

**Late Quaternary pelagic aragonite
preservation in the Arabian Sea and its
paleoceanographic implications**

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Abstract

In the course of the Quaternary the carbon dioxide concentrations of the atmosphere showed large fluctuations related to the oceanic carbon cycle and carbonate system. The production, accumulation, and dissolution of pelagic aragonite constitutes a considerable part of the oceanic carbonate system. Variations in water mass properties, atmospheric and oceanic circulation, which lead to changes in bioproductivity in the upwelling areas influence the preservation of aragonite and therefore the preservation of pteropod shells.

This project is concerned with Late Quaternary preservation of pteropods in sediments of the Arabian Sea. To this purpose 15 surface sediment samples and two high resolution sediment cores from the Arabian Sea have been analysed by means of the pteropod shell preservation index LDX (*Limacina inflata* dissolution index, Gerhard and Henrich, 2001) in respect to the aragonite preservation state. One objective was to test and apply the newly developed LDX on sediments from the Arabian Sea and to trace spatial and temporal variations in pteropod preservation.

The results show that pteropod preservation during the Late Pleistocene was better than during the Holocene and therefore reflects the Indo-Pacific carbonate preservation pattern with increased preservation during glacials and decreased preservation during interglacials. On millennial time scales, good pteropod preservation in the sediments of the Arabian Sea occurs during the time-equivalents of Heinrich events, stadials, Younger Dryas (YD), while poor preservation occurs during the interstadials.

The analyses of the surface sediment samples and the sediment core 137KA off Pakistan indicate: (1) Pteropod occurrence in surface sediment samples is linked to bioturbated sediments on the shelf and upper continental slope. Only well to perfectly preserved pteropods have been found. (2) Pteropod preservation in core 137KA is characterized by two extreme preservation modes:

(a) Good to excellent preservation occurs during times of enhanced intermediate water formation in the northern Arabian Sea (YD, H-equivalents and stadials). Increased NE monsoon activity induced deeper convective winter mixing (down to 600 m water depth). Consequently, ventilation of the Oxygen Minimum Zone (OMZ) dramatically improved the aragonite preservation potential.

(b) Very rare occurrence or even absence of pteropods represents times of weak intermediate water formation resulting in stable OMZ conditions (stadials, Late Holocene). Decreased NE monsoon activity and shallower deep winter mixing (at present-day down to water depths of roughly 150 m), which does not lead to a ventilation of the OMZ, cause strong dissolution of aragonite by the corrosive waters within the OMZ.

In contrast to the extreme preservation pattern off Pakistan, the variation in pteropod preservation in sediment core 905 off Somalia is more gradual. All in-between stages of the LDX have been found, ranging from good preservation during H-equivalents, stadials, YD (periods with decreased bioproductivity indicated by low C_{org} values) to intermediate to poor preservation during interstadials (periods with increased bioproductivity indicated by high C_{org} values). SW monsoon-driven upwelling increases the bioproductivity and subsequent remineralization of organic matter. Release of CO_2 to the subsurface waters and pore waters leads to strong aragonite dissolution. On the contrary, periods with decreased upwelling intensity are characterized by reduced bioproductivity and remineralization of organic matter improving the aragonite preservation potential. In addition, a change in intermediate water circulation on glacial/interglacial time scale could contribute to the variations in pteropod preservation.

The bulk aragonite content is dominated by high-Sr-aragonite (aragonite producing shallow marine organisms, e.g., algae and corals) as shown by aragonite needles found in the fine fraction of the bioturbated sediments of the Pakistan core, fragments of corals found in the coarse fraction of both cores, as well as high Sr/Ca ratios occurring in both cores. Hence, pteropods contribute much less to the bulk aragonite budget than expected.

The aragonite record of core 905 correlates on glacial/interglacial time scales with the global sea level record. High aragonite values occur during sea level highstands and low aragonite values during sea level lowstands. This observation can be explained by 'highstand shedding of carbonate platforms' (Schlager et al., 1994) i.e., high input of shallow marine aragonite in times of sea level highstands due to increased production areas on the shelf.

Besides the sea level control on input of aragonite, changes in preservation strongly influence the bulk aragonite record. In spite of the high sea level during the Late Holocene, a dramatic decrease in aragonite concentration occurs. This can be explained by strong dissolution of aragonite as indicated by very low Mg-calcite concentrations and pteropod abundances.

The correlation of the Mg-calcite record with the pteropod abundance and preservation records in core 905 confirms the use of Mg-calcite concentration as a carbonate dissolution proxy.

Zusammenfassung

Der Kohlendioxidgehalt der Atmosphäre unterlag im Verlauf des Quartärs starken Schwankungen, die im Zusammenhang mit dem ozeanischen Kohlenstoffkreislauf und dem Karbonatsystem stehen. Die Produktion, Akkumulation und Lösung von pelagischem Aragonit bildet dabei einen Teil des ozeanischen Karbonatsystems. Veränderungen der Eigenschaften der Wassermassen, der atmosphärischen und ozeanischen Zirkulation, die zur Variation in der Bioproduktion in den Auftriebsgebieten führen, haben einen Einfluss auf die Erhaltung des Aragonits und somit auf die Schalenerhaltung von Pteropoden (Flügel-schnecken).

Dieses Projekt beschäftigt sich mit der spätquartären Erhaltung von Pteropoden in Sedimenten des Arabischen Meers. Hierzu wurden 15 Oberflächenproben und zwei hochauflösende Sedimentkerne aus dem Arabischen Meer mit Hilfe des Schalenerhaltungsindex LDX und Zählungen von ganzen Pteropoden sowie deren Fragmente in Bezug auf ihre Erhaltung untersucht. Ein Ziel war dabei, die Anwendbarkeit des von Gerhard und Henrich (2001) im Südatlantik entwickelten LDX auf Sedimente des Arabischen Meeres zu erweitern und zu testen sowie dessen räumliche und zeitliche Veränderung im Arabischen Meer zu dokumentieren.

Dabei zeigt sich, dass die Pteropodenerhaltung im Spätpleistozän besser ist als im Holozän, und damit das indopazische Karbonaterhaltungsmuster mit guter Erhaltung während der Glaziale und schlechter Erhaltung während der Interglaziale repräsentiert.

Gute Pteropodenerhaltung in Sedimenten des Arabischen Meeres tritt außerdem während der zeitlichen Äquivalente der Heinrich-Events, der Stadiale und der Jüngeren Dryas (YD) auf, dagegen nimmt die Erhaltung während der Interstadiale stark ab.

Die Analysen der Oberflächensedimentproben und des Sedimentkernes 137KA vor Pakistan zeigen, dass (1) das Vorkommen von Pteropoden in Oberflächensedimentproben auf bioturbirte Sedimente auf dem Schelf und oberen Kontinentalhang beschränkt ist; (2) die Pteropodenerhaltung im Sedimentkern 137 KA durch zwei extreme Erhaltungsmuster gekennzeichnet wird:

- (a) Gute bis exzellente Erhaltung tritt in Phasen verstärkter Zwischenwasserbildung im nördlichen Arabischen Meer (während der YD, Heinrich-Äquivalente und Stadiale) auf. Verstärkte Nordostmonsunaktivität führt zur tieferen konvektiven Mischung der Wassermassen (bis zu Wassertiefen von 600 m). Daraus folgt eine Ventilation der Sauerstoffminimumzone (OMZ), die das Aragoniterhaltungspotential drastisch verbessert.
- (b) Sehr seltenes Auftreten bis völlige Abwesenheit von Pteropoden repräsentiert Zeiten mit schwacher Zwischenwasserbildung, die zu einer stabilen Sauerstoffminimumzone führt (während der Interstadiale und im späten Holozän). Abgeschwächte Nordostmonsunaktivität

induziert eine flachere konvektive Mischung der Wassermassen (heutzutage bis in eine Tiefe von 150 m), wodurch eine Ventilation der Sauerstoffminimumzone verhindert wird. Folglich tritt starke Aragonitlösung durch korrosive Wassermassen innerhalb der Sauerstoffminimumzone auf.

Im Gegensatz zu den extremen Erhaltungsbedingungen vor Pakistan ist die Variation der Pteropodenerhaltung im Sedimentkern 905 vor Somalia kontinuierlicher. Alle Zwischenstufen des LDX, von guter Erhaltung während der Heinrich-Äquivalente, Stadiale und YD (Phasen mit abgeschwächter Bioproduktion, die durch niedrige C_{org} -Gehalte in den Sedimenten gekennzeichnet sind) bis zu moderater und schlechter Erhaltung während der Interstadiale (Phasen mit verstärkter Bioproduktion und hohen C_{org} -Gehalten der Sedimente) sind vertreten.

Der vom Südwestmonsun induzierte Auftrieb verstärkt die Bioproduktion und anschließende Remineralisierung des organischen Materials im Zwischenwasser und Porenwasser. Das dabei freigesetzte CO_2 führt zu starker Aragonitlösung. Im Gegensatz dazu sind die Phasen mit abgeschwächter Auftriebsintensität durch reduzierte Bioproduktivität und Remineralisierung gekennzeichnet, wodurch sich das Aragoniterhaltungspotential verbessert. Zusätzlich könnte die geänderte Zwischenwasserzirkulation im Arabischen Meer auf Glazial/Interglazial-Ebene zur unterschiedlichen Aragoniterhaltung beigetragen haben.

Der Gesamtaragonitgehalt wird von Hoch-Strontium-Aragonit (d. h. von aragonitproduzierenden Algen und Korallen im flachmarinen Bereich) dominiert. Darauf deuten Aragonitnadeln in der Feinfraktion der bioturbirten Lagen des Sedimentkerns vor Pakistan, Korallenfragmente in der Grobfraktion beider Kerne einhergehend mit hohen Sr/Ca-Verhältnissen. Die Pteropoden bilden somit nur einen Bruchteil des Gesamtaragonitbudgets.

Der Aragonitgehalt des Sedimentkerns 905 korreliert auf Glazial/Interglazial-Ebene mit der globalen Meeresspiegelkurve. Hohe Aragonitgehalte treten während Meeresspiegelhochständen auf, niedrige dagegen während Meeresspiegeltiefständen. Diese Beobachtung kann mit dem sogenannten ‚highstand shedding‘ (Schlager et al., 1994) von Karbonatplattformen erklärt werden, d. h. bei Meeresspiegelhochständen erhöht sich der Aragoniteintrag, der sich durch vergrößerte Produktionsflächen im flachmarinen Bereich erklären lässt oder verursacht wird.

Zusätzlich beeinflussen Änderungen in der Erhaltung den Gesamtaragonitgehalt. So nimmt beispielsweise trotz des hohen Meeresspiegels während des späten Holozäns, der Gesamtaragonitgehalt in diesem Zeitraum drastisch ab. Dies kann mit starker Lösung erklärt werden, die durch sehr niedrige Mg-Kalzitgehalte und Pteropodenhäufigkeiten angezeigt wird. Die Korrelation von Mg-Kalzit mit Pteropodenhäufigkeiten bzw. Schalenerhaltung im Kern 905 bestätigt die Nutzbarkeit des Mg-Kalzitgehaltes als Karbonaterhaltungsproxy.

Part I Introduction

1. Motivation and objectives

The carbonate system of the oceans plays an important role in the global carbon cycle. Changes in the oceanic carbonate budget are crucial to understand variations in Late Quaternary atmospheric CO₂ concentrations. The study of pelagic aragonite production, accumulation, and preservation therefore provides important information about the dynamics of carbon cycling in upper and intermediate water masses as well as the associated changes in oceanic circulation patterns and climatic conditions.

Shelled pteropods are the principle pelagic producers of aragonite and contribute ~10% (Fabry, 1990; Fabry and Deuser, 1991, 1992) to 12 % (Bernier and Honjo, 1981) to the total CaCO₃ production. Aragonite, a metastable polymorph of CaCO₃, dissolves at shallower water depths than calcite due to the higher solubility in seawater (e.g., Morse et al., 1980; Millero, 1996; Morse and Arvidson, 2002). Hence, the Aragonite Compensation Depth (ACD) is located at a much shallower depth than the Calcite Compensation Depth (CCD). Hence, pteropods have been used to reconstruct changes in the ACD, which is the depth where pteropod shells disappear in seafloor sediments (e.g., Chen, 1964; Berger, 1977, 1978; Bernier, 1977; Rottman, 1979). The preservation state of pteropod tests has been established as a proxy for the aragonite saturation state of water masses (e.g., Almogi-Labin et al., 1986; Haddad and Droxler, 1996; Gerhardt and Henrich, 2001).

1.1. Previous studies on Late Quaternary paleoceanography and paleoclimate in the Indian Ocean and Arabian Sea

Recent paleoclimatic research documents the world-wide occurrence of millennial-scale variability in climate related to Dansgaard-Oeschger (D/O) cycles (~1500 years) and Heinrich events, which represent the Late Pleistocene climate variability over Greenland and the northern North Atlantic (Heinrich 1988; Johnsen et al., 1992; Bond et al., 1993; Dansgaard et al., 1993). A compilation of the world-wide distribution of millennial to centennial-scale records is given by Voelker (2002). Variations in the Asian monsoon system on D/O time scales have been reported from different sites in the Indian Ocean: from varved sediment sections off Pakistan (e.g., Reichert et al., 1998; Schulz et al., 1998; Suthhof et al., 2001),

from bioturbated high resolution sediment sections in the Arabian Sea (e.g., Sirocko et al., 1993, 1996; Altabet et al., 1995, 1999, 2002; Ivanova, 2000; Pourmand et al., 2004; Ivanochko et al., 2005) and from the Bengal Fan (Kudrass et al., 2001). These records reveal increased summer monsoons during interstadials, and increased winter monsoons during stadials (for details of the evolution and variability of the Asian monsoon system refer to the recent review given by Wang et al. 2005).

The link between the North Atlantic and the Arabian Sea, however, is poorly understood. The age models associated with these various archives are insufficient to assess the details of phasing among the monsoon records themselves nor the details of monsoon phasing relative to high-latitude climate change at the level necessary to determine which system initiates these abrupt transitions (Wang et al., 2005). Atmospheric teleconnections have been suggested by several authors (e.g., Porter and Zhisheng, 1995; von Rad et al., 1999, Pourmand et al., 2004) while others invoke teleconnections via oceanic circulation (e.g., Schulte et al., 1999).

Concerning the pelagic carbonate system, several studies in the Indian Ocean have concentrated on the preservation of calcite (e.g., Ninety-East Ridge, Petersen and Prell, 1985; Owen Ridge, Murray and Prell, 1992; Equatorial Indian Ocean, Bassinot et al., 1994) and on the preservation of aragonite (e.g., Pakistan continental margin, Berger, 1977, 1978; Reichart et al., 1998, 2002; von Rad et al., 1999; Murray Ridge, Reichart et al., 1997, 1998; Somalia margin, Ivanova, 2000; Gulf of Aden, Almogi-Labin et al., 2000). However, only few of these investigations deal with the preservation of aragonite on millennial time scales.

This study is focused on pelagic aragonite preservation in surface sediments and Late Quaternary sediment cores of the Arabian Sea. High resolution mineralogical (calcite, Mg-calcite, aragonite), geochemical (Sr/Ca ratios, total organic carbon and CaCO₃ content) and micropaleontological data (pteropod counts and shell preservation records) are presented and discussed. The objectives are:

- to study pteropod preservation in surface sediments and Late Quaternary high-resolution sediment cores from the Arabian Sea,
- quantify the contribution of aragonite to the bulk carbonate budget,
- to investigate the factors influencing the preservation of pteropods/aragonite,
- to trace spatial and temporal changes of aragonite production/preservation during the Late Pleistocene/Holocene and to study the influence of climate, bioproduction,

- upwelling intensity, water mass circulation, extent of the OMZ on aragonite production/preservation,
- to compare a sediment core taken from the Somalia transect with a sediment core taken from the Pakistan section regarding different production/preservation of aragonite,
- to test the applicability of the newly developed *Limacina* Dissolution Index (LDX, Gerhardt and Henrich, 2001) in the Arabian Sea and to compare pteropod dissolution proxies with another carbonate dissolution proxy (Mg-calcite %),
- to analyse the impact of millennial-scale variations in the strength of the SW monsoon and in relative sea level on resuspensional input, pelagic production, accumulation and preservation of carbonates off Somalia,
- to compare our record with previously published Indian Ocean carbonate dissolution records.

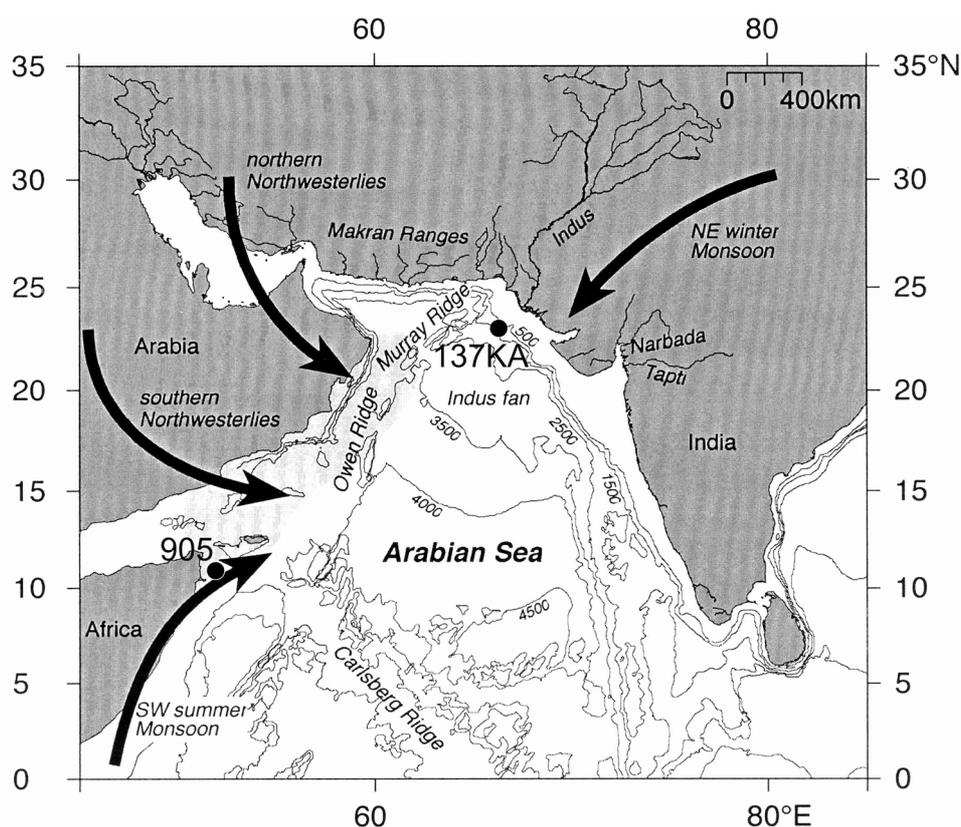


Fig. 1. Map of the wind systems controlling sedimentation processes (aeolian input), upwelling, and deep convective mixing in the Arabian Sea (modified after Leuschner et al., 2004).

The shaded area off Somalia and Arabia marks the region with enhanced biogenic surface water production due to SW monsoon induced upwelling. Significant river discharge (in particular by the Indus) is restricted to the Pakistan and Indian coast. Arrows illustrate direction of the main winds in the investigate area. Dots mark studied sites off Somalia (sediment core 905) and on the continental slope off Pakistan (sediment core 137 KA).

2. Climatic and oceanographic conditions

Seasonally reversing monsoonal winds characterize the climatic and oceanographic conditions in the Arabian Sea (Fig. 1). During boreal summer, sensible heating of the Asian landmass and condensational (latent) heating within the troposphere over Asia cause low pressure over Asia (Webster, 1987; Clemens et al., 1991). Latent heat is derived from surface evaporation over the southern subtropical Indian Ocean, transported across the equator and released during precipitation over Asia. The gradient between the low pressure over Asia relative to higher pressure over the southern subtropical Indian Ocean generates the warm and humid SW monsoon (Webster, 1987).

The strong monsoonal winds induce Ekman transport and upwelling of cold and nutrient-rich waters off Somalia and Oman (Wyrtki, 1973) and lead to a maximum in primary productivity between June and September (Conan et al., 2002). An Eastward drift of these nutrient-rich waters due to the clockwise surface water circulation results in high primary productivity in the northern part of the Arabian Sea (Banse, 1984).

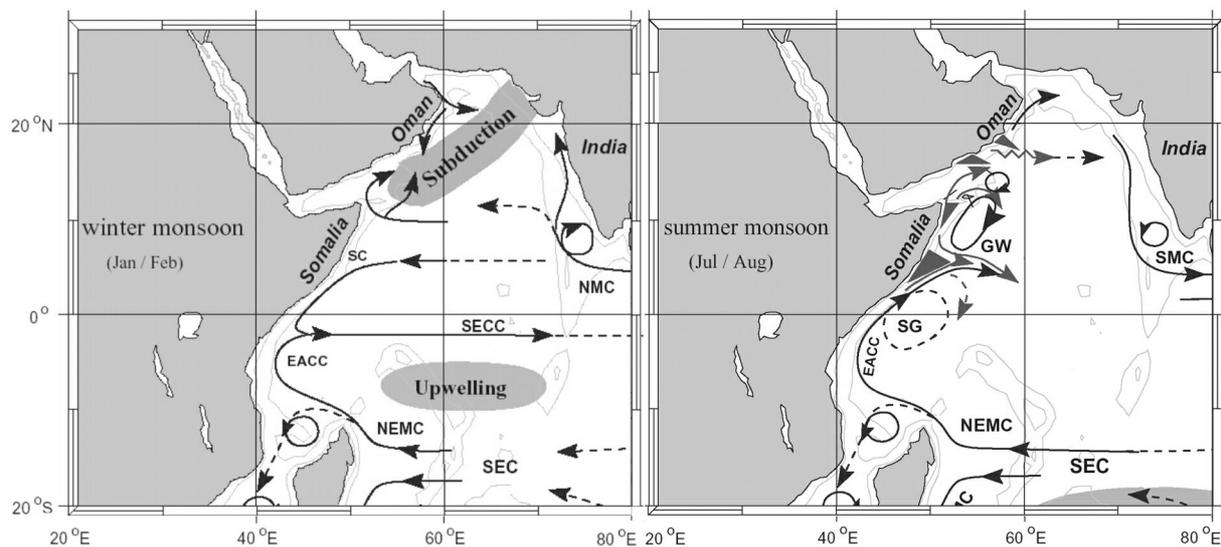


Fig. 2. A schematic map of the main surface currents during the Southwest and Northeast Monsoon (modified from Schott and McCreary, 2001). Marked are winter subduction area in the northern Arabian Sea, upwelling areas (dark grey). Note the seasonal change in the oceanic circulation due to the reversing atmospheric flow pattern. Current branches indicated are the South Equatorial Current (SEC), Northeast Madagascar Current (NEMC), East African Coast Current (EACC), Somali Current (SC), Southern Gyre (SG), Great Whirl (GW), Northeast and Southwest Monsoon Current (NMC and SMC) and South Equatorial Countercurrent (SECC).

In winter the atmospheric circulation pattern reverses. The cool and dry NE monsoon blowing from the Asian landmass causes deep convective mixing due to cooling of surface waters (Madhupratap et al., 1996) and injects nutrients to the surface leading to a second productivity maximum (Nair et al., 1989, Haake et al., 1993; Fig. 2).

High-surface water productivity (Qasim, 1977) and moderate rates of thermocline ventilation (You and Tomczak, 1993) generate a stable and pronounced mid-water Oxygen Minimum Zone (OMZ) between 150 - 1200 m (Wyrski, 1973; Deuser et al., 1978). Within the OMZ, high input and decay of organic matter raise dissolved inorganic carbon (DIC) concentrations in the subsurface waters and lower the pH (Millero et al., 1998), which results in a shallow aragonite saturation depth of 600 - 800 m in the Arabian Sea (Millero et al., 1998; Sabine et al., 2002). Below this depth bottom waters are undersaturated in respect to aragonite and aragonitic sediments start to dissolve (see chapter 3).

In addition, the release of metabolic CO₂ (due to export and subsequent decomposition of organic matter within the sediments) lowers the pore water pH and causes increased dissolution of carbonates (e.g., Emerson and Bender, 1981; Milliman et al., 1999) at the sediment/water interface and in the upper sediment layer.

Because of the intense variability in the circulation associated with the annual monsoon cycle, water mass structure in the upper kilometre of the Arabian Sea is extremely complex (Morrison, 2002). Arabian Sea Water (ASW, or Arabian Sea High-Salinity Water) is formed in the northern Arabian Sea during the NE Monsoon by subduction and spreads as salinity maximum underneath the surface-mixed layer (Morrison, 1997; Prasanna Kumar and Prasad, 1999; Schott and Fischer, 2000; Schott and McCreary Jr, 2001). Persian Gulf Water (PGW), which influence is restricted to the northern Arabian Sea (Schott and McCreary Jr, 2001) is a warm and saline near-surface water mass (~200 to 400 m water depth; Prasanna Kumar and Prasad, 1999). The high-salinity Red Sea Water (RSW) enters the Arabian Sea after mixing with the Gulf of Aden water and then spreads south through the passage between Socotra and the African continent (Schott and McCreary Jr, 2001). Off Somalia the core of RSW is located at 800 m depth (Shapiro and Meschanov, 1991). Indian Central Water (ICW) is formed in the subtropics of the southern hemisphere, spreads northward across the equator with the Somali Current supplying the upwelling water off Somalia and Arabia (Emery and Meincke, 1986; Schott and McCreary Jr, 2001). Aged ICW is termed North Indian Central Water (NICW, You and Tomczak, 1993).

The cold and low-salinity Circumpolar Deep Water (CDW) is found at greatest depths of the Somali basin (Schott and McCreary Jr, 2001; Dengler et al., 2002). Above the bottom water Indian Ocean Deep Water (IDW) is found between about 2000 and 3500 m (Warren, 1993). IDW flows in the density range just above CDW and is composed of upwelled CDW and mixed with older intermediate water masses (e.g., Warren and Johnson, 1992; Warren, 1993; Dengler et al., 2002).

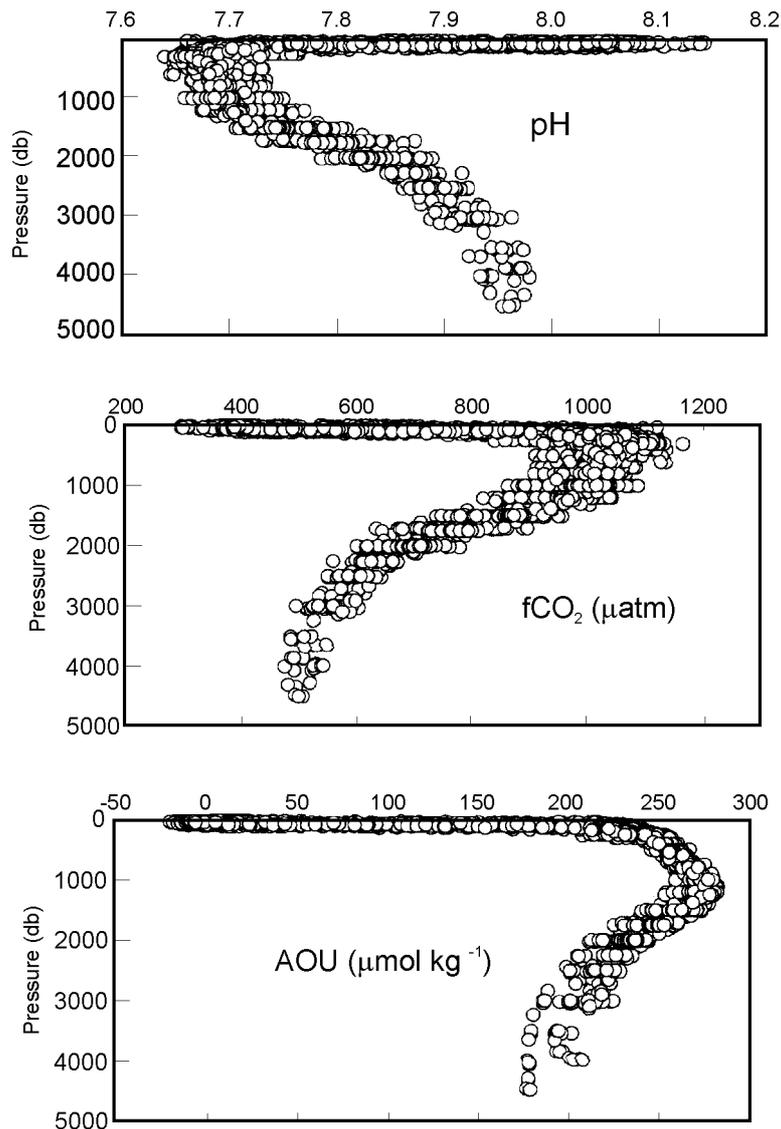


Fig. 3. Profiles of pH, fCO₂ and apparent oxygen utilisation (AOU) in the Arabian Sea measured in the WOCE/JGOFS studies (redrawn from Millero et al., 1998). Note the dramatic decrease in pH, increase in fCO₂ and AOU in the OMZ (200-1200 m). High organic matter decomposition rates in the OMZ (indicated by high AOU) lead to release of CO₂ to the subsurface waters and to a decrease in pH. For calculations of the pH, fCO₂ and saturation state refer to Millero et al., 1998.

3. Aragonite saturation depths derived from water column measurements

In the framework of the WOCE (World Ocean Circulation Experiment) and JGOFS (Joint Global Ocean Flux Study) programs measurements of the total inorganic carbon dioxide (TCO_2), total alkalinity (TA) and pH of water samples from the Arabian Sea have been performed (Fig. 3). The pH reaches a minimum and the carbon dioxide fugacity ($f\text{CO}_2$) a maximum in the OMZ (Millero et al., 1998). The profiles in the Arabian Sea are similar to those found in most oceans, but show a more pronounced minimum in pH and a maximum in $f\text{CO}_2$ (Millero et al., 1998).

This is due to increased rates of oxidation of organic matter as demonstrated by the profile of the apparent oxygen utilisation ($\text{AOU} = \text{O}_2(\text{saturation}) - \text{O}_2(\text{measured})$, Millero et al., 1998). These values of AOI are among the highest of those recorded in the open oceans as result of the extensive OMZ in the Arabian Sea.

All waters are undersaturated ($\Omega < 1$) with respect to aragonite below 600 m (and calcite below 3400 m, Millero et al., 1998; Fig. 4, Fig. 5). These values are in agreement with two previously published studies by George et al. (1994), who calculate 100 % aragonite saturation at 500 m and Mintrop et al. (1999), 600 ± 100 m water depth (3000-3200 m for calcite).

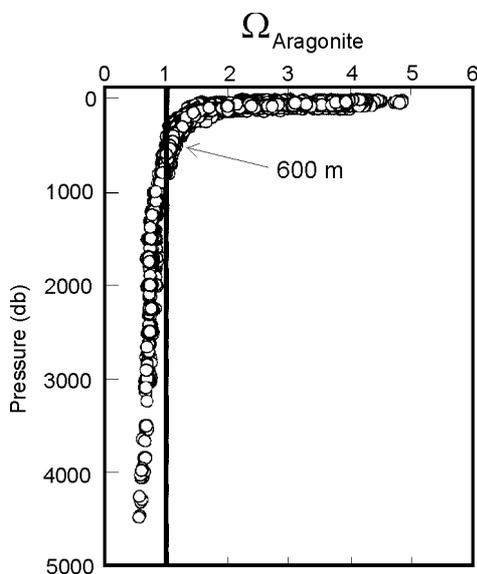


Fig. 4. The saturation state (Ω) of aragonite as a function of pressure in the Arabian Sea (redrawn from Millero et al., 1998). All waters are undersaturated ($\Omega < 1$) with respect to aragonite below 600 m. For calculations of the saturation state refer to Millero et al., 1998.

Note that the samples were taken in the central part of the northern Arabian Sea and do not include water samples from the locations of core 137 KA off Pakistan and core 905 off Somalia.

The ‘hydrographic’ aragonite lysocline (based on a kinetic approach and defined as the depth where aragonite saturation is 91%; Mintrop et al., 1999) is located at 800 – 1000 m.

Based on these depth-estimates, Millero et al. (1998) conclude that most of the increase in the observed normalised total alkalinity from surface to 3000 m depth is caused by the dissolution of aragonite in the water column and upper sediment layers.

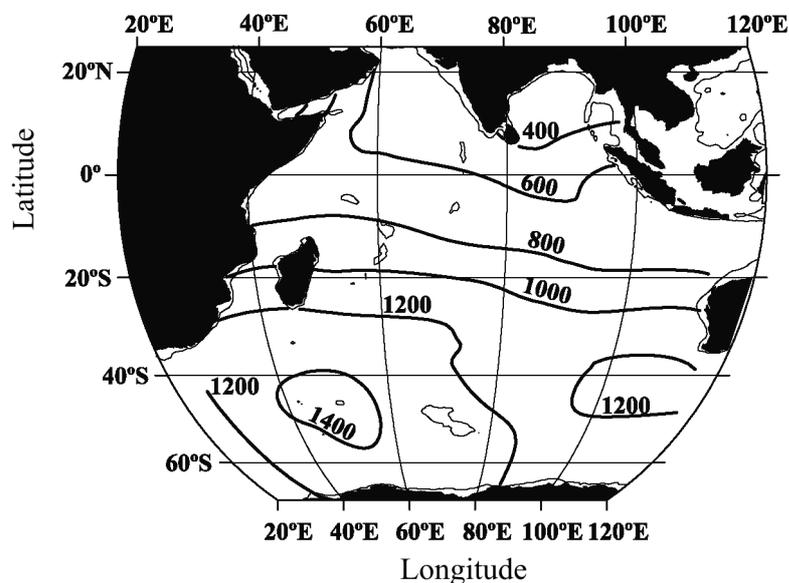


Fig. 5. Saturation depth in meters for aragonite derived from estimated water column dissolved inorganic carbon (DIC) and total alkalinity (TA) concentrations from the WOCE/JGOFS global CO₂ survey (modified after Sabine et al., 2002). The study uses nearly 25,000 carbon measurements from the Indian Ocean but lacks water samples from positions close to core 137 KA and core 905. The 800-m bathymetry is indicated by the thin line.

The WOCE results also show that within two decades (1974-1994, i.e., GEOSECS to WOCE) the aragonite saturation horizon shallowed significantly by 25-155 m in the Indian Ocean due to penetration of anthropogenic CO₂ into the subsurface water masses and due to increase in organic matter decomposition rates (Sarma et al., 2002). A comparison of the preindustrial and present-day saturation horizons by Feely et al. (2004) reveals that since preindustrial times saturation depths have shoaled increasingly north of 30°S in the Indian Ocean, so that aragonite saturation depths in the Arabian Sea and Bay of Bengal are now 100 to 200 m shallower than during preindustrial times.

4. Pteropods

Pteropods are small marine gastropods with a pelagic lifestyle, also known as ‘sea-butterflies’ because of their two fin-shaped wings (a transformation of the foot), which enable the animals to swim actively in the uppermost 500 m of the water column (Bé and Gilmer, 1977; Herman, 1978). During daytime, pteropods live in greater water depths (several hundred meters) and migrate vertically to shallower depths at night.

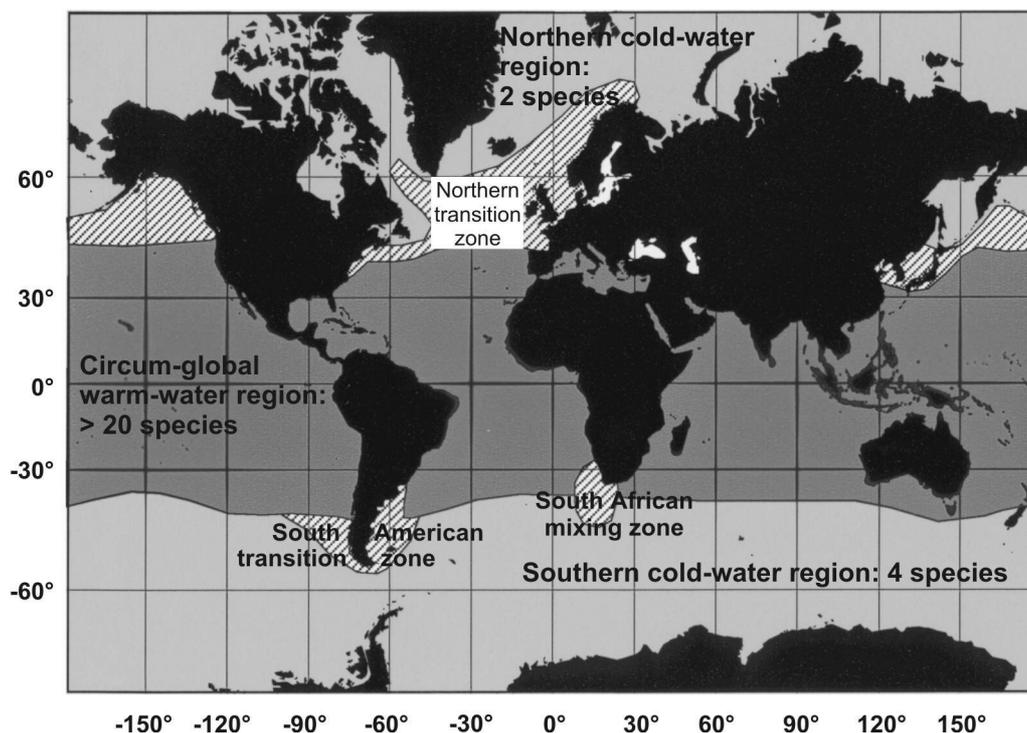


Fig. 6. Major biogeographic regions of pteropods in the modern oceans (modified after Bé and Gilmer, 1977; Gerhardt, 2001).

Pteropods are abundant in all oceans (Fig. 6). However, most species live in the tropical and subtropical warm-water region (more than 20 species), only few in the cold-temperate and polar regions (two species in the northern cold water region, four species in the southern cold water region; Bé and Gilmer, 1977; Herman, 1978).

4.1. Ecology and taxonomy

Pteropods are fast swimmers with observed escape speeds of up to 7 cm/s (*Diacria quadridentata*) or even 11-14 cm/s (for the *Cavolinia* species; Gilmer, 1974), which causes some difficulties to sample pteropods with plankton nets or water samplers. Euthecosomatous pteropods (Limacinidae and Cavolinidae) feed on phyto- and zooplankton (Bé and Gilmer, 1977; Herman, 1978). Therefore, their abundance is related to phytoplankton blooms and nutrient levels (Bé and Gilmer, 1977).

The phylogenetic classification distinguishes two orders: GYMNOSOMATA de Blainville, 1824 (naked pteropods; six families) and THECOSOMATA de Blainville, 1824 (mainly shelled pteropods, six families). For this study only shelled pteropods belonging to the two

families LIMACINIDAE Gray, 1847 (spiral and sinistrally coiled shells) and CAVOLINIIDAE Fischer, 1883 (uncoiled) are of interest. Pteropods are known since the Cretaceous, but in pre-Pleistocene sediments the preservation of the thin and fragile shells is rare due to the susceptibility to dissolution of aragonite.

Class GASTROPODA

Subclass OPISTHOBRANCHIATA

Order GYMNOSOMATA de Blainville, 1824 (naked, six families)

Order THECOSOMATA de Blainville, 1824 (mainly shelled pteropods)

Suborder PSEUDOTHECOSOMATA Meisenheimer, 1905

Family PERACLIDIDAE Tesch, 1913

Family CYMBULIIDAE Cantraine, 1841

Family DESMOPTERIDAE Chun, 1889

Family PROCYMBULIIDAE Tesch, 1913

Suborder EUTHECOSOMATA Meisenheimer, 1905

Family LIMACINIDAE Gray, 1847 (shell spirally coiled)

Family CAVOLINIIDAE Fischer, 1883 (shell uncoiled)

4.2. Shell structure

Pteropods (Limacinidae and Cavolinidae) possess aragonitic shells, which consist of minute CaCO₃ crystallites. The crystallites occur as 0.2 µm wide blocks (Bé and Gilmer, 1977, Bandel, 1990), which are arranged into elongated rods. These rods are arranged into a crossed-lamellar, helical, and prismatic structure (Bé and Gilmer, 1977, Bandel, 1990). The Limacinidae (with the exception of *L. inflata*) possess a crossed-lamellar microstructure with an inner prismatic aragonite layer (Bé and Gilmer, 1977). The width of the layers varies from individual to individual and from species to species. The Cavolinidae as well as *L. inflata* possess a helical aragonite microstructure.

Pteropod shell calcification depths vary between species and depend on environmental conditions (e.g., temperature, food availability, aragonite saturation state, Juranek et al., 2003). A recent study from the Sargasso Sea has shown that the calcification depths estimated from *L. inflata* δ¹⁸O values vary between 200 and 650 m water depth in late winter and spring, and between 50 and 250 m in late summer and autumn (Juranek et al., 2003). *S. subula* shows

similar seasonal variability with calcification depths between 250 and 600 m water depth in late winter and spring and 50–400 m in late summer and autumn. These results suggest that both species calcify across a greater range of depths than indicated by previous geochemical studies (e.g., Fabry and Deuser 1992), which give calcification depth estimates between 25 and 50 m throughout the year.

After the death of the organism, the shell settles rapidly to the sea floor due to its large size. Measurements of initial settling velocities in the laboratory by Byrne et al. (1984) range from 1.0 cm/s (*L. inflata*, juvenile stage) to 5 cm/s (*Cuvierina columnella*, adult stage). Thus, pteropods shells reach the sea floor within a few days (e.g., 1600 m, the water depth of core 905 off Somalia, in two days; 600 m, the water depth of core 137KA off Pakistan, in less than one day). Aragonite dissolution in the water column seems to be very unlikely for water depth < 2000m (as in this study), but has been observed by settling studies in deep waters of the Pacific Ocean (Byrne et al., 1984), which are strongly undersaturated in respect of aragonite. In the South Atlantic dissolution occurs mainly at the sea floor (Gerhardt, 2001).

4.3. Pteropods in the Indian Ocean

Plankton haul measurements indicate that euthecosomatous pteropods are abundant in the Indian Ocean with an increasing number of species from North to South (Sakthivel, 1976). A minimum of 12 species occurs in the northern Arabian Sea, a maximum of 20 species is found in the West Australian Sea (Sakthivel, 1976). The stable and pronounced OMZ in the Northern Arabian Sea could lead to suppression of pteropod productivity (Sakthivel, 1976). Sediment trap data off Pakistan show a maximum in pteropod production in late spring when nutrient concentrations have slightly decreased and no increase during the SW monsoon (Schulz et al., 2002). These results are corroborated by plankton haul data showing higher abundances of most pteropod species in the Northern Arabian Sea during the NE monsoon (Sakthivel, 1973, 1976).

In contrast, a broad maximum in pteropod productivity occurs during the SW monsoon off Somalia (Conan et al., 2002).

4.4. *Limacina inflata*

Limacina inflata (d'Orbigny, 1836; Fig. 7) is one of the most common warm-water cosmopolitan pteropods. It is widely distributed in the tropical and subtropical regions of all

oceans. In the Indian Ocean *L. inflata* is abundant in upwelling regions (e.g., off Somalia; Sakthivel, 1976).

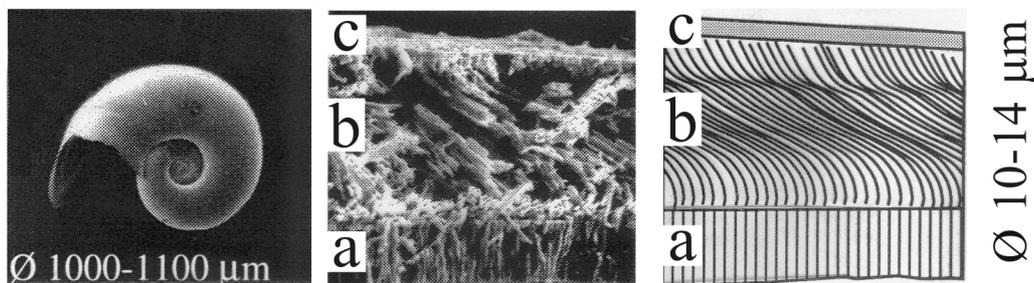


Fig. 7. Shell structure of *L. inflata*: SEM photographs of the whole shell, cross-section of the shell and schematic drawing. The thin shell ($\text{\O} 10\text{-}14 \mu\text{m}$) consists of an innermost prismatic layer (a) and a central helical layer (b). It is covered by the organic periostracum (c). Photo courtesy of S. Gerhardt.

L. inflata is an epipelagic species and lives primarily in the upper 300 m of the water column (Bé and Gilmer, 1977). Results from oxygen isotope studies suggest that the life cycle is several months or less (Fischer et al., 1999; Juranek et al., 2003). The almost planispiral sinistrally coiled shell of *L. inflata* has three whorls and shell diameters up to 1.5 mm. Its unaffected shell surface is smooth, transparent, and lustrous with gently developed growth lines from the second whorl onwards (Bandel et al., 1984). The aperture border of the adult is protruded to the so-called aperture tooth (Van der Spoel, 1967). The thin aragonitic shell is covered by the organic periostracum and consists of an innermost prismatic layer (Bé and Gilmer, 1977) and a central helical layer (Richter, 1976; Fig. 7). *L. inflata* is more fragile and susceptible to dissolution than the other three Limacinidae species (*L. bulimoides*, *L. lesueri*, *L. trochiformis*; Gerhardt, 2001). Only *L. inflata* has been chosen for the dissolution index LDX used in this study due to the rare appearance of the other members of the Limacinidae in samples from the Arabian Sea.

5. Material and methods

5.1. Material

To investigate the carbonate preservation state of modern (hemi-)pelagic sediments from the Arabian Sea, 25 surface sediment samples (Table 1, Part II), two high-sedimentation rate cores from the Pakistan and Somalia continental margin have been analysed. Piston core 905 ($10^{\circ}46.01\text{N}$, $51^{\circ}57.04\text{E}$, Fig. 1) was retrieved from 1586 m water depth off Somalia during the

C2 cruise of RV Tyro in the framework of the Netherland Indian Ocean Programme (NIOP, 1992 – 1993). The 15.26 m long core comprises a complete record of the last 90,000 years and has been sampled at 2.5-cm intervals for oxygen-isotope and pteropod analysis (average time resolution of about 150 years).

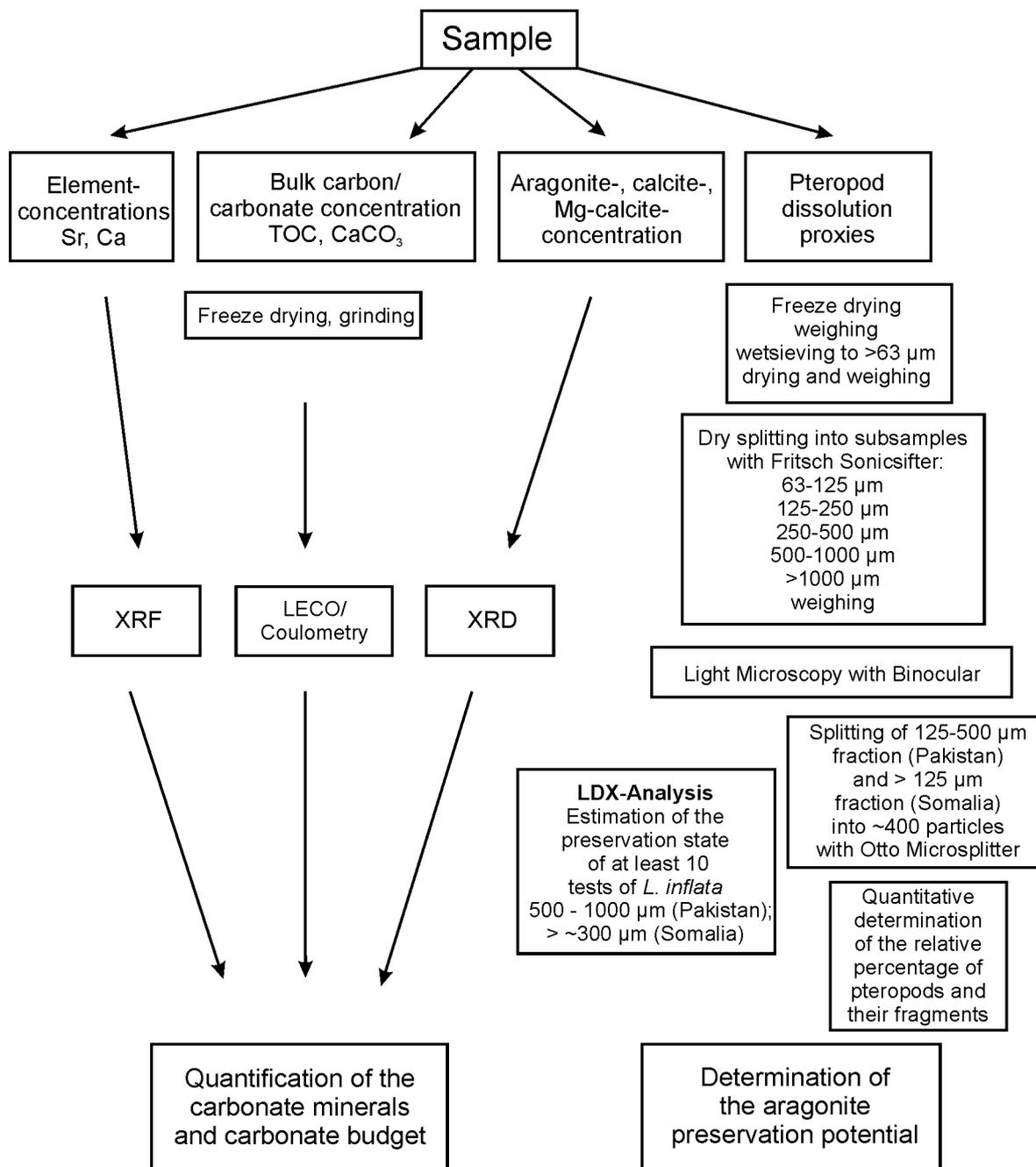


Fig. 8. Flowchart of sample preparation and analysis. For details of the XRD, XRF, LECO/Coulometry methods see method parts in Part II.

The 10 m long Kasten core SO90-137KA (Fig. 1) comprises a complete record of the past 30,000 years (taken during RV Sonne 90 cruise in 1993) and is located about 140 km southwest of the Indus delta at 573 m water depth in the centre of the OMZ (23°07.30N, 66°29.80E). Samples were taken at 10-cm intervals resulting in an average time resolution of about 300 years. The age models of both cores are based on oxygen isotope stratigraphy and radiocarbon dating (for detail see Part II).

5.2. Methods

To quantify the carbonate and aragonite budget and to estimate the state of preservation, the following methods were applied (Fig. 8): coarse fraction analysis (qualitative and quantitative determination of particles, quantification of pteropods and their fragments (including heteropods and their fragments), determination of the preservation state of pteropod tests (*Limacina* Dissolution Index, see chapters 5.2.1+5.2.2) using a light microscope (binocular). Element concentrations (Sr/Ca) were measured using a XRF/ICP, TOC and bulk CaCO₃ content utilizing a LECO element analyser and Coulometry. Determination of aragonite, calcite and Mg-calcite was performed by x-ray diffraction analysis (XRD, for details of the methods refer to the manuscripts).

Pteropod counts (core 905, core 137KA, surface sediment samples off Pakistan), estimation of the LDX (core 905, core 137KA, surface sediment samples off Pakistan), and LECO analysis (TOC and CaCO₃ concentrations of the surface sediment samples off Pakistan) have been performed by the author (R. Klöcker). XRD analysis and Sr/Ca ratios of core 905 have been measured by the co-author of the third manuscript, T. S. Ivanochko. All other data used in this study are taken from the literature as indicated in the manuscripts (refer to Part II).

5.2.1. Sample preparation for coarse fraction analysis and LDX

After freeze-drying and wetsieving the coarse fraction (> 63 µm fraction) of core 137KA was divided into subfractions (>1mm, 500-1000 µm, 250-500 µm, 125-250 µm and 63-125 µm) using a Fritsch sonic sifter. The 125-500 µm fraction of core 137KA and > 125 µm fraction of core 905 were split with a Otto Microsplitter into aliquots containing about 400 (600 for core 905) specimens for pteropod counts and estimation of the preservation state of pteropod shells. The 500-1000 µm fraction of core 137KA (> ~300 µm fraction of core 905) was used for determination of the LDX.

5.2.2. *Limacina* Dissolution Index

Based on the fact that pteropod tests display changing modes of preservation (e.g., Almogi-Labin et al., 1986; Haddad and Droxler, 1996), Gerhardt and Henrich (2001) developed a new proxy for aragonite dissolution, the so called *Limacina* Dissolution Index (LDX). The LDX is represented by six preservation stages, ranging from stage 0, best preservation, to stage 5, worst preservation (see Fig. 9):

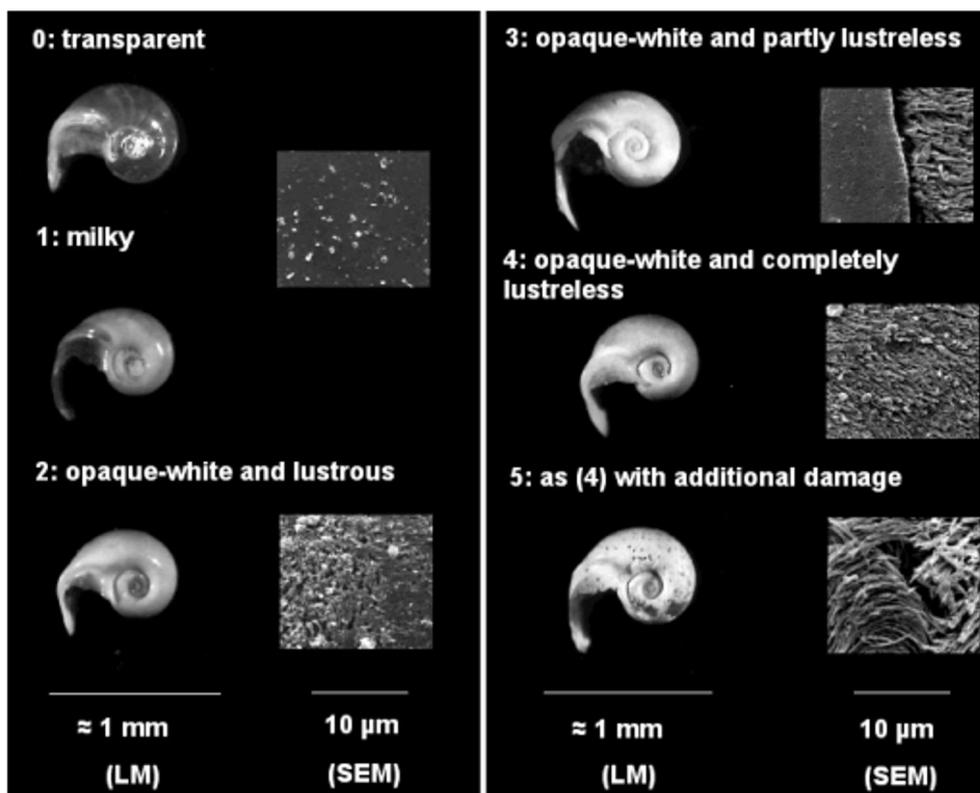


Fig. 9. Preservation stages of *L. inflata* according to the *L. inflata* Dissolution Index (LDX, Gerhardt and Henrich, 2001). Whole shell photographs are taken under the light microscope, enlargements of the shell surface by SEM (Gerhardt and Henrich, 2001). Note the characteristic smooth surface layer (stages 0 and 1) and the central helical layer with elongated aragonite rods (stages 3 to 5).

Stage 0, best preservation: Transparent shells

This stage indicates best preservation. Only the shells of living pteropods and originally preserved pteropod assemblages in the sediments show this mode of preservation.

Stage 1, very good preservation: Milky and cloudy shells, shells, lustrous shell surface

This stage is reached when either slight shell corrosion has taken place or the organic parts of the shell have become cloudy through oxidation (Haddad and Droxler, 1996).

Stage 2, good preservation: Opaque-white shells, lustrous shell surface

In this stage, pteropod shells are opaque and white, not just milky, which means they have truly experienced initial dissolution on the surface.

Stage 3, moderate preservation: Opaque-white shells, partly lustreless shell surface

In this stage parts of the surface layer have disappeared by dissolution. Consequently, the shell surface seems to be lustreless in those areas where the helical aragonite layer is exposed.

Stage 4, poor preservation: Opaque-white shells, totally lustreless shell surface

This stage is reached when the surface layer has been entirely removed by corrosion.

Stage 5, worst preservation: Opaque-white shells, totally lustreless and perforated shells

This stage is characterized by additional shell damage of any kind, neglecting the absence of the aperture tooth of *L. inflata* which is often broken off during sample preparation.

The LDX and the fragmentation ratio of pteropods were calculated according to the following equations:

$$LDX = \frac{\sum(n_p * p)}{\sum n_p}$$

where n_p is the number of investigated tests per preservation stage p (with $p = 0$ to 5) and $\sum n_p$ is at least 10 (tests of *L. inflata* $> 300 \mu\text{m}$ for the 905 samples and $> 500 \mu\text{m}$ for the samples from the Pakistan margin);

$$\text{fragmentation} = \frac{n_F}{(n_F + n_w)}$$

where n_F is the number of fragments and n_w is the number of whole tests (whole:= less than 50 % damaged, in most cases small juvenile limacinid pteropods).

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Part II Publications

Three manuscripts were submitted to international journals. My contribution to the manuscripts and their content is described in the following section.

Klöcker, R., Henrich, R. **Recent and Late Quaternary pteropod preservation on the Pakistan shelf and continental slope.**

Status: submitted **Journal:** Marine Geology
My contribution: analytical work (wetsieving, sonic-sifting, pteropod counts, estimation of the shell preservation, C_{org} and CaCO₃ analysis of the surface sediment samples), data processing, graphical presentation, and principal writing.

In this manuscript we analyse 15 surface sediment samples from the Pakistan shelf and upper continental slope and a Late Quaternary high-sedimentation rate core (573 m water depth, Pakistan continental margin) to improve the understanding of the factors influencing pteropod preservation in the northern Arabian Sea during the last 30 000 years. The LDX was applied on six surface sediment samples showing good to very good preservation (LDX: 2.2 to 1.3). The sedimentary record of core SO90-137 KA is characterized by alternations between bioturbated sediments (during the time-equivalents of Heinrich events, Younger Dryas (YD), and during the Early Holocene) and laminated sediments (during interstadials and Late Holocene). Well to perfectly preserved tests of *L. inflata* (LDX: 2.1-0.2) represent the bioturbated sediments, whereas only traces of pteropods occur in laminated intervals. The ‘extreme’ pteropod preservation pattern is interpreted with the repetitive occurrence of intermediate water formation in the northern Arabian Sea down to at least 600 m water depth in times of enhanced NE monsoons during YD, stadials and H-equivalents. Low amounts of pteropods in laminated sediments (interstadials, Late Holocene) and in the present-day OMZ indicate a weak NE monsoon, stable OMZ, and shallow ACD. The absence of moderate to poor pteropod preservation points to rapid shifts between the two ‘modes’ (OMZ dominance /intermediate water formation).

Klöcker, R, Ganssen, G., Jung, S.J.A., Kroon, D., Henrich, R. **Late Quaternary millennial-scale variability in pelagic aragonite preservation off Somalia.**

Status: submitted **Journal:** Marine Micropaleontology
My contribution: analytical work (pteropod counts, estimation of the shell preservation), data processing, graphical presentation, and principal writing.

This manuscript deals with Late Quaternary pteropod preservation in the western Arabian Sea during the last 90 000 years. We have investigated a high-resolution sediment core off Somalia. On glacial/interglacial time scales, the pteropod abundance corresponds to the ‘Indo-Pacific carbonate preservation type’ with poor preservation during interglacials and better preservation during glacials. On millennial time scales, pteropod preservation ranges from good preservation during the time equivalents of the H-events, stadials, and YD (periods with decreased bioproductivity indicated by low C_{org} values) to intermediate to poor preservation during interstadials (periods with increased bioproductivity indicated by high C_{org} values).

The variation in pteropod preservation can be explained as follows: SW monsoon-driven upwelling increases the bioproductivity and subsequent remineralization of organic matter. Release of CO_2 to the subsurface waters and pore waters leads to strong aragonite dissolution. On the contrary, periods with decreased upwelling intensity are characterized by reduced bioproductivity and remineralization of organic matter improving the aragonite preservation potential. Besides the regional monsoonal influence on deepwater chemistry, changes in deepwater circulation, occurring on glacial/interglacial and stadial/interstadial time scales, might have affected pteropod preservation.

Klöcker, R., Ivanochko, T.S., Brummer, G.-J.A., Jung, S.J.A., Ganssen, G., Kroon, D., Ganeshram, R.S., Henrich, R. **Variation in production, input and preservation of metastable calcium carbonate off Somalia during the last 90 000 years.**

Status: submitted **Journal:** Quaternary Science Reviews
My contribution analytical work (pteropod counts, estimation of the shell preservation), data processing, graphical presentation, and principal writing.

In this study we present high resolution mineralogical (calcite, Mg-calcite, aragonite), geochemical (Sr/Ca ratios, TOC, and CaCO₃ content) and micropaleontological data (pteropod counts and shell preservation records) from a Late Quaternary piston core off Somalia covering the last 90 000 years. We analyse the impact of variations in relative sea level on resuspensional input, accumulation and preservation of metastable carbonates. High Sr/Ca ratios combined with fragments of corals found in the coarse fraction indicate that most of the aragonite is of shallow water origin (high Sr-aragonite) and pteropods contribute much less to the bulk aragonite budget. The late Quaternary development is characterized by high resuspensional input of aragonite during sea level highstands (interglacials) and low input during lowstands (glacials). This observation can be explained by ‘highstand shedding of carbonate platforms’ (Schlager et al., 1994), i.e., high input of shallow marine aragonite in times of sea level highstands due to increased production areas on the shelf. Additionally, changes in preservation strongly influence the bulk aragonite record, e.g., in the Late Holocene. During this time characterized by a sea level highstand, a dramatic decrease in aragonite concentration occurs, which can be explained by strong dissolution of aragonite as indicated by very low Mg-calcite concentrations and pteropod abundances. The correlation of the Mg-calcite record with the pteropod abundance and preservation records confirms a multi-proxy approach using pteropod preservation proxies in conjunction with Mg-calcite measurements to reconstruct past fluctuations in dissolution of metastable carbonate.

Recent and Late Quaternary pteropod preservation on the Pakistan shelf and continental slope

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Abstract

Fifteen surface sediment samples from the Pakistan shelf and upper continental slope and a Late Quaternary high-sedimentation rate core (573 m water depth, Pakistan continental margin) have been analysed to improve the understanding of the factors influencing pteropod preservation. The aragonite compensation depth (ACD) is located at 250-400 m water depth, which corroborates previous observations of a very shallow ACD in the northern Arabian Sea. With the exception of the Hab transect off Karachi, the ACD coincides with the upper boundary of the OMZ located at 250 m water depth. The shell preservation index of the pteropod *Limacina inflata* (LDX) was applied on six surface sediment samples showing good to very good preservation (LDX: 2.2 to 1.3).

The 30 000 year long record of sediment core SO90-137 KA is characterized by alternations between bioturbated and laminated sediments. Bioturbated sediments occurring in the Early Holocene, Younger Dryas and time-equivalents of Heinrich events contain well to perfectly preserved tests of *L. inflata* (LDX: 2.1-0.2), whereas only traces of pteropods are found in laminated intervals.

The close linkage of pteropod preservation in the surface sediments and in core 137KA to well-oxygenated conditions can be explained by repetitive intermediate water formation in the Arabian Sea down to at least 600 m water depth in times of enhanced NE monsoons during stadials and H-equivalents. Low amounts of pteropods in laminated sediments (interstadials, Late Holocene) and in the present-day oxygen minimum zone (OMZ) indicate a weak NE monsoon, stable OMZ and shallow ACD. The absence of moderate to poor pteropod

preservation points to rapid shifts between OMZ dominance and intermediate water formation.

Keywords: Arabian sea; pteropods; *Limacina inflata*; aragonite dissolution; Late Quaternary; Pakistan

1. Introduction

Changes in the oceanic carbonate budget are crucial to understand past variations in atmospheric CO₂ concentrations. The study of pelagic aragonite production, accumulation, and preservation provides important information about the dynamics of carbon cycling in upper and intermediate water masses and the associated changes in oceanic circulation patterns and climatic conditions. Aragonite, a metastable polymorph of CaCO₃, dissolves at shallower water depths than calcite due to the higher solubility in seawater (Morse et al., 1980; Millero, 1996; Morse and Arvidson, 2002). Hence, the aragonite compensation depth (ACD) is located at a much shallower depth than the calcite compensation depth (CCD). Pteropods are important pelagic aragonite producers and have been used to reconstruct changes in the ACD, which is the depth where pteropod shells disappear in seafloor sediments (e.g., Chen, 1964; Berger, 1977, 1978; Berner, 1977; Rottman, 1979). The preservation state of pteropod tests has been established as a proxy for the aragonite saturation state of water masses (e.g., Almogi-Labin et al., 1986; Haddad and Droxler, 1996; Gerhardt and Henrich, 2001; Henrich et al., 2003).

Recent high-resolution studies on sediment cores from the Arabian Sea (Reichart et al., 1997, 1998; Ivanova, 2000; von Rad et al., 1999) display millennial-scale variations in aragonite preservation linked to the Dansgaard-Oeschger (D/O) cycles and Heinrich events in the North Atlantic. To improve the understanding of the driving factors behind the observed pteropod preservation spikes, we focus on pteropod preservation in surface sediments on the shelf and upper continental slope off Pakistan and a high sedimentation rate core from the Pakistan continental margin. The aims are to trace temporal and spatial changes in the preservation state of pteropod tests and to test the applicability of the newly developed *Limacina* Dissolution Index (LDX, Gerhardt and Henrich, 2001) in this area.

2. Regional setting

Climatic and oceanographic conditions in the Arabian Sea are strongly influenced by the monsoonal system and its seasonal reversals. During boreal summer, differential heating between the Tibetan plateau and the southern Indian Ocean (Cadet, 1979) results in a strong pressure gradient generating the warm and humid SW monsoon. These strong winds induce coastal and open-ocean upwelling off Somalia and Oman and lead to very high nutrient concentrations and primary productivity (Wyrki, 1973). Eastward drift of these nutrient-rich waters due to the clockwise surface water circulation also may support high primary productivity in the northern part of the Arabian Sea (Banse, 1984). In winter the atmospheric circulation pattern reverses. The cool and dry NE monsoon blowing from the Asian landmass causes deep convective mixing due to cooling of surface waters (Madhupratap et al., 1996) and injects nutrients to the surface leading to a second productivity maximum (Nair et al., 1989; Haake et al., 1993).

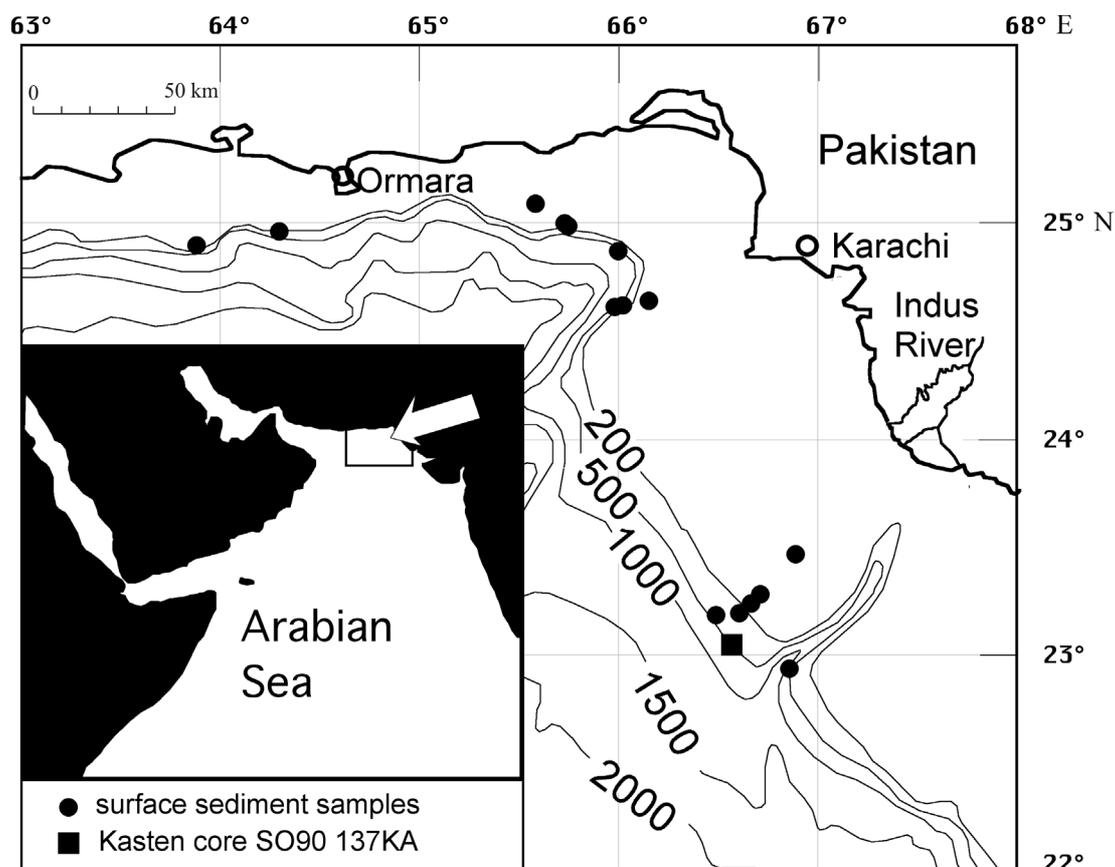


Fig. 1. Location of studied surface sediment samples and core SO90 137KA off Pakistan.

The combination of high-surface water productivity (Qasim, 1977) and moderate rates of thermocline ventilation (You and Tomczak, 1993) produces a stable and pronounced mid-water oxygen minimum zone (OMZ) between 150-2000 m (Wyrski, 1973). Within the OMZ, high input and decay of organic matter raise dissolved inorganic carbon (DIC) concentrations in the subsurface waters and lower the pH (Millero et al., 1998), which results in a shallow aragonite saturation depth of 500 m (George et al., 1994) or 600 m water depth (Millero et al., 1998; Mintrop et al., 1999).

Below this depth bottom waters are undersaturated in respect to aragonite and aragonitic sediments start to dissolve. Decomposition of organic matter within the sediments releases metabolic CO₂ to the pore water and lowers the pore water pH leading to a further increase in dissolution of carbonates (Emerson and Bender, 1981; Milliman et al., 1999).

3. Material and methods

The Kasten core SO90-137KA (23°07.30N, 66°29.80E) was taken during RV Sonne 90 cruise in 1993 and is located about 140 km southwest of the Indus delta at 573 m water depth in the centre of the OMZ (Fig. 1). The age model is based on oxygen isotope stratigraphy, radiocarbon dating and correlation with nearby cores 111KL and 136KL (see von Rad et al., 1999) and core 289KL (von Rad et al., 2002). The 10 m long core comprises a complete record of the past 30 000 years including Late Pleistocene and Holocene hemipelagic sediments. Samples were taken at 10-cm intervals resulting in an average time resolution of about 300 years. After freeze-drying and wetsieving the coarse fraction (> 63 µm fraction) of the 15 surface sediment samples and of core 137KA was divided into subfractions (>1mm, 500-1000 µm, 250-500 µm, 125-250 µm and 63-125 µm) using a Fritsch sonic sifter. The 125-500 µm fraction was split into aliquots containing about 400 specimens for coarse fraction analysis, e.g., qualitative and quantitative determination of particles, percentage of pteropods debris (including heteropods and their fragments), conventional fragmentation indices of pteropods (Gerhardt et al., 2000). The 500-1000 µm fraction of core 137KA was used for light-microscopic determination of the *Limacina* Dissolution Index (according to Gerhardt and Henrich, 2001). The *Limacina* Dissolution Index (LDX) distinguishes six preservation stages of the shells of the common pteropod *Limacina inflata* ranging from 0 (perfect preservation, transparent shells), 1 (very good preservation, milky shells), 2 (good preservation, opaque-white shells with lustrous shell surface), 3 (moderate preservation,

opaque-white shells with partly lustreless shell surface), 4 (poor preservation, opaque-white shells with totally lustreless shell surface) to 5 (worst preservation, opaque-white shells with totally lustreless shell surface and additional shell damage, Gerhardt and Henrich, 2001). The LDX and the fragmentation index of pteropods were calculated according to the equations:

$$LDX = \frac{\sum(n_p * p)}{\sum n_p}$$

where n_p is the number of investigated tests per preservation stage p (with $p = 0$ to 5) and $\sum n_p$ is at least 10;

$$\text{fragmentation} = \frac{n_F}{(n_F + n_w)}$$

where n_F is the number of fragments, n_w is the number of whole tests and $n_F + n_w > 15$. Data of the Sr concentration, TOC-, bulk CaCO_3 - and aragonite content of core 137KA were taken from the pangaea database (von Rad et al., 1999).

Site	Transect	Latitude (N)	Longitude (E)	Water depth (m)
SO130 255KG	Hab	25°5.02'	65°34.97'	25
SO130 264 KG	Hab	24°59.64'	65°43.75'	41
SO130 260 KG	Hab	24°58.85'	65°44.89'	95
SO90 120KG	Indus	23°27.99'	66°53.54'	96
SO90 66KG	Hab	24°38.31'	66°9.27'	120
SO90124KG	Indus	23°16.76'	66°42.77'	136
SO130 238KG	Ormara	24°53.54'	63 53.01'	137
SO90 129KG	Indus	23°14.29'	66°39.96'	185
SO90 18 KG	Ormara	24°57.43'	64°17.93'	228
SO90 44KG	Hab	24°37.02'	66°1.47'	258
S090 113 KG	Indus	23°11.49'	66°36.44'	287
SO90 42KG	Hab	24°36.52'	65°59.03'	313
SO90 180KG	Indus	22°56.02'	66°51.51'	398
SO90 135KG	Indus	23°11.02'	66°29.50'	402
SO90 35KG	Hab	24°51.95'	66°0.02'	416

Table 1. Locations of studied surface sediment samples.

For analysis of the surface sediments the upper 2 cm of 15 boxcores off Pakistan (Ormara transect, Hab-transect west of Karachi and Indus transect, Table 1) were freeze-dried and ground in an agate mortar. Total carbon (TC) and total organic carbon (TOC) contents were measured using a LECO 200 CS analyser. For TOC determination inorganic carbon was removed by addition of HCl. Bulk calcium carbonate (CaCO₃) contents were calculated using the relationship:

$$\text{CaCO}_3 = (\text{TC} - \text{TOC}) \times 8.33.$$

4. Results

4.1. Surface sediments off Ormara, Karachi(Hab-transect) and Indus

Pteropods and fragments of pteropods only occur in surface sediments deposited between 100 and 400 m water depth (Fig. 2d,e). Hence, recent pelagic aragonite preservation is restricted to the shelf region and the uppermost continental slope off Pakistan. These results confirm the findings of von Stackelberg (1972), who observed relative pteropod abundances > 1% only in 28 (from 53 m to 420 m water depth) of 88 surface sediment samples (ranging from 4 m to 4494 m water depth, Fig. 2h). Shell preservation applying the LDX could only be estimated on 6 of the 15 samples due to insufficient numbers of adult *L. inflata* (Fig. 2g). In all these samples the LDX indicates good to very good preservation (2.4 to 1.2). Each transect shows a downslope decrease in shell preservation: Ormara transect, one sample: 137 m water depth, LDX: 1.7; Hab transect, two samples: LDX: 1.3 to 1.6; from 120 m to 416 m water depth; Indus transect, three samples: LDX: 1.8; 2.1, 2.2 from 96 m, 136 m, 185 m water depth, respectively. Pteropod fragmentation decreases downslope (Fig. 2f). TOC contents are low (0.2-1.2 %) in surface sediment samples above 250 m water depth and high (1.6-2.5%) in samples within the OMZ (Fig. 2a). Bulk carbonate contents are low (11-20%) in samples from the inner shelf (<100 m water depth) and upper continental slope. Carbonate maxima (58-66%) occur in coarse-grained pteropod rich sediments on the outer shelf (100-200 m water depth, Fig. 2b,c).

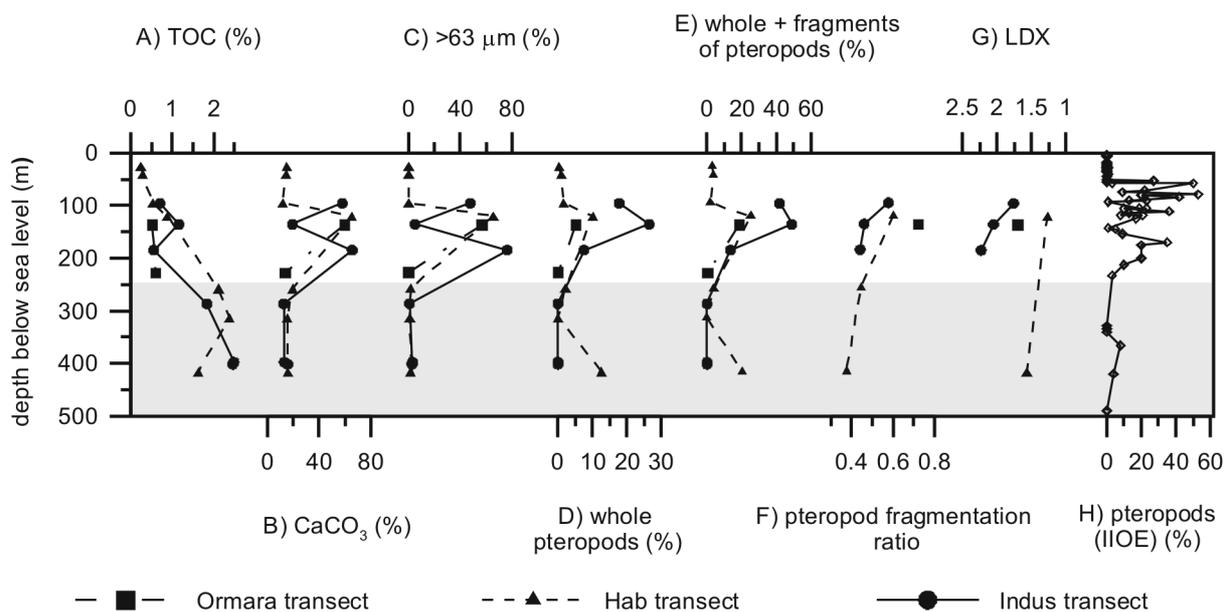


Fig. 2. Proxies from coarse fraction analysis of fifteen surface sediment samples off Pakistan (Ormara transect, Hab-transect west of Karachi and Indus transect) indicating aragonite dissolution: A) Total organic carbon (TOC) content; B) bulk calcium carbonate content; C) Coarse fraction content (>63 μm); D) relative abundance of whole pteropods and heteropods counted in the 125 μm -500 μm subfraction; E) relative abundance of whole pteropods and heteropods including fragments; F) pteropod fragmentation index: fragments/(fragments + whole tests); G) *Limacina inflata* dissolution index (LDX, 0 = best preservation, transparent shells, 1 = very good preservation, milky shells, 2 = good preservation, opaque-white shells with lustrous shell surface, 3 = moderate preservation, opaque-white shells with partly lustreless shell surface, Gerhardt and Henrich, 2001); H) relative pteropod abundance in surface sediments from the IIOE (von Stackelberg, 1972); grey shaded areas indicate upper part of the Oxygen Minimum Zone (OMZ).

4.2. Core 137 KA

Maxima in relative pteropod abundance in the 125-500 μm fraction of core 137KA (including heteropods and fragments of pteropods and heteropods) are found in the bioturbated intervals (up to 44 % in the Early Holocene, 7-10.5 ka; 40-60 % in the Younger Dryas, 11.7-13 ka and 20-45 % at the time equivalents of the Heinrich events, H1-equivalent, 15-17 ka; H2-equivalent, 23.5-24.2 ka; H3-equivalent, 29.3-30.2 ka and cold stadials between H2- and H3-equivalent, 25.5-26.0 and 28.0-28.5 ka (Fig. 3b,c). No pteropods are found in the upper part of the core (Late Holocene) and Preboreal. In the Bølling-Allerød the pteropod abundance is medium (< 20 %) during the LGM/IS 2 only small amounts of fragments occur.

The *Limacina* Dissolution Index was applied on 27 of the 93 samples due to nearly absence of pteropods in the laminated sediments and insufficient numbers of specimens of *L. inflata* in

some of the bioturbated sediments (Fig. 2g). Shell preservation ranges from 0.2 to 2.1 LDX values (perfect preservation to good preservation). No moderately or poorly preserved samples were found. During the Younger Dryas (LDX: 2.1-1.4), and H2-equivalent (LDX: 2.1-1.3) the LDX shows good to very good preservation, at H1-equivalent (LDX: 1.9-0.2) good to perfect preservation and at H3-equivalent (LDX: 0.7-0.2) the preservation is almost perfect (Fig. 3d).

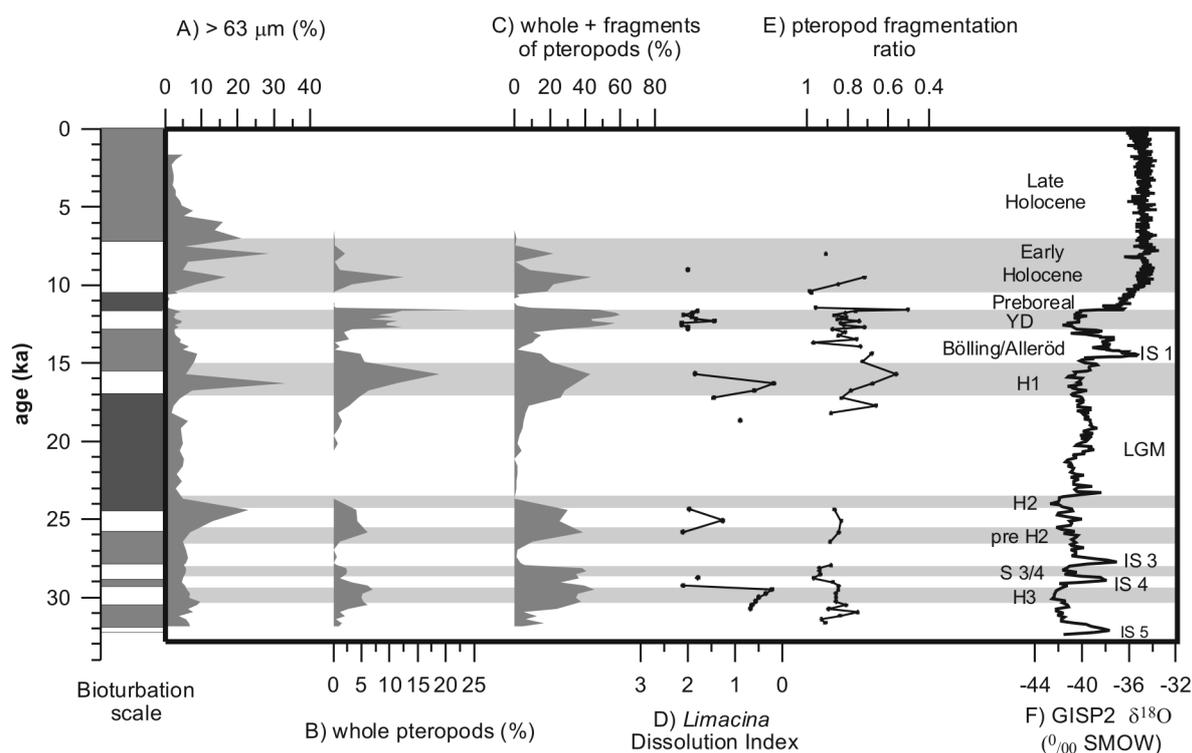


Fig. 3. Proxies from coarse fraction analysis of core 137KA indicating aragonite dissolution: A) Coarse fraction content (>63 μm); B) relative abundance of whole pteropods and heteropods counted in the 125 μm -500 μm subfraction; C) relative abundance whole pteropods and heteropods including fragments; D) *Limacina inflata* dissolution index (LDX, 0 = best preservation, transparent shells, 1 = very good preservation, milky shells, 2 = good preservation, opaque-white shells with lustrous shell surface, 3 = moderate preservation, opaque-white shells with partly lustreless shell surface, Gerhardt and Henrich, 2001); E) pteropod fragmentation index: fragments/(fragments + whole tests); F) GISP2 Greenland ice core record (Grootes et al., 1993); bioturbation scale: dark grey = distinctly to indistinctly laminated sediments, light grey = indistinctly laminated sediments, white = bioturbated sediments, modified after von Rad et al., 1999).

Pteropods are highly fragmented in all intervals of the core (Fig. 3e) due to the fact that pteropod tests are generally very fragile and thus susceptible to mechanical damage, despite careful treatment during washing and sieving of the sediment. Fragmentation slightly

decreases in the bioturbated intervals (Early Holocene, YD, H-equivalent) where also the LDX indicates a good preservation.

5. Discussion

5.1. Surface sediment samples

Analysis of 15 surface sediment samples from the Pakistan continental margin show that the ACD is located at 250-400 m water depth, which corroborates the previous observations of a very shallow ACD in the northern Arabian Sea (500 m, Berger, 1977; 500 ± 200 m von Rad et al., 1999). Assuming LDX values > 3 to portray deposition above the aragonite lysocline (as a previous study by Gerhard and Henrich, (2001) on South Atlantic surface sediments has shown), we interpret the good to very good preservation state (LDX: 2.4 to 1.2) of pteropods as deposition above the lysocline. However, in the investigated sample grid the position of the lysocline cannot be estimated precisely due to the absence of poorly preserved *L. inflata* tests and insufficient numbers of surface sediment samples from the critical depth range 250-500 m water depth. The CaCO_3 content covaries with the coarse fraction content and with the relative pteropod abundance (Fig. 2b-e). The strong decrease in CaCO_3 content, coarse fraction content, and relative pteropod abundance between 200 and 300 m water depth reflects the dissolution of pteropods. The very rapid decrease in pteropod abundance below 200 m water depth (previously reported by von Stackelberg, 1972) and the rise in TOC contents between 200 and 300 m water depth coincide with the upper boundary of the OMZ (Fig. 2a). This result combined with the difference between estimates of the ACD from observed pteropod abundance in surface sediments (400 m water depth for the Hab transect, 250 m water depth for the other transects) and chemically calculated saturation horizons, 500 m (George et al., 1994) or 600 m water depth (Millero et al., 1998; Mintrop et al., 1999), indicate that aragonite dissolution in modern sediments is mainly due to supralysoclineal dissolution.

5.2. Core 137KA

Pteropod abundance, their preservation state (LDX), and their fragmentation ratio in core SO90 137KA from the Pakistan continental margin clearly reflect repetitive preservation

spikes which are exclusively occurring in the bioturbated intervals. It is intriguing to find only well to perfectly preserved tests of *L. inflata* but no moderate to poor preservation. Based on analysis of a high-sedimentation rate piston core off Somalia showing all pteropod preservation stages from perfect to poor preservation (Klöcker et al., subm.), we exclude failure of the LDX applicability in 137KA.

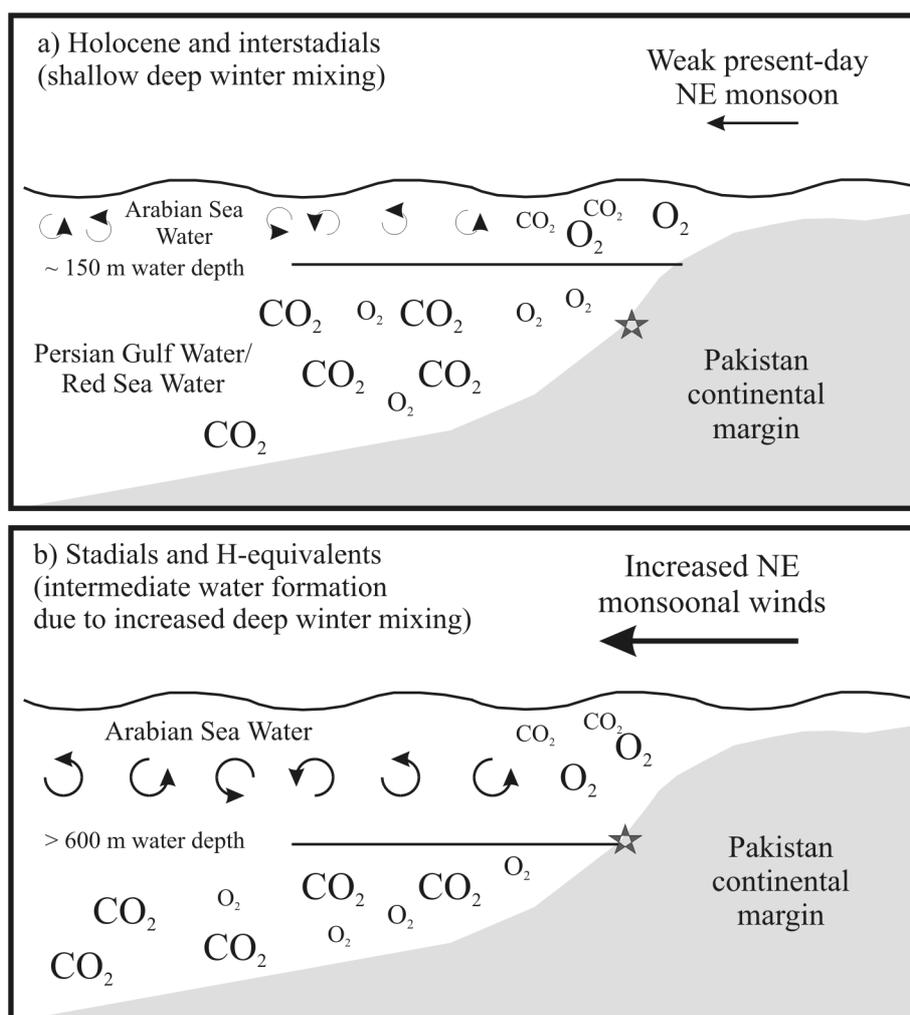


Fig. 4. Sketch showing the two pteropod preservation modes in sediment core 137 KA off Pakistan: a) Present-day situation with shallow deep winter mixing due to a weak NE monsoon, stable OMZ, absence of pteropods in core 137KA, pteropod occurrence restricted to shelf/upper continental slope; b) good to excellent preservation during times of intermediate water formation down to 600 m water depth.

We interpret the observed preservation pattern with the following model (Fig. 4):

The results from the surface sediments show that with the exception of the Hab transects, pteropods instantly disappear near the upper boundary of the OMZ at 250 m. All bioturbated intervals of 137KA contain pteropods. Both findings demonstrate a strong linkage to the

OMZ. Under present-day conditions with relative weak NE monsoonal winds, deep winter mixing is restricted to approximately 150 m water depth (Schulz et al., 2002). Therefore, the OMZ is very stable and the high DIC concentration/low pH within the OMZ leads to strong aragonite dissolution.

During stadials and H-equivalents, enhanced NE monsoon intensity (Pourmand et al., 2004) leads to deeper winter mixing and intermediate water formation in the Arabian Sea down to at least 600 m water depth (or 500 m, if one takes into account the lower sea level in the Late Pleistocene). Previous studies by Reichert et al. (1998, 2002) based on the presence of deep dwelling planktic foraminifer species *G. crassaformis* and *G. truncatulinoides* point to intermediate water formation up to 600 m water depth.

Pteropods found in 1470 m water depth (core NIOP464, Murray Ridge; Reichert et al., 1997) and 1000 m water depth (core 108KL, Pakistan continental slope; von Rad et al., 1999) indicate a dramatic deepening of the ACD. This would also explain the observation of well to perfectly preserved tests of *L. inflata* in core 137KA, as the distance to the ACD is then at least 1000 m. In addition, the bulk carbonate and the Sr and aragonite concentrations (von Rad et al., 1999; Fig. 5) show large fluctuations related to the occurrence of pteropods, although the high Sr values, aragonite needles in the fine fraction, and coral fragments in the coarse fraction indicate a high amount of resuspended shallow-water aragonite. We suggest that at least a significant part of the fluctuations in carbonate and aragonite concentrations are due to strong aragonite dissolution as indicated by the pteropod preservation pattern. However, higher input of resuspended shallow-marine aragonite in phases of enhanced NE monsoonal winds could contribute to high aragonite values during stadials and H-equivalents. The subsidence of well oxygenated and CO₂ poor surface waters to greater water depths increases O₂ concentrations of subsurface waters leading to a complete breakdown of OMZ conditions. Consequently, the increase in pH of subsurface waters leads to a deep ACD and improved pteropod preservation as indicated by the good to excellent preservation in this study. On the other hand, weak NE monsoonal winds are not capable of cooling surface waters enough to sink down to greater water depths. Under these stable OMZ conditions, represented by laminated sediments, a rise in ACD to 250-400 m water depth appears as indicated by absence of pteropods in core 137KA. Hence, there are only two pteropod preservation modes in core 137KA (573 m water depth): (1) good to excellent preservation during times of intermediate water formation down to 600 m water depth and (2) absence of pteropods in times of stable OMZ conditions (present-day situation). To conclude, the

‘extreme’ preservation pattern of the surface sediments and in core 137KA with an alternation of no preservation to well-perfectly preservation without intermediate stages fits perfectly to the ‘intermediate water formation model’.

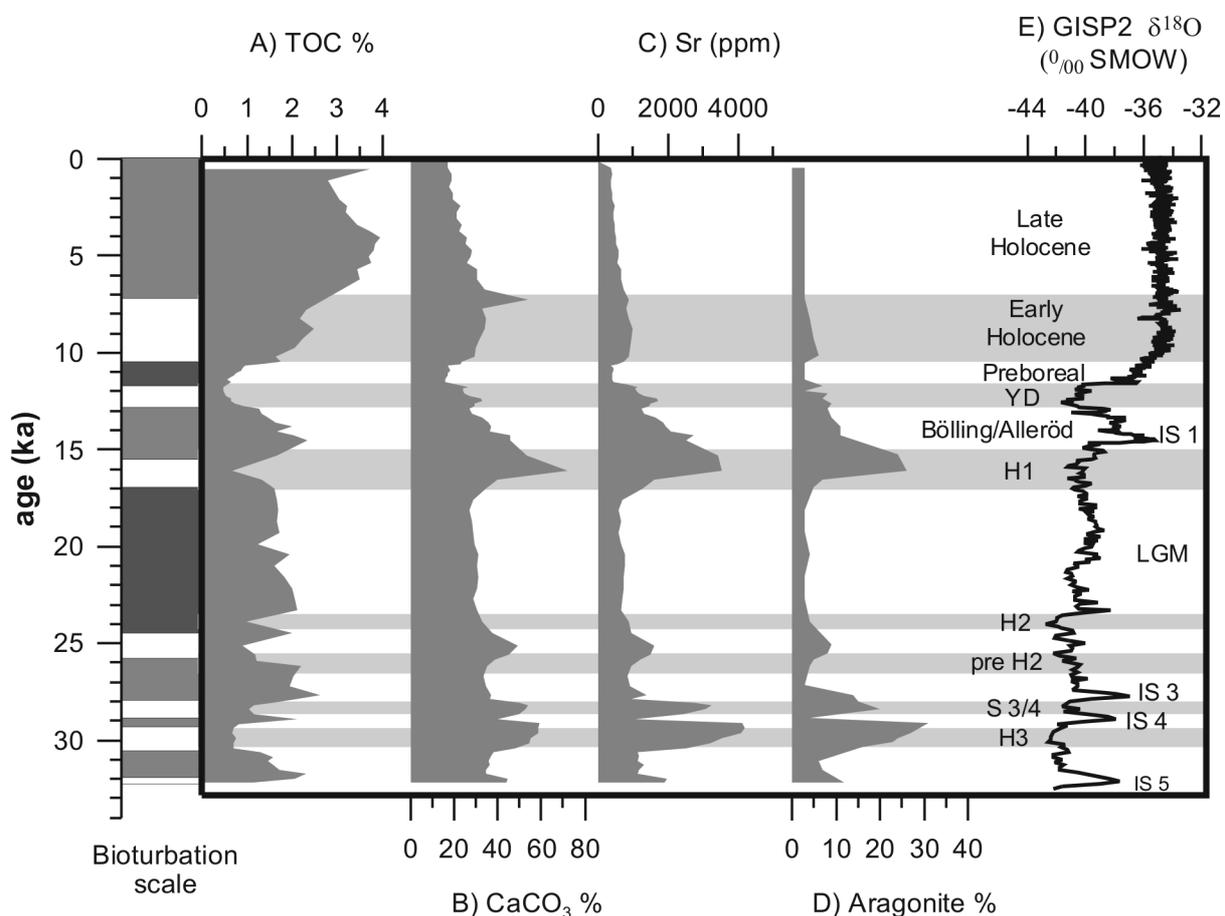


Fig. 5. Geochemical proxies of core 137KA indicating organic and carbonate productivity (modified after von Rad et al., 1999): A) Total organic carbon (TOC) content; B) bulk calcium carbonate content; C) strontium concentration; D) aragonite content; E) GISP2 Greenland ice core record (Grootes et al., 1993); bioturbation scale: dark grey = distinctly to indistinctly laminated sediments, light grey = indistinctly laminated sediments, white = bioturbated sediments, modified after von Rad et al., 1999).

5.3. Other possible factors influencing pteropod preservation

Pteropod preservation in 137KA could also be interpreted in terms of SW monsoon related bioproductivity with high input of organic matter in laminated sediments during interstadials and weaker bioproductivity during stadials. However, it is important to note that the Early Holocene is represented by bioturbated sediments containing pteropods, although SW monsoon intensity peaked during this period and TOC% is moderate-high in core 137KA.

Studies on planktic foraminifer have shown that the NE monsoon was also moderate-strong in the Early Holocene (Schulz et al., 2002). Thus, subsidence of O₂ rich, CO₂ poor surface water is more important for aragonite preservation than the variation in productivity and input of organic matter. This finding also underlines the importance of the NE monsoon for the Northern Arabian Sea that even under high productivity off Somalia and Oman the OMZ off Pakistan was not present at least down to 570 m water depth during that time. Breakdown of OMZ conditions is not caused by decreased productivity but by enhanced deep winter mixing and intermediate water formation.

The relative shallow position of the core and the rapid settling velocities of pteropods argue against dissolution within the water column. A proof to this is the observation of excellently preserved *L. inflata* tests in H3-equivalent. Furthermore, since the H3-equivalent section is situated between 8 m and 9.20 m core depth, significant diagenetic effects on aragonite preservation during sediment burial can be excluded. Aragonite dissolution seems to take place very close to the sediment water interface. Enhanced accumulation rates could also reduce the time pteropods are exposed to the bottom waters and therefore may increase preservation. However, mass accumulation rates during all H-equivalents in core 137 KA are in general much lower than in the laminated, organic rich intervals (von Rad et al., 1999). Hence, enhanced accumulation rates cannot explain the observed preservation pattern. Only during the Younger Dryas mass accumulation rates are very high and could have contributed to a better aragonite preservation.

6. Conclusions

Our results have shown that pteropod preservation in surface sediments and in core 137KA off Pakistan is related to well-oxygenated, bioturbated sediments. This can be explained by the influence of intermediate water formation in the Arabian Sea down to at least 600 m water depth in times of enhanced NE monsoons during stadials and H-equivalents. The absence of pteropods in laminated sediments (interstadials, Late Holocene) and in the present-day OMZ indicate a weak NE monsoon, stable OMZ, and shallow ACD. The extreme pteropod preservation pattern (well to excellent preservation in bioturbated sediments/ no preservation in laminated sediments, lack of moderate to poor pteropod preservation in surface sediments and in the core) point to rapid shifts between the two ‘modes’ (OMZ/Intermediate water formation).

In addition, supralysoclinal dissolution leads to a shallower present-day position of the ACD (250-400 m water depth) than expected from measurements of the water chemistry (aragonite saturation horizon: 500-600 m water depth in the Arabian Sea; George et al., 1994; Millero et al., 1998; Mintrop et al., 1999).

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Late Quaternary millennial-scale variability in pelagic aragonite preservation off Somalia

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Abstract

In order to better understand Late Quaternary pelagic aragonite preservation in the western Arabian Sea we have investigated a high-resolution sediment core 905 off Somalia. Pteropod preservation is enhanced in times of reduced monsoon-driven productivity, indicated by low amounts of C_{org} and low barium to aluminium (Ba/Al) ratios. All periods corresponding to Heinrich events in the North Atlantic are represented by maxima in shell preservation of the common pteropod *Limacina inflata* (LDX values < 2, except for H5-equivalent with a poorer shell preservation, LDX > 2.66). Good shell preservation is also found during stadials at 52.1-53.2 ka, 36 ka, 33.2 ka, and 31.9 ka. Relative abundance of pteropods and their fragments in the coarse fraction reaches maxima during Marine Isotope Stage (MIS) 5.2, during time-equivalents of Heinrich events 4-6 and in stadials at ~53 ka, ~42.5 ka, and 41.4 ka.

On longer time scales, the pteropod abundance corresponds to the 'Indo-Pacific carbonate preservation type' with poor preservation during interglacials and better preservation during glacials. Late MIS 5 to early MIS 4 sections (84.1-64.8 ka) and the Late Holocene interval (6.5-0 ka) of core 905 contain only traces of pteropods. The early Holocene (9.2-6.5 ka) part is characterized by low pteropod amounts. Between 64.8 ka and 9.2 ka the highest amounts in relative pteropod abundance are observed. Besides the regional monsoonal influence on deepwater chemistry, changes in deepwater circulation occurring on glacial/interglacial and

stadial/interstadial time scales, might have affected pteropod preservation. However, it remains elusive whether 1) deep water formation in the Arabian Sea, 2) inflow of Glacial North Atlantic Intermediate Water or 3) change in water mass properties of the Circumpolar Deep Water (which is the water mass currently bathing this site) contributed to the observed pteropod preservation pattern.

Keywords: Arabian sea; pteropods; *Limacina inflata*; aragonite dissolution; Late Quaternary; Somali basin

1. Introduction

Production, accumulation, and dissolution of pelagic carbonate sediments play an important role in the global carbon cycle. Fluctuations in the carbonate content and preservation state of carbonates are linked to climatic and oceanic circulation changes. Pteropods contribute ~10% (Fabry, 1990; Fabry and Deuser, 1991, 1992) to 12 % (Berner and Honjo, 1981) to the total CaCO₃ production. Aragonite, a metastable polymorph of CaCO₃, is 1.5 times more soluble than calcite in seawater (Morse et al., 1980; Millero, 1996; Morse and Arvidson, 2002). Therefore, the aragonite lysocline and the Aragonite Compensation Depth (ACD) are located at much shallower depths than the Calcite Compensation Depth (CCD).

The preservation state of pteropod tests reflects changes in the aragonite saturation state of seawater (e.g., Almogi-Labin et al., 1986; Haddad and Droxler, 1996; Gerhardt and Henrich, 2001; Henrich et al., 2003) and changes in the input and remineralization of organic matter in particular in high-productivity regions. Pteropods are also used to reconstruct changes in the aragonite lysocline and ACD, which are the depths where pteropod shells are strongly affected by dissolution or disappear in seafloor sediments, respectively (e.g., Chen, 1964; Berger, 1977, 1978; Berner, 1977; Rottman, 1979).

Several studies in the Indian Ocean have concentrated on the preservation of calcite (e.g., Ninety-East Ridge, Petersen and Prell, 1985; Owen Ridge, Murray and Prell, 1992; Equatorial Indian Ocean, Bassinot et al., 1994) and on the preservation of aragonite (e.g., Pakistan continental margin, Berger, 1977, 1978; Reichart et al., 1998, 2002; von Rad et al., 1999; Klöcker and Henrich, submitted; Murray Ridge, Reichart et al., 1997, 1998; Somalia margin, Ivanova, 2000; Gulf of Aden, Almogi-Labin et al., 2000). Most of these studies are focused

on glacial/interglacial time scales. However, only few investigations have been carried out so far on decadal to millennial time scales. In this paper we extend a high-resolution pteropod preservation record off Somalia back to 90 000 years. We discuss our results in terms of changing monsoon intensity and intermediate water circulation. We also evaluate the applicability of different aragonite dissolution proxies. Finally, we compare our record with previously published Indian Ocean carbonate dissolution records.

2. Climate and oceanography

Climatic and oceanographic conditions in the Arabian Sea are characterized by the seasonally reversing monsoonal wind system. Differential heating between the Tibetan plateau and the southern Indian Ocean during boreal summer results in a strong pressure gradient generating the warm and humid SW monsoon (Cadet, 1979). These strong winds induce Ekman transport and upwelling of cold and nutrient-rich waters off Somalia and Oman (Wyrтки, 1973) and lead to a maximum in primary productivity between June and September (Conan et al., 2002). In winter the cool and dry NE monsoon blowing from the Asian landmass leads to cooling of surface waters causing deep convective mixing (Madhupratap et al., 1996) and injection of nutrients to the surface resulting in a second productivity maximum (Nair et al., 1989; Haake et al., 1993).

High-surface water productivity (Qasim, 1977) and moderate rates of thermocline ventilation (You and Tomczak, 1993) generate a stable and pronounced mid-water Oxygen Minimum Zone (OMZ) between 150 - 1200 m (Wyrтки, 1973; Deuser et al., 1978). High input and decay of organic matter within the OMZ raise dissolved inorganic carbon (DIC) concentrations in the subsurface waters and lower the pH (Millero et al., 1998), which results in a shallow aragonite saturation depth of 600 m in the Arabian Sea (Millero et al., 1998). Below this depth bottom waters are undersaturated with respect to aragonite, and aragonitic sediments start to dissolve. In addition, release of metabolic CO₂ (due to export and subsequent decomposition of organic matter within the sediments) lower the pore water pH and increase dissolution of carbonates (Milliman et al., 1999) at the sediment/water interface and in the upper sediment layer.

At present there are 9 important water masses in the Somali basin. Arabian Sea Water (ASW, or Arabian Sea High-Salinity Water) is formed in the northern Arabian Sea during the northeast monsoon by subduction and spreads as salinity maximum underneath the surface-

mixed layer (Morrison, 1997; Schott and Fischer, 2000; Schott and McCreary Jr, 2001). ASW ranges from 0-100 m depth with salinity values between 35.3–36.7 psu and temperatures between 24°C and 28°C (Prasanna Kumar and Prasad, 1999). Persian Gulf Water (PGW) is a warm and saline near-surface water mass (35.1-37.9 psu, 13-19°C, at 200 to 400 m water depth; Prasanna Kumar and Prasad, 1999), which influence is restricted to the northern Arabian Sea (Schott and McCreary Jr, 2001). The high-salinity Red Sea Water (RSW) enters the Arabian Sea after mixing with the Gulf of Aden water and then spreads south through the passage between Socotra and the African continent (Schott and McCreary Jr, 2001). Off Somalia the core of RSW is located at 800 m depth with salinity values around 35.6 psu and temperatures of 11°C (Shapiro and Meschanov, 1991). Indian Central Water (ICW) is formed in the subtropics of the southern hemisphere, spreads northward across the equator with the Somali Current supplying the upwelling water off Somalia and Arabia (Schott and McCreary Jr, 2001). Temperatures and salinities range from 8-25°C and 34.60-35.80 psu, respectively (Emery and Meincke, 1986). Aged ICW is termed North Indian Central Water (NICW, You and Tomczak 1993). Salinities range from 34.84 to 35.10 psu and temperatures from 7.8 to 15.7°C.

The cold and low-salinity Circumpolar Deep Water (CDW) is found at greatest depths of the Somali basin (Schott and McCreary Jr, 2001; Dengler et al., 2002). It is formed in the Southern Ocean by mixing of Wedell Sea water, Pacific Indian intermediate waters, and North Atlantic Deep Water (45%, 30%, 25%, respectively; Emery and Meincke, 1986). Temperatures range from 0.1-3°C and salinity from 34.6-34.9 psu (Emery and Meincke, 1986). Above the bottom water Indian Ocean Deep Water (IDW) is found between about 2000 and 3500 m (Warren, 1993). IDW flows in the density range just above CDW and is composed of upwelled CDW and mixed with older intermediate water masses (e.g., Warren and Johnson, 1992; Warren, 1993; Dengler et al., 2002). The site of this investigation is today bathed in this water mass.

3. Material and methods

The high-sedimentation rate piston core 905 (10°46.01N, 51°57.04E; Fig. 1) was retrieved from 1586 m water depth off Somalia during the C2 cruise of RV Tyro in the framework of the Netherland Indian Ocean Programme (NIOP). The age model is based on 31 AMS ¹⁴C dates, high-resolution oxygen isotope stratigraphy (*N. dutertrei*), and 21 tie points with an

oxygen isotope record from Hoti cave (Jung et al., 2002a) and 17 tie points to the $\delta^{18}\text{O}$ GISP ice core record (Ivanochko et al., 2005). The 15.26 m long core consists of bioturbated homogenous calcareous ooze (Troelstra et al., 1995) and comprises a complete record of the last 90 000 years. Samples were taken at 2.5-cm intervals resulting in an average time resolution of about 150 years. Data of the C_{org} -content and barium to aluminium (Ba/Al) ratio were taken from Ivanochko et al., 2005.

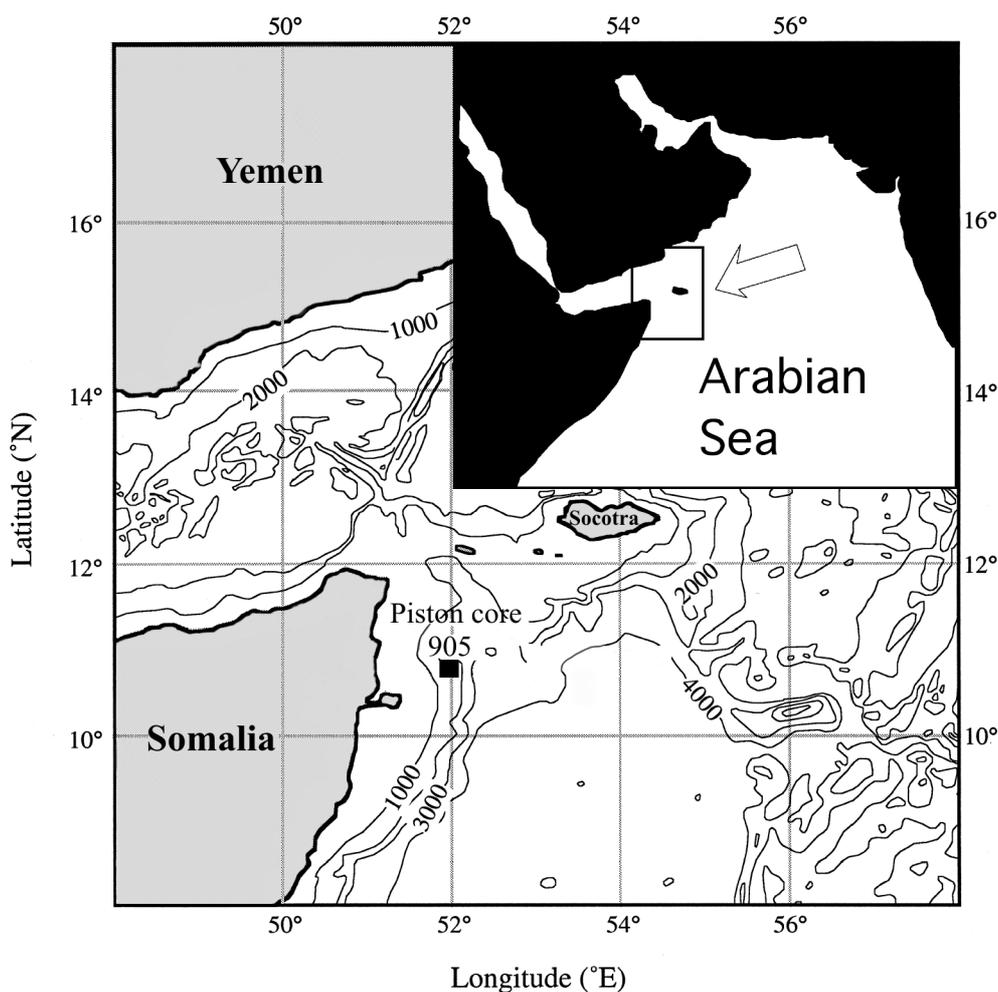


Fig. 1. Map showing the location of piston core 905 off Somalia.

3.1. Aragonite dissolution proxies

To study the preservation of aragonite throughout the core, different dissolution proxies have been applied. The $> 125 \mu\text{m}$ fraction was split into aliquots containing about 600 particles for quantitative light microscopic determination of percentages of pteropods and their fragments

(including heteropods and their fragments) and determination of the *Limacina* Dissolution Index (LDX, according to Gerhardt and Henrich, 2001). The percentage of whole pteropods (wp) is calculated as:

$$\text{whole pteropods (wp)} = \frac{\text{number of pteropods with less than 50 \% damage of the test}}{\text{all particles}}$$

The percentage of whole pteropods including fragments (wpf) is calculated as:

$$\text{wpf} = \frac{\text{number of pteropods with less than 50 \% damage of the test} + \text{fragments of pteropods}}{\text{all particles}}$$

The LDX distinguishes six preservation stages of the shells of the pteropod *Limacina inflata* ranging from 0 (best preservation, transparent shells), 1 (very good preservation, milky shells), 2 (good preservation, opaque-white shells with lustrous shell surface), 3 (moderate preservation, opaque-white shells with partly lustreless shell surface), 4 (poor preservation, opaque-white shells with totally lustreless shell surface) to 5 (worst preservation, opaque-white shells with totally lustreless shell surface and additional shell damage, Gerhardt and Henrich, 2001). *L. inflata* has been chosen because of its common appearance and susceptibility to dissolution. The LDX and the fragmentation ratio of pteropods were calculated according to the equations:

$$\text{LDX} = \frac{\sum(n_p * p)}{\sum n_p}$$

where n_p is the number of investigated tests per preservation stage p (with $p = 0$ to 5) and $\sum n_p$ is at least 10 (tests of *L. inflata* $> 300 \mu\text{m}$);

$$\text{fragmentation} = \frac{n_F}{(n_F + n_w)}$$

where n_F is the number of fragments and n_w is the number of whole tests (whole:= less than 50 % damaged, in most cases small juvenile limacinid pteropods).

Application of each dissolution proxy may imply certain advantages and disadvantages. The LDX and the percentage of whole pteropods appear to be the most reliable aragonite dissolution proxies in this study. Different other controls may have significant influence on the fragmentation ratio, i.e., fragmentation due to bottom currents, bioturbation, and during sample preparation. However the percentage of whole pteropods may also reflect fluctuations in the production rate of pteropods and, in addition, can differ because of variable production rates of foraminifers, a parameter which is very sensitive to changes in ecological conditions, e.g., glacial/interglacial boundary conditions and intensity of upwelling. The LDX is only based on the shell properties and not influenced by productivity changes and should therefore

solely reflect preservation. Unfortunately, even if pteropods are present in the sample, there are some gaps in the LDX record due to insufficient numbers of *L. inflata* tests.

4. Results

In general the relative abundance record of pteropods in the fraction $> 125 \mu\text{m}$ can be divided into 7 intervals (Fig. 2, Fig. 3f-h). The lowest part of the core (Marine Isotope Stage (MIS) 4 to 5.2) comprises three intervals VII-V- with two of them (V and VII) containing only traces of pteropods (interval VII: 88.7-87.2 ka, whole pteropods (wp) and whole pteropods including fragments (wpcf) $< 1\%$; interval V: 84.1-64.8 ka, wp $< 1\%$, wpcf $< 2\%$, some samples may contain up to 4% wpcf). Interval VI (87.2-84.1 ka) contains one broad spike (MIS 5.2: wp: 0-8%, average 4%, max. 8% at 85.8 ka; wpcf: 0-34%, average 21%, max. 34% at 85.3 ka).

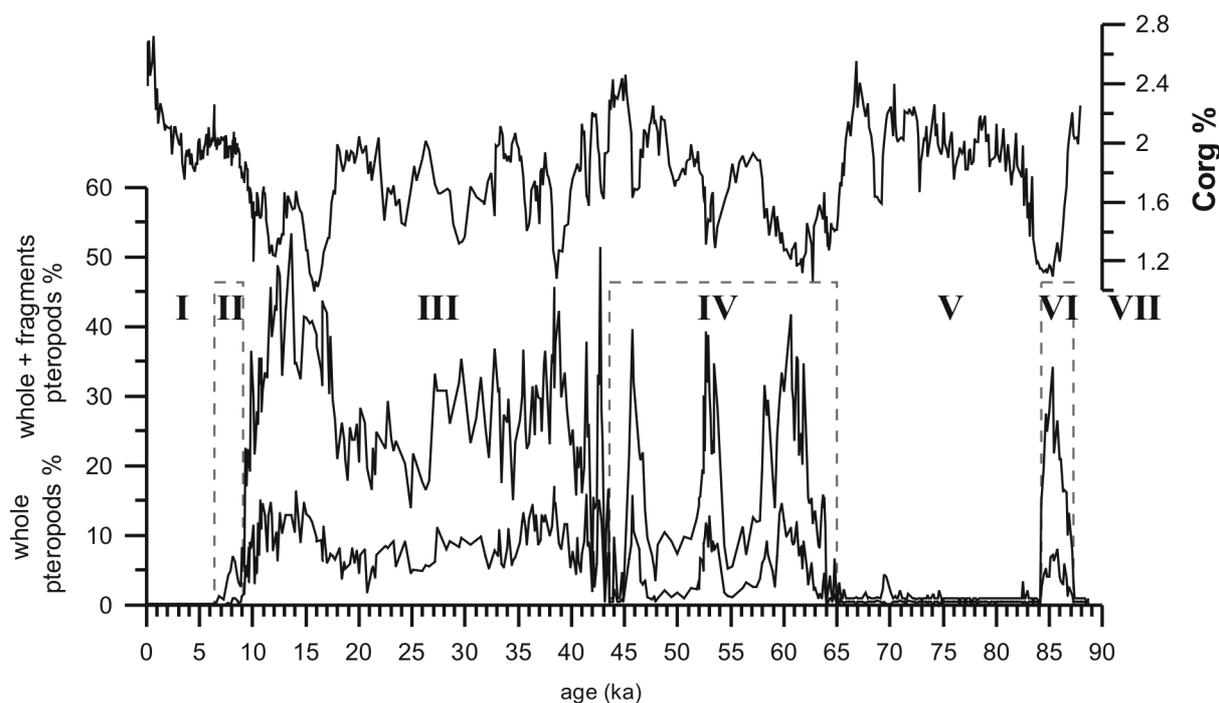


Fig. 2. Relative abundance of whole pteropods, whole pteropods including fragments in the coarse fraction ($> 125 \mu\text{m}$) in relation to the C_{org} content (Ivanochko et al., 2005) in core 905 off Somalia. Different pteropod preservation intervals are indicated by roman numbers.

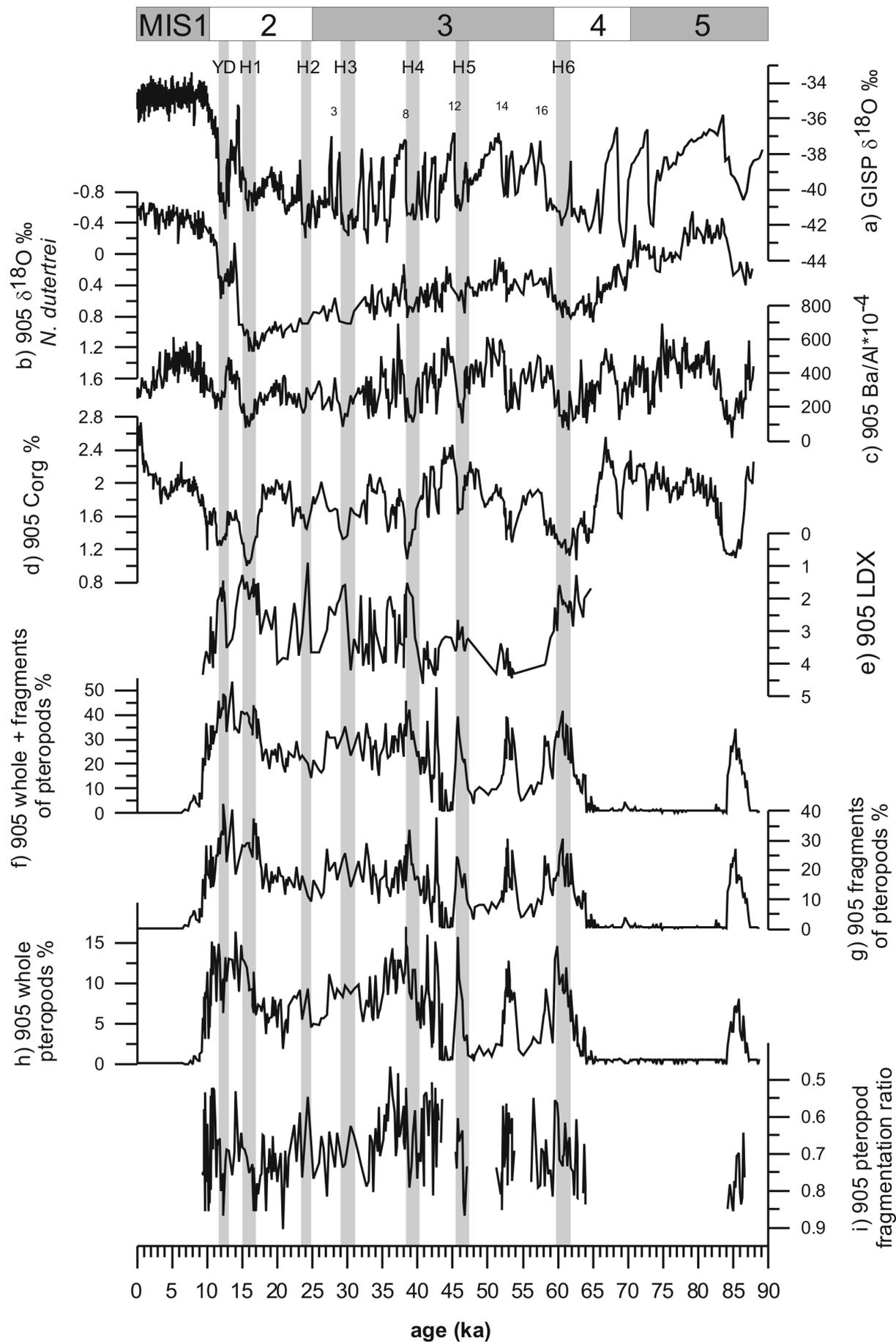


Fig. 3. Stratigraphy and proxies for bioproductivity and aragonite dissolution of core 905. A) $\delta^{18}\text{O}$ GISP2 Greenland ice core record (Grootes et al., 1993); B) $\delta^{18}\text{O}$ *N. dutertrei* record (Ivanochko et al., 2005) of piston core 905 off Somalia; C and D) productivity proxies $\text{Ba}/\text{Al} \cdot 10^{-4}$ and $\text{C}_{\text{org}} \%$ (Ivanochko et al., 2005); E) *Limacina inflata* dissolution index (LDX, 0 = best preservation, transparent shells, 1 = very good preservation, milky shells, 2 = good preservation, opaque-white shells with lustrous shell surface, 3 = moderate preservation, opaque-white shells with partly lustreless shell surface, 4 = poor preservation, opaque-white shells with totally lustreless shell surface, 5 = worst preservation, opaque-white shells with totally lustreless shell surface and additional shell damage, Gerhardt and Henrich, 2001); F, G, H) Relative abundance of whole pteropods including fragments, fragments, whole pteropods in the coarse fraction ($> 125 \mu\text{m}$); I) pteropod fragmentation index: fragments/(fragments + whole tests).

The intervals IV and III (64.8-43.4 ka and 43.4-9.2 ka, respectively) contain the highest percentage of pteropods in the core 905. In interval IV strong fluctuations are observed and an intermediate average abundance is revealed (wp: 1-16%, average 5%; wpf: 4-42%, average 18%). Three distinct spikes with high percentage of pteropods occur (H5-equivalent: wp: 16%, 45.76 ka, wpf: 40%, 45.76 ka; a double spike at the stadial14/15: wp: 13%, 53.03 ka, wpf: 39%, 52.7 ka; H6-equivalent: wp: 15%, 59.8 ka, wpf: 42%, 60.63 ka). Interval III is characterized by high average pteropod abundance (wp: 2-17%, average 9%; wpf: 14-53%, average 28%). Maxima which can be correlated to Heinrich events and stadials in the North Atlantic (Fig. 3a, f-h) occur at the end of MIS 2 (17.7-9.8 ka, H1-equivalent to Early Holocene) and during MIS 3 (H4-equivalent: wp: 17%, wpf: 46%, 38.35 ka; stadial 10: wp: 16%, wpf: 38%, 41.36 ka; stadial 11: wp: 15%, 42.5 ka, wpf: 51%, 42.72 ka).

In interval II (9.2-6.5, 'Early Holocene') only small amounts of whole pteropods (wp: 1-2%, average 1%) and whole pteropods including fragments occur (wpf: 1-8%, average 4 %). Interval I (6.5-0 ka, Late Holocene') is characterized by absence of pteropods in the coarse fraction.

The shell preservation record of *L. inflata* is quite similar to the relative abundance record but has a lower resolution due to insufficient numbers of adult *L. inflata* tests in some samples (Fig. 3e). Spikes with good to very good preservation (LDX values < 2) appear in the YD, H-equivalents and stadials (YD: 12.4-11.7 ka, LDX values min. 1.43; H1-equivalent: 17.4-14.5 ka, LDX min. 1.27; H2- equivalent: 24.28 ka, LDX 0.91; H3-equivalent: 29.7-29.4, LDX min. 1.57; three spikes at 31.87 ka, LDX 1.91, 33.2 ka, LDX 1.98, 36 ka, LDX 1.93; H4-equivalent: 39.4-38.2 ka; LDX min. 1.50; H6- equivalent: 64.8-60.1 ka, LDX max. 1.28). At H5-equivalent (46.3-45.8 ka) pteropods are slightly worse preserved (LDX > 2.66) than in the other H-equivalents intervals. Also pteropods during the 'pre IS14/IS15 stadial' (53.2-52.1 ka) show only moderate preservation (LDX > 3.50). In the time period from 11.7 to 9.4 ka

(Preboreal, Termination and earliest Holocene), Bølling-Allerød, and interstadials shell preservation of *L. inflata* is distinctly worse (LDX values > 2.5 to 4.6) than in the stadials and H-equivalents (with the exceptions mentioned above).

Productivity proxies percentage of organic carbon (C_{org} %) and the barium to aluminium (Ba/Al) ratio correlate very well throughout the whole core (except the last 3000 years where C_{org} % rises whereas Ba/Al decreases, Fig. 3c, d). This finding indicates that C_{org} % is a reliable productivity proxy at site 905. Therefore, we further focus on C_{org} % to compare productivity with pteropod preservation. In general, C_{org} % values are higher during interglacials (MIS 1,3,5) than during glacials (MIS 2 and 4). But also strong millennial scale fluctuations occur comparable to the D/O cycles with high values during interstadials and low values during stadials and H-equivalents.

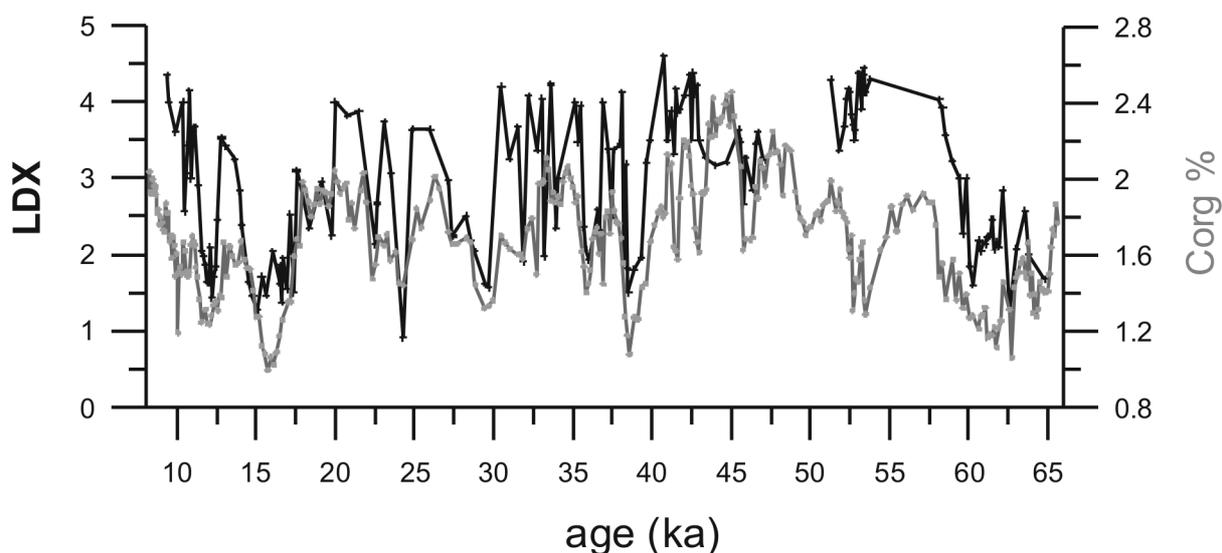


Fig. 4. Pteropod shell preservation (LDX) in relation to bioproductivity proxy C_{org} % (Ivanochko et al., 2005). Preservation spikes (low LDX values) correlate with low bioproductivity.

A striking anticorrelation to relative pteropod abundance and shell preservation (LDX) is visible (Fig. 2 and 4, respectively). The lower part of the core is rich in C_{org} in interval V (1.94 % on average) with very low pteropod percentage and low C_{org} (1.55 %) during the pteropod spike in interval VI. In intervals IV and III where relative pteropod abundance is highest C_{org} % is distinctly lower (average 1.71 % and 1.67 %, respectively).

The lowest C_{org} % concentrations (1.0-1.1%) are observed in the H-equivalents H1, H4, H6 and MIS 5.2. Also during YD, H3-equivalent and the stadial at 53.5 ka C_{org} % is low (1.2-

1.3%) whereas the interstadials are characterized by much higher values and low amounts of pteropods (e.g., interstadial 12, 45.0 ka, 2.46 % C_{org} with only traces of pteropods preserved). During intervals II and I where pteropods are few to absent, C_{org} % is high (9.2-6.5 ka: 1.72-2.08%, average 1.94 %; 6.5-0 ka: 1.75-2.73 %, 2.09 % on average).

The stable oxygen isotope ($\delta^{18}O$) record of the planktic foraminifer *N. dutertrei* shows the (typical) pattern with heavy values during the glacials and stadials and lighter values during interglacials and interstadials (-0.67 ‰, 0.8 ka, Late Holocene to 1.25 ‰, 16.7 ka, H1-equivalent, with a range of 1.92 ‰, Fig. 3b). Shell preservation (LDX) is in phase with $\delta^{18}O$ (Fig. 5), meaning best preservation at relative heavy $\delta^{18}O$ values. Maxima in relative pteropod abundance are also bound to relative heavy $\delta^{18}O$ values, but they seem to be shifted to the highest rate of change in $\delta^{18}O$ (Fig. 6), meaning rapid transitions from relative heavy values to relative lighter values, e.g., at 60 ka from MIS 4 to MIS 3 and at Termination I.

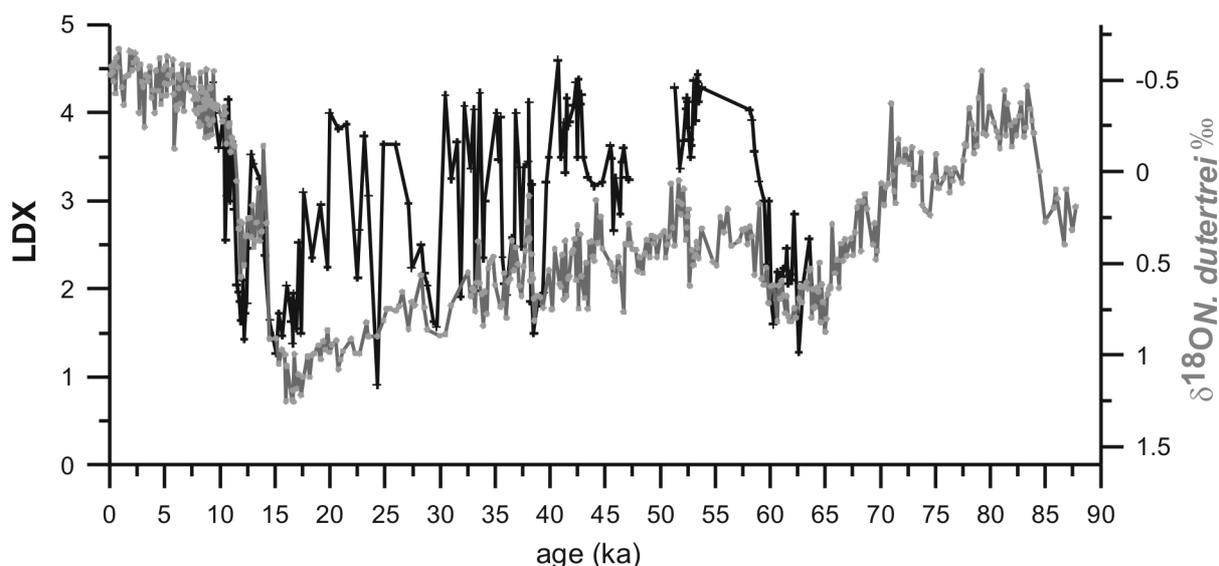


Fig. 5. Pteropod shell preservation (LDX) in relation to the $\delta^{18}O$ *N. dutertrei* record (Ivanochko et al., 2005) in core 905 off Somalia. Preservation spikes (low LDX values) occur during glacials and stadials.

5. Discussion

5.1. Pteropod abundance and preservation in relation to changes in monsoon strength

The relative abundance record of pteropods and the shell preservation record LDX show a clear opposite trend compared to productivity proxies (C_{org} %, Ba/Al ratio). Hence, aragonite

preservation is strongly influenced by the strength of the SW monsoon: During phases of enhanced SW monsoon activity (MIS 1 and 5, interstadials) pteropod preservation is poor whereas in times of reduced monsoon strength (H-equivalents, stadials) pteropod preservation is increased. Several studies in the Arabian Sea have shown that during the interglacials and interstadials the SW monsoon is enhanced which leads to an increase in upwelling and bioproductivity off Somalia and Oman (e.g., Sirocko et al., 1993; Reichert et al., 1998; Schulz et al., 1998; Schulte and Müller, 2001; Altabet et al., 2002; Pourmand et al., 2004). The high input and remineralization of organic matter leads to high DIC concentrations in the intermediate (subsurface) waters which lower the pH and dissolve aragonite (Millero et al., 1998). In addition, the higher export, burial, and decomposition of organic matter within the sediments lowers the pore water pH and contributes to dissolution of pteropods (supralysoclinal or biologically mediated carbonate dissolution; Milliman et al., 1999). In contrast, during periods of reduced SW monsoon intensity upwelling induced bioproductivity weakens and the preservation of pteropods increases due to the higher pH in intermediate and bottom waters. Also, the export flux of organic matter is reduced and supralysoclinal dissolution becomes less effective.

Long-term diagenetic trends can affect aragonite preservation. However, they are of minor importance for pteropod preservation in core 905, as pteropods in the preservation spike at H6-equivalent are as well preserved as pteropods in the H1-equivalent spike. Furthermore, the relative shallow position of the core 905 (1600 m water depth) and the rapid settling velocities of pteropods (1-2.5 cm/s according to Byrne et al., 1984) argue against dissolution within the water column. Hence, pteropod dissolution at site 905 seems to take place very close to the sediment water interface. In addition, the high sedimentation rates of core 905 may have contributed to increase the preservation of pteropods, because the exposure to undersaturated bottom waters and the time that pteropods stay within the oxygenated zones of the sediments decrease.

The observation, that pteropod shell preservation (LDX) is in phase with $\delta^{18}\text{O}$ (Fig. 5), but maxima in relative pteropod abundance seem to be shifted to the highest rate of change in $\delta^{18}\text{O}$ (in particular at the transition MIS 4 to MIS 3 and Termination I, Fig. 6), can be explained by optimum preservation conditions during glacials and stadials and optimum ecological conditions (highest pteropod productivity) at the transitions. This finding clearly supports our assumption that shell preservation (LDX) is a more reliable preservation proxy

than others. The relative pteropod abundance record mainly reflects the shell preservation, but in addition possesses an ecological (productivity) component.

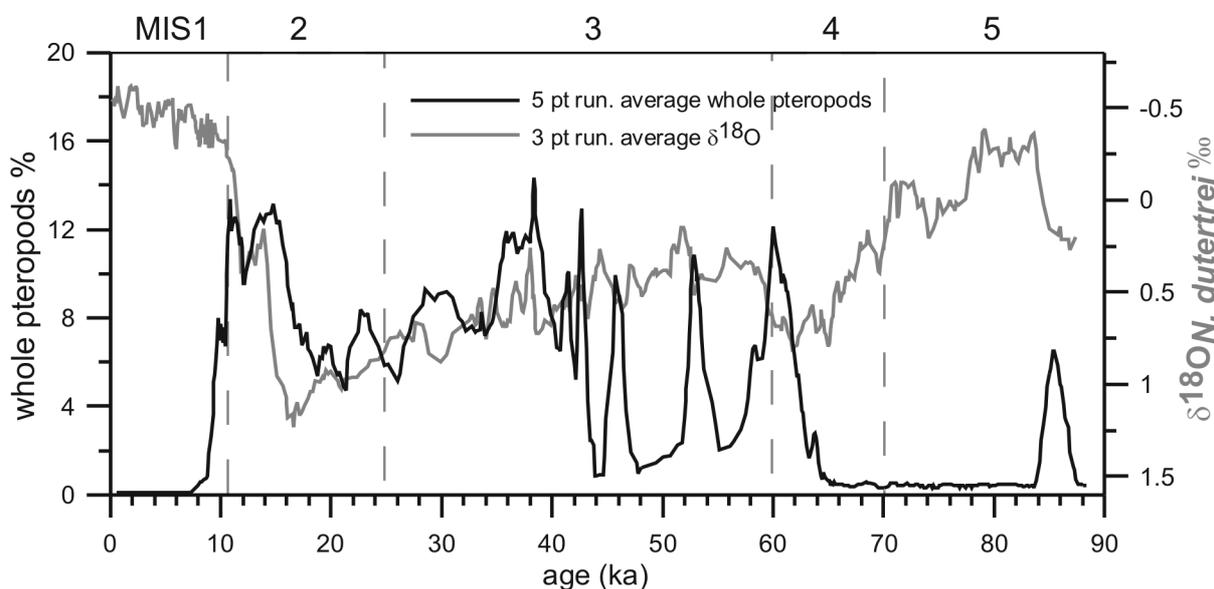


Fig. 6. Relative abundance of pteropods in the coarse fraction ($> 125 \mu\text{m}$) in relation to the $\delta^{18}\text{O}$ *N. dutertrei* record (Ivanochko et al., 2005) in core 905 off Somalia. Pteropod preservation spikes occur during glacial and stadials (partly shifted to transitions).

5.2. Recent pteropod productivity and the recent aragonite saturation depth

Calculations from DIC and alkalinity measurements have shown that the aragonite saturation horizon (ASH, water depth with 100% aragonite saturation) of the Somali Basin is positioned at 600 m (Millero et al., 1998; Sabine et al., 2002). Hence, core 905P was bathed at least during the Late Holocene in water masses which were undersaturated with regard to aragonite. Recently it has been observed that due to penetration of anthropogenic CO_2 into subsurface water masses ASHs of the oceans have shoaled (Feely et al., 2004; Sabine et al., 2004). In the Arabian Sea ASH has shoaled between the GEOSECS and WOCE measurements by about 100 m (Sabine et al., 2002). Thus in preindustrial times the saturation depth might have been distinctly deeper than the recently observed 600 m. However site 905 is located at 1600 m water depth and too deep to be already directly affected by anthropogenic CO_2 .

In two sediment traps off Somalia pteropods are abundant in the coarse fraction with a pteropod/planktic foraminifer ratio of about 40:60 (Conan et al., 2002). In addition,

unpublished records from a boxcore at a shallower site off Somalia (903B, 800 m water depth) show that during the Late Holocene pteropods were abundant off Somalia. Thus the absence of pteropods in the Late Holocene of 905P is not related to an interval with no production but refers to strong dissolution which appears to be reasonable since the site is located ~1000 m below the present ASH.

Poor pteropod preservation has been recorded from different upwelling regions in the world (Berger, 1978; Ganssen and Lutze, 1982; Gerhardt and Henrich, 2001). This study confirms the conclusion of Berger (1978) that dissolution and not lack of supply is responsible for low pteropod abundance in the sediments from high productivity regions. The sediment trap/surface sediment study off Somalia shows that only 25% of the planktic foraminifer flux is preserved in the surface sediments at site 905 which indicates supralysocline calcite dissolution during the Late Holocene (Conan et al., 2002). Aragonite dissolution could also partly be the result of the release of metabolic CO₂ to the pore waters, but as the ASH is located at a much shallower depth (around 600 m water depth) most of the dissolution should be due to the undersaturated bottom waters.

5.3. Pteropod preservation in relation to hydrographic changes

The core position is bathed at present-day (and during the Late Holocene) in CDW/IDW whereas during the Early Holocene the site could have been bathed in RSW (Jung et al., 2001). At 800 m water depth off Somalia RSW consists of a mixture between 25% Gulf of Aden subsurface water, 69% CDW, and 6% 'pure' RSW (Bab el Mandeb, Jung et al., 2001). Recently a 0.5‰ reduction in benthic foraminifer *C. kullenbergi* $\delta^{18}\text{O}$ between 10 and 6.5 ka has been observed and explained by either T-S changes in CDW (unlikely) or enhanced salinity of RSW (Jung et al., 2001). Changes in the evaporation-precipitation balance in the Red Sea region could have increased the density of 'source RSW' leading to a 800 m deeper settling of 'RSW off Somalia' than today (Jung et al., 2001). Pteropod abundance in core 905 is very low in the period from 9.2-6.5 ka and the intensity of the SW monsoon reached a maximum in the Early Holocene (Sirocko et al., 1993; Ivanova, 2000; Jung et al., 2002b). In the Late Holocene (0-6.5 ka) the SW monsoon was weaker but pteropods are absent. Jung et al. (2001) interpreted this finding as the result of the better preservation potential of RSW in contrast to the CDW/IDW. This shows that monsoon-driven changes in productivity are not sufficient to explain the fluctuations of relative pteropod abundance and shell preservation

alone. A Late Holocene rise of IDW/CDW could have induced a shoaling of the ACD off Somalia.

The lowering of sea level during the glacials shuts down the outflow of RSW almost completely because of the shallow sill depth (137m) at the Strait of Bab el Mandeb. In absence of RSW and PGW other intermediate/deep water masses become more important. Different concepts have been suggested:

(1) CDW bathing Site 905 during glacials seems unlikely due to the fact that the recent ACD is located at around 1500 m water depth (Ivanova, 2000) near the upper boundary of the IDW, representing its poor aragonite preservation potential. On the other hand, glacial CDW may have been less corrosive as indicated by better calcite preservation in the deep-sea of the Indian Ocean (e.g., Bassinot et al., 1994; Peterson and Prell, 1985).

(2) Boyle (Boyle et al., 1995; Boyle, 1997) suggested that Glacial North Atlantic Intermediate Water (GNAIW) was flowing round the tip of Africa into the Arabian Sea. GNAIW could have had a better preservation potential than CDW.

(3) Intermediate water formation within the northern Arabian Sea took place in times of increased winter monsoon (Reichart et al., 1998, 2002). Isotopic analysis from the Pakistan margin show that during times of increased NE monsoon strength due to enhanced deep winter mixing intermediate /deep water may have formed to greater water depths. This young and oxygen-rich/CO₂-poor water mass would have had an excellent preservation potential for aragonite and could explain the observed pteropod spikes and the fluctuations in the OMZ at the Pakistan continental margin.

5.4. The preservation record of the studied core 905 in comparison to other Indian Ocean carbonate preservation records

The pteropod preservation record of core 905 is in agreement with pteropod preservation records from the Pakistan margin which show preservation spikes during H-equivalents and stadials (Reichart et al., 1998, 2002; von Rad et al., 1999; Klöcker and Henrich, submitted). In addition, the glacial/interglacial preservation pattern agrees with the Murray Ridge records (NIOP 463 and 464; Reichart et al., 1997; den Dulk et al., 2000). Both cores (463 and 464) show preservation spikes at the transitions from glacials to interglacials (MIS 6/5, 4/3 and 2/1). In core 464, pteropods are much better preserved during MIS 6 than during MIS 5. A similar preservation pattern is also recorded in a Gulf of Aden core (KL15; Almogi-Labin et

al., 2000) where pteropods are nearly absent during interglacial stages (MIS 13,11,9,7,5,1). Spikes in total pteropod abundance occur at all transitions from glacial to interglacial stages with a maximum during stage 6.

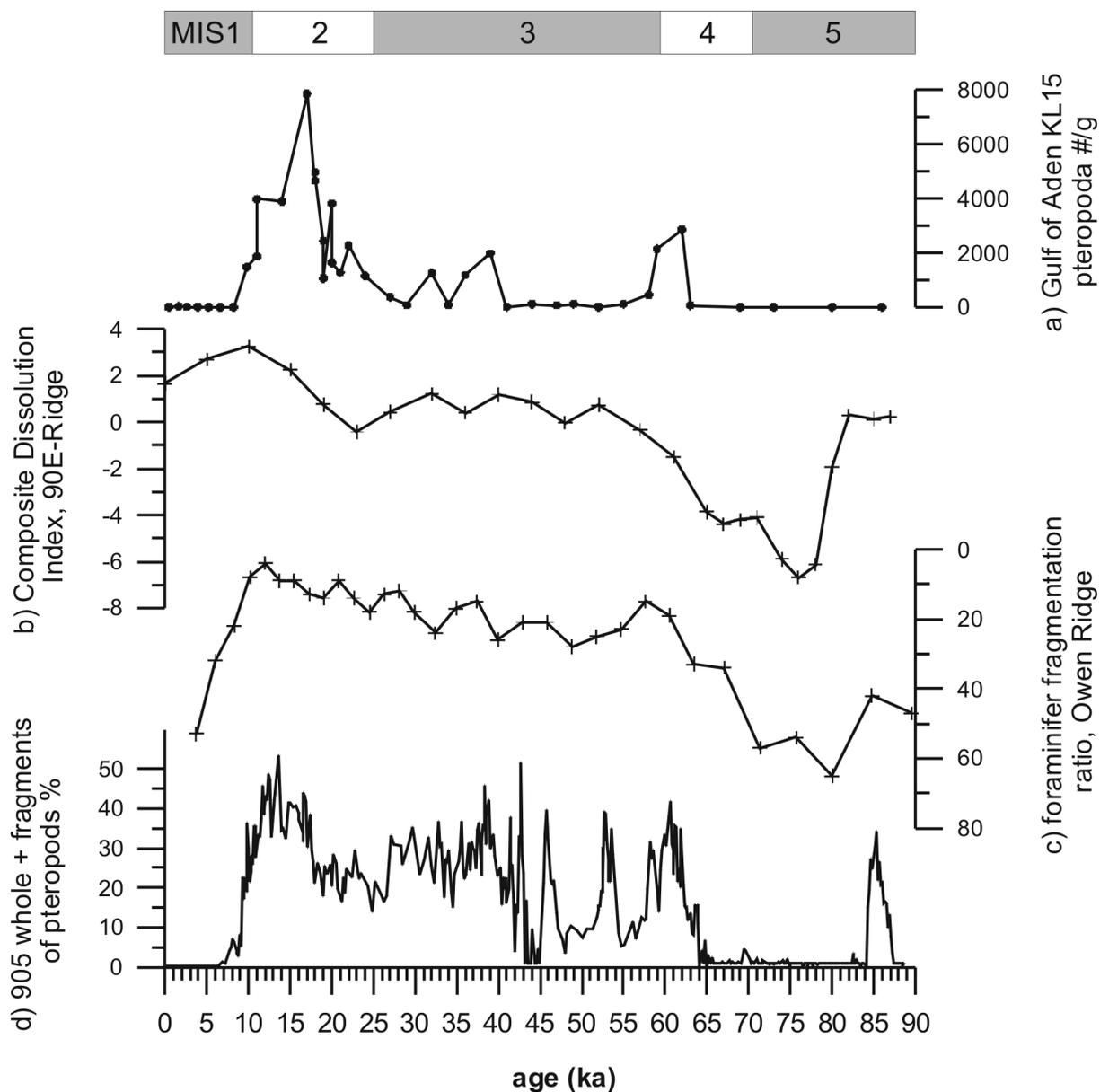


Fig. 7. Comparison between carbonate dissolution proxies from different sites in the Indian Ocean. a) total abundance of pteropods per g of core KL15 (1631 m water depth; Almogi-Labin et al., 2000) from the Gulf of Aden; b) Composite dissolution index of core V34-53 (3812 m water depth) from the Ninetyeast Ridge (after Peterson and Prell, 1985), higher values indicate better preservation; c) foraminiferal fragmentation index (fragments/(fragments+whole)) of core RC27-61 (1893 m water depth) from the Owen Ridge, northwestern Arabian Sea (after Murray and Prell, 1992); d) relative abundance of whole pteropods including fragments in the coarse fraction (> 125 μm) of core 905 off Somalia.

Compared to our record, the Gulf of Aden pteropod record for the last 90 000 years looks similar but spikes between 60 and 40 ka are missing in KL15 (Fig. 7a). The 905 LDX values during the same interval display poor pteropod preservation with high values in $C_{org}\%$. This could indicate that high-productivity caused the shallowing of the aragonite lysocline and the ACD. A broad primary productivity maximum between 60 and 40 ka has previously been observed at several sites in the Arabian Sea (e.g. Zahn and Pedersen, 1991; Hermelin and Shimmield, 1995; Reichart et al., 1997, 1998; den Dulk et al., 1998; Almogi-Labin et al., 2000; Schulte and Müller, 2001; Ivanova et al., 2003).

Spectral analysis of NIOP 464 pteropod record also demonstrates the monsoonal control on aragonite preservation in the Arabian Sea. Pteropod maxima occur in antiphase ($\sim 180^\circ$) relationship on precessional time scales to productivity proxies (*G. bulloides*, C_{org} , $\delta^{15}N$), which are in phase with maximum SW monsoon intensity (Reichart et al., 1998).

Additional evidence for monsoonal influence on carbonate preservation comes from a 350-kyr record of planktic foraminiferal fragmentation at the Owen Ridge (core RC27-61, 1893 m water depth, Murray and Prell, 1992). Supralysocline calcite dissolution appears in form of foraminiferal fragmentation which is nearly in phase with maximum bioproductivity (Murray and Prell, 1992).

Carbonate preservation spikes at the end of glacials have been observed in the Indian Ocean (Fig. 7b, Peterson and Prell, 1985; Fig. 7c, Murray and Prell, 1992), Pacific (Farrell and Prell, 1989) and South Atlantic (Hodell et al, 2001). A correlation of alternating maxima in carbonate preservation and dissolution with the maximum rate of change (first derivative) in benthic $\delta^{18}O$ has been observed (Peterson and Prell, 1985; Hodell et al, 2001). Global oceanic circulation changes (different modes of NADW production) that lead to shifts in basin-to-basin fractionation of the carbonate ion content of deep water have been invoked for this 'Indo-Pacific' type.

6. Conclusions

Investigation of a 90 000 year high-resolution sediment core 905 off Somalia has shown that pteropod preservation is enhanced in times of reduced monsoon-driven productivity as indicated by low percentages of C_{org} and low Ba/Al ratios. In contrast, periods of intensified monsoon activity characterized by high percentages of C_{org} and high Ba/Al ratios lead to dissolution of pteropods.

The low pteropod preservation potential during higher monsoon and upwelling activity is attributed to the high input and remineralization of organic matter, that lead to high DIC concentrations in the intermediate (subsurface) waters which lower the pH and dissolve aragonite. In addition, the higher export, burial and decomposition of organic matter within the sediments lowers the pore water pH and contributes to dissolution of pteropods (supralysoclineal dissolution; Milliman et al., 1999).

Shell preservation (LDX) is in phase with $\delta^{18}\text{O}$ (best preservation at relative heavy $\delta^{18}\text{O}$ values), whereas maxima in relative pteropod abundance are also bound to relative heavy $\delta^{18}\text{O}$ values, but they seem to be shifted to the highest rate of change in $\delta^{18}\text{O}$ (rapid transitions from relative heavy values to relative lighter values). This finding confirms our expectation that the LDX is a more reliable preservation proxy compared to the relative pteropod abundance record that mainly reflects the LDX preservation, but in addition possesses an ecological (productivity) component.

In addition to the monsoonal influence, changes in deepwater circulation occurring on glacial/interglacial and stadial/interstadial time scales might have affected pteropod preservation. The glacial/interglacial pteropod preservation pattern of 905 match the ‘Indo-Pacific carbonate preservation type’ with poor preservation during interglacials and better preservation during glacials.

Whether deep water formation in the Arabian Sea in times of enhanced NE monsoon intensity, inflow of Glacial North Atlantic Intermediate Water as suggested by Boyle (Boyle et al., 1995; Boyle, 1997) or an improved aragonite preservation potential of the CDW (which is the water mass currently bathing this site) contributed to better pteropod preservation remains elusive. Further work on benthic foraminifers (stable isotopes, Mg/Ca temperatures) is needed to answer this question.

Acknowledgments

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Variation in production, input and preservation of metastable calcium carbonate off Somalia during the last 90 000 years

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Abstract

To improve our understanding of the Late Pleistocene and Holocene carbonate system of the western Arabian Sea a high resolution sedimentary record off Somalia has been analysed. The 15.26 m long piston core 905 comprises a complete record of the last 90 000 years. We have measured concentrations of carbonate minerals, i.e., aragonite, calcite, Mg-calcite, and element ratios (Sr/Ca) together with pteropod counts and an estimation of the preservation state of pteropod shells to trace temporal changes in carbonate production and preservation.

The Sr/Ca ratio shows strong similarities to the aragonite percentage and the $\delta^{18}\text{O}$ record of the planktic foraminifer *N. dutertrei*. High Sr/Ca ratios together with fragments of corals found in the coarse fraction indicate that most of the aragonite is of shallow water origin (high Sr-aragonite) and pteropods contribute much less than expected. High resuspension input of

shallow marine aragonite occurs during sea level highstands (interglacials) and low input during lowstands (glacials).

The Mg-calcite concentration record resembles the whole pteropod abundance and pteropod shell preservation records confirming the use of Mg-calcite in combination with pteropod preservation proxies to reconstruct past fluctuations in carbonate dissolution. Preservation of aragonite and Mg-calcite increases during stadials, H-equivalents, YD and late Marine Isotope Stage (MIS) 3. During late MIS 5/early MIS 4 and in the Late Holocene absence or few pteropods as well as low Mg-calcite weight percentages point to strong dissolution of aragonite and Mg-calcite.

Keywords: Arabian sea; pteropods; highstand shedding; carbonate mineralogy; aragonite dissolution; Late Quaternary; Somali basin

1. Introduction

During the late Quaternary the Arabian Sea summer monsoon system showed strong millennial-scale fluctuations in relation to Dansgaard-Oeschger (D/O) cycles in the North Atlantic. Recent studies have focused on bioproductivity (Reichart et al., 1998; Schulz et al., 1998; Ivanova, 2000; Altabet et al., 2002; Ivanochko et al., 2005), terrigenous input (Pourmand et al., 2004; Ivanochko et al., 2005) or denitrification (Suthhof et al., 2001; Altabet et al., 2002; Ivanochko et al., 2005).

Only few investigations have been carried out on the millennial-scale variations in the carbonate system of the Arabian Sea (Reichart et al., 1997, 1998; von Rad et al., 1999; Ivanova, 2000). In this study we present high resolution mineralogical (calcite, Mg-calcite, aragonite), geochemical (Sr/Ca ratios) and micropaleontological data (pteropod counts and shell preservation records) from a piston core off Somalia. The main targets are to analyse the impact of millennial-scale variations in the strength of the SW monsoon and in relative sea level on resuspensional input as well as pelagic production, accumulation and preservation of carbonates.

1.1. General aspects of carbonate production and preservation in periplatform and continental slope settings

Aragonite, a metastable polymorph of CaCO_3 , is produced mainly by pteropods (pelagic aragonite, Fabry, 1990) or is of shallow water origin (e.g., corals, aragonite needles). Changes in the Aragonite Compensation Depth (ACD), which is the depth where pteropod shells disappear in seafloor sediments (Chen, 1964; Berger, 1977, 1978; Berner, 1977; Rottman, 1979), can be traced by the occurrence and absence of pteropods. Aragonite is 1.5 times more soluble than calcite in seawater (Morse et al., 1980; Millero, 1996; Morse and Arvidson, 2002). Hence, the aragonite lysocline and the ACD are generally located at a much shallower depth than the Calcite Compensation Depth (CCD).

The preservation state of aragonitic pteropod tests has been used as a proxy for the aragonite saturation state of seawater (Almogi-Labin et al., 1986; Haddad and Droxler, 1996; Gerhardt and Henrich, 2001; Henrich et al., 2003). Additionally, aragonite preservation is influenced by the input and remineralization of organic matter, particularly in high-productivity regions (Klöcker et al., *subm.*).

Furthermore, export of shallow marine aragonite and Mg-calcite (or high-magnesian calcite, > 4 mol-% MgCO_3 , typically 13-18 %, Droxler et al., 1991, hereafter Mg-calcite) increases the amount of carbonate buried in hemipelagic sediments near carbonate platforms (Droxler et al., 1988, 1991; Schlager et al., 1994; Haddad and Droxler, 1996; Dunbar et al., 2003). This material is transported by downslope gravity flows or settling through the water column after being suspended and transported offshore during high energy events (Droxler et al., 1988, 1991). Since no gravity flow deposits have been observed in core 905, resuspension and offshore transport (due to storms during the SW monsoon period, internal waves or activity of the gyre 'Great Whirl') control the input of shallow water aragonite and Mg-calcite to the site 905. Shallow water aragonite is generally enriched in strontium (>7,500 ppm) while calcitic components of planktic sources contain less strontium (< 2,000 ppm) (Milliman, 1974; Morse and Mackenzie, 1990). Pteropods incorporate much lower amounts of Sr into their shells (<2000 Sr ppm; Milliman 1974). Off Somalia the calcite and aragonite fraction of surface sediment samples contain on average ~1500 ppm Sr and ~7000 ppm Sr, respectively (Müller 1966, 1967).

Mg-calcite is more soluble in seawater than aragonite and low-magnesian calcite (hereafter calcite) and therefore has been used as a proxy for the carbonate saturation state at

intermediate water depths near the Bahamas and the Nicaragua Rise (Droxler et al., 1988, 1991; Haddad and Droxler, 1996). These authors also used a combination of Mg-calcite percentage, pteropod abundance, pteropod fragmentation and shell preservation in Late Quaternary sediment cores from the Caribbean and the Bahama Banks as a proxy of CaCO₃ dissolution (Haddad and Droxler, 1996).

Calcite is produced by pelagic carbonate-secreting organisms: e.g., coccolithophorids and planktic foraminifers. Calcite is much less susceptible to dissolution than aragonite and Mg-calcite. Since the piston core 905 is located at 1600m water depth far above the calcite saturation depth (~3200 m water depth; Sabine et al., 2002), possible dissolution should only be of supralysoclinal origin. In this study we will focus on the production and preservation of aragonite and Mg-calcite and will treat calcite as being stable due to the presence of pteropods in (most parts of) the core. However, the absence of pteropods in the Late Holocene as well as the results of a sediment trap/surface sediment study showing that only 25% of the planktic foraminifer flux is preserved at site 905 (Conan et al., 2002), indicate supralysoclinal calcite dissolution during the Late Holocene.

2. Climatic and oceanographic conditions

Seasonally reversing monsoonal winds characterize the climatic and oceanographic conditions in the Arabian Sea. During boreal summer a strong pressure gradient caused by differential heating between the Tibetan plateau and the southern Indian Ocean generates the warm and humid SW monsoon (Cadet, 1979). These strong winds induce Ekman transport and upwelling of cold and nutrient-rich waters off Somalia and Oman (Wyrтки, 1973) and lead to a maximum in primary productivity between June and September (Conan et al., 2002). In winter, the cool and dry NE monsoon blowing from the Asian landmass causes cooling of the surface waters resulting in deep convective mixing (Madhupratap et al., 1996) and the injection of nutrients to the surface leading to a second productivity maximum (Nair et al., 1989; Haake et al., 1993).

High-surface water productivity (Qasim, 1977) in combination with moderate thermocline ventilation rates (You and Tomczak, 1993) generate a stable and pronounced mid-water Oxygen Minimum Zone (OMZ) between 150 - 1200 m (Wyrтки, 1973; Deuser et al., 1978). Within the OMZ, high input and decay of organic matter raise dissolved inorganic carbon (DIC) concentrations in the subsurface waters and lower the pH (Millero et al., 1998), which

results in a shallow aragonite saturation depth of 600 m in the Arabian Sea (Millero et al., 1998). Below this depth bottom waters are undersaturated with respect to aragonite and aragonitic sediments start to dissolve. Additional decomposition of organic matter within the sediments ('respiratory dissolution') releases metabolic CO₂ to the pore water and lowers the pore water pH leading to a further increase in dissolution of carbonates (Emerson and Bender, 1981; Milliman et al., 1999).

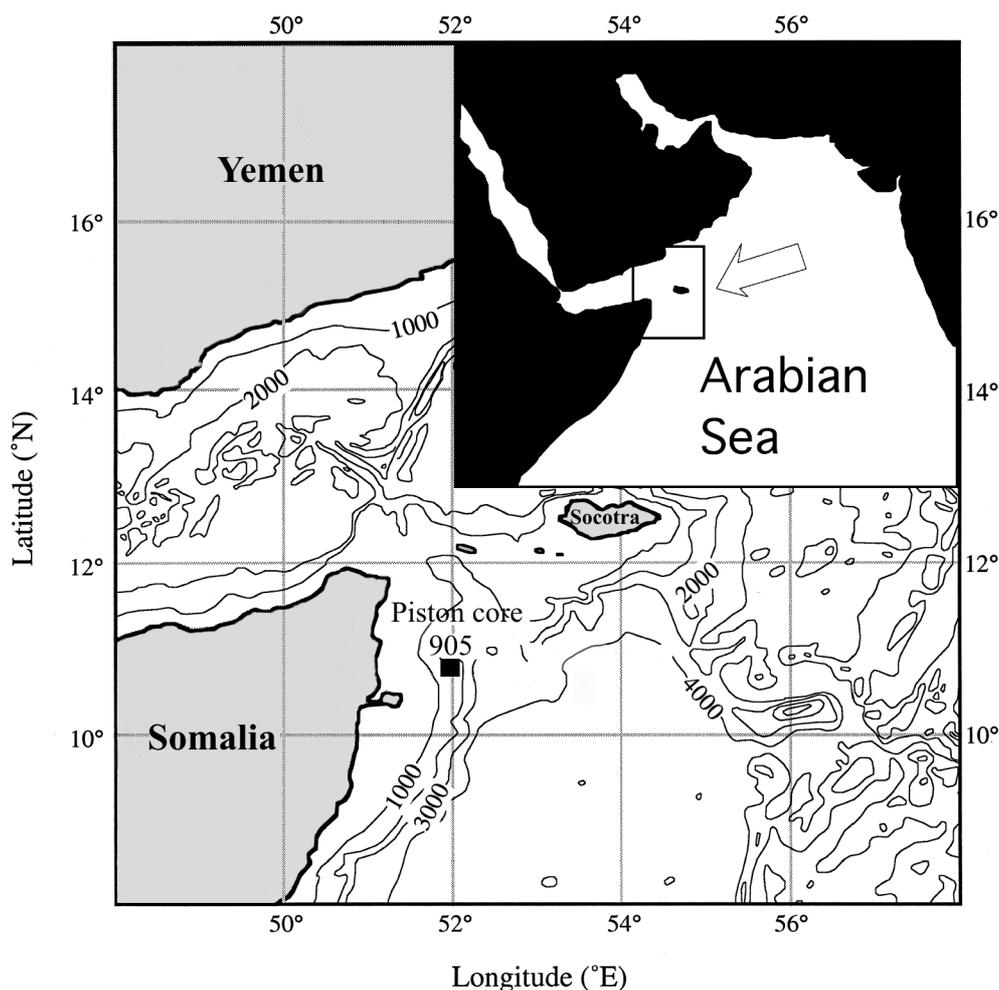


Fig. 1. Map showing the location of piston core 905 off Somalia.

3. Methods

The high-sedimentation rate piston core 905 (10°46.01N, 51°57.04E; Fig. 1) was retrieved from 1586 m water depth off Somalia (close to the present-day ACD, ~1600 m water depth; Ivanova, 2000) during the C2 cruise of RV Tyro in the framework of the Netherland Indian

Ocean Programme (NIOP). The age model is based on 31 AMS ^{14}C dates, high-resolution oxygen isotope stratigraphy (*N. dutertrei*; Fig. 2b) and 21 tie points with an oxygen isotope record from Hoti cave (Jung et al., 2002a) and 17 tie points to the $\delta^{18}\text{O}$ GISP ice core record (Ivanochko et al., 2005). The 15.26 m long core consists of bioturbated homogenous calcareous ooze (Troelstra et al., 1995) and comprises a complete record of the last 90 000 years.

3.1. XRD measurements + corrections Mineralogy

Qualitative measurements of the carbonate minerals present in the core 905 sediments were done by X-ray diffraction on a Philips PW1800 Automatic Powder Diffractometer at the University of Edinburgh. Powdered samples were compressed into uniformly made 3 mm deep containers and placed into the carousel. The peaks with the following D-spacing values have been used to identify the different carbonate minerals: calcite 303 pm, high Mg-calcite (Mg-calcite) 300 pm, aragonite 327 pm. Peak heights were corrected for the sensitivity of the machine using the following conversions: aragonite (5), low-Mg-calcite (calcite) (1.4) high Mg-calcite (Mg-calcite) (1.4). This analysis provides information on the proportion of aragonite and calcite in the sample. In order to get a more quantitative measurement of aragonite, calcite and Mg-calcite, these proportions were converted to weight % using total CaCO_3 (from coulometry, below).

3.2. TOC and CaCO_3

Weight % carbonate carbon (% Cinorg) for core 905 was determined on a Coulometrics 5012 coulometer at the University of Edinburgh (Ivanochko et al., 2005). Weighed sediment samples (~25 mg) were flushed for four minutes with CO_2 free air to remove atmospheric carbon dioxide contamination before dissolution in warm 10% HCl. The inorganic CO_2 released was converted to CaCO_3 using: % CaCO_3 = % Cinorg x 8.333.

Determination of Total Carbon: Approximately 15 mg of dried, homogenized sample were weighed into a tin cup for measurement by flash combustion gas chromatography on a Carlo Erba NA2500 Elemental Analyzer at the University of Edinburgh. For every carousel of fifty samples, five samples of acetanalide, with known % C and % N, and a weight range from

0.05 -2.00 mg were measured and two blanks were included and used as a zero standard for the carbon regressions. Generic marine sediment standard PACS-2 was used for carbon and nitrogen regressions. The concentration of organic carbon was calculated as the difference between total carbon and carbonate carbon.

3.3. Sr/Ca measurement

The concentrations of major (Ca) and minor (Sr) elements were determined on a Philips PW2404 wavelength dispersive automatic sequential X-ray Fluorescence Spectrometer fitted with a Rh-anode end window X-ray tube at the University of Edinburgh. International rock standards were used to calibrate the instrument and to monitor accuracy and precision during analysis.

Samples for major element analysis were pre-combusted overnight, combined with lithium borate flux and melted in platinum crucibles at 1100°C in a muffle furnace for 20 minutes. Upon cooling, additional flux was added to compensate for the weight lost from volatilized material. This mixture was re-melted in a flame and cast as a glass disc for XRF analysis. Samples for minor element analysis were prepared as pressed pellets using 1 g of powdered sediment. Salt titrations were done to determine the addition of sea salt Sr and Ca to each sample. All Sr and Ca values presented here are salt corrected. The error associated with the Sr measurements is 2.6 %.

3.4. Pteropod counts and shell preservation (LDX)

Aragonite preservation was studied by pteropod counts and by estimation of the preservation state of pteropod shells. After wetsieving the > 125 µm fraction was split into aliquots containing about 600 particles for quantitative light microscopic determination of percentages of pteropods (including heteropods) and determination of the *Limacina* Dissolution Index (LDX, according to Gerhardt and Henrich, 2001). The percentage of whole pteropods (wp) is calculated as:

whole pteropods (wp) = number of pteropods with less than 50 % damage of the test /all particles

The LDX distinguishes six preservation stages of the shells of the pteropod *Limacina inflata* ranging from 0 (best preservation, transparent shells), 1 (very good preservation, milky

shells), 2 (good preservation, opaque-white shells with lustrous shell surface), 3 (moderate preservation, opaque-white shells with partly lustreless shell surface), 4 (poor preservation, opaque-white shells with totally lustreless shell surface) to 5 (worst preservation, opaque-white shells with totally lustreless shell surface and additional shell damage; Gerhardt and Henrich, 2001). The LDX was calculated according to the equation:

$$\text{LDX} = \frac{\sum(n_p * p)}{\sum n_p}$$

where n_p is the number of investigated tests per preservation stage p (with $p = 0$ to 5) and $\sum n_p$ is at least 10 (tests of *L. inflata* > 300 μm). The whole pteropods percentage record has a resolution of ~ 290 years in the interval 88.5-6.6 ka, the LDX record covering the interval 64.8-9.4 ka has a slightly lower resolution (~ 340 years) due to insufficient numbers of *L. inflata* tests > $\sim 300 \mu\text{m}$ in some samples.

The LDX and the percentage of whole pteropods appear to be the most reliable aragonite dissolution proxies in this study. We did not include a pteropod fragmentation record (whole pteropods/(whole +fragments of pteropods)) because mechanical fragmentation due to bioturbation, strong bottom currents and during sample preparation seem to have a stronger influence on fragmentation than dissolution. The percentage of whole pteropods may also reflect fluctuations in the production rate of pteropods and foraminifers, which depend on changes in ecological conditions, e.g., glacial/interglacial boundary conditions and intensity of upwelling. In contrast the LDX is only based on shell properties and not influenced by productivity changes and should therefore reflect only preservation. Unfortunately even if pteropods are present in the sample there are gaps in the LDX record due to insufficient numbers of *L. inflata* tests.

4. Results

4.1. CaCO₃ and C_{org} concentrations

The bulk CaCO₃ content of core 905 is high ranging from 61.1 % to 84.7 % (Ivanochko et al., 2005; Fig. 2c). The Late Pleistocene is characterized by minor fluctuations (CaCO₃: 77-84.7%) with a pronounced minimum at 73.2 to 70 ka (71.6-76% carbonate).

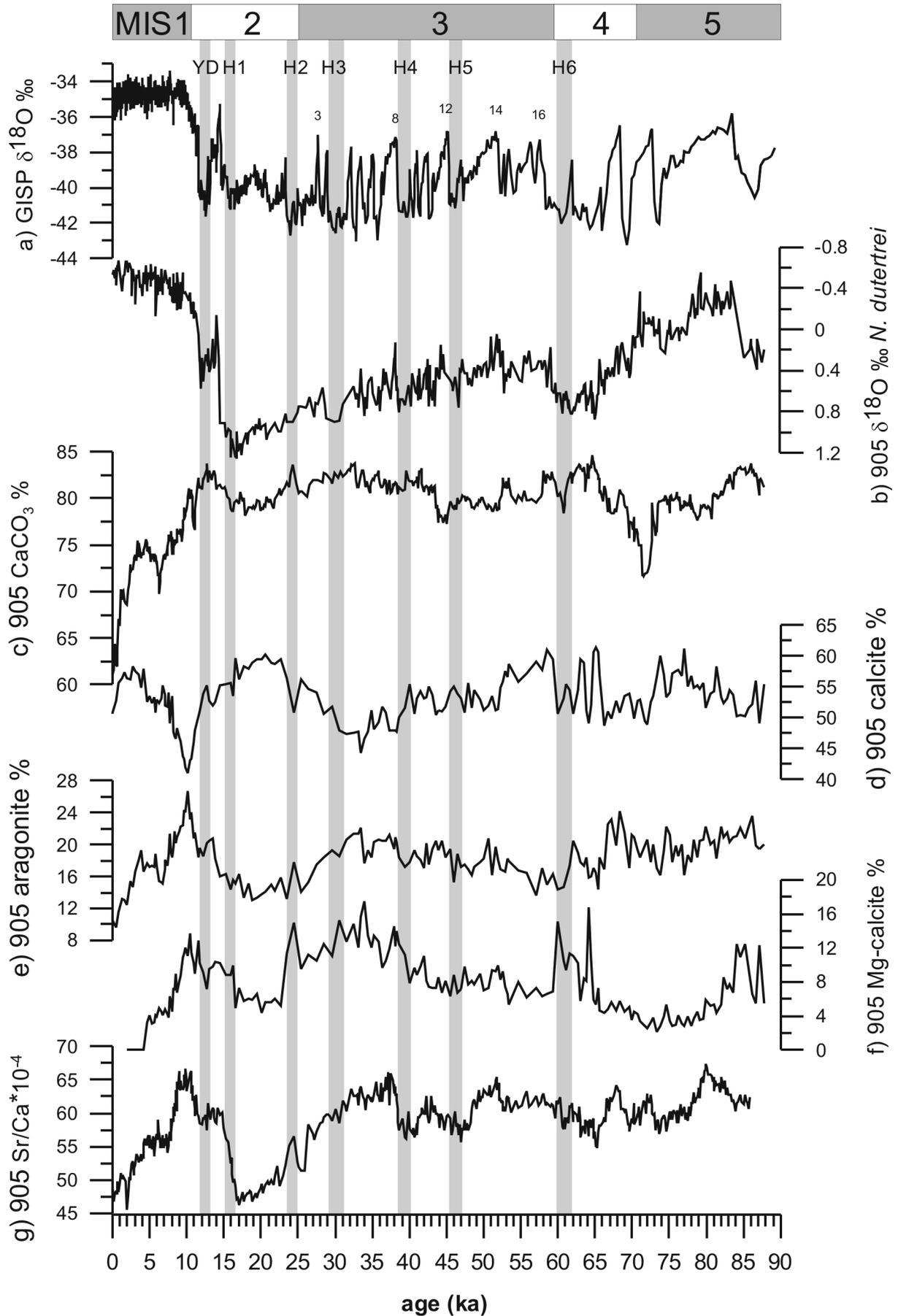


Fig. 2. Stratigraphy, bulk carbonate content, carbonate mineral concentrations and Sr/Ca ratio of core 905: a) $\delta^{18}\text{O}$ GISP2 Greenland ice core record (Grootes et al., 1993); b) $\delta^{18}\text{O}$ *N. dutertrei* record (Ivanochko et al., 2005); c) CaCO_3 % (Ivanochko et al., 2005); d) calcite %; e) aragonite %; f) Mg-calcite %; g) Sr/Ca ratio.

During the Holocene a distinct decrease from 80 % (Early Holocene) to 61.1 % (Late Holocene) is observed. The C_{org} content ranges from 1.0-2.7 % (Ivanochko et al., 2005; Fig. 3b), with minima occurring during glacials, stadials, and H-equivalents, maxima during interglacials and interstadials (described in detail in Ivanochko et al., 2005, Klöcker et al., subm.).

4.2. Calcite, aragonite and Mg-calcite concentrations

The calcite, aragonite and Mg-calcite contents range from 41 to 61.4 %, 9.7 to 26.7 % and 0 to 17.5 %, respectively (Fig. 2d, e, f). A maximum in the calcite concentration record of around 57 % occurs in late Marine Isotope Stage (MIS) 5 followed by a minimum during MIS 4 containing strong fluctuations (49–61 %). A steady decrease in calcite percentage from 61 to 44 % (58.6-33.5 ka) is observed during MIS 3. In MIS 2 another maximum of 58-60% in calcite content occurs from 22.7-16.7 ka (LGM) followed by a dramatic drop to 43% at the end of MIS 2. The Holocene is characterized by a strong increase in relative calcite percentage from a 41-44 % Early Holocene minimum at 10.7-9.4 ka to 52-54% at 8.1-4.6 ka and further rise to a Late Holocene (2.8-0.8 ka) maximum of 56-58%.

Strong fluctuations in the aragonite content are observed from MIS 3-5. While the late MIS 5 is characterized by higher values (~16-24 %), the aragonite content drops down immediately after 67 ka to relative low values in MIS 4 (~14-19 %) and continuously increases to higher values during MIS 3 (~16-21 %). Aragonite percentages are low in early MIS 2 (13-16 %, 25.4-14.5 ka) and moderate in late MIS 2 (18-24%, 14-10.4 ka). During the Holocene aragonite decreases from 26.7 % at 10.1 ka to 15-18 % (7.4-4.3 ka) to 10-13 % (2-0 ka).

The Mg-calcite record starts with high values around 85 ka (maximum from 87.3-84.1 ka, up to 12.5 %), drops to ~3-5% in Late MIS 5 and shows a long term increase to 10-18 % in late MIS 3 (interrupted by a maximum from 64.2-60 ka with more than 11 % Mg-calcite). The Mg-calcite content is relative low in early MIS 2 (5-7 %, 22.7-16.6 ka) and moderate in late MIS 2 (9-10 %, 16.2-11.8 ka). During the Holocene Mg-calcite contents decrease from 10-13 % (11.5-9.4 ka) to 3-5 % (8.1-4.6 ka) and finally to 0 % after 4.6 ka.

4.3. Sr/Ca ratio

The Sr/Ca ratio varies between $45.6 \cdot 10^{-4}$ and $67.3 \cdot 10^{-4}$ (Fig. 2g) and shows strong similarities to the aragonite percentage record (Fig. 2e). Large fluctuations between values of 55 and $67 \cdot 10^{-4}$ are observed during MIS 3-5. Maxima occur at 80.0, 72.5, 67.9, 51.8 and 42.3 ka, minima at 73.7, 69.7, 65.3, 47 and 39.6 ka. Sr/Ca values decrease dramatically from a maximum of $66 \cdot 10^{-4}$ at 37.2 ka (late MIS 3) to minimum values of $46-49 \cdot 10^{-4}$ at the LGM (including a minor minimum at ~ 26 ka with values of $51.4 \cdot 10^{-4}$). A rapid increase occurs from the LGM minimum to moderate values of $58-61 \cdot 10^{-4}$ during the YD and Bölling/Alleröd (14.8-11.4 ka) followed by a second sharp rise to the maximum at Termination 1b ($66.2 \cdot 10^{-4}$ at 10.6 ka).

The Holocene is characterized by a decrease from a Early Holocene maximum of $66 \cdot 10^{-4}$ (at 10.6-8.9 ka) to values around $54-57 \cdot 10^{-4}$ during the middle Holocene (7.8-4.3 ka) and finally to low values around $46-51 \cdot 10^{-4}$ (2.5-0 ka). Except for the Holocene, the Sr/Ca record also shows striking similarities to the $\delta^{18}\text{O}$ record of the planktic foraminifer *N. dutertrei*.

4.4. Pteropod shell preservation

The shell preservation record of the pteropod *L. inflata* (LDX) shows strong millennial-scale fluctuations in relation to D/O cycles and Heinrich event (H)-equivalents (Fig. 3d). Spikes with good to very good preservation (LDX values < 2) appear during H6- and H1-4-equivalents (**H6-equivalent**: 60.1-64.8 ka, LDX max. 1.28; **H4-equivalent**: 38.2-39.4 ka; LDX min. 1.50; **H3-equivalent**: 29.4-29.68, LDX min. 1.57; **H2-equivalent**: 24.28 ka, LDX 0.91 and **H1-equivalent**: 14.5-17.35 ka, LDX min. 1.27) and stadials (36 ka, LDX 1.93; 33.2 ka, LDX 1.98 and 31.87 ka, LDX 1.91) and in the YD (12.4-11.7 ka, LDX values min. 1.43). During H5-equivalent (46.3-45.8 ka) pteropods are not as well preserved (LDX > 2.66) as they are during other H-equivalent intervals. Pteropods from IS14/IS15 (53.2-52.1 ka) show only moderate preservation (LDX > 3.50). In the interstadials, Bölling/Alleröd and during the period from 11.7 to 9.4 ka (Preboreal, Termination and earliest Holocene) shell preservation is distinctly worse (LDX values > 2.5 to 4.6) than in the stadials and H-equivalents.

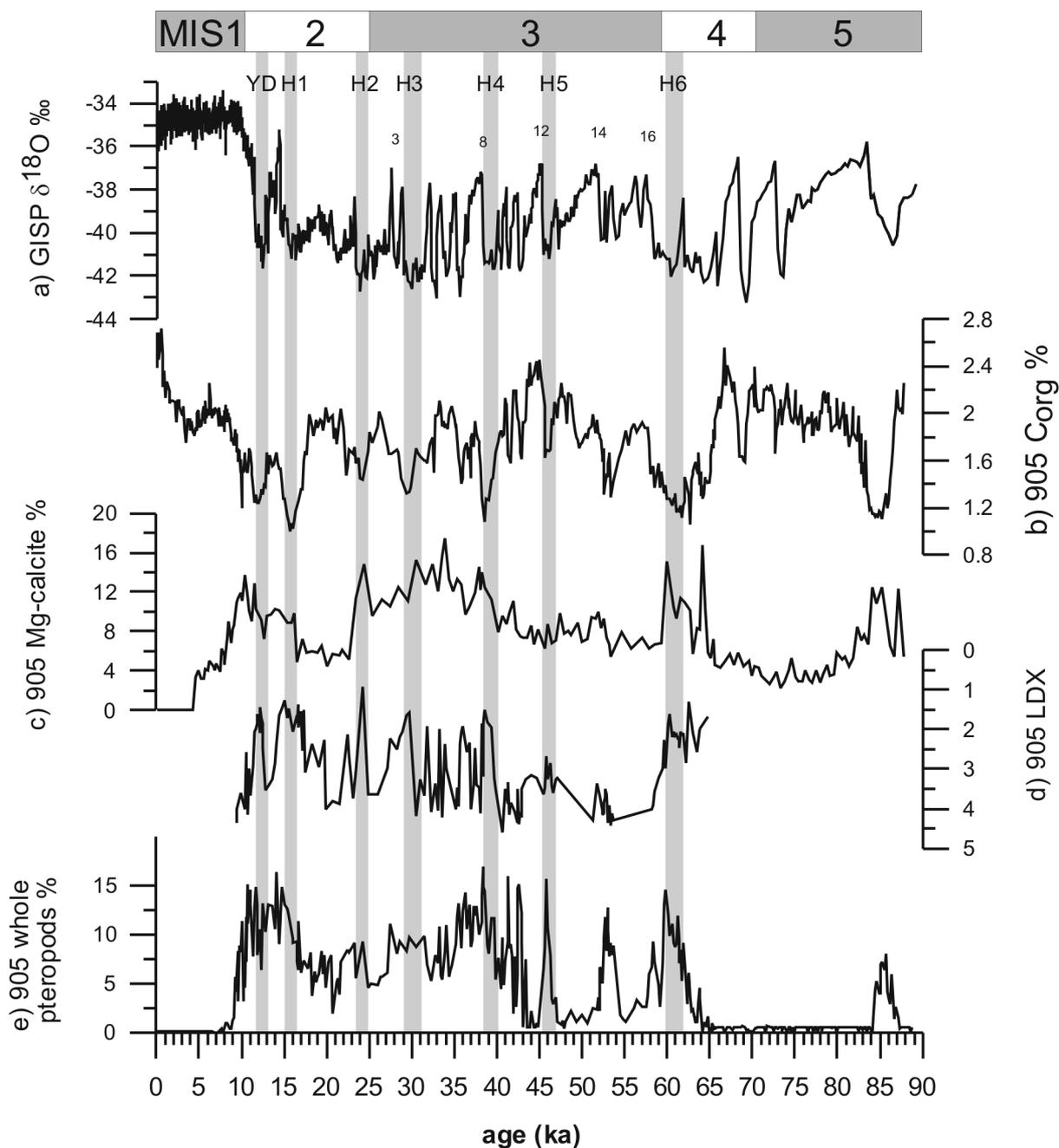


Fig. 3. Pteropod preservation proxies, C_{org} and Mg-calcite concentration of core 905: a) $\delta^{18}O$ GISP2 Greenland ice core record (Grootes et al., 1993); b) C_{org} % (Ivanochko et al., 2005); c) Mg-calcite %; d) *Limacina inflata* dissolution index (LDX, 0 = best preservation, transparent shells, 1 = very good preservation, milky shells, 2 = good preservation, opaque-white shells with lustrous shell surface, 3 = moderate preservation, opaque-white shells with partly lustreless shell surface, 4 = poor preservation, opaque-white shells with totally lustreless shell surface, 5 = worst preservation, opaque-white shells with totally lustreless shell surface and additional shell damage, Gerhardt and Henrich, 2001); e) whole pteropods %.

4.5. Whole pteropod abundance

Comparable to the LDX record strong fluctuations in relation to (inter-)stadials and H-equivalents occur in the late Pleistocene (Fig. 3e). From 87.2-64.8 ka only traces of pteropods occur (whole pteropods (wp) < 1%) including one broad spike at MIS 5.2 (wp: 0-8 %, average 4%, max. 8% at 85.8 ka). MIS 3 and MIS 2 (64.8-9.2 ka) contain the highest percentage of pteropods (64.8-43.4 ka, wp: 1-16%, average 5%, 43.4-9.2 ka, wp: 2-17%, average 9%). Maxima in whole pteropod abundance are observed at H6-equivalent (wp: 15%, 59.8 ka), stadials 14/15 (wp: 13%, 53.03 ka), H5-equivalent (wp: 16%, 45.76 ka), stadial 11 (wp: 15%, 42.5 ka), 10 (wp: 16%, 41.36 ka), H4-equivalent (wp: 17%, 38.35 ka) and also at the end of MIS 2 (17.7-9.8 ka, H1-equivalent to Early Holocene). The early Holocene (9.2-6.5 ka, wp: 1-2%, average 1%) contains only small amounts of pteropods, while pteropods are absent during the late Holocene (6.5-0 ka).

5. Discussion

For further discussion of variations in the carbonate system off Somalia during the Late Pleistocene and Holocene, we will interpret the mineralogical, geochemical and pteropod data in terms of variations in production/input of the different carbonate minerals and in terms of variations in dissolution/preservation of aragonite and Mg-calcite.

5.1. Variation in production/input of carbonate minerals (calcite, Mg-calcite, aragonite)

Variations in sedimentary aragonite concentrations can be interpreted as changes in a) relative productivity of pteropods in relation to bulk calcite productivity, b) the production and input of shallow marine aragonite (shelf/upper slope derived aragonite, e.g., predominantly aragonite needles or coral fragments) in relation to sea level fluctuations, or c) aragonite preservation (see next chapter).

An interpretation based on pteropods alone may be misleading due to the following observations: (1) fragments of corals are present in the coarse fraction of 905; (2) the Sr/Ca ratios are too high to be explained only by pteropods; (3) sediment trap data show a big resuspension event of shelf/upper slope material (shallow water aragonite, Mg-calcite) dominating the bulk flux at the 905 site (G.-J. Brummer pers. comm.); (4) pteropod flux rates

of the upper part of the core (Ivanova, 2000) increase during H-equivalents and decrease during interstadials, but the aragonite concentration record indicates a minimum rather than a maximum during H-equivalents. However, it should be mentioned that it is difficult to transfer numbers of pteropod fragments into mass, as the mass of the fragments increases exponentially with increasing size (Fabry, 1990). To conclude, we think that most of the aragonite in core 905 is not of pteropod but of shallow water origin.

Aragonite production on carbonate platforms increases during sea level highstands due to an increase in the production area ('highstand shedding theory'; Schlager et al., 1994). Export of this shallow marine aragonite to the continental slope by resuspension increases the amount of aragonite buried at 905 and raises also the Sr/Ca ratio due to the input of high-Sr aragonite. In contrast, production of shallow marine aragonite is reduced during lowstands (due to a decrease in production area) leading to lower aragonite concentrations and Sr/Ca ratios in 905.

As was to be expected the Sr/Ca record shows strong similarities to the aragonite record (Fig 2g and 2e, respectively). Small deviations are due to the fact that the bulk aragonite is a mixture of high-Sr shallow marine aragonite and low-Sr pteropod aragonite with a variable ratio of the two. If we assume that ~1500 ppm Sr (determined from surface sediment samples off Somalia by Müller 1966, 1967) is a representative value for the calcite fraction of our core and if this value is also more or less representative (and constant) for the Late Pleistocene, then the Sr content of the aragonite fraction must be ~3000-7000 ppm, if we neglect any Sr in the Mg-calcite and terrigenous fraction. Therefore, we think that a large part of the bulk aragonite fraction is made of high Sr-aragonite and pteropods contribute much less than expected for this pelagic sediments. High Sr/Ca ratios have previously been reported from the Pakistan margin and underline the importance of non-pteropod aragonite for (hemi-)pelagic sediments (see discussion in Reichert et al., 2004).

Comparison of aragonite % with the relative sea level curve (Siddall et al., 2003) shows that in general aragonite % is high during periods with relative sea level highstands (interglacials) and low during periods with lowstands (glacials). The strong increase in aragonite concentration at Termination I can be attributed to the rapid sea level rise during this time. During MIS 3 the aragonite record steadily increases together with an increase in whole pteropod abundance, while the relative sea level record shows an opposite trend, a decrease from early to late MIS 3. Hence, during MIS 3 aragonite percentage seems to be controlled by preservation rather than sea level. The comparably small sea level fluctuations during this

period did not cause a significant change of the shallow-marine aragonite production on the shelf. Therefore, the increase in aragonite concentration reflects the higher amount of preserved shallow-marine aragonite as indicated by the increase in pteropod preservation. We suggest that sea level fluctuations are important, but other factors, i.e., dissolution (see discussion below), variation in wind speeds, prolongation/shortening of the summer monsoon season, variation in deep water circulation, internal waves, and eddy activity, all contribute to changes in the resuspensional input to site 905. In addition, the susceptibility to sea level variations depends on the morphology of the shelf. Phase lags of the aragonite concentration relative to the sea level record could also be due to the readjustment time that the shallow-marine aragonite producers need after environmental changes.

The bulk carbonate record shows a Holocene minimum that is interpreted as dilution by non-carbonate material as the Holocene sedimentation rates are distinctly higher (28.5 cm/ka) than the late Pleistocene sedimentation rates (15.6 cm/ka). It might be possible that the strong decrease of the bulk carbonate concentration record in the Late Holocene at least partly reflects the aragonite and Mg-calcite dissolution (see discussion below).

5.2. Variation in preservation/dissolution of aragonite and Mg-calcite

The records of shell preservation, LDX, and whole pteropod abundance in the coarse fraction indicate good aragonite preservation during stadials and H-equivalents and poor preservation during interstadials which has been explained by variations in input and remineralization of organic matter (Klöcker et al., submitted). During interstadials, high C_{org} % and Ba/Al ratios indicate increased monsoon induced upwelling off Somalia and enhanced primary productivity (Ivanova, 2000; Jung et al., 2002b; Ivanochko et al., 2005). On longer time scales, the pteropod abundance corresponds to the ‘Indo-Pacific carbonate preservation type’ with poor preservation during interglacials and better preservation during glacials, which indicates that besides the regional monsoonal influence on deepwater chemistry, changes in deepwater circulation occurring on glacial/interglacial and stadial/interstadial time scales, might have affected pteropod preservation (for detail see discussion in Klöcker et al., submitted).

Mg-calcite is more soluble in seawater than aragonite and calcite and therefore the Mg-calcite% record has been used to monitor changes in the preservation state of carbonate sediments (Haddad and Droxler, 1996). Not surprisingly, the Mg-calcite record shows a

similar pattern compared to the pteropod preservation proxies with high values in the MIS 5.2 at H6-, H4-, H2-, H1-equivalent, and YD (Fig. 3c, d, e; Fig. 4).

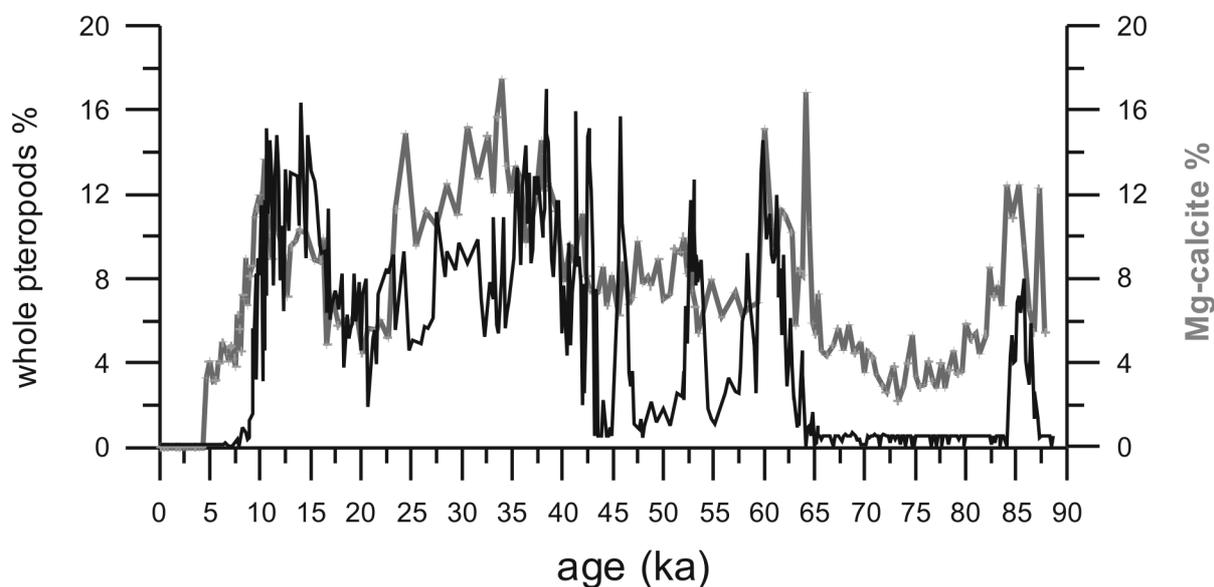


Fig. 4. Comparison of whole pteropod % and Mg-calcite % in core 905.

As pteropods are absent in the core 905 sediments during 82-65.5 ka (late MIS 5/early MIS 4) and in the Late Holocene, the corresponding low % Mg-calcite values are interpreted as a signal of strong Mg-calcite dissolution. It is possible that the Mg-calcite % record could also reflect variations in the production and input of Mg-calcite in comparison to aragonite and calcite. However, the ratio of Mg-calcite to Mg-calcite+ calcite (Fig. 5b) shows a similar pattern to the ratio of Mg-calcite to Mg-calcite+ aragonite (Fig. 5c), and to the Mg-calcite % record (Fig. 5d). Therefore, the use of Mg-calcite % as a proxy for carbonate dissolution is confirmed.

The similarities between the aragonite % and the sea level record (Fig. 5e and 5f) and the similarities between aragonite % and the pteropod record (Fig. 6) point to a combination of variation in input of aragonite (in relation to calcite) and dissolution of aragonite as the controlling factors of the aragonite % in 905.

The distinct increase in aragonite % from low values during MIS 2 to high values in the Early Holocene reflect the rise in sea level and therefore the increase in production area on the shelf. The long-term increase in aragonite % during MIS 3, accompanied by a long-term decrease in sea level and increase in pteropod % and Mg-calcite%, indicates preservation control.

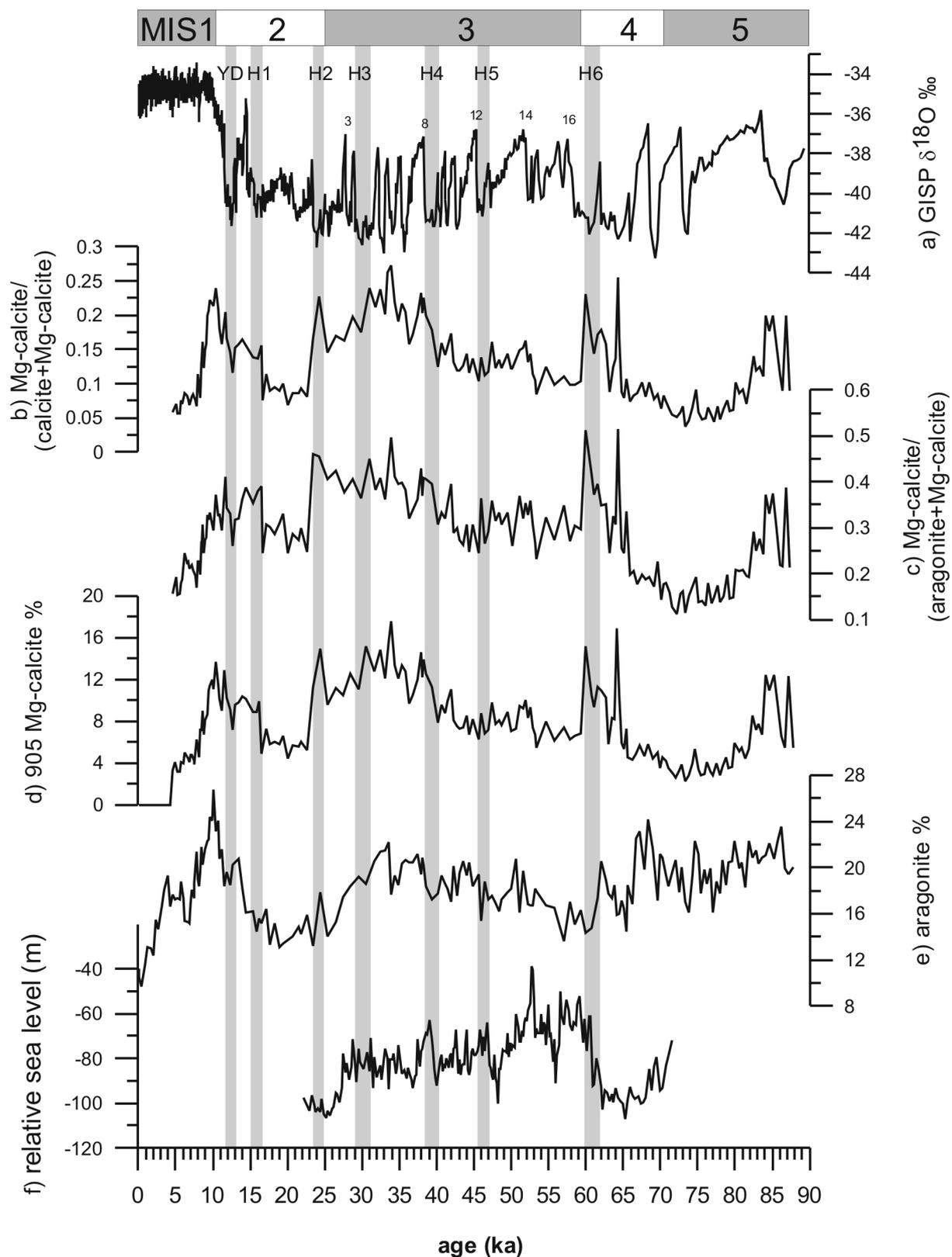


Fig. 5. Aragonite concentration in relation to relative sea level during MIS2 and 3 and comparison of different Mg-calcite ratios of core 905: a) $\delta^{18}\text{O}$ GISP2 Greenland ice core record (Grootes et al., 1993); b) Mg-calcite/(calcite+Mg-calcite); c) Mg-calcite/(aragonite+Mg-calcite); d) Mg-calcite %. e) aragonite %; f) relative sea level (after Siddall et al., 2003);

The sharp decrease in aragonite % from the early Holocene maximum to a Late Holocene minimum accompanied by a (relative) constant sea level again points to dissolution (Fig 6). Hence, we suggest that the aragonite % record of 905 can be convincingly generated by using a variable input ratio of aragonite+Mg-calcite to calcite (high during sea level highstands, low during lowstand) and variable preservation of the aragonite+Mg-calcite (indicated by the pteropod preservation, see Fig. 6).

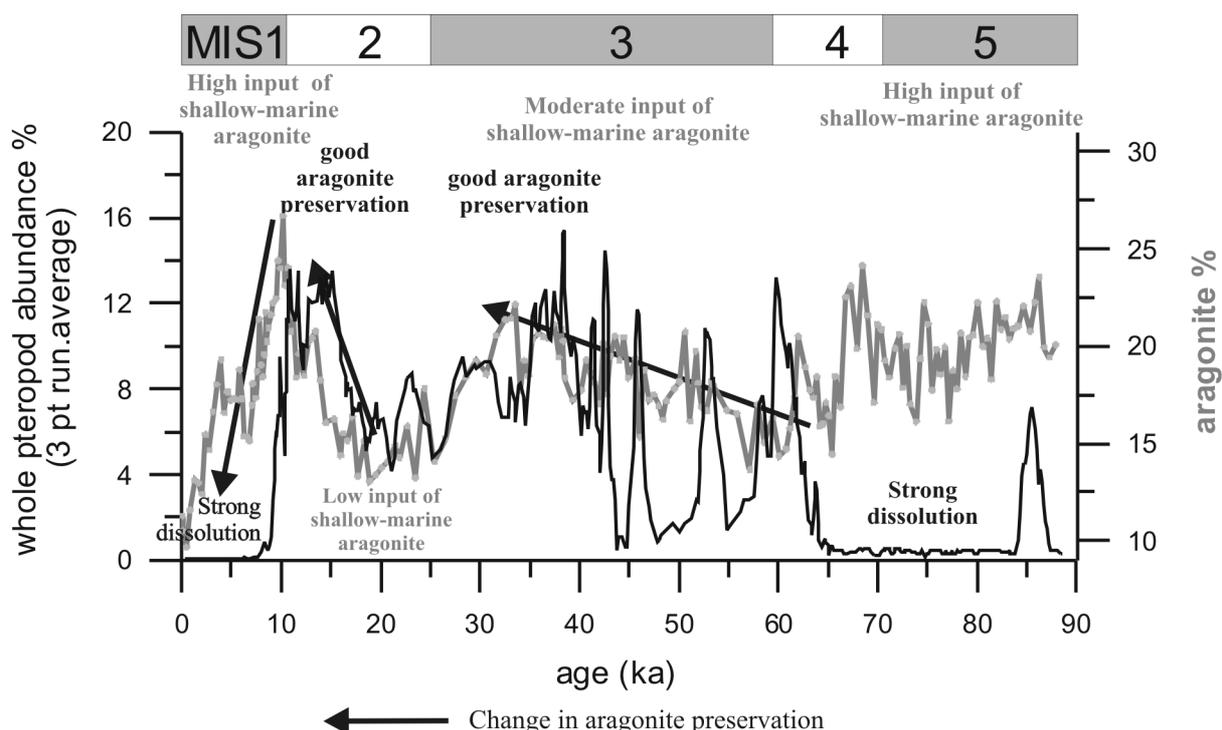


Fig. 6. Late Quaternary evolution of the aragonite system in core 905 off Somalia.

6. Summary and conclusions

This study confirms a multi-proxy approach using shell preservation of pteropods and pteropod counts in connection with Mg-calcite measurements to reconstruct past fluctuations in carbonate dissolution. The Mg-calcite record of core 905 shows strong similarities to the pteropod abundance record. The aragonite concentration record partly reflects dissolution but appears to be dominated by sea level controlled input of aragonite derived from shallow water sources. High Sr/Ca ratios together with fragments of corals found in the coarse fraction indicate that most of the aragonite of 905 is of shallow water origin (high Sr-aragonite) and

pteropods contribute much less than expected. The late Quaternary (last 90 ka) development of the carbonate system off Somalia is characterized by high resuspensional input of aragonite during sea level highstands (interglacials) and low input during lowstands (glacials). Absence or few pteropods as well as low Mg-calcite weight percentages during late MIS 5/early MIS 4 and in the Late Holocene point to strong dissolution of aragonite and Mg-calcite. Good aragonite preservation indicated by increased relative abundance of whole pteropods and shell preservation occurs during stadials, H-equivalents, YD and late MIS 3.

Acknowledgments

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Part III Summary and outlook

1. Results and conclusion

In order to improve our understanding of the Late Quaternary oceanic carbonate system, 15 surface sediment samples and two high-resolution sediment cores from the Arabian Sea have been investigated with special emphasis on the budget and preservation potential of aragonite. In this multi-proxy approach bulk carbonate and C_{org} content, percentages of carbonate minerals, i.e., aragonite, calcite, Mg-calcite, and element ratios (Sr/Ca) have been determined in combination with pteropod counts and an estimation of the preservation state of pteropod shells. Spatial and temporal changes in carbonate production and preservation were traced. The applicability of the pteropod shell preservation proxy *Limacina* Dissolution Index (LDX, Gerhardt and Henrich, 2001) has been successfully tested and applied on sediments from the Arabian Sea.

The results show that large fluctuations in pteropod preservation have occurred in the course of the Late Pleistocene and Holocene. A relation occurs to the high-frequent Dansgaard-Oeschger (D/O) cycles and Heinrich-events in the North Atlantic with good pteropod preservation in the sediments of the Arabian Sea during the time-equivalents of Heinrich events, stadials, Younger Dryas (YD), and poor pteropod preservation during the interstadials. On longer time scales, the results show that pteropod preservation during the Late Pleistocene was enhanced compared to the Holocene, in particular to the Late Holocene. Pteropod preservation therefore reflects the Indo-Pacific carbonate preservation pattern with increased preservation during glacials and decreased preservation during interglacials.

In sediment core 137KA off Pakistan the change in pteropod preservation is more dramatic than off Somalia. In the well-oxygenated bioturbated sediments preservation is good to very good, whereas in the suboxic, laminated sediments pteropods are very rare or even absent. In the surface sediment samples pteropods are bound to bioturbated sediments and the preservation is good to very good. No moderately to poorly preserved pteropods have been found neither in surface sediment samples nor in samples from the core 137KA off Pakistan.

The observed preservation pattern can be explained with enhanced intermediate water formation in phases of increased NE monsoon activity that lead to deeper convective winter mixing in the northern Arabian Sea. While today the deep winter mixing is restricted to water depths of roughly 150 m, which does not lead to a ventilation of the pronounced Oxygen

Minimum Zone (OMZ, 250-1200 m water depth), during the H-equivalents an increase in intermediate water formation to water depths > 600 m has been proposed by Reichert et al., (1998, 2002) and would explain the excellent preservation of the pteropods found in the bioturbated sediments. During the periods with weak intermediate water formation (analogue to the present-day situation) the pteropod preservation is restricted to the shelf and upper continental slope.

The corrosiveness of the waters within the OMZ can be explained by an enrichment in CO₂ (leading to a relative low pH) which is caused by the relative old age of the intermediate water mass in the northern Arabian Sea, the slow circulation, the addition of CO₂ while moving through the high-productivity areas off Somalia and Oman, and the landlocked position (water exchange possible only from the South).

In core 905 off Somalia the variation in pteropod preservation is more gradual with all in-between stages of the LDX ranging from good preservation during H-equivalents, stadials, YD to intermediate to poor preservation during interstadials.

A clear relation to the C_{org} content is found, i.e., in periods with increased SW monsoon induced upwelling the bioproductivity and subsequent remineralization of organic matter lead to a release of CO₂ to the subsurface waters and pore waters. Consequently, poor preservation of pteropods is observed, whereas in times of decreased bioproductivity (indicated by low C_{org} percentages) pteropod preservation improves.

In addition to the monsoonal influence on deepwater chemistry, pteropod preservation might have been affected by changes in deepwater circulation occurring on glacial/interglacial and stadial/interstadial time scales. Whether (1) deep water formation in the Arabian Sea, (2) inflow of Glacial North Atlantic Intermediate Water, or (3) change in water mass properties of the Circumpolar Deep Water (which is the water mass currently bathing this site) contributed to the observed pteropod preservation pattern is left as an open question.

Fragments of corals in the coarse fraction and high Sr/Ca ratios of the Somalia core show that the bulk aragonite record is dominated by high-Sr-aragonite (aragonite producing shallow marine organisms, algae and corals) and pteropods contribute much less than expected.

Similarities between the aragonite record and the sea level record point to a sea level control on the input of this shallow marine aragonite ('highstand shedding of carbonate platforms', Schlager et al., 1994), i.e., high input in times of sea level highstands due to increased production areas on the shelf. In general, fine shallow marine aragonite and Mg-calcite can be transported by downslope gravity flows or settling through the water column after being

suspended and transported offshore during high energy events. Since no gravity flow deposits have been observed in core 905, resuspension and offshore transport (due to storms during the SW monsoon period, internal waves or activity of the gyre ‘Great Whirl’) control the input of shallow water aragonite and Mg-calcite to the site 905.

But preservation has also a great influence on the bulk aragonite content, e.g., increased preservation in MIS3, a period characterized by falling sea level but increasing aragonite, Mg-calcite and pteropod concentrations. Strong dissolution occurs in the Late Holocene, a period characterized by high sea level but strong decrease in aragonite, Mg-calcite and pteropod concentration. Dissolution of Mg-calcite occurs in late MIS5/early MIS4 and during the Late Holocene, in contrast the preservation of Mg-calcite increases at the end of MIS4 and 2, during MIS3 a steady increase in Mg-calcite preservation is observed. Preservation spikes occur during the H-equivalents 6, 4, and 2.

This study confirms a multi-proxy approach using shell preservation of pteropods (LDX) and pteropod counts combined with Mg-calcite measurements to reconstruct past fluctuations in carbonate dissolution. However, the evaluation of the different carbonate dissolution proxies shows that application of each carbonate dissolution proxy may imply certain advantages and disadvantages. The LDX and the relative abundance record of whole pteropods appear to be the most reliable aragonite dissolution proxies. A pteropod fragmentation record (whole pteropods/(whole + fragments of pteropods)) was not included because mechanical fragmentation due to bioturbation, strong bottom currents, and sample preparation seem to have a stronger influence on fragmentation than dissolution. The percentage of whole pteropods may also reflect fluctuations in the production rate of pteropods and foraminifers, which depend on changes in ecological conditions, e.g., glacial/interglacial boundary conditions and the intensity of upwelling. Contrasting this, the LDX is only based on shell properties and not influenced by productivity changes and should therefore reflect preservation only. Unfortunately, even if pteropods are present in the sample there are gaps in the LDX record due to insufficient numbers of *L. inflata* tests.

Mg-calcite concentrations can be used as a carbonate dissolution proxy as shown by the correlation of the Mg-calcite record with the pteropod abundance and preservation records in core 905. However, the sea level controlled input of Mg-calcite in relation to aragonite and calcite has also a big influence on the Mg-calcite concentration. In addition, variations in pelagic calcite productivity (coccolithophorids and planktic foraminifers) dilute the relative Mg-calcite concentration record. To circumvent these effects, a ratio of Mg-calcite to Mg-

calcite+aragonite can be used as an additional carbonate dissolution proxy, that is independent of calcite dilution.

This study also confirms the importance of resuspensional input of shallow marine aragonite and Mg-calcite to hemipelagic sediments on the continental slopes. The study shows that millennial-scale variations related to D/O cycles and H-events in the North Atlantic effect pteropod preservation and (at least partly) Mg-calcite preservation in the Arabian Sea, which demonstrates the high variability of the oceanic carbonate system.

The close relationship between LDX and C_{org} in core 905 off Somalia indicates that in upwelling areas pteropod preservation strongly depends on the intensity of the bioproductivity and the subsequent remineralization of organic matter.

2. Outlook

Current paleoceanographic research on oxygen isotopes of planktic and benthic foraminifers and Mg/Ca temperature reconstruction from benthic foraminifers will add further information on the influence of changes in deep water circulation on pteropod preservation in the Arabian Sea. To quantify the pteropod content in absolute values by XRD analysis, sediment cores containing only aragonite of pteropod origin (and not of shallow marine origin) should be used, e.g., sediments from oceanic ridges.

Based upon the successful application of the LDX on sediments from the Atlantic Ocean and Caribbean Sea (Gerhardt et al., 2000; Gerhardt and Henrich, 2001) and Arabian Sea (this study), Late Quaternary sediments from the Indian (outside the Arabian Sea) and Pacific Ocean should be investigated in respect to aragonite preservation. However, due to the shallow aragonite saturation depths in these oceans (mostly < 500 to 1000 m water depth, Feely et al., 2004), only sediments from the (upper) continental margin and oceanic ridges seem to be promising. Focus should be directed to the glacial parts, since aragonite preservation increases (and saturation depths deepen) during glacial periods (Reichart et al., 1998, this study). There is also a lack of high-resolution Late Pleistocene pteropod preservation studies (outside the Arabian Sea). Millennial-scale variability in pteropod preservation should be confirmed on high sedimentation rate sediment cores. To expand the use of pteropod shell preservation to the cold-water regions, the applicability of the LDX on other species of the family Limacinidae should be tested, e.g., *Limacina helicina* (an arctic/antarctic species) and *L. retroversa* (a subarctic/subantarctic species). For those

sediments where fragmentation is low also the species from the family Cavoliniidae could be used for a pteropod dissolution proxy.

3. Data

All data presented in this study are archived in the PANGAEA database (<http://www.pangaea.de/>) or available from the corresponding authors by request.

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