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Climate of the Past Discussions

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

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We thank Edward T. Tipper for his overall positive and constructive review, which led to an improved version of our paper. In the following detailed answers to the individual comments are provided.

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

Our reply: We thank the reviewer for this very constructive comment. We moved text regarding detrital material to section 3 (Magnesium isotope analysis) and text regarding the fluid inclusions is moved to the results section 5.1 (Stalagmite AH-1, Atta Cave, Germany). Neither silicon nor aluminium were measured for these speleothems, thus the identification of detrital material was only macro- and microscopically.

Comment 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.

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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?

Our reply: We thank the reviewer for his detailed comment and fully appreciate the complexity of weathering rates and other processes in the soil and aquifer zone. We agree that there is no easy and direct relation between Mg and weathering and state this in the paper. We politely disagree with the reviewer's statement regarding the lack of Sr and its bearing on weathering and source material. Buhl et al. (2007) show a combined Sr and Mg data set from Morocco (shown here, GDA) and document a strong correlation between changes in 87Sr/86Sr and 26Mg. Hence, we do show data albeit not from all sites. Second, the probably best studied case example is Bunker Cave (Riechelmann et al., 2012) and there we do show a detailed data set including rain water, soil water, karst water, drip water and speleothem calcite. In essence, we do NOT ignore isotopic fractionation and these data are published. At present we undertake leaching experiments using different carbonate and soil materials. In this sense, the present paper is a status report that requires updating with new data. For clarification, we added a short paragraph in section 4 (Environmental, equilibrium and disequilibrium factors affecting the Mg isotope fractionation in continental karst systems) regarding the connection between climate and silicate versus carbonate weathering as reported in the study by Riechelmann et al. (2012).

Comment 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

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affecting Mg isotopes. This should be clarified. Just because it rains less, doesn't mean to say that subsurface waters cease to flow altogether.

Our reply: We appreciate the suggestion of the reviewer to separate the facts from the hypotheses and more speculative interpretations in this section. However, we think a separation of different facts supporting one or several hypotheses or leading to different interpretations should not be done, because we fear to unnecessarily confuse the reader on this complex topic. Furthermore, it would lead to a change in style compared to the previous sections of the discussion. Of course, the reviewer is right regarding the increase of silicate weathering due to enhanced soil respiration. Therefore, we added a few sentences to this topic in chapter 6.3 (Warm-humid climate: speleothem time series delta26Mg data from Germany). We tried to clarify the text for the Austrian samples on pp. 1854, line 20.

Comment 4: Technical corrections 4.1. 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.

Our reply: With respect to the stalagmites, it is correct that NC-A and NC-B have the highest value. But the reviewer is right that SPA 52 has the highest value, when all speleothems (including stalagmites and flowstones) are compared. We clarified this by changing the sentence to "...stalagmites from Peru show the highest mean value of all stalagmites..."

4.2. Line 9: Should be relative to the DSM3 standard, not using Our reply: We changed the sentence to "...by measuring the mono-elemental solution Cambridge 1 against DSM3 standard solution repeatedly..."

4.3. Are the uncertainties quoted on line 10 2S.D. or 2sigma?

Our reply: We added 2sigma after the uncertainties.

4.4. line 26: Depleted relative to what? This occurs throughout the manuscript. De-

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pleted is a relative term, and it is essential that this ambiguous terminology is corrected.

Our reply: We completely agree with the reviewer. We corrected this throughout the manuscript according to Sharp (2007; Principles of stable isotope geochemistry).

4.5. 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)?

Our reply: We added a new figure summarizing the Mg isotope time series data of AH-1 and BU 4, because they were compared in the discussion. Since no further comparison between the different speleothems takes place we decided against a figure containing all speleothems.

4.6. 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.

Our reply: We thank the reviewer for this comment and added text according to the reference in section 4 (Environmental, equilibrium and disequilibrium factors affecting the Mg isotope fractionation in continental karst systems).

4.7. pp1844, lines 29. replace increasing with higher.

Our reply: We changed the sentence to "…weathering is relatively higher during warmer…"

4.8. pp1845, lines 19. I am sure there are more references about carbonate and silicate weathering.

Our reply: We added more references as the reviewer suggested.

4.9. pp1845, lines 23 onwards. What about the formation of clay minerals, and not just their dissolution?

Our reply: This is an interesting point. However, as far as we know, there is no study yet, which addresses the potential influence of the formation of clay minerals on the Mg-isotopes of these clay minerals, water, etc.

4.10. 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.

Our reply: We added a sentence to give this explanation more weight in the discussion as the reviewer suggested.

4.11. pp1847, lines 18. Note that dust will also likely affect the Mg isotope composition as it provides another source of Mg.

Our reply: The reviewer is right about this statement; however, the study of Larrasoaña et al. (2003) is a climatic reconstruction of the time when the speleothem probably grew and we only wanted to compare the interpretations of both studies.

4.12. pp1848 line 8. Replace siliceous with silicate.

Our reply: We changed this as suggested.

The authors

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