Nutrient Proxies

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Introduction

The distribution of marine nutrients in the past is of interest to paleoceanographers for two main reasons. First, nutrients control oceanic primary productivity, which is believed to be an important control on atmospheric CO2 on glacial-interglacial timescales. Second, nutrients are useful tracers of deep-water masses, and changes in the modes and locations of deep-water formation are believed to have fundamentally influenced Quaternary climates. Reconstruction of paleonutrients relies mainly on five proxies that are recorded in marine sediments: foraminiferal δ13C, Cd/Ca, Ba/Ca, and Zn/Ca; and organic matter δ15N.

Carbon-13

Systematics

Dissolved inorganic carbon (DIC), also known as ΣCO2, is composed of three dominant species in seawater: dissolved carbon dioxide (CO2(aq)), bicarbonate (HCO3−), and carbonate (CO32−), having relative concentrations on the order of 1%, 90%, and 10%, respectively. Furthermore, carbon has two stable isotopes: 12C (98.9%) and 13C (1.1%). Fractionation between these two isotopes is expressed in delta notation:

$$\delta^{13}C = \left(\frac{^{13}C/^{12}C}_{\text{sample}} / ^{13}C/^{12}C_{\text{standard}} - 1\right) \times 1000 \ [1]$$

where the standard is a calcium carbonate, usually referenced to the Pee Dee Belemnite standard. On this scale, the δ13C of DIC ranges between about −1‰ and 2.5‰ in the world’s oceans (Kroopnick, 1985). Photosynthetic fixation of carbon preferentially utilizes 12C such that primary marine organic matter δ13C is typically between −20‰ and −30‰. This leaves the remaining surface ocean DIC pool slightly enriched in δ13C. As organic matter sinks through the water column and decays, its 12C-rich carbon is regenerated along with other nutrients such as phosphate and nitrate, resulting in a water column δ13C profile that is inversely correlated with these nutrients (Figure 1). If biogeochemical cycling were the only process acting on the DIC pool, δ13C would decrease by about 1.1‰ for each 1 μmol kg−1 increase in dissolved phosphate, and an oceanic range of about 3.3‰ would be possible (Lynch-Stieglitz et al., 1995). Regional differences in the δ13C of marine organic matter may alter the slope of this relationship.

In addition to biogeochemical cycling, the δ13C of surface ocean DIC is significantly affected by air-sea exchange of CO2. If DIC were at isotopic equilibrium with atmospheric CO2, it would be enriched by about 8% relative to the atmosphere at 20 °C. This value results from the dominance of HCO3−, which is enriched by 8.5‰ relative to the atmosphere, with smaller contributions from CO32− (6‰) and CO2(aq) (−1‰) (Lynch-Stieglitz et al., 1993). The enrichment for HCO3− (and therefore DIC) increases by about 0.1‰ per degree of cooling. However, isotopic equilibration between the surface ocean mixed layer and the atmosphere is never reached because the time required (on the order of a decade) is longer than surface ocean mixing times. The extent of equilibration may be increased through longer air-sea contact time or high winds, which would increase DIC δ13C. A final air-sea effect occurs in areas where there is net movement of CO2 into or out of the surface ocean. Both CO2(aq) and atmospheric CO2 are isotopically light compared to DIC. Regions that absorb CO2 from the atmosphere, such as the low-pCO2 North Atlantic, therefore experience δ13C depletion. Areas that emit CO2 to the atmosphere, such as the high-pCO2 eastern equatorial Pacific, experience δ13C enrichment. The net effect of the various air-sea exchange processes spans a surface ocean range of about 2‰ (Lynch-Stieglitz et al., 1995). In addition, the anthropogenic evolution of atmospheric CO2 toward lower δ13C values, known as the Suess effect, results in a progressive lowering of surface water δ13C that has already propagated into the deep North Atlantic (Olsen and Ninnemann, 2010).

Paleoceanographic Reconstruction

Reconstruction of past ocean δ13C relies mainly on the calcitic (CaCO3) tests of protozoa called Foraminifera. Foraminiferal calcite carbon is presumed to be derived from dissolved HCO3−, and may therefore be expected to record the δ13C of DIC, in the absence of complicating biological effects. Core-top calibrations show that various taxa of benthic Foraminifera faithfully reflect the δ13C of bottom water DIC (Duplessy et al., 1984). Epifaunal species are preferred for reconstructions because infaunal taxa record pore water values, which are typically lower than those of bottom waters due to organic matter remineralization (Zahn et al., 1986). However, the δ13C of even epifaunal species may be lower than that of bottom waters in regions where organic matter rain rates are very high (Mackensen et al., 1993).

Benthic foraminiferal δ13C provides a picture of the past distribution of deep-water masses. Biogeochemical cycling and air-sea exchange cause most surface waters, particularly those stripped of nutrients, to be more enriched in δ13C compared to the deep ocean. North Atlantic Deep Water (NADW) is today formed from such low-nutrient waters, and therefore carries a high-δ13C signature (Figure 2). In contrast, Antarctic Bottom Water (AABW) and Antarctic Intermediate Water (AAIW) are formed from poorly ventilated surface waters and therefore carry low-δ13C signatures. Lowest δ13C values are found today in the deep North Pacific, far from the well-ventilated NADW source.

Today NADW transports a large amount of heat into the North Atlantic, and past changes in its formation are believed to have strongly impacted regional climates. The most extensively studied period in this regard is the Last Glacial Maximum.
(LGM, ∼20 ka BP), for which meridional Atlantic δ13C sections have been created. Such reconstructions suggest that low-δ13C AABW expanded into the North Atlantic and that its boundary with high-δ13C NADW shoaled from a water depth of 4 to ∼2–3 km (Figure 3; Curry and Oppo, 2005; Duplessy et al., 1988). This reorganization was long assumed to be due to a reduction in the formation rate of NADW, but other more rate-sensitive proxies have since underscored the fact that paleonutrients constrain only the spatial extent of water masses and not their fluxes. The glacial form of NADW, dubbed Glacial North Atlantic Intermediate Water (GNAIW), likely formed significantly southward of its modern deep convection regions. This migration may therefore have cooled high latitudes even if formation rates were not reduced. On longer Quaternary timescales, the δ13C gradient between the North Atlantic and Pacific has been used to monitor NADW extent. As during the LGM, NADW volume was apparently reduced during all Northern Hemisphere glaciations.

One interesting aspect of the glacial δ13C distribution is that the lowest values occurred in the deep Southern Ocean, rather

Figure 1 Modern seawater profiles of the main nutrient proxies. (a) δ13C of DIC (Kroopnick, 1985) compared to dissolved phosphate (Broecker et al., 1982) in the central North Pacific; (b) Dissolved Cd compared to dissolved phosphate in the eastern North Pacific (Bruland, 1980); (c) Dissolved Ba (Ostlund et al., 1987) compared to total alkalinity (Broecker et al., 1982) in the central North Pacific; (d) Dissolved Zn compared to dissolved silica in the eastern North Pacific (Bruland, 1980); (e) δ15N of dissolved nitrate compared to dissolved nitrate in the Indian sector of the Southern Ocean (Sigman et al., 1999).

Figure 2 Meridional section of the δ13C of DIC in the western Atlantic Ocean during the 1970s (reproduced from Kroopnick PM (1985) The distribution of 13C of ΣCO2 in the world oceans. Deep-Sea Research 32: 57–84). Major water masses are indicated, and the numbers at the top refer to oceanographic cruise stations. Preindustrial δ13C values were slightly higher at the sea surface and in the North Atlantic, shallower than ∼2 km (Olsen and Ninnemann, 2010).
than in the North Pacific as they do today. Glacial production of a North Pacific Deep Water could explain the pattern, but such a water mass is difficult to document, in part because of the poor preservation of calcite in the North Pacific. Some have attributed low Southern Ocean δ¹³C values to an organic matter microhabitat effect (Mackensen et al., 1993), noting that Cd/Ca (see Section ‘Cadmium’) does not support a very high-nutrient glacial AABW (Boyle, 1992). However, the relative uniformity of glacial δ¹³C in the Atlantic sector of the Southern Ocean suggests that the values are probably reliable (Ninnemann and Charles, 2002). Independent estimates of deep sea salinity and temperature require glacial AABW to have been particularly dense, so perhaps GNAIW avoided extensive mixing in the Southern Ocean en route to the North Pacific, leaving AABW anomalously low in δ¹³C. Reduced vertical mixing between these two water masses is supported by an enhanced oxygen isotope vertical gradient in the deep Atlantic (Lund et al., 2011).

The δ¹³C pattern in the glacial Atlantic implies that there was a net shift of DIC from the upper ocean into the deep ocean. A comparable δ¹³C shift has been documented in the glacial Indian Ocean, and although data coverage in the Pacific is comparatively poor, an intermediate- to mid-depth δ¹³C gradient is generally supported (Herguera et al., 2010). Glacial DIC deepening may have acted to lower atmospheric CO₂, through both the direct effect of decreased surface ocean DIC and the compounding effect of increased oceanic alkalinity due to greater dissolution of seafloor CaCO₃ (Sigman et al., 2010).

Reconstruction of surface water δ¹³C appears to be more complicated than deep-water work because of confounding influences on planktic foraminiferal δ¹³C (Keigwin and Boyle, 1989; Spero, 1998). For example, culture work shows that photosymbionts, respiration, and carbonate chemistry affect the δ¹³C of various taxa. Nevertheless, planktonic-benthic comparisons may record past shifts of DIC partitioning between the upper and deep oceans, with the implications for atmospheric CO₂ mentioned earlier (Shackleton et al., 1983). A widespread planktonic δ¹³C minimum during the last deglaciation may represent the release of DIC that was stored in the isotopically light and isolated AABW during glacial times (Spero and Lea, 2002).

On glacial-interglacial timescales, the partitioning of carbon between land and ocean must also be considered. It is estimated from benthic Foraminifera that the average δ¹³C value of the world’s oceans was 0.3‰ lower during the LGM (Duplessy et al., 1988). This estimate is subject to considerable error because of the scarcity of data in some regions, particularly the North Pacific. Assuming an average terrestrial carbon isotopic composition of −25‰, the glacial lowering could be explained by a transfer of 400–500 Gt (10¹⁵ g) of carbon from land into the ocean, or about 20% of the terrestrial biomass (Crowley, 1995). Independent reconstructions of the LGM terrestrial biosphere, based on paleoecological data, argue for a greater reduction, by up to two or three times that inferred from mean ocean δ¹³C. Factors that might reconcile these disparate estimates include glacial carbon storage on exposed continental shelves or in isotopically light methane hydrates.

### Trace Metals: Cadmium, Barium, and Zinc

Numerous dissolved trace elements in the ocean exhibit vertical profiles that resemble those of nutrients. That is, they are at low concentrations in surface waters and at greater concentrations at depth. In some cases, this behavior is linked to the element’s importance as a micronutrient. For example, iron is essential for the synthesis of chlorophyll and various algal proteins and is the limiting nutrient in some regions of the ocean. In other cases, nutrient-like behavior may result simply from adsorption onto particulate organic matter in the photic zone and co-remineralization in the deep sea. Regardless of biogeochemical mechanisms, such elements may be useful as nutrient and water mass tracers. Paleoreconstruction relies on the fact that various elements are incorporated into foraminiferal calcite during precipitation. In particular, divalent cations are believed to substitute for calcium in the calcite crystal matrix. Three divalent trace metals have been developed as paleonutrient tracers: cadmium (Cd), barium (Ba), and zinc (Zn).
Cadmium

Dissolved Cd has an oceanic distribution very similar to that of the major nutrient phosphate (Figure 1). Both are nearly completely removed from most surface waters and regenerated at depth, with an intermediate-depth concentration maximum near 1 km. Cd therefore behaves like a labile (easily remineralized) nutrient, and its concentration increases about fivefold between the deep North Atlantic and North Pacific. Although Cd has been linked to at least one important algal metalloenzyme, it is not clear if this use is sufficient to explain its oceanwide nutrient-like behavior. The global correlation between Cd and phosphate follows a slight curve that may be explained by preferential uptake of Cd over phosphate by particulate organic matter (Elderfield and Rickaby, 2000).

Benthic foraminiferal Cd/Ca ratios reflect seawater Cd concentrations (Boyle, 1992). The relationship between foraminiferal Cd/Ca and seawater Cd is expressed in terms of the partition coefficient:

\[
D_{\text{Cd}} = \frac{(\text{Cd}/\text{Ca})_{\text{foramin}}}{(\text{Cd}/\text{Ca})_{\text{seawater}}}
\]

Calcitic benthic foraminiferal \( D_{\text{Cd}} \) varies with water depth, from \(~1.3\) in the upper ocean to \(2.9\) below 3 km. The aragonitic benthic foraminifer Hoeglundina elegans has a \( D_{\text{Cd}} \) of 1.0, invariant with depth. Calcitic partition coefficients also appear to be reduced in waters that are very undersaturated with respect to calcite, such as in the deep Pacific (McCorkle et al., 1995).

Cd/Ca generally supports \( \delta^{13}\text{C} \) observations indicating that low-nutrient NADW was less extensive in the glacial Atlantic Ocean and was present as the shallower GNAIW (Figure 4; Boyle and Keigwin, 1987; Marchitto and Broecker, 2006). A notable difference between the two proxies is the already mentioned deep Southern Ocean discrepancy, where glacial \( \delta^{13}\text{C} \) shows very low values in contrast to Cd/Ca, which is similar to the current value. An undersaturation effect on Cd/Ca and/or a microhabitat effect on \( \delta^{13}\text{C} \) might explain some of the difference. Alternatively, large-scale changes in deep-water ventilation might have decoupled the two tracers such that AABW was depleted in \( \delta^{13}\text{C} \) without being significantly enriched in Cd.

The Southern Ocean problem highlights the fact that because \( \delta^{13}\text{C} \) and Cd behave somewhat differently in the modern ocean, unique information may be derived from paired measurements that is not available from either tracer alone. Specifically, air–sea exchange affects \( \delta^{15}\text{N} \) but not Cd, so combining the two can potentially reveal past air–sea processes (Lynch-Stieglitz and Fairbanks, 1994). Paired measurements from various regions of the glacial ocean suggest that different deep-water masses had distinct air–sea signatures, allowing for the separation of biogeochemical aging and water mass mixing. LGM Atlantic observations may be largely explained by mixing between well-ventilated GNAIW and poorly ventilated AABW (Marchitto and Broecker, 2006).

Planktonic Foraminifera incorporate Cd with a similar range of partition coefficients as benthics (Delaney, 1989), but less paleoceanographic work has been done with planktonics. Cd/Ca from a polar species suggests that LGM nutrient levels in the high-latitude North and South Atlantic were not much different from today, arguing against changes in NADW and AABW end member properties as explaining the deep sea record (Keigwin and Boyle, 1989). Temperature appears to affect the incorporation of Cd in at least one planktonic species (Rickaby and Elderfield, 1999), and correction for this influence implies that glacial Southern Ocean surface nutrient levels were elevated south of the modern Polar Front, but relatively unchanged north of it (Elderfield and Rickaby, 2000), seemingly in contradiction with \( \delta^{15}\text{N} \) data (see Section ‘Nitrate Utilization’).

Barium

Dissolved Ba is moderately depleted in surface waters and reaches maximum concentrations below \(~2\) km (Figure 1). Its distribution resembles that of alkalinity, but the association is coincidental (Lea and Boyle, 1989). Ba is removed from shallow waters mainly by barite formation in decaying organic matter, while alkalinity is removed mainly by CaCO₃ formation. Both are regenerated at depth as their carrier phases dissolve, and deep-water masses have characteristic Ba and alkalinity values, with Ba increasing about threefold between the deep North Atlantic and North Pacific. Due to its refractory (less easily remineralized) behavior, Ba may offer information that is distinct from the more labile Cd. Ba is incorporated into several taxa of calcitic benthic Foraminifera with a partition coefficient of \(~0.4\) (Lea and Boyle, 1989), and there is
evidence that this value is reduced in strongly undersaturated waters (McCorkle et al., 1995).

For the LGM Atlantic, benthic Ba/Ca supports the view that low-nutrient NADW was replaced by the shallower GNAIW (Figure 5; Lea and Boyle, 1990b). Low intermediate-depth Ba/Ca also appears to rule out the Mediterranean Sea as an important contributor to GNAIW, since water from that basin carries high Ba concentrations. In contrast to δ¹³C and Cd/Ca, however, there was no apparent glacial Ba gradient between the deep Atlantic and the Pacific. Deep ocean Ba may have become decoupled from the other nutrient tracers because of an increase in barite regeneration at the seafloor, possibly associated with increased productivity (Lea and Boyle, 1990b).

**Zinc**

Dissolved Zn has an oceanic distribution very similar to that of the nutrient silica (Figure 1). Both are nearly completely removed from most surface waters, but unlike the labile Cd and phosphate, they lack intermediate-depth concentration maxima. Zn therefore behaves like a refractory nutrient, with maximum concentrations below ~1–2 km water depth. Zn is an essential micronutrient for many marine organisms, second only to iron among the biologically important trace metals. In particular, its use by diatoms (algal protists with siliceous shells) in the enzyme carbonic anhydrase may explain its oceanic association with silica. Zn concentrations increase more than tenfold between the deep North Atlantic and North Pacific, and there is a sevenfold meridional increase within the deep Atlantic alone. Zn/Ca may therefore be a very sensitive tracer of past interactions between NADW and AABW (Marchitto et al., 2002).

At least two species of calcitic benthic Foraminifera incorporate Zn with a partition coefficient that depends strongly on the saturation state. In sufficiently supersaturated waters $D_{Zn}$ is ~9, but it may be as low as ~4 in the corrosive deep Pacific. The glacial increase in deep North Atlantic Zn due to the increased presence of AABW was therefore partially muted in Zn/Ca because of AABW’s lower saturation state (Marchitto et al., 2002). Nevertheless, paired Zn/Ca and Cd/Ca measurements provide strong evidence for glacial AABW expansion, and not some independent change in NADW nutrient content.

**Nitrogen-15**

**Nitrate Utilization**

Along with carbon and phosphate, nitrate (NO₃⁻) is an essential major nutrient for marine primary production, and is often the limiting nutrient in the open ocean. Like carbon, nitrogen has two stable isotopes: ¹⁴N (99.6%) and ¹⁵N (0.4%). Fractionation is again expressed in delta notation:

$$\delta^{15}N = \left(\frac{^{15}N/^{14}N}_{\text{sample}}/^{15}N/^{14}N_{\text{standard}} - 1\right) \times 1000$$  \[3\]

where the standard is atmospheric N₂. Phytoplankton preferentially incorporate the lighter isotope, leading to $\delta^{15}N$ enrichment of the remaining dissolved NO₃⁻ pool. In regions where
the NO$_3^-$ supply is heavily utilized, the surface ocean isotopic enrichment can be relatively large (order of 10‰; Figure 1), and organic matter $\delta^{15}N$ increases in parallel. To the first order, the $\delta^{15}N$ of sedimentary organic matter may therefore be used to reconstruct past surface ocean NO$_3^-$ $\delta^{15}N$, and thus the degree of NO$_3^-$ utilization (Altabet and Francois, 1994). There are indications that sedimentary bulk organic matter $\delta^{15}N$ may be subject to diagenetic alteration in some environments, which might be avoidable by measuring diatom-bound $\delta^{15}N$ (Robinson and Sigman, 2008).

Past NO$_3^-$ utilization is of particular interest in the Southern Ocean, the largest area of incomplete consumption of NO$_3^-$ and phosphate by phytoplankton in the modern oceans. Here, deep waters charged with nutrients and DIC upwell to the surface, but they are subducted again before their nutrient loads can be efficiently extracted, resulting in a missed opportunity for the ocean’s ‘biological pump’ to sequester CO$_2$ (Sigman et al., 2010). Hypothetically, the resulting leak of CO$_2$ into the atmosphere could have been stemmed during glacial times either by increased biological productivity or by reduced vertical mixing. Both processes would be recorded as increases in $\delta^{15}N$ due to a more complete NO$_3^-$ utilization. South of the modern Polar Front, $\delta^{15}N$ data indeed suggest that NO$_3^-$ utilization was enhanced during the last glaciation (Figure 6), and proxy evidence for reduced export production confirms that this change was related to reduced upwelling and/or stronger surface stratification (Francois et al., 1997; Robinson and Sigman, 2008). North of the modern Polar Front, export production increased, but NO$_3^-$ utilization apparently did not rise as much as it did south of the front, implying that the

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**Figure 7** Sedimentary $\delta^{15}N$ records from off southern Chile (c) (Robinson et al., 2007), California (d) (Hendy et al., 2004), and Oman (e) (Altabet et al., 2002), compared to $\delta^{18}O$ of ice (a proxy for air temperature) in Greenland (a) and Antarctica (b). Numbers at the top indicate marine isotope stages, and gray bars denote millennial-scale warm events in Antarctica. Also shown (on a reversed scale) is $\delta^{15}N$ in the subantarctic zone of the Southern Ocean (f). Reproduced from Robinson RS, Mix A, and Martinez P (2007) Southern Ocean control on the extent of denitrification in the southeast Pacific over the last 70 ka. Quaternary Science Reviews 26: 201–212.

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enhanced productivity could have resulted from increased upwelling. It has been suggested that the changes south of the Polar Front had a greater impact on the atmosphere, contributing to glacial CO₂ lowering.

### Denitrification

A second important influence on the δ¹⁵N of dissolved NO₃⁻ is water column denitrification, which represents an important loss of fixed nitrogen from the oceans. Under suboxic conditions, NO₃⁻ may be used by certain bacteria as an electron acceptor during organic matter degradation, producing N₂O and N₂. Like NO₃⁻ utilization, this process preferentially uses ¹⁴N and results in δ¹⁵N enrichment of the remaining NO₃⁻ pool. While well-oxygenated deep waters are typically ~3–6‰ in δ¹⁵N, denitrification may drive the values above 18‰. Today, denitrification occurs primarily in the intermediate-depth oxygen minimum zones (OMZs) of the eastern tropical North and South Pacific, and the Arabian Sea.

Along the western Mexico continental margin, bulk sediment δ¹⁵N was about 2–3‰ lower during late Quaternary glacial intervals, indicative of reduced denitrification in this region (Ganesham et al., 2002). Other sediment cores from the eastern tropical North Pacific exhibit reduced organic carbon content and increased bioturbation during glacial times, consistent with erosion of the regional OMZ. Arabian Sea sedimentary δ¹⁵N was similarly reduced (Altabet et al., 2002), suggesting that global rates of denitrification were significantly lower during glacial periods. This may have resulted in an increased oceanic inventory of NO₃⁻, possibly stimulating primary production in oligotrophic (subtropical gyre) regions and contributing to the glacial drawdown of atmospheric CO₂. However, phosphate limitation likely became important, reducing overall NO₃⁻ fixation and limiting the biological impact of reduced denitrification (Ganesham et al., 2002).

OMZ weakening during glacial periods may have resulted from decreased upwelling-driven productivity in those regions, and/or increased ventilation by high-oxygen intermediate waters. In the Arabian Sea, sediment δ¹⁵N also decreased during millennial-scale intervals corresponding to the Northern Hemisphere cold stages of the last Ice Age, the so-called Dansgaard–Oeschger stadials (Figure 7(a) and (c); Altabet et al., 2002). Reduced denitrification at these times was likely due to reduced summer upwelling and productivity in response to a weakened southwest Indian monsoon. δ¹⁵N off southern Chile also displayed millennial-scale variability during the last Ice Age, but with a timing that more closely mimics the temperature history of Antarctica (Figure 7(b) and (c); Robinson et al., 2007). δ¹⁵N records from the eastern North Pacific OMZ appear to transition from Antarctic-like timing near the equator to Greenland-like timing further north (Figure 7(d); Hendy et al., 2004; Robinson et al., 2007; Pichevin et al., 2010), pointing to some combination of southern and northern forcing along this margin. Enhanced ventilation of Subantarctic Mode Water during Antarctic cold phases may have delivered more oxygen to the eastern tropical and South Pacific OMZs, resulting in less denitrification. Furthermore, if enhanced NO₃⁻ utilization occurred in the Subantarctic Southern Ocean during cold phases, as suggested by higher diatom-bound δ¹⁵N (Figure 7(f); Robinson et al., 2007), then nutrient delivery to the low-latitude world ocean would have been reduced, leading to lower productivity and less demand for oxygen in the regions of the modern OMZs. In contrast to the Southern Ocean, changes in upwelling and productivity above the low-latitude OMZs are believed to exert little leverage on atmospheric CO₂ because nutrients upwelled there are completely utilized eventually (Sigman et al., 2010).


### References


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