Magnesium isotope fractionation during dolostone weathering

Ting Gao^a, Shan Ke^{a*}, Fang-Zhen Teng^{b*}, Shouming Chen^a, Yongsheng He^a,
Shu-Guang Li^a

^aState Key Laboratory of Geological Processes and Mineral Resources, and School of Earth Sciences and Resources, China University of Geosciences, Beijing 100083, China

^bIsotope Laboratory, Department of Earth and Space Sciences, University of Washington, Seattle, WA 98195, USA

Abstract: 351 words

Text: 5242 words

Table: 1

Figures: 9

Chemical Geology
(Revised version)

*Corresponding authors: email: keshan@cugb.edu.cn (Shan Ke),
fteng@u.washington.edu (F.-Z. Teng)

Abstract

The element, Mg and Sr isotope ratios of a weathering profile from Hubei, China have been measured in order to document the behavior of Mg isotopes during dolostone weathering. The profile is developed in the joint system, and the weathering intensity increases from the least weathered dolostone towards the joint plane. According to the element and isotope ratios, the weathering profile can be divided into the weakly and intensely weathered zones. In the weakly weathered zone, Mg/Al (atomic) ratios decrease from 4.99 to 1.75 with increasing weathering intensity, while

Ca/Al ratios slightly decrease from 13.70 to 9.02. These suggest massive loss of Mg and simultaneous conservation of Ca. $\delta^{26}\text{Mg}$ values in the weakly weathered zone slightly decrease from -1.90‰ to -2.22‰, lighter than the corresponding protolith (-1.90‰). These element and isotope variations are likely caused by the cooccurrence of dolomite dissolution and calcite re-precipitation, suggesting that the fluids co-existing with the dolostone are saturated with respect to calcite while not saturated with respect to dolomite. By contrast, both Mg/Al and Ca/Al ratios of intensely weathered samples display a decreasing trend towards the joint plane, ranging from 1.62 to 0.16 and 10.24 to 2.05, respectively. The significant loss of Mg and Ca indicates the considerable dissolution of both dolomite and calcite. $\delta^{26}\text{Mg}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ values increase from -2.22‰ to -0.41‰ and from 0.71128 to 0.71368, respectively. These observations demonstrate that the isotope compositions of the intensely weathered residues are dominantly controlled by the increasing silicate fractions after carbonate dissolution, given that silicates have considerably high $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{26}\text{Mg}$ values relative to the carbonates. Overall, our study reveals large Mg isotope fractionation during dolostone weathering. The direction and extent of Mg isotope fractionation are mainly governed by the dissolution and re-precipitation of carbonate minerals, which are further controlled by the fluid's saturation with respect to carbonate minerals (calcite and dolomite). Therefore, cautions should be taken when using whole rock Mg isotope data of dolostones to trace paleoclimate change and dolostone genesis. Primary dolomite could be partially reserved in weakly weathered dolostones and step-leaching experiments may help to reveal its bearing Mg isotope signals.

Key words: Mg isotopes; dolostone weathering; dolomite dissolution; calcite re-precipitation; saturation

1. Introduction

Magnesium isotope composition of dolostone has been increasingly employed to constrain the evolution of seawater chemistry, paleoclimate environments and the origin of dolostone (Pokrovsky et al., 2011; Kasemann et al., 2014; Liu et al., 2014a; Geske et al., 2015a, b; Huang et al., 2015; Husson et al., 2015) due to the following geochemical characteristics. Firstly, a large fractionation between ^{26}Mg and ^{24}Mg is expected at low temperatures due to ~ 8% relative mass difference, which has been shown between natural/synthetic inorganic/biogenic carbonates and solutions ($\Delta^{26}\text{Mg} = \delta^{26}\text{Mg}_{\text{carbonate}} - \delta^{26}\text{Mg}_{\text{solution}} = -1 \sim -3\text{‰}$, e.g. Higgins and Schrag, 2010; Immenhauser et al., 2010; Wombacher et al., 2011; Li et al., 2012b, 2015; Mavromatis et al., 2013; Wang et al., 2013; Saenger and Wang, 2014). Secondly, Mg is a major element in dolomite, and the potential Mg sources for dolostone formation, including carbonate sediments, terrestrial silicates, and seawater, have very distinct Mg isotope compositions (Tipper et al., 2006b; Li et al., 2012b; Huang et al., 2013; Wang et al., 2015). Thirdly, Mg isotope composition of the modern seawater is homogeneous (Foster et al., 2010; Ling et al., 2011), consistent with the long residence time (~ 13 Ma) of Mg in the ocean (Li, 1982). Finally, the change of Mg isotope composition in

marine carbonates on million-year scale is controlled by isotope composition of Mg in the oceans. The main source of Mg to the oceans is the weathering of carbonates and silicate rocks. These characteristics make Mg isotopes, combined with other stable isotopes (e.g. carbon, boron) and radiogenic strontium isotopes, potentially be an excellent tracer for chemical evolution of oceans and for paleoclimate environments, such as sea regression and transgression (Pokrovsky et al., 2011), ocean acidification event (Kasemann et al., 2014), seawater and climate evolution during post-‘Snowball Earth’ event (Liu et al., 2014a; Husson et al., 2015). In addition, Mg isotopes may provide a promising insight into the origin of dolostone (Geske et al., 2015a, b; Huang et al., 2015).

Nonetheless, dolostone can be altered due to recrystallization and chemical weathering (Land, 1985; Machel, 1997; Al-Aasm and Packard, 2000; Warren, 2000), which are usually accompanied by the element migration (e.g. Mg, Ca and Sr) and possible isotope fractionation (e.g. Mg, O and C; Land, 1985; Montanez and Read, 1992; Malone et al., 1994; Yoo and Lee, 1998; Fantle and Higgins, 2014). Knowledge about Mg isotope fractionation during diagenesis and weathering processes thus is a prerequisite to use Mg isotope as a proxy to reconstruct paleoclimate environments and study the origin of dolostone. Thus far, only a few studies have been carried out to constrain Mg isotope fractionation during diagenesis of dolostone and the results are debated. Fantle and Higgins (2014) showed that limestone diagenesis and dolomitization significantly fractionate Mg isotopes, implying that the diagenesis of carbonates may greatly alter their $\delta^{26}\text{Mg}$ values. By contrast, Geske et al. (2012) and Azmy et al. (2013) found that diagenesis would alter the texture of the dolomite while the Mg isotope signals remain intact. With respect to Mg isotope fractionation during dolostone weathering, only one study has been carried out. Jacobson et al. (2010) investigated the fractionation mechanism during dedolomitization reactions such as dolomite dissolution, calcite precipitation and Mg-for-Na ion ion-exchange, mainly based on water samples. They concluded that dolomite recrystallization and calcite precipitation did not significantly fractionate Mg isotopes, while the preferential uptake of ^{24}Mg during Mg-for-Na ion-exchange was responsible for the observed isotope variation. In order to understand Mg isotope fractionation during dolostone weathering and its relevant controlling mechanisms, more case studies on natural weathering profiles are thus needed.

Here, we report Mg isotope data from a well-exposed weathering profile that developed on the Ca-dolostone from Cambrian strata in Changyang county of Hubei, China. The weathering intensity along the profile changes gradually. Thus the profile is well suitable for systematical investigation of the behaviors of Mg isotopes during dolostone weathering. We found large (up to 1.8‰) Mg isotope variation along the weathering profile and both the direction and extent of fractionation vary with the weathering intensity. The fluid’s saturation with respect to carbonate minerals (calcite and dolomite) dominates the dissolution and re-precipitation of carbonates and thus controls the Mg isotope fractionation.

2. Samples

The profile studied here is from the lower Cambrian Shuijingtuo Formation in Xijiaao village, Changyang county, Hubei Province, South China (111° 08' 35.41" E, 30° 31' 49.82" N; Fig. 1A). This area is predominately covered by carbonates and shales. Carbonate rocks in this area are extensively developed with joints (Fig. 1B). The dolostone weathering profile is ~ 17 cm long (the least weathered zone is defined as 0 cm). The weathering degree increases gradually from the least weathered end towards joint plane with the color from black to yellow (Fig. 2). Petrographic study shows that the least weathered dolostone consists of dolomite, calcite and small amounts of silicates (dolomite + calcite = 90-95%, silicates = 5-10%, Fig. 3A). Alteration and carbonate recrystallization are not widely present in the least weathered dolostone. With the enhancement of weathering, the proportion of carbonate minerals decreases from 90-95% to 5-10% and that of silicate minerals increases from 5-10% to 90-95% (Fig. 3. B, C, D). Besides, the grain diameter of carbonate minerals reduces and the clayzation becomes more intense on the mineral surface.

SL, DL1, DL2, DL3 and DL4 are five different deposition layers. To avoid the contamination from other deposition layers, fourteen samples (HY-PM3-3 to HY-PM3-16) were drilled from the same deposition layer (SL) (Fig. 2). To compare the geochemical composition of different deposition layers, another four samples (HY-1, HY-2, HY-3 and HY-4) were collected from four different deposition layers (DL1, DL2, DL3 and DL4) in the least weathered end (Fig. 2).

3. Analytical methods

The analyses of element ratios, Mg and Sr isotopes were performed at the Isotope Laboratory of the China University of Geosciences, Beijing. The procedures for sample digestion, column chemistry and instrumental analysis are described below.

3.1 Sample digestion

Based on the Mg content of samples, 1 ~ 10 mg of rock power was weighted in Savillex screw-top beakers and was digested by using a combination of single-distilled HCl, HF, HNO₃ and HClO₄. The digestion procedures are as follows: (1) sample powders were dissolved by concentrated HF-HNO₃ (3:1, v/v) as well as 3 ~ 4 drops of HClO₄ at 140 °C for 1 ~ 2 days, and then dried at 190 °C; (2) the residues were refluxed by concentrated HCl-HNO₃ (3:1, v/v) and concentrated HNO₃ at 140 °C consequently; (3) Three solution splits were prepared in 3% HNO₃, 1 N HNO₃, and 2.5 N HCl for element ratio analysis, Mg and Sr isotope column chemistry, respectively.

3.2 Element ratio (Mg/Al, Ca/Al and Mg/Ca) analysis

Magnesium, Ca and Al concentrations were determined and monitored by ²⁴Mg, ²⁷Al and ⁴⁴Ca intensities on a Neptune plus MC-ICP-MS. Each measurement comprises of 10 cycles. A 400 ppb Mg, Al and Ca mixed solution, prepared by pure

single element standard solutions from “GSB standard”, was used for calibration. The primary data are listed in [Appendix A](#). Element ratios can be calculated by using the following formula:

$$M / N = (M_{smp} / N_{smp}) \times (N_{std} / M_{std})$$

M and N refer to intensities of two monitoring isotopes; smp and std refer to sample and standard, respectively.

3.3 Magnesium isotope analysis

Magnesium was purified for isotope analysis through cation exchange chromatograph with Bio-Rad 200-400 mesh AG50W-X8 resin ([Ke et al., 2016](#)), by following previously established methods ([Teng et al., 2007, 2010a, 2015](#); [Yang et al., 2009](#); [Li et al., 2010](#); [Liu et al., 2010](#)). The resin was cleaned by 6 N HCl, 1 N HNO₃, 1 N HF and Milli-Q (18.2 MΩ) water alternatively before loading samples. Magnesium was eluted by 1 N HNO₃ and the Mg yield was between 99.5 and 99.9% based on the analyses of pure Mg solutions as well as reference materials (BHVO-2, BCR-2 and AGV-2). The whole procedure blank is < 10 ng, having a negligible contribution to samples. To obtain a sufficiently pure Mg fraction, each sample was passed through the column twice.

Magnesium isotope compositions were measured by the standard-sample bracketing method using a Neptune Plus MC-ICP-MS. A “wet” sample introduction system, equipped with a quartz spray chamber and a 50 ul/min PFA nebulizer, and low-resolution mode were adopted for Mg isotope analysis. Samples were introduced as 400 ppb solutions in 3% HNO₃ and concentrations of samples and standards are matched within ±10%. A 400 ppb solution typically yields beam intensity of ~ 6 V for ²⁴Mg, with background Mg signals of < 10⁻⁴ V. The standard-sample sequence was repeated 4 times for each sample to get a better reproducibility. Magnesium isotope ratios of samples are expressed as deviations between sample and standard DSM3 ([Galy et al., 2003](#)):

$$\delta^x Mg = \left[\left(\frac{{}^x Mg / {}^{24} Mg}{({}^x Mg / {}^{24} Mg)_{DSM3}} - 1 \right) \right] \times 1000$$

where x refers to mass 25 or 26. Long term external reproducibility is 0.06‰ for $\delta^{26}Mg$ (2SD; [Ke et al., 2016](#)). Duplicated measurement of the seawater standard (Hawaiian seawater) yields results (average $\delta^{26}Mg = -0.83 \pm 0.03\text{‰}$, 2SD, $n = 2$) consistent with the previously reported values ([Foster et al., 2010](#); [Ling et al., 2011](#); [Teng et al., 2015](#)).

3.4 Strontium isotope analysis

Strontium was purified by cation exchange chromatography with columns filled with 2 ml Bio-Rad AG50W-X12 resin (200-400 mesh). Before separation, the resin was cleaned by 20 ml 6 N HCl and 5 ml Milli-Q water. Samples were loaded on 0.5 ml 2.5 N HCl, followed by 1.5 ml 2.5 N HCl and 15 ml 4 N HCl. Thereafter, Sr was

collected by 7 ml 4 N HCl and 4 ml 6 N HCl. Strontium isotope ratios were measured on the Neptune Plus MC-ICP-MS. Each measurement comprises 30 s baseline measurement at half mass positions (85.5 and 86.5) and 160 cycles of 4.198 second integration. ^{85}Rb and ^{83}Kr were monitored for the correction of the ^{87}Rb contribution on ^{87}Sr and ^{86}Kr on ^{86}Sr . Mass bias correction was corrected against $^{88}\text{Sr}/^{86}\text{Sr} = 8.375209$, assuming an exponential law. The measured $^{87}\text{Sr}/^{86}\text{Sr}$ of NIST SRM987 during this measurement has an average value of 0.71028 ± 0.000031 (2SD, $n = 3$), showing good agreement with published data (e.g. [Li et al., 2012a](#) and references therein).

4. Results

Element ratios (Mg/Al, Ca/Al and Mg/Ca), Mg and Sr isotope compositions are listed in [Table 1](#) for all the samples.

4.1 Compositions of the different deposition layers

The samples from the five different deposition layers (SL, DL1, DL2, DL3, DL4) represent five deposition characteristics and have different element and isotope compositions ([Fig. 4](#)). All the weathering profile samples were collected from the surface layer (SL). The least weathered dolostone from the SL has the Mg/Ca, Mg/Al and Ca/Al ratios of 0.46, 5.64 and 12.22, respectively. $\delta^{26}\text{Mg}$ ratio is -1.90‰ and falls in the range of $\delta^{26}\text{Mg}$ ratios of the typical dolostones ([Pokrovsky et al., 2011; Azmy et al., 2013; Kasemann et al., 2014; Liu et al., 2014a; Geske et al., 2015a; Huang et al., 2015; Husson et al., 2015](#)). $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is 0.71091, higher than that of the seawater at 520 ~ 525 Ma ([Kaufman et al., 1996; McArthur et al., 2012](#)), reflecting the contribution of silicate fractions.

The layers DL1 and SL have similar element ratios (Mg/Ca = 0.41 ~ 0.46, Mg/Al = 5.64 ~ 6.00, Ca/Al = 12.22 ~ 14.58) and isotope compositions ($\delta^{26}\text{Mg} = -1.98\text{‰} \sim -1.90\text{‰}$, $^{87}\text{Sr}/^{86}\text{Sr} = 0.71088 \sim 0.71091$) ([Fig. 4](#)). By contrast, DL2, DL3 and DL4 have rather different element ratios (Mg/Ca = 0.11 ~ 0.34, Mg/Al = 2.88 ~ 8.15, Ca/Al = 12.38 ~ 25.83) and isotope compositions ($\delta^{26}\text{Mg} = -1.61\text{‰} \sim -2.08\text{‰}$, $^{87}\text{Sr}/^{86}\text{Sr} = 0.70971 \sim 0.71095$). These geochemical variations among different deposition layers suggest that it is important to collect samples within the same layer when studying Mg isotope fractionation mechanisms during dolostone weathering. All 14 samples of the weathering profile were strictly sampled along the layer SL to avoid any disturbance from the other deposition layers. Moreover, the layer SL has similar composition to the next layer DL1, which further minimizes the possible contamination effects.

4.2 Compositions of the weathering profile

Several immobile elements (e.g. Al, Ti, Zr and Nd) can be used to evaluate the relative depletion or enrichment of mobile elements during chemical weathering. Similar to a previous study ([Rudnick et al., 2004](#)), Al was chosen here because it is

one of the least mobile elements and more prone to be enriched in weathered residues. The dolostone weathering profile is divided into two different weathering zones, namely weakly weathered and intensely weathered zones, based on element ratios (Mg/Al, Ca/Al and Mg/Ca, Fig. 5) and isotope compositions ($\delta^{26}\text{Mg}$ and $^{87}\text{Sr}/^{86}\text{Sr}$, Fig. 6).

In the weakly weathered zone, Mg/Al and Mg/Ca ratios are lower than the least weathered dolostone and show a decreasing trend with increasing weathering intensity, ranging from 4.99 to 1.75 and 0.44 to 0.19, respectively (Fig. 5A, B). By contrast, Ca/Al ratios slightly decrease from 13.70 to 9.02 (Fig. 5C). $\delta^{26}\text{Mg}$ values are lower than the least weathered dolostone and successively decrease from -1.90‰ to -2.22‰, while $^{87}\text{Sr}/^{86}\text{Sr}$ ratios slightly increase from 0.71097 to 0.71161 (Fig. 6).

In the intensely weathered zone, Mg/Al, Ca/Al and Mg/Ca ratios all decrease as weathering intensity increases, ranging from 1.62 to 0.16, 10.24 to 2.05 and 0.16 to 0.07, respectively (Fig. 5). $\delta^{26}\text{Mg}$ values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios increase significantly, varying from -2.22‰ to -0.41‰ and 0.71128 to 0.71368, respectively (Fig. 6).

5. Discussion

Chemical weathering is a process in which primary minerals are progressively dissolved and secondary minerals are formed. Mobile elements (e.g. Mg and Ca) during weathering are redistributed in primary minerals, secondary minerals and solutions (Nesbitt and Markovics, 1980). For example, the Mg/Al and Ca/Al ratios in the dolostone weathering profile here vary up to 97% and 83%, respectively, suggesting that nearly all Mg and most of Ca in the most intensely weathered samples have been removed to the solution and the rest of them may be absorbed or incorporated into secondary minerals. Large Mg isotope fractionation had been found during weathering of igneous rocks and shales (Tipper et al., 2006a, b; Pogge von Strandmann et al., 2008; Teng et al., 2010b; Wimpenny et al., 2010; Ryu et al., 2011; Huang et al., 2012; Opfergelt et al., 2012, 2014; Pogge von Strandmann et al., 2012; Liu et al., 2014b; Ma et al., 2015). The dolostone weathering profile yields a $\delta^{26}\text{Mg}$ variation up to 1.81‰. Particularly, those two samples near the joint plane have rather heavy Mg isotope compositions (-0.41‰ ~ -0.64‰), which are close to those of igneous rocks (Teng et al., 2007, 2010a; Shen et al., 2009; Li et al., 2010; Yang et al., 2012). The large variations of element ratio and Mg isotope composition most likely reflect the dissolution of primary minerals and formation of secondary minerals. Below, we first discuss the behaviors of carbonate minerals and the nature of the fluids, and then reveal and model the Mg isotope fractionation mechanisms during dolostone weathering.

5.1 Behaviors of carbonate minerals during dolostone weathering

The weakly weathered zone is characterized by lower Mg/Al ratios (1.75 to 4.99) and slight variation of Ca/Al ratios (9.02 to 13.70) when compared to the least weathered dolostone (Fig. 5). The Mg/Al ratios decrease with increasing weathering

intensity, suggesting that a large amount of initial Mg has been gradually lost as weathering progresses. For example, the sample HY-PM3-11 has the Mg/Al ratio of 1.75, indicating that approximately up to 70% of Mg was lost. Such huge loss of Mg suggests substantial dissolution of dolomite since dolomite is the dominant Mg-bearing mineral in dolostone. In addition to dolomite dissolution, the less variation of Ca/Al ratios and the significant decrease of Mg/Ca ratios indicate that calcite re-precipitation occurs simultaneously with dolomite dissolution to compensate Ca and keep Ca/Al ratios with less variation.

In contrast to the weakly weathered zone, both Mg/Al and Ca/Al ratios in the intensely weathered zone show a decreasing trend as weathering progresses, varying from 1.62 to 0.16 and from 10.24 to 2.05, respectively (Fig. 5). Again, dolomite dissolution is required to explain the decreasing Mg/Al ratios but it alone cannot explain the decrease in both Mg/Al and Ca/Al ratios. Even dolomite in the least weathered dolostone has been completely dissolved during weathering, only approximately 46% of the bulk Ca would be lost, which cannot explain the actual 80% loss of total Ca calculated by Ca/Al ratios (from 10.24 to 2.05) in the most intensely weathered samples. Therefore, calcite dissolution is also needed to further lower the Ca/Al ratios in the intensely weathered zone as calcite is the only dominant Ca hosting mineral other than dolomite. Dolomite and calcite dissolution are thus concurrent in the intensely weathered zone. These conclusions are consistent with the petrographic study that the content of carbonate minerals in the intensely weathered samples is much lower than the least weathered dolostone.

The fluid-dolostone reactions involve dissolution and re-precipitation of carbonate minerals depending on the saturation state of fluids with respect to carbonate minerals. The dolomite dissolution and calcite re-precipitation as suggested in the weakly weathered zone were also observed in Chinese Loess Plateau samples (Jeong et al., 2008; Wimpenny et al., 2014a). The re-precipitation of secondary calcite is likely attributed to the saturation of fluids with respect to calcite given that large amounts of primary calcite and dolomite are dissolved causing high concentration of Ca^{2+} and CO_3^{2-} in fluids. In addition, this cooccurrence of dolomite dissolution and calcite re-precipitation occurs in carbonate regions where gypsum or anhydrite is present (Plummer and Back, 1980; Back et al., 1983; Jacobson and Wasserburg, 2005; Jacobson et al., 2010). The irreversible dissolution of gypsum or anhydrite would make the fluid reach saturation with respect to calcite and then drive the calcite re-precipitation. The calcite re-precipitation decreases the pH and removes CO_3^{2-} from fluids, thereby causing the dissolution of dolomite. As to the weathering profile in this study, no gypsum or anhydrite was present. Therefore, another process is needed to explain the behaviors of dolomite dissolution and calcite re-precipitation.

Jin et al. (2008) found that dolomite continuously dissolved after calcite equilibrium, because the solubility of dolomite is higher than calcite. Saturation index (SI) of the fluids with respect to calcite is defined as $\text{SI} = \text{Log}([\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] / K_{\text{calcite}})$, where $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{2-}]$ are activities of Ca^{2+} and CO_3^{2-} , and K_{calcite} is the solubility constant of calcite. Saturation index of calcite is controlled by K_{calcite} and concentrations of Ca^{2+} and CO_3^{2-} . The intensely weathered zone is near the joint plane.

Fluids, like the rain waters, are poor in Ca^{2+} , Mg^{2+} , and CO_3^{2-} and thus could be undersaturated with respect to both dolomite and calcite, which could lead to substantial dissolution of dolomite and calcite in the intensely weathered zone close to the joint plane (Fig. 7). Most fluid after water-rock interaction may drain away along the joint and a small fraction of fluid infiltrates the dolostone because of the hydrostatic pressure, which would infiltrate the dolostone deeply and continue to dissolve carbonates. Massive dissolution of dolomite and calcite in the intensely weathered zone would concentrate Ca^{2+} and CO_3^{2-} in the fluids. This could drive the infiltration fluid saturated with respect to calcite in the boundary between the weakly weathered and intensely weathered zone, whereas keep undersaturated with respect to dolomite because of the higher equilibrium constant for dolomite than that for calcite at temperatures $< 30^\circ\text{C}$ (Langmuir, 1997). Thus, dolomite could continue dissolving while calcite begins to re-precipitate in the weakly weathered zone. Once calcite re-precipitation begins, Ca^{2+} and CO_3^{2-} would be reduced, and thereby leading to a feedback of accelerating dolomite dissolution.

5.2 Magnesium isotope fractionation during dolostone weathering

The chemical weathering of dolostone mainly involves the dissolution of primary carbonate minerals (e.g. dolomite and calcite) and formation of secondary minerals (e.g. calcite). These processes also control the Mg isotope fractionation in the dolostone weathering profile. The intensely and weakly weathered zones display different fractionation directions driven by different fractionation mechanisms. Below, we discuss the behaviors of Mg isotopes in these two zones, respectively.

5.2.1 The intensely weathered zone

The least weathered dolostone is mainly composed of carbonates (90-95%) with trace amounts of silicates (5-10%). The intensely weathered zone is characterized by great dissolution of both dolomite and calcite due to its direct contact with externally undersaturated fluids such as rain waters. As carbonates are more reactive and soluble than silicates (Horton et al., 1999; White et al., 2005), the carbonates to silicates ratio largely decreases with increasing weathering intensity. This is supported by the much higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.71128 ~ 0.71368) of samples from the intensely weathered zone than the least weathered dolostone (0.71091). Since silicates have higher $\delta^{26}\text{Mg}$ values than carbonates (Huang et al., 2013; Wimpenny et al., 2014a; Wang et al., 2015), $\delta^{26}\text{Mg}$ values of the weathered products therefore depend on the Mg proportion between carbonates and silicates as well as their $\delta^{26}\text{Mg}$ values. This interpretation agrees with the general increase of $\delta^{26}\text{Mg}$ (-2.22‰ ~ -0.41‰, Fig. 6) with the increasing degree of weathering. In particular, the two most intensely weathered samples (HY-PM3-15 and HY-PM3-16) have extremely heavy Mg isotope compositions up to -0.41‰ and -0.64‰ that are close to igneous rocks (Teng et al., 2007, 2010a; Shen et al., 2009; Li et al., 2010; Yang et al., 2012). This suggests the Mg budget of the whole rocks is dominated by silicates and a nearly complete loss of

carbonates, which was also found in studies of loess and paleosol (Wimpenny et al., 2014a).

5.2.2 The weakly weathered zone

In contrast to the intensely weathered zone, calcite re-precipitates simultaneously with dolomite dissolution in the weakly weathered zone. The positive correlation between $\delta^{26}\text{Mg}$ and Mg/Al (Fig. 8A) suggests that the heavy Mg isotopes are preferentially lost during chemical weathering. Four possible mechanisms could explain this fractionation of Mg isotopes: (1) preferential release of heavy Mg isotopes during dolomite dissolution; (2) preferential selection of ^{24}Mg over ^{26}Mg during Mg-for-Na ion-exchange; (3) decrease in ratio of dolomite to calcite; and (4) preferential incorporation of isotopically light Mg during secondary calcite precipitation.

Previously published data indicated that dolomite tends to have lighter Mg isotope composition than its co-existing solution (Higgins and Schrag, 2010; Fantle and Higgins, 2014; Huang et al., 2015; Li et al., 2015). However, no isotope fractionation is expected during dissolution of dolomite as shown by previous studies. River waters draining dolostones were found to have Mg isotope composition similar to that of dolostones (Tipper et al., 2006b). Step leaching experiments revealed that the leachates from dolostone have constant $\delta^{26}\text{Mg}$ values (Liu et al., 2014a). In this case, dolomite dissolution is not likely to be responsible for the isotope fractionation of Mg.

Mg for Na ion-exchange process has been tentatively called to explain Mg isotope variation in groundwater samples as fluids preferentially remove ^{24}Mg during Mg-for-Na ion-exchange (Jacobson et al., 2010). This process, however, cannot be the main process altering Mg isotope composition of dolostone given that (1) silicate content in dolostone is much lower than carbonate and (2) the abundance of Na in dolostone is extremely limited ($\text{Na}/\text{Al} \leq 0.06$, see Appendix A) and (3) the abundance of Na in dolostone remain unchanged as weathering intensity changes.

Instead, $\delta^{26}\text{Mg}$ decline in the weakly weathered zone is likely caused by the decrease of dolomite to calcite ratio and precipitation of secondary calcite. Given that the calcite has lighter Mg isotope composition than dolomite (Galy et al., 2002; Tipper et al., 2006b), dolomite dissolution would decrease the dolomite to calcite ratio and thus lower $\delta^{26}\text{Mg}$ values of whole rocks. This agrees with the positive correlations between Mg/Al vs. $\delta^{26}\text{Mg}$ as well as Mg/Ca vs. $\delta^{26}\text{Mg}$ (Fig. 8). In addition, the secondary calcite that precipitates from the infiltration fluid preferentially incorporates ^{24}Mg (Galy et al., 2002; Immenhauser et al., 2010), thereby possibly further lowering $\delta^{26}\text{Mg}$ values of the dolostone.

Below, we quantitatively assess whether combined dolomite dissolution and calcite re-precipitation processes can produce the Mg isotope fractionation observed in the weakly weathered samples. In such a process, Mg isotope fractionation of weathered dolostone is determined by the input and output mass fluxes and their isotope compositions. As discussed above, the output flux of Mg from the weakly weathered dolostone is governed by dolomite dissolution while the input flux is due to calcite

re-precipitation. Based on mass balance, the isotope deviation of a weathered dolostone from the least weathered dolostone ($\Delta_{\text{weathered-protolith}}$) can be expressed by:

$$\Delta_{\text{weathered-protolith}} = \frac{\delta_{\text{protolith}} + F_{\text{cal.r}} \times \delta_{\text{cal.r}} - F_{\text{dol}} \times \delta_{\text{dol}}}{1 + F_{\text{cal.r}} - F_{\text{dol}}} - \delta_{\text{protolith}} \quad (\text{I})$$

where δ is the $\delta^{26}\text{Mg}$ value, F is the Mg fraction, *cal.r* is the secondary calcite, *dol* is the dissolved dolomite, *weathered* is the weathered dolostone, and *protolith* is the least weathered dolostone. The Mg fraction (F) is normalized by Mg/Al ratio of the least weathered dolostone. Here, Mg isotope exchange between silicate fraction and infiltration fluid is not considered, as no evidence indicates that such isotope exchange is important given that Mg sink in silicates is considerably low relative to dolomites and such contribution to the bulk dolostone could not alter $\delta^{26}\text{Mg}$ values of dolostone. $\delta_{\text{protolith}}$ is defined as -1.90‰, a value of the least weathered dolostone in our field study. Mg isotope composition of secondary calcite ($\delta_{\text{cal.r}}$) can be expressed by:

$$\delta_{\text{cal.r}} = \delta_{\text{sol.r}} + \Delta_{\text{cal.r-sol.r}} \quad (\text{II})$$

where *sol.r* refers to the infiltration fluid, and $\Delta_{\text{cal.r-sol.r}}$ refers to the fractionation factor between *cal.r* and *sol.r*. As (1) Mg in *sol.r* mainly comes from dolomite and no fractionation occurs between dolomite and the fluid, and (2) the rather small amount of Mg is incorporated into secondary calcite, we assume that $\delta_{\text{sol.r}}$ is similar to δ_{dol} and keeps constant during weathering. Eq. (II) can be re-expressed by:

$$\delta_{\text{cal.r}} = \delta_{\text{dol}} + \Delta_{\text{cal.r-sol.r}} \quad (\text{III})$$

In Eq. (III), $\Delta_{\text{cal.r-sol.r}}$ is adopted as -2.6‰ based on the experimental calibration of temperature dependence by Li et al. (2012b) and local annual average temperature of 18 °C (Hu et al., 2008). Seasonal and/or annual temperature fluctuations have negligible influence on $\Delta_{\text{cal.r-sol.r}}$ due to its insensitive temperature dependence ($0.011 \pm 0.002\text{‰}/^\circ\text{C}$ in Li et al. 2012b). Given that Ca/Al ratios display limited variation in the weakly weathered zone, we assume that the Ca influx and outflux are balanced in this model, then $F_{\text{cal.r}}$ can be calculated by:

$$F_{\text{cal.r}} = \frac{F_{\text{dol}} \times X_{\text{Mg/(Mg+Ca)}}}{1 - X_{\text{Mg/(Mg+Ca)}}} \quad (\text{IV})$$

where $X_{\text{Mg/(Mg+Ca)}}$ is the proportion of MgCO_3 in calcite.

The modeling results indicate that the Mg isotope fractionation is mainly controlled by the ratio of influx to outflux Mg and the isotope composition of primary dolomite (Fig. 9): (1) the higher ratio of reprecipitated Mg to dissolved Mg, the larger magnitude of fractionation; (2) the heavier Mg isotope composition of dolomite, the easier to achieve the observed fractionation. Our data ideally fall in the modeled lines (Fig. 9), supporting the interpretation that the concurrence of dolomite dissolution and calcite re-precipitation could lead to the observed Mg isotope fractionation. In addition, these models appear to indicate that the secondary calcite is low Mg calcite ($X_{\text{Mg/(Mg+Ca)}} < 0.05$) and the δ_{dol} lies between -1.75‰ and -1.90‰.

The occurrence of both dolomite dissolution and calcite precipitation in the weakly

weathered zone was termed as the “dedolomitization” which commonly occurs in the surface or near-surface settings (Raines and Dewers, 1997; Ronchi et al., 2004). This process is in opposite to dolomitization that is characterized by the formation of dolomite and decomposition of calcite. Fantle and Higgins (2014) found that dolomitization of limestone could lead to 1.3‰ Mg isotope fractionation, much larger than the 0.3‰ variation induced by dedolomitization observed in this study. The difference of Mg isotope fractionation between dolomitization and dedolomitization may depend on Mg influx and outflux, diagenetic fractionation factors, and fluid properties. For example, dolomitization will bring much external Mg into the Mg-depleted limestone and lead to a large diagenetic isotope fractionation up to -2‰, which can significantly change whole rock Mg isotope compositions (Fantle and Higgins, 2014). By contrast, dolomite dissolution does not appreciably fractionate Mg isotopes as discussed above. Additionally, samples in Fantle and Higgins (2014) were collected from an ocean drilling core and the dolomitization process occurred in an open system with a high fluid to solid mass ratio. By contrast, dedolomitization in this study took place under a surface environment with a low fluid to solid mass ratio. The fluids formed in these two different environments are probably distinct as well. The fluid during dolomitization of limestone in Fantle and Higgins (2014) is seawater-like, with Mg isotope composition much heavier than carbonates. However, dedolomitization fluid in this study has $\delta^{26}\text{Mg}$ value similar to dolostone as discussed above.

6. Implications

Our study of the dolostone weathering profile demonstrates that chemical weathering can significantly fractionate Mg isotopes even at the scale (~ 17 cm) of a hand specimen, with the direction and magnitude of isotope fractionation varying in different weathering stages. Therefore, the weathering influence has to be considered when using Mg isotopes of carbonates to trace paleoclimate change and the origin of dolostone.

The isotope fractionation produced in the intensely weathered zone is very large (~ 1.8‰), which can easily compromise the fractionation caused by other processes. Nonetheless, intensely weathered samples could be easily identified and avoided during sampling because of their distinct petrographic features such as color, hardness, and porosity. For example, the intensely weathered samples in this study have yellow color, are soft with very high porosity because of the substantial dissolution of carbonate minerals. Although the Mg isotope fractionation found in the weakly weathered zone is small (~ 0.3‰), it is still significant when compared to the variation observed in dolostone strata (e.g. 0.7‰ in Kasemann et al. 2014 and 0.4‰ in Liu et al. 2014a). The weakly weathered dolostones, prevalent in dolostone strata, are difficult to identify through petrographic studies and chemical analyses because of the highly variable compositions in primary dolostone. Therefore, evaluating and minimizing the weakly weathering effects are critical for using Mg isotopes in dolomites to trace dolostone genesis and paleoclimate change. Our study reveals that

the Mg isotope fractionation in the weakly weathered dolostones is mainly caused by dedolomitization, during which process the dissolution of the primary dolomite is unidirectional with calcite as the only secondary phase. Therefore, in the weakly weathered dolostones, primary dolomite can still be partially preserved. Then the step-leaching experiments can be used to identify the primary Mg isotope signature of the weathered dolostones because behaviors of dolomite, calcite and silicates are different to acid leaching, as shown in previous studies (Liu et al., 2014a; Wen et al., 2015).

7. Conclusions

Extreme Mg depletion (~ 97%) and Mg isotope fractionation ($\delta^{26}\text{Mg}$ up to 1.8‰) are observed in a dolostone weathering profile from Hubei, China. The weathering profile is divided into the weakly and intensely weathered zones based on the element and isotope ratios. In the weakly weathered zone, whole rock $\delta^{26}\text{Mg}$ decreases from -1.90‰ to -2.22‰ with decreasing Mg/Al ratios and nearly constant Ca/Al ratios, reflecting the cooccurrence of dolomite dissolution and calcite re-precipitation, decrease in dolomite to calcite ratio, and preferential incorporation of ^{24}Mg into secondary calcite. Significant loss of both Mg and Ca is evident in the intensely weathered zone. Accordingly, $\delta^{26}\text{Mg}$ increases from -2.22‰ to -0.41‰, and $^{87}\text{Sr}/^{86}\text{Sr}$ from 0.71128 to 0.71368, which likely result from the increasing ratio of silicates to carbonates in the weathered residues. Our study suggests that both direction and magnitude of Mg isotope fractionation during dolostone weathering are controlled by dissolution and re-precipitation of carbonate minerals, as well as the saturation of carbonate minerals in the co-existing fluids. Possible weathering effect thus shall be carefully evaluated and minimized before using Mg isotopes of dolostone to trace dolostone genesis and paleoclimate change in the future work. Primary dolomite could be partially preserved in the weakly weathered dolostones and can be identified by step-leaching experiments.

Acknowledgements

We thank Dr. Lijuan Xu, Zijian Li, Xu-Nan Meng and Ruiying Li for help during sample analysis, and Zhengrong Wang, Lixin Jin, Jianming Zhu, Sheng-Ao Liu, Bing Shen, Kangjun Huang, Xianguo Lang, Yinghuai Lu, Pengfei Li, Chuanwei Zhu, and Ruoqi Wan for discussions. The constructive comments by Josh Wimpenny and two anonymous reviewers are greatly appreciated. This work was supported by the National Nature Scientific Foundation of China (No. 41103010, No. 41202010 and No. 41328004), the Fundamental Research Funds for the Central Universities (No. 2652014035) and the National Science Foundation (EAR 1340160).

References

Al-Aasm, I.S., Packard, J.J., 2000. Stabilization of early-formed dolomite: a tale of divergence from two Mississippian dolomites. *Sedimentary Geology* 131,

97-108.

Azmy, K., Lavoie, D., Wang, Z., Brand, U., Al-Aasm, I., Jackson, S., Girard, I., 2013. Magnesium-isotope and REE compositions of Lower Ordovician carbonates from eastern Laurentia: implications for the origin of dolomites and limestones. *Chemical Geology* 356, 64-75.

Back, W., Hanshaw, B.B., Plummer, L.N., Rahn, P.H., Rightmire, C.T., Rubin, M., 1983. Process and rate of dedolomitization: mass transfer and ^{14}C dating in a regional carbonate aquifer. *Geological Society of America Bulletin* 94, 1415-1429.

Fantle, M.S., Higgins, J., 2014. The effects of diagenesis and dolomitization on Ca and Mg isotopes in marine platform carbonates: Implications for the geochemical cycles of Ca and Mg. *Geochimica et Cosmochimica Acta* 142, 458-481.

Foster, G.L., Pogge von Strandmann, P.A.E., Rae, J.W.B., 2010. Boron and magnesium isotopic composition of seawater. *Geochemistry, Geophysics, Geosystems* 11, Q08015. doi:10.1029/2010GC003201.

Galy, A., Bar-Matthews, M., Halicz, L., O'Nions, R.K., 2002. Mg isotopic composition of carbonate: insight from speleothem formation. *Earth and Planetary Science Letters* 201, 105-115.

Galy, A., Yoffe, O., Janney, P.E., Williams, R.W., Cloquet, C., Alard, O., Carignan, J., 2003. Magnesium isotope heterogeneity of the isotopic standard SRM980 and new reference materials for magnesium-isotope-ratio measurements. *Journal of Analytical Atomic Spectrometry* 18, 1352-1356.

Geske, A., Zorlu, J., Richter, D.K., Buhl, D., Niedermayr, A., Immenhauser, A., 2012. Impact of diagenesis and low grade metamorphism on isotope ($\delta^{26}\text{Mg}$, $\delta^{13}\text{C}$, $\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$) and elemental (Ca, Mg, Mn, Fe and Sr) signatures of Triassic sabkha dolomites. *Chemical Geology* 332, 45-64.

Geske, A., Goldstein, R.H., Mavromatis, V., Richter, D.K., Buhl, D., Kluge, T., Immenhauser, A., 2015a. The magnesium isotope ($\delta^{26}\text{Mg}$) signature of dolomites. *Geochimica et Cosmochimica Acta* 149, 131-151.

Geske, A., Lokier, S., Dietzel, M., Richter, D.K., Buhl, D., Immenhauser, A., 2015b. Magnesium isotope composition of sabkha porewater and related (Sub-) Recent stoichiometric dolomites, Abu Dhabi (UAE). *Chemical Geology* 393, 112-124.

Higgins, J., Schrag, D., 2010. Constraining magnesium cycling in marine sediments using magnesium isotopes. *Geochimica et Cosmochimica Acta* 74, 5039-5053.

Horton, T.W., Chamberlain, C.P., Fantle, M., Blum, J.D., 1999. Chemical weathering and lithologic controls of water chemistry in a high-elevation river system: Clark's Fork of the Yellowstone River, Wyoming and Montana. *Water Resources Research* 35, 1643-1655.

Hu, C., Henderson, G., Huang, J., Chen, Z., Johnson, K., 2008. Report of a three-year monitoring programme at Heshang Cave, Central China. *International Journal of Speleology* 37, 143-151.

Huang, K.-J., Teng, F.-Z., Wei, G.-J., Ma, J.-L., Bao, Z.-Y., 2012. Adsorption- and

586 desorption-controlled magnesium isotope fractionation during extreme
 587 weathering of basalt in Hainan Island, China. *Earth and Planetary Science*
 588 *Letters* 359, 73-83.
 589 Huang, K.-J., Teng, F.-Z., Elsenouy, A., Li, W.-Y., Bao, Z.-Y., 2013. Magnesium
 590 isotopic variations in loess: Origins and implications. *Earth and Planetary*
 591 *Science Letters* 374, 60-70.
 592 Huang, K.-J., Shen, B., Lang, X.G., Tang, W.B., Peng, Y., Ke, S., Li, F.B., 2015.
 593 Magnesium isotopic compositions of the Mesoproterozoic dolostones:
 594 Implications for Mg isotopic systematics of marine carbonate. *Geochimica et*
 595 *Cosmochimica Acta* 164, 333-351.
 596 Husson, J.M., Higgins, J.A., Maloof, A.C., Schoene, B., 2015. Ca and Mg isotope
 597 constraints on the origin of Earth's deepest $\delta^{13}\text{C}$ excursion. *Geochimica et*
 598 *Cosmochimica Acta* 160, 243-266.
 599 Immenhauser, A., Buhl, D., Richter, D., Niedermayr, A., Riechelmann, D., Dietzel, M.,
 600 Schulte, U., 2010. Magnesium-isotope fractionation during low-Mg calcite
 601 precipitation in a limestone cave—Field study and experiments. *Geochimica et*
 602 *Cosmochimica Acta* 74, 4346-4364.
 603 Jacobson, A., Wasserburg, G., 2005. Anhydrite and the Sr isotope evolution of
 604 groundwater in a carbonate aquifer. *Chemical Geology* 214, 331-350.
 605 Jacobson, A.D., Zhang, Z., Lundstrom, C., Huang, F., 2010. Behavior of Mg isotopes
 606 during dedolomitization in the Madison Aquifer, South Dakota. *Earth and*
 607 *Planetary Science Letters* 297, 446-452.
 608 Jeong G.Y., Hillier S., Kemp R.A., 2008. Quantitative bulk and single-particle
 609 mineralogy of a thick Chinese loess-paleosol section: implications for loess
 610 provenance and weathering. *Quaternary Science Reviews* 27, 1271-1287.
 611 Jiang, G., Wang, X., Shi, X., Xiao, S., Zhang, S., Dong, J., 2012. The origin of
 612 decoupled carbonate and organic carbon isotope signatures in the early
 613 Cambrian (ca. 542–520Ma) Yangtze platform. *Earth and Planetary Science*
 614 *Letters* 317, 96-110.
 615 Jin, L., Williams, E.L., Szramek, K.J., Walter, L.M., & Hamilton, S.K., 2008. Silicate
 616 and carbonate mineral weathering in soil profiles developed on Pleistocene
 617 glacial drift (Michigan, USA): Mass balances based on soil water
 618 geochemistry. *Geochimica et Cosmochimica Acta* 72, 1027-1042.
 619 Kasemann, S.A., Pogge von Strandmann, P.A.E., Prave, A.R., Fallick, A.E., Elliott, T.,
 620 Hoffmann, K.H., 2014. Continental weathering following a Cryogenian
 621 glaciation: Evidence from calcium and magnesium isotopes. *Earth and*
 622 *Planetary Science Letters* 396, 66-77.
 623 Kaufman, A.J., Knoll, A.H., Semikhatov, M.A., Grotzinger, J.P., Jacobsen, S.B.,
 624 Adams, W., 1996. Integrated chronostratigraphy of Proterozoic–Cambrian
 625 boundary beds in the western Anabar region, northern Siberia. *Geological*
 626 *Magazine* 133, 509-533.
 627 Ke, S., Teng, F.-Z., Li, S., Gao, T., Liu, S.-A., He, Y., Mo, X., 2016. Mg, Sr, and O
 628 isotope geochemistry of syenites from northwest Xinjiang, China: Tracing
 629 carbonate recycling during Tethyan oceanic subduction. *Chemical Geology* 37,

109-119..

Land, L.S., 1985. The origin of massive dolomite. *Journal of Geological Education* 33, 112-125.

Langmuir, D., 1997. *Aqueous Environmental Geochemistry*. Prentice Hall, Upper Saddle River, NY, 600 p.

Li, C.F., Li, X.H., Li, Q.L., Guo, J.H., Li, X.H., Yang, Y.H., 2012a. Rapid and precise determination of Sr and Nd isotopic ratios in geological samples from the same filament loading by thermal ionization mass spectrometry employing a single-step separation scheme. *Analytica Chimica Acta* 727, 54-60.

Li, W., Chakraborty, S., Beard, B.L., Romanek, C.S., Johnson, C.M., 2012b. Magnesium isotope fractionation during precipitation of inorganic calcite under laboratory conditions. *Earth and Planetary Science Letters* 333, 304-316.

Li, W., Beard, B.L., Li, C., Xu, H., Johnson, C.M., 2015. Experimental calibration of Mg isotope fractionation between dolomite and aqueous solution and its geological implications. *Geochimica et Cosmochimica Acta* 157, 164-181.

Li, W.-Y., Teng, F.-Z., Ke, S., Rudnick, R.L., Gao, S., Wu, F.Y., Chappell, B.W., 2010. Heterogeneous magnesium isotopic composition of the upper continental crust. *Geochimica et Cosmochimica Acta* 74, 6867-6884.

Li Y.H., 1982. A brief discussion on the mean oceanic residence time of elements. *Geochimica et Cosmochimica Acta* 46, 2671-2675.

Ling, M.X., Sedaghatpour, F., Teng, F.-Z., Hays, P.D., Strauss, J., Sun, W., 2011. Homogeneous magnesium isotopic composition of seawater: an excellent geostandard for Mg isotope analysis. *Rapid Communications in Mass Spectrometry* 25, 2828-2836.

Liu, C., Wang, Z., Raub, T.D., Macdonald, F.A., Evans, D.A., 2014a. Neoproterozoic cap-dolostone deposition in stratified glacial meltwater plume. *Earth and Planetary Science Letters* 404, 22-32.

Liu, S.-A., Teng, F.-Z., He, Y., Ke, S., Li, S.-G., 2010. Investigation of magnesium isotope fractionation during granite differentiation: Implication for Mg isotopic composition of the continental crust. *Earth and Planetary Science Letters* 297, 646-654.

Liu, X.-M., Teng, F.-Z., Rudnick, R.L., McDonough, W.F., Cummings, M.L., 2014b. Massive magnesium depletion and isotope fractionation in weathered basalts. *Geochimica et Cosmochimica Acta* 135, 336-349.

Ma, L., Teng, F.-Z., Jin, L., Ke, S., Yang, W., Gu, H.O., Brantley, S.L., 2015. Magnesium isotope fractionation during shale weathering in the Shale Hills Critical Zone Observatory: Accumulation of light Mg isotopes in soils by clay mineral transformation. *Chemical Geology* 397, 37-50.

Machel, H.G., 1997. Recrystallization versus neomorphism, and the concept of 'significant recrystallization' in dolomite research. *Sedimentary Geology* 113, 161-168.

Malone, M.J., Baker, P.A., Burns, S.J., 1994. Recrystallization of dolomite: evidence from the Monterey Formation (Miocene), California. *Sedimentology* 41,

1223-1239.

Mavromatis, V., Gautier, Q., Bosc, O., Schott, J., 2013. Kinetics of Mg partition and Mg stable isotope fractionation during its incorporation in calcite. *Geochimica et Cosmochimica Acta* 114, 188-203.

McArthur, J.M., Howarth, R.J., Shields, G.A., 2012. Strontium isotope stratigraphy. In: Gradstein, F.M., Ogg, J.G., Schmitz, M.D. Ogg, G.M. (Eds), *The Geologic Time Scale*. Elsevier, pp. 127-144.

Montanez, I.P., Read, J.F., 1992. Fluid-rock interaction history during stabilization of early dolomites, upper Knox Group (Lower Ordovician), US Appalachians. *Journal of Sedimentary Research* 62, 753-778.

Nesbitt, H.W., Markovics, G., 1980. Chemical processes affecting alkalis and alkaline earths during continental weathering. *Geochimica et Cosmochimica Acta* 44, 1659-1666.

Opfergelt, S., Georg, R.B., Delvaux, B., Cabidoche, Y.M., Burton, K.W., Halliday, A.N., 2012. Mechanisms of magnesium isotope fractionation in volcanic soil weathering sequences, Guadeloupe. *Earth and Planetary Science Letters* 341, 176-185.

Opfergelt, S., Burton, K.W., Georg, R.B., West, A.J., Guicharnaud, R.A., Sigfusson, B., Halliday, A.N., 2014. Magnesium retention on the soil exchange complex controlling Mg isotope variations in soils, soil solutions and vegetation in volcanic soils, Iceland. *Geochimica et Cosmochimica Acta* 125, 110-130.

Plummer, L.N., Back, W., 1980. The mass balance approach: application to interpreting the chemical evolution of hydrologic systems. *American Journal of Science* 280, 130-142.

Pogge von Strandmann, P.A.E., Burton, K.W., James, R.H., van Calsteren, P., Gislason, S.R., Sigfússon, B., 2008. The influence of weathering processes on riverine magnesium isotopes in a basaltic terrain. *Earth and Planetary Science Letters* 276, 187-197.

Pogge von Strandmann, P.A.E., Opfergelt, S., Lai, Y.J., Sigfússon, B., Gislason, S.R., Burton, K.W., 2012. Lithium, magnesium and silicon isotope behaviour accompanying weathering in a basaltic soil and pore water profile in Iceland. *Earth and Planetary Science Letters* 339, 11-23.

Pokrovsky, B.G., Mavromatis, V., Pokrovsky, O.S., 2011. Co-variation of Mg and C isotopes in late Precambrian carbonates of the Siberian Platform: A new tool for tracing the change in weathering regime? *Chemical Geology* 290, 67-74.

Raines M.A., Dewers T.A., 1997. Dedolomitization as a driving mechanism for karst generation in Permian Blaine Formation, southwestern Oklahoma, USA. *Carbonates and Evaporites* 12, 24-31.

Ronchi P., Jadoul F., Savino R., 2004. Quaternary dedolomitization along fracture systems in a late triassic dolomitized platform (Western Southern Alps, Italy). *Carbonates and Evaporites* 19, 51-66.

Rudnick, R.L., Tomascak, P.B., Njo, H.B., Gardner, L.R., 2004. Extreme lithium isotopic fractionation during continental weathering revealed in saprolites from South Carolina. *Chemical Geology* 212, 45-57.

- Ryu, J.-S., Jacobson, A.D., Holmden, C., Lundstrom, C., Zhang, Z., 2011. The major ion, $\delta^{44/40}\text{Ca}$, $\delta^{44/42}\text{Ca}$, and $\delta^{26/24}\text{Mg}$ geochemistry of granite weathering at pH=1 and T=25°C: power-law processes and the relative reactivity of minerals. *Geochimica et Cosmochimica Acta* 75, 6004-6026.
- Saenger, C., Wang, Z., 2014. Magnesium isotope fractionation in biogenic and abiogenic carbonates: implications for paleoenvironmental proxies. *Quaternary Science Reviews* 90, 1-21.
- Schauble, E.A., 2011. First-principles estimates of equilibrium magnesium isotope fractionation in silicate, oxide, carbonate and hexaaquamagnesium (2+) crystals. *Geochimica et Cosmochimica Acta* 75, 844-869.
- Shen, B., Jacobsen, B., Lee, C.-T.A., Yin, Q.-Z., Morton, D.M., 2009. The Mg isotopic systematics of granitoids in continental arcs and implications for the role of chemical weathering in crust formation. *Proceedings of the National Academy of Sciences* 106, 20652-20657.
- Teng, F.-Z., Wadhwa, M., Helz, R.T., 2007. Investigation of magnesium isotope fractionation during basalt differentiation: Implications for a chondritic composition of the terrestrial mantle. *Earth and Planetary Science Letters* 261, 84-92.
- Teng, F.-Z., Li, W.-Y., Ke, S., Marty, B., Dauphas, N., Huang, S., Pourmand, A., 2010a. Magnesium isotopic composition of the Earth and chondrites. *Geochimica et Cosmochimica Acta* 74, 4150-4166.
- Teng, F.-Z., Li, W.-Y., Rudnick, R.L., Gardner, L.R., 2010b. Contrasting lithium and magnesium isotope fractionation during continental weathering. *Earth and Planetary Science Letters* 300, 63-71.
- Teng, F.-Z., Li, W.-Y., Ke, S., Yang, W., Liu, S.-A., Sedaghatpour, F., Xiao, Y., 2015. Magnesium Isotopic Compositions of International Geological Reference Materials. *Geostandards and Geoanalytical Research* 39, 329-339.
- Tipper, E., Galy, A., Bickle, M., 2006a. Riverine evidence for a fractionated reservoir of Ca and Mg on the continents: Implications for the oceanic Ca cycle. *Earth and Planetary Science Letters* 247, 267-279.
- Tipper, E., Galy, A., Gaillardet, J., Bickle, M.J., Elderfield, H., Carder, E.A., 2006b. The magnesium isotope budget of the modern ocean: Constraints from riverine magnesium isotope ratios. *Earth and Planetary Science Letters* 250, 241-253.
- Wang, S.-J., Teng, F.-Z., Rudnick, R.L., Li, S.-G., 2015. The behavior of magnesium isotopes in low-grade metamorphosed mudrocks. *Geochimica et Cosmochimica Acta* 165, 435-448.
- Wang, Z., Hu, P., Gaetani, G., Liu, C., Saenger, C., Cohen, A., Hart, S., 2013. Experimental calibration of Mg isotope fractionation between aragonite and seawater. *Geochimica et Cosmochimica Acta* 102, 113-123.
- Warren, J., 2000. Dolomite: occurrence, evolution and economically important associations. *Earth-Science Reviews* 52, 1-81.
- Wen B., Evans D.A.D., Li Y.X., Wang, Z., Liu, C., 2015. Newly discovered Neoproterozoic diamictite and cap carbonate (DCC) couplet in Tarim Craton, NW China: Stratigraphy, geochemistry, and paleoenvironment. *Precambrian*

- Research 271, 278-294.
- White, A.F., Schulz, M.S., Lowenstern, J.B., Vivit, D.V., Bullen, T.D., 2005. The ubiquitous nature of accessory calcite in granitoid rocks: implications for weathering, solute evolution, and petrogenesis. *Geochimica et Cosmochimica Acta* 69, 1455-1471.
- Wimpenny, J., Gíslason, S.R., James, R.H., Gannoun, A., Pogge von Strandmann, P.A.E., Burton, K.W., 2010. The behaviour of Li and Mg isotopes during primary phase dissolution and secondary mineral formation in basalt. *Geochimica et Cosmochimica Acta* 74, 5259-5279.
- Wimpenny, J., Yin, Q.-Z., Tollstrup, D., Xie, L.-W., Sun, J., 2014a. Using Mg isotope ratios to trace Cenozoic weathering changes: A case study from the Chinese Loess Plateau. *Chemical Geology* 376, 31-43.
- Wimpenny, J., Colla, C.A., Yin, Q.-Z., Rustad, J.R., Casey, W.H., 2014b. Investigating the behaviour of Mg isotopes during the formation of clay minerals. *Geochimica et Cosmochimica Acta* 128, 178-194.
- Wombacher, F., Eisenhauer, A., Böhm, F., Gussone, N., Regenberg, M., Dullo, W.C., Rüggeberg, A., 2011. Magnesium stable isotope fractionation in marine biogenic calcite and aragonite. *Geochimica et Cosmochimica Acta* 75, 5797-5818.
- Yang, W., Teng, F.-Z., Zhang, H.-F., 2009. Chondritic magnesium isotopic composition of the terrestrial mantle: a case study of peridotite xenoliths from the North China craton. *Earth and Planetary Science Letters* 288, 475-482.
- Yang, W., Teng, F.-Z., Zhang, H.-F., Li, S.-G., 2012. Magnesium isotopic systematics of continental basalts from the North China craton: Implications for tracing subducted carbonate in the mantle. *Chemical Geology* 328, 185-194.
- Yoo, C.M., Lee, Y.I., 1998. Origin and modification of early dolomites in cyclic shallow platform carbonates, Yeongheung Formation (Middle Ordovician), Korea. *Sedimentary Geology* 118, 141-157.

Table 1: Element ratios and isotope compositions of standards and weathered dolostone samples from Hubei, China.

Layer ID	Sample ID	Distance (cm)	Mg/Ca	Mg/Al	Ca/Al	$^{87}\text{Sr}/^{86}\text{Sr}$	$\delta^{25}\text{Mg}$ (‰)	2SD	$\delta^{26}\text{Mg}$ (‰)	2SD
SL	HY-PM3-3*	0.0	0.46	5.64	12.22	0.71091	-1.02	0.04	-1.90	0.04
	HY-PM3-4	2.0	0.44	4.47	10.11	0.71118	-0.99	0.03	-1.90	0.03
	HY-PM3-5	4.0	0.40	4.99	12.54	0.71097	-0.98	0.08	-1.92	0.08
	HY-PM3-6	7.7	0.24	3.02	12.42	0.71161	-1.04	0.05	-2.02	0.05
	HY-PM3-7	9.4	0.32	3.41	10.77	0.71152	-1.02	0.05	-1.99	0.05
	HY-PM3-8	10.0	0.21	2.86	13.70	0.71130	-1.10	0.08	-2.11	0.08
	HY-PM3-9	10.7	0.21	2.78	12.98	0.71129	-1.07	0.04	-2.06	0.04
	HY-PM3-10	11.7	0.21	2.34	11.13	0.71125	-1.12	0.06	-2.17	0.06
	HY-PM3-11	12.7	0.19	1.75	9.02	0.71137	-1.15	0.06	-2.22	0.06
	HY-PM3-12	13.7	0.16	1.62	10.24	0.71128	-1.14	0.06	-2.22	0.06
	HY-PM3-13	14.7	0.13	1.04	8.06	0.71143	-1.12	0.01	-2.17	0.03
	HY-PM3-14	15.7	0.12	0.28	2.23	0.71353	-0.73	0.01	-1.41	0.01
	HY-PM3-15	16.2	0.07	0.16	2.22	0.71249	-0.21	0.03	-0.41	0.01
	HY-PM3-16	16.7	0.09	0.17	2.05	0.71368	-0.34	0.07	-0.64	0.03
DL1	HY-1	/	0.41	6.00	14.58	0.71088	-1.01	0.04	-1.98	0.05
DL2	HY-2	/	0.11	2.88	25.83	0.70971	-1.06	0.09	-2.08	0.03
DL3	HY-3	/	0.34	8.15	23.88	0.71018	-0.83	0.03	-1.61	0.10
DL4	HY-4	/	0.30	3.77	12.38	0.71095	-1.00	0.09	-1.95	0.07
/	Seawater	/	/	/	/	/	-0.43	0.07	-0.84	0.07
	Seawater	/	/	/	/	/	-0.40	0.07	-0.82	0.06
	Average	/	/	/	/	/	-0.42	0.04	-0.83	0.03
	SRM987	/	/	/	/	0.71029	/	/	/	/
	SRM987	/	/	/	/	0.71028	/	/	/	/
	SRM987	/	/	/	/	0.71026	/	/	/	/
	Average	/	/	/	/	0.71028	/	/	/	/

$\delta^x\text{Mg} = [({}^x\text{Mg}/{}^{24}\text{Mg})_{\text{sample}}/({}^x\text{Mg}/{}^{24}\text{Mg})_{\text{DSM3}} - 1] \times 1000$, where $x=25$ or 26 and DSM3 is Mg solution made from pure Mg metal (Galy et al., 2003). 2SD = 2 times the standard deviation of population analyzed. “*” represents the least weathered dolostone. “/” represents the inexistence or no measurements.

Figure Captions

Figure 1: (A) Geological map of the study area in Hubei Province, South China (modified after Jiang et al., 2012). The star represents the study area. (B) The photo of weathering profile in the field. The arrow represents the sample location.

Figure 2: Photograph of the specimen (A) and sketch (B) of the dolostone weathering profile in Hubei Province of South China. SL represents the sampling layer. 14 samples were successively taken from the least weathered end to the most weathered end in this layer. DL1, DL2, DL3 and DL4 represent different layers paralleling to the SL layer, and one sample was taken from each layer in the least weathered end.

Figure 3: Photomicrographs of the samples in different weathering zones. (A) the least weathered dolostone; (B) and (C) samples in the weakly weathered zone; (D) a sample in the intensely weathered zone. The relative proportions of each section are described as follows: (A) carbonates = 90-95%, silicates = 5-10%; (B) carbonates = 80-85%, silicates = 15-20%; (C) carbonates = 75-80%, silicates = 20-25%; (D) carbonates = 5-10%, silicates = 90-95%.

Figure 4: The element ratios (Mg/Ca, Mg/Al, Ca/Al) and isotope compositions ($^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{26}\text{Mg}$) of different deposition layers (SL, DL1, DL2, DL3 and DL4). Data are reported in Table 1.

Figure 5: Mg/Al (A), Ca/Al (B), Mg/Ca (C) as a function of distance in the dolostone weathering profile. The star represents the least weathered dolostone. Error bars represent 2SD uncertainties. Data are reported in Table 1.

Figure 6: $\delta^{26}\text{Mg}$ (A) and $^{87}\text{Sr}/^{86}\text{Sr}$ (B) as a function of distance in the dolostone weathering profile. The star represents the least weathered dolostone. Error bars represent 2SD uncertainties. Data are reported in Table 1.

Figure 7: Schematic diagram of carbonate mineral behaviors and fluid's properties along the dolostone weathering profile. In the intensely weathered zone, the fluids from the joint are undersaturated with respect to both dolomite and calcite. In the weakly weathered zone, the fluids become saturated with respect to calcite but undersaturated with respect to dolomite after interaction with dolomites and calcites in the intensely weathered zone.

Figure 8: Mg/Al (A) and Mg/Ca (B) as a function of $\delta^{26}\text{Mg}$. The star represents the least weathered dolostone. Error bars represent 2SD uncertainties. Data are reported in Table 1.

Figure 9: $\sum F_i$ vs. $\Delta_{\text{weathered-protolith}}$ of the weakly weathered zone in dolostone weathering profile. $\sum F_i$ is the sum of Mg fraction: $\sum F_i = 1 + F_{\text{cal.r}} - F_{\text{dol}}$. $\Delta_{\text{weathered-protolith}} = \delta_{\text{weathered}} - \delta_{\text{protolith}}$, *weathered* and *protolith* represent the weathered and the least weathered dolostone, respectively. (A) $\delta_{\text{dol}} = -1.90\text{‰}$; (B) $\delta_{\text{dol}} = -1.80\text{‰}$; (C) $\delta_{\text{dol}} = -1.75\text{‰}$.

Gao et al. Figure 1

(A)

(B)

Gao et al. Figure 2

(A)

(B)

Gao et al. Figure 3

Gao et al. Figure 4

Gao et al. Figure 5

Gao et al. Figure 6

Gao et al. Figure 7

Gao et al. Figure 8

Gao et al. Figure 9