Stable Magnesium Isotopes

12	24,31
Mg	
Magnesium	

General aspects of magnesium

Magnesium is the ninth most abundant element in the universe, the eighth most abundant element in the earth's crust and the fourth most common element in the bulk composition of the earth. As an alkaline earth metal, it belongs to group 3 in the periodic table. In nature magnesium only occurs combined with other elements, where it always has an oxidation state of +2. Magnesium is incorporated during growth of biogenic $CaCO_3$ and plays an essential role during photosynthesis, which indicates that biological fractionation plays an important role for Mg isotopes (Hoefs 2018).

Isotopes of magnesium

^{24}Mg   78,99%

^{25}Mg   10,00%

^{26}Mg   11,01%

According to Rosman and Taylor (1998), magnesium is composed of three isotopes. Only the introduction of the multicollector-inductively coupled-plasma mass spectrometry (MC-ICP-MS) allowed proper research of the natural Mg isotope variations (Galy et al. 2002) The δ^{25}Mg and δ^{26}Mg values are reported relative to the DSM-3 standard (Teng et al 2015a). Young and Galy (2004) proposed that the relationship between ^{25}Mg/^{24}Mg and ^{26}Mg/^{24}Mg ratios is diagnostic of kinetic versus equilibrium fractionations. Equilibrium processes should therefore show a slope close to 0.521 on a three-isotope diagram, whereas kinetic processes result in a slope closer to 0.511. Figure 1 summarizes the natural δ^{26}Mg isotope variations relative to DSM-3.
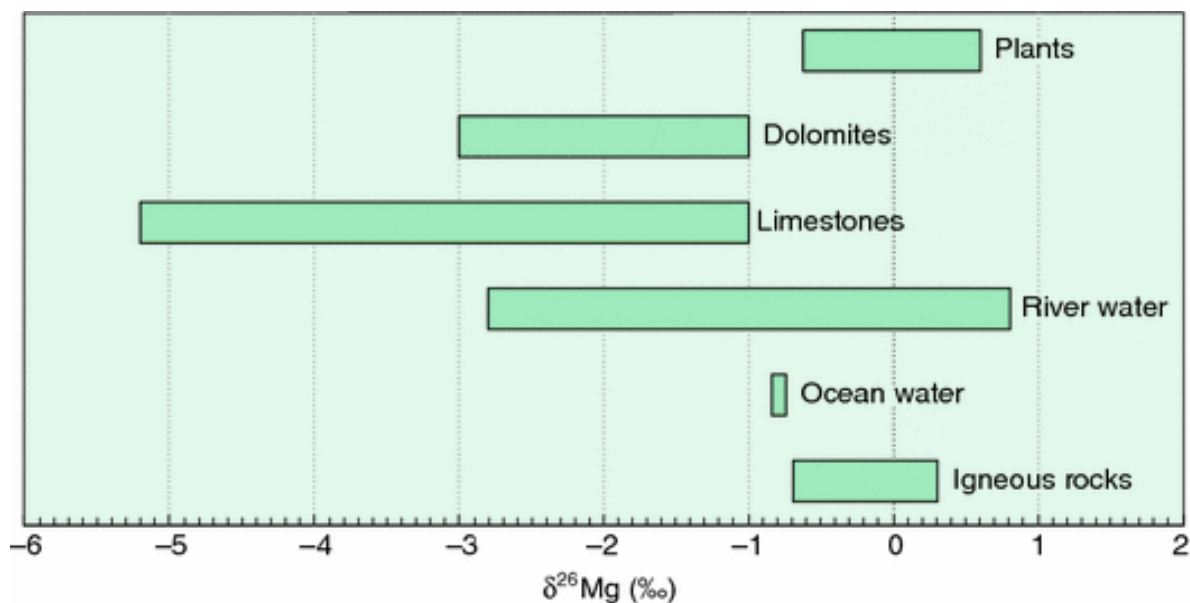

Figure 1: δ^{26}Mg values of important geological reservoirs (Hoefs 2018).

Fractionation Processes

High-Temperature Fractionations

Fractionations are controlled by the coordination number of Mg in minerals, tetrahedral sites tend to have higher $^{26}Mg/^{24}Mg$ ratios than octahedral sites. In olivine, orthopyroxene, clinopyroxene, hornblende and biotite the coordination number of Mg is 6, resulting in limited isotope fractionations among these minerals. In spinel the coordination of Mg is 4 and in garnet it is 8. Therefore, pyrope is depleted in heavy Mg isotopes relative to pyroxenes and olivine, whereas spinel is enriched relative to the coordination of 6 (Hoefs 2018). Schauble (2011) calculated that ^{26}Mg isotope fractionations among silicates, carbonates and oxides result in enrichment in the order magnesite, dolomite, forsterite, orthoenstatite, diopside, periclase and spinel.

Fractionations During Weathering

Weathering has a rather complex effect on the fractionation of magnesium isotopes (Huang et al. 2012). Mg is soluble and mobile during weathering, potentially inducing small fractionations during dissolution and precipitation of minerals. Experiments on basalt resulted in an enriched residue due to light Mg isotopes being preferentially released during dissolution. Other experiments reported only little fractionation during dissolution of granite.

The isotopes show an even more complex behaviour during secondary formation of Mg minerals (Huang et al. 2012). Several studies showed that soil and clays are generally heavier than their parent rocks suggesting that heavier Mg isotopes are preferentially incorporated into the structure of clay minerals or absorbed in soils (Hoefs 2018).

The large variation of Mg isotopes in river waters depicted in Figure 1 results from this complex behaviour during weathering. Li et al. (2012) suggested that the range of $\delta^{26}Mg$ values is reflecting differences of catchment lithologies particularly in the proportions of carbonate to silicate rocks. Another study by Tipper et al. (2006) observed a smaller variation and concluded that the lithology in the drainage area is of limited significance and the major part of the variability has to be the result of fractionations in the weathering environment.

This leads to the conclusion that the different behaviour of Mg isotopes during weathering may be due to crystallographic differences of Mg-sites in minerals (Hoefs 2018).

Mg Isotopes of Different Settings

Mantle Rocks

Peridotites have a rather constant Mg isotope composition suggesting a homogeneous mantle with a $\delta^{26}Mg$ value of-0,25‰ (Hu et al. 2016) that is used as the average Mg isotope composition of the mantle and bulk earth. Different studies found that there is a lack of Mg isotope fractionation during crystal melt fractionation.

Diffusion processes on the other hand play an important role in causing Mg isotope variations in mantle rocks. The interdiffusion exchange of Mg and Fe in olivine results in lighter Fe isotopes diffusing in and lighter Mg isotopes diffusing out of the crystal and thereby causes negatively coupled isotope variations from rim to core (Hoefs 2018).

Metasomatism produces Mg isotope variations in the lithospheric mantle. Wang et al. (2016) demonstrated that the continental lithosphere is heterogeneous in its Mg isotope composition, with xenoliths from the middle, lower crust and from the lithospheric mantle exhibiting values from -1,23 to 0,01‰. Low $\delta^{26}Mg$ values have been interpreted to indicate metasomatism by carbonate rich fluids.

Continental Crust

Shen et al. (2009) showed that the upper continental crust is heterogeneous in Mg isotope composition and on average slightly heavier than the mantle. The largest variations occur in sediments (more than 2,5‰), which are due to mixing of isotopically light carbonates with heavy silicates (Hoefs 2018).
Clastic sediments are, overall, enriched in heavy Mg isotopes with δ^{26}Mg values up to 0,92‰ (Li et al. 2010). During subduction, clastic sediments generally retain their Mg isotope composition and thus will enrich the mantle in heavy Mg isotopes. Carbonates on the other hand are significantly depleted in heavy Mg isotopes. Light isotope values could therefore be interpreted as result of carbonate recycling.

Ocean Water

River input is the major source for Mg in the ocean. Major sinks are removal by hydrothermal fluids, dolomite formation and low-temperature clay formation during alteration of the oceanic crust. The riverine input has an average δ^{26}Mg value of -1,09‰ (Tipper et al 2006). Due to its long mean residence time, ocean water has a constant isotope composition of -0,80‰ that is slightly higher than the average river water. This is the result of Mg uptake into silicate minerals during weathering. Other than hydrothermal interaction with the oceanic crust, dolomitisation affects the sea water and drives it to heavier values (Hoefs 2018).

Carbonates

Mg is present in $CaCO_3$ in the form of high Mg calcite, low Mg calcite and to a minor extent as aragonite. Marine organisms produce a wide range of δ^{26}Mg values from -5 to -1‰ that are species dependent. Since the extent of Mg substitution into $CaCO_3$ is temperature dependent, Mg/Ca ratios can be used as thermometer for oceanic temperatures. This temperature dependence, however, does not play a major role in determining Mg isotope ratios. The observed variability can instead be attributed to mineralogy (Hippler et al. 2009). The fractionation between water and carbonate follows the sequence aragonite < dolomite < magnesite < calcite. (Hoefs 2018).
Most recent benthic and planktonic foraminifera show nearly identical δ^{26}Mg ratios, making them suitable for investigating past isotopic variations of ocean water. The change in the past 40 Ma in planktonic foraminifera concluded that seawater Mg has changed from δ^{26}Mg of -0,83‰ at present to 0‰ at 15 Ma (Pogge von Standmann et al. 2008).
Dolomite is one of the major rock-forming Mg-bearing carbonates that forms under specific environmental conditions. As Figure 1 implies, the range of dolomite is rather large. Geske et al (2015) argued that Mg isotope ratios are affected by a variety of factors, making the application of Mg isotopes as a proxy for their depositional and diagenetic environment problematic. Other studies on the other hand observed, that early diagenetic dolomite inherits its isotope signature from precursor carbonates and diagenetic fluids. Later formed diagenetic dolomite phases may be slightly enriched in ^{26}Mg suggesting that temperature is not the decisive factor, but instead the Mg-isotope composition of the interacting fluid upon diagenesis.

Hydroisotop

References

Galy A, Bar-Matthews M, Halicz L, O'Nions RK (2002): Mg isotopic composition of carbonate: insight from speleothem formation. Earth Planet Sci Lett 201:105-115

Geske A, Goldstein RH, Mavromatis V, Richter DK, Buhl D, Kluge T, John CM, Immenhauser A (2015): The magnesium isotope (δ^{26}Mg) signature of dolomites. Geochim Cosmochim Acta 149:131-151

Hippler D, Buhl D, Wibaard R, Richter DK, Immenhauser A (2009): Towards a better understanding of magnesium-isotope ratios from marine skeletal carbonates. Geochim Cosmochim Acta 73:6134-6146

Hoefs J (2018): Stable Isotope Geochemistry: Eighth Edition. Springer Tesxbooks in Earth Sciences, Geography and Environment:102-106

Hu Y, Teng FZ, Zhang HF, Xiao Y, Su BX (2016): Metasomatism-induced mantle magnesium isotopic heterogeneity: evidence from pyroxenites. Geochim Cosmochim Acta 185:88-111

Huang KJ, Teng FZ, Wei GJ, Ma JL, Bao ZY (2012): Adsorption- and desorption- controlled magnesium isotope fractionation during extreme weathering of basalt in Hainan Island, China. Earth Planet Sci Lett 359-360:73-83

Li W-Y, Teng F-Z, Ke S, Rudnick R, Gao S, Wu F-Y, Chappell B (2010): Heterogeneous magnesium isotopic composition of the upper continental crust. Geochim Cosmochim Acta 74:6867-6884

Li W, Chakraborty S, Beard BL, Romanek CS, Johnson CM (2012): Magnesium isotope fractionation during precipitation of inorganic calcite under laboratory conditions. Earth Planet Sci Lett 333-314:304-316

Pogge von Standmann PA, Burton KW, James RH, van Calsteren P, Gislason SR, Sigfusson B (2008): The influence of weathering processes on riverine magnesium isotopes in a basaltic terrain. Earth Planet Sci Lett 276:187-197

Rosman JR, Taylor PD (1998): Isotopic composition of the elements (technical report): commission on atomic weights and isotopic abundances. Pure Appl Chem 70:217-235

Schaubl EA (2011): First principles estimates of equilibrium magnesium isotope fractionation in silicate, oxide, carbonate, hexaaquamagnesium(2+) crystals. Geochim Cosmochim Acta 75:844-869

Shen B, Jacobson B, Lee CT, Yin QZ, Mourton DM (2009): The Mg isotopic systematics of granitoids in continental arcs and implications for the role of chemical weathering in crust formation. PNAS 106:20652-20657

Teng FZ et al (2015): Magnesium isotopic compositions of international geological reference materials. Geostand Geoanal Res 39:329-339

Tipper ET, Galy A, Bickle MJ (2006): Riverine evidence for a fractionated reservoir of Ca and Mg on the continents: implications for the oceanic Ca cycle. Earth Planet Sci Lett 247:267-279

Young ED, Galy A (2004): The isotope geochemistry and cosmochemistry of magnesium. Rev Mineral Geochem 55:197-230