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3. Low-Temperature Isotope Geochemistry

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3. Low-Temperature Isotope Geochemistry

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3.1

Late Albian Carbon Isotope Stratigraphy and new Insights into mid-Cretaceous Paleoceanography

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We present new $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ data from the Late Albian succession of the Umbria-Marche Basin showing the evolution of the ocean-climate system under the mid-Cretaceous greenhouse conditions. We observe long eccentricity cycles recorded both in the $\delta^{13}\text{C}_{\text{carb}}$ and in the $\delta^{13}\text{C}_{\text{org}}$ records, suggesting that orbital forcing affected both oceans and terrestrial environments. These cycles occur together with very variegated facies, with cyclic, thin black shale layers, suggesting that the oceanic circulation was unstable, very sensitive to orbital forcing, and prone to anoxic episodes.

During the Late Albian we observe the occurrence of more homogeneous and carbonate-rich sedimentation, accompanied by a stabilization of the $\delta^{13}\text{C}_{\text{carb}}$ curve. This suggests a switch of the global oceanic system into a more stable circulation mode, with deeper thermocline and permanent deep-water ventilation. On the other hand this change does not occur in the $\delta^{13}\text{C}_{\text{org}}$ record dominated by terrestrial organic matter, showing that this event concerned the oceanic but not the terrestrial system.

In the lattermost Albian, after the onset of the more stable circulation mode, the ocean was pushed back again into the unstable mode for a relatively short time. This event occurred at global scale, it was accompanied by a slight increase in carbon burial and was considered one of the minor Cretaceous Oceanic Anoxic Events (OAE 1d).

We hypothesize that the transition into the stable circulation mode was an oceanographic response to the opening and deepening of gateways during the mid-Cretaceous. On the other hand the short-term switch back to the unstable mode was due to a period of prolonged, exceptionally strong orbital forcing and/or to changes in atmospheric CO_2 concentrations. Our results show that anoxic conditions during the mid-Cretaceous could occur in response to different forcings, favored by the peculiar paleoceanographic conditions.

3.2

Calibration and application of the 'clumped-isotope' thermometer to foraminifera for high-resolution climate reconstructions of the last 500 years from the Mediterranean Sea

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Clumped-isotope thermometry allows determination of the precipitation temperature of calcite via measurements of the abundance of ¹³C-¹⁸O bonds in carbonate and at the same time an estimation of the $\delta^{18}\text{O}$ of seawater in which the organism lived.

At ETH Zurich we utilize a newly developed technique for clumped-isotope measurements of small samples (Schmid and Bernasconi, 2010), which allows for the first time to produce combined high-resolution $\delta^{18}\text{O}$ and clumped-isotope records from sediment cores. In this contribution we present a calibration study on 8 species of foraminifera with growth temperatures ranging from 0.6°C to 29°C.

Our results are in good agreement with the published calibrations of Ghosh et al. (2006) and Tripathi et al. (2010). The clumped-isotope temperatures of the surface-dwelling planktonic foraminifera are similar to the measured sea surface temperatures (SST's), while the benthonic and deep-dwelling planktonic species show a larger variation, suggesting that they may not always precipitate their shells in isotopic equilibrium with seawater.

We also show that our measuring technique on small samples of foraminifera can be used to obtain high-resolution $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ time series, and at the same time to reconstruct lower-resolution clumped-isotope temperature records.

We present our $\delta^{18}\text{O}$ and clumped-isotope measurements of *Globigerinoides ruber (white)* from a short sediment core covering the last 500 years, at 3.5 years resolution, from the Gulf of Taranto (Mediterranean Sea). As it records both, marine and riverine influences, we deem this region well suited for reconstructing Holocene climate variability, especially for evaluating the potential of anthropogenic influence on climate.

The obtained clumped-isotope temperatures are in good agreement with measured SST's with accuracy of $\pm 2^\circ\text{C}$ over the last 50 years. This demonstrates that our method can serve as a robust new tool for reconstructing changes in temperature and $\delta^{18}\text{O}$ of seawater, and hence salinity, on the same sample.

We observe that SST's do not change significantly over the last 500 years. However, changes in salinity in the order of 1-2 PSU are common, which suggests changes in circulation and freshwater runoff. Additional analyses of core top samples and water samples from the same area support our calibration of the clumped-isotope signatures of *G. ruber (white)*.

REFERENCES

- Ghosh, P., Adkins, J., Affek, H., Balta, B., Guo, W., Schauble, E., Schrag, D., Eiler, J. (2006). ¹³C-¹⁸O bonds in carbonate minerals: A new kind of paleothermometer. *Geochim. Cosmochim. Acta* 70, 1439-1456.
- Schmid, T.W., Bernasconi, S.M. (2010). An automated method for 'clumped-isotope' measurements on small carbonate samples. *Rapid Comm. Mass Spectrom.* 24, 1955-1963.
- Tripathi, A.K., Eagle, R.A., Thiagarajan, N., Gagnon, A.C., Bauch, H., Halloran, P.R., Eiler, J.M. (2010). ¹³C-¹⁸O isotope signatures and 'clumped-isotope' thermometry in foraminifera and coccoliths. *Geochim. Cosmochim. Acta* 74, 5697-5717.

3.3

Solution speciation controls mercury isotope fractionation during sorption of Hg(II) to goethite

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Mercury is a pollutant of global concern because of its potential to be transported over long distances through the atmosphere and to form highly toxic organometallic molecules (e.g., methyl-Hg) which biomagnify along the food chain. Soils are the most important terrestrial sinks for atmospherically deposited Hg. Iron(oxyhydr)oxides are common soil minerals and can play an important role in the immobilization of Hg, especially in mineral soils with low organic matter content. Environmental changes like acidification, salinization, or land use change can lead to a leaching of mineral-bound mercury. The analysis of stable Hg isotope ratios has developed rapidly in the past years and represents a promising tool for pollution source identification and tracing the biogeochemical behavior of mercury. We use stable Hg isotopes to investigate the biogeochemical Hg cycle in soils. However, to interpret natural Hg isotope ratios, a better understanding of the processes causing Hg isotope fractionation in soils is needed. Therefore, we investigated the sorption of Hg(II) to goethite (α-FeOOH), an important Fe(III)-oxyhydroxide mineral in most soils, and the corresponding isotope fractionation mechanisms.

We performed laboratory scale sorption experiments with dissolved Hg(II) (nitrate salt) and goethite under different pH conditions (buffered at pH 7 with 2.5 mM MOPS, or unbuffered at pH 3-6), different Cl⁻ concentrations (0 and 0.5 mM) and different SO₄²⁻ concentrations (0 and 1M). Equilibration experiments from 18h to 30d were performed. The dissolved Hg was separated from the goethite by centrifugation and filtration, and the sorbed fraction was measured after dissolving the goethite in 6M HCl. Concentrations of Hg were measured by CV-AFS and isotope ratios by CV-MC-ICPMS (Nu Plasma) yielding a standard reproducibility of ±0.09 ‰ (2SD for δ²⁰²Hg, 16 measurements over 12 months) using Tl mass bias correction and sample-standard bracketing.

The experimental data revealed systematic mass dependent fractionation (MDF) during the equilibration experiments (72 h) with an enrichment of light Hg isotopes at the goethite surface (δ²⁰²Hg_{diss} - δ²⁰²Hg_{sorb} = 0.4 ‰). Low pH and increased Cl⁻ concentration reduced the sorbed fraction of Hg(II), but did not affect the isotope fractionation factor compared with pH 7. The amendment of 1M SO₄²⁻, resulting in a change of the Hg sorption complex from bidentate to monodentate (Kim et al., 2004), did not show any effect on the Hg isotope fractionation. Different equilibration times (18h – 30 d) did also not affect the observed isotope effect. These results strongly suggest that the observed isotope effect during sorption of Hg(II) to goethite is controlled by an equilibrium isotope effect between solution species. Computational chemistry calculations of mass-dependent and nuclear volume fractionation factors between solution species (Wiederhold et al., 2010) support this hypothesis by predicting for the sorption active Hg-cations (e.g. HgOH⁺) an enrichment of the lighter isotopes in the order of the experimentally observed 0.4 ‰ for δ²⁰²Hg relative to the dominant neutral solution species (e.g. Hg(OH)₂).

In combination with the previous findings on Hg(II) sorption to thiol groups (Wiederhold et al., 2010), a model study for sorption to organic matter, our data suggest that light Hg isotopes are preferentially sequestered in soils and one could expect an enrichment of heavy Hg isotopes in the mobile fraction which is leached from soils into surrounding ecosystems.

REFERENCES

- Kim, C.S., Rytuba, J., Brown, G.E. 2004: EXAFS study of mercury(II) sorption to Fe- and Al-(hydr)oxides – II. Effects of chloride and sulfate. *Journal of Colloid and Interface Science*, 270, 9-20.
- Wiederhold, J.G., Cramer, C.J., Daniel, K., Infante, I., Bourdon, B., Kretzschmar, R. 2010: Equilibrium Mercury Isotope Fractionation between Dissolved Hg(II) Species and Thiol-Bound Hg. *Environ. Sci. Technol.* 44, 4149-4197.

3.4

Geochemical composition of marine vertebrates from Sidi Chenanne (Ouled Abdoun Basin, Morocco)

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Phosphate rich sediments are mined in several regions in Morocco. The most actively mined area is the Ouled Abdoun Basin which one of the largest producing mines in the world. The phosphate series cover a time span of about 25 million years from the Maastrichtian to early Lutetian. These layers are very rich in vertebrate remains, which often form bonebeds. The far most frequent fossils are shark teeth and bony fish remains, but several other groups like crocodiles, turtles, mosasaurs are also quite common in certain beds. Some of the rare curiosities are the fossils of pterosaurs, «dinosaurs», birds and mammals. The fossil richness of these beds has drawn the attention of many scientists for years, and not only paleontologists but also geochemists (e.g. Grandjean et al. 1988; Lécuyer et al. 1993; McFadden et al. 2004). These later studies mainly focused on oxygen isotope and rare earth element (REE) compositions of the vertebrate fossils in order to assess paleo-environmental conditions (climate, oceanography, early diagenesis).

Here, a similar but a more detailed study, involving also carbon isotope composition of the remains, has been carried out in the Sidi Chennane area. The different phosphate layers were systematically sampled largely for shark teeth and coprolites, and prepared for the geochemical analyses. One of the main aims of our study is to test whether the fossils reflect or preserved any of the observed perturbations in the carbon cycle during and after the Paleocene-Eocene (P/E) boundary, namely the abrupt negative carbon isotope shifts at different hyperthermals (cf. Lourens et al. 2005).

Shark teeth enameloid yielded often positive $\delta^{13}\text{C}$ values possibly reflecting dissolved inorganic carbon (DIC) of seawater at the time, while the $\delta^{13}\text{C}$ values of coprolites, bones and dentin are very negative linking to burial conditions and reflecting the special environment of phosphate formation with the intensive recycling of organic matter. The variation is quite large along the series in these fossils, especially in some of the bonebeds that is maybe due to reworked specimens and also maybe enhanced oxidation of organic matter at these levels. Between the phosphate layer-I and -II, that are Ypresian and Danian-Thanetian in age, more negative values appear which might relate to the P/E boundary event.

Oxygen isotope composition of shark teeth show habitat related variations, while along the series a general decreasing trend is observed till the top of layer-I possibly linking to warmer conditions.

Rare earth elements in apatite fossils originate almost entirely from early diagenetic pore fluid and thus they can be used as a fingerprint of burial conditions and they often applied in taphonomical studies (Trueman & Tuross, 2002). In the Sidi Chennane fossils the REE distribution is quite alike for the whole series showing typical seawater pattern with negative Ce-anomaly and heavy REE enrichment. Ypresian and Maastrichtian fossils are separated on La/Sm vs. La/Yb plot, while the Paleocene ones overlap between them.

REFERENCES

- Grandjean, P., Cappetta, H. & Albarède, F. 1988: The REE and eNd of 40–70 Ma old fish debris from the West-African platform. *Geophys. Res. Lett.*, 15, 389–392.
- Lécuyer, C., Grandjean, P., O'Neil, J.R., Cappetta, H. & Martineau, F. 1993: Thermal excursions in the ocean at the Cretaceous–Tertiary boundary (northern Morocco): $\delta^{18}\text{O}$ record of phosphatic fish debris. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 105, 235–243.
- Lourens, L.J., Sluijs, A., Kroon, D., Zachos, J.C., Thomas, E., Röhl, U., Bowles, J. & Raffi, I. 2005: Astronomical pacing of late Palaeocene to early Eocene global warming events. *Nature*, 435, 1083–1087.
- MacFadden, B.J., Labs-Hochstein, J., Quitmyer, I. & Jones, D.S. 2004: Incremental growth and diagenesis of skeletal parts of the lamnoid shark *Otodus obliquus* from the early Eocene (Ypresian) of Morocco. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*, 206, 179–192.
- Trueman, C.N. & Tuross, N. 2002: Trace elements in recent and fossil bone apatite. In: Kohn, J.M., Rakovan, J., Hughes, J.M. (Eds.), *Review in Mineralogy and Geochemistry*, vol. 48, pp. 489–521.

3.5

Clumped isotope analysis of Pozalagua hydrothermal dolomite system (N Spain)

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Carbonate clumped isotope geochemistry is an innovative technique that allows to estimate the precipitation temperature of carbonate minerals. In addition, the determined clumped isotope temperatures in combination with the $\delta^{18}\text{O}$ values of carbonates permit us to calculate the $\delta^{18}\text{O}$ of the fluid in equilibrium with the carbonate mineral. We tested this new tool in well-exposed outcrops of the hydrothermal dolomite system of the Asón Valley (Basque-Cantabrian Basin, western Pyrenees) to better characterize its thermal and fluid history.

The methodology used in the Stable Isotope Laboratory at ETH Zurich follows that described in Schmid and Bernasconi (2010). We measure the clumped isotope composition in multiple carbonate generations that were previously studied by microscopy and by fluid inclusion geochemistry. We analysed hydrothermal dolomites (saddle and fine replacive dolomites), early and late calcites, and host limestones at different burial depths and distances from the main dolomite body. The different generations of carbonates show a large range of D_{47} ranging between 0.356 and 0.590‰ corresponding to temperatures between approximately 40 and 200°C, using the Guo et al. (2009) theoretical calibration.

Dolomites give temperatures ranging from 117 to 169°C and reconstructed $\delta^{18}\text{O}$ water values from -3.6‰ to 6.6‰, indicating that they are the product of different fluid sources (hypersaline brines, marine and mixture of meteoric and marine waters). Yellow calcite filling transpressional Alpine fractures shows the lowest temperature value (40°C) with quite negative $\delta^{18}\text{O}$ water value (-12.4‰) indicating a late shallow depth origin influenced by meteoric waters. These results are in agreement with macroscopic (outcrop) and microscopic (petrography) analysis of the dolomites (López-Horgue et al., 2010). Host rock samples give the highest temperatures ranging from 130 to 200°C. Presuming a loading of sediments before Alpine compression of 1900 m, the paleogeothermal gradient obtained is 68.4 – 105.3°C km⁻¹. This elevated paleogeothermal gradient is related to extreme crustal thinning during the Mesozoic rifting stage previously documented in the Basque Cantabrian Basin (e.g.: García-Mondéjar et al., 2005).

The temperature reconstructions combined with petrographic and oxygen isotopic analysis provide an ideal opportunity to trace thermal and fluid history of the hydrothermal system of the Valle Asón in extraordinary quantitative detail. This study shows the great potential of the clumped isotope method to improve our understanding of low temperature hydrothermal systems and to trace thermal histories of sedimentary basins.

REFERENCES

- García-Mondéjar, J., López-Horgue, M. A., Aranburu, A., & Fernández-Mendiola, P. A. 2005: Pulsating subsidence during a rift episode: stratigraphic and tectonic consequences (Aptian-Albian, northern Spain): *Terra Nova* 17 (6), 517-525.
- Guo, W. F., Mosenfelder, J. L., Goddard, W. A., & Eiler, J. M. 2009: Isotopic fractionations associated with phosphoric acid digestion of carbonate minerals: Insights from first-principles theoretical modeling and clumped isotope measurements: *Geochimica Et Cosmochimica Acta*, 73 (24), 7203-7225.
- López-Horgue, M. A., Iriarte, E., Schröder, S., Fernández-Mendiola, P. A., Caline, B., Corneyllie, H., Frémont, J., Sudrie, M., & Zerti, S. 2010: Structurally controlled hydrothermal dolomites in Albian carbonates of the Asón valley, Basque Cantabrian Basin, Northern Spain: *Marine and Petroleum Geology*, 27 (5), 1069-1092.
- Schmid, T. W., & Bernasconi, S. M. 2010: An automated method for 'clumped-isotope' measurements on small carbonate samples: *Rapid Communications in Mass Spectrometry*, 24 (14), 1955-1963.

3.6

Molybdenum scavenging from anoxic waters of the modern Black and Baltic Seas

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The isotope signature of molybdenum (Mo) is a relatively new proxy for paleo-redox conditions of the oceanic system. Mo is a redox-sensitive trace metal which is present in seawater as molybdate oxyanion with a long residence time of about 800 ka, resulting in a homogeneous seawater Mo isotope composition (Siebert et al. 2003). However, Mo is efficiently removed in the presence of sulfide and thus often enriched in reducing sediments. We analyzed samples from the Black Sea, the largest permanently euxinic basin and the type-system for sediment formation under anoxic conditions. Euxinic conditions prevail below the chemocline, at ~120 m water depth. A complementary sample set was taken from the Baltic Sea, the largest brackish basin of the world. Here, in two anoxic basins, the Gotland Deep and the Landsort Deep, have been included in the study. Most of the time, the water bodies are well stratified with a permanent pycnocline between 60 and 80 m depth. Water column profiles as well as surface sediment samples, were recovered from different water depths.

Dissolved Mo in all water samples is enriched in the heavy isotope ($\delta^{98}\text{Mo}$ values up to +2.9‰; $\delta^{98}\text{Mo}$ = deviation of $^{98}\text{Mo}/^{95}\text{Mo}$ from standard) compared to published isotope data of sedimentary Mo from the same water depths (Neubert et al. 2008). Furthermore, $\delta^{98}\text{Mo}$ values of all water samples from the Black Sea and anoxic deeps of the Baltic Sea are heavier than open ocean water (mean ocean Mo (MOMo) = +2.3 ‰). Near total removal of Mo from the water column is reached at aquatic sulfide concentration of ~11 μM (Erickson & Helz 2000). In the Black Sea this corresponds to a water depth of about 400 m. The corresponding sediment samples carry the signature of the main Mo source, ocean water, as expected from the mass balance. However, shallower sediments deposited under lower aquatic sulfide concentrations show significant Mo isotope fractionation. The sulfidity in the two deeps of the Baltic Sea is comparable to the Black Sea above 400m depth, and, as expected, the surface sediments show a similar Mo isotope fractionation.

While the observations are consistent, open questions remain concerning the of scavenging process: First, the extent to which Mo scavenging occurs in pore waters or within the sulfidic water column is still a matter of debate. Second, it is unclear whether the process is bidirectional (equilibrium) or unidirectional. Finally, the relative importance of the different oxythiomolybdates is not sufficiently constrained. These questions are approached applying a model (Nägler et al., 2011) involving published ab initio calculations of Mo isotope fractionation (Tossell 2005) and thermodynamic thiomolybdate distributions parameters (Erickson & Helz 2000). The model results indicate that the observed isotope fractionation between sediments and the anoxic water column of the Black Sea can readily be explained as decreasing importance of mono-, di-, or tri- thiomolybdate scavenging with increasing $\text{H}_2\text{S}_{\text{aq}}$. The model results further imply that Mo isotopic composition of the waters is in equilibrium with that of the sediments. The apparent equilibrium fractionation factor depends on the relative abundances of the different thiomolybdates, and thus $\text{H}_2\text{S}_{\text{aq}}$ abundance. An extrapolation to a theoretical pure MoS_4^{2-} solution indicates a fractionation factor between MoS_4^{2-} and authigenic solid Mo of $0.5 \pm 0.3\%$. Results from the Baltic Sea are in principle agreement with the model predictions, but may be affected by occasional large scale inflow events which lead to temporary disequilibrium distribution of thiomolybdates, due to the slow reaction kinetics of the MoOS_3^{2-} to MoS_4^{2-} transition.

$\delta^{98}\text{Mo}$ values of the upper mostly oxic waters of both basins are higher, and the Mo concentrations lower, than predicted by mixing models based on salinity. The results can be explained by non-conservative behavior of Mo under suboxic to anoxic conditions on the continental shelves, which, in case of the Black Sea, represent about 25% of its surface area. The suboxic to anoxic bottom water conditions favor preferential scavenging of lighter isotopes, leaving behind a heavy Mo isotopic composition in solution. Further, upwelling of deep saline water with heavy Mo isotopic signature and low Mo concentration may contribute to the $\delta^{98}\text{Mo}$ values of the upper waters.

In conclusion: 1) Data from euxinic water columns indicate in situ fractionation of Mo isotopes. 2) $\delta^{98}\text{Mo}$ of sulfidic waters and sediments are consistent with: a) Mo scavenging from the water column b) thiomolybdates scavenging c) equilibrium Mo isotope fractionation. 3) The apparent fractionation factor depends on relative abundances of the thiomolybdates and thus H_2S . The $\delta^{98}\text{Mo}$ between MoS_4^{2-} and sedimentary Mo is 0.5% +/- 0.3% . 4) $\delta^{98}\text{Mo}$ values of the upper waters of both basins indicate non-conservative behavior. This is most probably due to suboxic to anoxic Mo scavenging on the shelves.

REFERENCES

- Erickson, B.E., & Helz, G.R., 2000: Molybdenum(VI) speciation in sulfidic waters: Stability and lability of thiomolybdates, *Geochim. Cosmochim. Acta* 64, 1149-1158.
- Nägler, Th.F, Neubert, N., Böttcher, M.E., Dellwig, O. & Schnetger, B. 2011: Molybdenum isotope fractionation in pelagic euxinia: Evidence from the modern Black and Baltic Seas, *Chem. Geol.*, doi: 10.1016/j.chemgeo.2011.07.001
- Neubert, N., Nægler, T.F. & Böttcher, M.E. 2008: Sulphidity controls Molybdenum Isotope Fractionation into Euxinic Sediments: Evidence from the Modern Black Sea. *Geology*, 36; 10; 775–778
- Siebert, C., Nægler, T. F., von Blanckenburg, F., & Kramers, J. D., 2003: Molybdenum isotope records as a potential new proxy for paleoceanography, *Earth Planet. Sci. Lett.* 211, 159-171.
- Tossell, J.A., 2005: Calculating the partitioning of the isotopes of Mo between oxidic and sulfidic species in aqueous solution. *Geochim. Cosmochim. Acta* 69, 2981-2993.

3.7

Barium isotope fractionation in carbonates

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In this study, we present first results from a current research on barium isotope fractionation in marine carbonates. This isotopic system could allow a better understanding of the evolution of oceanic water masses. In particular the Ba isotopic signature in carbonates could be linked with paleo productivity, given that Ba reacts like a nutrient in the water column. Further, continental weathering and upwelling influence the oceanic cycle of Ba. A Ba(NO₃)₂ standard solution and standard natural limestone BSC-CRM 393, obtained from the Bureau of Analysed Samples, Ltd., Middlesborough, England, have been analyzed to set up and optimize analytical procedures for the determination of Ba isotopes in carbonates.

We developed a method to separate Ba and measure its isotopic composition with sufficient precision to discriminate the expected variations in natural environments. Samples were dissolved in acids of different molarity in order to determine the most efficient method. A ¹³⁰Ba/¹³⁵Ba double spike (von Allmen et al., 2010) was added to all samples. Chemical separation on cation columns only made use of PTFE vessels to avoid the contamination introduced by softeners in other plastic materials. Measurements were carried out on a Nu Instruments multicollector ICP-MS. Sample digestion with hot concentrated acid (6.4 M HCl; 12h on the hot plate), yield isotopic compositions consistent within ±0.11 ‰ (2 standard deviation, referring to the ¹³⁷Ba/¹³⁴Ba ratio), while the use of 2.5 M HCl causes a significant fractionation to lighter isotopic compositions. Similarly, Ba concentrations determined on hot concentrated acid attacks are in line with independent concentration determinations, while 2.5 M HCl attacks recovered only about 50% of the Ba. These indications point to incomplete dissolution in the 2.5 M HCl attack. Probably disseminated small barites are present in the carbonate standard, with a Ba isotopic composition different from that of a coexisting, more soluble Ba phase. The internal reproducibility of the standard solution is 0.1 ‰ 2SD (N=14).

The precision and reproducibility of our refined method encourages us to measure natural carbonates, such as a vertical transect along a fossil carbonate platform (to constrain the oceanic evolution with depth), or corals (to constrain the influence of water masses on skeletal Ba).

REFERENCES

- von Allmen, K., Böttcher, M., Samankassou, E., Nægler, F.T. 2010: Barium isotope fractionation in the global barium cycle: First evidence from barium minerals and precipitation experiments, *Chemical Geology*, 277, 70-77.

3.8

Forest use and damages recorded by trace elements and stable isotopes in recent speleothems from Milandre cave (JU)

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To test the suitability of speleothems from Milandre Cave (Boncourt, JU) for paleoclimatic and paleoenvironmental research, we analysed oxygen and carbon isotopes and a large range of trace elements in stalagmite M4 covering the period between 1822-2006 AC (chronology based on laminae counting).

Although many trace elements are probably of anthropogenic origin, the patterns of many pollution related trace elements do not correspond to the evolution of the concentrations in recognized archives for industrial pollution (e.g. Pb, Cu, Zn; cf. Fig 1). However, the sulphur in M4 corresponds to the SO₂ emissions (FOS) when considering an offset of about 30 years related to retention of S in the soil zone. The S-isotopic signature confirms a change in S-origin. The overlying soil acts thus probably as a reservoir for airborne and bedrock-derived elements. Mobilization of anthropogenic (e.g. Pb, Cu) and geogenic (e.g. Al, Ti) trace elements as solutes, colloids or particles is controlled mainly by soil stability and high infiltration events.

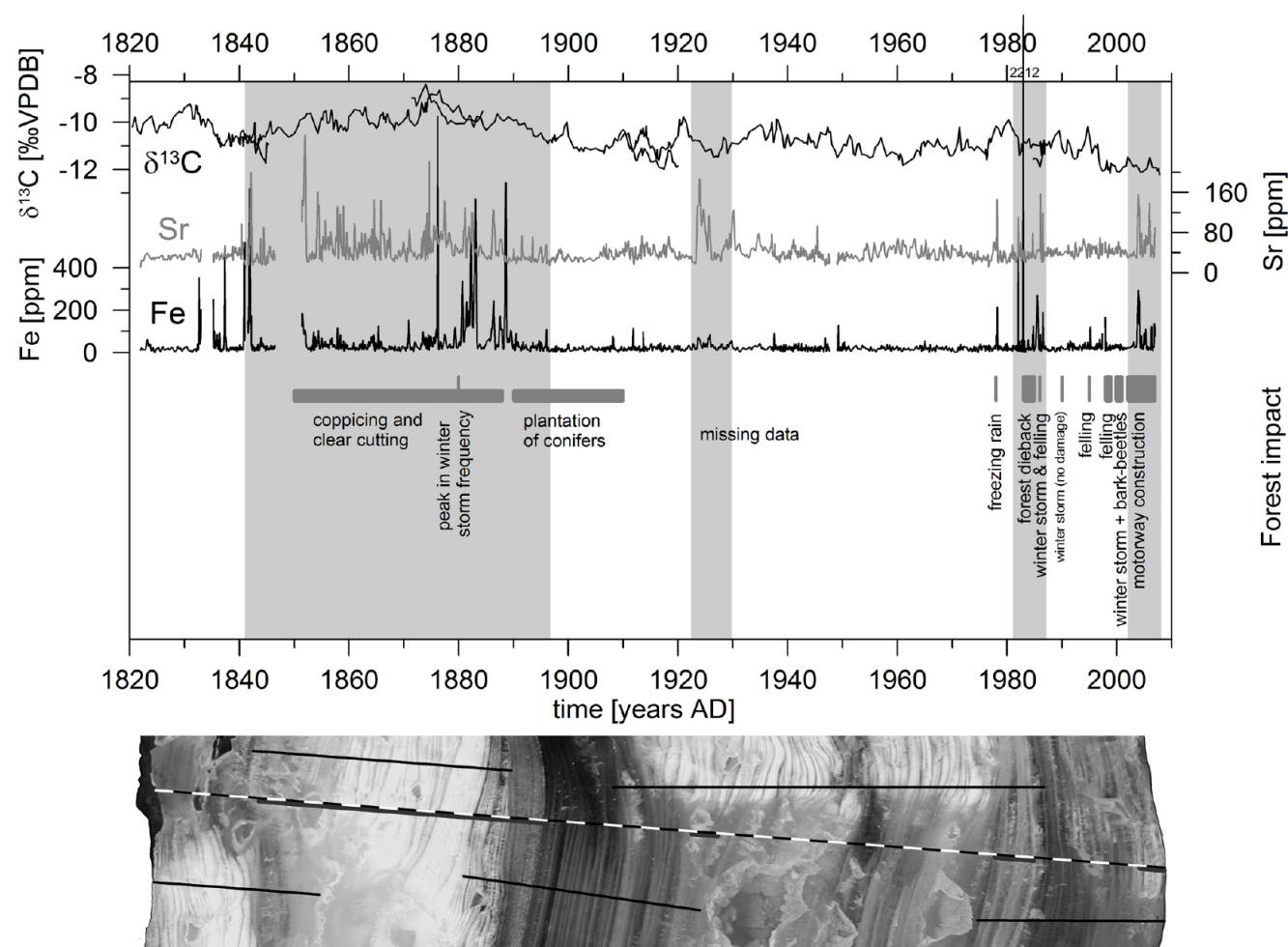


Figure 1. Comparison of Pb and S in stalagmite M4 from Milandre Cave with SO₂ emissions and an archive for anthropogenic Pb pollution (see legend for details). For Pb, no correlation is visible, S seems to record SO₂ air pollution with an offset of about 30 years.

Extreme events such as destructive storms (e.g. Lothar in 1999; winter storms in 1986), forest dieback due to air pollution (1980's), repeated coppicing and wood pasturing (19th century) are known to have affected the local forest and correspond well with the recorded high trace element concentrations in stalagmite M4 (Sr, Fe and many others ; Fig. 2). Stalagmite M4 is thus an appropriated archive for forest damages by extreme events and thus allows to extend the series of extreme events into the past. Some of them are confirmed by the reconstruction of forest damages (national level) by Usbeck et al. (2010).

The decrease in $\delta^{13}\text{C}$ in stalagmite M4 corresponds to a significant forest build-up and to increasing growing stock (i.e. forest density), confirming the importance of forest management practices and the soil for the M4 archive and the pertinence of $\delta^{13}\text{C}$ as a proxy for vegetation development in the Milandre Cave.

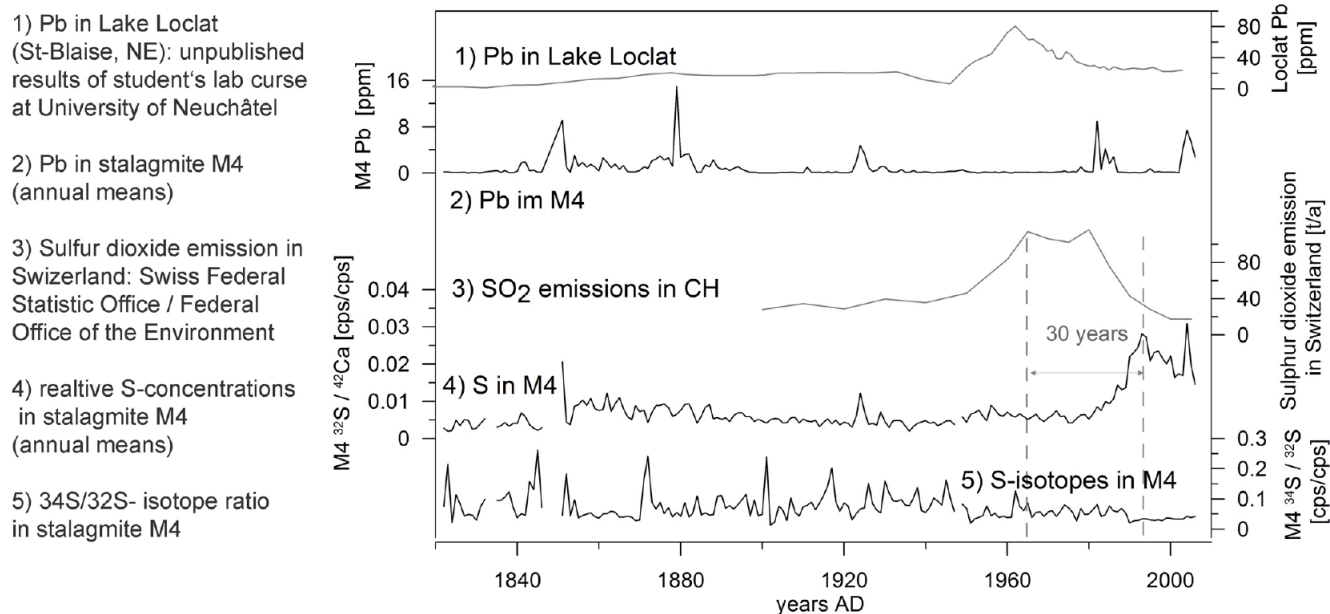


Figure 2:

$\delta^{13}\text{C}$, Sr and Fe concentrations in stalagmite M4 from Milandre Cave. Human and natural impact on the nearby forest (Augsburger & Monnin, 2009, personal communication). The sampling tracks for trace elements (1mm-scale bar) and stable isotopes (black lines) are indicated on a scan of M4.

REFERENCES

- Federal Office of Statistics (FOS) / Federal Office of the Environment (FOEN), www.bfs.admin.ch/bfs/portal/de/index/themen/02/06/indindicator.139201.1380.html
- Usbeck, T., Wohlgemuth, T., Dobbertin, M., Pfister C., Bürgi, A. & Rebetez, M. (2010). Increasing storm damage to forests in Switzerland from 1858 to 2007, *Agricultural and Forest Meteorology* 150, 47-55.

3.9

Molybdenum isotopes in river water: sources, fractionation processes and their importance for Mo cycling in the marine environment

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The fluxes of most elements from continents to oceans are largely controlled by river transport. The marine isotope inventory is thus strongly dependent on fractionation processes during continental weathering and subsequent river transport to the ocean basins. In the case of the highly redox sensitive molybdenum (Mo), the continental contribution accounts for the predominant part of the marine Mo budget. Mo isotopes ($\delta^{98/95}\text{Mo}$) in marine sediments have been used to investigate the evolution of atmospheric O_2 and to quantify the extent of ocean anoxia in the geological record. Such models strongly rely on accurate assumptions regarding the riverine Mo isotope input signature. In the past, its isotopic composition has been assumed to be fairly stable, reflecting the $\delta^{98/95}\text{Mo}$ of igneous crustal rocks (-0.1 to +0.3‰). Recent studies by Archer & Vance (2008), Pearce et al. (2010), Neubert et al. (2011) and Voegelin et al., (submitted), however, have revealed not only a general preferential enrichment of river waters in the heavy Mo isotopes but also a large $\delta^{98/95}\text{Mo}$ variability (-0.13 to +2.3‰). This pronounced discrepancy between the assumed crustal background and the aquatic signature emphasizes the need for a better understanding of Mo behavior during weathering and transport.

We present a compilation of our recent findings on Mo sources and fractionation processes in the terrestrial weathering environment. We discuss data of samples collected in river catchments in Switzerland (Entlebuch and Aare) and France (Massif Central). Sampling was selected to monitor potential controlling factors, i.e. basement geology, fractionation during weathering, within river precipitation and soil retention of Mo. The sampling locations differ with respect to their bedrock lithologies: while the streams in the French Massif Central are underlain exclusively by igneous crustal rocks, the bedrock in the Entlebuch and Aare catchments comprise evaporites, marine sediments and molasses.

Generally, the Mo isotope data of water samples and their associated bedrocks have revealed that, independent of source rock type, the observed $\delta^{98/95}\text{Mo}$ variations of 0 to +1.9‰ are primarily controlled by bedrock lithology. In the case of the Swiss river systems, the heavy Mo isotopic compositions of the sedimentary rocks have shown to be reflected in the river water $\delta^{98/95}\text{Mo}$. Thereby two very prominent effects were identified to control the aquatic Mo signature: weathering of sedimentary (evaporitic) sulfates and oxidative weathering of sulfides. In the case of the French catchment, the heavy stream water $\delta^{98/95}\text{Mo}$ signatures do not reflect the bedrock composition. Given that the bulk rock $\delta^{98/95}\text{Mo}$ reflects a value typical for crustal magmatic rocks (ca. 0.1‰), Mo fractionation during incongruent rock dissolution can explain the observed isotopically heavy aquatic Mo signatures. The dominance of this process is supported by the excellent agreement of the stream water data with those of Mo released during experimental basalt leaching. Results of mass balance calculations, based on single grain and matrix laser ablation data, identify the rare, but in part highly Mo-enriched sulfide melt inclusions as the principal, isotopically heavy Mo source for the leach solutions and hence the stream waters. Incongruent crustal bedrock weathering may thus cause a preferential release of heavy Mo isotopes. This, however, is highly dependent on the primary bedrock mineralogy.

Despite being a potential pathway for the removal of light isotopes, soil retention of Mo or its adsorption to the particulate load do not play a dominant role in driving the river water Mo towards the heavy signatures observed in the catchments investigated here. Generally speaking, the isotopically heavy Mo of river waters is most likely the result of a complex interplay between various processes involved, and the mass balance between the competing factors likely controls the aquatic $\delta^{98/95}\text{Mo}$. The local system is thus highly dependent on rock mineralogy, degree of rock weathering and soil development, secondary mineral precipitation and adsorption. The finding that catchment geology exerts a primary control on the delivery of Mo to seawater indicates that the flux and isotope composition of molybdenum to seawater has likely varied in the geologic past. These variations are closely linked to e.g. the continents' configuration, the average age of the sediments exposed to erosion, weathering intensity and climate.

REFERENCES

- Archer, C. & Vance D., 2008: The isotopic signature of the global riverine molybdenum flux and anoxia in the ancient oceans. *Nature Geoscience* 1, 597–600.
- Neubert, N., Heri, A. R., Voegelin, A. R., Nägler, T. F., Schlunegger, F. & Villa, I. M. 2011: The molybdenum isotopic composition in river water: Constraints from small catchments, *Earth and Planetary Science Letters*, 304, 180-190.
- Pearce, C. R., Burton, K. W., Pogge von Strandmann, A. E., James, R. H. & Gislason, S. R. 2010: Molybdenum isotope behaviour accompanying weathering and riverine transport in a basaltic terrain, *Earth and Planetary Science Letters*, 295, 104-114.
- Voegelin, A. R., Nägler, T. F., Pettke, T., Neubert, N., Steinmann, M., Pourret, O. & Villa, I. M. submitted: The impact of igneous bedrock weathering on the Mo isotopic composition of stream waters: Natural samples and laboratory experiments.

3.10

Mass-dependent and mass-independent fractionation of stable mercury isotopes as tracer for anthropogenic pollution in the environment

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Mercury (Hg) is a toxic heavy metal that represents a serious hazard for human and ecosystem health at local and global scales. Anthropogenic activities (e.g., combustion, industry, mining) have increased global Hg cycling by about a factor of three compared with pre-industrial times. Although the biogeochemical cycling of mercury in the environment has been studied extensively over the last decades, many questions concerning sources, transformations, and the fate of Hg species in natural ecosystems still remain unclear.

The recent improvement of analytical methods, namely cold-vapor multicollector inductively-coupled plasma mass spectrometry (CV-MC-ICP-MS), has resulted in the detection of significant variations of Hg isotope ratios in natural samples caused by fractionation processes (Blum et al. 2011). Thus, stable Hg isotope signatures represent a promising new tool to trace Hg cycling in the environment by providing information on source materials and transformation processes which fractionate Hg isotope by various mechanisms.

The stable Hg isotope system is different compared to most other metal stable isotopes due to the occurrence of both mass-dependent (MDF) and mass-independent (MIF) fractionation which are affecting the even- and odd-mass Hg isotopes to a different extent (Figure 1). Thus, the Hg isotope signature of a natural sample contains multiple dimensions which can be exploited to track sources and transformation processes of Hg in nature.

Mass-independent fractionation of Hg isotopes was first reported for photochemical reactions (Bergquist & Blum 2007) which are also responsible for large MIF signatures in natural samples and probably caused by magnetic isotope effects during kinetic radical-pair reactions affecting only the odd-mass Hg isotopes which possess nuclear spin and a magnetic moment (Buchachenko 2009). In addition, smaller MIF effects of Hg isotopes can be caused by nuclear volume fractionation (Schauble 2007; Wiederhold et al. 2010) due to the non-linear increase of nuclear charge radii with isotopic mass.

Here, we present Hg isotope data from different anthropogenically polluted field systems (e.g., mining environments, sediments polluted by industrial sources) measured by CV-MC-ICP-MS to demonstrate the potential of Hg isotopes as environmental tracer and discuss ongoing laboratory studies to determine fractionation mechanisms and factors for individual Hg species transformations.

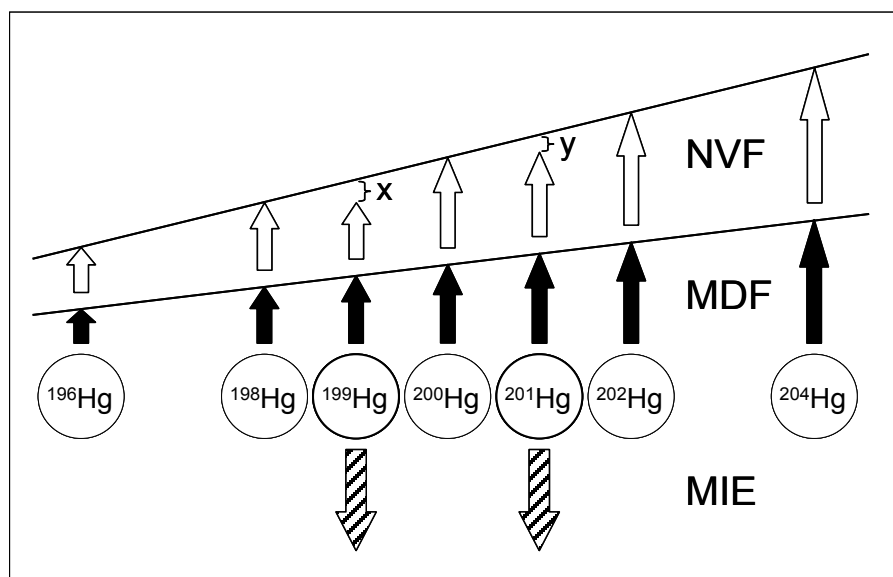


Figure 1. Schematic picture of stable Hg isotope fractionation by mass-dependent fractionation (MDF), nuclear volume fractionation (NVF), and magnetic isotope effect (MIE). Mass-independent fractionation (MIF) can be caused either by NVF (non-linear increase of nuclear charge radii with $x/y \sim 1.65$) or MIE (odd-mass isotopes with nuclear spin and magnetic moment are fractionated in kinetic radical-pair reactions relative to even-mass isotopes).

REFERENCES

- Bergquist, B.A. & Blum, J.D. 2007: Mass-dependent and -independent fractionation of Hg isotopes by photoreduction in aquatic systems. *Science* 318, 417-420.
- Blum, J.D. 2011: Application of stable mercury isotopes to biogeochemistry. In: *Handbook of environmental isotope geochemistry* (Ed. by Baskaran, M.), Springer, Chapter 12, 229-245.
- Buchachenko, A.L., 2009: Mercury isotope effects in the environmental chemistry and biochemistry of mercury-containing compounds. *Russian Chemical Reviews*, 78, 319-328.
- Schauble, E.A. 2007: Role of nuclear volume in driving equilibrium stable isotope fractionation of mercury, thallium, and other very heavy elements. *Geochimica et Cosmochimica Acta*, 71, 2170-2189.
- Wiederhold, J.G., Cramer, C.J., Daniel, K., Infante, I., Bourdon, B., Kretzschmar, R. 2010: Equilibrium mercury isotope fractionation between dissolved Hg(II) species and thiol-bound Hg. *Environmental Science and Technology*, 44, 4191-4197.

3.11

Silicon isotopic fractionation in marine sponges: A new paradigm and model for understanding silicon isotopic variations in sponges

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The modern Southern Ocean plays a pivotal role in determine the air-sea balance of CO₂ and global biological production. However, there is debate regarding nutrient utilisation in Southern Ocean surface waters and how this transfers through to the deeper Southern Ocean, especially during the past. To fill this gap we have determined the silicon isotope composition of deep-sea sponges collected from near Antarctica, subantarctic waters (Tasmania Seamounts) and subtropical waters north of New Zealand with the aim of developing a new paleo-nutrient proxy. For deep-sea sponges, $\delta^{30}\text{Si}$ values widely between 0.87 ‰ and -3.40 ‰ (vs NBS). Depth profiles show that sponge $\delta^{30}\text{Si}$ compositions trend to lighter values with increasing depth. This is exemplified by sponges from the Tasmanian Seamounts which vary from 0.87 ‰ to -3.13 ‰ over a depth range from 100 to 1200 m. We find that silicon isotope fractionation ($\delta^{30}\text{Si}$ sponge - $\delta^{30}\text{Si}$ seawater) varies with seawater silicon concentration with more fractionated (lighter) isotope values being associated with specimens collected from water high in silicon. A mass-balance based model for silicon isotope fractionation is consistent with $\delta^{30}\text{Si}$ fractionation driven by changes in the difference between the silicon influx and efflux from the sponge. At higher seawater silicon concentrations efflux is correspondingly higher, and with $\delta^{30}\text{Si}$ having an apparent greater internal fractionation, this results in lighter $\delta^{30}\text{Si}$ spicule values. This model can also explain $\delta^{30}\text{Si}$ fractionation in diatoms and be used to reconstruct past seawater silicon concentrations from the $\delta^{30}\text{Si}$ signature of fossil sponges and diatoms.

P 3.1

A volcanically induced climate warming and floral change preceded the onset of OAE1a (Early Cretaceous)

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The Aptian Oceanic Anoxic Event 1a (OAE1a) is preceded by a prominent negative C-isotope excursion (NCIE) attributed to major volcanism on the Ontong-Java plateau that is supposed to lead to a $p\text{CO}_2$ increase and a climate change. Lower Aptian sporomorph assemblages in two pelagic sections from the southern Tethys margin (N-Italy) were analysed in order to test if the postulated climate changes affected the terrestrial vegetation.

At the base of the NCIE the sporomorph assemblages comprise abundant bisaccate pollen reflecting a warm-temperate climate (Fig. 1). Several tens of kiloyears (ka) after the start of the NCIE decreasing bisaccate pollen and increasing *Classopollis* spp. and *Araucariacites* spp. suggest the beginning of a long-term temperature rise (Fig. 2). Palynomorphs indicate that maximum temperatures were reached several tens of ka after the end of the NCIE and the onset of OAE1a. The highest temperatures coincide with arid conditions, which could reflect a northward shift of the hot-arid Northern Gondwana floral province as a result of an increasing $p\text{CO}_2$. Over 200 ka after the onset of OAE1a reduced volcanic activity and/or increased black shale deposition allowed for a drawdown of most of the excess CO_2 and a southward shift of floral belts.

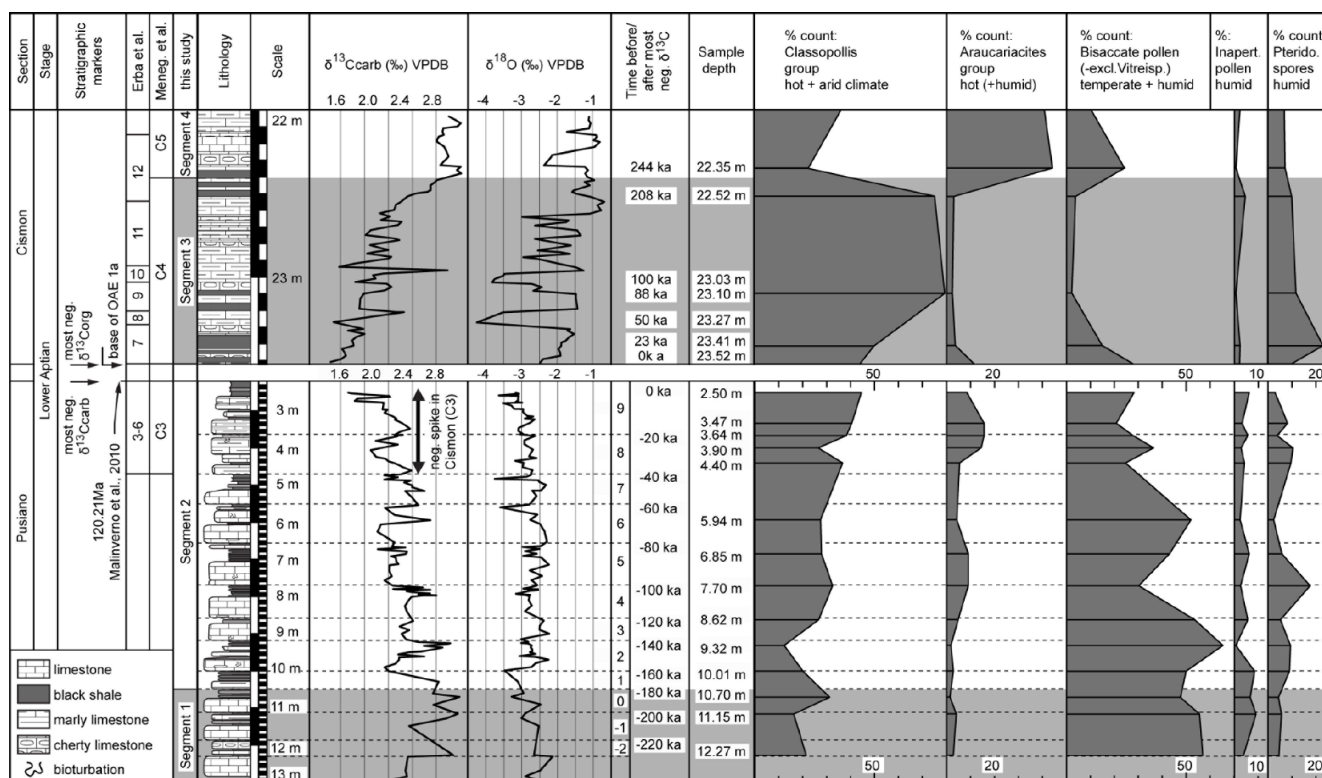


Figure 1 (Keller et al. 2011). Composite section of Pusiano and Cision showing the C_{carb} - and O-isotopes and the succession of sporomorph assemblages (%) through the negative C-isotope excursion (NCIE; Pusiano section, segment 2) and the onset of Oceanic Anoxic Event 1a (OAE1a; Cision section, segments 3–4, from Hochuli et al. 1999). Limestone-black shale couplets in Pusiano are considered to reflect orbital precession (~20 kiloyears (ka)). Timing for Pusiano: number of limestone-black shale couplets / time in estimated ka before the end of the NCIE. Timing for Cision: ka after onset of OAE1a (sedimentation rate from Malinverno et al., 2010). For further information see Keller et al. (2011).

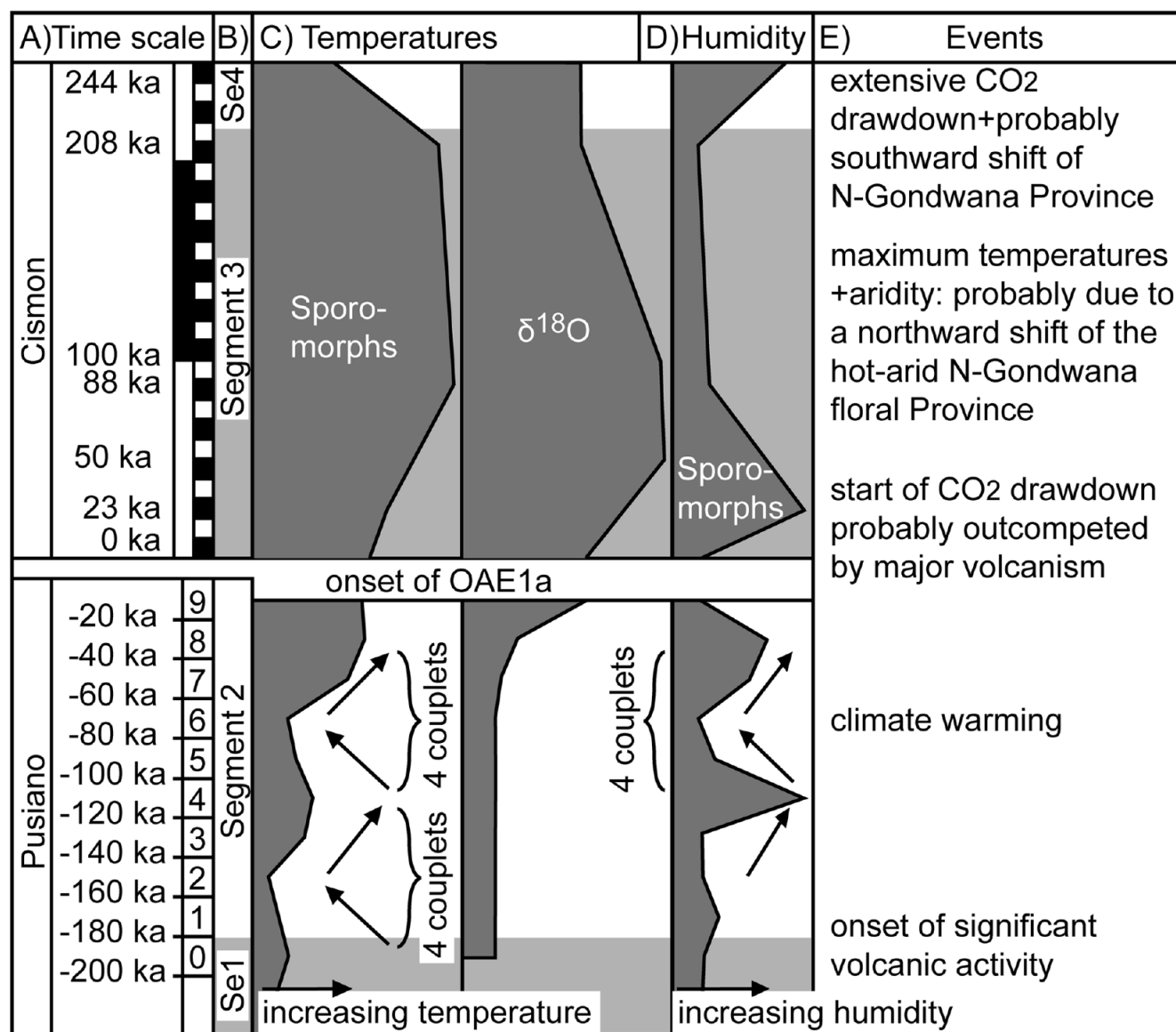


Figure 2 (Keller et al. 2011). Estimated evolution of temperature and humidity for the composite section of Pusiano and Cismon. A) Time scale. B) Segments (see Fig. 1). C) Relative temperature changes inferred from sporomorphs and $\delta^{18}O$. D) Relative humidity changes. E) Climate-related events. For further information see Keller et al. (2011).

REFERENCES

- Hochuli, P.A., Menegatti, A.P., Weissert, H., Riva, A., Erba, E. & Silva, I.P. 1999: Episodes of high productivity and cooling in the early Aptian Alpine Tethys. *Geology*, 27, 657–660.
- Keller, C.E., Hochuli, P.A., Weissert, H., Bernasconi, S.M., Giorgioni, M. & Garcia, T.I. 2011: A volcanically induced climate warming and floral change preceded the onset of OAE1a (Early Cretaceous). *Palaeogeography, Palaeoclimatology, Palaeoecology*, 305, 43–49, doi:10.1016/j.palaeo.2011.02.011.
- Malinverno, A., Erba, E. & Herbert, T.D. 2010: Orbital tuning as an inverse problem: Chronology of the early Aptian oceanic anoxic event 1a (Selli Level) in the Cismon APTICORE. *Paleoceanography*, 25, PA2203, doi:10.1029/2009PA001769.

P 3.2

In the Tethys Ocean black shales commonly formed prior to Oceanic Anoxic Event 1a (OAE1a, Early Aptian, ~120 Ma ago)

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The Early Aptian Oceanic Anoxic Event 1a (OAE1a) is attributed to increasing oxygen deficiency in the ocean waters as a result of climate changes triggered by major volcanic outgassing related to the formation of the Ontong Java plateau. However, onset of black shale deposition was not globally simultaneous and under specific palaeogeographic and palaeoceanographic conditions occurred already before OAE1a. In order to identify conditions favouring pre-OAE1a black shale formation, we compared four pelagic Tethyan sections (northern Italy and Switzerland), in which we analysed the evolution of CaCO₃/total organic carbon (TOC) content before and at the onset of OAE1a.

Throughout the studied stratigraphic interval, the sections record frequent precession controlled changes in carbonate content, which are reflected by limestone-marlstone alternations in the shallower sections and by limestone-black shale couplets in the deepest section, at the locality of Pusiano. Depth controlled suboxic to anoxic conditions in the water column are also suggested by the prominent OAE1a black shales, which occurred first in the deeper Pie del Dosso and Roter Sattel sections and only subsequently in the shallower Cismon section. However, contrary to expectations, the deepest Pusiano section exhibits – instead of an earliest onset of prominent OAE1a black shales – only a minor increase in TOC with a corresponding decrease in carbonate content.

This suggests that the orbitally driven climate changes most strongly influenced water stratification and hence are most prominently expressed in the deepest sections. Conversely, the volcanically induced long-term climate changes seemed to more strongly affect organic matter production, the extension of the oxygen minimum zone and hence had the strongest impact on sections at intermediate depth.

P 3.3

Mercury Isotope Fractionation as Biogeochemical Tracer in Ore Waste

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High concentrations of mercury (Hg) can often be found in the environment around inactive Hg mines. During mine operation, rock containing the primary ore mineral HgS was crushed and heated in furnaces to temperatures of ~ 700 °C (calcination). Most of the resulting elemental Hg vapor was condensed and collected for various industrial uses. The remaining mine tailings (calcines) were then piled on site. This removal process was not complete and significant amounts of Hg remained in the calcines. Large pieces of calcine often exhibit a characteristic internal layering, with dark-grey cores, light-grey outer rims, and red outer surface layers. Previous studies have shown that Hg speciation in calcines is dominated by stable α -HgS & β -HgS, but consists of a small proportion of more soluble secondary Hg phases. The speciation of the Hg-bearing compounds in these wastes determines the solubility, volatility, and thus mobility of the Hg remaining in the calcines (Kim *et al.* 2004; Jew *et al.* 2011).

Various environmental processes fractionate the stable Hg isotopes via mass-dependent (MDF) and/or mass-independent fractionation (MIF); however, the controlling mechanisms are not fully understood. These fractionation signatures are a potentially useful “two-dimensional” tool to study the biogeochemical cycling of Hg and its transformations and fluxes from highly contaminated mining environments (Stetson *et al.* 2009). Here we report stable Hg isotope results for different layers in calcine cobbles collected from two sampling locations from the former New Idria Hg mine, San Benito County, CA, USA.

Differently colored layers in the calcines were carefully separated using a diamond saw or were chipped with chisels. The horizon pieces were then ground to a powder using a tungsten carbide rotary disk mill, followed by a total digestion in aqua regia. Mercury concentration analyses were conducted using cold vapor-AFS and isotopic analyses were performed on a Nu Plasma MC-ICP-MS with cold vapor introduction. Mass bias was corrected by a combination of standard-sample bracketing and Tl addition. Data for MDF are reported as $\delta^{202}\text{Hg}$ relative to the NIST-3133 standard. MDF is calculated by the following formula:

$$\delta^{202}\text{Hg} [\text{‰}] = 1000 \left(\left[\frac{(^{202}\text{Hg}/^{198}\text{Hg})_{\text{sample}}}{(^{202}\text{Hg}/^{198}\text{Hg})_{3133}} \right] - 1 \right)$$

Our analyses revealed significant concentration gradients across the different layers, with higher Hg concentrations in outer rims and lower concentrations in inner regions. Bulk calcine samples from one area sampled are isotopically heavier than ore and unroasted ore wastes, and significant MDF $\delta^{202}\text{Hg}$ gradients exist from isotopically heavy centers to lighter rims. Bulk samples from a second sampling site display smaller magnitude fractionation and the opposite MDF trend, with isotopically lighter centers and heavier rims. These findings suggest that incomplete roasting of ore rocks led to pronounced Hg isotope gradients which were presumably caused by kinetic effects during diffusive processes. The highly fractionated Hg isotope ratios of calcine materials, together with the higher solubility of secondary Hg phases which have formed during or after roasting, will have important implications for the isotope signature of Hg which is exported from the former mine into the surrounding ecosystems.

REFERENCES

- Jew, A.D., Kim, C.S., Rytuba, J.J., Gustin, M.S., Brown, G.E. 2011: New technique for quantification of elemental Hg in mine wastes and its implications for mercury evasion into the atmosphere. *Environmental Science and Technology*, 45, 412-417.
- Kim C.S., Rytuba, J.J., Brown, G.E. 2004: Geological and anthropogenic factors influencing mercury speciation in mine wastes: an EXAFS spectroscopy study. *Applied Geochemistry*, 19, 379-393.
- Stetson, S.J., Gray, J. E., Wanty, R.B., Macalady, D.L. 2009: Isotopic Variability of Mercury in Ore, Mine-Waste Calcine and Leachates of Mine-Waste Calcine from Areas Mined for Mercury. *Environmental Science and Technology* 43, 7331-7336.

