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Adsorption- and desorption-controlled magnesium isotope fractionation during extreme weathering of basalt in Hainan Island, China

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ABSTRACT

Magnesium isotopic compositions of a set of clay-rich saprolites developed on the Neogene tholeiitic basalt from Hainan Island in southern China have been measured in order to document the behavior of Mg isotopes during continental weathering. Compared with unaltered basalts (δ^{26}Mg$=-0.36$‰), the overlying saprolites are strongly depleted in Mg (i.e., $\tau_{\mathrm{Th,Mg}}=-99.1\%$ to -92.9%), and display highly variable δ^{26}Mg, ranging from -0.49‰ to $+0.40$‰. Magnesium concentration and δ^{26}Mg value of the saprolites display a general increasing trend upwards in the lower part of the profile, but a decreasing trend towards the surface in the upper part. The variations of Mg concentration and isotopic composition in this weathering profile can be explained through adsorption and desorption processes: (1) adsorption of Mg to kaolin minerals (kaolinite and halloysite), with preferential uptake of heavy Mg isotopes onto kaolin minerals; and (2) desorption of Mg through cation exchange of Mg with the relatively lower hydration energy cations in the upper profile. Evidence for adsorption is supported by the positive correlation between δ^{26}Mg and the modal abundance of kaolin minerals in saprolite of the lower profile, while negative correlations between δ^{26}Mg and concentrations of lower hydration energy cations (e.g., Sr and Cs) in the upper profile support the desorption process. Our results highlight that adsorption and desorption of Mg on clay minerals play an important role in behavior of Mg isotopes during extreme weathering, which may help to explain the large variation in Mg isotopic composition of river waters.

1. Introduction

The chemical weathering of silicate rocks results in drawdown of atmospheric CO_2 through precipitation of Ca and Mg bearing carbonate minerals, and hence regulates the earth's climate on a geological time scale (Berner et al., 1983; Gaillardet et al., 1999). As one of the most easily weathered Ca–Mg-rich silicate rocks on the earth's surface, basalts play a major role in the global carbon cycle, with about 30% of atmospheric CO_2 consumed by the weathering of continental basalts (Dessert et al., 2003).

Reconstruction of the global CO_2 cycle over long-term from the geological archives requires suitable geochemical proxies of silicate weathering. The stable isotopes of Mg have several advantages as a promising tracer of silicate weathering. Magnesium is a fluid-mobile, major element in both the mantle and the crust, and has three isotopes with relative mass difference of ~8% between ^{24}Mg and ^{26}Mg, which can potentially lead to large mass-dependent Mg isotope fractionation (Young and Galy, 2004). Previous studies have revealed that Mg isotope fractionation is small during magmatic differentiation (Teng et al., 2007, 2010a; Liu et al., 2010), but large during biological processes such as plant growth (Black et al., 2008; Bolou-Bi et al., 2010, 2012) and during silicate weathering process (Tipper et al., 2006a, 2008; Pogge von Strandmann et al., 2008a, 2008b, 2012; Li et al., 2010; Teng et al., 2010b; Wimpenny et al., 2010, 2011; Opfergelt et al., 2012). However, the magnitude and mechanisms of Mg isotope fractionation during chemical weathering of silicate rocks are still poorly understood.

Chemical weathering of silicate rocks involves the dissolution of primary minerals and the formation of secondary minerals. Studies of Mg isotopes during primary mineral dissolution show conflicting results. Wimpenny et al. (2010) carried out dissolution experiments and found that light Mg isotopes are preferentially released into the dissolved phase during dissolution of basalt glass and forsterite. This conclusion agrees with studies of weathering profile developed on a diabase dike, which shows that Mg isotopic compositions of saprolites evolve towards heavy values with increased degree of weathering, suggesting that light Mg

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isotopes were preferentially released into the hydrosphere during continental weathering (Teng et al., 2010b). By contrast, another experimental study found limited Mg isotope fractionation during granite mineral dissolution and the large Mg isotopic variation in the output solution during granite dissolution mainly reflects preferential dissolution of isotopically distinct minerals (Ryu et al., 2011). The different behaviors of Mg isotopes during mineral dissolution are uncertain and may reflect the difference in Mg crystalline sites in different minerals.

When compared to primary mineral dissolution, the behavior of Mg isotopes during secondary mineral formation is more complex. Soil and clay fractions are isotopically heavier than their parent rocks (Tipper et al., 2006a, 2010; Brenot et al., 2008; Teng et al., 2010b; Opfergelt et al., 2012; Pogge von Strandmann et al., 2012), suggesting that heavy Mg isotopes are preferentially incorporated into the structure of secondary mineral or adsorbed onto the soil exchange complex. By contrast, allophane, a secondary mineral formed during the weathering of basalt, appears to prefer light Mg isotopes to heavy ones (e.g., Pogge von Strandmann et al., 2008a). Experimental studies also show that some phyllosilicates have an affinity for light Mg isotopes during water-rock interactions (e.g., Wimpenny et al., 2010). These discrepancies are still unclear and more studies are needed to address them.

To improve our knowledge of behaviors of Mg isotopes during continental weathering, especially to understand the role of secondary minerals on Mg isotope fractionation, we studied a well-characterized saprolite profile that developed on Neogene basalt in a tropical climate on Hainan Island in southern China. This saprolite profile is ideally suited for investigating behaviors of Mg isotopes during secondary mineral formation, because (1) the weathering input of Mg is derived predominantly from a single silicate mineral (pyroxene); (2) primary minerals have almost completely broken down and secondary minerals dominate the saprolites due to extreme weathering (Ma et al., 2007). Our results demonstrate that Mg isotope fractionation during extreme weathering of basalt involves a two-step process: preferential adsorption of heavy Mg isotopes onto the surface of secondary minerals and preferential desorption of previously adsorbed heavy Mg isotopes from the secondary minerals into pore water, due to high rain infiltration in the upper profile.

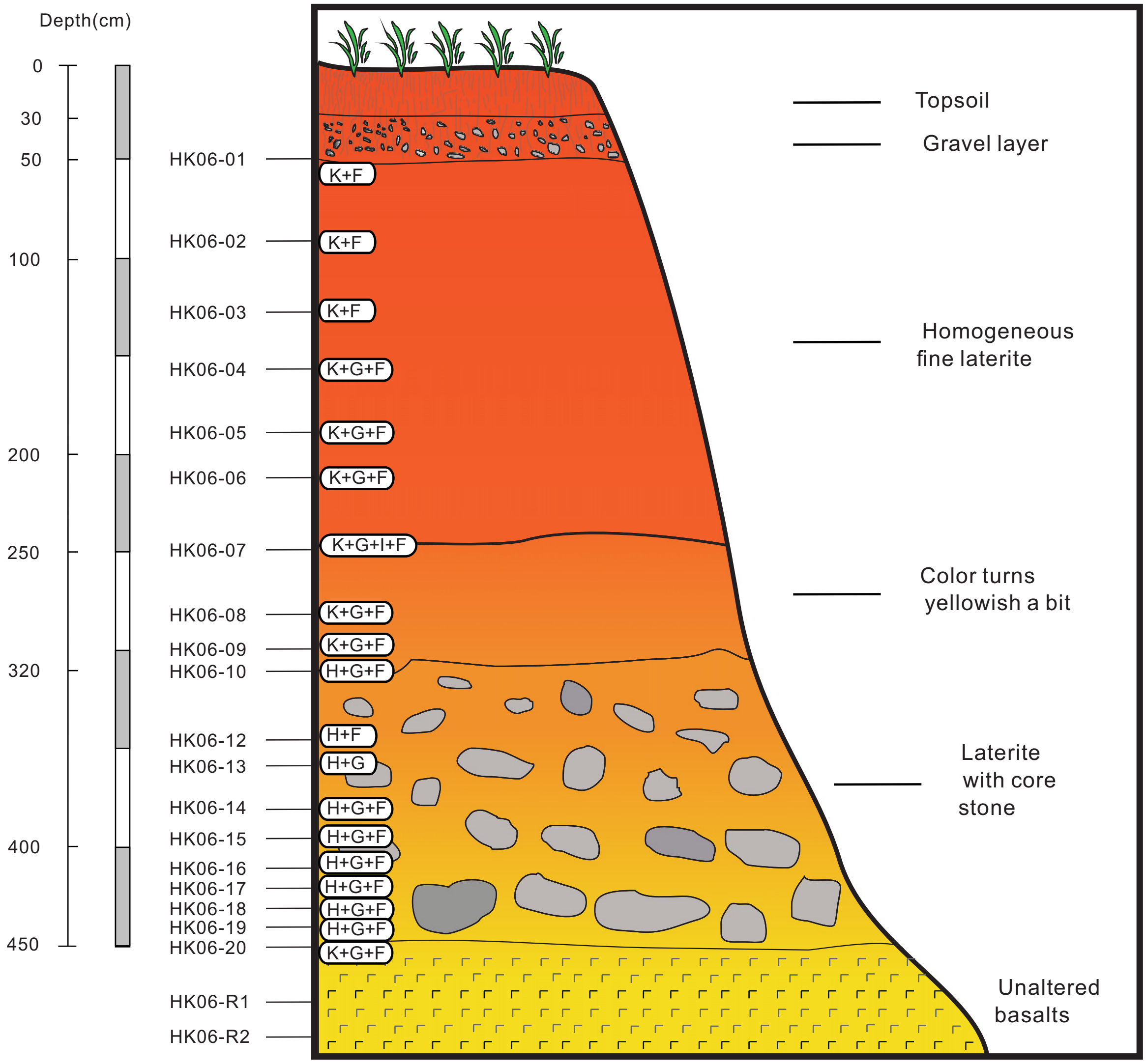

Fig. 1. (Color online) Sketch section of the basalt weathering profile in the northern region of Hainan Island, China (after Ma et al., 2007). According to the texture and color, six different horizons are identified within the profile, but all boundaries between these horizons are essentially gradational. The numbers represent the sample ID and their sampling position in the profile. The letters within the profile represent clay mineral distribution in the different horizons (*F*=Fe-oxy-hydroxides; *H*=halloysite; *G*=gibbsite; *I*=illite; *K*=kaolinite).