



The temporal evolution of magnesium isotope fractionation during hydromagnesite dissolution, precipitation, and at equilibrium

Eric H. Oelkers^{a,b,*}, Ulf-Niklas Berninger^{a,c}, Andrea Pérez-Fernández^a, Jérôme Chmeleff^a, Vasileios Mavromatis^{a,d}

^a *Géosciences Environnement Toulouse, CNRS-UPS-OMP, 14 av. Édouard Belin, 31400 Toulouse, France*

^b *Department of Earth Sciences, UCL, Gower Street, WC1E 6BT London, United Kingdom*

^c *Department für Geo- und Umweltwissenschaften, LMU, Theresienstr. 41, 80333 München, Germany*

^d *Institute of Applied Geosciences, Graz University of Technology, Rechbauerstrasse 12, 8010 Graz, Austria*

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Abstract

This study provides experimental evidence of the resetting of the magnesium (Mg) isotope signatures of hydromagnesite in the presence of an aqueous fluid during its congruent dissolution, precipitation, and at equilibrium at ambient temperatures over month-long timescales. All experiments were performed in batch reactors in aqueous sodium carbonate buffer solutions having a pH from 7.8 to 9.2. The fluid phase in all experiments attained bulk chemical equilibrium within analytical uncertainty with hydromagnesite within several days, but the experiments were allowed to continue for up to 575 days. During congruent hydromagnesite dissolution, the fluid first became enriched in isotopically light Mg compared to the dissolving hydromagnesite, but this Mg isotope composition became heavier after the fluid attained chemical equilibrium with the mineral. The $\delta^{26}\text{Mg}$ composition of the fluid was up to $\sim 0.35\%$ heavier than the initial dissolving hydromagnesite at the end of the dissolution experiments. Hydromagnesite precipitation was provoked during one experiment by increasing the reaction temperature from 4 to 50 °C. The $\delta^{26}\text{Mg}$ composition of the fluid increased as hydromagnesite precipitated and continued to increase after the fluid attained bulk equilibrium with this phase. These observations are consistent with the hypothesis that mineral-fluid equilibrium is dynamic (i.e. dissolution and precipitation occur at equal, non-zero rates at equilibrium). Moreover the results presented in this study confirm (1) that the transfer of material from the solid to the fluid phase may not be conservative during stoichiometric dissolution, and (2) that the isotopic compositions of carbonate minerals can evolve even when the mineral is in bulk chemical equilibrium with its coexisting fluid. This latter observation suggests that the preservation of isotopic signatures of carbonate minerals in the geological record may require a combination of the isolation of fluid-mineral system from external chemical input and/or the existence of a yet to be defined dissolution/precipitation inhibition mechanism.

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1. INTRODUCTION

The magnesium isotopic signatures preserved in the geologic record have been applied by the Earth Science community to characterize a plethora of natural processes and environments. For example, Mg isotopes have been used

* Corresponding author at: Department of Earth Sciences, UCL, Gower Street, WC1E 6BT London, United Kingdom.

E-mail address: oelkers@get.omp.eu (E.H. Oelkers).

in an attempt to constrain Mg cycling in marine sediments (Higgins and Schrag, 2010), provide insight into past and present continental weathering processes (Pogge von Strandmann et al., 2008; Pokrovsky et al., 2011; Wimpenny et al., 2011; Mavromatis et al., 2014b), quantify carbonate diagenesis (Fantle and Higgins, 2014), define ancient climatic events (Kasemann et al., 2014), and as paleoenvironmental proxies (Pogge von Strandmann et al., 2014; Geske et al., 2015; Riechelmann et al., 2016). Critical to most of these applications is that magnesium isotopic ratios are preserved over significant and in some cases over geologic timeframes. The preservation of stable isotopic signatures in minerals, however, has been questioned by a number of studies in a variety of systems (e.g. Curti et al., 2010; Gorski and Fantle, 2017; Perez-Fernandez et al., 2017). For example, Pearce et al. (2012) observed that Mg isotopic signatures continued to evolve between an aqueous fluid and coexisting magnesite at 150 and 200 °C after bulk chemical equilibrium was attained in this fluid – mineral system. Mavromatis et al. (2012) and Shirokova et al. (2013) observed a continuous re-equilibration of Mg isotopes between the hydrous Mg carbonate minerals nesquehonite and dypingite, and its co-existing aqueous fluid at ambient temperatures during experiments that lasted no more than 4 weeks. In a follow-up study, Mavromatis et al. (2015) reported the continuous re-equilibration of C isotopes between nesquehonite and dypingite and its co-existing aqueous fluid at the same conditions. Mavromatis et al. (2016b) reported the resetting of the Ba isotopic composition of witherite (BaCO_3) in contact with an aqueous fluid over the course of one week at 25 °C. The rapid exchange and resetting of Fe, Mn and O isotopic compositions have been reported during mineral-fluid reactions by Friedrich et al. (2015, 2016). A significant number of observations also suggest that the divalent carbonate isotopic signatures can be reset in natural systems over geological timeframes (Fantle and DePaolo, 2007; Fantle et al., 2010; Druhan et al., 2013; Mavromatis et al., 2017c). Similar isotopic signature resetting was reported at ambient temperature during water-barite interaction by Curti et al. (2010), during water-epsomite interaction by Li et al. (2011), and during water-brucite interaction by Li et al. (2014). Building upon these past works, the present study provides further insight into the resetting of isotopic compositions through observations of the temporal evolution of Mg isotopic composition of fluids and coexisting hydromagnesite during its dissolution, precipitation, and at equilibrium.

This study is centered on the reactivity of hydromagnesite, a hydrous Mg-carbonate. Despite the fact that their formation is thermodynamically favored (Benezeth et al., 2011), the formation of anhydrous Mg-carbonate minerals such as magnesite is unlikely to occur at ambient temperatures due to the strong hydration of aqueous magnesium (i.e. Lippmann, 1973; Saldi et al., 2009, 2012; Mavromatis et al., 2013; Gautier et al., 2014). As such, hydrous magnesium carbonate minerals, such as hydromagnesite and nesquehonite are relatively common in natural environments, where they occur as weathering products of mafic or ultramafic rocks (Deelman, 2011), within evaporate deposits (Aldermann and Von der Borch, 1960; Goto

et al., 2003) and within speleotherms (Northrup et al., 2001). Hydromagnesite has also been observed to precipitate in microbial mats or stromatolites in a number of alkaline lakes (Power et al., 2007, 2014; Shirokova et al., 2011, 2013; Mavromatis et al., 2012, 2015). The formation of these minerals can be catalyzed by bacterial activity (Thompson and Ferris, 1990; Power et al., 2007, 2009, 2014; Shirokova et al., 2013).

The formation of hydrous magnesium carbonates, such as hydromagnesite and nesquehonite has recently attracted interest due to their potential use in geological CO_2 storage, particularly at ambient temperature conditions where magnesite does not form (Teir et al., 2009; King et al., 2010; Hovelmann et al., 2012; Oskierski et al., 2013; McCutcheon et al., 2014; Power et al., 2014). Notably, field observations have shown that passive CO_2 storage may occur in ultramafic mine tailings through the weathering of Mg-silicates and precipitation of hydrous Mg-carbonates (Wilson et al., 2009, 2014; Pronost et al., 2011). Such observations have motivated a number of experimental studies characterizing the formation conditions, reactivity, and thermal stability of the hydrous Mg-carbonates (Frost et al., 2008; Hänchen et al., 2008; Ballirano et al., 2010; Berninger et al., 2014; Gautier et al., 2014). Other studies have investigated the mechanisms of hydromagnesite or nesquehonite formation during the carbonation of serpentine (Park and Fan, 2004; Teir et al., 2007, 2009) and brucite (Zhao et al., 2009; Schaefer et al., 2011; Loring et al., 2012).

Numerous studies have focused on characterizing Mg isotope fractionation among anhydrous carbonate minerals and their co-existing fluids. For example, Mg isotope fractionation between fluids and co-existing magnesite and dolomite at elevated temperatures has been reported by Pearce et al. (2012) and Li et al. (2015), respectively. In each case, light Mg was found to be preferentially incorporated into the solid phase. Corresponding fractionation has been measured for Mg in calcite at ambient temperatures (Li et al., 2012; Mavromatis et al., 2013, 2017a,b). Work on Mg fractionation during hydrous Mg carbonate water interaction include that of Mavromatis et al. (2012) on dypingite at ambient temperatures and that of Shirokova et al. (2013) on the hydromagnesite stromatolites of Lake Salda, Turkey. These studies suggest that at equilibrium Mg in these hydromagnesite phases is $\sim 1.0\%$ lighter than their co-existing aqueous fluid phases. It should be emphasized, however, that the equilibrium distribution of Mg isotopes among minerals and their co-existing aqueous fluids depends strongly on the fluid composition (Schott et al., 2016); the presence of substantial carbonate or aqueous organic species can alter these equilibrium fraction factors by up to several per mil. Due to these non-zero fractionation factors, the congruent dissolution of hydromagnesite could lead to an isotopic disequilibrium between the remaining hydromagnesite and an originally Mg-free fluid phase. This study takes advantage of this isotopic disequilibrium to assess how rapidly such Mg isotopic signatures may re-equilibrate isotopically with their co-existing fluid phase through a series of batch reactor experiments performed under strictly defined physicochemical conditions for up to 575 days.

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