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Oxygen, strontium, and neodymium isotope composition of fossil shark teeth as a proxy for the palaeoceanography and palaeoclimatology of the Miocene northern Alpine Paratethys

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Abstract

The Upper Marine Molasse sediments of southern Germany were deposited during the Early to Middle Miocene, a period of significant change for the global Miocene palaeoceanography, palaeoclimate, and the regional palaeogeography because of the ongoing Alpine–Himalayan orogeny. To address the influence of the Alpine uplift on climate and oceanography of the northern Alpine molasse basin, a combined O-, Sr-, and Nd-isotope study was undertaken on fossil teeth from sharks (*Synodontaspis* sp., *Galeocerdo* cf. *aduncus*, *Chaenogaleus* sp.), and button-like teeth from the bony fish of the Upper Marine Molasse (*Chrysophrys molassica*). Average $\delta^{18}\text{O}$ values for hydroxyapatite of teeth from two sites are 20.3‰ ($1\sigma = 0.6$) and 21.2‰ ($1\sigma = 0.5$), while their average $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios are 0.70850 (± 0.00001 , 2σ) and 0.70882 (± 0.00003 , 2σ), and 0.51220, and 0.51223 (both at ± 0.00001 , 2σ), respectively. By comparison to the Sr-evolution curve for the global ocean, the Sr-isotope compositions suggest ages of about 22 and 17 Ma for the teeth. These ages are in good agreement with the depositional ages, which suggests open marine conditions. Open marine conditions are also compatible with (1) lower average $\delta^{18}\text{O}$ values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the one site compared to higher $\delta^{18}\text{O}$ values and higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the other site, (2) estimates for seawater temperatures which are similar to other estimates from deposits of similar latitude and age, (3) a comparison of seawater temperatures with average ambient air temperature estimates deduced from continental palaeoclimate indicators. Nd-isotope compositions are compatible with an influence of the North Atlantic on the Paratethys. Assuming constant salinity and seawater oxygen isotope composition, a 4°C cooling can be inferred from average $\delta^{18}\text{O}$ values of the teeth between 22 and 17 Ma. This is similar to trends observed for foraminiferal records from the Mediterranean Tethys, but different from foraminiferal and molluscan records of the North Atlantic and the North Sea during this period, and allows for the possibility that the Alpine orogeny had an influence on the regional, circum-Alpine climate. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is intuitively obvious that major orogenies have an important influence on the regional and perhaps also the global climate. Studies of direct links between orogenies and variations in climate are, however, relatively few. Tertiary molasse sediments of southern Germany which were shed into the Paratethys, an epicontinental sea separated from the Tethys Ocean during the Alpine–Himalayan orogeny, provide an opportunity to investigate links between mountain uplift and variations in climate. The geology and palaeontology of the classic foreland basin molasse sediments have been well characterized (e.g. Lemcke, 1984; Steininger et al., 1985; Geyer and Gwinner, 1991; Bachmann and Müller, 1992; Berger, 1992; Laubscher, 1992), but data on the palaeoclimatic and also palaeoceanographic conditions under which the marine sediments of the molasse were deposited are few.

To determine the influence of the Alpine orogeny on the palaeoceanographic and palaeoclimatic evolution of the north Alpine Paratethys, we have examined the O-, Sr-, and Nd-isotope compositions of shark teeth from two localities within the Early Miocene molasse sediments of southern Germany. Isotopic analyses of marine phosphates have gained increasing recognition as oceanographic proxies (e.g. Longinelli and Nuti, 1973; Staudigel et al., 1985; Grandjean et al., 1987; Kolodny and Luz, 1991; Ingram, 1995). Among marine phosphatic samples, shark teeth are of particular interest because they are readily classified on taxonomic level, the enamel and dentine of the teeth has good crystallinity and physical hardness, and the teeth are continually replaced by the sharks. Once the tooth is lost, it is sedimented generally with little or no residual organic matter attached, limiting enzyme-mediated recrystallization (e.g. Boyer, 1978), which may be common for phosphate from bones. Biogenic phosphate in shark teeth is thus commonly judged to be robust to post-depositional diagenetic alteration (e.g. Kolodny et al., 1983; Kolodny and Raab, 1988; Grandjean and Albarède, 1989; Lécuyer et al., 1993), although such alteration cannot be mutually excluded (McArthur and Herczeg, 1990; Shemesh, 1990; Kolodny and Luz, 1991).

Provided that the primary chemical and isotopic composition of the phosphatic material from marine

fish teeth has been preserved, the isotopic composition thereof is a function of the isotopic composition of the ambient seawater and, in the case of oxygen, also of temperature. Oxygen isotope fractionation between seawater and marine fish phosphatic precipitates has been well documented at various temperatures by Longinelli and Nuti (1973) and Kolodny et al. (1983), and can be expressed by the following equation:

$$t = 111.4 - 4.3(\delta^{18}\text{O}_P - \delta^{18}\text{O}_W) \quad (1)$$

where t is the temperature in °C, and $\delta^{18}\text{O}_P$, and $\delta^{18}\text{O}_W$ are the oxygen isotope compositions of marine phosphate and seawater, respectively, expressed in the familiar δ -notation relative to VSMOW (standard mean ocean water whose isotopic composition has been defined in Vienna). Measurement of the $\delta^{18}\text{O}_P$ and assumptions on the $\delta^{18}\text{O}_W$ values (where $\delta^{18}\text{O}_W$ is commonly between 0 and -1% for open marine conditions during glacial and interglacial periods) will allow ambient seawater temperatures to be calculated.

Sr- and Nd-isotope studies have shown that fish teeth record the isotope composition of the ambient seawater (Piepgras et al., 1979; Piepgras and Wasserburg, 1980; Staudigel et al., 1985; Grandjean et al., 1987; Ingram et al., 1994; Ingram, 1995). However, while these elements are contributed to the seawater by weathering and erosion of the continental crust and hydrothermal alteration of the oceanic crust, Sr- and Nd-isotope compositions reflect different behaviour of the elements in seawater. Owing to the long residence time of Sr in seawater (about 2×10^6 years), which is much longer than the mixing time of the Earth's oceans (about 10^3 years), it has been demonstrated that the Sr-isotope composition ($^{87}\text{Sr}/^{86}\text{Sr}$) of seawater is similar for the oceans and many semi-restricted basins at any particular time (Peterman et al., 1970; Veizer and Compston, 1974; Burke et al., 1982; DePaolo and Ingram, 1985; Veizer, 1989). The long residence time of Sr in seawater has permitted the construction of a Sr-isotope evolution curve through analysis of sediments and fossils from the open ocean (e.g. Koepnick et al., 1985; DePaolo and Ingram, 1985; DePaolo, 1986; Veizer, 1989; Hodell et al., 1991). The reverse of this is that measurements of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for marine phosphate or carbonate material permits indirect dat-

ing of the sediments, for periods during which the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio changes with time (Ingram, 1995). This is particularly the case for the Tertiary. Indirect dating is only possible, though, if the sediments were deposited under open marine conditions and not in isolated or restricted basins.

In the case of Nd-isotope compositions, the residence time is similar to the mixing time of the oceans and hence the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio reflects regional (typically the scale of a basin) rather than global conditions (e.g. Turner and Whitfield, 1979; Piepgras et al., 1979; Piepgras and Wasserburg, 1980; Palmer and Elderfield, 1985; Staudigel et al., 1985; Grandjean et al., 1987).

A combined O-, Sr- and Nd-isotope study of fossil fish teeth from the south German molasse and comparison to concurrent global changes may elucidate questions on the thermal and oceanographic development of the basin in response to the Alpine orogeny. Our interest in the Upper Marine Molasse is primarily stimulated by its deposition during the Middle to Upper Miocene, which is a period of pronounced global oceanographic and climatic change (e.g. Kennett, 1985).

2. Geologic setting

Sediments of the Tertiary molasse basin of southern Germany were deposited in a classical foreland basin whose present outcrop extends from Lake Geneva to lower Austria (Fig. 1; Lemcke, 1984; Bachmann and Müller, 1992). The Tertiary sedimentary record is characterized by two major transgressive–regressive cycles, which in turn can be subdivided into two smaller cycles: the Lower Marine and Freshwater Molasse (Eocene to Early Miocene), and the Upper Marine and Freshwater Molasse (Early to Late Miocene; Fig. 2). The major sedimentary units correlate with the sea-level curve of Haq et al. (1988), suggesting a eustatic control on the sedimentation, but with additional influence by sediment loading and flexural subsidence related to the uplift of the Alps (Jin et al., 1995). Predominantly marine sediments such as shales and marls within each cycle pass unconformably upwards into more continental sandstones of shallow marine, deltaic and alluvial fan origin (Fig. 2; Lemcke, 1984; Bachmann and Müller, 1992). For most of the marine depositional cycles shallow water conditions existed, although depths of 800 to 1000 m have also been estimated (Lemcke, 1984; Bachmann and Müller, 1992).

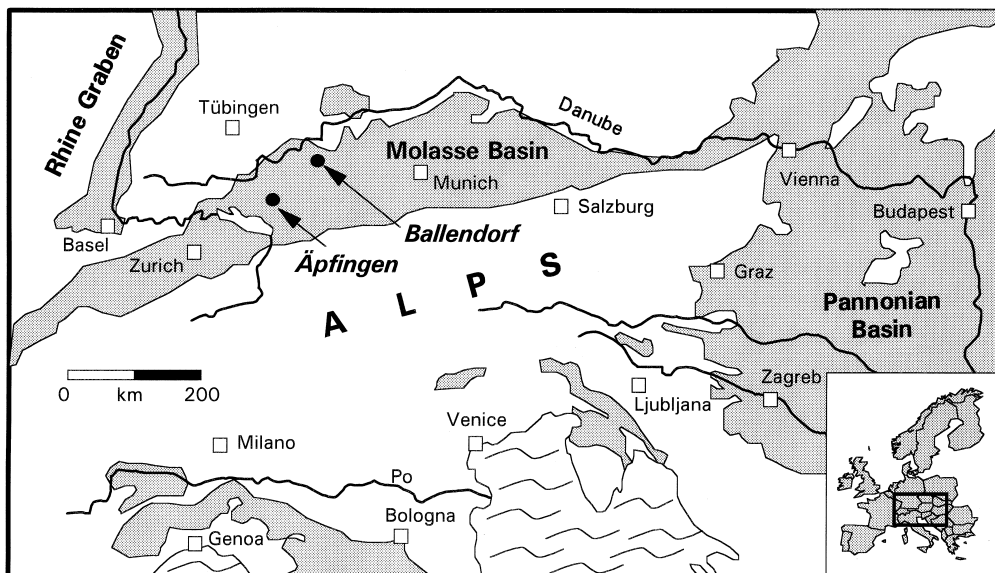


Fig. 1. Schematic map of the Molasse Basin, the Pannonian Basin, and the Rhine Graben. Shaded portions represent approximate present outcrop of the Tertiary sediments. Also indicated are the sample localities of Äpfingen and Ballendorf.

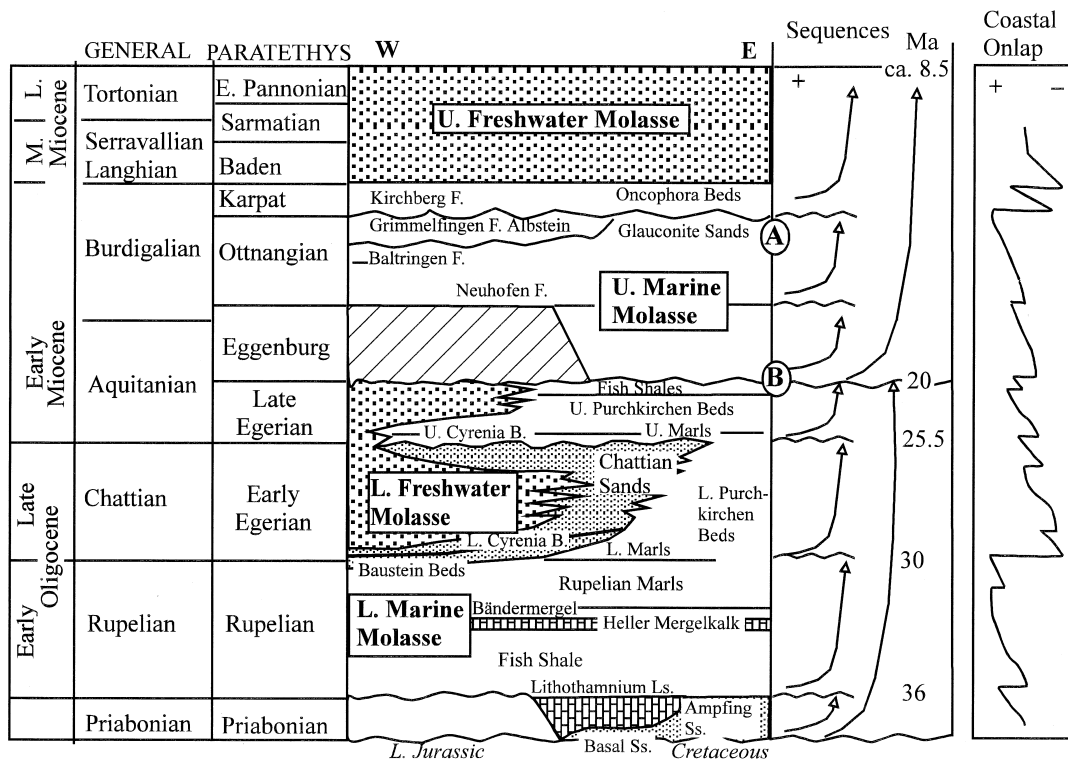


Fig. 2. Stratigraphy of the Molasse Basin sediments after Bachmann and Müller (1992). Coastal onlap curve is after Haq et al. (1988). Sample localities are shown as A (Äpfingen) and B (Ballendorf).

Of interest to this study are the Upper Marine Molasse sediments (OMM, Obere Meeresmolasse; to avoid confusion with the existing literature, the German abbreviation is used), which are characterized by marls and fine- to coarse-grained sand layers with occasional conglomerates in the southern, Swiss part of the basin, as well as the lower Austrian sections. The sandy layers of the OMM are noted for their abundance of shark teeth with only subordinate amounts of carbonate fossils. In the north, the OMM sediments border against the Late Jurassic limestones which have formed the northern shoreline of this part of the Paratethys. Much of the northern OMM sediments were removed during subsequent erosion.

3. Sampling and analytical techniques

Samples for this study were collected from two localities within the OMM: the villages of Äpfin-

gen and Ballendorf (Figs. 1 and 2). At each locality approximately 2 m³ of generally loose, unconsolidated sediment was sieved and shark teeth were selected for analysis. Scanning electron microscope images of the teeth reveal a crystallinity of the teeth that matches that of modern specimens (T. Jones, unpublished data). Oxygen isotope analyses of the teeth followed a technique adapted after Crowson et al. (1991) and O'Neil et al. (1994). Individual teeth, or portions thereof, were soaked for 12 h in 2.5% NaOCl to remove much of the organic matter, washed several times in distilled water and then soaked for another 48 h in NaOH to remove humic acids not removed by NaOCl. After several rinse cycles with distilled water, the phosphate was dissolved in HF, the eluate neutralized with KOH and subsequently precipitated as Ag₃PO₄ by the addition of a solution of ammoniacal silver nitrate. Filtered crystals of Ag₃PO₄ were washed several times in distilled water, dried at 50°C overnight and reacted with known amounts of graphite in sealed

silica tubes to produce CO₂. For several samples the Ag₃PO₄ was also reacted with BrF₅ on a silicate extraction line and the released O₂ quantitatively converted to CO₂. The oxygen isotope composition of the CO₂ was measured on a Finnigan MAT 252 mass spectrometer, and it directly reflects the oxygen isotope composition of the hydroxyapatite of the tooth. Oxygen isotope compositions are expressed in the δ -notation relative to VSMOW: $\delta^{18}\text{O} = \left[\frac{(^{18}\text{O}/^{16}\text{O})_{\text{Sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{VSMOW}}} - 1 \right] \times 1000$. Replicate analyses of NBS-120c gave values of $21.5\% \pm 0.2\%$, consistent with measurements of this standard by Lécuyer et al. (1993, 1996) and O'Neil et al. (1994). Repeated measurements were within $\pm 0.2\%$ for both the reaction with graphite and the fluorination techniques.

Sr- and Nd-concentrations as well as their isotopic compositions were determined on the same sample powders used for oxygen analyses. About 5 mg of sample powder was decomposed in dilute HNO₃ and the elements were separated using conventional cation exchange chromatography (Hegner et al., 1995). The concentrations of Sr and Nd were determined by isotope dilution using ¹⁵⁰Nd–¹⁴⁹Sm and ⁸⁴Sr tracer solutions. Total procedure blanks are <30 pg for Nd and Sm, and <100 pg for Sr. The isotopic ratios were determined on a Finnigan MAT 262 using a dynamic multiple mass data collection routine. Analysis of NBS-SRM 987 Sr standard yielded ⁸⁷Sr/⁸⁶Sr = 0.710238 ± 10 (2σ , external, $n = 90$). The La Jolla Nd standard yielded ¹⁴³Nd/¹⁴⁴Nd = 0.511852 ± 10 (2σ , external, $n = 25$). ⁸⁷Sr/⁸⁶Sr ratios are relative to ⁸⁶Sr/⁸⁸Sr = 0.1194 and ¹⁴³Nd/¹⁴⁴Nd ratios to ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219.

ϵ_{Nd} values are corrected for an age of 20 Ma and are given as:

$$\epsilon_{\text{Nd}}^t = \left[\frac{(^{143}\text{Nd}/^{144}\text{Nd})_{\text{measured}}}{(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}}^t} - 1 \right] \times 10^4$$

where ¹⁴³Nd/¹⁴⁴Nd for present day CHUR is 0.512638 and ¹⁴⁷Sm/¹⁴⁴Nd is 0.1967 (Jacobsen and Wasserburg, 1980).

4. Results

The results of the present study on shark teeth from several taxa (*Synodontaspis* sp., *Galeocerdo* cf.

aduncus, *Chaenogaleus* sp.) and button teeth of the bony fish *Chrysophrys molassica* are summarized in Table 1. Average $\delta^{18}\text{O}$ values of the teeth for Äpfingen are 21.2‰ ($1\sigma = 0.6\%$), while those for Ballendorf average 20.3‰ ($1\sigma = 0.5\%$). Analyses of different parts of the same tooth (enameloid-dominated tip, orthodontine and osteodontine mid- to lower sections) give $\delta^{18}\text{O}$ values that are indistinguishable within the analytical error (Fig. 3 and Table 1). Different teeth from the same taxa within each locality, however, have different $\delta^{18}\text{O}$ values, varying by up to 1.6‰. There is no discernible correlation between tooth size nor tooth type (taxa) and $\delta^{18}\text{O}$ values (Fig. 3).

The Sr-isotope compositions and Sr concentrations differ significantly between the two localities (Fig. 4). Samples from Äpfingen have similar ⁸⁷Sr/⁸⁶Sr ratios with an average of 0.70882 (± 0.00003 , 2σ). The Sr-concentrations of the samples range from about 2000 to 3000 ppm. The samples from Ballendorf also have uniform ⁸⁷Sr/⁸⁶Sr ratios with an average of 0.70850 (± 0.00001 , 2σ). The ⁸⁷Sr/⁸⁶Sr ratios of samples from Ballendorf are significantly lower than those for samples from Äpfingen (Fig. 4b). The Sr concentrations of the Ballendorf samples range from about 1400 to 1800 ppm, which are also lower than those from Äpfingen. Similarly, the Nd isotope compositions differ significantly between samples from the two localities (Fig. 5) with Äpfingen having ¹⁴³Nd/¹⁴⁴Nd ratios ranging from 0.51222 to 0.51225, while samples from Ballendorf have lower values of 0.51220 to 0.51221. No difference is observed in the Nd concentrations of samples from the two localities. Both Sr and Nd concentrations overlap the values reported for shark teeth in other well-preserved marine sections (e.g. Staudigel et al., 1985; Shaw and Wasserburg, 1985; Grandjean et al., 1987).

5. Discussion

5.1. Open versus restricted marine basin

In order to use isotopic analyses of marine sediments from the molasse of southern Germany for reconstructions of the palaeoceanography and palaeoclimate, it is important to establish whether they

Table 1

O-, Sr-, and Nd-isotope compositions of shark teeth from the Miocene Upper Marine Molasse of southern Germany

Sample	Genus and species	Part of tooth	$\delta^{18}\text{O}$ (‰)	Sr (ppm)	$^{87}\text{Sr}/^{86}\text{Sr}$	Nd (ppm)	Sm (ppm)	$^{143}\text{Nd}/^{144}\text{Nd}$	$^{147}\text{Sm}/^{144}\text{Nd}$	ϵ_{Nd} ^a
<i>Äpfingen (eastern edge of the village)</i>										
A1	<i>Synodontaspis</i> sp.	Top 2 mm	21.9	2010	0.708762	–	–	0.512226	–	–8.0
A6	<i>Chaenogaleus</i> sp.	Complete	21.4	2670	0.708861	32.56	6.03	0.512236	0.1120	–7.6
A7	<i>Chrysophrys molassica</i>	Half of 'button'	20.2	2635	0.708855	–	–	0.512248	–	–7.6
A8	<i>Chrysophrys molassica</i>	Half of 'button'	21.1	2965	0.708816	32.03	6.44	0.512226	0.1206	–7.8
A9a	<i>Chaenogaleus</i> sp.	Top 2 mm	21.7							
A9b	<i>Chaenogaleus</i> sp.	Mid 2 mm	21.2							
A9c(1)	<i>Chaenogaleus</i> sp.	Bottom-dentine	21.7	2480	0.708811	8.92	1.56	0.512232	0.1055	–7.7
A9c(2)	<i>Chaenogaleus</i> sp.	Bottom-dentine	21.7	2390	0.708810					
A10	<i>Synodontaspis</i> sp.	Top 3 mm	20.4							
A11	<i>Synodontaspis</i> sp.	Top 4 mm	20.7							
A12	<i>Synodontaspis</i> sp.	Complete	21.6	2200	0.708846	8.34	1.54	0.512220	0.1116	–7.9
A13	<i>Chaenogaleus</i> sp.	Complete	21.3	2725	0.708835	–	–	0.512253	–	–7.5
<i>Ballendorf (region of Langenau)</i>										
B1	<i>Synodontaspis</i> sp.	Top 7 mm	20.1	1390	0.708487	25.54	4.40	0.512201	0.1042	–8.3
B4a	<i>Synodontaspis</i> sp.	Top 7 mm	21.1	1800	0.708518	17.42	3.09	0.512202	0.1071	–8.3
B4b	<i>Synodontaspis</i> sp.	Bottom-dentine	20.9	1810	0.708503	25.53	4.27	0.512203	0.1011	–8.3
B5(1)	<i>Chaenogaleus</i> sp.	Complete	19.8	1620	0.708496	39.12	7.33	0.512199	0.1132	–8.4
B5(2)	<i>Chaenogaleus</i> sp.	Complete	19.8	1700	0.708494					
B6(1)	<i>Galeocerdo</i> cf. <i>aduncus</i>	Complete	20.0	1570	0.708476	–	–	0.512210	–	–8.3
B6(2)	<i>Galeocerdo</i> cf. <i>aduncus</i>	Complete	20.5							
B6(3)	<i>Galeocerdo</i> cf. <i>aduncus</i>	Complete	20.1							

^a Uncertainty is about 0.2 ϵ -units; value is calculated for 20 Ma, except for samples where no Nd and Sm concentrations are given and the ϵ -value is given for present-day $^{143}\text{Nd}/^{144}\text{Nd}$. Correcting for 20 Ma changes the ϵ -value by about +0.2.

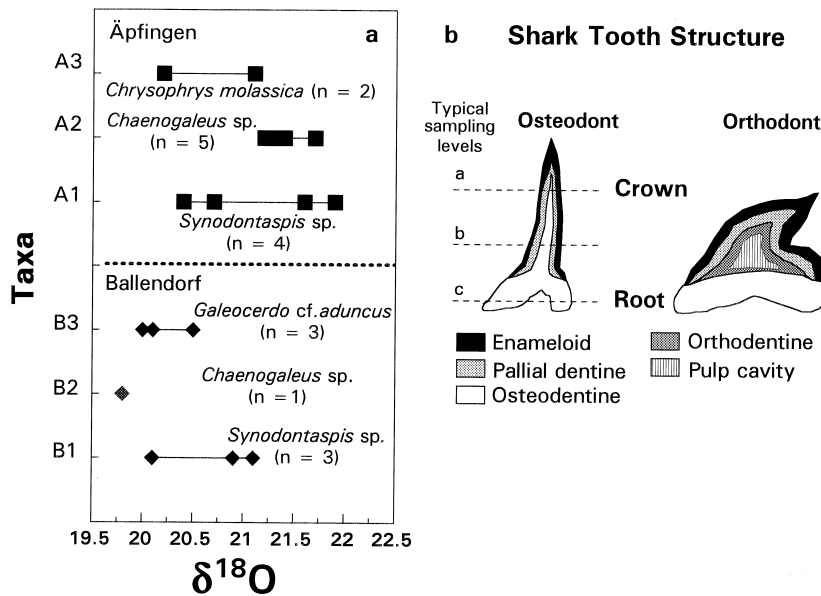


Fig. 3. Oxygen isotope compositions of shark teeth from Äpfingen and Ballendorf in permil relative to VSMOW (a). Also shown in (b) are typical structures for osteodont- and orthodont-type shark teeth with typical sampling levels corresponding to sample number suffix in Table 1.

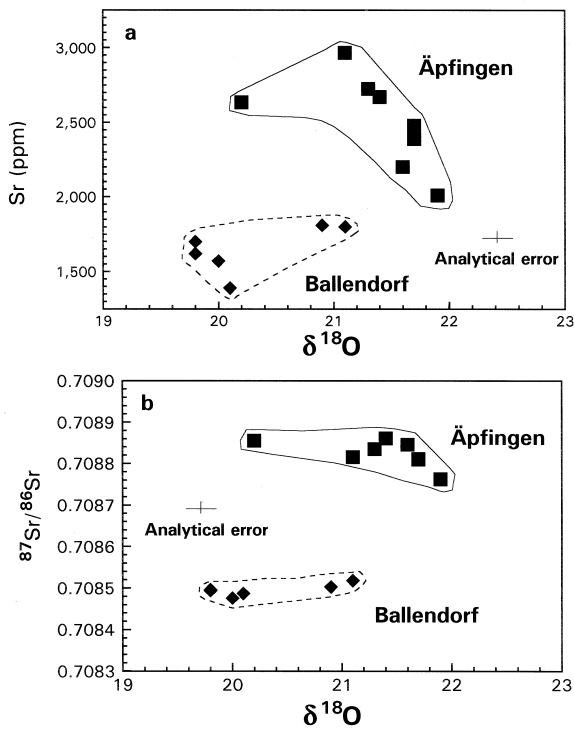


Fig. 4. Comparison between the $\delta^{18}\text{O}$ values of shark teeth and their Sr concentrations (a) and Sr-isotope compositions (b).

were deposited in a basin open to the global oceans, a restricted, or even isolated marine basin. The inferred shallow marine conditions prevalent during sedimentation of much of the marine molasse sediments, together with palaeogeographic and palinspastic reconstructions of the Tertiary Paratethys (e.g. Steininger and Rögl, 1984), open up the possibility that the molasse basin may have been a marine basin with limited connection to the global oceans. If this were to be the case, then the O-, Sr-, and Nd-isotope composition of the seawater would be characterized by local environmental conditions. For example, a significant addition of meteoric water would lower the $\delta^{18}\text{O}$ value of the seawater in a closed basin, much like it is observed for the Baltic Sea at present (e.g. Förstel, 1983). Alternatively, if the climate was arid, strong evaporation could lead to an enrichment in ^{18}O of the seawater. A modern example for this is the Red Sea (Craig, 1966).

Samples from the locality of Ballendorf were taken in the vicinity of outcrops of the Lower Fresh-

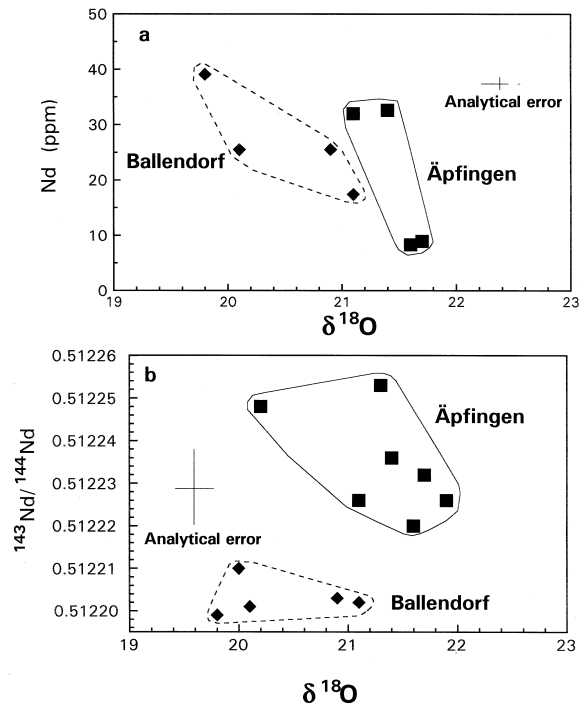


Fig. 5. Comparison between the $\delta^{18}\text{O}$ values of shark teeth and their Nd concentrations (a) and Nd-isotope compositions (b).

water Molasse while those for Äpfingen were, along strike, found to be in contact with the Upper Freshwater Molasse. This geologic relation implies that samples from the locality of Äpfingen are stratigraphically above those for Ballendorf (Fig. 2). The measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the two localities and a comparison of these ratios with the Sr-isotope evolution curves for Neogene seawater (e.g., Koepnick et al., 1985; DePaolo, 1986; Hodell et al., 1991), are compatible with the stratigraphic position of the samples, that is, samples from Äpfingen have higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios relative to those from Ballendorf (Table 1). In Fig. 6, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the two OMM localities are compared to high-precision data from the open ocean (DePaolo, 1986) and to biochronologic estimates of the depositional age of the OMM (Bachmann and Müller, 1992). Latter estimates are based on detailed biostratigraphic work within the molasse sequence. By comparison to the Sr isotope evolution curve from site 590B of the Deep Sea Drilling Project (DSDP; DePaolo, 1986) shown in Fig. 6, the measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for

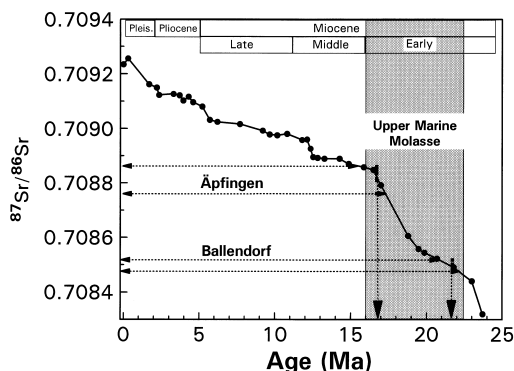


Fig. 6. Comparison between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured on shark teeth from Äpfingen and Ballendorf (shown as small filled squares and depicted by the horizontal arrows) and the Sr-isotope evolution curve for the ocean after DePaolo (1986; data points shown as filled circles). The shaded area represents the depositional age for the Upper Marine Molasse (after Bachmann and Müller, 1992).

the locality of Ballendorf can be assigned to average ages of 21.7 ± 1 Ma and those for Äpfingen 16.8 ± 1 Ma. Uncertainties in the ages include the analytical error, as well as errors that derive from fitting the data to the Sr-evolution curve of DePaolo (1986). Given that the residence time for Sr in the oceans during the Neogene was similar to that of today, then the isotopic variations measured by DePaolo (1986) can be assumed representative for the Sr-isotope variation of the global oceans. Subsequent measurements of $^{87}\text{Sr}/^{86}\text{Sr}$ on other DSDP sites (e.g. Hodell et al., 1991; Miller et al., 1991), have been found to be in good agreement with those measured by DePaolo (1986), confirming that the oceans were indeed homogeneous in their $^{87}\text{Sr}/^{86}\text{Sr}$ ratio throughout the Neogene. However, while the overall shape of the Sr-isotope evolution curves are very similar, small differences in the bio- and magnetostratigraphic constraints at individual sites as well as questions on local diagenetic alterations, result in a Sr-evolution band rather than a curve, producing differences in absolute ages of ± 2 Ma. Thus even though the relative difference in measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between well preserved samples can resolve stratigraphic differences as small as 0.2 Ma (equal to the analytical error), the assigned absolute ages determined for the teeth from the OMM are only meaningful to within ± 2 Ma. Nonetheless, the as-

signed ages for the teeth of about 22 and 17 Ma are in good agreement with depositional ages estimated for the OMM (Bachmann and Müller, 1992; Berger, 1992). This agreement may be taken as evidence for deposition of the OMM sediments in an open marine basin which was not significantly affected by contributions of terrestrial Sr from Alpine lithologies.

To determine the influence of Sr and Nd contributions from the Alpine crust on the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of the seawater within the molasse basin, it is necessary to know the proportions of the lithologies that contribute sediment, as well as the Sr and Nd concentrations, and the Sr- and Nd-isotopic compositions of the lithologies. Mineralogic composition of the sands and conglomerates of the OMM of southern Germany indicate that the sediment input is dominated by recycled Mesozoic chemical sediments, with subordinate amounts of metamorphic and granitic (Variscan) components (approximate proportions of 56 : 27 : 17; Haag, 1991). Similar lithologies and proportions thereof were estimated by Henry et al. (1997) to supply sediment to the OMM in the Swiss and French parts of the molasse basin, although their estimate includes significant proportions of alkaline granites, which are not known to occur in the more central parts of the Alps (Brügel et al., 1997). Given lithologic proportions similar to those estimated by Haag (1991) and typical Sr concentrations for chemical sediments, metamorphic, and granitic rocks (610 ppm, 250 ppm, and 300 ppm, respectively; Mason and Moore, 1982), as well as $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for such rocks (0.7078, 0.7194, and 0.7110, respectively; Faure et al., 1978; Liew and Hofmann, 1988; Hunziker et al., 1992), then simple mass balance calculations predict that the Sr contributed to the seawater from the Alpine crust would have an average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7099. This ratio is higher than the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for the global ocean at the time of molasse sedimentation (Koepnick et al., 1985; DePaolo, 1986; Hodell et al., 1991). Significant continental influence on a restricted or closed marine basin would thus tend to increase the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the ambient seawater to values above those for the global ocean.

A similar calculation for the Nd-isotope composition of Alpine crust which may have shed sediment into the molasse basin gives an average ϵ_{Nd} value of -9.9 (Nd concentrations of 6, 20, and 26 ppm, and

ϵ_{Nd} of -10.9 , -8.1 , and -8.2 , respectively; Mason and Moore, 1982; Liew and Hofmann, 1988; Henry et al., 1997). This is somewhat lower than the ϵ_{Nd} values estimated for the Tethys and North Atlantic between about 24 and 15 Ma (Stille et al., 1996, and references therein), and hence a significant crustal influence on the Nd-isotopic composition of the molasse basin seawater would tend to lower the ϵ_{Nd} value.

These calculations are very simplistic, however, in that the sediment source rocks, their Sr- and Nd-concentrations and isotopic composition, as well as the susceptibility of these rocks to weathering and erosion is little constrained. For example, Sr may be preferentially contributed from chemical sediments compared to the silicic rocks of the Alps. Preferential erosion of chemical sediments would raise the proportion of Sr with low $^{87}\text{Sr}/^{86}\text{Sr}$. This could lead to a crustally derived bulk $^{87}\text{Sr}/^{86}\text{Sr}$ ratio similar to that for global ocean water at the time of molasse sedimentation. Under such circumstances the Sr-isotopic composition of the molasse basin seawater would not be sensitive to Alpine crustal contributions. Furthermore, the above mass balance calculations have also neglected a significant sediment input from the postulated northern and northeastern shoreline to the OMM (e.g. crystalline rocks from the Bohemian Massif). Clearly, more detailed studies of sediment sources and their isotopic compositions are required before models on the crustal contribution of Sr and Nd to the molasse basin seawater can be refined.

Given, for the present study, that the above modelling is appropriate, then a further argument for the OMM basin having good connections with the global oceans is given by a comparison of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with the $\delta^{18}\text{O}$ values (Fig. 4b). The palaeoflora of time-equivalent lithologies of the lower Rhine area suggests that much of Germany experienced a warm and humid climate with mean annual temperatures of about 16 to 21°C, and precipitation of about 1300 mm (Mosbrugger, 1994). This implies that if the connections between the molasse basin and the open oceans were restricted, a significant input of meteoric water would have lowered the $^{18}\text{O}/^{16}\text{O}$ ratio of the seawater as meteoric water is depleted in ^{18}O relative to water from the open oceans. Warm, humid conditions would also lead to increased weathering and erosion of the Alpine hinterland. On the basis

of the above modelling, the effect of this crustal contribution of Sr on a closed basin would be higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the seawater of the molasse basin compared to the open ocean at the time of sediment deposition. However, *higher* average $\delta^{18}\text{O}$ values and *higher* average $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the locality of Äpfingen compared to that of Ballendorf (Fig. 4b), are compatible with open marine conditions rather than a restricted marine basin.

A comparison of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios for the localities are also helpful for distinguishing open versus restricted marine conditions. If both of these ratios were mutually controlled by regional crustal input, as would be the case for a restricted or isolated marine basin, a sample with higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios would have lower $^{143}\text{Nd}/^{144}\text{Nd}$ ratios. This is not observed though as Äpfingen has both higher $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios when compared to Ballendorf.

5.2. Palaeothermometry

Using the temperature calibration of Kolodny et al. (1983), and assuming a $\delta^{18}\text{O}$ value for the open ocean of -1‰ (a value typical for the pre-glacial ocean), then the average $\delta^{18}\text{O}$ values of teeth from Äpfingen and Ballendorf would correspond to ambient seawater temperatures of 16°C and 20°C ($\pm 4^\circ\text{C}$ in both cases), respectively. This temperature calculation is made without allowance for variations in salinity nor seawater $\delta^{18}\text{O}$ values. While changes in salinity are difficult to constrain, data from Shackleton and Kennett (1975) and Savin et al. (1975) indicate that the major build-up of the Antarctic ice sheet, and hence significant changes in the $\delta^{18}\text{O}$ values of the oceans, did not occur until about the Middle Miocene at about 14 Ma. The calculated absolute temperatures of 16 to 20°C are in good agreement with estimates of temperature from continental palaeontologic records (Mosbrugger, 1994), and are also very similar to those determined for shark teeth from other Miocene fish deposits (Fig. 7 and Kolodny and Luz, 1991). Of particular interest are the deposits from the Middle Miocene Atlantic of western France, which represent samples from a similar latitude to those considered in this study (Lécuyer et al., 1996). $\delta^{18}\text{O}$ values for fish teeth and bones from these deposits are between 21.4 and

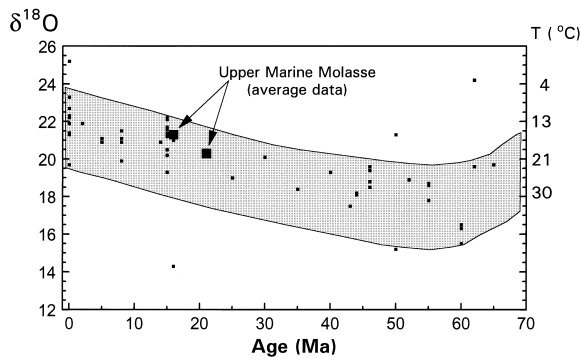


Fig. 7. Secular variation of the $\delta^{18}\text{O}$ values of phosphatic material from marine fish during the last 70 Ma (small squares, data from Kolodny and Luz, 1991). Average $\delta^{18}\text{O}$ values for the shark teeth from Äpfingen and Ballendorf are depicted as large filled squares. Temperatures given on the right side of the figure were calculated using the equation of Kolodny et al. (1983) and assuming ambient seawater with a $\delta^{18}\text{O}$ value of -1‰ .

22.7‰ (Lécuyer et al., 1996). These values are similar to those measured for the shark teeth of the present study, and hence would correspond to similar temperatures.

It is of interest to note that the Sr concentration of the teeth from the two localities also differ (Fig. 4a). If the incorporation of Sr into the hydroxyapatite structure follows a similar behaviour as the incorporation of Sr in marine calcite and aragonite, then this difference would also be compatible with temperature differences at the time of the hydroxyapatite formation. It has been observed by Kinsman (1969) that with decreasing temperature the Sr concentration in crystalline carbonates increases. No such difference is observed in the Nd-concentration of the teeth though (Fig. 5a), where no such temperature relation is known to exist.

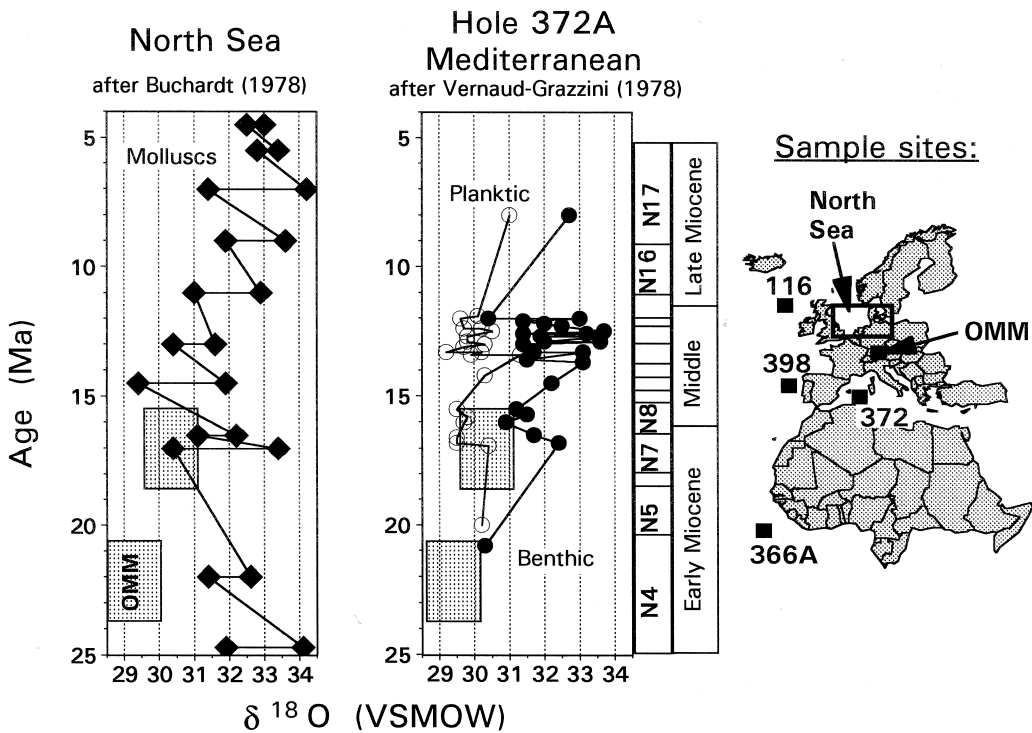
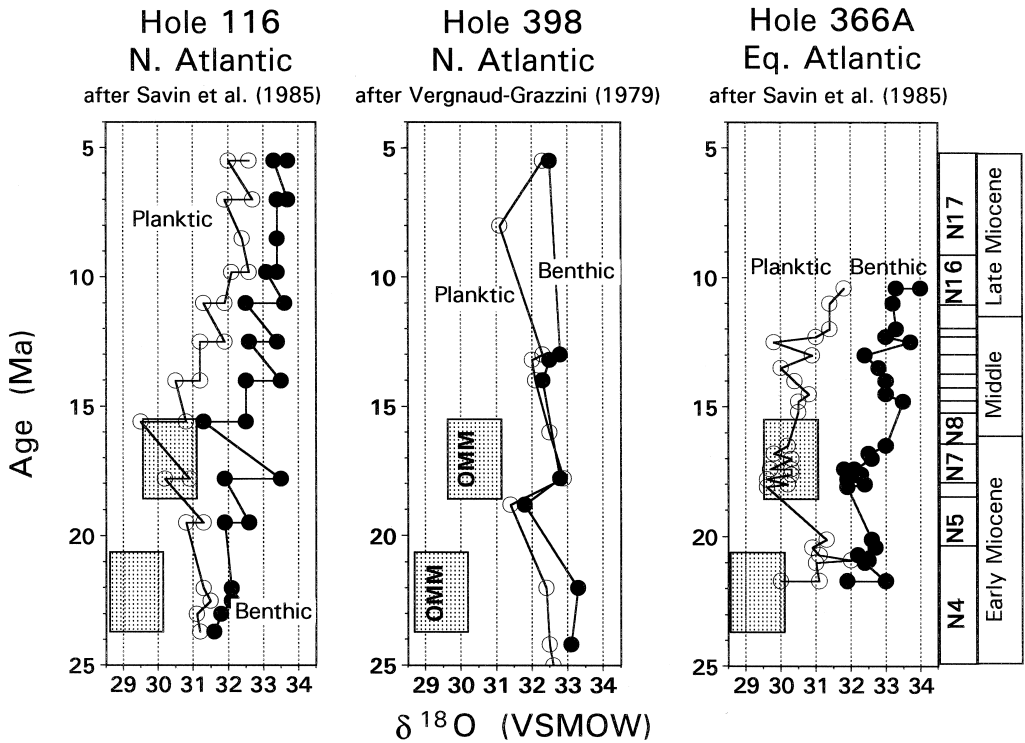
The fairly large differences in $\delta^{18}\text{O}$ values between different shark teeth from the same locality are surprising and lead to fairly large errors in average temperature estimates for each locality. Several reasons lead us to believe that this range in $\delta^{18}\text{O}$ val-

ues is not caused by diagenesis, but instead reflects real short-term differences in temperature, salinity, or O-isotope composition of the ambient seawater.

Partial recrystallization of phosphatic samples can result in heterogeneous $\delta^{18}\text{O}$ values, even for samples from the same bone (e.g. Shemesh, 1990; Iacumin et al., 1996). It has also been suggested (e.g. Ayliffe et al., 1994) that dentine is more prone to recrystallization compared to enamel. In contrast, complete recrystallization in the presence of a diagenetic fluid would tend to homogenize originally distinct $\delta^{18}\text{O}$ values. For the present study, however, individual teeth are found to be homogeneous in oxygen isotope composition, that is, dentine-dominated lower portions of the teeth are similar in isotopic composition to portions dominated by enamel-rich top portions (Table 1). This suggests that partial recrystallization of the teeth may not be the cause for variable $\delta^{18}\text{O}$ values. Complete recrystallization of all the teeth is also considered unlikely as different teeth from the same sediment batch have different $\delta^{18}\text{O}$ values. The variation in O-isotope compositions of the shark teeth from the same sediment batch is also not unusual for samples from marine sections as carbonates from DSDP sections, judged to be unaffected by diagenetic alteration (see below), show similar variations.

Also, while the Sr concentration of freshwater, which may be important during diagenesis, is very low, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios thereof can be high, owing to the contribution of radiogenic Sr from old continental crust. Diagenetic recrystallization of the phosphate in the presence of freshwater solutions is thus likely to generate higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the recrystallized phosphate. This was observed to be the case for altered phosphatic material by McArthur and Herczeg (1990), who reported a negative correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and $\delta^{18}\text{O}$ values for altered phosphatic material. However, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of different teeth from the same sample site of this study have very similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratios but dif-

Fig. 8. Comparison of the average $\delta^{18}\text{O}$ values of the shark teeth of this study with those of benthonic and planktonic foraminifera from DSDP drilling sites, and $\delta^{18}\text{O}$ values for molluscs from the Tertiary North Sea. 9‰ has been added to the $\delta^{18}\text{O}$ values of the shark teeth because it approximately corresponds to the equilibrium fractionation between carbonate and phosphate at temperatures of 10 to 30°C (Longinelli and Nuti, 1973; Craig, 1965). Their range in $\delta^{18}\text{O}$ values for a given time span are depicted as shaded boxes. For simplicity, at any one age, only the range in $\delta^{18}\text{O}$ values of the carbonates are shown rather than individual data points. Data are from Buchardt (1978), Vergnaud-Grazzini (1978, 1979) and Savin et al. (1985).



ferent $\delta^{18}\text{O}$ values, and the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are also compatible with Miocene seawater compositions.

Absolute ambient seawater temperature estimates through analyses of phosphates and carbonates must always be interpreted with caution. The reason for this is that the oxygen isotope composition of the seawater, its salinity and the subsequent diagenetic effects imposed on fossilized phosphates and carbonates, can all influence the oxygen isotope compositions, and all are difficult to constrain. More emphasis is, therefore, placed on the trends in $\delta^{18}\text{O}$ values and their implied changes in temperature. Present results for the oxygen isotope analyses of the shark teeth are compatible with 4°C cooling of the western Paratethys between 22 and 17 Ma. This trend is similar to that for Tertiary phosphate (Fig. 7) and carbonate samples on a global scale (e.g. Shackleton and Kennett, 1975; Savin et al., 1975; Buchardt, 1978; Savin et al., 1985; Kolodny and Luz, 1991). However, on a regional scale some differences between the results of this study and those from oxygen isotope analyses of foraminifera and molluscs become apparent. This is illustrated in Fig. 8 where variations in $\delta^{18}\text{O}$ values of benthonic and planktonic foraminifera from several DSDP sites of the Atlantic Ocean and the Mediterranean Sea, as well as $\delta^{18}\text{O}$ values of molluscs from the North Sea are compared to those of the shark teeth of this study. For the purpose of comparison, 9‰ have been added to the average $\delta^{18}\text{O}$ values of the shark teeth (approximate equilibrium fractionation between coprecipitated phosphate and carbonate at temperatures between 10 to 30°C ; Longinelli and Nuti, 1973; Craig, 1965). The range in $\delta^{18}\text{O}$ values and inferred ages for the shark teeth are also shown in Fig. 8. As plotted in this figure, coprecipitated phosphates and carbonates would overlap. In more detail, given the nektonic habitat of the sharks investigated, it may be expected that their $\delta^{18}\text{O}$ values would fall between those of the planktonic and benthonic foraminifera, in deep basins probably closer to those of the planktonic foraminifera.

The oxygen isotope data for Atlantic sites shown are compatible with either constant temperatures (Site 398) or with a slight warming (N. Atlantic Site 116 and tropical Atlantic Site 366A) of bottom as well as surface waters during the Early Miocene (Fig. 8, and Savin et al., 1985). This is also the case

for the mollusc data from the Early Miocene North Sea (Buchardt, 1978). The trend for the shark teeth of this study is different, however, and is compatible with overall cooling. The $\delta^{18}\text{O}$ values of the 17 Ma site of Äpfingen do overlap with the planktonic foraminifera of the Atlantic DSDP sites 116 and 366A, as well as with the molluscs from the North Sea though. Hence, these phosphate and carbonate phases would predict similar seawater temperatures for this period only.

Samples from the Mediterranean DSDP Site 372A are similar to the shark teeth of the OMM, in that they show similar trends in $\delta^{18}\text{O}$ values. Furthermore, the oxygen isotope composition of the teeth is also similar to that expected for phosphate in equilibrium with the carbonate for this site, implying similar absolute temperatures for similar oxygen isotope compositions and salinity of the ambient seawater. The overall similarity in both absolute temperature estimates and thermal evolution of the Mediterranean site and the OMM basin, but their difference to the estimates for the Atlantic sites and the Tertiary North Sea, opens up the possibility that the Alpine orogeny may have had a regional thermal effect.

5.3. Palaeoceanography

Comparing the Nd-isotope compositions of the shark teeth with those suggested for the North Atlantic and the Tethys (Fig. 9), a small increase in $^{143}\text{Nd}/^{144}\text{Nd}$ (or ϵ_{Nd}) observed for Äpfingen relative to Ballendorf, may be explained by influence of the North Atlantic on the isotopic composition of the Paratethys of the molasse basin. While there is abundant overlap between the ϵ_{Nd} values of the Tethys and the North Atlantic between 20 and 15 Ma (Stille et al., 1996), the ϵ_{Nd} values for shark teeth from this study as well as those from glauconites from the Swiss part of the OMM (Stille and Fischer, 1990) mimic the trend shown by the North Atlantic rather than the Tethys. An influence of the North Atlantic on the Tethys at about 16 to 18 Ma has also been suggested on the basis of palaeontologic studies of the molasse sediments, where various molluscs typical for the Atlantic fauna begin to emerge in many of the Alpine marine molasse sediments (F. Rögl, pers. commun., 1997). While a connection between

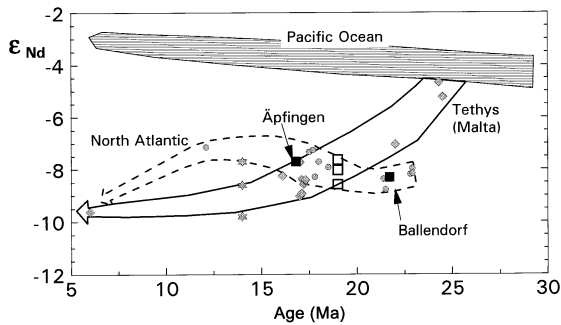


Fig. 9. Variations of ϵ_{Nd} values of Pacific, North Atlantic and Tethys seawater during the past 30 Ma. Data for the North Atlantic (shaded circles), the Tethys (shaded diamonds), and the Pacific Ocean are from Stille and Fischer (1990), Stille et al. (1996, and references therein). Data from Grandjean et al. (1987) for sediments in southern France are shown as shaded stars. Data for the Upper Marine Molasse of Switzerland are shown as open squares (after Stille and Fischer, 1990) while those for the Upper Marine Molasse of southern Germany (this study) are shown as solid squares.

the Paratethys and the North Atlantic is most commonly described as being via the Rhône basin and the Mediterranean Tethys, the contrasting trends in ϵ_{Nd} between our data and those from the Tethys as represented by a section sampled in Malta (Stille et al., 1996), may suggest a connection between the Paratethys and the North Atlantic via the Rhine Graben and the North German lowlands. Alternatively, the Mediterranean Tethys and the western Paratethys of the molasse basin had different sediment sources.

It is interesting to point out that the small but significant increase in the ϵ_{Nd} values between Ballendorf (average $\epsilon_{Nd} = -8.3$) and Äpfingen (-7.7) is similar to that measured on Burdigalian sediments by Henry et al. (1997) for the French and Swiss molasse sediments deposited further towards the southwest. Henry et al. (1997) argued that the increase in ϵ_{Nd} values resulted from erosion of late Variscan alkaline granites with ϵ_{Nd} values of about -2 to -5 . Compared to the typically S- or I-type Variscan granitoids that make up the largest proportion of the Variscan granitoid rocks in the Alps (e.g. Finger and Steyrer, 1990), alkali granites are rare and have not been observed in the central portions of the Alps, nor has detritus from such rock types been found in the south German molasse sediments (Brügel et al., 1997).

6. Conclusions

The results of this study allow for the following conclusions.

(1) By comparison with the Neogene marine Sr-evolution 'curve', the absolute ages for the teeth from Ballendorf are 22 ± 2 Ma while those for Äpfingen are 17 ± 2 Ma. This range in ages is in good agreement with the biostratigraphic record for the molasse sediments.

(2) The combined $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{18}\text{O}/^{16}\text{O}$ ratios of the shark teeth from the south German OMM are compatible with an unrestricted connection between the Paratethys of the molasse basin and the global ocean system.

(3) Assuming constant salinity and pre-Antarctic glaciation seawater oxygen isotope compositions of -1‰ , the shark teeth of the OMM suggest decreasing average seawater temperatures of about 4°C between 22 and 17 Ma. This is similar to temperature changes calculated from other marine phosphates (e.g. Kolodny and Luz, 1991) and from foraminiferal records for the Mediterranean Tethys (Vergnaud-Grazzini, 1978). It is different from records for the North and Equatorial Atlantic and the North Sea (e.g. Buchardt, 1978; Savin et al., 1985). The thermal evolution of the Paratethys may have been similar to that of the North Atlantic and/or the North Sea at about 17 Ma, in accord with an Atlantic influence on the Tethys–Paratethys at that time.

(4) The data presented in this study allow for the interpretation that the Alpine orogeny had an effect on the regional circum-Alpine palaeoclimate. Further studies are required to verify this interpretation.

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