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Fractionation of Mg isotopes by clay formation and calcite precipitation in groundwater with long residence times in a sandstone aquifer, Ordos Basin, China

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Abstract

Compared with the numerous studies on river and soil waters, studies on Mg isotopes of groundwater are limited. In this study, a sandstone aquifer in the Ordos Basin, China with contrast contents of Mg in shallow and deep groundwater is selected to examine the behavior of Mg isotopes during groundwater circulation. The δ^{26}Mg values of shallow groundwater are within the range of widely reported results of groundwater, while those of deep groundwater are found to be as light as −3.30‰ to −2.13‰. Assuming that shallow groundwater is an endmember, ^{87}Sr/^{86}Sr ratios show that calcite dissolution has contribution to low δ^{26}Mg of deep groundwater, but mixing alone cannot explain the coupled low δ^{26}Mg and low Mg contents. The removal of Mg in deep groundwater is found to be mainly caused by incorporating into neoformed clay minerals, which further lowers δ^{26}Mg. For the deep groundwater samples denoted as G1 and G3, the relationship between δ^{26}Mg and 1/Mg has been quantitatively explained by the superposition of calcite dissolution and clay formation with a fractionation factor ($\alpha_{clay-water}$) of 1.0003. For samples denoted as G2, in addition to calcite dissolution and clay formation, high proportion of Mg in the residual solution are further removed via precipitation of low-Mg calcite, which leads to increased δ_{26}Mg. There are increasingly stronger degrees of clay formation in G3, G1, and G2 due to the increasingly longer travel distances and travel times of groundwater from recharge to discharge areas. This study enhances understanding on the factors controlling Mg isotopes of groundwater, as well as the geochemical processes of subsurface water-rock interactions in sandstone aquifers.

Keywords: Groundwater geochemistry; Magnesium isotopes; Rayleigh distillation; Residence time; Groundwater circulation; Flowing well

1. INTRODUCTION

The water cycle is a fundamental process involving movement of water and transport of elements on the Earth. The water-rock interactions during the water cycle could lead to different hydrochemical and isotopic compositions of water (Ingebritsen et al., 2006; Edmunds and Shand, 2008). As a major element in water, magnesium participates in various geochemical processes, which could cause significant fractionation of Mg isotopes (^{24}Mg, ^{25}Mg and ^{26}Mg) (Tipper et al., 2010). Therefore, Mg isotopes, which belong to stable isotopes, have been widely applied to trace geochemical processes in river water and soil water (Pogge von Strandmann et al., 2012; Mavromatis et al.,

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2016). In previous studies, Mg isotopes of river and/or soil water are found to be controlled by dissolution of minerals (Brenot et al., 2008; Tipper et al., 2010, 2012a), precipitation of carbonates (Lee et al., 2014; Fan et al., 2016), neoformation of clay minerals (Tipper et al., 2010, 2012a, 2012b; Wimpenny et al., 2014), adsorption onto clay minerals (Pogge von Strandmann et al., 2012; Huang et al., 2012; Ma et al., 2015) and uptake by plants (Pogge von Strandmann et al., 2008; Bolou-Bi et al., 2012). Due to the simultaneous controls by several factors, the dominant controls on the fractionation of Mg isotopes in water remain unclear, and the predictive capacity of Mg isotope geochemistry is limited compared with other widely utilized isotopes such as Sr isotopes (Jacobson et al., 2010; Tipper et al., 2012b).

Although groundwater circulation is an indispensable component of the water cycle, there are limited studies on Mg isotopes of groundwater. In order to reveal the behavior of Mg isotopes during groundwater circulation from recharge to discharge areas, intensive sampling in both recharge and discharge areas is a prerequisite. In a recent field study in the sandstone aquifer of the Ordos Basin, Wang et al. (2015a) found that deep groundwater in discharge areas has much lower Mg contents than shallow groundwater in recharge areas, which provides a unique opportunity to examine the behavior of Mg isotopes accompanying with Mg removal. Therefore, the sandstone aquifer of the Ordos Basin is selected as the current study area. The δ^{26}Mg values of shallow groundwater are found to be within the normal range between −1.63‰ and −0.59‰ (Fig. 1) as reported in previous studies with a total of 20 groundwater samples (Jacobson et al., 2010; Immenhauser et al., 2010; Tipper et al., 2012a, 2012b; Geske et al., 2015; Ma et al., 2015). However, the δ^{26}Mg values of deep groundwater in the discharge areas of the current study are all found to be below the lower limit of reported values in groundwater. This study aims to quantitatively examine the major processes controlling the low δ^{26}Mg and low Mg contents in deep groundwater with the aid of major ions and ^{87}Sr/^{86}Sr ratios of groundwater.

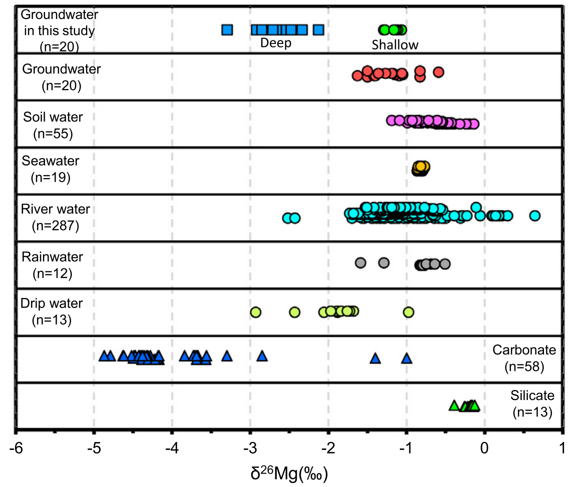

Fig. 1. A comparison of published δ^{26}Mg values of different waters and rocks. Data of groundwater is from Jacobson et al. (2010), Immenhauser et al. (2010), Tipper et al. (2012a, 2012b) Geske et al. (2015), Ma et al. (2015); data of soil water is from Tipper et al. (2010, 2012b), Pogge von Strandmann et al. (2012), Ma et al. (2015); data of seawater is from Young and Galy (2004), Hippler et al. (2009), Teng et al. (2010), Tipper et al. (2010), Mavromatis et al. (2016); data of river water is from Tipper et al. (2006), Brenot et al. (2008), Pogge von Strandmann et al. (2008), Jacobson et al. (2010), Wimpenny et al. (2011), Tipper et al. (2012a, 2012b), Lee et al. (2014), Fan et al. (2016), Mavromatis et al. (2016); data of rainwater is from Tipper et al. (2010, 2012b), Bolou-Bi et al. (2012); data of drip water is from Young and Galy. (2004), Immenhauser et al. (2010); data of carbonates is from Buhl et al. (2007), Brenot et al. (2008), Immenhauser et al. (2010); and data of silicates is from Huang et al. (2009), Liu et al. (2010). The δ^{26}Mg values of groundwater measured in the current study are also shown in the top of the figure.

2. METHODS

2.1. Study area

The Ordos Basin located in northwestern China is the second largest sedimentary basin of China. Due to the semi-arid climate, groundwater is the main water supply in the basin (Hou et al., 2008; Jiang et al., 2018). In the north part of the Ordos Basin, the thick Cretaceous sandstone with sporadic clay lenses is the main aquifer. The thin unconsolidated Quaternary sediments overlying the Cretaceous sandstone also constitute an aquifer in topographic lows with shallow water table.

The study sites of the current study include the Dosit River Watershed and the Wudu Lake Catchment (Fig. 2). The Dosit River Watershed covering an area of around 11,000 km^2 can be considered as a sub-basin of the Ordos Basin, with the Dosit River being the lowest discharge points and the major surface water body. The Wudu Lake Catchment adjacent to the Dosit River Watershed covers an area of around 200 km^2 and is one of the numerous small catchments in the Ordos Basin, with Wudu Lake being the lowest discharge point and the only surface water body. In both study sites, there are numerous wells with different depths drilled into the Cretaceous sandstone or the Quarternary sediments for irrigation and domestic uses, which provide an excellent opportunity for intensive groundwater sampling in both recharge and discharge areas. More detailed descriptions of the Dosit River Watershed can be found in Jiang et al. (2014) and Wang et al. (2015a), and of the Wudu Lake Catchment can be found in Wang et al. (2015b) and Jiang et al. (2017). Note that both groundwater and surface water are alkaline in the north part of the Ordos Basin, which is one of the few regions with numerous soda lakes due to its arid climate.

2.2. Sampling

In the summers of 2015 and 2016, 20 groundwater samples were collected in the study area. Among them, 16 samples were from the Dosit River Watershed, and 4 were from the Wudu Lake Catchment. Before sampling, electrical conductivity (EC), temperature, and pH were measured