4. Aqueous fingerprinting of the middle to late Miocene Yecua wetland environment

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Abstract

Strontium isotopic ratios of ostracodes and foraminifera from the Miocene Yecua Formation of the Bolivian Chaco foreland basin suggest that a short-lived marine incursion invaded the lacustrine environment of the Miocene Chaco Basin whose water consisted of a mixture of dominant Brazilian Shield-derived and minor Andean-derived freshwater. Molluscan oxygen and carbon isotopes indicate that freshwater-dominated waters modified the original ^{12}C isotopic value of foraminifera, which show shallow marine environments. Sedimentary facies analysis, which reconstruct frequent changes between brackish marine and coastal lacustrine environments, agree with the geochemical observations.

4.1 Introduction

Middle to late Miocene sedimentary deposits of the Yecua Formation within the northern part of the southern Bolivian Chaco foreland basin contain controversial information about the timing and extent of eastward Andean growth and represent a detailed biostratigraphic record of central South American palaeoclimatic history (Marshall and Sempere, 1991; Marshall et al., 1993; Hulka et al., in press). Hulka et al. (in press) argued that the middle to late Miocene basin (14-7 Ma) was dominated by coastal marine environments including semiarid floodplains, shoreline, tidal and shallow marine facies. Marshall et al. (1993) suggested a shallow restricted marine environment between 10 and 8 Ma.

Based on strontium, oxygen, and carbon isotopic analyses of well-preserved ostracodes and foraminifera we aim to distinguish between marine and freshwater influences of various provenances.

4.2 Data and methods

We sampled ostracodes and abundant foraminifera from shell-hash coquinas and fine-grained sandstones, interbedded with marls and vary-colored mudstones, in two sections of the Yecua

Formation of the northern Chaco Basin. The section Angostura, on the banks the Rio Piray, is located approximately 30 km north of Santa Cruz, near the village Angostura. The section Abapó at the Rio Grande is about 200 km south of Santa Cruz, near the village Abapó (Fig. 4.1).

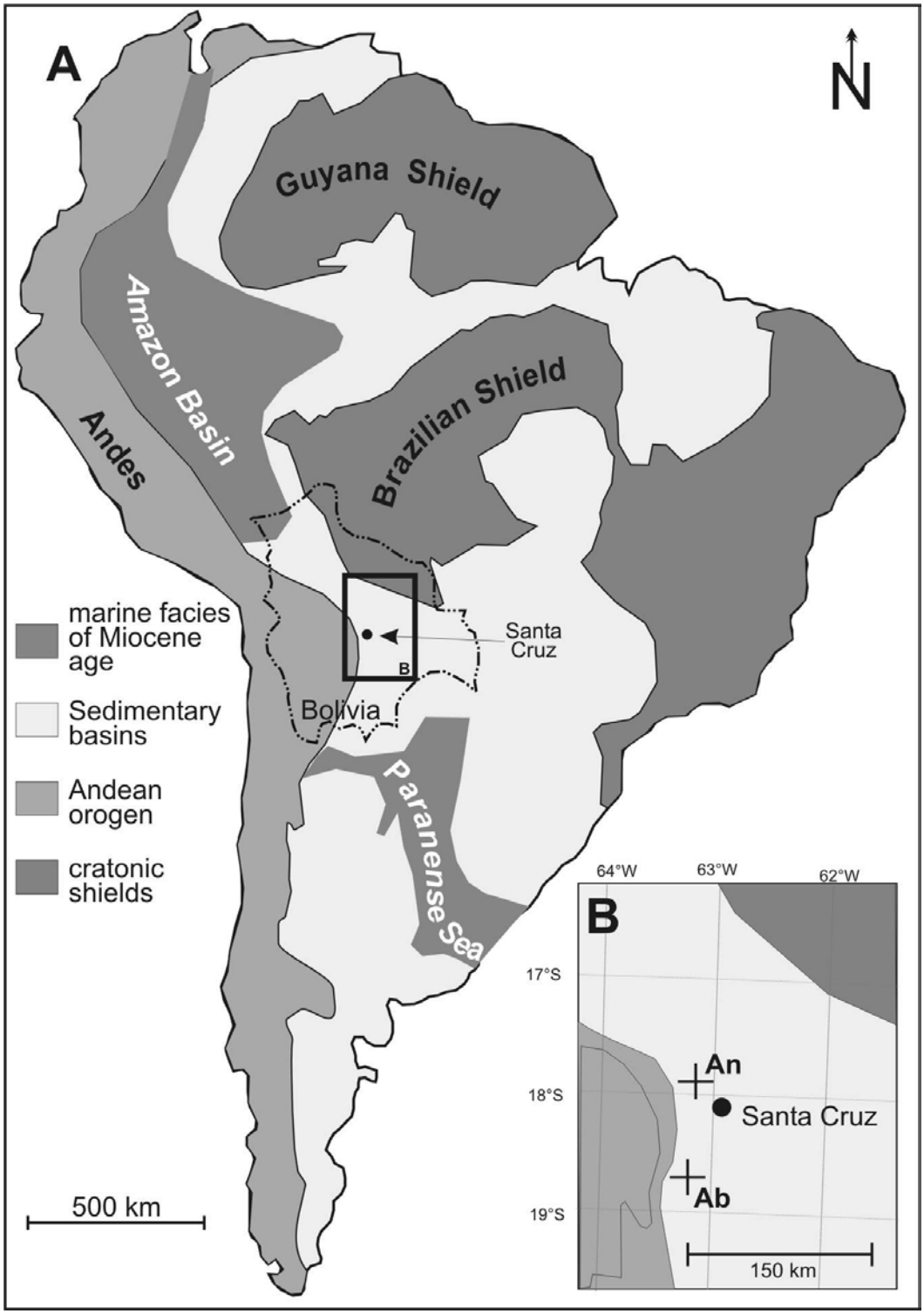

Fig. 4.1: (A) Geological map of South America showing the major geological units (Andes, cratons, and sedimentary basins) and major cities (SC = Santa Cruz). (B) Inset map shows the location of the samples (An = Angostura, Ab = Abapó)

Our database consists of samples interpreted by Hulka et al. (in press) as marginal marine.

4.2.1 Data

Foraminifera (*Anomalinoides* cf. *salinasensis*, *Cibicidoides* cf. *cushmani*, *Cibicidoides* aff. *mckannai*, *Gyroidina rosaformis*, *Holmanella valmonteensis*, *Nonionella miocenica*, *Pseudoparella californica*, *Hansenisca multicamerat*a, and *Holmanella baggi*) are middle to late Miocene in age (14-7 Ma; Finger, 1990; Finger, 1992) and collectively suggest sedimentation on a shallow marine shelf (Hulka et al., in press). In contrast, the ostracode *Cyprideis* aff. *torosa* is characteristic of meso- to polyhaline environments of up to 80% palaeosalinity. *Cyprideis* aff. *amazonica* and *Cyprideis* aff. *truncata* may occur in freshwater to fully marine environments (Oliver, 1992).

Based on the micropalaeontological record, Hulka et al. (in press) suggested an overall mixohaline environment with occasional influence by shallow marine incursions.

4.2.2 Methods

Before the measurement, we selected foraminifera and ostracodes and cleaned the microfossils with methanol. We measured $^{87}Sr/^{86}Sr$-ratios from foraminifera and ostracodes using a thermionic mass spectrometer (Finnigan 261 MAT) at the Department of Geological Sciences of the Freie Universität Berlin. For these measurements, we chose nine specimens of three species: *Cibicidoides cushmani* (foraminifera from section Angostura), *Nonionella miocenica* (foraminifera from section Abapó), and *Cyprideis truncata* (ostracode from section Abapó). In order to improve the homogeneity of the samples, we picked three specimens of each species and therefore obtained three results for each species. $^{18}O/^{16}O$- and $^{13}C/^{12}C$-ratios were determined at the GeoBio-Center of the Universität München using an Isotope-Ratio-Mass-Spectrometer. For this measurement, we sampled 30 specimens of three species (*Cibicidoides cushmani*, *Nonionella miocenica*, and *Cyprideis truncata*).

In isotope geochemistry, it is common to express the isotopic composition of oxygen and carbon in term of δ-values (delta). These values are expressed in per mil (‰) and are defined as differences in isotopic composition relative to a standard:

$$\delta^{18}O = (R_{Sample/}\ R_{Standard} - 1)* 1000 \qquad R = {}^{18}O/{}^{16}O$$
$$\delta^{18}O = (R_{Sample/}\ R_{Standard} - 1)* 1000 \qquad R = {}^{13}C/{}^{12}C$$

Positive δ-values demonstrate that the samples are enriched in the heavier isotope compared to the standard while negative δ-values represent depletion of the heavier isotope compared to the standard.

There are two international reference standards used to report variations in oxygen isotope ratios: PDB (Peedee Belemnite) and SMOW (Standard Mean Ocean Water). In our study, δ-values of C and O refer to CO_2 produced from Cretaceous belemnites of the Peedee Formation (PDB) in South Carolina. The PDB standard went through several generations (PDB II and PDB III) but no longer exists physically. Coplen et al. (1983) reported the conversion to the SMOW with the equation:

$$\delta^{18}O_{\ SMOW} = 1.03091\ \delta^{18}O_{\ PDB} + 30.91$$

The SMOW standard first existed as a hypothetical water sample with hydrogen and oxygen isotope ratios. To resolve the problem of SMOW being only a virtual standard, Craig (1961) distilled a large sample of ocean water and adjusted its isotopic composition until this water had the oxygen and hydrogen isotope ratios of SMOW.

4.3 Results

The results of the isotope measurements are listed in Tab. 4.1 for $^{87}Sr/^{86}Sr$-ratio and in Tab. 4.2 for $\delta^{18}O$- and $\delta^{13}C$-values.

Tab. 4.1: Isotopic results from foraminifera and ostracode calcite from samples of the middle to late Miocene Yecua Formation, Chaco Basin, southern Bolivia:

Sample	Fauna	Species	$^{87}Sr/^{86}Sr$ (± 2σ)
Angostura 1-1	Foraminifera	Cibicidoides cushmani	0.714539 ± 69
Angostura 1-2	Foraminifera	Cibicidoides cushmani	0.714446 ± 33
Angostura 1-3	Foraminifera	Cibicidoides cushmani	0.714574 ± 42
Abapó 1-1	Foraminifera	Nonionella miocenica	0.714726 ± 71
Abapó 1-2	Foraminifera	Nonionella miocenica	0.714810 ± 61
Abapó 1-3	Foraminifera	Nonionella miocenica	0.715800 ± 144
Abapó 2-1	Ostracodes	Cyprideis truncata	0.715090 ± 87
Abapó 2-2	Ostracodes	Cyprideis truncata	0.714886 ± 69
Abapó 2-3	Ostracodes	Cyprideis truncata	0.714692 ± 36

The $^{87}Sr/^{86}Sr$ -ratios for all measurements range between 0.7145 and 0.7158 (Tab. 4.1). The $^{87}Sr/^{86}Sr$-ratios from Angostura (0.7145 to 0.7146) are slightly lower than the $^{87}Sr/^{86}Sr$-ratios from Abapó (0.714692 to 0.715800). The $^{87}Sr/^{86}Sr$ ratio of the aliquot Abapó 1-3 is extremely high and does not fit with the other aliquots from Abapó 1-1, Abapó 1-2, and the other samples. Besides, exhibit Abapó 1-3 an unusually high standard deviation (Fig. 4.2).

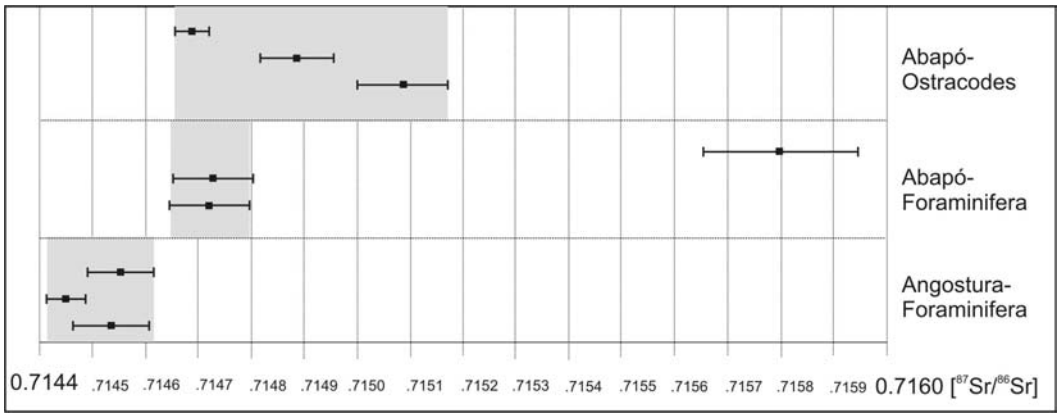

Fig. 4.2: Mean values and 2σ-standard deviations of strontium isotopic ratios from ostracodes and foraminifera from the Yecua Formation, Chaco Foreland Basin, Bolivia.

The $\delta^{18}O$-values of the microfossils from the Yecua Formation range between -6.86 (± 0.05) to -4.82 (± 0.23); the $\delta^{13}C$-values range between -8.01 (± 0.19) to -4.17 (± 0.15) (Tab. 4.2).

Tab. 4.2: Isotopic results from foraminifera and ostracode calcite from samples of the middle to late Miocene Yecua Formation, Chaco Basin, southern Bolivia:

Sample	Fauna	Species	$\delta^{18}O$	$\delta^{13}C$
Angostura-A	Foraminifera	Cibicidoides cushmani	-4.82 ± 0.23	-4.17 ± 0.15
Abapó-A	Foraminifera	Nonionella miocenic*a*	-5.95 ± 0.12	-8.01 ± 0.19
Abapó-B	Ostracodes	Cyprideis truncata	-6.86 ± 0.05	-5.38 ± 0.04

4.4 Discussion

4.4.1 Strontium systematics

Three major source regions are available for the middle to late Miocene water system within the Chaco Basin: Andean freshwater, Brazilian Shield-derived freshwater and middle to late Miocene sea-water.

Firstly, Andean freshwater runoff dominates the modern catchment of the Chaco Basin (Gubbels et al., 1993; Horton and DeCelles, 2001; Uba et al., in revision) with a low $^{87}Sr/^{86}Sr$ ratio of 0.7077 and a strontium concentration of 0.05 ppm (Palmer and Edmond, 1992; Fig. 4.3). Because the composition of the exposed Central Andean basement has not profoundly changed since the Miocene, Vonhof et al. (2003) assumed only insignificant change through time in these values delivered to the Andean foreland basins.

A second possible water provenance to the catchment area may have been runoff from Precambrian rocks of the Brazilian Shield. These streams show a present-day high $^{87}Sr/^{86}Sr$-ratio of 0.7300 with a very low strontium concentration of 0.01 ppm (Palmer and Edmond, 1992; Fig. 4.3). The tectonically stable setting in the center of the South America continent suggests that these values have not changed notably since the Miocene (Vonhof et al., 2003).

Thirdly, middle to late Miocene sea-water may have contributed to the Yecua environment. The $^{87}Sr/^{86}Sr$-ratio of middle to late Miocene sea-water ranges between 0.7088 and 0.7090 (Veizer et al., 1999) but is characterized by a very high strontium concentration of 7.89 ppm (Palmer and Edmond, 1992; Fig. 4.3).

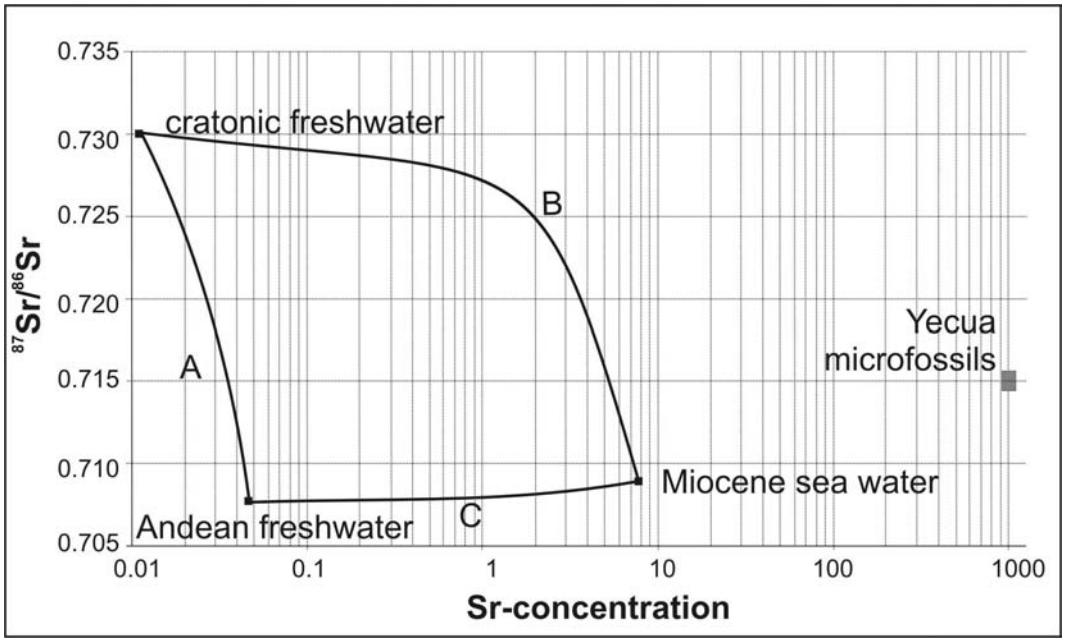

Fig. 4.3: Isotopic fingerprints of potential water sources to the Miocene Chaco basin using $^{87}Sr/^{86}Sr$-ratios and strontium concentrations. The plot show data of the Yecua microfossils (grey rectangle) and the assumed values for the three most likely water sources (black square after Palmer and Edmond, 1992; Veizer et al., 1999) from the middle to late Miocene basin and their mixing lines (A = cratonic freshwater - Andean freshwater, B = cratonic freshwater – Miocene sea-water, C = Andean freshwater - Miocene sea-water). Note logarithmic scale for strontium concentrations; black mixing lines would be strongly curved in linear scale. The precision of the $^{87}Sr/^{86}Sr$-ratios is better than ± 0.0001 while the Sr-concentration values are generally precise to <0.5 % (Palmer and Edmond, 1992).

Scasso et al. (2001), Li et al. (2002), and Kinsman (1969) published primary strontium concentrations for microfossils between 500 and 2000 ppm, whereas most benthic foraminifera and ostracodes have a strontium content of 1000 ppm. Therefore we assume for our samples a strontium content of 1000 ppm (Fig. 4.3), similar to the strontium content of microfossils of the Amazon Basin (Vonhof et al., 1998).

A strontium concentration of 1000 ppm in the shells of the Yecua Formation suggest an enrichment factor of > 100 for pure sea-water, > 20000 for pure Andean freshwater, and > 90000 for pure cratonic freshwater.

The very high $^{87}Sr/^{86}Sr$-ratios of the middle to late Miocene microfossils allow three mixing options. One option is a mixture between cratonic fresh water and Miocene sea-water (Fig. 4.4.A), a second possibility is a mixture of cratonic fresh water and Andean freshwater (Fig. 4.4.B), and a third alternative may be a mixture between all three potential water sources. A mixture between Andean freshwater and Miocene sea-water (line "C" in Fig. 4.3) would not yield measured $^{87}Sr/^{86}Sr$.

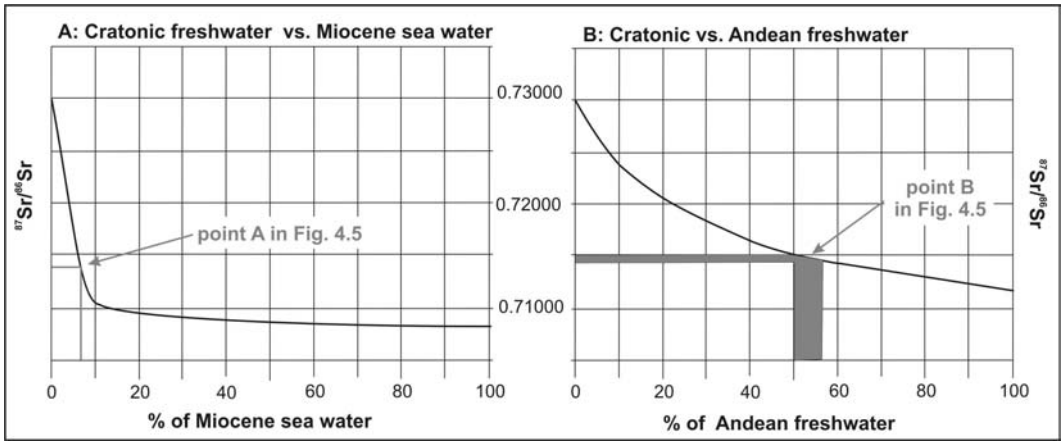

Fig. 4.4: Mixing curves (black lines) between theoretical water source end members. (A) Brazilian craton vs. sea-water. (B) Cratonic freshwater vs. Andean freshwater. The grey lines demonstrate the measured $^{87}Sr/^{86}Sr$-ratios from the microfossils of the section Angostura and the section Abapó.

Because the $^{87}Sr/^{86}Sr$-ratio from Angostura microfossils is slightly lower than that from Abapó, mixing models from these two locations differ slightly. For the binary system of cratonic runoff and Miocene sea-water (Fig. 4.4A), modeling yielded a mix of 7.5 % (Angostura) to 7 % (Abapó) sea-water combined with 92.5 to 93 % cratonic water (Fig. 4.4A). The binary system of cratonic runoff and Andean freshwater (Fig. 4.4B) indicates a mix of 56 % (Angostura) to 50 % (Abapó) of Andean freshwater with 46 to 50 % cratonic water (Fig. 4.4B).

If no diagenetic processes had occurred the original $^{87}Sr/^{86}Sr$-ratios of shells would reflect the $^{87}Sr/^{86}Sr$-ratio of the host water. Biological fractionation does not affect the values (Faure, 1986). However, clay material in the fossils' chamber may lead to enrichment of the heavy ^{87}Sr by radiogenic development of ^{87}Rb. Assuming that this was not the case, we consider two possibilities:

1. Microfossils shells incorporated an $^{87}Sr/^{86}Sr$-ratio of 0.714, which would indicate that the contribution of sea-water was less than 7 % to the aqueous environment (Fig. 4.4A). However, biostratigraphy suggests a marginal marine or shallow marine environment for the foraminifera (Hulka et al., in press). In this case, the biostratigraphic facies must be reconsidered and modified to include brackish environment.

2. Marine microfossil shells incorporated the primary marine signal of an $^{87}Sr/^{86}Sr$-ratio of 0.707. Early diagenetic substitution of the original calcite by calcite carrying cratonic freshwater isotopic ratios elevated the $^{87}Sr/^{86}Sr$ to the measured values. This must have taken place before the massive reduction in permeability associated with shale diagenesis, i.e. during very early diagenesis, characteristic for a brackish milieu. Scasso et al. (2001) discuss a similar process for microfossils of the Paranense Sea in eastern Argentina.

4.4.2 Stable isotopes: Oxygen and Carbon systematics

The stable $\delta^{18}O$- and $\delta^{13}C$-values of foraminifera and ostracodes show disequilibrium fractionation between their shells and the host water. All organisms show a temperature-sensitive fractionation between the host water and their shells. Wefer (1985) described, as many others before, that most living organisms (including benthic foraminifera and ostracodes) fractionate oxygen isotopes in accordance to the $\delta^{18}O$ temperature relationship established by Epstein et al. (1953). If the water temperature reaches 16.4°C, the isotopic signatures of the shells reflect their host water signature. With increasing temperature the $\delta^{18}O$ signal decreases with respect to the host water, and the $\delta^{18}O$ signal increases with respect to the surrounding water respectively (Epstein et al., 1953). Urey et al. (1951) was the first who suggested, in additional to the temperature-dependent fractionation, the so-called 'vital effects' which cause deviation of the isotopic composition of fossils compared to the expected isotopic composition of host water. Chivas et al. (1993) describe for a variety of organisms living in the same environment of constant temperature vital effects that cause offsets in the oxygen-isotope fractionation between biogenic carbonates and the host water. McConnaughey (1989) identified two diagenetic disequilibrium pattern, designated kinetic and metabolic. Kinetic discrimination against the heavy isotopes ^{18}O and ^{13}C occurs during CO_2-hydration and hydroxylation. In corals, rapid skeletogenesis favors strong kinetic effects and leads to isotopic depletion. Additional positive or negative modulation of skeletal $\delta^{13}C$ reflects changes in the $\delta^{13}C$ of dissolved inorganic carbon, which are caused by metabolic effects such as photosynthesis and respiration (McConnaughey, 1989).

However, reported isotopic deviations between living organisms and their host water seldom exceed 2.5 ‰ (Fritz and Poplawski, 1974; Tanaka et al., 1986; Fastovsky et al., 1993). Therefore, we assume in the following pages that the stable isotopic ratios of the shells reflect the signatures of their host water within these limits.

Fig. 4.5 illustrates a three end-member water system with the corresponding $\delta^{18}O$- and $\delta^{13}C$-values of the present-day Andean fresh water source, the present-day Brazilian craton runoff, and the middle to late Miocene $\delta^{18}O$- and $\delta^{13}C$-values for sea-water (Longinelli and Edmond, 1983; Bandel and Hoefs, 1975). Also integrated are the measured $\delta^{18}O$- and $\delta^{13}C$-values of the two foraminifera samples and the one ostracode sample and the proportion of mixture for the three water systems of the $^{87}Sr/^{86}Sr$ analysis (Tab.4.2).

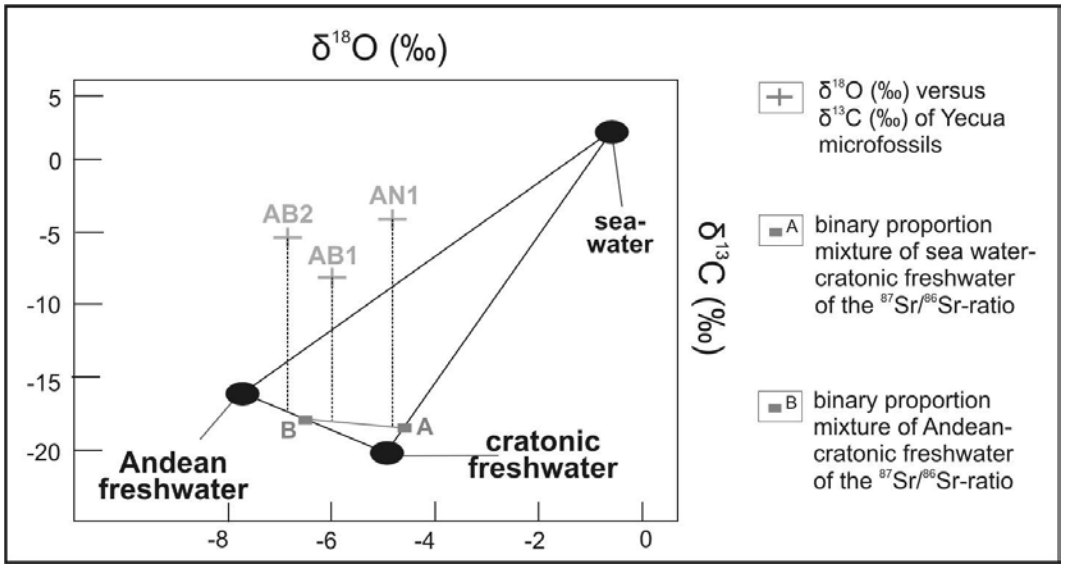

Fig. 4.5: $\delta^{18}O$- and $\delta^{13}C$-values (PDB) of Yecua Formation microfossils (grey crosses), compared with isotopic composition of potential water sources: Miocene sea-water (Veizer et al., 1999), modern Andean freshwater (Longinelli and Edmond, 1983) and Brazilian-craton freshwater (Longinelli and Edmond, 1983). Grey boxes A and B represent the estimated $\delta^{18}O$ and $\delta^{13}C$ isotopic composition of Yecua water due to water mixing, calculated from Sr-isotopic data.

$\delta^{18}O$- and $\delta^{13}C$-values of the Miocene microfossils (Fig. 4.5) should be situated within a the three end-member triangle defined by sea-water, Andean and cratonic water runoff. While the $\delta^{18}O$-values of the Yecua foraminifera are situated within the suggested range, the $\delta^{13}C$-values are highly enriched. This enrichment may be due to preferential removal of ^{12}C from water by plant growth, by anaerobic decomposition of organic matter, or by intensive exchange between aqueous and atmospheric CO_2 (Vonhof et al., 1998). Indeed, aquatic plant fossils and anoxic black shales in Yecua outcrops indicate anaerobic decomposition of organic matter (Hulka et al., in press) and may have contributed to the observed ^{13}C enrichment in Yecua microfossils. Furthermore, the Yecua lithofacies suggests a shallow water system in a coastal environment, which is prone to intensive exchange between aqueous and atmospheric CO_2.

Enrichment of $\delta^{13}C$ is well known from literature: Schmidlowski et al. (1976) described preferred withdrawal of ^{12}C by organic material in closed basins. Vonhof et al. (1998) observed that the general enrichment in ^{13}C (relative to their estimated values) is similar to the observed ^{13}C enrichment of long-lived lakes relative to their source river systems.

The proportion mixture of the $^{87}Sr/^{86}Sr$-ratios of the two binary water systems (A: cratonic freshwater vs. sea-water, B: cratonic freshwater vs. Andean freshwater; Fig. 4.4) are shown in Fig. 4.5 by a straight line (connecting points A and B) that represent the proportion mixture of $^{87}Sr/^{86}Sr$-ratios for the ternary system. This line falls in the range for the $\delta^{18}O$-values of the foraminifera samples. The $\delta^{18}O$-values for sample Abapó-B is slightly enriched (by 0.5 ‰), with respect to the end point B on line A-B.

4.5 Conclusions

4.5.1 Composition and provenance of the Yecua Formation water body; implications for regional paleogeographic reconstructions

The $^{87}Sr/^{86}Sr$-ratio of fossils within the marine-influenced horizons in the Yecua Formation reflects either (1) a mix of insignificant sea-water with dominant cratonic freshwater or (2) an approximately equal mix of Andean freshwater with cratonic freshwater. The data exclude the possibility of an open marine system for the Chaco Basin in the middle to late Miocene. Also, perhaps more realistically, and supported by the lithostratigraphic and paleontological data, a three-component mix may be likely. The postulated marine incursion was probably short in duration and appeared to transgress into (or over) a stable and dominant lacustrine environment. Such a scenario would also explain the occurrence of lacustrine microfossils close to the apparently marine bio- and lithofacies.

Combining all the results, we conclude that the analyzed microfossil shells show secondary depletion of carbon and oxygen soon after deposition, compared to their primary marine isotopic values.

The depletion of the $\delta^{18}O$- and $\delta^{13}C$-values with respect to the $^{87}Sr/^{86}Sr$-ratio suggests a mix of cratonic freshwater from the Brazilian Shield with Andean freshwater. Possibly (and only indicated by a trend defined by two geographic localities) the cratonic freshwater influence decreased from north toward the south, compatible with lithostratigraphic regional reconstructions (Hulka et al., in press).

However, the enrichment in $\delta^{13}C$ compared to the available water systems argue for a long-lived lacustrine environment following (and probably also prior to) the marine incursion. A similar time-equivalent palaeoenvironment is known for the Amazon Basin (Pebas Formation; Schmidlowski et al., 1976; Hoorn, 1993; Vonhof et al., 1998; Wesselingh et al., 2002). Vonhof et al. (1998) estimated a composition of approximately 10-15 % Miocene sea-water mixed with approx. 90-85 % cratonic freshwater for this basin. Because Andean freshwater shows a distinctive, very low $^{87}Sr/^{86}Sr$-ratio, these authors exclude a significant Andean-derived freshwater contribution. Our results are compatible and allow a southward continuation of this aqueous system into the Chaco Basin with less influence of Miocene sea-water ($\leq$ 7%) and higher Andean freshwater (56-50 %).

In contrast, south of the Chaco Basin, the Paranense Sea, a middle to late Miocene marine estuary system reaching from Uruguay to the north eastern part of Argentina (Aceñolaza and Sprechmann, 2002), shows a distinct development. A possible relation with the Yecua Formation of the Chaco Basin cannot be substantiated through our results.

Paleontological and lithofacies data from the Bolivian Yecua Formation, reported by Hulka et al. (in press), were ultimately inconclusive in quantifying the degree of marine influence from the north (Amazon Basin; Pebas Formation; Räsänen et al., 1995), the southeast (Paraguay Embayment; “Paranense Sea”; Aceñolaza and Sprechmann, 2002) or from both, as postulated in form of an “intercontinental seaway” by Webb (1995) and Ihering (1927). Our new $^{87}Sr/^{86}Sr$ data now exclude an open-marine origin of the Yecua basin and permit only a minor role of marine water entering a long-lived lacustrine environment, probably with decreasing southward influence. Should there have ever existed a connection from the Yecua basin to the south or southeastern Paranense Sea, characterized by Aceñolaza (2000) and Sprechmann et al. (2000) as an open sea, it is likely that this connection existed only during a short time period.

4.5.2 Tectonic implications

Can we infer from the limited isotopic data whether the Yecua Sea formed in a forebulge or a back-bulge basin?

Uba et al. (in revision) favored a distal foredeep origin of the Yecua Formation due to the interpretation of the underlying Petaca Formation having formed in a stable basin during a period of limited or non-sedimentation, and the overlying Tariquia Formation representing deposits in a foredeep depocenter. The oxygen isotopes from this study suggest a low to medium contribution of Andean freshwater to the Yecua environments and therefore imply that the distal foredeep, probably close to the forebulge, may have been low in relief or traversed by streams.

The decrease in sea-water and cratonic-shield influence and a corresponding increase in Andean fresh water component toward the south is only constrained by two data points and requires confirmation by additional data.

Acknowledgements

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