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Late Glacial temperature and precipitation changes in the lowland Neotropics by tandem measurement of δ¹⁸O in biogenic carbonate and gypsum hydration water

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Abstract

We applied a new method to reconstruct paleotemperature in the tropics during the last deglaciation by measuring oxygen isotopes of co-occurring gypsum hydration water and biogenic carbonate in sediment cores from two lakes on the Yucatan Peninsula. Oxygen and hydrogen isotope values of interstitial and gypsum hydration water indicate that the crystallization water preserves the isotopic signal of the lake water, and has not undergone post-depositional isotopic exchange with sediment pore water. The estimated lake water δ¹⁸O is combined with carbonate δ¹⁸O to calculate paleotemperature. Three paired measurements of 1200-yr-old gypsum and gastropod aragonite from Lake Chichancanab, Mexico, yielded a mean temperature of 26°C (range 23–29.5°C), which is consistent with the mean and range of mean annual temperatures (MAT) in the region today. Paired measurements of ostracods, gastropods, and gypsum hydration water samples were measured in cores from Lake Petén Itzá, Guatemala, spanning the Late Glacial and early Holocene period (18.5–10.4 ka). The lowest recorded temperatures occurred at the start of Heinrich Stadial (HS) 1 at 18.5 ka. Inferrred temperatures from benthic ostracods ranged from 16 to 20 °C during HS 1, which is 6–10 °C cooler than MAT in the region today, whereas temperatures derived from shallow-water gastropods were generally warmer (20–25 °C), reflecting epilimnetic temperatures. The derived temperatures support previous findings of greater tropical cooling on land in Central America during the Late Glacial than indicated by nearby marine records. Temperature increased in two steps during the last deglaciation. The first occurred during the Bolling-Allerod (B-A; from 14.7 to 13 ka) when temperature rose to 20–24 °C towards the end of this period. The second step occurred at 10.4 ka near the beginning of the Holocene when ostracod-inferred temperature rose to 26 °C, reflecting modern hypolimnetic temperature set during winter, whereas gastropod-derived temperature attained 30 °C, reflecting modern summer epilimnetic temperature.

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1. INTRODUCTION AND BACKGROUND

1.1. Statement of the problem

A fundamental problem in oxygen isotope paleothermometry is the carbonate mineral–water temperature equation is often under-constrained. Both the oxygen isotopic composition of the carbonate mineral and the lake water from which it precipitated must be known to calculate temperature. Gypsum (CaSO\textsubscript{4}·2H\textsubscript{2}O) is a hydrated mineral containing 20.9% water by weight that records the oxygen and hydrogen isotopic signature of the water from which it formed. Gypsum is a moderately soluble mineral (2.0–2.5 g L\textsuperscript{-1} H\textsubscript{2}O) that forms during evaporation of sulfate- and calcium-bearing water, and is found commonly in lacustrine and marine deposits that have undergone evaporation. The δ\textsuperscript{18}O and δD of the water from which gypsum was precipitated can be determined by measuring gypsum hydration water if: (i) isotopic equilibrium is achieved between the mother and hydration water; (ii) the fractionation factors during gypsum formation are known and temperature-independent, and (iii) no isotope exchange has occurred between environmental and hydration water after gypsum deposition. By measuring the δ\textsuperscript{18}O of gypsum hydration water and calcite or aragonite from the same samples, a unique temperature estimate can be derived. Here we demonstrate the method in sediment cores from two lakes on the Yucatan Peninsula, Lake Chichancanab, Mexico and Lake Petén Itzá, Guatemala (Fig. 1), and derive estimates of deglacial temperature fluctuations in the lowland Neotropics.

1.2. History of gypsum hydration water isotope measurements

Some of the first measurements of stable isotopes in gypsum hydration water were made in the early 1950s (Baertschi, 1953; Taube, 1954), and seminal papers in the early 1960s established the fractionation factors for oxygen (Gonfiantini and Fontes, 1963) and hydrogen (Fontes and Gonfiantini, 1967) between gypsum hydration water and the water from which it formed. Most applications of oxygen and hydrogen isotope analysis of gypsum hydration water have focused on understanding the origin and formation of gypsum in soils and sediments (Matsubaya and Sakai, 1973; Sofer, 1978; Halas and Krouse, 1982; Khademi et al., 1997). Despite the ubiquitous occurrence of gypsum in the sedimentary record, relatively few studies have utilized hydration water for paleoclimate reconstruction. This reticence stems from concerns that the isotopic composition of gypsum hydration water can be altered by postdepositional recrystallization (dissolution and recrystallization) or isotopic exchange with environmental water (Sofer, 1978).

Sofer (1978) characterized the isotopic composition of gypsum hydration water from a wide spectrum of environments. He concluded gypsum hydration water retains its isotopic composition under dry conditions (e.g., Negev Desert), but under humid conditions, only the history of young gypsum deposits can be studied. Thus, he concluded that the method is limited to primary gypsum that has not undergone dehydration, exchange, or recrystallization and thus has retained its original water isotopic composition.

Various methods have been employed to measure the δ\textsuperscript{18}O and δD of gypsum hydration water. Early methods involved extraction of water followed by CO\textsubscript{2} equilibration to measure δ\textsuperscript{18}O (Fontes, 1965), which had a distinct disadvantage in that very large sample sizes (7–25 g of gypsum) were required. Playa et al. (2005) developed an extraction method for oxygen isotopic analysis of gypsum hydration water using guanidine hydrochloride, which reduced sample size requirements to 20–25 mg. Hydrogen isotopes have been measured mainly by reduction to H\textsubscript{2} gas using native metals (e.g., uranium, zinc) or thermal conversion using glassy carbon (Sharp et al., 2001). Rohrssen et al. (2008) developed an on-line method for rapid analysis of both δ\textsuperscript{18}O and δD using a carbon reducing furnace connected to a continuous-flow mass spectrometer system. Here we extracted the gypsum hydration water offline with subsequent isotope analysis of both oxygen and hydrogen by cavity ringdown laser spectroscopy (CRDS) using a Picarro water isotope analyzer.

1.3. Site locations and settings

Lake Chichancanab is located in the northern Yucatan Peninsula, Mexico, and is a moderately saline lake (~4000 mg/L) that is saturated today for gypsum, calcite, aragonite, dolomite and celestite (SrSO\textsubscript{4}) (Perry et al., 2002). Maximum water depth is 15 m and lake temperature averaged ~26 °C throughout the water column in March 2004 (Fig. 2), which approximates the mean annual air temperature of 25.9 °C in the region today. Mean annual precipitation averages 1268 mm. A depth profile of water in 2004 yielded mean δ\textsuperscript{18}O and δD values of 2.8‰ and 12.3‰, respectively (Fig. 2). Perry et al. (2003) reported...
δ¹⁸O and δD values for surface waters of 3.0‰ and 15.4‰, respectively, in 1998.

The paleoclimate history of Lake Chichancanab is well documented from previous study of sediment cores (Covich and Stuiver, 1974; Hodell et al., 1995, 2001, 2005). Here we measured three samples of gypsum for stable isotopes of hydration water between 67 and 71 cm in Core CH-25-VI-93, which is 4.9-m long and was raised in 6.9 m of water in 1993 (Hodell et al., 1995). The 6-cm thick gypsum bed and a concomitant increase in δ¹⁸O of gastropod and ostracod shells provided the first physical evidence for an intensified period of drought during the Terminal Classic Period (ca 800–1000 AD), which coincided with the demise of Classic Maya civilization (Hodell et al., 1995).

Lake Petén Itzá, located in northern Guatemala at 16°55′ N, 89°50′ W, was the focus of a drilling campaign in 2006 sponsored by the International Continental Drilling Program (Hodell et al., 2006). It is the largest (100 km²) and deepest (160 m) lake in the Central Petén Lake District. The lake appears to be oligomictic today and probably circulates during abnormally cold winters. Epilimnetic temperatures during summer reach ~24°C, and there is a well-developed thermocline between ~20 and 30 m (Fig. 3). Hypolimnetic temperatures average ~25°C and are set by air temperature during times of winter mixing. The lake is thermally stratified throughout much of the year. This, along with the failure of the water column to fully mix annually, contributes to oxygen depletion in hypolimnetic waters. Mean annual air temperature at Flores, an island in the southern basin of Petén Itzá, is 26°C, with mean monthly temperatures reaching as low as 19°C during winter (associated with the passage of cold fronts or nortes) and as high as 31°C during summer. Precipitation averages 1600 mm yr⁻¹, with the majority of the rain falling in the summer months from May to October.

The mean oxygen and hydrogen isotope compositions of Lake Petén Itzá water today are ~2.7‰ and 15.2‰, respectively (Fig. 3). Surface waters on August 13, 2002 were slightly more enriched in the heavier isotope than deep water because of evaporation. The modern lake water is dilute (400 mg/L) and dominated by bicarbonate and sulfate anions and calcium and magnesium cations. Lake water pH is high (~8.0) and saturated with respect to calcite, aragonite and dolomite. The lake water is undersaturated with respect to calcium sulfate today, but the occurrence of gypsum deposits at depth in sediment cores indicates that the water was oversaturated at times during the past (Hillesheim et al., 2005; Hodell et al., 2008; Mueller et al., 2010). High dissolved sulfate concentrations in the lake derive from the dissolution of gypsum from bedrock in the watershed.

Site PI-6 was drilled in a water depth of 71 m. The lithostratigraphy of the cores was described by Hodell et al. (2008) and Mueller et al. (2010), and we adopt the radiocarbon chronology of Escobar (2010). The core consists of alternating layers of gypsum and clay of varying thickness (Fig. 4), reflecting times of drier and wetter climate conditions, respectively. Thirty-four samples of gypsum hydration water were measured in cores from Site PI-6 between 21 and 11.3 m composite depth (mcd) representing the Late Glacial period between ~18.5 and 10.8 ka (Electronic annex EA1). Five gypsum samples were measured from the earliest Holocene (10.5 to 10.4 ka) of Core 8-VI-02 Station 11A in 58.2 m of water (Hillesheim et al., 2005). Gypsum is absent in intervals that are clay-dominated, such as the LGM (~23–19 ka), Bolling-Allerod (~14.7–13 ka), and most of the Holocene (~10–0 ka).

Fig. 2. Hydrographic profiles of Lake Chichancanab collected in March 2004 including temperature (black diamonds), dissolved oxygen concentrations (green open circles), and δD (blue squares) and δ¹⁸O (red filled circles) of water. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
2. METHODS

2.1. Gypsum hydration water

Sediment samples were disaggregated in a solution of deionized water at room temperature for 12 h. Samples were then washed through a 63-μm sieve and the coarse fraction was collected on filter paper and dried at room temperature for one week. Because gypsum has been reported to possibly lose hydration water at temperatures as low as 42 °C in aqueous systems at atmospheric pressure (D’Ans, 1968; Braitsch, 1971; Deer et al., 1983), we tested...
if the sample drying procedure caused any loss of hydration water or isotopic fractionation. We took a new set of samples from the same levels in the core to test whether sample disaggregation, washing, or drying had any effect on the isotopic composition of the extracted hydration water. For the disaggregation experiment, raw samples were split into three aliquots. One aliquot was sieved immediately using deionized water with no soaking, one was disaggregated by standing in deionized water (\(\delta^{18}O = -7.4; \deltaD = -49.2\)) for 24 h, and the other was disaggregated in 3% H\(_2\)O\(_2\) (\(\delta^{18}O = -7.2; \deltaD = -52.4\)) for 24 h. For the drying experiment, raw samples were split in two aliquots and dried at room temperature (20 °C) and in an oven at 50 °C for a week. We found no significant differences in the \(\delta^{18}O\), \(\deltaD\), or the weight percent of hydration water extracted among the sediment washing and drying methods (EA1).

Gypsum crystals were picked from the sediment under a binocular microscope from the >350-μm size fraction and adhering particles were removed. About 300-400 mg of clean gypsum was gently ground, loaded into glass boats, and placed in a vacuum extraction line and evacuated to a pressure of 10\(^{-2}\) mbars. Samples were pumped on for 3 h at room temperature with a liquid nitrogen trap fitted above a stainless-steel screen in the squeezer and water emanated from a hole at the base of the unit, where a plastic syringe was fitted with a 0.45-μm disposable filter. Interstitial water samples were separated into two aliquots: 5 mL for pH and alkalinity measurements in the field and the remainder for major ions and stable isotope analysis. All water samples were analyzed by CRDS using a L1102-i Picarro water isotope analyzer and A0211 high-precision vaporizer.

2.2. Precipitation, meteoric and lake water samples

We report isotopic results of a large number of water samples collected from Mexico and Guatemala. Samples include rain, river, spring, groundwater, cave drip, and lake water (EA2–5). Rainwater is mostly from a meteorological station in northern Yucatan established at Rancho Hobonil near Tzucacab, Mexico (20°09'99; 89°1'22'). All water samples were collected and stored in Qorpak bottles with Poly-seal cone-lined caps to prevent evaporation.

Pore water samples were obtained from several drill sites during the Petén Itzá Scientific Drilling Project, using a stainless-steel hydraulic squeezer. Core-catcher samples were placed onto a tray where the outer surface was scraped with a spatula to remove potential contamination. Interstitial water was passed through a Whatman No. 1 filter fitted above a stainless-steel screen in the squeezer and water emanated from a hole at the base of the unit, where a plastic syringe was fitted with a 0.45-μm disposable filter. Interstitial water samples were separated into two aliquots: 5 mL for pH and alkalinity measurements in the field and the remainder for major ions and stable isotope analysis. All water samples were analyzed by CRDS using a L1102-i Picarro water isotope analyzer and A0211 high-precision vaporizer.

2.3. Biogenic carbonate

Oxygen isotopes of calcite were measured on carapaces of the benthic ostracode *Lmnocythere opesta* (Escobar, 2010), which lives from the littoral zone to a maximum depth of ~40 m near the base of the thermocline (Perez et al., 2010). Adult ostracod specimens were picked from the ~212-μm fraction using a binocular microscope. Prior to isotopic analysis, ostracod specimens were cleaned using 15% H\(_2\)O\(_2\) to remove organic material, and then rinsed in methanol before drying. Approximately 12-20 individual ostracod carapaces, weighing a total of ~20–55 μg, were placed into glass vials and CO\(_2\) was evolved by reaction with phosphoric acid using a Kiel III carbonate preparation device attached to a Finnigan-MAT 252 isotope ratio mass spectrometer (IRMS) at the University of Florida. Analyt-
ical error was estimated by analysis of NBS-19 and yielded 1 standard deviation values of ±0.08‰ for δ18O and ±0.04‰ for δ13C.

Shells and shell fragments of the gastropod Cochliopina sp. were picked from samples that contained sufficient numbers for analysis. Stable isotopes of the aragonitic shell were measured using a Multiprep device coupled to either a Prism or Sira IRMS in the Godwin Laboratory for Palaeoclimate Research at the University of Cambridge. Analytical error was estimated by repeated analysis of Carrara Marble and yielded 1 standard deviation values of ±0.08‰ for δ18O and ±0.06‰ for δ13C.

3. RESULTS

3.1. Meteoric and lake water

Oxygen and hydrogen isotopes of rain, surface and groundwater define a local meteoric water line (δD = 7.18 + δ18O + 8.1) (Fig. 5), which is nearly the same as the one derived by Lachniet and Patterson (2009) using surface waters from Guatemala and Belize (δD = 8.0 + δ18O + 8.7). The hydrology of lakes on the Yucatan Peninsula ranges from completely open and connected to the water table to effectively closed basins, the latter losing water almost entirely to evaporation. The varying degree of evaporative loss among lakes is reflected in the wide range of δ18O (−3.9‰ to +6.8‰) and δD (−17‰ to +28.2‰) values measured in lakes throughout the peninsula. The δ18O and δD of these lakes define an evaporative line where δD = 5.0δ18O − 1.3 (Figs. 5 and 6). The evaporative line intersects the local meteoric water line at about δ18O = −4‰ and δD = −23‰, which are close to the average values for groundwater in the region.

3.2. Interstitial water

The δ18O and δD of interstitial pore waters in the Petén Itzá cores increase from lake water values at the sediment–water interface to maximum values between ~25 and 50 mcd, and decrease to the bottom of each hole (Fig. 7). Maximum pore-water values are 3.7‰ for δ18O and 21‰ for δD. The profile reflects the δ18O and δD history of the overlying lake water, subsequently attenuated by diffusion and advection. The pattern is analogous to marine pore water δ18O profiles that preserve the seawater signal of the last glacial period (McDuff, 1984; Schrag and DePaolo, 1993; Schrag et al., 2002; Adkins et al., 2002). The high δ18O and δD of pore water between 25 and 50 m thus reflect the isotopic enrichment of lake water during the last glacial

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Fig. 5. δ18O and δD of rain, surface water, and ground water (black crosses), lake water (blue open circles), gypsum hydration water as measured from Lakes Chichancanab (red open diamonds) and Petén Itzá (green open squares), and predicted paleo-lake water values for Chichancanab (red closed diamonds) and Petén Itzá (green closed squares) after correction for fractionation factors. Solid black line represents the local meteoric water line estimated by least-squares linear regression through rain, surface and groundwater data. Blue line represents the evaporative line estimated by least-squares linear regression using lake data. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
period when Petén climate was drier than today. The $\delta^{18}O$ and $\deltaD$ of the glacial lake water were considerably greater than the maximum recorded by the pore waters today because of diffusion within pore waters attenuating the signal. In Section 4.6, we use a diffusion-advection model to estimate the unattenuated $\delta^{18}O$ and $\deltaD$ value of lake water during the last glacial period. The relation between pore-water $\delta^{18}O$ and $\deltaD$ values define a trend with a slope of 5.5 that is close to the lake-water evaporative line defined by regional closed-basin lakes (Fig. 6).

### 3.3. Gypsum hydration water

Three gypsum samples were measured from between 67 and 70 cm depth in Chichancanab Core CH-25-VI-93. This interval was radiocarbon dated to 1140 ± 35 14C yrs BP (Hodell et al., 1995). The measured $\delta^{18}O$ of gypsum hydration water ranged from 7.5‰ to 8.9‰ and $\deltaD$ from −3.3‰ to 2.0‰. When corrected for isotopic fractionation factors between mother water and hydration water, the $\delta^{18}O$ of paleolake water is estimated to have ranged between 3.5‰ and 4.9‰, and $\deltaD$ from 17‰ to 22.5‰, compared to modern $\delta^{18}O$ and $\deltaD$ values of about −3‰ and 15‰.

<table>
<thead>
<tr>
<th>$\delta^{18}O$ (SMOW)</th>
<th>$\deltaD$ (SMOW)</th>
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<tbody>
<tr>
<td>Lateglacial</td>
<td>8.8‰ to 11.0‰</td>
</tr>
<tr>
<td>Holocene</td>
<td>2.1‰ to 2.0‰</td>
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Fig. 6. Details of $\delta^{18}O$ and $\deltaD$ data relative to the evaporative line with slope = 5 (bold blue line), including extant lakes with varying hydrologic budgets and evaporative losses (blue open circles), Petén Itzá pore waters (red closed diamonds), and Late Glacial-early Holocene paleo-lake water values predicted from gypsum hydration water (closed green squares). The modern $\delta^{18}O$ and $\deltaD$ of Petén Itzá is indicated by closed black circle. Note the lake water values calculated from gypsum hydration water lie on a projection of the evaporative line based on regional extant lakes. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Thirty-four samples of gypsum hydration water were measured in samples from the core taken at Site PI-6 in Lake Petén Itzá. The samples span the Late Glacial to early Holocene interval, between 18.5 and 10.4 ka. The measured $\delta^{18}O$ of gypsum hydration water ranged from 6.8‰ to 11‰ and $\deltaD$ from 2.1‰ to 16‰ (EA1; Fig. 8). When corrected for isotopic fractionation factors between mother water and hydration water, the $\delta^{18}O$ of paleolake water is estimated to have ranged between 4.8‰ and 7‰, relative to an average value of 2.7‰ for lake water today, and the $\deltaD$ varied from 22.5‰ to 37‰, relative to a modern average value of 15‰.

Elemental variations measured by core-scanning XRF reflect changes in the relative proportion of clay (high Ti) and gypsum (high S) (Hodell et al., 2008; Fig. 8A and B). From 18.5 to 17.5 ka, gypsum dominated and $\delta^{18}O$ and $\deltaD$ of lake water averaged ~6‰ and 7‰, respectively (Fig. 8D). Isotope values generally increase between 17.5 and 16 ka, reaching the greatest $\delta^{18}O$ and $\deltaD$ values of 7‰ and 37‰, respectively, between ~16 and 15 ka. Values of $\delta^{18}O$ and $\deltaD$ decrease during the Bolling-Allerod to 6‰ and 29‰, respectively, and sediment composition switches from gypsum to clay between 15 and 13.3 ka. At ~13.2 ka, $\delta^{18}O$ and $\deltaD$ increase to 6.5‰ and 31‰, as gypsum deposition resumed at the start of the Younger Dryas. Values gradually decrease from the Younger Dryas into the
Preboreal Period before decreasing abruptly at 10.5 ka when $\delta^{18}O$ and $\delta^D$ average 5.8$\%$ and 24.2$\%$, respectively, during the earliest Holocene.

3.4. Sediment composition and $\delta^{18}O$ of biogenic carbonate

During the Last Glacial Maximum (LGM) from ~23 to 19 ka, clay deposition prevailed, with $\delta^{18}O$ of ostracod calcite averaging 5.8$\%$ at 17 ka. An abrupt decrease of ~2.8$\%$ in ostracod calcite $\delta^{18}O$ occurred at 16.8 ka, coinciding with an increase in clay deposition that lasted until ~15.9 ka. Between 15.9 and 14.7 ka, the oxygen isotope composition of ostracod calcite was high, with $\delta^{18}O$ exceeding 6.8$\%$ and coincident with sediments dominated by gypsum. The $\delta^{18}O$ of the ostracod calcite decreased abruptly at 14.7 ka, marking the return of clay deposition during the Bolling-Allerod, which lasted until 13.0 ka. The $\delta^{18}O$ of the ostracod calcite increased and gypsum deposition returned again at the beginning of the Younger Dryas at ~13.0 ka, and lasted until the start of the Holocene at 10.5 ka when $\delta^{18}O$ decreased to 3.5$\%$, and clay deposition resumed. No gypsum was deposited in Lake Petén Itzá after 10.35 ka (Hillesheim et al., 2005). The oxygen isotope record of gastropod aragonite is spotty and, where present, values are similar to ostracods.

3.5. Paleotemperature estimates

For calcite, temperature was calculated with the equation of Anderson and Arthur (1983), using $\delta^{18}O$ of ostracod calcite and gypsum hydration water to estimate $\delta^{18}O_{\text{calcite}}$ and $\delta^{18}O_{\text{water}}$, respectively:

$$T^{\circ}C = 16 - 4.14 \times (\delta^{18}O_{\text{calcite}} - \delta^{18}O_{\text{water}}) + 0.13 \times (\delta^{18}O_{\text{calcite}} - \delta^{18}O_{\text{water}})^2$$

Late glacial temperatures were considerably cooler than the mean annual temperature of 26 $^\circ$C in the region today. During HS1 from 18.5 to 15 ka, temperatures were cool, averaging 19 $^\circ$C with minimum values of 16–17 $^\circ$C recorded between 17 and 17.5 ka (Fig. 8F). Warming occurred in the middle of HS1 at 16.9 ka when temperature rose as high as 22.3 $^\circ$C, coincident with an increase in sediment clay content. At 16 ka, temperatures cooled again to a low of 18 $^\circ$C at 15.5 ka. At 14.7 ka, gypsum precipitation ceased and sediments became dominated by clay during the Bolling-Allerod, from 14.7 to 13.0 ka. We have no temperature estimates for the periods when no gypsum was deposited, but temperatures towards the end of the B-A averaged 26 $^\circ$C. These values fall in the range of modern lake temperatures (Fig. 3). Temperatures cooled again during the Younger Dryas and Preboreal Period, from 13 to 10.5 ka. At 10.5 ka, temperatures increased to an average of 26 $^\circ$C, which is equal to the hypolimnetic temperature today.
today, temperature can exceed 30 °C in summer (Fig. 3). Gastropods can be transported from the littoral zone into deeper water by downslope processes or development of a gas bubble upon death, which is trapped inside the shell causing it to float. The greatest concentrations of gastropod shells occur during lake level lowstands when the littoral zone was closer to the coring site.

In Core PI-6 from Lake Petén Itzá, gastropods are most abundant during HS 1, where they generally record higher temperature than ostracods from the same samples. Coldest temperatures, between 16 and 20 °C, occurred early in HSI from ~18.5 to 18.0 ka. Gastropod-derived temperatures increase throughout H1, yielding a maximum of ~25 °C at 16 ka before decreasing to 22 °C at 15 ka. The occurrence of gastropods is very spotty thereafter, with a temperature of 25 °C recorded at 12 ka. One sample from the early Holocene at 10.5 ka yielded a temperature of 30 °C, which is similar to the epilimnetic summer temperature today (Fig. 8).

4. DISCUSSION

Estimation of temperature using tandem measurements of δ18O carbonate and gypsum hydration water requires several assumptions: (i) fractionation factors must be known; (ii) The isotopic signature of the gypsum hydration water must be in equilibrium with the lake water at the time of formation and no post-depositional alteration or exchange of oxygen isotopes with other minerals or pore water can have occurred; (iii) δ18O of mineral carbonate must have formed in equilibrium with the same water as the gypsum and cannot have undergone diagenetic exchange. Next, we evaluate the validity of each assumption and discuss the implications of the results with respect to paleoclimate.

4.1. Fractionation factors

The fractionation factors for oxygen and hydrogen isotopes between gypsum hydration water and mother water have been reported to be 1.004 ± 0.0002 for δ18O and 0.98 for δD (Gonfiantini and Fontes, 1963; Fontes and Gonfiantini, 1967; Sofer, 1975). The fractionation factors are not believed to be temperature-sensitive nor are they affected by the “salt effect” at ion concentrations of gypsum saturation (Sofer and Gat, 1972). We re-determined the fractionation factors by converting anhydrite to gypsum in a sealed flask containing water of known isotopic composition, in the presence of 0.5 M sodium sulfate, which acts as an activator (Conley and Bundy, 1958). The experiment was conducted at three temperatures: 12, 20 and 37 °C (Table 4), covering the complete range of past temperatures on the Yucatan Peninsula. After stirring the solution for 24 h, the gypsum was filtered, dried in a petri dish at 50 °C for one week, and hydration water was extracted and measured with the Picarro water isotope analyzer.

The fractionation factor for oxygen averaged 1.0039 ± 0.0002, which is indistinguishable from the published value of 1.004 ± 0.0002 (Gonfiantini and Fontes, 1963; Sofer, 1975). No significant temperature dependence
was found between 12 and 37 °C. An error in the fractionation factor of ±0.0002 translates into an error in δ18Owater of ±0.2, which is equivalent to ±1 °C.

The isotope fractionation factor for hydrogen isotopes during our experiment averaged 0.981 ± 0.001, which is analytically indistinguishable from the previously determined value of 0.98 (Sofer, 1975). There may be a slight temperature dependence (0.00012 per °C) but additional experiments are needed to confirm this observation.

### 4.2. Isotopic exchange and recrystallization

Post-depositional isotopic exchange of hydration water can occur if gypsum is in contact with water that is isotopically different from its hydration water. In the case of Lake Petén Itzá, the measured δ18O of the hydration water varies between 8.9‰ and 11‰, whereas the maximum pore water value is 3.7‰ (Fig. 7). The δ18O of the lake water from which the gypsum originally crystallized was 4.8‰ to 7‰ (factoring in the isotope fractionation on gypsum formation), so the gypsum is now in contact with water of a different isotopic composition. Similarly, the δD of the hydration water is significantly lower than the pore water by about 20‰ (Fig. 7). The effect of isotopic exchange would be to lower the δ18Owater, estimate from hydration water and thus increase the δ18Ocalcite-δ18Owater difference, thereby resulting in a temperature estimate that was too low.

The isotopic exchange reactions for oxygen and hydrogen isotopes between gypsum hydration water and pore water are:

\[
\begin{align*}
&\text{CaSO}_4 \cdot \text{H}_{218}^1\text{O} + \text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot \text{H}_{18}^1\text{O} + \text{H}_2\text{O} \\
&\text{CaSO}_4 \cdot \text{H}_{218}^1\text{O} + \text{HD}_{16}^1\text{O} \rightarrow \text{CaSO}_4 \cdot \text{HD}_{16}^1\text{O} + \text{H}_2\text{O}
\end{align*}
\]

The conditions governing the kinetics of these exchange reactions are not well understood, but exchange likely depends upon factors such as temperature, pressure, humidity, crystal size, time, etc. The rate of exchange and isotope fractionation are likely to be different for oxygen than hydrogen isotopes. For example, the diffusion of H216O and DH18O into the gypsum crystal would differ, as would the exchangeability and fractionation factors for oxygen and hydrogen atoms of the hydration water in the gypsum lattice. Thus, we expect that as isotope exchange proceeded, the ΔδD/Δδ18O relationship would deviate from its original value.

The oxygen and hydrogen isotopic composition of the gypsum hydration waters plot on a line that has the same slope as the evaporative line (~5), but is enriched in 18O (by ~4‰) and depleted in D (by ~20‰) due to the respective fractionation factors (Fig. 5). When measured values of gypsum hydration water are corrected for the isotope fractionation factors, the calculated lake water values plot on the projection of the evaporative line defined by regional closed-basin lakes (Fig. 6). This line describes the evolution of lake water δ18O and δD with progressive evaporation starting from modern values, and assuming evaporation under similar conditions as today. The fact that the predicted lake water values fall on the regional evaporative line, and not on a line with a different slope, lends support to the notion that hydration water has not exchanged isotopically with interstitial water.

The isotopic composition of the hydration water can also be altered by dissolution and secondary precipitation of gypsum in sediment pore waters. The hydration water of the recrystallized gypsum will have an isotopic composition in equilibrium with sediment pore waters. Assuming a δ18O and δD of pore water of 3‰ and 20‰, respectively, for the interval in which gypsum samples were measured (Fig. 7), the δ18O and δD of gypsum hydration water precipitated in equilibrium with pore water would be approximately 7‰ and 0‰, respectively. This compares with a measured mean δ18O and δD values of hydration water of ~10.1‰ and 10.6‰, respectively. If, for example, 10% of
the gypsum in a sample were derived from secondary gypsum equilibrated with pore waters, then the original \( \delta^{18}O \) would be lowered by \( \sim 0.3\%_o \), and the \( \delta D \) raised by \( \sim 1\%_o \). Such a change would result in an underestimation of the \( \delta^{18}O \) of lake water and the temperature derived from the oxygen isotope composition of calcite or aragonite would be about \( \sim 1\,^\circ C \) too cold.

Pore waters are undersaturated for gypsum at the sediment–water interface but increase rapidly to saturation within the top 10 m of sediment. Pore waters are entirely saturated in the interval measured in this study (11–21 m); thus, the amount of dissolution over this depth is likely to be minimal. Extensive recrystallization is not indicated as gypsum crystals exhibit primary features – i.e., clear, euhedral in shape, growing in clusters with swallow-tail twinning. In addition, there’s little evidence for gypsum entombing sediment as might be expected if it recrystallized in sediment pore waters.

Two other observations also argue against resetting of the isotopic composition of gypsum hydration water in Lakes Petén Itzá and Chichancanab. First, using the \( \delta^{18}O \) of gypsum and co-occurring carbonate, near modern temperatures were calculated for the early Holocene of Petén Itzá and late Holocene in Chichancanab. Second, in Section 4.6, we show that modeling of the pore water \( \delta^{18}O \) profile gives a calculated glacial lake water \( \delta^{18}O \) of 6.2\%oo, which equals the average lake water value estimated using gypsum hydration water (after correcting for isotope fractionation).

We suggest that the gypsum hydration water in Lakes Chichancanab and Petén Itzá sediment cores have retained their primary isotopic composition because: (i) the gypsum is young and is not buried deeply (<20 m), resulting in little compaction or dewatering, leading to good preservation at near-lake-bottom temperatures; (ii) sediments have been continually bathed in pore water and have never been exposed to waters (e.g., meteoric) that are vastly different isotopically or chemically (e.g., gypsum undersaturation) from the conditions under which the gypsum was originally deposited; (iii) pore waters are saturated for gypsum, thereby discouraging dissolution and re-precipitation; and (iv) gypsum grains are coarse, which impedes diffusion of water into the crystal, thereby retarding exchange reactions (Hallas and Krouse, 1982).

It has been previously assumed that gypsum retains its original isotopic composition only under arid conditions (Sofer, 1978). Here we suggest that under the right aqueous conditions, young lacustrine, and possibly marine, deposits that have been never been exposed or deeply buried may also retain their original isotopic composition. We caution, however, that Lakes Peten Itza and Chichancanab may be exceptions rather than the norm in terms of gypsum preserving the lake water signal.

### 4.3. Vital effects

The gypsum–calcite tandem method assumes that the measured \( \delta^{18}O \) of calcite or aragonite is in isotopic equilibrium with water in which it formed. Organisms often do not precipitate their carbonate in equilibrium with the host water and the offset is termed the “vital effect.” The “vital effect” of \( L. opesta \) was estimated by comparing \( \delta^{18}O \) in core-top specimens of \( L. opesta \) with the \( \delta^{18}O \) of the overlying lake water. Although specimens of \( L. opesta \) are found from the littoral zone to a maximum water depth of 160 m, living male and female specimens with well-preserved soft parts were only collected from the littoral zone to a maximum water depth of \( \sim 40 \) m, near the base of the thermocline (Perez et al., 2010). We varied the disequilibrium offset until the best match was obtained with the profile of equilibrium calcite (Fig. 9). An estimated correction of \( \sim 0.58\%_o \) was applied downcore to all \( \delta^{18}O \) measurements of \( L. opesta \) to derive the value of equilibrium calcite. The estimate could be improved by culturing \( L. opesta \) in the laboratory to determine the offset from oxygen isotope equilibrium.

Aragonite disequilibrium was assessed for gastropods by comparing \( \delta^{18}O \) in core-top specimens of \( Cochliopina \), and \( Pyrgophorus \) with equilibrium \( \delta^{18}O \) values calculated with temperature and \( \delta^{18}O \) of modern lake water. We found that both \( Cochliopina \) and \( Pyrgophorus \) precipitate aragonite in near isotopic equilibrium with lake water (Fig. 9). Both snail species are gill-breathing gastropods (i.e., Prosobranchia – Hydrobiidae) and this group has been reported to precipitate aragonite in the range of predicted equilibrium (Shanahan et al., 2005). Similarly, Curtis et al. (1998) found that \( Cochliopina \) and \( Pyrgophorus \) precipitated aragonite in near oxygen isotope equilibrium based on comparison of core-top specimens in Lake Petén Itzá; therefore, no correction was applied.

### 4.4. Comparison with other paleotemperature estimates

Paleotemperature has been estimated using pollen in sediment cores from Lake Petén Itzá (Bush et al., 2009) and nearby Lake Queexil (Leyden et al., 1993, 1994). The stratigraphy of the Lake Queexil core was reinterpreted in light of the more detailed radiocarbon chronology in Petén Itzá cores (Bush et al., 2009). Vegetation during the LGM consisted of a pine-oak forest, reflecting an estimated cooling or 3–5 \(^\circ C\) relative to present. We have no isotope-based temperature estimate for the LGM because deposits of the time period lack gypsum. The deglacial period represented the coldest, driest conditions for which Leyden et al. (1993) estimated a cooling of 6.5–8 \(^\circ C\) relative to today. This estimate is similar to the 6–10 \(^\circ C\) cooling suggested from ostracod calcite and slightly less than the cooling inferred from gastropod aragonite (Fig. 8). The lower temperature estimates derived from benthic ostracods probably reflect cool hypolimnetic temperature, which are set during winter isothermy. The oxygen isotope temperature estimates suggest that hypolimnetic and epilimnetic temperatures rose to 26 and 30 \(^\circ C\), respectively, in the early Holocene, which is consistent with the modern lake temperature profile during summer stratification (Fig. 3).

Additional evidence for cooling during the last glacial period comes from the Guatemalan highlands (Altos de Cuchumatanes), which hosted a \(~ 60 \) km² ice cap above 3400 masl (Roy and Lachniet, 2010). Although there are no dates on the moraines resulting from this glacial
advance, the estimated equilibrium line altitude was lowered to 1100–1435 m, which has been calculated to be equivalent to 5.9–7.6 °C of cooling. This falls within the range of glacial temperatures estimated by pollen and oxygen isotope paleothermometry.

We compared our estimated temperature from Petén Itzá at 17°N with two SST records estimated using Mg/Ca of the foraminifer *Globigerinoides ruber*, one from the Cariaco Basin at 11°N (Lea et al., 2003) and the other from the Orca Basin in the Gulf of Mexico at 27°N (Williams et al., 2010) (Fig. 10). Although Petén and Cariaco temperatures agree for the early Holocene, the two records diverge greatly during the Late Glacial when ostracod-inferred temperatures from Petén Itzá were significantly colder than Cariaco SST estimates. This discrepancy illustrates the well-known problem, i.e. that temperature proxies for the last glacial period from terrestrial archives yield much colder estimates than those from marine sediment records (for a review, see Rind and Peteet, 1985; Colinvaux et al., 1996). Comparison of Petén Itzá lake temperature with SST from the Gulf of Mexico yields better agreement between absolute temperatures, although minimum ostracod-derived temperatures in Petén Itzá are still lower than those from the Orca Basin (Fig. 10).

Some land-sea temperature differences are to be expected, as the land surface often undergoes larger temperature changes than those of the surrounding oceans (Joshi et al., 2008); however, the differences between Cariaco and Petén are too large to be explained entirely by physical climate processes. Either the marine temperature proxies underestimate the degree of cooling or terrestrial proxies overestimate it, or both. Seasonality is likely an important cause of the discrepancy. For example, some terrestrial proxies may be biased towards the cold season, whereas...
marine proxies may have a warm-season bias. In Lake Petén Itzá, temperatures estimated using benthic ostracods likely record winter conditions because hypolimnetic temperatures reflect those of the water column during winter isothermy. Only epilimnetic waters warm during summer stratification. Gastropods, on the other hand, live above the thermocline and therefore generally record warmer temperatures than ostracods. Because our method can only be applied when gypsum and calcite co-occur in the sediment, we only report temperature estimates for the coldest, driest conditions, when lake water is saturated for gypsum. The Mg/Ca data from the Cariaco and Orca Basins were measured on G. ruber, which generally records mean annual temperature, except in the higher latitudes and upwelling regions. During the glacial, it may have calcified in the warm season. There may also be a significant salinity effect on Mg/Ca values that has not been accounted for. In the modern ocean, shell Mg/Ca ratios are significantly elevated above expected values in the saline subtropical gyres (Arbuszewski et al., 2010). Prell et al. (1976) reported that the planktonic foraminifer assemblages in the glacial Caribbean resembled some of those of the subtropical gyre today, suggesting greater salinity. Applying a salinity correction to the Cariaco Mg/Ca data would lower the glacial SST estimates, thereby reducing the apparent offset with Petén Itzá temperatures (Fig. 10).

4.5. Paleolake water δ18O, δD and d-excess

The power of the tandem gypsum–calcite δ18O approach is that it provides a direct measure of the δ18O and δD of paleo-lake water, and permits deconvolution of the δ18O calcite signal into its temperature and δ18Owater components. It also allows calculation of another environmental parameter from the paleo-lake, the deuterium excess (d-excess = δD – 8×δ18O) (Craig, 1961). Changes in the δ18O and δD of lake water are controlled by the balance between water input and evaporative loss from a lake, and the δ18O of precipitation in the drainage basin. Increased evaporative loss from the lake surface leaves the residual water enriched in D and 18O, evolving along an evaporative line in δD–18O space. The d-excess reflects the deviation from the global meteoric water line, with lower values resulting from increased evaporation. Isotopic fractionation during evaporation of water from the lake surface is affected by temperature, wind speed, salinity, and most importantly, humidity. Many factors can affect the δ18O and δD of precipitation, including the isotopic composition at the source, distance of transport, and the temperature and amount of rainfall. The moisture source for Petén is the Caribbean, where surface water was enriched in δ18O by >1.2‰ during the glacial period because of increased ice volume.

In the case of Chichancab, the estimated δ18O and δD of lake water during the terminal Classic drought was between 3.5‰ and 4.0‰ and δD from 11.3‰ to 17.0‰, respectively, compared to modern δ18O and δD values of 2.8‰ and 12.3‰ respectively. Lake water δ18O was enriched by about 1.0‰ during the drought, which is supported by gypsum deposition at that time. Because the calculated temperature was the same as today during the terminal Classic Period, the entire δ18O increase of 1.0‰ is attributed to an increase in the δ18O of lake water as a result of increased E/P. This interpretation is supported by d-excess that averaged −14 for the terminal Classic Period compared to a value of −10 today (Fig. 8).

For Lake Petén Itzá, the Late Glacial and early Holocene values were 2–4‰ enriched in δ18O and 10–24‰ enriched in δD with respect to modern values. d-excess varied between −22 and −16 (Fig. 8), which is considerably less than the modern value of −6. Variations in the δ18O of lake water generally follow the δ18O of ostracod calcite, but there are some notable differences resulting from varying temperature effects. For example, the time periods of the most positive values of δ18O and δD of lake water occurred between ~16 and 15 ka and at the beginning of the Younger Dryas at ~13 ka. Lake-water δ18O and δD decreased during the earlier Holocene, but was still enriched in the heavier isotope relative to today’s values of 2.7‰ and 15.0‰, respectively, indicating that a ~2‰ decrease in δ18O occurred in the Holocene, most likely between ~7 and 5 ka (Curtis et al., 1998).

Because climate oscillated between warm-wet and cold-dry conditions, the temperature and δ18Owater effects were additive in the δ18O calcite signal. The total range in calcite δ18O over the deglacial period was ~3.5‰ (i.e., greatest values at ~15.5 ka minus the values at 10.4 ka), whereas the range in δ18O water was ~2‰. This means ~1.5‰ can be attributed to temperature change between 15.5 and 10.4 ka, or about 6°C. Although proportions of the δ18Owater and temperature signal vary from one event to another, about half of the change in the ostracod δ18O was due to temperature and the half can be attributed to δ18Owater.

4.6. Glacial δ18O and δD from sediment pore fluid profiles

An independent approach to calculating the δ18O and δD of the paleo-lake water can be made through diffusive-advective modeling of the isotope composition of the water in the pore fluid. The approach is similar to the method used for calculating the δ18O and δD of the deep ocean at the last glacial maximum using changes in the δ18O and δD of sedimentary pore fluids (e.g., McDuff, 1984; Schrag and DePaolo, 1993; Schrag et al., 1996, 2002; Adkins et al., 2002). The equation for the movement of a fluid through sedimentary pore space via diffusion and advection, following the seminal work by Berner (1980) and based on the law of mass conservation, is (for δ18O but analogous for δD):

\[
\phi(z) \frac{\partial (\delta^{18}O)}{\partial t} = \frac{\partial}{\partial z} \left( \phi(z) D(z) \frac{\partial (\delta^{18}O)}{\partial z} \right) - \frac{\partial}{\partial z} (\phi(z) \omega(z) \delta^{18}O(z))
\]

where \( \phi \) is sediment porosity, \( \omega \) is advection in units of length per time, \( D \) is the diffusion coefficient for H2O. This equation describes the movement of water through sedimentary pore fluids through diffusion (the first term) and advection (largely through compaction, the second term). The model was initialized for 100-kyr with a constant δ18O with depth and fixed boundary conditions (upper boundary δ18O = 2.6‰ and δD = 15‰lower boundary δ18O = 1.5‰ and δD = 7‰, as per the data). After the pore
fluid water isotopes had reached steady state, the upper boundary condition was forced using a 100-kyr forcing for one glacial-interglacial cycle for the oxygen and hydrogen isotope composition of the lake water with a minimum of 2.6‰ for δ18O and 15‰ for δD (modern values) and a maximum at the LGM of 3.5‰ for δ18O and 20‰ for δD. The forcing function mimicked the evaporation/precipitation changes inferred by Hodell et al. (2006) and Escobar (2010); that is, the δ18O and δD increased in value until ∼50 ka, then remained relatively high until 18 ka, then decreased to modern values by 6 ka. Fig. 11 shows these forward model results, indicating the pore fluid isotope data are consistent with an average glacial δ18O value of 6.2‰ and δD of 31‰. These estimated values are in good agreement with the average δ18O and δD values of lake water calculated from measurement of gypsum hydration water. The millennial-scale variations in δ18O and δD of lake water recorded in hydration water (Fig. 8) have been smoothed out in the pore water profiles by diffusion.

4.7. Paleoclimate implications

In general, temperature and rainfall were tightly coupled during the Late Glacial, as indicated by synchronous changes in δ18O, δD and temperature (Fig. 8). Climate alternated between cold-dry and warm-moist conditions, which is not surprising considering water vapor pressure increases non-linearly with temperature, according to the Clausius-Clapeyron equation. In addition, Folkins and Braun (2003) proposed a SST threshold for tropical convection, with no observed dependence between tropical rainfall and SST in the range from 19 to 26 °C, followed by an abrupt increase by a factor of 5 as SSTs increase from 26 to 29 °C (see also Johnson and Xie, 2010). In the Caribbean and Mexico, convection and precipitation are tightly coupled and related to the seasonal development of the Atlantic warm pool (Wang and Enfield 2001, 2003), when temperatures exceed 28.5 °C during late summer. A large warm pool leads to an increase in rainfall in the Caribbean and Mexico. Petén Itzá at 17° N is particularly sensitive to convective threshold effects because it is close to the boundary between the convective tropics, marked by persistent deep convection, and the subtropics, marked by no deep convection (Seager et al., 2000). We suggest that rainfall during the Late Glacial and early Holocene was linked to Caribbean SST. When SST fell below a critical threshold for tropical convection (∼26 °C), such as during HSI and the Younger Dryas, aridity abruptly increased in the Petén owing to increased stability of the troposphere. During the Bolling-Allerod and Holocene, the minimum SST threshold for convection was surpassed, resulting in atmospheric instability and increased rainfall. The ultimate cause of temperature and precipitation changes in the circum-Caribbean may have been related to freshwater forcing to the North Atlantic and Gulf of Mexico during the last deglaciation, which affected Atlantic Meridional Overturning Circulation, sea ice extent, and the position of the Atlantic Intertropical Convergence Zone (Hodell et al., 2008).

5. CONCLUSIONS

With carefully selected samples, tandem measurements of δ18O of biogenic carbonate and gypsum hydration water offer a potential means for reconstructing past lake water temperature, δ18O, δD, and d-excess. The method permits deconvolution of the δ18O signal of biogenic or authigenic carbonate into its temperature and δ18Owater components. Proof of the method is offered by the calculation of modern lake temperatures for both a 1200-yr gypsum deposit in Lake Chichancanab and early Holocene gypsum beds in Lake Petén Itzá. Further support is lent by the observation that δ18O and δD of gypsum hydration water falls on a projection of the evaporative line derived for extant regional lakes. The estimated mean glacial δ18O and δD values based on modeling of pore water profiles are consistent with the average values derived from gypsum hydration water.

The last deglaciation between ∼19 and 10 ka was a time of major reorganization of Earth’s climate system, yet little is known about the magnitude and temporal pattern of temperature change in the tropics. The gypsum–calcite δ18O record from Petén Itzá provides a temperature history for the last deglaciation in the lowland Neotropics at 17° N, 90° W. Temperature inferred from ostracod δ18O during the Late Glacial period (18–10.7 ka) averaged ∼19 °C
(range 16–23 °C), which is 7 °C cooler than MAT today (~26 °C). These estimates are similar to cooling inferred from pollen and depression of equilibrium line altitude of glaciers. Terrestrial estimates for cooling are significantly greater than those inferred from Mg/Ca in the Cariaco Basin and somewhat greater than temperatures inferred from the Orca Basin, Gulf of Mexico. By 10.5 ka in the early Holocene, Lake Petén-Itzá temperatures had risen to near modern values.

We suggest the numerous rapid switches from cold-arid to warm-moist climate in the Late Glacial and early Holocene may have been caused by a convective threshold effect related to Caribbean SST, and ultimately forced by freshwater routing that affected Atlantic Meridional Overturning Circulation, sea ice extent, and the position of the Atlantic Intertropical Convergence Zone (Hodell et al., 2008).

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.gca.2011.11.026.

REFERENCES


Oxygen and hydrogen isotopes of gypsum hydration water


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