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High δ^{26}Mg in an early Cambrian palaeosol reveals a terrestrial clay mineral factory

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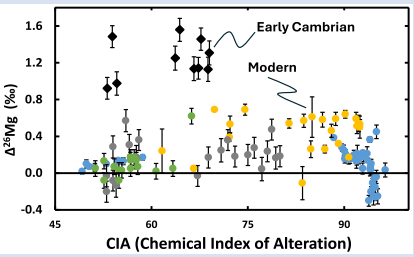
Abstract



The Mg isotopic signature of a palaeosol developed through the Great Unconformity has been analysed to elucidate the silicate weathering conditions on the Wyoming Craton during the early and middle Cambrian. The bulk saprolite shows substantially increased δ^{26}Mg signatures, ranging from -0.32 ± 0.09 ‰ in the pristine granitic parent to a maximum of $+1.24 \pm 0.09$ ‰ in the saprolite, which are significantly heavier in comparison to the upper continental crust and all modern granitic soils reported in literature. Our results suggest that formation of clay minerals in the saprolite during intensive chemical weathering served as the main control on the δ^{26}Mg isotopic composition. The high δ^{26}Mg signature in the lower saprolite was likely caused by the preferential scavenging of heavy Mg into clay minerals from the contemporaneous soil solution and palaeo-groundwater. Our results indicate that Mg isotopes may serve as a useful tool for tracking clay production in deep time and serve to direct further studies on well preserved palaeosols for more comprehensive understanding of the Mg isotope weathering proxy in palaeo-weathering systems.

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Introduction

The late Precambrian is marked by a series of global glaciation events known collectively as the snowball earth, when glaciation extending to the equator (Hoffman and Schrag, 2002). Subsequent intense chemical weathering and continental erosion, promoted by the high atmospheric CO_2 concentration (pCO_2) during the terminal Cryogenian, likely contributed to the diversification of the marine biosphere in the Early and Middle Cambrian Ocean (*e.g.*, Sahoo *et al.*, 2012). However, the specific weathering processes and weathering regimes during the late Precambrian and early Cambrian have not been well constrained.

Weathering intensities are usually inferred by studying terrigenous marine sediments regarded as the products of continental weathering. However, palaeo-weathering evidence in sediments can be obscured by heterogeneous source lithologies, transient storage on continental shelves, and authigenic marine clay formation through reverse weathering (Isson and Rauzi, 2024). In contrast, preserved *in situ* Precambrian and Cambrian-aged palaeosols formed directly at the Earth's surface and provide an opportunity for direct palaeo-climatic and environmental reconstructions (Sheldon and Tabor, 2009 and references therein). Palaeosol profiles in North America developed during the early Cambrian on the Great Unconformity are relatively under-represented in the literature as they were largely eroded away by the transgressing Cambrian Ocean (*e.g.*, Peters and Gaines, 2012).

Magnesium isotopes fractionate during silicate mineral dissolution (Wimpenny *et al.*, 2010) and clay mineral formation (Wimpenny *et al.*, 2014), where weathering residuals retain isotopically heavier ^{26}Mg with increasing chemical weathering intensity (Teng *et al.*, 2010). Relevant to this observation is that Mg isotopic fractionation during low grade metamorphism and diagenesis is limited in siliciclastic sediments (Wang *et al.*, 2015), making the Mg isotope system ideal for tracking Earth's pedogenic processes in deep time. Although Mg isotopes have been used to examine weathering intensity and regimes from modern weathering and saprolite profiles (*e.g.*, Liu *et al.*, 2014), δ^{26}Mg has not been reported for Precambrian or Cambrian-aged palaeosols. Mg isotope systematics are controlled by clay mineralogy in modern felsic saprolites (Li *et al.*, 2021), suggesting that Mg isotopes may serve as an important tool to track terrestrial clay production in palaeosols.

Here, we present the Mg isotopic composition of bulk and clay-sized ($r < \sim 2$ µm) portions of saprolites from a Cambrian age palaeosol outcrop developed on the Wyoming Craton to evaluate the ancient weathering regimes and clay mineral formation in North America during the Precambrian-Cambrian transition.

Results

Elevated δ^{26}Mg in the saprolites. The weathering profile is developed on the meta-granitic basement of the Archean Wyoming Craton and recognised as the erosional remnant of the Great Unconformity, where it was subsequently buried by the Middle Cambrian Flathead Sandstone. The weathering processes that produced the saprolite thus immediately preceded

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the deposition of the Flathead Sandstone during the middle Cambrian. The palaeosol has been previously described and the profile contains both slightly weathered saprocks that still retain crystalline structure of the bedrock, and saprolites that experienced more intensive chemical weathering with a maximum Chemical Index of Alteration (CIA) of 69 and a Plagioclase Index of Alteration (PIA) reaching 98 (Z. Huang *et al.*, 2024).

The unweathered basement has a measured δ^{26}Mg (−0.33 ‰) that is similar to the average composition of the upper continental crust (−0.22 ‰; Li *et al.*, 2010). Both saprolites and moderately weathered saprock samples show elevated ^{26}Mg values compared to their granitic parent, with a maximum δ^{26}Mg of +1.24 ‰ in the saprolite (Fig. 1). The δ^{26}Mg values in the saprolite do not show a simple linear increasing trend from less weathered samples to more intensively weathered samples. Instead, the lower saprolite samples generally have higher δ^{26}Mg values than the more intensively weathered samples from higher in the profile (from +1.14 ‰ in the lowest saprolite to +0.81 ‰ in the highest saprolite; Fig. 1a). The δ^{26}Mg values of the Cambrian palaeosol are considerably higher than the published data from modern granitic weathering profiles, even though the CIA values of the palaeosol suggest that the weathering intensity is relatively unremarkable compared to some of the most weathered samples (Fig. 1c).

The clay-sized fraction of the saprolites contains higher total Mg content and Mg/Al values compared to the bulk sample (Table S-2), indicating that the formation of terrestrial clay minerals, such as kaolinite, smectite, illite, and pedogenic chlorite/vermiculite, was responsible for the retention of Mg during palaeosol development. Such enrichment pattern is also observed in modern felsic soils (Li *et al.*, 2021). Clay-sized fractions also exhibit a high δ^{26}Mg composition that persists through the entire saprolite, with a maximum δ^{26}Mg at +1.39 ‰. The magnesium isotopic composition is even heavier compared to their bulk counterparts (Fig. 1a). Like the bulk saprolite samples, there is no clear correlation between δ^{26}Mg and the Mg content in the clay-sized fraction. Such observations confirm that the isotopically heavy ^{26}Mg preferentially partitions into the clay minerals during chemical weathering.

Surprisingly, even the least weathered saprock samples that represent the incipient weathering stage during palaeosol development have significantly isotopically heavier ^{26}Mg compared to the pristine basement. This isotopic composition also suggests that the weathering intensity was likely not the only factor influencing the δ^{26}Mg of the palaeosol. SEM images of thin sections of these moderately weathered bedrock samples in the lower profile show Mg-rich fine grained clay minerals in the cracks of fractured and physically altered primary silicate minerals such as plagioclase and quartz (Fig. S-2a,b), suggesting downward transport of clay minerals in the profile. This hypothesis is supported by a recent study on a modern granitic soil where the vertical transportation of kaolinite is likely responsible for the enrichment of ^{26}Mg in the lowest weathering profile (Song *et al.*, 2025). In addition, previous studies have shown a preferential adsorption of isotopically heavier ^{26}Mg as an exchangeable form during the weathering and transformation of chlorite to vermiculite in saprocks during the incipient stage of granite weathering (Li *et al.*, 2021). Therefore, both the downward transport of Mg-containing clays with higher δ^{26}Mg from the upper saprolite of the weathering profile, and adsorption process during the initial chlorite-vermiculite transformation likely elevated the δ^{26}Mg values in saprock samples that otherwise have evidence of relatively low weathering intensity with low CIA.

Diagenetic and authigenic influences. Cambrian and Precambrian-aged palaeosol and sedimentary records are often overprinted by post-weathering metasomatism (Nesbitt and Young, 1989), where interactions of palaeosols and sediments with seawater, including reverse weathering and carbonate precipitation, could result in the authigenic addition of Fe, Mg, Na, and Ca (Isson and Planavsky, 2018). Metasomatism through post-burial illitisation is common in North American Cambrian and Precambrian palaeosols (*e.g.*, Medaris *et al.*, 2022). Since metasomatic overprinting could potentially modify the Mg content and Mg isotopic signature, it is thus important to evaluate diagenetic influence on this palaeosol.

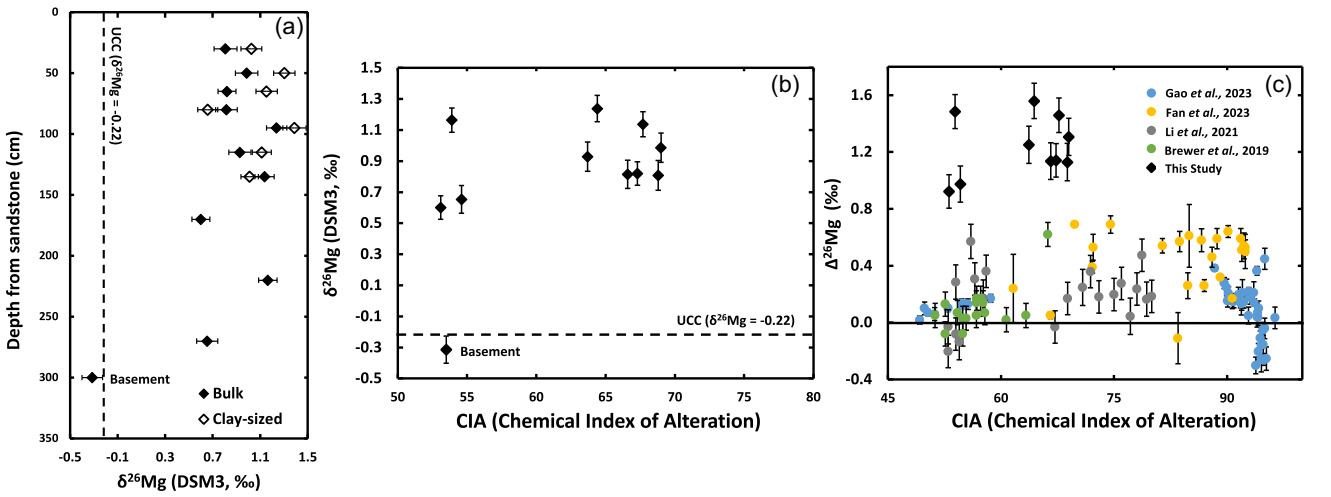

Figure 1 **(a)** Magnesium isotopic composition of the bulk and clay-sized fractions of the saprolite profile plotted against depth from the overlying sandstone. **(b)** Magnesium isotopic compositions plotted against CIA (Chemical Index of Alteration; Z. Huang *et al.*, 2024) for the δ^{26}Mg values for the Cambrian palaeosol on the Great Unconformity. **(c)** The magnesium isotope difference ($\Delta^{26}Mg_{saprolite\text{-}bedrock}$) between the parental bedrock and corresponding regolith, including data from this study and the literature on modern granitic soil profiles (Brewer *et al.*, 2018; Fan *et al.*, 2023; Gao *et al.*, 2023; Li *et al.*, 2021). All error bars are 2σ, and error bars in **(c)** are calculated using the formula $2\sigma = \sqrt{(2\sigma)^2_{saprolite} + (2\sigma)^2_{bedrock}}$.

While the Wind River Canyon palaeosol shows moderate enrichment in bulk K content compared to the unweathered basement, there is no significant addition of Na and Ca in saprolites (Z. Huang *et al.*, 2024), and no diagenetic plagioclase or authigenic carbonate mineral precipitation observed or detected in bulk saprolite samples, consistent with the lack of Na and Ca metasomatism in the Wind River Canyon saprolite. It is likely that moderate K metasomatism overprinted the Wind River Canyon saprolite with illite, partially or completely replacing smectite and kaolinite in upper saprolite samples, forming illitised kaolinite and interstratified illite-smectite (Fig. S-2c,d). The metasomatic process could potentially influence the Mg isotopic composition through the equilibrium fractionation between Mg-enriched smectite and illite. While there are strong to moderate positive correlations between K and Mg contents (Fig. 2a), the molar K/Al ratio shows no correlation with δ^{26}Mg in neither bulk nor clay-sized fraction of the saprolites (Fig. 3b), indicating that the degree of K addition during metasomatism may have limited effects on the δ^{26}Mg values, particularly in the clay-sized fraction of the weathering profile. The lack of isotopic fractionation due to post-burial K metasomatism also agrees with observations of the Mg isotopic system in other siliciclastic Neoproterozoic-aged sediments (Huang *et al.*, 2016; Zhang *et al.*, 2021).

Processes controlling the Mg isotope behaviour. Overall, there is a moderate positive correlation between the bulk δ^{26}Mg values of saprolites and the abundance of the clay-sized fraction (Fig. 4a), except for one saprock sample with an unusually high δ^{26}Mg value. This pattern supports the hypothesis that the formation of secondary clay minerals likely controlled the

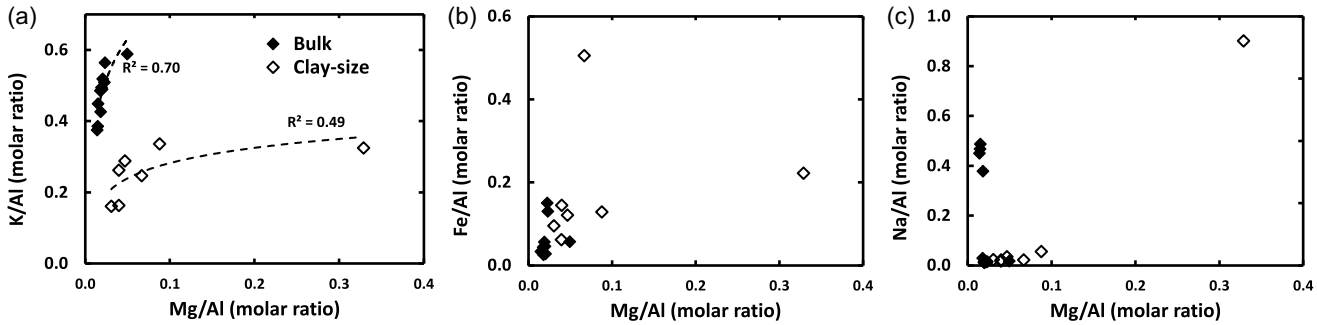

Figure 2 Cross plots for the molar ratios of **(a)** K/Al, **(b)** Fe/Al and **(c)** Na/Al *vs.* Mg/Al of both bulk and clay-sized portions of the saprolite.

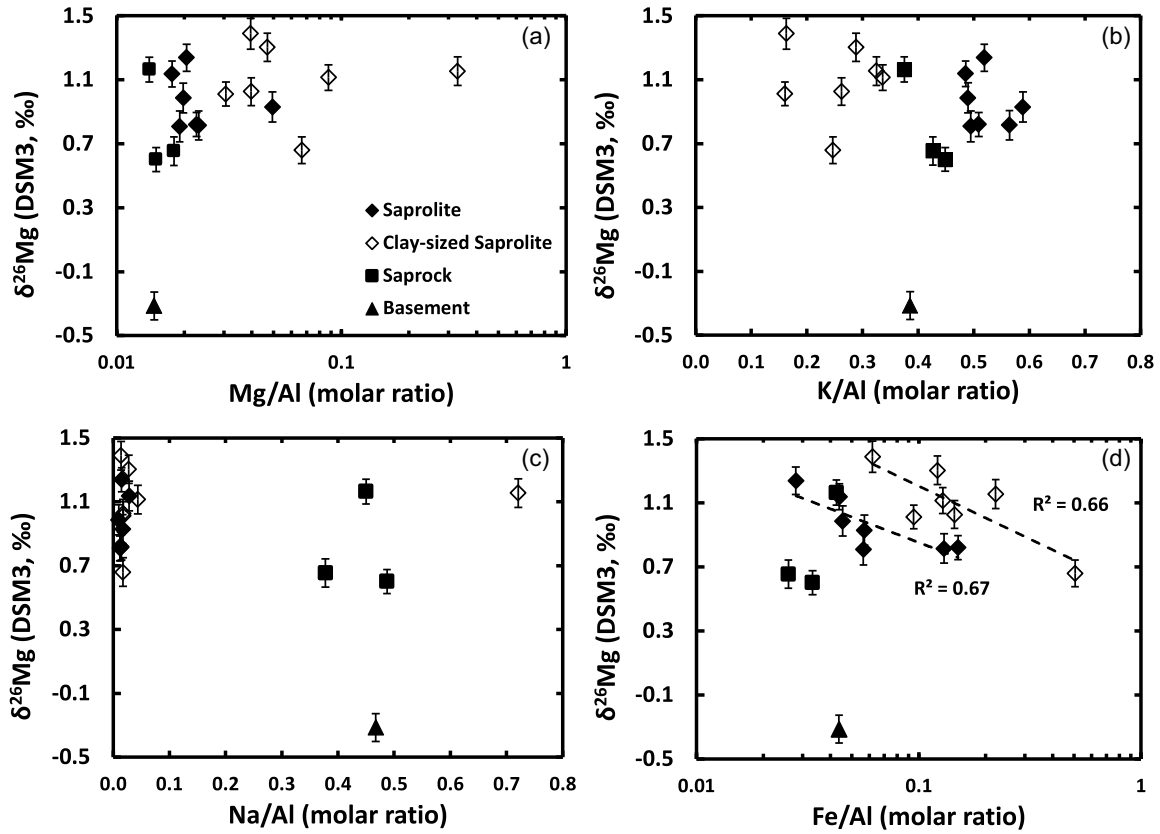

Figure 3 Cross plots for the molar ratios of **(a)** Mg/Al (semi-log), **(b)** K/Al, **(c)** Na/Al and **(d)** Fe/Al (semi-log) *vs.* δ^{26}Mg values of both bulk and clay-sized portion of the saprolite.

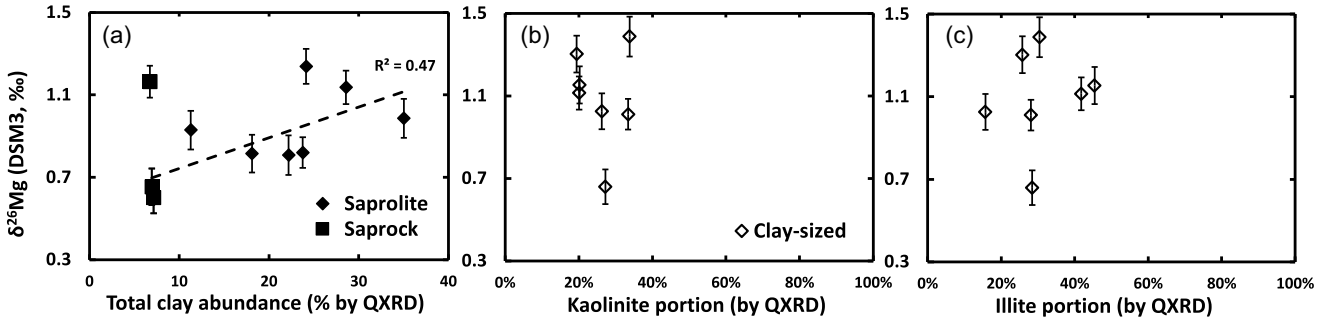

Figure 4 Cross plots of the δ^{26}Mg values of bulk and clay-sized portions with the abundance of **(a)** total secondary clay abundance detected by XRD (sum of all secondary phyllosilicates), **(b)** kaolinite fraction of the total clay abundance and **(c)** illite fraction of the total clay abundance.

^{26}Mg enrichment of the saprolite. However, plots of two pedogenic clay mineral abundances (illite and kaolinite) do not display a significant correlation with the δ^{26}Mg values of the clay-sized portion of saprolites (Fig. 4b,c). Recent studies have shown that Mg isotopes fractionate differently among various clay mineral formation pathways during supergene chemical weathering processes. For example, smectite minerals with low Al such as saponite and stevensite, preferentially uptake ^{24}Mg in a laboratory setting (Hindshaw *et al.*, 2020). Complications could also arise from adsorption-desorption processes of Mg ions from soil solution onto clay minerals where both ^{24}Mg and ^{26}Mg may be preferentially incorporated (Opfergelt *et al.*, 2012). Hence, a more comprehensive examination of the role of clay minerals in controlling Mg isotopes in palaeosol profiles is needed.

The Fe content in the saprolite shows moderate negative correlations with the δ^{26}Mg values for both bulk and clay-sized fraction of the saprolite (Fig. 3d). Iron oxide minerals, such as goethite and hematite, were detected by XRD and observed in SEM images of thin sections (Z. Huang *et al.*, 2024). Since there is no clear correlation between Mg and Fe contents in both bulk saprolites and the clay fraction (Fig. 2b), the negative correlation between Fe and δ^{26}Mg may be caused by heterogeneous sorption onto precipitated hematite or goethite in upper saprolites, instead of the formation of Mg and Fe-rich clay minerals such as chlorite and vermiculite. Fe oxides and oxyhydroxides increase the overall cation exchange capacity, which has a higher affinity for ^{24}Mg (Gao *et al.*, 2018). Such a pattern is observed in modern granitic soils (*e.g.*, Fan *et al.*, 2023), where ^{24}Mg is preferentially adsorbed onto goethite and hematite in an exchangeable form while ^{26}Mg is substituted into the Fe oxide structure. Further investigations through a sequential extraction experiment may therefore needed to investigate the distribution of Mg in different phases and estimate the influence of secondary Fe minerals on the Mg isotopic composition in palaeosols.

The Wind River Canyon palaeosol isotopic patterns compare favourably with those observed in modern granitic weathering profiles. Specifically, Mg isotopic fractionation in a granitic soil developed under a modern subtropical setting (Li *et al.*, 2021), also shows minimally weathered saprock samples with elevated δ^{26}Mg compared to intensively weathered saprolite. Mass balance calculations for Mg (τMg_{Zr}) indicates a strong enrichment of Mg in one of the lower saprolite samples with an overall decreasing pattern towards the upper saprolite (Z. Huang *et al.*, 2024; Fig. S-1b). Secondary phyllosilicate may be dissolved during the advanced stage of weathering in the upper weathering profile, mobilising the heavier δ^{26}Mg that was incorporated into clays. According to the overall enrichment pattern and clay abundance in the lower saprolite, we consider that the dissolution of phyllosilicates with higher δ^{26}Mg values in intensively weathered upper palaeosol induced a vertical mobilisation of ^{26}Mg-enriched soil solution from the upper weathering profile, allowing the incorporation of heavier ^{26}Mg into neo-formed clay minerals in lower saprolite. However, further investigations may be required on other palaeosol profiles as the uppermost section of the Wind River Canyon palaeosol is likely lost due to erosional processes that formed the Great Unconformity.

Alternatively, the increase in both Mg abundance and the δ^{26}Mg in the lower saprolite may be explained by external contributions from the palaeo-groundwater. It is likely that the *in situ* weathering of the upper weathering profile did not provide all the Mg needed for the observed Mg-enrichment in the lower saprolite. The Mg flux contributed by palaeo-groundwater could enrich the Mg in the lower saprolite. However, groundwater generally contains a relatively lighter Mg isotopic composition compared to the weathering residuals (Tipper *et al.*, 2012) that are substantially influenced by their respective parental minerals (Chapela Lara *et al.*, 2017). Therefore, the observed high δ^{26}Mg and Mg abundance in the lower saprolite cannot solely be explained by the influx of Mg from the palaeo-groundwater, as it could not directly provide abundant ^{26}Mg for all the saprolite and saprock samples. Instead, the palaeo-groundwater may have contributed a minor amount to the abundance of Mg in the less weathered lower saprolite and the saprock.

Implications

Preserved marine sediments including sandstones and siltstones, derived from the continental erosion during the termination of the Marinoan glaciation, have distinctively positive δ^{26}Mg values ranging from +0.56 ‰ to +0.95 ‰ (Huang *et al.*, 2016). Similarly, black shales deposited in modern southern China during the middle Cambrian and late Precambrian also exhibit extremely high δ^{26}Mg values (Zhang *et al.*, 2021). The high δ^{26}Mg values of these sediments were interpreted as the result of intensive continental weathering under a warm and humid climate during the early/middle Cambrian and the post-snowball earth deglaciation. However, as suggested by other studies (*e.g.*, T. Huang *et al.*, 2024), the weathering intensity may only be precisely constrained from the Mg isotopic signature through also assessing the clay mineralogy from contemporaneous palaeo-weathering profiles. Here we can confirm that all these sediments possess δ^{26}Mg values similar to those observed in an *in situ* contemporaneous weathering profile, preserved as the Wind River Canyon palaeosol (+1.0 ‰ to + 1.5 ‰).

Recent studies have shown that the earliest Phanerozoic is marked as an incipient stage of increased terrestrial clay production known as the clay mineral factory, coupled with the

emergence of terrestrial microbial activities (Isson and Rauzi, 2024; Kennedy *et al.*, 2006). Following the break-up of Rodinia, a large volume of felsic rocks was emplaced in the upper continental crust and exposed to weathering and erosional processes (Keller *et al.*, 2019). The lithological shift in the late Precambrian coupled with an extreme global greenhouse condition during the termination of a global glaciation likely enhanced clay mineral formation through incongruent felsic rock weathering. While our study agrees with the previously established interpretation that weathered products and residuals retain the isotopically heavier ^{26}Mg, considering the poor linear relationship between CIA and $\delta^{26}Mg$, we suggest that heavier Mg isotopic composition may have an indirect and nonlinear connection to a higher weathering intensity in palaeo-weathering profiles. We further hypothesise that the intensive continental weathering inferred from the elevated $\delta^{26}Mg$ in sediments from the Ediacaran-Cambrian boundary was likely accompanied by the enhanced terrestrial clay mineral production induced by the weathering of the newly exposed felsic rocks.

Conclusions

The early/middle Cambrian Wind River Canyon palaeosol on the Great Unconformity in the Bighorn Basin, Wyoming records some of the heaviest Mg isotopic compositions reported in chemical weathering processes of felsic rocks. This study confirms that the Mg isotopes strongly fractionate in palaeo-weathering profiles and could potentially be used to reconstruct palaeo-weathering regimes in deep time. The elevated $\delta^{26}Mg$ composition in the saprolite was likely controlled by the formation of clay minerals in the lower saprolite where ^{26}Mg was likely preferentially scavenged from the contemporary soil solution. Due to the poor correlation with CIA values, heavy $\delta^{26}Mg$ record in palaeosol or siliciclastic sediment records may not be treated as a direct indicator for palaeo-weathering intensity, but as an indicator of enhanced terrestrial clay mineral productions. This is the first time Mg isotopes have been reported for a Cambrian or Precambrian-aged weathering profile. With further investigations on different palaeosols from the same geologic period, the Mg isotopic system may potentially serve as an important tool to reconstruct palaeo-weathering regimes.

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Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2521.

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