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## Paleotemperatures

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### Definition

A paleotemperature is the temperature of a location, either on land or in the ocean, at a specific time in the geologic past. Scientists use paleothermometers to reconstruct past temperature records from archives – natural features of the Earth that preserve clues about past climate and environmental change. Examples of archives include marine and lacustrine sediment, glacial ice, and corals. Paleothermometers are often referred to as temperature proxies, which are measurable physical, geological, geochemical, or biological characteristics that get preserved in archives, standing in for instrumental measurements. Each proxy is associated with a calibration that transforms the proxy measurements into the parameter of interest, which in this case is temperature.

Scientists rely on proxy measurements from archives because direct observations of temperature extend back only as far as the middle of the nineteenth century (Smith et al. 2008). Direct temperature measurements of the ocean extend back even less. These limits to the length of instrumental records make it difficult to constrain the range of natural climate variability, the degree of twentieth century warming, and climate sensitivity to greenhouse gas forcing. Accurate paleotemperature reconstructions are the only way to extend the short observational period farther into the past.

This entry describes paleotemperature proxies from marine and terrestrial archives. The paleotemperature proxies presented here are by no means an exhaustive list, but instead highlight the geochemical proxies that are used most frequently for paleotemperature reconstructions.

### Assemblages of Planktonic Foraminifera

Foraminifera are marine protozoa (unicellular zooplankton) that can either be found free-floating in the open, upper layers of the ocean (planktonic), or living on or in seafloor sediment (benthic). They secrete characteristic tests, or shells, often composed of calcium carbonate (calcite, $CaCO_3$), that accumulate on the seafloor after death. There are ~50 living species of planktonic foraminifera in the modern oceans, and they are found in diverse oceanic regions from the warm tropics to cold polar waters (Kucera 2007). The greatest planktonic species diversity can be found in the tropics, with diversity generally decreasing with increasing latitude. Differences in the species composition, or assemblage, of planktonic foraminifera contain information about the temperature of the waters they inhabit (Murray 1897). Statistical techniques can be used to determine sea surface temperature (SST) from assemblages, including transfer functions (Imbrie and Kipp 1971) and the modern analog technique (Hutson 1980; Howard and Prell 1992). Studies comparing both methods find little difference between them (Ortiz and Mix 1997), but there are limitations to the overall approach. Both methods are based on the assumption that temperature is the main control on the assemblages; other factors, such as food availability, light requirements, and ocean circulation changes can also alter species distributions (Wefer et al. 1999). Finally, there is uncertainty in relating habitat (depth and seasonal) to SST at a certain time of the year.

### Mg/Ca Ratios

Mg/Ca ratios in benthic and planktonic foraminifera have become widely used proxies for reconstructing bottom and

upper water column paleotemperatures, respectively. The underlying basis for Mg/Ca paleothermometry is that the substitution of $Mg^{2+}$ for $Ca^{2+}$ in calcite is endothermic and therefore favored at higher temperatures. As a result, the Mg/Ca ratio of foraminiferal calcite increases with increasing temperature.

The temperature dependence on Mg uptake into planktonic foraminiferal tests has been determined using culture-based, sediment trap, and core-top calibrations. Culture-based calibrations rely on growing planktonic foraminifera under controlled laboratory conditions in which the temperature is fixed independently of other environmental parameters (e.g., Nürnberg et al. 1996; Lea et al. 1999; Russell et al. 2004; Allen et al. 2016). Sediment trap calibrations measure planktonic foraminifera collected in sediment trap time series from regions with high seasonal temperature variability (e.g., Anand et al. 2003). Core-top calibrations measure Mg/Ca ratios of modern or recently deposited planktonic foraminifera from the seafloor and then calibrate the ratios against the water column temperature overlying the sediment core site based on the foraminifera's preferred depth habitat (e.g., Lea et al. 2000; Dekens et al. 2002). Core-top calibrations are used most often to determine the relationship between Mg/Ca ratios in benthic foraminifera and bottom water temperature (Rosenthal et al. 1997; Lear et al. 2002; Bryan and Marchitto 2008).

Despite differences between calibration methods, studies show that most species of planktonic foraminifera have a temperature sensitivity of a ~9–10% exponential increase in Mg/Ca per degree Celsius (Lea et al. 1999; Elderfield and Ganssen 2000; Dekens et al. 2002; Anand et al. 2003). Culturing studies find that salinity also influences the uptake of Mg into planktonic foraminiferal tests, with Mg/Ca ratios increasing by 3–8% per salinity unit increase (Nürnberg et al. 1996; Lea et al. 1999; Hertzberg and Schmidt 2013; Hönisch et al. 2013; Allen et al. 2016). In contrast, the sensitivity of Mg/Ca to temperature in benthic foraminifera is more variable between species and may be influenced by other factors, including bottom water carbonate ion concentration (Lear et al. 2002; Elderfield et al. 2006; Bryan and Marchitto 2008). As benthic foraminifera dwell on the bottom of the ocean, where temperatures are lower than at the sea surface, their Mg/Ca ratios tend to fall on the lower end of the exponential relationship with temperature. Thus, the Mg/Ca paleothermometer for benthic foraminifera is less sensitive than for planktonic foraminifera, often making bottom water Mg/Ca-temperature estimates more difficult.

Postdepositional processes can alter Mg/Ca ratios in planktonic foraminifera because saturation with respect to calcite decreases in the ocean with increasing depth. Depth transect studies show that, in general, Mg/Ca ratios decrease with increasing water depth, especially below the regional lysocline (Brown and Elderfield 1996; Lea et al. 2000;

Dekens et al. 2002; Regenberg et al. 2014). Partial dissolution of foraminifera tests can bias Mg/Ca ratios due to the heterogeneous distribution of Mg within the test and the higher solubility of Mg-rich calcite (Brown and Elderfield 1996; Dekens et al. 2002). However, methods have been developed to account for this effect (Rosenthal and Lohmann 2002; Dekens et al. 2002; Regenberg et al. 2014).

Recent advances in Mg/Ca paleothermometry include the analysis of multiple planktonic species that live at a range of depths and the analysis of individual foraminiferal tests from the same stratigraphic interval. By analyzing species with a range of depth habitats, scientists can reconstruct past changes in the vertical temperature profile of the ocean (Schmidt et al. 2012; Parker et al. 2015). To gain insight into short-term variability at times in the past, scientists are now using individual planktonic foraminifera Mg/Ca analyses from a single depth horizon in a sediment core (Ford et al. 2015). This approach allows scientist to reconstruct past changes in overall temperature variability and has provided insight into past changes in seasonality and El Niño Southern Oscillation variability.

Mg/Ca ratios in ostracods can be also used to reconstruct bottom water temperatures (e.g., Cronin et al. 2000). Ostracods are benthic bivalved Crustacea that secrete calcite shells during molting. Similar to foraminifera, the amount of magnesium in the calcite shells is largely controlled by the water temperature in which the organism secreted the shell (Dwyer et al. 2002). A positive correlation between water temperature and Mg/Ca in ostracods has been observed, although postdepositional processes such as dissolution also impact Mg/Ca ratios (Cronin et al. 2000). The main difference between foraminifera and ostracod Mg/Ca paleothermometry is that the calibration between temperature and Mg/Ca in ostracods is linear, as opposed to exponential for foraminifera.

## Oxygen Isotopic Composition of Foraminifera

The oxygen isotopic composition of both planktonic and benthic foraminiferal calcite has been used for decades as a proxy for reconstructing past SSTs (Emiliani 1955). It is expressed as $\delta^{18}O_{Calcite}$ ($\delta^{18}O_C$), the deviation of the $^{18}O/^{16}O$ ratio relative to the VPDB standard in per mil (‰). Based on laboratory and natural experiments, a number of general and species-specific foraminiferal relationships between SST and $\delta^{18}O_C$ have been published (Epstein et al. 1953; Shackleton 1974; Erez and Luz 1983; Kim and O'Neil 1997; Bemis et al. 1998; Marchitto et al. 2014). In general, $\delta^{18}O_C$ decreases by ~0.21–0.23 ‰ for a 1 °C increase in temperature (Ravelo and Hillaire-Marcel 2007). However, foraminiferal $\delta^{18}O_C$ values are a function of both temperature and the oxygen isotopic composition of the seawater ($\delta^{18}O_{SW}$) in which they grow. Furthermore, $\delta^{18}O_{SW}$ varies

with changes in salinity, as evaporation and precipitation cause local $\delta^{18}O_{SW}$ to increase and decrease, respectively. On longer timescales, changes in continental ice volume cause $\delta^{18}O_{SW}$ to decrease globally with melting of ice and increase globally with ice sheet growth. Mixing of water masses with different $\delta^{18}O_{SW}$ values can also influence local $\delta^{18}O_{SW}$. Thus, only if $\delta^{18}O_{SW}$ is known (or at least constrained) can $\delta^{18}O_C$ provide unique paleotemperatures. Other limitations to the $\delta^{18}O_C$ temperature proxy are vital effects such as photosynthetic activity of algal symbionts (Duplessy et al. 1970; Bemis et al. 1998), changing depth habitats of planktonic foraminifera, and the carbonate ion concentration of seawater (Spero et al. 1997).

Because $\delta^{18}O_C$ is a function of both temperature and $\delta^{18}O_{SW}$, researchers developed a method using paired Mg/Ca temperatures and $\delta^{18}O_C$ measurements on foraminifera to reconstruct past $\delta^{18}O_{SW}$ variability. When applied to surface-dwelling planktonic foraminifera, this method has been shown to be a robust proxy for reconstructing sea surface salinity variability once changes in continental ice volume are taken into account (Schmidt et al. 2006; Schmidt and Lynch-Stieglitz 2011). Researchers have also used this method with benthic foraminifera to reconstruct bottom water $\delta^{18}O_{SW}$ change as a proxy for continental ice volume variability over the past 1.5 Ma (Elderfield et al. 2012). The most significant advantage of this approach to calculate $\delta^{18}O_{SW}$ variability is that Mg/Ca can be measured on the same shells that carry $\delta^{18}O_C$ information, so there is no ambiguity in timing between the signals.

## Clumped Isotopes in Carbonates

Recently, a considerable amount of interest has been invested in the development of a paleothermometer based on clumped stable isotope analyses of $CaCO_3$. Although the multiply substituted isotopologue ($^{13}C^{16}O^{18}O$) is rare and difficult to measure, the approach is based on the thermodynamic prediction that the abundance of multiple isotope substitutions in $CaCO_3$ increases as temperature decreases (Schauble et al. 2006; Passey et al. 2010). Therefore, unlike for temperature reconstructions based on $\delta^{18}O$ values, temperature reconstructions based on this method are not influenced by changes in the $^{18}O/^{16}O$ ratio of the water from which the mineral was precipitated. Initially, synthetically grown carbonates were used to identify the relationship between temperature and $\Delta_{47}$ values (Ghosh et al. 2006). Since then, calibration efforts have extended to shallow and deepwater corals, mollusks, and fish otoliths (Ghosh et al. 2006, 2007; Came et al. 2007; Thiagarajan et al. 2011). In addition, recent work has included the initial development of clumped isotopes in foraminifera and coccolithophores (Tripati et al. 2010, 2014). The resulting

relationship for both inorganic and organic calcite shows a sensitivity of ~0.004–0.005 ‰ per $^\circ$C.

Although clumped isotopes are becoming a more widely applied tool for geosciences, its application to the field of paleoceanography has been somewhat limited because of several factors. First, large sample sizes are required for a single analysis (in the range of 3–8 mg $CaCO_3$). Second, because the measurement of $\Delta_{47}$ is analytically challenging, it is necessary to replicate each measurement three to five times in order to reduce the standard error to less than $\pm 2\,^\circ$C. Third, only limited calibration data is available, especially for temperatures below 15 $^\circ$C.

The abundance of $^{13}C$–$^{18}O$ bonds in a $CaCO_3$ sample is measured on the $CO_2$ liberated from the sample in phosphoric acid using gas source mass spectrometry (Ghosh et al. 2006; Guo et al. 2009). This allows for both $\Delta_{47}$ and $\delta^{18}O$ analysis on the same sample, resulting in the determination of both calcification temperature and the $\delta^{18}O$ value of the water from which the mineral precipitated. Therefore, as analytical methods continue to improve, this technique has considerable potential for becoming an important paleothermometer for future paleoceangraphic studies.

## Biomarker Proxies: Alkenones and TEX$_{86}$

Although the Mg/Ca paleothermometer has advantages compared with the $\delta^{18}O_C$ proxy, it also has limitations including the influences of dissolution, calibrations based only on modern species, geographic limitations to regions inhabited by foraminifera, and temporal variability in seawater Mg/Ca ratios over millions of years. Biomarker-based SST proxies, such as the alkenone $U^{k'}_{37}$ (Brassell et al. 1986; Prahl and Wakeham 1987) and TEX$_{86}$ (Schouten et al. 2002) indices, can overcome some of these limitations due to the ubiquitous appearance of the associated biomarkers in marine sediments temporally and spatially, especially during times and in regions where foraminifera do not exist. Similar to foraminifera-based proxies, the carriers of biomarkers accumulate and get preserved on the seafloor and can be sampled and extracted from sediment cores.

Alkenones are long-chain organic compounds produced by marine haptophyte algae (phytoplankton) known as coccolithophores. Because algae require sunlight to perform photosynthesis, they reside at or near the sea surface, making them a useful tool for reconstructing SST. The $U^{k'}_{37}$ index is based on the proportions of di- and tri-unsaturated ketones within the alkenones and varies positively with growth temperature. A decrease in temperature leads to an increase in the degree of unsaturation. Prahl and Wakeham (1987) and Prahl et al. (1988) developed the first quantitative calibration of alkenone unsaturation to growth temperature based on coccolithophores grown in the laboratory at known

temperatures, and it appeared to reliably estimate SST based on samples collected from the ocean. Since then, large datasets of core-top $U^{k'}_{37}$ SST calibrations have been developed and show strong convergence with the original laboratory based calibration (Conte et al. 2006). Unfortunately, one of the main drawbacks to the $U^{k'}_{37}$ paleotemperature proxy is that it has an upper temperature limit of ~28 °C and a lower limit of ~1 °C (Herbert 2014). This precludes SST reconstructions based on the $U^{k'}_{37}$ index from the coldest and warmest regions of the ocean and from exceptionally warm periods in Earth's history.

Other ambiguities related to the alkenone paleotemperature proxy are depth and seasonal variations of alkenone-producing species in the ocean (Herbert 2014) and the potential for postdepositional transport of fine-grained alkenone carriers (Ohkouchi et al. 2002). Sunlight can penetrate to depths below the sea surface; thus, alkenones can be produced at a range of depths as long as light is sufficient for photosynthesis. Another drawback to this proxy is that phytoplankton production is seasonal in most ocean locations, so the $U^{k'}_{37}$ temperatures can be biased to the season of maximum production.

The $TEX_{86}$ paleothermometer is another biomarker-based proxy developed more recently and holds promise for overcoming the temperature limitations of the alkenone temperature proxy. The $TEX_{86}$ (TetraEther indeX of 86 carbons) index is based on the number of cyclopentane rings in membrane lipids, known as glycerol dialkyl glycerol tetraethers (GDGTs), which are produced by marine Thaumarchaeota (Schouten et al. 2002). The $TEX_{86}$ paleothermometer is based on observations from culturing and mesocosm experiments that the number of cyclopentane rings in GDGTs increases with increasing growth temperature (Wuchter et al. 2004). Schouten et al. (2002) noted a relationship between the number of rings in the GDGTS in marine surface samples and overlying SST and developed the first $TEX_{86}$ temperature calibration based on 40-sediment core-top samples from 15 locations. Subsequent calibrations involving the addition of hundreds of core-top samples all note the highest correlation between the $TEX_{86}$ index and SST (Kim et al. 2010). However, other studies have noted a bias in $TEX_{86}$ temperatures where they are representative of subsurface rather than sea surface temperatures (Hertzberg et al. 2016). Unlike coccolithophorids that live near the sea surface, archaea live throughout the water column, which may help explain the subsurface signal (Schouten et al. 2002). While the exact cause of the subsurface bias is still unknown, a new calibration to subsurface temperature has been developed (Tierney and Tingley 2015). Despite this uncertainty, the $TEX_{86}$ temperature proxy, which can reconstruct warmer temperatures than the alkenone SST proxy, has been used to reconstruct SSTs from the early Eocene when atmospheric $pCO_2$ levels may have reached ~2000 ppmv (Bijl et al. 2009).

The $TEX_{86}$ paleothermometer can also be applied to lacustrine sediments for reconstructions of terrestrial temperatures, as GDGT-producing Thaumarchaeota also exist in lakes (Powers et al. 2004). The mechanistic basis of the proxy is the same in these systems, although separate calibrations are necessary (Tierney et al. 2010). In addition, soil GDGTs and methanogenic archaea can potentially complicate $TEX_{86}$ in lakes, but these effects do not appear to be systematic (Tierney 2014). Nevertheless, the lacustrine $TEX_{86}$ paleothermometer has been applied to a number of lakes, in, for example, Africa (Tierney et al. 2008).

## Sr/Ca Ratios in Corals

Corals associated with reefs (as opposed to deep-sea corals) grow in regions of warm SST making them a useful archive for tropical SST reconstructions. These corals secrete aragonite in annual bands, so high-resolution paleotemperature reconstructions are possible. $Sr^{2+}$ substitution in corals has inverse temperature dependence due to the exothermic nature of the reaction in which $Sr^{2+}$ substitutes for $Ca^{2+}$ in aragonite. Typically, Sr/Ca ratios are first calibrated with modern instrumental SST records to establish a coral-specific Sr/Ca-temperature relationship, which is then applied to the older skeleton of the same coral, or to fossil corals for reconstructions past SST (e.g., Felis et al. 2009; Hereid et al. 2013).

Coral Sr/Ca ratios appear to also be strongly influenced by vital effects (Alpert et al. 2016). Growth rate and symbiotic activity have a marked influence on coral Sr/Ca, and culture studies have shown that coral Sr/Ca responds to changes in seawater pH and light. Researchers have also noted offsets in temperature sensitivity and mean Sr/Ca ratios in neighboring colonies collected from the same reef (Goodkin et al. 2005; Alpert et al. 2016). A potential explanation for these vital effects is that corals accrete their skeleton within an isolated calcifying fluid that is continuously depleted in Sr/Ca as aragonite precipitation proceeds (Cohen et al. 2006). Changes in the carbonate ion concentration of the calcifying fluid can drive variations in the amount of aragonite precipitation and cause variations in the magnitude of calcifying fluid Sr/Ca depletion. DeCarlo et al. (2016) developed a method to account for these vital effects by combining Sr/Ca with U/Ca ratios, which decrease as carbonate ion concentrations increase. This new method, termed coral Sr-U thermometry, has the potential to offer significantly improved reliability for reconstructing past ocean temperatures from corals.

## Terrestrial Temperature Proxies

Terrestrial temperature proxies provide information on Earth's surface air temperature. Geochemical proxies such

as oxygen ($\delta^{18}O$) and deuterium ($\delta D$) isotopic values of glacial ice, and nitrogen and argon isotopic ratios of air bubbles trapped in ice, can be used to estimate past atmospheric temperatures.

Ice cores are a valuable paleoclimate archive because of the large number of variables that can be derived from both the ice and the air that is trapped within the ice as it forms. In addition to temperature, ice cores are used for reconstructions of atmospheric $CO_2$ and $CH_4$ concentrations, dust, and concentrations of salts, to name a few. Ice cores can be drilled from the polar regions of Greenland and Antarctica and from high-altitude tropical and subtropical locations. Oxygen and deuterium isotopes measured in ice can be used as a temperature proxy because isotopic fractions of the heavier $^{18}O$ and $^2H$ in snowfall are temperature dependent, and there is a strong spatial correlation between mean annual temperature and the mean isotopic fraction of $^{18}O$ or $^2H$ in precipitation (Dansgaard et al. 1993; Grootes et al. 1993). Evaporation fractionation, which depends on surface conditions (e.g., SST, wind speed, relative humidity), controls the isotopic composition of atmospheric water vapor. Fractionation occurs as an air mass moves poleward, cooling and condensing, which leads to fractionation as the air mass progressively loses heavy isotopes from the water vapor. As a result of this process, known as Rayleigh distillation, the predominant control on the polar isotopic composition of water vapor is the temperature difference between the evaporative source and the final region of deposition (Masson-Delmotte, et al. 2006). Thus, past changes in evaporation conditions or atmospheric transport can induce biases in temperature reconstructions based on $\delta^{18}O$ or $\delta D$. A parameter known as deuterium excess (d = $\delta D$ – 8($\delta^{18}O$)) takes advantage of the combined measurements of $\delta^{18}O$ and $\delta D$ to correct past temperature reconstructions from changes in evaporation conditions (Cuffey and Vimeux 2001). Prominent ice core temperature records from Greenland include GRIP (Greenland Ice-core Project Members 1993; Dansgaard et al. 1993), GISP2 (Grootes et al. 1993), and NGRIP (North Greenland Ice Core Project members 2004) and from Antarctica include Vostok (Petit et al. 1999), EPICA Dome C (EPICA community members 2004), and WAIS Divide (WAIS Divide Project Members 2013). Note that this is not a complete list of all available ice core records.

Measurements of the $\delta^{15}N$ and $\delta^{40}Ar$ of air bubbles trapped in ice cores can be used for temperature reconstructions during periods of abrupt temperature change. When rapid temperature change occurs, a transient temperature gradient is established in the firn (the region of partially compacted snow) until a stable depth temperature gradient in the upper part of the ice is restored. Under a vertical temperature gradient, the gases in the firn undergo a thermal fractionation, with the heaviest species being concentrated at the coldest end (Masson-Delmotte et al. 2006). Analyses of

$\delta^{15}N$ and $\delta^{40}Ar$ in ice core air bubbles, which are constant in the atmosphere over long timescales, can be combined with firn modeling to provide estimates of past abrupt temperature changes (Severinghaus et al. 1998). This method has proven especially useful for reconstructing temperature changes from Greenland ice cores across abrupt climate change intervals such as Dansgaard-Oeschger events of the last glacial period and the millennial-scale events of the last deglaciation (Severinghaus and Brook 1999; Landais et al. 2004).

## Conclusions

Each paleotemperature proxy has a unique set of advantages and disadvantages. Depending on the location and time period of interest, scientists will use the proxies that best suit their needs. Often, reconstructing temperature using two or more proxies can help to make climate records more robust. If the paleotemperatures measured using multiple proxies disagree, it may indicate an environmental control on the proxy unrelated to temperature. Finally, robust and reliable age models are key to any paleotemperature reconstruction. Temperature proxies also continue to undergo refinement as new discoveries are made and better technologies and methods are made available for measurements. The geochemical paleotemperature proxies discussed in this entry are by no means an exhaustive list, and the reader is encouraged to consult the references for more details.

## Cross-References

▶ Carbonate Sediments
▶ Oxygen Isotopes
▶ Paleoclimatology
▶ Paleoenvironments
▶ Paleoproductivity
▶ Stable Isotope Geochemistry

## References

Allen KA, Hönisch B, Eggins M, Haynes LL, Rosenthal Y, Yu J (2016) Trace element proxies for surface ocean conditions: a synthesis of culture calibrations with planktonic foraminifera. Geochim Cosmochim Acta 193:197–221

Alpert AE, Cohen AL, Oppo D, DeCarlo TM, Gove J, Young C (2016) Comparison of equatorial Pacific sea surface temperature variability and trends with Sr/Ca records from multiple corals. Paleoceanography 31:252–265

Anand P, Elderfield H, Conte MH (2003) Calibration of Mg/Ca thermometry in planktonic foraminifera from a sediment trap time series. Paleoceanography 18:1050

Bemis BE, Spero HJ, Bijma J, Lea DW (1998) Reevaluation of the oxygen isotopic composition of planktonic foraminifera:

experimental results and revised paleotemperature equations. Paleoceanography 13:150–160

Bijl PK, Schouten S, Sluijs A, Reichart G, Zachos JC, Brinkhuis H (2009) Early Palaeogene temperature evolution of the southwest Pacific Ocean. Nature 461:776–779

Brassell SC, Eglinton G, Marlowe IT, Pflaumann U, Sarnthein M (1986) Molecular stratigraphy: a new tool for climatic assessment. Nature 320:129–133

Brown SJ, Elderfield H (1996) Variations in Mg/Ca and Sr/Ca ratios of planktonic foraminifera caused by postdepositional dissolution: evidence of shallow Mg-dependent dissolution. Paleoceanography 11:543–551

Bryan SP, Marchitto TM (2008) Mg/Ca–temperature proxy in benthic foraminifera: new calibrations from the Florida Straits and a hypothesis regarding Mg/Li. Paleoceanography 23:PA2220

Came R, Eiler J, Veizer J, Azmy K, Brand U, Weidman C (2007) Coupling of surface temperatures and atmospheric $CO_2$ concentrations during the Palaeozoic era. Nature 449:198–201

Cohen AL, Gaetani GA, Lundalv T, Corliss BH, George RY (2006) Compositional variability in a cold-water scleractinian, *Lophelia pertusa*: new insights into "vital effects". Geochem Geophys Geosyst 7:Q12004

Conte MH, Sicre M, Rühlemann C, Weber JC, Schulte S, Schulz-Bull D, Blanz T (2006) Global temperature calibration of the alkenone unsaturation index ($U^{K'}_{37}$) in surface waters and comparison with surface sediments. Geochem Geophys Geosyst 7:Q02005

Cronin TM, Dwyer GS, Baker PA, Rodriguez-Lazaro J, DeMartino DM (2000) Orbital and suborbital variability in deep North Atlantic bottom water temperature obtained from Mg/Ca ratios in the ostracode Krithe. Palaeogeogr Palaeoclimatol Palaeoecol 162:45–57

Cuffey KM, Vimeux F (2001) Covariation of carbon dioxide and temperature from the Vostok ice core after deuterium-excess correction. Nature 412:523–527

Dansgaard W, Johnsen SJ, Clausen HB, Dahl-Jensen D, Gundestrup NS, Hammer CU, Hvidberg CS, Steffensen JP, Sveinbjoornsdottie AE, Jouzel J, Bond G (1993) Evidence for general instability of past climate from a 250-kyr ice-core record. Nature 364:218–220

DeCarlo TM, Gaetani GA, Cohen AL, Foster GL, Alpert AE, Stewart JA (2016) Coral Sr-U thermometry. Paleoceanography 31:626–638

Dekens PS, Lea DW, Pak DK, Spero HJ (2002) Core top calibration of Mg/Ca in tropical foraminifera: refining paleotemperature estimation. Geochem Geophys Geosyst 3:1–29

Duplessy JC, Lalou C, Vinot AC (1970) Differential isotopic fractionation in benthic foraminifera and paleotemperatures reassessed. Science 168:250–251

Dwyer GS, Cronin TM, Baker PA (2002) Trace elements in ostracodes. In: Holmes JA, Chivas AR (eds) Applications of the Ostracoda to Quaternary research. American Geophysical Union, Washington, DC, pp 205–225

Elderfield H, Ganssen G (2000) Past temperature and $\delta^{18}O$ of surface ocean waters inferred from foraminiferal Mg/Ca ratios. Nature 405:442–445

Elderfield H, Yu J, Anand P, Kiefer T, Nyland B (2006) Calibrations for benthic foraminiferal Mg/Ca paleothermometry and the carbonate ion hypothesis. Earth Planet Sci Lett 250:633–649

Elderfield H, Ferretti P, Greaves M, Crowhurst S, McCave IN, Hodell D, Piotrowski AM (2012) Evolution of ocean temperature and ice volume through the Mid-Pleistocene climate transition. Science 337:704–709

Emiliani C (1955) Pleistocene temperatures. J Geol 63:538–578

EPICA community members (2004) Eight glacial cycles from an Antarctic ice core. Nature 429:623–628

Epstein S, Buchsbaum R, Lowenstam HA, Urey HC (1953) Revised carbonate-water isotopic temperature scale. Geol Soc Am Bull 64:1315–1325

Erez J, Luz B (1983) Experimental paleotemperature equation for planktonic foraminifera. Geochim Cosmochim Acta 47:1025–1031

Felis T, Suzuki A, Kuhnert H, Dima M, Lohmann G, Kawahata H (2009) Subtropical coral reveals abrupt early-twentieth-century freshening in the western North Pacific Ocean. Geology 37:527–530

Ford HL, Ravelo AC, Polissar PJ (2015) Reduced El Niño-Southern Oscillation during the Last Glacial Maximum. Science 347:255–258

Ghosh P, Adkins J, Affek H, Balta B, Guo W, Schauble E, Schrag D, Eiler J (2006) $^{13}C$-$^{18}O$ bonds in carbonate minerals: a new kind of paleothermometer. Geochim Cosmochim Acta 70:1439–1456

Ghosh P, Eiler J, Campana S, Feeney R (2007) Calibration of the carbonate 'clumped isotope' paleothermometer for otoliths. Geochim Cosmochim Acta 71:2736–2744

Goodkin NF, Hughen KA, Cohen AL, Smith SR (2005) Record of Little Ice Age sea surface temperatures at Bermuda using a growth-dependent calibration of coral Sr/Ca. Paleoceanography 20:PA4016

Greenland Ice-core Project (GRIP) Members (1993) Climate instability during the last interglacial period recorded in the GRIP ice core. Nature 364:203–207

Grootes PM, Stuiver M, White JWC, Johnsen S, Jouzel J (1993) Comparison of oxygen isotope records from the GISP2 and GRIP Greenland ice cores. Nature 366:552–554

Guo W, Mosenfelder JL, Goddard WA, Eiler J (2009) Isotope fractionations associated with phosphoric acid digestion of carbonate minerals: insights from first principles theoretical modeling and clumped isotope measurements. Geochim Cosmochim Acta 73:7203–7225

Herbert TD (2014) 8.15: alkenone paleotemperature determinations. In: Holland HD, Turekian KK (eds) Treatise on geochemistry, 2nd edn. Elsevier, Oxford, pp 399–433

Hereid KA, Quinn TM, Taylor FW, Shen CC, Edwards RL, Cheng H (2013) Coral record of reduced El Nino activity in the early 15th to middle 17th centuries. Geology 41:51–54

Hertzberg JE, Schmidt MW, Bianchi TS, Smith RW, Shields MR, Marcantonio F (2016) Comparison of eastern tropical Pacific $TEX_{86}$ and *Globigerinoides ruber* Mg/Ca derived sea surface temperatures: insights from the Holocene and Last Glacial Maximum. Earth Planet Sci Lett 434:320–332

Hertzberg JE, Schmidt MW (2013) Refining *Globigerinoides ruber* Mg/Ca paleothermometry in the Atlantic Ocean. Earth Planet Sci Lett 383:123–133

Hönisch B, Allen KA, Lea DW, Spero HJ, Eggins SM, Arbuszewski J, deMenocal P, Rosenthal Y, Russell AD, Elderfield H (2013) The influence of salinity on Mg/Ca in planktic foraminifers – evidence from cultures, core-top sediments and complimentary $\delta^{18}O$. Geochim Cosmochim Acta 121:196–213

Howard WR, Prell WL (1992) Late quaternary surface circulation of the southern Indian Ocean and its relationship to orbital variations. Paleoceanography 7:79–117

Hutson WH (1980) The Agulhas current during the late Pleistocene: analysis of modern faunal analogs. Science 207:64–66

Imbrie J, Kipp NG (1971) A new micropaleontological method for quantitative paleoclimatology: application to a late Pleistocene Caribbean core. In: Turekian KK (ed) The Late Cenozoic glacial ages. Yale University Press, Connecticut, pp 71–181

Kim JH, van der Meer J, Schouten S, Helmke P, Willmott V, Sangiorgi F, Koc N, Hopmans E, Sinninghe Damsté JS (2010) New indices and calibrations derived from the distribution of crenarchaeal isoprenoid tetraether lipids: implications for past sea surface temperature reconstructions. Geochim Cosmochim Acta 74:4639–4654

Kim ST, O'Neil JR (1997) Equilibrium and nonequilibrium oxygen isotope effects in synthetic carbonates. Geochim Cosmochim Acta 61:3461–3475

Kucera M (2007) Planktonic foraminifera as tracers of past oceanic environments, Chapter 6. In: Hillaire-Marcel C, de Vernal A (eds) Developments in marine geology. Elsevier, Oxford, pp 213–262

Landais A, Caillon N, Grachev A, Barnola JM, Chapellaz J, Jouzel J, Masson-Delmotte V, Leuenberger M (2004) Quantification of rapid temperature change during DO event 12 and phasing with methane inferred from air isotopic measurements. Earth Planet Sci Lett 225:221–232

Lea DW, Mashiotta TA, Spero HJ (1999) Controls on magnesium and strontium uptake in planktonic foraminifera determined by live culturing. Geochim Cosmochim Acta 63:2369–2379

Lea DW, Pak DK, Spero HJ (2000) Climate impact of Late Quaternary Equatorial Pacific sea surface temperature variations. Science 289:1719–1724

Lear CH, Rosenthal Y, Slowey N (2002) Benthic foraminiferal Mg/Ca-paleothermometry: a revised core-top calibration. Geochim Cosmochim Acta 66:3375–3387

Marchitto TM, Curry WB, Lynch-Stieglitz J, Bryan SP, Cobb KM, Lund DC (2014) Improved oxygen isotope temperature calibrations for cosmopolitan benthic foraminifera. Geochim Cosmochim Acta 130:1–11

Masson-Delmotte V, Dreyfus G, Braconnot P, Johnsen S, Jouzel J, Kageyama M, Landais A, Loutre M-F, Nouet J, Parrenin F, Raynaud D, Stenni B, Tuenter E (2006) Past temperature reconstructions from deep ice cores: relevance for future climate change. Clim Past 2:145–165

Murray J (1897) On the distribution of the pelagic foraminifera at the surface and on the floor of the ocean. Nat Sci (Ecology) 11:17–27

North Greenland Ice Core Project members (2004) High-resolution record of Northern Hemisphere climate extending into the last interglacial period. Nature 431:147–151

Nürnberg D, Bijma J, Hemleben C (1996) Assessing the reliability of magnesium in foraminiferal calcite as a proxy for water mass temperatures. Geochim Cosmochim Acta 60:803–814

Ohkouchi N, Eglinton TI, Keigwin LD, Hayes JM (2002) Spatial and temporal offsets between proxy records in a sediment drift. Science 298:1224–1227

Ortiz JD, Mix AC (1997) Comparison of Imbrie-Kipp transfer function and modern analog temperature estimates using sediment trap and core top foraminiferal faunas. Paleoceanography 5:43–54

Parker AO, Schmidt MW, Chang P (2015) Tropical North Atlantic subsurface warming events as a fingerprint for AMOC variability during Marine Isotope Stage 3. Paleoceanography 30:1425–1436

Passey BH, Levin NE, Cerling TE, Brown FH, Eiler JM (2010) High-temperature environments of human evolution in East Africa based on bond ordering in paleosol carbonates. Proc Natl Acad Sci 107:11245–11249

Petit JR, Jouzel J, Raynaud D, Barkov NI, Barnola J-M, Basile I, Bender M, Chappellaz J, David M, Delaygue G, Delmotte M, Kotlyakov VM, Legrand M, Lipenkov VY, Lorius C, Pepin L, Ritz C, Saltzman E, Stievenard M (1999) Climate and atmospheric history of the past 420,000 years from the Vostok ice core, Antarctica. Nature 399:429–436

Powers LA, Werne JP, Johnson TC, Hopmans EC, Sinninghe Damste JS, Schouten S (2004) Crenarchaeotal membrane lipids in lake sediments: a new paleotemperature proxy for continental paleoclimate reconstruction? Geology 32:613–616

Prahl FG, Muehlhausen LA, Zahnle DL (1988) Further evaluation of long-chain alkenones as indicators of paleoceanographic conditions. Geochim Cosmochim Acta 52:2303–2310

Prahl FG, Wakeham SG (1987) Calibration of unsaturation patterns in long-chain ketone compositions for paleotemperature assessment. Nature 330:367–369

Ravelo AC, Hillaire-Marcel C (2007) The use of oxygen and carbon isotopes of foraminifera in paleoceanography, Chapter 18. In: Hillaire-Marcel C, de Vernal A (eds) Developments in marine geology. Elsevier, Oxford, pp 735–764

Regenberg M, Regenberg A, Garbe-Schönberg D, Lea DW (2014) Global dissolution effects on planktonic foraminiferal Mg/Ca ratios controlled by the calcite-saturation state of bottom waters. Paleoceanography 29:127–142

Rosenthal Y, Boyle EA, Slowey N (1997) Temperature control on the incorporation of magnesium, strontium, fluorine, and cadmium into benthic foraminiferal shells from Little Bahama Bank: prospects for thermocline paleoceanography. Geochim Cosmochim Acta 61:3633–3643

Rosenthal Y, Lohmann GP (2002) Accurate estimation of sea-surface temperatures using dissolution corrected calibrations for Mg/Ca paleothermometry. Paleoceanography 17:1044

Russell AD, Hönisch B, Spero HJ, Lea DW (2004) Effects of seawater carbonate ion concentration and temperature on shell U, Mg, and Sr in cultured planktonic foraminifera. Geochim Cosmochim Acta 68:4347–4361

Schauble E, Ghosh P, Eiler J (2006) Preferential formation of $^{13}C$-$^{18}O$ bonds in carbonate minerals, estimated using first-principles lattice dynamics. Geochim Cosmochim Acta 70:1439–1456

Schmidt MW, Vautravers MJ, Spero HJ (2006) Rapid subtropical North Atlantic salinity oscillations across Dansgaard-Oeschger cycles. Nature 443:561–564

Schmidt MW, Lynch-Stieglitz J (2011) Florida Straits deglacial temperature and salinity change: implications for tropical hydrologic cycle variability during the Younger Dryas. Paleoceanography 26:PA4205

Schmidt MW, Chang P, Hertzberg JE, Them TR, Ji L, Otto-Bliesner BL (2012) Impact of abrupt deglacial climate change on tropical Atlantic subsurface temperatures. Proc Natl Acad Sci 109:14348–14352

Schouten S, Hopmans EC, Schefuß E, Sinninghe Damsté JS (2002) Distributional variations in marine crenarchaeotal membrane lipids: a new tool for reconstructing ancient sea water temperatures? Earth Planet Sci Lett 204:265–274

Severinghaus JP, Sowers T, Brook EJ, Alley RB, Bender ML (1998) Timing of abrupt climate change at the end of the Younger Dryas interval from thermally fractionated gases in polar ice. Nature 391:141–146

Severinghaus JP, Brook E (1999) Simultaneous tropical-Arctic abrupt climate change at the end of the last glacial period inferred from trapped air in polar ice. Science 286:930–934

Shackleton NJ (1974) Attainment of isotopic equilibrium between ocean water and the benthonic foraminifera genus *Uvigerina*: isotopic changes in the ocean during the last glacial. In: Labeyrie J (ed) Les méthodes quantitatives d'étude des variations du climat au cours du Pléistocene. Colloques Int. duc. N. R. S, Paris, pp 203–209

Smith TM, Reynolds RW, Peterson TC, Lawrimore J (2008) Improvements to NOAA's historical merged land-ocean surface temperature analysis. J Climate 21:2283–2296

Spero HJ, Bijma J, Lea DW, Bemis BE (1997) Effect of seawater carbonate concentration on foraminiferal carbon and oxygen isotopes. Nature 390:497–500

Thiagarajan N, Adkins J, Eiler J (2011) Carbonate clumped isotope thermometry of deep-sea corals and implications for vital effects. Geochim Cosmochim Acta 75:4416–4425

Tierney JE, Russell JM, Huang Y, Sinninghe Damste JS, Hopmans EC, Cohen AC (2008) Northern Hemisphere controls on tropical southeast African climate during the past 60,000 years. Science 322:252–255

Tierney JE, Russell JM, Eggermont H, Hopmans EC, Verschuren D, Sinninghe Damste JS (2010) Environmental controls on branched tetraether lipid distributions in tropical East African lake sediments. Geochim Cosmochim Acta 74:4902–4918

Tierney JE (2014) Biomarker-based inferences of past climate: the $TEX_{86}$ paleotemperature proxy. In: Turekian KK, Holland HD (eds) Treatise on geochemistry, Organic geochemistry, vol 12, 2nd edn. Elsevier, Oxford, pp 379–393

Tierney JE, Tingley MP (2015) A $TEX_{86}$ surface sediment database and extended Bayesian calibration. Sci Data 2:150029

Tripati A, Eagle R, Thiagarajan N, Gagnon A, Bauch H, Halloran P, Eiler J (2010) $^{13}$C-$^{18}$O isotope signatures and 'clumped isotope' thermometry in foraminifera and coccoliths. Geochim Cosmochim Acta 74:5697–5717

Tripati A, Sahany S, Pittman D, Eagle RA, Neelin JD, Mitchell JL, Beaufort L (2014) Modern and glacial tropical snowlines controlled by sea surface temperature and atmospheric mixing. Nat Geosci 7:205–209

WAIS Divide Project Members (2013) Onset of deglacial warming in West Antarctica driven by local orbital forcing. Nature 500:440–444

Wefer G, Berger WH, Bijma J, Fischer G (1999) Clues to ocean history: a brief overview of proxies. In: Fischer G, Wefer G (eds) Use of proxies in paleoceanography: examples from the South Atlantic. Springer, Berlin, pp 1–68

Wuchter C, Shouten S, Coolen MJL, Sinninghe Damsté JS (2004) Temperature-dependent variation in the distribution of tetraether membrane lipids of marine Crenarchaeota: implications for TEX$_{86}$ paleothermometry. Paleoceanography 19:PA4028