

## ***Interactive comment on “The magnesium isotope record of cave carbonate archives” by S. Riechelmann et al.***

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### **1 General Comments**

In this manuscript Riechelmann et al present magnesium isotope data ( $^{26}\text{Mg}/^{24}\text{Mg}$  expressed in delta notation relative to the DSM3 standard) from six different speleothem calcite archives from Germany, Morocco and Peru, in addition to two flowstone records from Austria. Although Mg is a trace element in the calcite forming in cave stalagmites, it is a major element in the drip waters from which the cave mineralisation occurs, and it is a major element in the soil environments that are likely to control the Mg content of soil pore-waters. The fundamental rationale behind the manuscript is that the physico-chemical processes controlling the chemical reactions in soils are depen-

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dent on climate, such as temperature and supply of water by rainfall. The Mg isotope composition of pore and ground waters is therefore also likely dependent on climate, because the numerous processes that control Mg in waters likely influence Mg isotopes also. It is then required that speleothem calcite then faithfully preserves the Mg isotope composition of pore-water, and hence climatic information. Although complex, the same rationale has been successfully applied for a series of better understood isotopic systems such as carbon, oxygen and strontium. Less is known about Mg isotopes, but there is hope that they will provide a wealth of information. This manuscript reads quite like a review and does an admirable job of summarising what is currently known, or unknown, and what we might hope to learn from such novel isotopic systems. Because the subject is in its infancy, there are many uncertainties, and although the limitations are clearly stated, I think these could be given greater weight, compared to the sometimes speculative interpretation. I think in some cases this might lead to a simplification. In general the manuscript is well written, but I can't help but feel that this work could be better articulated with just a little more work.

### **2 Specific Comments**

#### **2.1 Detrital layers and fluid inclusions**

At several places in the manuscript it is discussed that fluid inclusions and detrital material present in the speleothem calcite influence (albeit in a subtle way for fluid inclusions) the Mg isotope composition of the bulk speleothem calcite. I find this a distraction when it comes to the interpretation, and don't think it should really feature in the discussion at all, but rather in the results or methods section. From a point of view of extracting any information pertaining to climate, this is not particularly relevant. Rather, the samples need to be carefully processed and screened for such effects. In the case of detrital material, one would imagine that measuring the aluminium or silicon

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content would provide a suitable method for screening out such problems.

## 2.2 Interpretation of the Mg isotope data

The principal idea behind using Mg isotope data in speleothems to extract climate information is that Mg isotopes might be a proxy for carbonate to silicate weathering, and that the relative amounts of carbonate and silicate weathering occurring are dependent on climate. This is an interesting and plausible idea, but as yet not well tested. Looking at the problem from a weathering point of view, one might interpret the data in a very different way. I think what the majority of weathering studies on Mg isotopes show (and there are not very many) is that Mg isotopes are not a simple tracer of carbonate to silicate weathering, but rather are strongly controlled by processes inducing isotopic fractionation (probably linked to clay). For example, Mg isotope ratios rarely correlate with the Si/Ca ratio or Sr isotope ratios in natural waters. A recent study has shown that small Alpine streams show 1 per mil variation in Mg isotope ratios, that is dependent on climate, but entirely independent of the proportion of carbonate to silicate weathering, because there was no carbonate material in the system. In the case of karstic systems there will always be carbonate material in the host rock by definition. Hence there will always be a source effect of carbonate to silicate material. The question is really whether this source effect provides the dominant signal, or whether the first order observations are controlled by isotopic fractionation related to changing physico-chemical reactions (that are climate dependent). This for me is the weakest point of the whole manuscript, because the potential controls are never really set out in a concise and clear way. Isotopic fractionation is largely ignored, and this may be the major signal. A sceptic might ask, why not use Sr isotopes that are not affected by isotopic fractionation to infer the proportion of carbonate to silicate weathering? Finally, is the link between carbonate and silicate weathering and climate well understood?

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## 2.3 Warm-humid climate speleothems

The authors acknowledge that these are the most complex settings, and perhaps this is where the interpretation needs to proceed with the greatest caution. I would suggest trying to separate the facts from the hypotheses and more speculative interpretations in this section. I wonder if it could be written as a series of testable questions to clarify what we know, and what we don't know. For example, doesn't soil respiration also increase silicate weathering? I don't understand the argument for the Austrian samples on pp1854 line 20, about rain not affecting Mg isotopes. This should be clarified. Just because it rains less, doesn't mean to say that subsurface waters cease to flow altogether.

## 3 Technical corrections

1. Abstract, Line 17: Does NC-A and NC-B really have the highest value? On line 22 of the abstract SPA 52 seems to have a higher value.
2. Line 9: Should be relative to the DSM3 standard, not using
3. Are the uncertainties quoted on line 10 2S.D. or 2sigma?
4. line 26: Depleted relative to what? This occurs throughout the manuscript. Depleted is a relative term, and it is essential that this ambiguous terminology is corrected.
5. The results section is rather terse to read, covering each case study separately but just stating the values. I wonder if there might be a better way of presenting this section? Perhaps a summary figure of all the Mg isotope data would help (an expanded Fig. 2)?

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6. PP1844, lines 16. There is some additional discussion on the controls of rain water in Tipper et al., Chem Geol 2012. This wouldn't have been published when the present manuscript was in prep, but it might be of interest.
7. pp1844, lines 29. replace increasing with higher.
8. pp1845, lines 19. I am sure there are more references about carbonate and silicate weathering.
9. pp1845, lines 23 onwards. What about the formation of clay minerals, and not just their dissolution?
10. pp1846, lines 26 onwards. I think the calcite aragonite explanation is a very plausible and simple one. I would be tempted to give it more weight.
11. pp1847, lines 18. Note that dust will also likely affect the Mg isotope composition as it provides another source of Mg.
12. pp1848 line 8. Replace siliceous with silicate.

#### **4 Summary**

Overall, this work should be published subject to relatively minor revisions that improve the way this work is presented and communicated.

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Interactive comment on Clim. Past Discuss., 8, 1835, 2012.