

# *EUG XI*



Symposium EVO7

Geological History of Sea-Water

Convenors

Heide Zimmermann  
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# EVO7

## Geological History of Sea-Water

### Sunday PO Session

#### EVO7 : SUPO01 : PO Hauterivian-Barremian Sea Level Fluctuations in Central Part of Northern Caucasus-Scythian Platform Area

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The study of Hauterivian - Barremian evolution of Northern Caucasus - Scythian Platform basin is based on detailed investigation and correlation of 11 outcrops and about 400 boreholes in the central - eastern part of the region. Hauterivian and Barremian sediments of this region are represented by shallow marine terrigenous and carbonate-terrigenous succession, which reaches 500 m in thickness. It was recognised that accumulation of the succession was controlled mainly by sea-level changes. The Hauterivian and Barremian deposits are subdivided into four formations, which coincide with system tracts of the same sequence. The lower Korinsk Formation (Acanthodiscus radiatus ammonite Zone) consists of clays and silts. It was formed during fast sea-level rise and continues latest Valanginian transgression. The sea transgressed onto different structures and moved in the northern direction. The following Argudan Formation (Cricoceratites loryi Zone) consists of sandstones with silty detritic and oolitic limestones. The deposits are distributed wider and indicate sea-level rising. The Baksan Formation (Speonoceras inversum Zone) is build up of sandstones and covers larger area. The Uruk Formation (Craspedodiscus discolifolius Zone of Uppermost Hauterivian to Barremian) consists of obliquely laminated oolitic sandstones, clays and limestones with insignificant disconformities. It was formed during termination of transgression and then under regressive conditions in a shallow basin with active hydrodynamics. The latter phase was finished in the late Barremian (the base of Imerites giraudi Zone), when the condense sections and avandeltaic facies were formed. The coarseness of terrigenous material increases north- westwards in each system tract where, as we suggest, the land has existed. Thus the Hauterivian part of the succession was formed under transgressive conditions, which is in a good agreement with the eustatic curve. However, the Barremian part does not fit well in the eustatic curve: it began with the transgressive phase, which in the middle late Barremian was changed into regression. The maximum of the highstand coincides with the beginning of the late Barremian. This conclusion is confirmed by the most extensive distribution of Lower Barremian Moutoniceras moutonianum Zone sediments. The area of their distribution is limited by Mineralovodskiy Uplift in the west and by Manych Trough in the north. The lowstand coincides with Valanginian / Hauterivian, Lower / Late Hauterivian and Barremian / Aptian boundaries, which is also in agreement with the eustatic curve.

#### EVO7 : SUPO02 : PO Lithological Cycles- Sedimentological Proxy for Researching of Late Cretaceous Paleogeography

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22 sections of mostly carbonate rocks of Upper Cretaceous were investigated on the Russian craton and NW Caucasus (Russia) and SW Crimea (Ukraine) by complex of petromagnetic, petrographic, geochemical, geophysical and paleontological methods. Described sections were divided into cyclic, non-cyclic and cryptocyclic (periodic fluctuations of petromagnetic parameters in the visually non-cyclic section). In the cyclic parts of sections 16 types of lithological cycles were observed: sand, sandstone - carbonate sandstone (1); sandstone-clay (2); sandstone-marl (3); sandstone-limestone (4); clay-marl (5); sandy marl-marl (6); marl-marl (7); marl-limestone (8); limestone-limestone (9); limestone-clay (10); chalk-clay (11); chalk-marl (12); chalk-chalk (13); sandstone-silty clay-clay silt (14); sandstone-clay-limestone (15); marl-cherty marl-sandy marl (16). 13 paleogeographic models and 3 main mechanisms of origin of rhythms (dilution, solution and bioproductivity cycles) were discussed for 16 types of lithological cycles from 22 investigated sections

(Russian craton; Betovo, Chernetovo, Fokino, Stoylesky GOK, Sengeley, Hvalynsk, Volsk, Shikhany, Nizhnaya Bannovka; Caucasus: Andreevsky Pereval, Aderbyevka, Betta, Kolhoznaya Stchel; Crimea: Maloe Sadovoe, Besh-Kosh, Kizil-Chigir, Aksu-Dere, Mender, Selbuhra (1-3), Kacha). Comparing data with data from 28 sections of Upper Cretaceous deposits of Euroasia (Zumaya, Relleu, Agost, Speeton, Compton Bay, Calver Cliff, Eastburn, Dover, Blan-Nez, Vergons, St. Lion, Enci, Leeks, Misburg, Zalzgitter-Zalder, Baddikenshtadt, Hoppenshtadt, Lengerich, Rein, Vandsdorf, Umbria, Castagne, Cismon, Gamba Zong Shan), Africa (Kalaat Senan), North America (WIB, Alabama, Gulf of Mexico) and Australia (Exmouth Plateau) time-space distribution of lithological cycles, mechanisms and paleogeographic models were analyzed. 1. The most abundant type of cycles are limestone-marl alteration. 2. 16 types of lithological cycles can be classified into 5 groups (shallow marine-hemipelagic (1), hemipelagic (2), hemipelagic-pelagic (3), shallow marine and pelagic (4) and "cosmopolitan"(5)). 3. The maximal diversity of rhythms characterizes shallow marine and pelagic conditions. 4. Paleogeographic models can be divided into 3 classes: shallow marine-hemipelagic (1), hemipelagic-pelagic (2) and "cosmopolitan"(3). 5. Number of types of rhythms varies during Late Cretaceous: Cenomanian - 8 types, Turonian - 14 types, Coniacian - 3 types, Santonian - 3 types, Campanian - 5 types, Maastrichtian - 10 types. Turonian and Maastrichtian peaks of diversity correlates with the regressive trends of the long term eustatic curve (Hardenbol, 1998). 6. Quantity of types of paleogeographic models proposed changes in time: Cenomanian - 7 types, Turonian - 6 types, Coniacian - 2 types, Santonian - 4 types, Campanian - 3 types, Maastrichtian - 5 types. 7. Main factor responsible for rhythm's forming is thought to be dilution cycles (16 types of lithological cycles). Solution cycles promote the occurrence of 13 types of rhythms. Bioproductivity cycles cause appearance of 6 types of rhythms. Founded laws of bathymetric and time distribution of cycles, mechanisms and paleogeographic models are proposed to analyze the changes in the Late Cretaceous paleogeography.

#### EVO7 : SUPO03 : PO Mn/Fe-Concretions Record the Last 4300 Years of Pb-Isotope Variations in Baltic Seawater

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Increasing attention has been directed to Baltic Mn/Fe-enrichment, because of their potential use as geochemical archive for heavy-metal pollution of the Baltic Sea over post-glacial times. However, earlier attempts to reconstruct Baltic seawater history lag high resolution time series of environmental sensitive proxies and precise absolute chronologies. Latter problem has recently been overcome by the development of the <sup>226</sup>Ra<sub>0</sub>/Ba-dating technique, which provide an absolute chronology for Baltic Mn/Fe-concretions (Liebetrau et al., 1999). In this study we present Pb-isotope measurements (TIMS) in order to test whether or not the Pb-isotopic record can be used as a monitor for natural versus anthropogenic induced chemical changes of the Baltic seawater composition. For our investigations we have chosen a Mn/Fe-concretion (VL-99/2) from the Mecklenburg Bay (54°10'N, 11°21'E, 20 m water depth) which was recently dated by the <sup>226</sup>Ra<sub>0</sub>/Ba-dating technique to be about 4300 years old (Liebetrau et al., 1999).

The <sup>206</sup>Pb/<sup>207</sup>Pb ratios of crust VL-99/2 remained constant around 1.28 from about 4300 to about 2500 years BP. A drastic drop of the <sup>206</sup>Pb/<sup>207</sup>Pb signal to ratios around 1.23 occurred from about 2500 to 1700 years BP. Then, in the time interval from 1700 to 1000 years BP, the signal remained fairly constant on that level. Starting at about 1000 years BP it declined towards the present value of about 1.19. The pattern of our <sup>206</sup>Pb/<sup>207</sup>Pb record is fairly similar to the <sup>206</sup>Pb/<sup>207</sup>Pb record of Shotyk et al. (1998) for a peat bog (Jura Mountains, Switzerland) which is interpreted to reflect anthropogenic perturbations of the natural Pb-cycle. Given that our record may also reflect anthropogenic perturbations of the Pb-cycle rather than being

simply due to diagenetic alteration, Baltic Mn/Fe-concretions can be considered to be an archive for past, in particular historical geochemical variations in the water column of the Baltic Sea. However, further measurements and independent verification are required before final conclusions can be drawn.

Shotyk W, Weiss D, Appleby PG, Cheburkin AK, Frei R, Gloor M, Kramers JD, Reese S & Van Der Knaap WO, *Science*, **281**, 1635-1640, (1998).  
Liebetrau V, Eisenhauer A, Gussone N, Wörner G & Hansen BT, *EOS Trans. Am. Geophys. Union*, **80**, 538, (1999).

#### EVO7 : SUPO04 : PO The Effects of Declining Ocean Salinity on Climate during the Phanerozoic

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Assuming that evaporites on land follow the same rates of sedimentary cycling as other sedimentary materials, it is possible to determine both the original size of the deposits and to calculate the flux of salts to the sea as they have been eroded. We assume that salt removals into the deep offshore, continental margin, and marginal sea deposits are not yet part of the recycling system. The reconstructions indicate that during most of the Phanerozoic salinities have been higher than they are today. Each of the major salt extractions into the offshore has caused a rapid decrease of oceanic salinity by a few per mille. In the Early Cretaceous mean ocean salinities ranged between 38 and 42, and the Jurassic and Triassic they were between 43 and 48. Paleozoic salinities were in the low 50's. The Phanerozoic decline in mean ocean salinity may have played a significant role in the development of climate. Below a salinity of 24.7, the freezing point of water lies below the temperature of maximum density. Above salinity 24.7 the freezing point lies above the temperature of maximum density. At today's average ocean salinity, 34.7, the density of seawater changes only very slightly as the freezing point is approached, but at salinities of 45 or higher, the change of density as seawater cools to the freezing point is significant and continuous. At salinities in the upper 40's or lower 50's, seawater will become denser as it cools and will sink. This means that during the Paleozoic and perhaps Triassic, deep water formation would have taken place wherever the water is coolest, i.e. in the polar regions. As the salinity declined during the Jurassic and Cretaceous toward modern values the density increase required to make water sink is achieved through salinization via either of two processes: sea-ice formation or evaporation. Both of these processes involve large transfers of latent heat between the ocean and atmosphere. The effect is to closely couple the atmosphere and ocean heat transport systems. In particular, this coupling served to limit the energy transport through the ocean's thermohaline circulation to less than 10% of the total meridional energy transfer. This limiting condition may not have existed in the earlier Phanerozoic. These changes imply significantly different changes in the role of the atmosphere and ocean in global climate regulation prior to the Jurassic.

# EVO7

## Geological History of Sea-Water

### Monday PM Session

**EVO7 : MOPm21 : F5**  
**Seawater Composition, BIF Deposition, Glaciation and the Rise of Oxygen: Major Changes Linked by a Late Archaean/Early Proterozoic Change in the Internal Behaviour of the Earth**

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The interval 2.45-2.2 Ga saw a uniquely vast deposition of BIF (banded iron-formation). It also marks, globally, a still-empty age-gap both for greenstone belts and for orogenic granitoids. What was going on?

During the preceding 500 Ma, from about 2.9 Ga, there was major acceleration in the rate of crustal addition to cratons. This process (Osmaston, 1999a), involved the widespread intrusion of successive greenstone belts by TTG granitoids, derived from subduction interface melts whenever 'flat-slab' subduction beneath was interrupted. So it advectively deprived the mantle of heat which subduction would otherwise have returned to the mantle budget. This, in turn, rendered subduction even more susceptible to interruption, thus accelerating the repetition (Osmaston, 2000). The increasing depositional water-depth of inter-pillow sediments on greenstone belts during this time is consistent with declining mantle heat. It is therefore reasonable to attribute the gap in greenstone and granitoid dates to a 'hiatus' in upper mantle convective overturn (Osmaston, 1999b). How did this affect seawater?

Accelerated deposition of oxide-facies BIF, beginning about 2.75 Ga, was clearly not due to a sudden increase in Fe<sup>++</sup> from MORs, especially if these were declining; it must have been accumulating in solution. The same applies to the even greater amount of silica in the BIF. These requirements, together with studies of Cameron crater lakes, suggest the following 'specification' for ocean water at ~2.75 Ga. Below a chemocline, the fumarole-maintained pH was ~4.5, Fe<sup>++</sup> content was over 80 ppm and the mean temperature (to the floor) was ~25°C, with an inverted temperature gradient maintained by the Fe<sup>++</sup> density gradient.

The following history then emerges. Throughout the Archaean, a low-pH ocean (topped by a shallow oxygenated water layer beneath a dense CO<sub>2</sub>+N atmosphere) accumulated Fe<sup>++</sup> in solution. At ~2.8 Ga the ocean floor began to deepen, exposing the cratons to massive weathering. This lowered CO<sub>2</sub>, resulting in the Earth's first glaciation at 2.65 Ga, followed at 2.35 Ga by the major Huronian glaciation during the 4 km+ lowering of sea-level during the actual hiatus. During the hiatus the MOR supply of reducing gases was shut off and oxygenic life was at last enabled to win its battle against the Earth's reducing power. BIF deposition was the result. Carbonates with a major positive excursion in δ<sup>13</sup>C at 2.2 Ga mark the florescence of oxygenic life, presented with non-acid shallow seas over planated cratons, as renewed MOR activity raised sea-level. Thus the lowering of atmospheric CO<sub>2</sub>, the rise of oxygen and the change in seawater chemistry stem from changes in the Earth's internal behaviour, not from biological innovation.

Osmaston MF, *IUGG99, Birmingham, UK, Abstr.B*, B.74 (B.75 in Abst.Update CD), (1999a).

Osmaston MF, *IUGG99, Internat. Union Geod. Geophys., Birmingham, UK, Abstr.B*, B.261, (1999b).

Osmaston MF, *31st Int. Geol. Congr., Rio de Janeiro, Abstr.CD-ROM*, Gen.Symp.9-2, (2000).

**EVO7 : MOPm22 : F5**  
**The Chemical Evolution of Seawater during the Phanerozoic: Record from Primary Fluid Inclusions in Marine Halite**

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The Mg<sup>2+</sup> concentration of seawater has varied significantly during the Phanerozoic. Evidence from the chemistry of fluid inclusions in marine halite indicates that the composition of seawater during the Permian and Neoproterozoic was similar to that of present-day seawater. Seawater was severely depleted in MgSO<sub>4</sub> and enriched in CaCl<sub>2</sub> from the Cambrian to the Devonian and from the Jurassic to the Eocene. The long-term variations in seawater composition correlate well with variations in the stand of sea level. During high stands of sea level cycling of seawater through MORs was probably more rapid and flooding of the continents tended to produce extensive shallow-water carbonate platforms. Intense Mg<sup>2+</sup> loss to MORs and to dolomitization on carbonate platforms drew down the Mg<sup>2+</sup> content of seawater during these periods.

Since the Eocene the concentration of Mg<sup>2+</sup> in seawater has increased by 18 mmol/kg H<sub>2</sub>O and has probably been accompanied by a considerable increase in the concentration of SO<sub>4</sub><sup>2-</sup> (Zimmermann, 2000). Because the rate of seafloor spreading has been nearly constant during the last 40 Ma, it is unlikely that the cycling of seawater through MORs accounts for a significant fraction of the observed depletion of Mg<sup>2+</sup> during this period. The increase in the Mg<sup>2+</sup> concentration of seawater during the Tertiary seems to be related to a decrease in the rate of dolomite formation in more recent carbonate sediments. This is due to the progressive transfer of the site of CaCO<sub>3</sub> deposition from shallow to deep-water settings where dolomitization is minor (Holland and Zimmermann, 2000).

Zimmermann H, *Am. J. Sci.*, in press, (2000).

Holland HD & Zimmermann H, *Int. Geol. Rev.*, **42**, 481-490, (2000).

**EVO7 : MOPm23 : F5**  
**Variation in Seawater Chemistry during the Permian and Triassic**

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The data on the chemical composition of primary fluid inclusions (brine inclusions) in primary-bedded halite from many evaporite formations showed that during the Phanerozoic the seawater chemistry oscillated, and that in Permian and Triassic the Na-K-Mg-Cl-SO<sub>4</sub> type occurred (Kovalevych et al., 1998). However, also within that time interval important variation of the relative content of SO<sub>4</sub> ion (as expressed in the Jänecke units) existed. This conclusion is based on study of fluid inclusions that are related to sedimentary or early diagenetic halite in marine primary-bedded halite, occurring below the potash salts or in the sections where the potash salts are lacking. The reason of such a selection was that only such data allow the reconstruction of the chemical composition of ancient oceans. During Early Permian, the content of SO<sub>4</sub> ion was 4.4 - 14.5 (average 8.5) in the Asselian of the Dnipro-Donets basin of Ukraine and 6.7 - 15.5 (average 9.7) in the Sakmarian of the Dvina-Sukhona basin of Russia and the Dnipro-Donets basin of Ukraine. This content dropped to 0.4 - 10.1 (average 3.3) in the Kungurian of the Prikaspiian basin and Solikamsk basin of Russia. A similar concentration (average 3.8) was recorded in the Leonardian of Kansas (Horita et al., 1991). The highest relative content of SO<sub>4</sub> ion was recorded in the Upper Permian Delaware Basin and the Upper Permian Zechstein Basin: 10.2 - 17.9 (average 14.2) and 10.0 - 17.4 (average 13.8), respectively (Kovalevych et al., 2000; Horita et al., 1991). A slightly lower content of this ion (5.7 - 13.3, average 10.4) was recorded in the Lower Triassic. The decreasing trend continued in the Middle Triassic Muschelkalk halite of northern Switzerland where the content of SO<sub>4</sub> ion is 7.1 - 8.7 (Kovalevych & Hauber, 2000). In fluid inclusions from the Lower Carnian Keuper of Lorraine the content of SO<sub>4</sub> ion was relatively

the lowest in the Triassic (1.4 - 11.1, average 4.2) (Fanlo & Ayora, 1998). Accordingly, starting from the Late Permian, the content of SO<sub>4</sub> ion was decreasing in the brines of marine evaporite basins what in turn was related to the decrease of SO<sub>4</sub> ion content in seawater. This conclusion is based on that the seawater evaporation path defined by modern brines closely approximates the brine evolution during formation of marine evaporites. In the Late Permian, the SO<sub>4</sub> ion content in seawater was close to (but slightly lower than) the value characteristic for modern seawater. The trend of decrease of SO<sub>4</sub> ion has been continued in the Triassic.

Fanlo I & Ayora C, *Chem. Geol.*, **146**, 135-154

Horita J, Friedman T, Lazar B & Holland HD, *Geochim. Cosmochim. Acta*, **55**, 417-432

Kovalevych VM, Peryt TM & Petrichenko OI, *J. Geol.*, **106**, 695-712

Kovalevych VM, Czapowski G, Halas S & Peryt TM, *Przeglad Geol.*, **48**, 448-454

Kovalevych V & Hauber L, *8th World Salt Symp.*, **1**, 143-148

**EVO7 : MOPm24 : F5**  
**Did the Ocean Change in Composition during the Phanerozoic? Learning from Fluid Inclusions and Potash Sequences**

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The chemical evolution of several European Mesozoic and Tertiary evaporite basins was reconstructed by using mineral associations, primary fluid-inclusion analyses and numerical simulations of evaporation scenarios. The solute proportion recorded in the fluid inclusions can be explained by the evaporation of present-day seawater as a major recharge. The sulfate depletion in the brines is responsible for the type of potash deposit formed, potassium-magnesium sulfates or sylvite. This sulfate depletion can be due either to dolomitization or to the addition of a CaCl<sub>2</sub>-rich solution to the basin. The sulfate depletion occurred in varying intensity in basins of the same age, as well as throughout the evolution of the same basin. Therefore, changes in potash mineralogy and sulfate depletion in fluid inclusions are not conclusive arguments in favor of secular variations in the composition of the ocean, as recently proposed by several authors.

**EVO7 : MOPm25 : F5**  
**Extensive and Rapid Changes in Seawater Chemistry during Phanerozoic: Evidence from Br Contents in Basal Halite**

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Br concentration in primary marine basal halites was used to indicate variations in seawater composition during the past 550 Ma. Based on the thermodynamic formulation of the partition coefficient it can be shown, that every change in the composition of seawater must influence the incorporation of Br in halite (Siemann & Schramm, 2000). This influence was verified by evaporation experiments with natural recent as well as with synthetic seawaters. The latter were increasingly depleted in MgSO<sub>4</sub> and enriched in KCl and CaCl<sub>2</sub>. The more the seawater was changed, the lower the Br concentrations in the precipitated halite were. The experimentally obtained Br contents in the first precipitated (basal) halite can be correlated to the chemical composition of the unevaporated seawater. A combination of this correlation with time dependent models for ocean chemistry (Hardie, 1996) leads to a prediction of Br in basal halite during Phanerozoic. These are in good agreement with data from different ancient evaporation basins. It is important to note, that only those data were used from the literature, where evidence from sedimentological, petrological, or geochemical data was available, proving that the halite section have not been altered by secondary processes. In addition, the evaporate sections have to be in close contact to basal anhydrite and the entire Br profiles document the typical pattern of primary marine halite formations. Inspection of these data unequivocally demonstrates that the predicted Br curve and the Br contents in primary basal halites is in good agreement. However, minimum

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concentration of Br in first precipitated halite can be predicted for the Early Cretaceous and Middle Cambrian whereas contents close to that expected from modern seawater are likely for Early Jurassic, Late Permian to Early Triassic, Early Permian, Late Mississippian to Early Pennsylvanian, and Late Neoproterozoic to Early Cambrian. The model also implies constantly increasing Br contents in halite during Late Mesozoic and Cenozoic to recent. Rapidly changing concentrations are predicted for Late Paleozoic and Early Mesozoic whereas the Br concentrations in basal halites of Early Paleozoic may be relatively constant. Based on the increasing Br contents in basal halite from Early Cretaceous to recent, an extensive change in the composition of the seawater is inferred. This change in composition must have been much stronger than those caused by dolomitization or  $MgSO_4$ -depletion. Rapid changes of seawater composition can be observed in Late Permian (Zechstein Formation, Germany) and in Pennsylvanian (Paradox Formation, U.S.A.), but in different directions. Br data give evidence for rapid and massive changes in seawater chemistry during Phanerozoic, which could not have been produced by dolomitization.

Siemann MG & Schramm M, *Geochim. Cosmochim. Acta*, **64**, 1681-1693, (2000).  
Hardie LA, *Geology*, **24**, 279-283, (1996).

#### EVO7 : MOPm26 : F5 The Sulphur Isotopic Composition of Phanerozoic Seawater Sulfate- New Data and Preliminary Modeling

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Earth system evolution can be monitored through the isotopic evolution of seawater. Thereby, secular variations of the global sulfur cycle are documented in the isotopic composition of marine sulfate. A temporal record for the sulfur isotopic composition of Phanerozoic seawater sulfate is being presented, based on the analysis of 156 biogenic carbonates and 102 whole rock carbonates of Paleozoic and Mesozoic age. This acknowledges the fact, that sulfate represents an important trace constituent in marine calcites with quantities ranging from a few tens to several thousand ppm. This sulfate is present in the crystal structure of calcite. All samples studied are biostratigraphically well constrained and were screened for possible diagenetic overprints. In addition, sufficient work on recent biogenic carbonates and on modern seawater was performed to assure the suitability of the analytical and conceptual approach. For the Cenozoic, this record was supplemented with data from the literature.

Secular variations in the sulfur isotopic composition of seawater sulfate on different time scales are clearly discernible for the Phanerozoic. The long-term temporal record, as already documented through the analysis of marine evaporitic sulfates, has been duplicated and provides the frame work for further discussions. It shows maximum sulfur isotope values around +35 ‰ for the Cambrian followed by a decline to minimum values around +13 ‰ for the Permian and an increase to a value close to +21 ‰ for dissolved sulfate in the modern ocean. Additional temporal variations exist on much shorter times, many of which were previously not documented as a consequence of poor time resolution. In particular, the Paleozoic sulfur isotope record was significantly improved through numerous new results.

The long-term evolution for the sulfur isotopic composition of Phanerozoic seawater sulfate is constrained by a moving average (20 Ma time window, 5 Ma steps) where the 95% confidence level defines a band width between 1 and 5 ‰ for most of the Phanerozoic. Modeling of this new temporal record, based on the inversion of the measured seawater sulfate isotopic composition, indicates that the secular variations reflect changes in the magnitude of bacterial sulfate reduction. The evolution of the sulfur isotopic composition of seawater is interpreted in terms of a decrease in the burial flux of reduced sulfur until late Carboniferous by a factor of 2.5, followed by a 40% increase towards the

present day. These fluctuations are within reasonable limits when compared to modern marine burial fluxes. No substantial input of mantle sulfur at any given time is calculated.

#### EVO7 : MOPm29 : F5 Tournaisian Whole Rock Carbon Isotope Stratigraphy in Europe and Laurentia

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A Kinderhookian positive delta 13-C excursion is known from bulk rock analyses of the Lodgepole Limestone in Utah and Wyoming (Budai et al., 1987). Recently, Salzmann et al. (2000) reported similar data from the Joana Limestone of southeastern Nevada. Additionally, brachiopod data from Iowa and western Europe indicate a widespread occurrence of this excursion during the Siphonodella isosticha-Upper crenulata conodont Zone. We sampled sections in western Canada (Banff area), Nevada (Arrow Canyon), and from several places in Europe (Austria, Belgium, France, Germany). Our dataset comprises several hundred analyses of carbon isotopes of carbonates and organic carbon. We examined bulk rock samples and selected compounds (e.g. matrix of mudstones and wackestones, echinoderms, brachiopods, cements). All sections yield a large positive carbon isotope excursion of several permil delta 13-C, regardless whether we examine organic or inorganic carbon of mudstones and wackestones, or even inorganic carbon of grainstones. Only in few cases, early subaerial exposure or fresh water diagenesis suppressed the original signal or produced a considerable negative shift (for instance at the top of the Battleship Wash Formation, Arrow Canyon). A more detailed look at the carbon excursion of the Siphonodella isosticha-Upper crenulata Zone of the Canadian sections exhibits the following geometry: A negative shift, only seen in inorganic carbon, precedes the main positive excursion. The excursion itself is characterized by a continuous increase of delta 13-C in organic and inorganic carbon, a sharp drop and a second smaller peak, which may fall into the typicus Zone already. Salzmann et al. (2000) argued that the positive shift in delta 13-C is a result of high organic carbon burial rates in the Antler foreland basin. In Europe, widespread deposition of black shale (Liegende Alaunschiefer, Russchiefer, Maurenne) provides evidence for (global?) sea level rise during the crucial time interval.

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#### EVO7 : MOPm30 : F5 delta 18-O of Carbonate, Quartz and Phosphate from Belemnite Guards: Implications for the Isotopic Record of Old Fossils and the Isotopic Composition of Ancient Seawater

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Belemnite guards of Cretaceous and Jurassic age were found to contain variable though relatively large amounts of secondary quartz deposited on the external surface and inside the rostra by solutions percolating through microfractures and/or along the apical canal. The oxygen isotopic composition of coexisting carbonate, quartz and phosphate from the same rostrum was measured according to well established techniques. None of these compounds showed isotopic values at equilibrium with one another. Assuming an oxygen isotope value of the water percolating through the belemnite rostra close to -7 per mil (V-SMOW) the quartz oxygen isotope values yield temperatures in agreement with the apparent secondary origin of this phase. The carbonate oxygen isotope values range with a certain continuity between -10.8 and +0.97 (PDB) with most of the intermediate values being, as usual, within the range of the carbonate isotopic values of Mesozoic fossils. The most positive isotopic results were obtained from phosphate (about +23 to +24 per mil [V-SMOW]). They can hardly be related to a secondary origin of the phosphate, or to the presence of secondary diagenetic effects, since these results are among the most positive ever measured on phosphate, and as far as we know there is no widespread diagenetic process determining an oxygen-18 enrichment

of phosphate. The very low concentration of phosphate in belemnite rostra (similar to that found nowadays in the cuttlebones of the modern Belemnite counterpart, Sepia officinalis) did not allow the determination of its mineralogical composition. This phosphate may be present as apatite, but it may also be related to the presence of organic matter. However, the oxygen isotopic compositions of carbonate and phosphate in Sepia cuttlebones are in isotopic equilibrium with seawater at their mean growth temperature. Whatever the origin of the belemnite phosphate, if an isotope exchange took place between the rostra and diagenetic water, the observed oxygen isotope values of both carbonates and phosphates must have shifted towards lighter values, even though at different rates. Since very positive oxygen isotope values were obtained repeatedly during the past from carbonate and phosphate of Mesozoic and Palaeozoic fossils, these values and the most positive results reported here can be explained only by assuming that the oxygen isotopic composition of ocean water during the past was isotopically heavier than modern ocean water by at least 2-3 per mil. Different rates of diagenetic alteration of carbonate and phosphate would justify the isotopic values which are usually obtained from Mesozoic and older fossils.

#### EVO7 : MOPm31 : F5 The Oxygen Isotopic Composition of Palaeozoic Seawater- The Apatite delta 18-O Record

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The oxygen isotopic composition of ancient oceans is one of the most controversial issues in stable isotope geochemistry (Land, 1995; Veizer, 1995). The fact that the oxygen isotopic composition of well-preserved brachiopod shells becomes more depleted with increasing age of the brachiopods was interpreted by a secular change in seawater delta 18-O (Veizer et al., 1999). If the oxygen isotopic composition of seawater changed during the Phanerozoic, biogenic apatite is expected to show a comparable secular decrease in delta 18-O.

We analysed the oxygen isotopic composition of Silurian, Devonian and Carboniferous conodont apatite using a laser-based microsampling technique (Wenzel et al., 2000). delta 18-O values of Silurian conodonts from Gotland range from +17.5 to +19.5‰ V-SMOW. In contrast, average delta 18-O values of coeval brachiopod shells range from ?2.4 to -5.9‰ V-PDB. If calcite and apatite were precipitated in isotopic equilibrium with ambient sea water, calcite should be enriched in 18-O by 8.5 to 9.0‰ relative to apatite (t = 15 to 40°C). Opposite to this expected offset of approximately 9‰, the Silurian brachiopods are enriched in 18-O by only 7.0 to 8.5‰ relative to conodont apatite. Comparable observations are made for Middle Devonian conodonts and coeval brachiopods. Givetian conodont apatite delta 18-O values range from 18.0 to 19.4‰ V-SMOW with brachiopod calcite being enriched in 18-O by only 6.6‰.

The lower than expected offset between calcite and apatite delta 18-O can neither be explained by a diagenetic overprint of the brachiopod shells nor by non-equilibrium fractionation of one or both minerals. All brachiopod shells have been carefully checked for their geochemical and structural preservation. Modern brachiopods are interpreted to precipitate calcite close to oxygen isotope equilibrium with sea water. Since conodonts became extinct in the Triassic, equilibrium fractionation during precipitation of conodont apatite cannot be proven. However, the analysis of Upper Devonian conodont and coeval fish teeth reveals comparable delta 18-O values for conodont and fish teeth apatite. Since modern fish precipitate apatite in oxygen isotopic equilibrium with sea water, a non-equilibrium fractionation for Palaeozoic conodonts seems unlikely.

The Silurian delta 18-O\_apatite and delta 18-O\_calcite data show parallel trends. This correlation is expected if the delta 18-O variations in both phases are related to primary environmental changes. Interestingly, if a +1‰ correction is applied to account for an ice-free Silurian or Devonian world, the conodont delta 18-O values are virtually identical to values of modern tropical fish teeth and invertebrate shells and translate into palaeotemperatures ranging from 26 to 32°C.

## EVO7

### Geological History of Sea-Water

To our understanding, these observations are remarkable since the conodont  $\delta^{18}\text{O}$  data do not corroborate hypotheses that the average oxygen isotopic composition of Palaeozoic sea water was significantly different from the  $\delta^{18}\text{O}$  signature of modern oceans.

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#### EVO7 : MOPm32 : F5

##### The Variation of Ca Isotopic Composition in Marine Phosphates and Carbonates during the Tertiary

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Only a few studies dealing with variations in the isotopic composition of marine calcium in Tertiary time actually exist. Skulan et al., (1997) and De La Rocha and DePaolo, (2000) showed that, similar to Sr, the variations of Ca isotopic compositions might yield important information about the Ca budget in seawater, especially about carbonate sedimentation and changes in the ratio of silicate to carbonate weathering. Measurement on Atlantic seawater samples yield very homogeneous  $^{42}\text{Ca}/^{44}\text{Ca}$  ratios ( $0.30570 \pm 15$ ) (Schmitt et al. 2000) which is in agreement with earlier observations suggesting that the Ca isotopic composition in present day seawater is very homogeneous (Zhu and Mac Dougall, 1998 and De La Rocha and DePaolo, 2000). This strong isotopic homogeneity might be due to the residence time of Ca which is far longer than the oceans mixing time. Recently published Ca isotope data of marine carbonates show variations in the marine calcium cycle over the last 80 million years (Skulan et al., 1997; De La Rocha and DePaolo, 2000). Most important changes towards low  $\delta^{44}\text{Ca}$  are observable at about 36 and 18 Ma and have been correlated with global cooling. We performed a similar study not on carbonates but on authigenic marine phosphates which apparently integrated and conserved the Sr and Nd isotopic composition of seawater of the time of their formation (Stille et al., 1996). These phosphates cover the timespan between present-day and 25 Ma. They do not show the rapid decrease of  $\delta^{44}\text{Ca}$  at 18 Ma. They yield rather similar  $\delta^{44}\text{Ca}$  values ranging between -1.11 and -1.20 with respect to seawater. Thus, the question rises whether marine phosphates and carbonates furnish the same geochemical information. The different isotopic composition might be due to different fractionation processes occurring during formation, sedimentation or early diagenesis of these phosphates and carbonates.

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#### EVO7 : MOPm33 : F5

##### Rare Earth Element Evolution of Phanerozoic Seawater Recorded in Biogenic Apatites

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Rare Earth Element (REE) contents of marine biogenic apatites record the evolution of Phanerozoic seawater composition provided no alteration of the original signature has occurred. We show how the available dataset for phanerozoic times can be cleaned up from altered samples, which are characterized by very low La/Sm ratios acquired during apatite recrystallization. The filtered data reveal that two types of REE patterns are recorded, one characteristic of ancient (pre-Aptian) seawaters and of present-day organic matter rich estuarine waters and the other characteristic of present-day open seawaters. A progressive change between these two chemistries is observed from the Aptian until late Cretaceous (Campanian), where the REE chemistry of seawater reached a steady-state until present-day. The evolution of seawater REE chemistry during the Cretaceous could result from the colonization of the pelagic realm by the calcareous plankton within the frame of the opening of the Atlantic ocean. Changes in the mechanism of REE fractionation inside the water column could reflect the challenging role of organic vs inorganic primary carriers. Possible mechanisms and implications for the early mesozoic and paleozoic ocean chemistry will be discussed.

#### EVO7 : MOPm34 : F5

##### Rhenium and Osmium Budgets on Limestone and the Os-Isotope Composition of Middle Devonian Seawater

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The chemical and isotopic composition of marine sediments reflect the changing composition and physical conditions of the seawater in which they accumulated. Marine sediments therefore preserve a record of the changes that have occurred with respect to the global inputs into the ocean (e.g. spilitization, cosmic catastrophies, continental runoff etc.). Os is an especially sensitive proxy for these. Cosmic impacts may point to events which have caused mass extinctions (like the Kellwasser event). Osmium isotopes, Re - Os concentration data, and rhenium - osmium budgets have been obtained on samples from one suite of layered shale, white and black limestone of middle Devonian age (Kellwasser sequence, southern Kellerwald, Germany).

The interpretation of Re - Os bulk rock data is still hampered by the limited understanding of the distribution of rhenium and osmium in sediments and limestone in particular. Although Re - Os data have been obtained on sedimentary rocks before (e.g. Ravizza & Esser, 1993; Peucker-Ehrenbrink & Ravizza, 1996; Cohen et al., 1999), this study presents new results:

1. Re and Os bearing components in the selected limestone samples are identified, establishing the basis for an understanding of how the measured isotope ratios can be interpreted. These particular limestone samples are characterised by very radiogenic and significantly varying  $^{187}\text{Os}/^{186}\text{Os}$  ratios between 23.2 (black "Kellwasser" limestone) and 75.4 (white limestone),

2. conodonts were identified as potential Os-bearing component, that may allow the reconstruction of the Os - isotopic composition in Devonian seawater.

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