Geodynamic impact on the stable isotope signatures in a shallow epicontinental sea

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ABSTRACT
Analyses were made of a mollusc-based meta dataset of 859 δ13C and δ18O data of Miocene nearshore settings in the European Paratethys Sea and its descendant Lake Pannon. The observed trends document a strong tie to geodynamics, which are largely decoupled from Miocene open ocean isotope curves. Semi- to fully enclosed, initially marine water bodies such as the Paratethys Sea are prone to switching seawater isotope signatures because they respond rapidly to changes in the evaporation/precipitation ratio. Two phases of positive deviations of oxygen isotope values of water (relative to the modern ocean value, SMOW) occurred during the Middle Miocene; both were initiated by tectonic constrictions of the seaways and became amplified by global warming and regionally decreasing precipitation. With the final disintegration of the Paratethys, the marine isotope signatures vanish. Instead, the observed isotope trends suggest a comparably simple system of an alkaline lake with steadily declining salinity. The ‘ocean-derived’ Paratethys Sea may thus act as a key for understanding isotope trends in epicontinental seas.

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Introduction
The marine Miocene deposits of Central Europe are a heritage of the Paratethys Sea (Fig. 1). During its maximum extent this sea spread from the Rhône Basin in France towards Inner Asia. As a northern satellite sea of the Western Tethys (= Proto-Mediterranean) it originated during the latest Eocene and Early Oligocene due to the rising Alpine island chains, which acted as geographical barriers (Rögl, 1998). The Central Paratethys existed throughout the Early and Middle Miocene. Already during the latest Middle Miocene, marine connections to adjacent seas were strongly narrowed. Finally, at 11.6 Ma, the western part of that sea became isolated within the Pannonian Basin system and Lake Pannon formed (Magyar et al., 1999). In this evolving system, severe changes in the composition of the Paratethyan nearshore faunas were triggered by climatic and geodynamic developments (Harzhauser et al., 2003). The latter are indicated by repeated isolation events with highly endemic faunas (Rögl, 1998).

Methods, samples and study area
1. As no generally accepted standard procedure of sample treatment prior to isotope analyses exists, we avoided any pre-treatment (e.g. roasting) of the shells to exclude any artificial alteration. Multiple samples were taken in ontogenetic sequence from apex to aperture with a 0.3-mm drill. Very small shells were crushed. All samples were reacted with 100% phosphoric acid at 70°C in a Thermo-Finnigan Kiel II automated reaction system and measured with a Thermo-Finnigan Delta Plus isotope-ratio mass spectrometer at the Institute of Earth Sciences, University of Graz. Repeated measurements of NBS-19 and an internal laboratory standard yielded a standard deviation of 0.1‰ for both δ18O and δ13C. Values are given in permil relative to V-PDB. The shell mineralogy and microstructures were investigated by XRD (X-ray diffraction) and SEM (Scanning Electron Microscopy) to detect diagenetic alteration (see Latal et al., 2004, 2006a for techniques, methodology and exemplary SEM photographs).

As no alteration in the original shell material was detected we assume that no modification of the original isotope composition occurred. This is an essential assumption, because moluscs generally precipitate their shells in oxygen isotope equilibrium or near equilibrium (Grossman and Ku, 1986). Accordingly, oxygen and carbon isotope data may be applied for paleoenvironmental and paleotemperature reconstructions. δ18O values in gastropod shells are mainly controlled by the temperature and δ18O of the ambient water, whereas δ13C values are influenced by a multitude of factors, e.g. upwelling, seasonal productivity, diet, living mode, growth rate, reproductive status (Geary et al., 1992 and references therein; Bonadonna et al., 1999). Global climate is one of the main factors that influence the oxygen isotope value of seawater in open oceans, whereas local environmental conditions are more important in marginal seas or coastal areas. Freshwater δ18O values are primarily controlled by the isotopic composition of the rainwater.

2. In total, 859 δ13C and δ18O data were measured in gastropod and bivalve shells from the Central Paratethys Sea and Lake Pannon. Fluvial and lacustrine taxa (e.g. Melanopsis, Lymnaea, Unio, Margaritifera) provide data for the freshwater endmembers and are used to discriminate between marine, brackish and purely freshwater values. The samples were collected in the
Stable isotopes of an epicontinental sea  

North Alpine Foreland Basin and the Pannonian Basin System (Vienna B., Korneuburg B., Styrian Basin; Fig. 1). Additional literature data are derived from the Hungarian and Rumanian part of the Pannonian Basin system (Kisaföld B., Transylvanian B.; Fig. 1). Nine time slices have been selected: ~20 Ma (Eggenburgian), ~16.5 Ma (late Karpatian), ~15 Ma (early/middle Badenian), ~14 Ma (late Badenian), ~12.5 Ma (early Sarmatian), ~12 Ma (late Sarmatian), ~11.5 Ma (early Pannonian), ~11–10 Ma (middle Pannonian), ~9–6 Ma (late Pannonian) (Fig. 2). Usually, serial samples per specimen were obtained by microdrilling. The same method was applied by all cited earlier studies. In the following, the number of samples is indicated as n and the number of shells as s.

The dataset (n = 37, s = 3) of the oldest samples is derived from litoral gastropod species (one batillariid; two muricids) of lower Lower Miocene (=Eggenburgian) deposits. The second dataset (n = 234, s = 22) comes from upper Lower Miocene (=Karpatian) deposits published by Latal et al. (2006a) and includes litoral (batillariid, potamidid, ocenebrid) and sublittoral (turritellid) gastropods. For the lower Middle Miocene (=Badenian), 175 measurements (s = 22) were collected, supplementing published data from Latal et al. (2006b) and Mátyás et al. (1996). A broad range of taxa was measured, including litoral batillariids and potamidids, shallow sublittoral turritel lids, nassariids, naticids, etc. and deeper sublittoral thyasirid bivalves. The late mid-Miocene Sarmatian is covered by 235 (s = 32) measurements taken from Latal et al. (2004), Piller and Harzhauser (2005), Geary et al. (1989), Mátyás et al. (1996) and new analyses. Litoral potamidids and batillariids along with hydrobiids are represented along with shallow marine cardids. The Late Miocene (=Pannonian and ‘Pontian’) data are based on 178 (s = 69) measurements derived from bivalves published in Harzhauser et al. (2007) and 87 measurements (bivalves and gastropods) from Geary et al. (1989) and Mátyás et al. (1996). Coastal faunas are represented by melanospid gastropods and various dreissenids; sublittoral environments are covered by cardids and the endemic dreissenid Congeria.

The entire dataset with detailed taxonomic, paleoenvironmental and geographic information and references is available online (http://www.Content.Node/forschung/geologie/mitarbeiter/pdfs/H arzhauser_et_al_TerraNova.xls).

Results

Miocene nearshore isotope values are plotted within a stratigraphic frame in Fig. 2. To avoid a bias by data lumping, the analysed taxa were separated according to their environmental requirements. Consequently, pure freshwater dwellers tend to be separated from the marine taxa by their usually lower δ13C and δ18O values. This trend is more obvious for δ13C than for δ18O values. During the early Late Miocene, however, the freshwater oxygen values of unionid bivalves are equal to or greater than those of litoral taxa of Lake Pannon. An aberrant Pannonian pattern is also evident from the average δ18O values of sublittoral taxa. These steadily increase from the Early Miocene to the Middle Miocene, with an early Sarmatian maximum of +1.74‰ at ~12.5 Ma. After a strong δ18O decrease during the late Sarmatian (~12 Ma) with a rather negative value of −1.2‰, a slight increase is evident again during the early Pannonian (~11.5–10.5 Ma) coinciding with the formation of Lake Pannon. Afterwards, a continuous decrease sets in. A generally similar trend is reflected by δ13C average values. A focus on the maximum δ13C values reveals an excursion at ~12 Ma during the Sarmatian. This positive peak of +6.8‰ contrasts with Early to Middle Miocene carbon maxima between +3 and 4‰. The distribution pattern of the stable isotope values is best visualized in frequency diagrams based on 799 δ18O/δ13C measurements (Fig. 3). They document a shift of the δ18O maximum from the Karpatian to the Badenian towards the heavy tail, while the δ13C frequency curves lack a distinct shift. During the Sarmatian and Pannonian, the δ18O maxima switch back to values comparable with the Karpatian ones. A marked shift towards negative values for both stable isotopes does not occur before the late Pannonian.
1. A clear weakness of the ‘holistic’ approach is the inhomogeneity of the available data per time slice. Nevertheless, some general trends seem to be robust. Oxygen isotope values of extant shallow marine molluscs have maxima between $-2$ and $+1\permil$ (Goodwin et al., 2001; Rodríguez et al., 2001; Keller et al., 2002; Kobashi and Grossman, 2003; Reinhardt et al., 2003). More negative values due to freshwater influx by river run-off or seasonal increases in precipitation are also commonly described (e.g. Rodríguez et al., 2001; Kobashi and Grossman, 2003; Reinhardt et al., 2003). Minimum SSTs (Sea Surface Temperature) for the Karpatian have been estimated at around 14 $\degree C$ (Latal et al., 2006b) and from 15 to 17 $\degree C$ for the early Badenian based on mollusc (Harzhauser et al., 2003) and planktic foraminifers (Gonera et al., 2000). Hence, both time intervals display fairly similar SSTs. The recorded shift can therefore only be explained by a switch of the isotope composition of the ambient seawater.

2. A $\delta^{18}O$ of the open ocean seawater of $c. -1.0\permil$ is indicated for the Middle Miocene climatic optimum by Lear et al. (2000). Our data suggest that this open ocean value cannot be uncritically adopted for epicontinental seas such as the Paratethys. Calculating the proxy data-based minimum SSTs against the measured $\delta^{18}O$ values of the mollusc carbonate (Grossman and Ku, 1986) indicates an isotopically negative seawater system ($\sim -1\permil$) in the Early Miocene and a positive one ($\sim +1\permil$) in the Middle Miocene (Fig. 4). This change is considered to be geodynamically induced.
and climatically enforced. During that time, the Paratethyan basins transformed from west–east-trending deep-water basins towards shallow intra-mountain basins (Rögl, 1998). A highly structured archipelago sea was formed with decreasing connections to the open ocean. In addition, the high precipitation during the Karpatian (2000 mm year$^{-1}$; Meller, 1998) was replaced by less humid conditions and increasing seasonality (Bohme, 2003). Thus, similar to the modern Red Sea or Persian Gulf, the oxygen isotope composition of this semi-enclosed sea shifted towards positive values, amplified by the high temperatures of the MMCO. The reverse trend during the late Badenian and the early Sarmatian was initiated by the mid-Miocene climate transition, as suggested by the decline of the reef systems (Pisera, 1996) and surface water cooling (Baldi, 2005). The calculated $\delta^{18}$O values of the early Sarmatian seawater might have additionally been influenced by the ingress of eastern Paratethyan waters after the re-connection with the Asian part of the Paratethys. The renewed positive peak during the late Sarmatian again reflects geodynamic and climatic interplay. A short warming phase, as indicated by the global curve of Zachos et al. (2001), is reflected in the Paratethys by a highly productive Sarmatian carbonate factory in the subtropical climate (Piller and Harzhauser, 2005). The sea became completely sealed and was thus prone to evaporation, which shifted the $\delta^{18}$O values to around $+1\%_o$ (Fig. 4). These evaporation effects are emphasized by a characteristic peak of very heavy
oxygen isotope values, pointing to even hypersaline waters in coastal areas (Latal et al., 2004). The increasing trend of $\delta^{13}C$ maxima during the Sarmatian fits well to a lowered sea level accompanied by advanced evaporation in coastal areas. Indeed, the Sarmatian maximum extension of the Paratethys Sea occurred during the early Sarmatian, whilst the late Sarmatian with oolite shoals corresponds to a lowered sea level (Harzhauser and Piller, 2004). These conditions would support a better vertical mixing, promoting surface productivity, and in turn would increase the $\delta^{13}C$ value (Li and Ku, 1997). Again, geological data support this scenario: laminated marls of the early Sarmatian point to a stratified water body, whereas carbonate sedimentation of the late Sarmatian lacks evidence for pronounced stratification (Piller and Harzhauser, 2005).

3. The onset of Lake Pannon corresponds to a parallel decrease in both stable isotope trends. This simply seems to reflect gradual freshening of the lake water, which started as a brackish remnant of the Paratethys Sea. Increasing freshwater discharge soon turned the lake into a near-freshwater system. Fossil-water analyses of well-logs support this interpretation (Ma´tya´s et al., 1996). The abrupt decline towards negative values is unique in the entire dataset. Nevertheless, a dominant carbon regime supported still rather high values between $-0.5$ and $+1\%$. A brackish water scenario, as calculated from the oxygen values, cannot explain the high $\delta^{13}C$ values. In modern lake systems such high $\delta^{13}C$ values strongly correlate with elevated $pH$ values. This would yield a $pH$ value of 9–10 for the initial Lake Pannon based on the empiric data plot of Bade et al. (2003). Lake Pannon would thus have started as an alkaline lake.

Conclusions

The Paratethyan isotope patterns reflect a severe impact by an interconnected system of geodynamics and regional climate. The resulting trends are often decoupled from global isotope curves and are bound to the considerable fluctuations of the isotope composition of the Paratethys Sea. First constrictions of the seaways in the Middle Miocene are reflected immediately by a major positive shift in oxygen isotope values. That trend was positively amplified by the global warming of the mid-Miocene Climatic Optimum and by a decrease in humidity on the regional scale. The cooling during the Miocene climate deterioration led to a swing back towards balanced values, which attain nearly...
Stable isotopes of an epicontinental sea

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fits well to the coeval peak in
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ings. The final disintegration of the
isotopes, is impossible without inde-
phases a straightforward calculation
which gave rise to a fully endemic
brackish lake and a rather high alka-

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0‰ deviation from the SMOW in the
early Sarmatian, probably due to the
influx of water with negative δ18O and
δ13C values from the eastern Para-
tethys. A second sealing of the connec-
tions, coinciding with a short-termed
warm interval and a lowered sea level
in the late Sarmatian, caused a second
phase with positive δ18O and δ13C values
for Paratethyan waters. Wide-
spread ooid formation at that time
hints at increased alkalinity, which
fits well to the coeval peak in δ13C
maxima in molluscs from littoral set-
tings. The final disintegration of the
sea is followed by the formation of
Lake Pannon. The aberrant, positive
δ18O and δ13C values of the early lake
stage suggest elevated salinity in a
brackish lake and a rather high alka-
linity. Both factors may account for
the big faunal turnover at that time,
which gave rise to a fully endemic mollusc radiation. During all these
phases a straightforward calculation
of SRT, based only on the mollusc isotopes, is impossible without inde-
pendent proxy data.

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