (aq) isotope composition can thus be strongly influenced by its

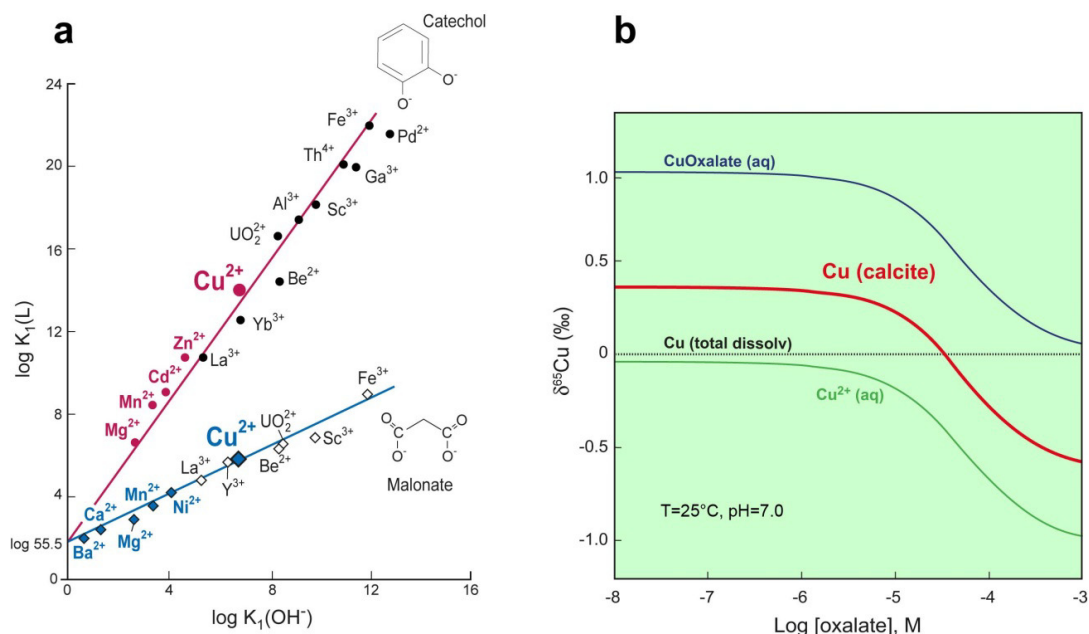


Fig. 2. Impact on the isotopic composition of Cu co-precipitated with calcite of the concentration of oxalic acid in the parent solution. a) Linear free energy relationships for a variety of metals ions between the logarithm of the formation constant of their complex with catechol and malonate and the logarithm of the formation constant of their hydroxide complex (from Martell and Hancock [8]). b) Calculated equilibrium isotopic composition at  $25^\circ\text{C}$  and  $\text{pH} = 7$  of Cu co-precipitated with calcite,  $\text{Cu}^{2+}(\text{aq})$  and  $\text{CuOxalate}(\text{aq})$  as a function of oxalate concentration in the parent solution. Calculations were performed for total dissolved  $\text{Cu}(\text{II}) = 2.10^{-6} \text{ M}$ , Alkalinity =  $2.5.10^{-3} \text{ M}$  and  $\text{Cl}^- = 10^{-2} \text{ M}$  using the CRITICAL data base for computing Cu aqueous speciation, and the reduced partition functions of  $\text{Cu}(\text{II})$  aqueous species from [9].  $\text{Cu}^{2+}$  isotopic fractionation between calcite and the fluid was assumed to be  $\Delta^{65}\text{Cu}_{\text{calcite-fluid}} = +0.4 \text{ ‰}$ .

complexation with aqueous carboxylic acids. For example, based on the  $\beta$  values proposed by Fujii et al. [9] for Cu-oxalate complexes, it can be seen in Fig. 2b that the presence of only a few ppm of oxalate is sufficient to change the Cu fractionation between calcite and the aqueous fluid by 1‰ and to make calcite enriched in light Cu instead of heavy Cu. It is likely that the very strong chelates formed by  $\text{Cu}^{2+}$  with hydroxyl-carboxyl or phenolic groups will make Cu isotopic compositions an accurate probe of past biomineralisation.

### 3. Concluding remarks

- The isotopic composition of divalent metal (Mg, Zn, Cu, Ni...) impurities in calcite (and potentially aragonite) may provide new and improved chemical probes to access past environmental conditions including ocean pH and ocean chemical composition, and the degree of biotic processes.
- The interpretation of Mg isotopes signatures via 3-isotope plots can yield  $\text{CaCO}_3$  growth rates and thus estimates of the fluid saturation state with respect to the precipitated solid.
- A critical factor governing our ability to interpret the isotope signatures in carbonate minerals is the degree to which they are preserved over geological time; experimental observations suggest that this requires limited fluid-mineral contact as these signatures have been observed to change significantly in the laboratory over time frames of weeks to months.

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