Time series of $\delta^{26}$Mg variability in precipitation of north-west Germany

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Abstract
This study presents $\delta^{26}$Mg values, Mg$^{2+}$ concentrations, $\delta^{18}$O and $\delta^{2}$H values of monthly collected rain and snow samples between 2014 and 2017 from north-west Germany. The $\delta^{26}$Mg values of snow are similar to those of rain. Unlike $\delta^{18}$O and $\delta^{2}$H, neither $\delta^{26}$Mg$_{\text{precipitation}}$ values nor Mg$^{2+}$ concentrations display a relationship with air temperature. In contrast, $\delta^{26}$Mg$_{\text{precipitation}}$ values and Mg$^{2+}$ concentrations are correlated with precipitation amount. As previously suggested by other studies but now based on a larger data set, it is proposed that the $\delta^{26}$Mg$_{\text{precipitation}}$ values and Mg$^{2+}$ concentrations are affected by the mineralogical composition and amount of airborne dust. Consequently, a small number of random precipitation samples cannot represent the complex processes influencing the $\delta^{26}$Mg$_{\text{precipitation}}$ values. $\delta^{26}$Mg$_{\text{precipitation}}$ can be used to differentiate between seawater aerosols, carbonate and silicate dust. Silicate dust is typified by higher Mg concentrations and $\delta^{26}$Mg values compared to carbonate dust. Concerning carbonates, dolostone dust has higher Mg concentrations and $\delta^{26}$Mg values, while limestone dust is Mg-lean with lower $\delta^{26}$Mg values. Dust of anthropogenic origin in the region can come from active limestone and dolostone quarries, surface mining of siliciclastics, and agriculture on silicate-rich soils. Although dust of this mineralogy can also be of natural origin, most natural dust consists of airborne silicates transported by wind systems from the Sahara to Europe. Higher $\delta^{26}$Mg$_{\text{precipitation}}$ values would indicate silicate or dolostone dust influx. Lower $\delta^{26}$Mg$_{\text{precipitation}}$ values suggest lower dust concentrations and a predominantly calcitic dust mineralogy. It appears that $\delta^{26}$Mg$_{\text{precipitation}}$ is most probably influenced by changes in weather conditions and natural and anthropogenic dust origin. This study implies that $\delta^{26}$Mg$_{\text{precipitation}}$ is a potential proxy for dust mineralogy and fluxes. Nevertheless, further research should include the determination of atmospheric dust mineralogy and their fractions as well as air mass back trajectory analysis to identify the source(s) of dust.

KEYWORDS
air temperature, anthropogenic influence, dust, magnesium isotopes, precipitation
1 | INTRODUCTION

Magnesium is the eighth most abundant element of the Earth’s crust and a major constituent of numerous minerals, including carbonates and silicates. Thus, it plays an essential role in mineral and rock formation (Okrusch & Matthes, 2005) and geochemical cycles (Tipper et al., 2006b). Moreover, Mg is important in biological and hydrological systems given that it is a common element in plant material, seawater, groundwater, as well as dust and aerosols (Appelo & Postma, 2005; Black et al., 2008; Bolou-Bi et al., 2010; Négrel & Roy, 1998; Sigg & Stumm, 2011). As a consequence, the number of studies focussing on the magnesium isotope composition (δ26Mg) of carbonate and silicate rocks, plants, river water, groundwater, seawater and biogenic shell material has rapidly increased over the last decades (Black et al., 2008; Geske et al., 2015; Hu et al., 2021; Kimmig et al., 2018; Li et al., 2019; Murray et al., 2021; Novak et al., 2020; Pogge von Strandmann et al., 2008; Riechelmann et al., 2012, 2016, 2018; Rollion-Bard et al., 2016; Teng et al., 2010; Teng, 2017 and references therein; Tipper et al., 2006a; Wombacher et al., 2011).

The Mg isotopic composition of rain (openfall and throughfall) and snow (δ26Mgprecipitation), however, is comparably underexplored, and the published database is small (less than six data points per study site; Bolou-Bi et al., 2012; Chapela Lara et al., 2014, 2017; Dessert et al., 2015; Fries et al., 2019; Kimmig et al., 2018; Mavromatis et al., 2014; Novak et al., 2020; Pogge von Strandmann et al., 2008; Riechelmann et al., 2012, 2016, 2018; Rollion-Bard et al., 2016; Teng et al., 2010; Teng, 2017 and references therein; Tipper et al., 2010, 2012). This is surprising because rainwater contributes significantly to soil water, groundwater, river and lake water and undergoes geochemical changes in soils and aquifer rocks. Soil water, for example, may represent a mixture of rainwater Mg, Mg derived from weathering processes in soils, from the dissolution of host rock minerals, cation exchange processes and may also be influenced by vegetation (Bolou-Bi et al., 2012; Chapela Lara et al., 2014, 2017; Dessert et al., 2015; Fries et al., 2019; Kimmig et al., 2018; Mavromatis et al., 2014; Novak et al., 2020; Pogge von Strandmann et al., 2008; Riechelmann et al., 2012; Tipper et al., 2010, 2012). This mixture is reflected in the Mg isotopic values of a given soil water sample and shows the importance of land-surface processes such as weathering (Chapela Lara et al., 2014, 2017; Dessert et al., 2015; Fries et al., 2019; Tipper et al., 2010). This mixture is reflected in the Mg isotopic values of a given soil water sample and shows the importance of land-surface processes such as weathering (Chapela Lara et al., 2014, 2017; Dessert et al., 2015; Fries et al., 2019; Tipper et al., 2010).

Riverine δ26Mg values commonly reflect the mixing of at least two water sources, with δ26Mgprecipitation being one component and δ26Mg of the weathering end-member (e.g. soil water, groundwater) the other under the premise that riverine water has drained Mg-lean rocks (Chapela Lara et al., 2014, 2017; Dessert et al., 2015; Mavromatis et al., 2014; Tipper et al., 2012). Otherwise, the δ26Mgriver water reflects the Mg isotope signature of the lithologies in the catchment (Dessert et al., 2015; Kimmig et al., 2018; Mavromatis et al., 2014; Tipper et al., 2008). The input of Mg precipitation to riverine water is particularly high during heavy rain or storm events reflected in δ26Mgriver water being closer to the δ26Mgprecipitation value, for example, in tropical catchment areas of Puerto Rico (USA) and Guadeloupe (French West Indies) (Chapela Lara et al., 2014, 2017; Dessert et al., 2015). Fries et al. (2019), however, reported no influence of δ26Mgprecipitation on δ26Mgriver water during storm events for the same site. The Mg2+ concentration of precipitation is most commonly too low to have a considerable impact on the δ26Mgriver water value (Bolou-Bi et al., 2012; Mavromatis et al., 2014).

The origin of Mg in precipitation and its isotopic variability has been attributed to aerosols and dust in the atmosphere. The Mg isotope signature of coastal precipitation is suggested to reflect the Mg isotope value of seawater (Chapela Lara et al., 2014, 2017, rainwater; Dessert et al., 2015, rainwater; Fries et al., 2019, throughfall; Pogge von Strandmann et al., 2008, glacial ice; Tipper et al., 2010, rainwater). Rainwater collected further inland in the Rhenish Slate Mountains (north-west Germany, 250 km from the coast) displays Mg isotope values of −0.90 to −0.59‰, whereas snow yielded a value of −1.35‰. This might suggest a temperature dependency of the Mg isotope system (Riechelmann et al., 2012). Furthermore, Riechelmann et al. (2012) suggested that dust and aerosols in the atmosphere affect δ26Mgbranwater. Rain and snow samples collected in the Vosges Mountains (France) and Central Siberia (Russia) show similar values between −0.75 and −0.51‰ (Bolou-Bi et al., 2012; Mavromatis et al., 2014). The enrichment in the heavy Mg isotope of these precipitation samples is attributed to an influx of silicate dust (Bolou-Bi et al., 2012). Rainwater collected in the Swiss Alps and Canada displays significantly lower values (−1.59 to −1.29‰ and −2.76 to −1.30‰ respectively), potentially due to the influence of carbonate dust (Kimmig et al., 2018; Tipper et al., 2012). Variations in the δ26Mgthroughfall values are attributed to differences in Mg input from the canopy, which can be either accumulated carbonate or silicate dust (Fries et al., 2019; Kimmig et al., 2018). In conclusion, the impact of δ26Mgprecipitation on the Mg isotope signatures of the different components of the hydrosphere is underexplored in particular regarding the source(s) of Mg in precipitation and the factors driving δ26Mg variability therein.

Here, time-series data of Mg2+ concentration and δ26Mg values of monthly precipitation in north-west Germany over 2.5 years are presented. Precipitation amount and air temperature data of a nearby meteorological station were used to calibrate δ26Mgprecipitation. In addition, δ18O and δ2H values of precipitation were analysed from the same samples and provide circumstantial evidence. The aims of this paper are (i) to significantly add to the δ26Mg database
of precipitation, (ii) to document the seasonal and annual variability of $\delta^{26}\text{Mg}\text{precipitation}$ at a stationary site, (iii) and to propose potential source(s) and the process(es) that affect $\delta^{26}\text{Mg}$ precipitation values.

2 | STUDY SITE, MATERIALS AND METHODS

2.1 | Study site

North-west Germany is located in the temperate climate zone characterised by warm summers but lacks a distinct dry season (Cfb climate in the Köppen classification; Peel et al., 2007). Consequently, rainfall is more or less equally distributed over the year but still shows variability between months. The mean air temperature of the warmest month is below 22°C, and air temperatures exceed 10°C for more than four months (Peel et al., 2007).

The precipitation collection site was installed in the village of Gevelsberg (north-west Germany, 51.32°N, 7.32°E) at 206 m above sea level (a.s.l.; Figure 1). Gevelsberg is located at the northern margin of the Remscheid-Altena Anticline belonging to the Rhenish Massif of North-Rhine Westphalia (Figure 1). The geology of the region consists mainly of siliciclastic materials such as claystone, siltstone and sandstone. However, massive limestone of Middle to Upper Devonian age also occurs, which is partly dolomitised (Gillhaus et al., 2003). Active quarries in this unit are located close to the towns Hagen and Wuppertal (Figure 1). Open-pit mining of Palaeogene siliciclastics occurs in the region close to the Rhine river (Figure 1).

The soil covering NRW consists mainly of siliciclastic brown soil and a lesser amount of brown calcareous soil (BGR (Bundesanstalt für Geowissenschaften und Rohstoffe), 2021; Fuchs & Krusch, 1911). Around 42% of the whole area of NRW is used for farming, with 72% used for cultivation of land and 28% used as grazing land (Information und Technik Nordrhein-Westfalen, 2017).

2.2 | Sample collection, preparation and meteorological data

Precipitation was collected monthly from December 2014 to June 2017. A 5 litre PET canister equipped with a funnel was used to collect rainwater and, when occurring, snow. The funnel was permanently open to the atmosphere. Consequently, also dry deposition was collected between precipitation events. The water was filtered daily and stored in clean, tightly closed 5 litre PET canisters in a refrigerator to minimise evaporation. Depending on the amount of the collected water, a second canister was used, and the water was subsequently mixed in a 10 litre PET canister. When possible, daily snow samples were collected separately in 500 ml PET bottles at the end of each snow event. Therefore, snow was collected from the surface of a meadow 5 m from the precipitation collection site using a small scoop. The full thickness of the snow layer was sampled. Afterwards, snow was melted at room temperature, filtered and stored in a refrigerator. At the end of each month, rainwater and melted snow were filtered using 0.45 µm cellulose-acetate filters (Sartorius). The filters were washed with deionised water before filtering. The samples were transferred into 100–500 ml PET bottles, filled to the rim and stored in a refrigerator to minimise evaporation. These subsamples were used for the analysis of Mg concentration and the $^{26}\text{Mg}/^{24}\text{Mg}$ and $^{25}\text{Mg}/^{24}\text{Mg}$ ratios. Subsamples for the analysis of $\delta^{18}\text{O}$ and $\delta^{2}\text{H}$ values were filled into 2 ml vials without head space and closed with caps with a septum then stored in a refrigerator. Data regarding the air temperature and precipitation amount was collected at the meteorological station Gevelsberg-Oberbrocking (51.33°N, 7.34°E, 205 m a.s.l.; www.meteogroup.com; www.dwd.de) 2.5 km to the north-east of the precipitation collection site.

2.3 | Oxygen and hydrogen isotope analyses

The $\delta^{18}\text{O}$ and $\delta^{2}\text{H}$ values of the rain and snow water samples were determined using cavity ring-down spectrometry (L2140i, Picarro) at Innsbruck University, Austria. Standardisation was accomplished using VSMOW, GISP2 and SLAP reference solutions. Delta values are given against ‰ VSMOW. The 1σ-reproducibility is 0.1‰ for $\delta^{18}\text{O}$ and 0.6‰ for $\delta^{2}\text{H}$.

2.4 | Magnesium concentration analyses

Magnesium concentrations of water samples were analysed using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Thermo Fisher Scientific iCAP 6500 DUO) in the laboratories of the Ruhr-University Bochum, Germany. About 1 ml of each sample was used for the measurement, and 1 ml deionised H₂O and 1 ml 3 M HNO₃ were added. The 1σ-reproducibility of the standards BCS-CRM512 (dolomite; $n = 112$) and BCS-CRM513 (limestone, $n = 110$; Bureau of Analyzed Samples Ltd) for Mg²⁺ was 0.09% and 0.003% respectively.
2.5 Magnesium isotope analyses

Magnesium isotope ($\delta^{26}\text{Mg}$) values were analysed at Ruhr-University Bochum, Germany, using a Thermo Fisher Scientific Neptune multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS). Depending on the Mg concentration, 5–122 ml of the water was filled into PFA beakers and evaporated to dryness at 125°C. Subsequently, 1 ml of a 1:1 mixture of HNO$_3$ and H$_2$O$_2$ (65%:30%) was added to destroy organic compounds and prevent the complexation of cations. These samples were again dried on a hot plate at 60°C and then re-dissolved in 1 ml 1.25 M HCl.

The magnesium fraction was recovered using BioRad ion exchange resin AG50W-X12 (200–400 mesh) and quartz glass columns. The Mg yield exceeded 98%. The Mg fraction was dried, and a 500 ppb solution was prepared by adding 3.5% HNO$_3$. The Mg isotope signatures of the samples are determined by the standard-sample bracketing method using DSM3 as the standard solution.

$$\delta^{26}\text{Mg}_{\text{smp}} = \left( \frac{\delta^{26}\text{Mg}}{\delta^{24}\text{Mg}}_{\text{smp}} - 1 \right) \times 1000 \left[ \%_{\text{ee}} \right]$$ (1)

with $x$ referring to either 25 or 26. Each delta value consists of a sequence of five repetitions, and each repetition represents 25 values. The internal precision of the measurements is given as ±2σ. The external precision (without chemical sample separation) was determined by repeatedly measuring the mono-elemental solution Cambridge1 ($\delta^{25}\text{Mg} = -1.34 \pm 0.02 \text{ 2}\sigma$ and $\delta^{26}\text{Mg} = -2.60 \pm 0.04 \text{ 2}\sigma$, $n = 171$, 2015–2017). Reference materials undergoing the chemical sample separation result in (i) $\delta^{25}\text{Mg} = -0.42 \pm 0.05 \text{ 2}\sigma$ and $\delta^{26}\text{Mg} = -0.80 \pm 0.09 \text{ 2}\sigma$ for IAPSO seawater ($n = 42$), and (ii) $\delta^{25}\text{Mg} = -1.02 \pm 0.02 \text{ 2}\sigma$ and $\delta^{26}\text{Mg} = -1.96 \pm 0.05 \text{ 2}\sigma$ for JCP-1 ($n = 5$). These values agree with previously published values (Immenhauser et al., 2010; Teng, 2017; Teng et al., 2015). For further details regarding the Mg isotope analysis, the reader is referred to Immenhauser et al. (2010) and Riechelmann et al. (2018).

It was not possible to analyse the $\delta^{26}\text{Mg}$ value of one snow sample (March 7, 2016) because the Mg$^{2+}$ concentration was too low (0.004 mg/L) and the sample size was insufficient.

2.6 Data analysis

Pearson correlation coefficients ($r$) between $\delta^{18}\text{O}$ values, $\delta^2\text{H}$ values, Mg$^{2+}$ concentrations, $\delta^{26}\text{Mg}$ values, air temperature and precipitation amount were calculated without weighting using the software OriginPro 2017G. In order to validate the correlations, the $p$-value is given with $p < 0.05$ (95% significance level), indicating significant correlations. Additionally, principal component analysis (PCA; Navarra & Simoncini, 2010; von Storch & Zwiers, 2004) was used to determine the components/factors influencing the different proxies studied here. Therefore, the data were first standardised and then analysed using PAST3 (Hammer et al., 2001).
3 | RESULTS

Values of samples given with the subscript precipitation consist of rainwater (liquid phase) and snow (solid phase). In contrast, the subscript snow represents only the solid phase and subscript rainwater represents only the liquid phase.

3.1 | Air temperature and precipitation amount

The precipitation sum was 1,008 mm in 2015 and 902 mm in 2016. The precipitation sum for the months January to June of 2017 of 324 mm is comparable to the first six months of 2015, characterised by a precipitation sum of 377 mm. The first six months of 2016 were wetter with a precipitation sum of 607 mm. This is reversed for the second six months of 2016, which are drier (precipitation sum 296 mm) than the second six months of 2015 (precipitation sum 631 mm). The driest month was September 2016, with a precipitation amount of only 15 mm. The wettest month was August 2015, with a precipitation amount of 147 mm (Figure 2A and Table S1). Snowfall occurred on a few days in January and February of 2015, 2016 and 2017, as well as in March 2017 (Table 1 and Figure 3). The highest amount of snow fell from 13 to 16 January in 2017 and the lowest amount on 2 January in 2017.

The annual mean air temperature was 10.5°C in 2015 and 10.3°C in 2016. The first six months of 2017 were characterised by a mean air temperature of 9.1°C, a value comparable with the mean air temperatures of the first six months of 2015 (8.0°C) and 2016 (8.5°C). The second six months of 2015 and 2016 are characterised by higher mean air temperatures of 13.0 and 12.0°C respectively. The warmest month was August 2015, with a mean air temperature of 19.0°C. The coldest month was January 2017, with a mean air temperature of 0°C (Figure 2A and Table S1). The warmest daily air temperature was 24°C on 23 February 2015, and the lowest daily air temperature (−1.4°C) was measured on 17 January 2016, during snowfall (Figure 3A and Table S1).

3.2 | Oxygen and hydrogen isotope composition of precipitation

The δ18O and δ2H values of precipitation range between −13.15 and −4.72‰ and −93.0 to −27.0‰ respectively.

![Graphs showing precipitation amount and air temperature, δ18O and δ2H values of precipitation, Mg²⁺ concentrations and δ26Mg values of precipitation from December 2014 to June 2017. Error bars are within the size of the data points](image-url)
The lowest values were recorded in October 2015 and the highest values in July 2015. The mean δ\(^{18}\)O value is −7.82 ± 1.87‰ (1σ SD; \(n = 28\)) and the mean δ\(^{2}\)H value is −52.3 ± 14.4‰ (1σ SD; \(n = 28\)). Both isotope values are higher in summer and lower in winter (Figure 2B and Table 1). The local meteoric water line (LMWL) is

| Sample       | δ\(^{18}\)O (‰ VSMOW) ±1σ | δ\(^{2}\)H (‰ VSMOW) ±1σ | Mg\(^{2+}\) (mg/L) ±1σ | δ\(^{26}\)Mg (‰ DSM3) ±2σ |
|--------------|-----------------------------|---------------------------|-------------------------|-----------------------------|
| Rainwater    |                             |                           |                         |                             |
| RW 12/14     | −8.75 ± 0.02                | −55.8 ± 0.4               | 0.10 ± 0.003            | −1.12 ± 0.03                |
| RW 01/15     | −9.15 ± 0.09                | −59.1 ± 0.4               | 0.14 ± 0.002            | −0.91 ± 0.02                |
| RW 02/15     | −11.65 ± 0.08               | −82.3 ± 0.6               | 0.15 ± 0.003            | −2.03 ± 0.04                |
| RW 03/15     | −6.83 ± 0.04                | −43.6 ± 0.4               | 0.16 ± 0.002            | −2.29 ± 0.03                |
| RW 04/15     | −7.73 ± 0.07                | −47.3 ± 0.4               | 0.20 ± 0.002            | −1.83 ± 0.03                |
| RW 05/15     | −6.66 ± 0.08                | −47.9 ± 0.8               | 0.18 ± 0.002            | −1.36 ± 0.03                |
| RW 06/15     | −7.00 ± 0.09                | −46.3 ± 0.6               | 0.20 ± 0.004            | −2.19 ± 0.08                |
| RW 07/15     | −4.72 ± 0.06                | −27.0 ± 1.3               | 0.17 ± 0.003            | −1.28 ± 0.03                |
| RW 08/15     | −8.01 ± 0.10                | −52.9 ± 0.8               | 0.19 ± 0.003            | −1.85 ± 0.03                |
| RW 09/15     | −7.29 ± 0.14                | −44.3 ± 0.5               | 0.15 ± 0.002            | −1.32 ± 0.05                |
| RW 10/15     | −13.15 ± 0.05               | −93.0 ± 0.2               | 0.17 ± 0.002            | −1.62 ± 0.03                |
| RW 11/15     | −6.43 ± 0.04                | −38.9 ± 0.4               | 0.14 ± 0.004            | −1.60 ± 0.03                |
| RW 12/15     | −6.66 ± 0.04                | −41.7 ± 0.2               | 0.09 ± 0.001            | −1.47 ± 0.04                |
| RW 01/16     | −10.37 ± 0.10               | −71.5 ± 0.5               | 0.08 ± 0.002            | −1.27 ± 0.02                |
| RW 02/16     | −8.12 ± 0.04                | −55.8 ± 0.3               | 0.10 ± 0.001            | −1.17 ± 0.01                |
| RW 03/16     | 0.13 ± 0.002                | −27.0 ± 1.3               | 0.17 ± 0.003            | −1.14 ± 0.06                |
| RW 04/16     | −9.85 ± 0.09                | −66.1 ± 0.7               | 0.20 ± 0.004            | −1.13 ± 0.04                |
| RW 05/16     | −6.22 ± 0.09                | −40.2 ± 0.4               | 0.15 ± 0.004            | −1.43 ± 0.06                |
| RW 06/16     | −7.05 ± 0.12                | −50.2 ± 0.5               | 0.07 ± 0.002            | −1.28 ± 0.05                |
| RW 07/16     | −6.01 ± 0.03                | −39.9 ± 0.2               | 0.22 ± 0.004            | −1.58 ± 0.06                |
| RW 08/16     | −4.97 ± 0.02                | −31.3 ± 0.4               | 0.10 ± 0.004            | −1.64 ± 0.03                |
| RW 09/16     | −6.72 ± 0.05                | −45.3 ± 0.2               | 0.25 ± 0.002            | −1.72 ± 0.06                |
| RW 10/16     | −7.29 ± 0.03                | −55.8 ± 0.2               | 0.15 ± 0.002            | −1.66 ± 0.05                |
| RW 11/16     | 0.08 ± 0.002                | −27.0 ± 1.3               | 0.17 ± 0.003            | −2.16 ± 0.03                |
| RW 12/16     | −6.73 ± 0.07                | −44.0 ± 0.4               | 0.23 ± 0.002            | −1.48 ± 0.02                |
| RW 01/17     | −9.83 ± 0.05                | −65.5 ± 0.3               | 0.25 ± 0.003            | −1.40 ± 0.03                |
| RW 02/17     | −7.14 ± 0.04                | −47.5 ± 0.4               | 0.10 ± 0.001            | −1.73 ± 0.04                |
| RW 03/17     | −8.10 ± 0.07                | −55.5 ± 0.1               | 0.13 ± 0.003            | −2.34 ± 0.07                |
| RW 04/17     | −7.98 ± 0.07                | −50.6 ± 0.1               | 0.23 ± 0.003            | −2.85 ± 0.02                |
| RW 05/17     | −8.52 ± 0.05                | −65.1 ± 0.3               | 0.09 ± 0.002            | −2.01 ± 0.03                |
| RW 06/17     | 0.13 ± 0.003                | −27.0 ± 1.3               | 0.17 ± 0.003            | −2.04 ± 0.03                |
| Snow         |                             |                           |                         |                             |
| 24.01.2015   | −12.50 ± 0.08               | −87.4 ± 0.7               | 0.07 ± 0.002            | −1.80 ± 0.03                |
| 30.01.2015   | −12.20 ± 0.08               | −79.9 ± 0.6               | 0.18 ± 0.002            | −1.15 ± 0.02                |
| 23.02.2015   | −15.78 ± 0.02               | −119.4 ± 1.0              | 0.02 ± 0.001            | −1.15 ± 0.05                |
| 17.01.2016   | 0.55 ± 0.004                | −12.6 ± 0.01              | 0.00 ± 0.001            | −1.26 ± 0.02                |
| 15.02.2016   | −12.69 ± 0.02               | −89.4 ± 0.06              | 0.10 ± 0.002            | −1.47 ± 0.03                |
| 07.03.2016   | −20.89 ± 0.06               | −155.9 ± 0.2              | 0.004 ± 0.002           | −1.45 ± 0.04                |
| 02.01.2017   | −11.69 ± 0.06               | −80.1 ± 0.1               | 0.15 ± 0.002            | −1.61 ± 0.04                |
| 13.16.01.17  | −7.95 ± 0.06                | −52.0 ± 0.3               | 0.43 ± 0.006            | −1.61 ± 0.04                |
defined by $\delta^2H = 7.51 \pm 0.31 \times \delta^{18}O + 6.39 \pm 2.52$ with a significant correlation of $r = 0.98$ ($p = 0$; Table 2 and Figure S1) and is comparable with the LMWL of rainwater monitoring at Iserlohn located 23 km east of Gevelsberg ($\delta^2H = 7.72 \times \delta^{18}O + 7.14$; (Riechelmann et al., 2017) and the 130 km distant GNIP station Bad Salzuflen ($\delta^2H = 7.72 \times \delta^{18}O + 5.7$; Stumpp et al., 2014).

The $\delta^{18}O$ and $\delta^2H$ values of snowfall range between −20.89 and −7.95‰ and −155.9 and −52.0‰ respectively. The mean values of $\delta^{18}O$ and $\delta^2H$ of snow are $-13.39 \pm 4.02$‰ ($\sigma$ SD, $n = 7$) and $-94.9 \pm 33.4$‰ ($\sigma$ SD; $n = 7$) respectively (Figure 3B and Table 1). Generally, snowfall represents the lowest $\delta^{18}O$ and $\delta^2H$ values of precipitation collected over the monitoring period (Figure 3B and Figure S1, and Table 1).

3.3 Mg²⁺ concentrations and $\delta^{26}$Mg values of precipitation

Magnesium concentrations of precipitation range from 0.07 to 0.25 mg/L (lowest value June 2016; highest value September 2016) with a mean value of 0.15 ± 0.05 mg/L ($\sigma$ SD; $n = 31$). Generally, higher Mg²⁺ concentrations occurred during the summer months and lower concentrations in the winter months from 2014 to mid-2016. Other than that, no obvious pattern was found (Figure 2C and Table 1). The Mg²⁺ concentrations of snow are between 0.004 and 0.55 mg/L with a mean of 0.19 ± 0.20 mg/L ($\sigma$ SD; $n = 8$) (Figure 3C and Table 1). Most Mg²⁺ concentrations for snow are within the range of precipitation values presented above (Table 1); however, two snow samples yielded much higher concentrations (0.43 and 0.55 mg/L; Figure 3C).

The $\delta^{26}$Mg values of precipitation are between −2.85 and −0.91‰ (lowest value April 2017; highest value January 2015) with a $\delta^{26}$Mg mean value of $-1.64 \pm 0.88$ ($2\sigma$ SD; $n = 31$). In general, higher $\delta^{26}$Mg values were observed in winter, whereas lower $\delta^{26}$Mg values were found for summer (Figure 2C and Table 1). Magnesium isotope values of snow range from −1.80 to −1.15‰ with a mean of $-1.41 \pm 0.48$ ($2\sigma$ SD; $n = 7$). This value is slightly higher than the mean of $\delta^{26}$Mg precipitation but indistinguishable within error. The Mg isotope values of snowfall are in the same range as $\delta^{26}$Mg precipitation (Figure 3C and Table 1).

**FIGURE 3** (A) Precipitation amount and air temperature. (B) $\delta^{18}$O and $\delta^2H$ values of snow. (C) Mg²⁺ concentrations and $\delta^{26}$Mg values of snow on days with snowfall (December 2014 to June 2017). Error bars are within the size of the data points.
3.4 Pearson correlations and PCA

There is no significant correlation between δ²⁶Mg values and Mg²⁺ concentrations, δ¹⁸O values, or δ²⁶Mg and δ²H precipitation values (Table 2 and Figure S2). Both δ¹⁸O and δ²H values show a significant positive correlation with air temperature (Table 2 and Figure S3), whereas neither Mg²⁺ concentrations nor δ²⁶Mg values correlate with air temperature (Table 2 and Figure S3). On the other hand, the Mg²⁺ concentrations of precipitation show a significant negative correlation with precipitation amount, while δ²⁶Mg precipitation values display a significant positive correlation with precipitation amount (Table 2 and Figure S4). The δ¹⁸O precipitation and δ²H precipitation values show no correlation with precipitation amount (Table 2 and Figure S4).

The PCA resulted in three components/factors explaining the total variability of δ¹⁸O precipitation and δ²H precipitation values, Mg²⁺ concentrations and δ²⁶Mg precipitation values. The PC 1 explains 47.4% of total variability that influences δ¹⁸O and δ²H values only, but not Mg²⁺ concentrations and δ²⁶Mg values. Both δ¹⁸O and δ²H values show a positive correlation with PC 1 (Figure 4A). On the other hand, neither δ¹⁸O nor δ²H values are controlled by PC 2 (31.0%) or PC 3 (21.1%; Figure 4). In contrast, δ²⁶Mg values and Mg²⁺ concentrations are influenced by PC 2 and PC 3, showing a positive correlation in the case of δ²⁶Mg values and a negative correlation for Mg²⁺ concentrations for PC 2 and a positive correlation for both for PC 3 (Figure 4).

4 INTERPRETATION AND DISCUSSION

The LMWL reported in this study agrees with MWL’s of Central Europe (Rozanski et al., 1982, 1993; Figure S1). Both δ¹⁸O and δ²H values are dependent on air temperature, as proven by their significant positive Pearson correlations (Figure S3). The dependency on air temperature is because cold air cannot keep as much moisture as warm air. Additionally, the isotopic fractionation between water vapour (cloud) and condensate (rain) increases with decreasing temperature. Consequently, the water vapour is increasingly enriched in the light isotopes (¹⁶O/¹H) at colder temperatures, and this is transferred to the δ¹⁸O and δ²H values of rain and snow (Sharp, 2007). The correlation between temperature and δ¹⁸O and δ²H values of precipitation agrees with previous findings for this region (Riechelmann et al., 2011, 2017). Since both isotope values show a positive correlation with PC 1 and neither Mg²⁺ concentrations nor δ²⁶Mg values correlate with PC 1 (Figure 4A) or air temperature, it is possible to conclude that PC 1 represents air temperature.

When comparing the δ²⁶Mg precipitation values of this study with those reported previously, the extensive range of δ²⁶Mg precipitation values documented for north-west Germany stands out as a prominent feature (Figure 5). This may partly reflect the fact that previous studies were based only on a few rain/snow samples (Bolou-Bi et al., 2012; Chapela Lara et al., 2014, 2017; Dessert et al., 2015; Fries et al., 2019; Kimmig et al., 2018; Mavromatis et al., 2014; Novak et al., 2020; Pogge von Strandmann et al., 2008; Riechelmann et al., 2012; Tipper et al., 2010, 2012). The current study presents a time series of 2.5 years with 38 samples for one stationary site and documents the high variability of δ²⁶Mg precipitation values. A similar range for δ²⁶Mg precipitation (rainwater and throughfall) is only known from Québec in Canada (Figure 5; Kimmig et al., 2018). However, the range is probably biased by the two throughfall samples being influenced by the wash-off of leaves (Kimmig et al., 2018). The observation of the current study raises questions regarding (i) the source(s) of Mg in precipitation, and (ii) the factors influencing δ²⁶Mg precipitation variability.

The values of magnesium isotopes from rain and glacial ice in coastal areas (Iceland, California—USA, Puerto Rico, Guadeloupe) display δ²⁶Mg values similar to that of seawater (−0.83 ± 0.09‰; Foster et al., 2010; Ling et al., 2011; Figure 5) and previous authors agreed that the source of δ²⁶Mg precipitation is seawater (Chapela

|                | Air temperature | Precipitation amount | δ¹⁸O | δ²H | Mg²⁺ conc. |
|----------------|-----------------|----------------------|------|-----|------------|
| Air temperature| −0.08           | 0.56                 | 0.01 | 0.50| 0.08       |
| Precipitation amount | 0.05         | −0.60               | 0.03 | 0.08| −0.19     |
| δ¹⁸O           | 0.43            | −0.02               | 0    | 0   |
| δ²H            |                 |                      |      |     |
| Mg²⁺ conc.     |                 |                      |      |     |
| δ²⁶Mg          |                 |                      |      |     |

Note: Values printed in bold are significant correlations with p < 0.05.
Lara et al., 2014, 2017; Dessert et al., 2015; Pogge von Strandmann et al., 2008; Tipper et al., 2010). The sampling site used in this study is approximately 250 km from the coast, and δ²⁶Mg_{precipitation} values are depleted in ²⁶Mg compared to seawater (Figure 5). Analyses of chloride concentrations and chloride isotope signatures of rain and cave drip water in the region do not support a marine source of elements in rainwater (Münsterer et al., 2012; Riechelmann et al., 2011). It is thus proposed that seawater is not a dominant source for the variability of δ²⁶Mg_{precipitation} in this region.

Comparing δ²⁶Mg_{snow} with δ²⁶Mg_{rainwater} of the current study, no systematic difference was found between the two aggregate states (Figures 2C, 3C and 5, Table 1). An aspect, however, that has to be kept in mind for this study site is that the snow samples are collected per snow event (daily), while rainwater samples represent precipitation of a whole month. Support for this observation comes from the daily collection of rainwater and snow in France (Bolou-Bi et al., 2007) and the collection of rain events and monthly snow samples in Central Siberia (Mavromatis et al., 2014; Figure 5). There, rain and snow also display similar Mg isotope values. However, two of the snow samples might have been contaminated by road salt containing magnesium chloride, magnesium sulphate and/or clay minerals. Specifically, the samples taken on 17 January 2016, and 13 to 16 January 2017 have elevated Mg²⁺ concentrations (0.55 and 0.43 mg/L respectively) compared to all other precipitation samples (Figure 3C and Table 1). These two samples also display elevated Na⁺ concentrations suggesting an anthropogenic influence, probably aerosols containing salt from the nearby road.
The Mg$^{2+}$ concentrations and $\delta^{26}$Mg$_{\text{precipitation}}$ values display no relationship with air temperature (Figure S3) or PC 1 (temperature component; Figure 4A). Furthermore, $\delta^{26}$Mg values do not correlate with $\delta^{18}$O or $\delta^{2}$H values, which are both temperature dependent. Riechelmann et al. (2012) originally suggested that $\delta^{26}$Mg$_{\text{precipitation}}$ values in north-west Germany are influenced by the air temperature. Arguments for this are based on the observation that the $\delta^{26}$Mg$_{\text{snow}}$ value ($-1.35\%$) is significantly depleted in $^{26}$Mg compared to the $\delta^{26}$Mg$_{\text{rainwater}}$ values ($-0.59$ to $-0.90\%$; Figure 5). The $\delta^{26}$Mg$_{\text{snow}}$ value published by Riechelmann et al. (2012) is in the range of the Mg isotope values of snow observed in the current study. In contrast, the range of previously published Mg isotope values of rain overlap with, or are enriched in, $^{26}$Mg compared to data shown in this study for the same region (Figure 5). Therefore, based on the data provided in this study, it can be concluded that the $\delta^{26}$Mg$_{\text{precipitation}}$ values are not temperature dependent.

Both Mg$^{2+}$ concentrations and $\delta^{26}$Mg values significantly correlate with precipitation amount (Figure S4). Magnesium concentrations correlate negatively with precipitation amount, whereas $\delta^{26}$Mg values correlate positively with precipitation amount (Figure S4). The same pattern is found for the PCA showing a negative correlation between Mg$^{2+}$ concentrations and PC 2 and a positive one between $\delta^{26}$Mg values and PC 2 (Figure 4A). Consequently, it is proposed that PC 2 represents the precipitation amount. This is confirmed by the lack of correlation between $\delta^{18}$O and $\delta^{2}$H values with precipitation amount and PC 2 (Figure 4A and Figure S4). At least part of the variability of both Mg$^{2+}$ concentrations and $\delta^{26}$Mg values is driven by precipitation amount. Surprisingly, there is no correlation between Mg$^{2+}$ concentrations and $\delta^{26}$Mg values, although both parameters correlate with precipitation amount. This is probably because both proxies correlate positively with PC 3 but negatively (Mg$^{2+}$ concentrations)/positively ($\delta^{26}$Mg) with precipitation amount (PC 2; Figure 4). This opposite behaviour between Mg$^{2+}$ concentrations and $\delta^{26}$Mg values and their main controlling factors blurs the correlation between the two parameters.

In the case of PC 3, dust seems the most probable explanation and both, Mg$^{2+}$ concentrations and $\delta^{26}$Mg values correlate positively, as shown by the PCA (Figure 4B). In general, carbonates display $^{26}$Mg-depleted values and lower Mg concentrations than silicate minerals (Schauble, 2011; Tipper et al., 2006b). However, more complexity is found when comparing low-Mg calcites with lower $\delta^{26}$Mg values and Mg-carbonates such as dolomite with higher $\delta^{26}$Mg values (Tipper et al., 2006b). Consequently, higher Mg concentrations and higher $\delta^{26}$Mg$_{\text{precipitation}}$ values suggest silicate or dolostone dust, whereas lower Mg concentrations and lower $\delta^{26}$Mg$_{\text{precipitation}}$ values suggest limestone dust in the atmosphere (Figure 5). If this concept holds true, the positive correlation of Mg$^{2+}$ concentration/$\delta^{26}$Mg values with PC 3 (Figure 4B) can be explained.
Dust as a factor controlling $\delta^{26}\text{Mg}_{\text{precipitation}}$ is in agreement with previous studies (Bolou-Bi et al., 2012; Kimmig et al., 2018; Riechelmann et al., 2012; Tipper et al., 2012). Magnesium isotope signatures of rainwater in Switzerland, Québec (Canada), and the Czech Republic display similarly low values, as shown here (Figure 5; Kimmig et al., 2018; Novak et al., 2020; Tipper et al., 2012). Carbonate dust was suggested to influence the Mg isotopic signature of rainwater, albeit based on a significantly smaller data set (Kimmig et al., 2018; Tipper et al., 2012). Similarly, $\delta^{26}\text{Mg}_{\text{precipitation}}$ values from France are elevated and most probably influenced by silicate dust in the atmosphere (Bolou-Bi et al., 2012; Figure 5). Active quarries in Devonian limestone and dolostone units are found about 30 km west-southwest and east of the sampling location (Figure 1). Open-pit mining of Palaeogene siliciclastics takes place some 65 km south-west of the precipitation collection point (Figure 1). Wind directions in the study region are typically southerly to westerly and less commonly northerly to easterly (Riechelmann et al., 2019). An additional local origin of dust in the atmosphere is farming, contributing mainly silicate minerals (Fuchs & Krusch, 1911). Since almost half of the area of North Rhine-Westphalia is used for farming (Information und Technik Nordrhein-Westfalen, 2017), this is a very probable explanation for anthropogenically derived silicate dust. Summing up, anthropogenically derived dust from quarries and farms may represent a significant factor influencing $\delta^{26}\text{Mg}_{\text{precipitation}}$ values and their variability. This raises questions regarding the applicability of these data and their relevance for pre-anthropogenic rainfall.

A natural origin of airborne dust includes mineral dust erosion in arid environments (Boucher et al., 2013). Saharan dust, for example, contributes to increased aerosol levels over Central Europe and is transported over several thousands of kilometres (DWD (Deutscher Wetterdienst), 2017; Pey et al., 2013). In Germany, Saharan dust influx is commonly recorded during the spring and summer months (Flentje et al., 2015). Saharan dust is mainly composed of aluminosilicates, iron oxides and quartz, and to a lesser degree of calcite and gypsum (Sokolik & Toon, 1999). Throughout July 2015, increased levels of Saharan dust were recorded (DWD, 2017). The $\delta^{26}\text{Mg}_{\text{precipitation}}$ values in July 2015 are enriched in $^{26}\text{Mg}$ ($-1.28 \pm 0.03\%$) compared to most other months, a feature that is best explained by an increased input of silicate minerals to the locally occurring carbonate dust in the region. Slightly increased levels of Saharan dust levels are also recorded for March and April 2016 (DWD, 2017). Precipitation during these two months shows $\delta^{26}\text{Mg}$ values of $-1.14 \pm 0.06$ and $-1.13 \pm 0.04\%$, respectively. Saharan dust levels were lower for most of the remaining monitoring period (DWD, 2017), and $\delta^{26}\text{Mg}_{\text{precipitation}}$ values seem not to be influenced by this dust origin.

In general, dust in the atmosphere settles by either dry deposition (sedimentation, impaction) or wet deposition (rain, snow, etc.; DWD, 2017). The $\text{Mg}^{2+}$ concentrations display a significant correlation with precipitation amount (Figure S4). High $\text{Mg}^{2+}$ concentrations are found when the precipitation amount is low and vice versa (Figure 2C). This is probably due to the accumulation of Mg-bearing dust in the atmosphere during dry, and washout (dilution) during wet periods (Figure 2). Generally, the $\delta^{26}\text{Mg}_{\text{precipitation}}$ value is lower during drier conditions and higher under wetter conditions. The correlation between the $\delta^{26}\text{Mg}_{\text{precipitation}}$ values and precipitation amount is weak but significant (Table 2 and Figure S4D). The best explanation for this relationship is probably washout or dust accumulation in the atmosphere from a different origin. It is proposed that $\delta^{26}\text{Mg}$ values strongly depend on dust mineralogy and concentration affected by the prevailing weather conditions during the precipitation event (e.g. wind direction, wind speed, precipitation amount). This aspect requires further research. Additionally, farming and surface mining represents a significant anthropogenic dust component that probably affects the data reported in this study.

A detailed interpretation for the $\delta^{26}\text{Mg}_{\text{precipitation}}$ patterns must, at present, remain elusive but generally is consistent with natural or anthropogenic derived dust, its mineralogy and concentration. The $\delta^{26}\text{Mg}_{\text{precipitation}}$ value is most probably a reliable indicator of the origin (mineralogical composition, amount) of dust/aerosols in the atmosphere, reflecting the significant difference in $\delta^{26}\text{Mg}$ values of seawater, carbonate and silicate minerals. The high variability of $\delta^{26}\text{Mg}_{\text{precipitation}}$ over the monitoring period suggests that the Mg isotope system in the atmosphere is susceptible to changing patterns in dust origin, mineralogy and concentration and, thus, random sampling of a small number of precipitation events is inadequate to capture these processes. Future research on the Mg isotope composition of precipitation should include dry deposition collectors to quantify the dust and determine its mineralogy. Further analyses of cations and anions (e.g. chloride) could also provide helpful insight into dust mineralogy and its influence on the $\delta^{26}\text{Mg}_{\text{precipitation}}$. Air mass back trajectory analysis might also be a useful tool to determine the source region(s) of dust, especially for individual rain events.

5 | CONCLUSIONS

Monthly $\delta^{18}\text{O}$, $\delta^2\text{H}$ and $\delta^{26}\text{Mg}$ values and $\text{Mg}^{2+}$ concentrations of precipitation from December 2014 to June 2017 are documented and interpreted. High temporal variability
was found in $\delta^{26}$Mg values between $-2.85$ and $-0.91$‰ ($\delta^{26}$Mg$_{\text{mean}}$: $-1.64 \pm 0.88$‰ 2SD) at the sample collection site in north-west Germany. Oxygen and hydrogen isotope values also display high temporal variability, which is driven by changes in air temperature. Furthermore, the observed LMWL agrees with the GMWL and other LMWLs of the region.

The data show that Mg$^{2+}$ concentrations and the $\delta^{26}$Mg$_{\text{precipitation}}$ values are not influenced by air temperature, as is the case for $\delta^{18}$O and $\delta^{2}H$ values. The $\delta^{26}$Mg values of snow are in the same range as the $\delta^{26}$Mg values of rainwater.

Previous studies suggested that the Mg isotope composition of precipitation probably is influenced by the mineralogical composition of the dust in the atmosphere. Based on a more comprehensive data collection, it is suggested that both, Mg$^{2+}$ concentrations and $\delta^{26}$Mg$_{\text{precipitation}}$ values are related to precipitation amount and the mineralogical composition and the concentration of dust/aerosol particles in the atmosphere. A higher input of silicate dust to precipitation leads to higher $\delta^{26}$Mg values, whereas a higher input of carbonate dust results in lower $\delta^{26}$Mg values. Additional complexity is found when comparing dolostone and limestone dust. Anthropogenically induced dust in the study area can be produced by active quarries in limestone and dolostone. Siliciclastic dust can be derived from farming, while natural sources include mainly Saharan dust (mainly silicates). Higher $\delta^{26}$Mg$_{\text{precipitation}}$ values point to a higher abundance of silicate or dolostone dust in the atmosphere, and lower $\delta^{26}$Mg$_{\text{precipitation}}$ values point to limestone dust. Consequently, $\delta^{26}$Mg$_{\text{precipitation}}$ values can be used as an indicator to differentiate between seawater aerosols, carbonate and silicate dust due to their different $\delta^{26}$Mg values. Future research should focus on the dust mineralogy combined with air mass back trajectory analysis to determine the dust’s source region(s).

Based on the data set shown here, $\delta^{26}$Mg$_{\text{precipitation}}$ values appear to serve as a proxy for dust mineralogy and concentration. This influences all hydrospheric systems such as soil waters, ground waters, river waters and cave waters, which are recharged by Mg-bearing rainwater.

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The authors declare that there exists no conflict of interest. We thank two anonymous reviewers for their feedback on the manuscript.

**DATA AVAILABILITY STATEMENT**

All data used in this study are provided in Table 1 and Table S1. The data set of this paper has been archived in the PANGAEA database: https://doi.pangaea.de/10.1594/PANGAEA.937577.

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**REFERENCES**

Appelo, C.A.J. & Postma, D. (2005) Geochemistry, groundwater and pollution. Amsterdam: A.A. Balkema Publishers.

BGR (Bundesanstalt für Geowissenschaften und Rohstoffe) (2021) Bodenatlas [Online]. Available from: https://geoviewer.bgr.de/mapapp4/resources/apps/bodenatlas/index.html?lang=de&tab=boedenDeutschlands [Accessed 3 September 2021].

Black, J.R., Epstein, E., Rains, W.D., Yin, Q.-Z. & Casey, W.H. (2008) Magnesium-isotope fractionation during plant growth. *Environmental Science and Technology*, 42, 7831–7836. https://doi.org/10.1021/es8012722.

Bolou-Bi, E.B., Poszwa, A., Leyval, C. & Vigier, N. (2010) Experimental determination of magnesium isotope fractionation during higher plant growth. *Geochimica et Cosmochimica Acta*, 74, 2523–2537. https://doi.org/10.1016/j.gca.2010.02.010.

Bolou-Bi, E.B., Vigier, N., Poszwa, A., Boudot, J.P. & Dambrine, E. (2012) Effects of biogeochemical processes on magnesium isotope variations in a forested catchment in the Vosges Mountains (France). *Geochimica et Cosmochimica Acta*, 87, 341–355. https://doi.org/10.1016/j.gca.2012.04.005.

Bolou-Bi, E.B., Vigier, N., Poszwa, A. & Brenot, A. (2007) Compared Mg isotope compositions of plants, rocks and waters. *Geochimica et Cosmochimica Acta*, 71, A106.

Boucher, O., Randall, D., Artaxo, P., Bretherton, C., Feingold, G., Forster, P., Kerminen, V.M., Kono, Y., Liao, H., Lohmann, U., Rasch, P., Satheesh, S.K., Sherwood, S., Stevens, B. & Zhang, X.Y. (2013) Clouds and aerosols. In: Stocker, T.F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S.K., Boschung, J., Nauels, A., Xia, Y., Bex, V. & Midgley, P.M. (Eds.) *Climate change 2013: the physical science basis*. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge and New York, NY: Cambridge University Press, pp. 571–657.

Chapela Lara, M., Buss, H.L., Pogge von Strandmann, P.A.E., Dessert, C. & Gaillardet, J. (2014) Controls on the Mg cycle in the tropics: insights from a case study at the Luquillo Critical Zone Observatory. *Procedia Earth and Planetary Science*, 10, 200–203. https://doi.org/10.1016/j.proeps.2014.08.019.
Chapela Lara, M., Buss, H.L., Pogge von Strandmann, P.A.E., Schuessler, I.A. & Moore, O.W. (2017) The influence of critical zone processes on the Mg isotope budget in a tropical, highly weathered andesitic catchment. *Geochimica et Cosmochimica Acta*, 202, 77–100. https://doi.org/10.1016/j.gca.2016.12.032

Dessert, C., Lajeunesse, E., Lloret, E., Clergue, C., Crisi, O., Gorge, C. & Quidelleur, X. (2015) Controls on chemical weathering on a mountainous volcanic tropical island: Guadeloupe (French West Indies). *Geochimica et Cosmochimica Acta*, 171, 216–237. https://doi.org/10.1016/j.gca.2015.09.009

DWD (Deutscher Wetterdienst) (2017) Saharan dust [online]. Available from: https://www.dwd.de/EN/research/observing_atmosphere/composition_atmosphere/aerosol/cont_nav/saharan_dust_node.html [Accessed 3 April 2020].

Fletsch, H., Briel, B., Beck, C., Collaud Coen, M., Fricke, M., Cyrys, J., Gu, J., Pitz, M., Thomas, W. (2015) Identification and monitoring of Saharan dust: an inventory representative for southern Germany since 1997. *Atmospheric Environment*, 109, 87–96. https://doi.org/10.1016/j.atmosenv.2015.02.023

Foster, G.L., Pogge von Strandmann, P.A.E. & Rae, J.W.B. (2010) Boron and magnesium isotope composition of seawater. *Geochemistry Geophysics Geosystems*, 11, 10. https://doi.org/10.1029/2010gc003201.

Fries, D.M., James, R.H., Dessert, C., Bouchez, J., Beaumais, A. & Pearce, C.R. (2019) The response of Li and Mg isotopes to rain events in a highly-weathered catchment. *Chemical Geology*, 519, 68–82. https://doi.org/10.1016/j.chemgeo.2019.04.023

Fuchs, A. & Krusch, F. (1911) Blatt 4610 Hagen Erläuterungen, *Mitteilungen der Gesellschaft der Geologie- und Bergbaustudenten in Österreich*, 46, 51–66.

Hammer, Ø., Harper, D.A.T. & Ryan, P.D. (2001) PAST: paleontological statistics software package for education and data analysis. *Palaeontologia Electronica*, 4, 9.

Hu, Z., Bialik, O.M., Hohl, S.V., Xia, Z., Waldmann, N.D., Liu, C. & Li, W. (2021) Response of Mg isotopes to dolomitization during fluctuations in sea level: constraints on the hydrological conditions of massive dolomitization systems. *Sedimentary Geology*, 420, 105922. https://doi.org/10.1016/j.sedgeo.2021.105922.

Immenhauser, A., Buhl, D., Richter, D.K., Niedermayr, A., Riechelmann, D., Dietzel, M. & Schulte, U. (2010) Magnesium-isotope fractionation during low-Mg calcite precipitation in a limestone cave – field study and experiments. *Geochemistry et Cosmochimica Acta*, 74, 4346–4364. https://doi.org/10.1016/j.gca.2010.05.006

IT.NRW (Information und Technik Nordrhein-Westfalen) (2017) Statistische Berichte – Bodennutzung in Nordrhein-Westfalen 2017 Endgültiges Ergebnis [Online]. Available from: https://www.statistischesbibliothek.de/mir/servlets/MCRFileNodeServlet/NWHeft_derivate_00010708/c113201700_A.pdf?jsess...
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