Glendonites as Paleoclimatic and Paleoceanographic Indicators: A Case Study from the Glacially Influenced Permian System of Eastern Australia*

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Abstract

Glendonites, pseudomorphs after ikaite ($CaCO_3$. $6H_2O$), feature prominently in Permian glaciomarine strata of eastern Australia. Because ikaite formation requires near-freezing temperatures, high alkalinity, and elevated orthophosphate, the presence of glendonites implies a particular array of paleoenvironmental conditions. The utility of glendonites as paleoenvironmental proxies was assessed via petrographic and isotopic study. The glendonites possess a granular internal fabric consisting of concentrically zoned calcite grains that "float" in a matrix of enclosing calcite cements. The zoned calcite grains represent the ikaite replacement phase, based on the ubiquitous presence of such grains in modern and ancient glendonites from many localities and their petrographic relationships with enclosing phases. The ikaite replacement phase possesses the highest $\delta^{18}O$ and lowest $\delta^{13}C$ values, which lie at one end of a trend toward progressively lower $\delta^{18}O$ and higher $\delta^{13}C$ values of enclosing phases. The low $\delta^{13}C$ values implicate organic matter, and possibly methane, as the main carbon source for ikaite precipitation.

The results are consistent with observations from the modern, which suggest that ikaite is an early diagenetic phase that forms in the zone of suboxic diagenesis in organic matter (OM) rich sediments. Given ikaite's proclivity for forming in OM-rich sediments, glendonites may be considered useful indicators of paleoproductivity, paleo-upwelling, and potential hydrocarbon source rocks. In addition, the $\delta^{13}C$ values from the ikaite replacement phase may also be useful indicators of the presence or absence of paleomethane seeps. Interpretations of oxygen isotope data from the ikaite replacement phase reflect precipitation from cold waters, but more quantitative interpretations are encumbered by assumptions about temperature and fluid composition.

Glendonites as paleoclimatic & paleoceanographic indicators:

a case study from the glacially influenced Permian System of eastern Australia

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Notes by Presenter Follows

1

Glendonites are calcite pseudomorphs after ikaite ($CaCO_3 \cdot 6H_2O$)

- **Where?**
  - High latitude shelves, deep sea, alkaline lakes
  - Neoproterozoic - Recent
- **How?**
  - Displacive growth below sediment-water interface
- **Conditions?**
  - Cold temps. (<7°C)
  - High alkalinity (10 x SW)
  - High orthophosphate (>50 x SW)

Ikaite from Kola Peninsula, Russia

Notes by Presenter: Purpose of this slide is to let people know what glendonites are, where it's found forming in nature, and the conditions that favor precipitation. It is also important to point out that glendonites are known from the Neoproterozoic to Recent.

Because the focus here is on the forms that grow displacively in unconsolidated sediment, I'm leaving off mention of tufa towers.

1

Glendonites can be most prominent form of $CaCO_3$ in high-latitude shelf deposits

- Presence alone indicates near-freezing depositional conditions

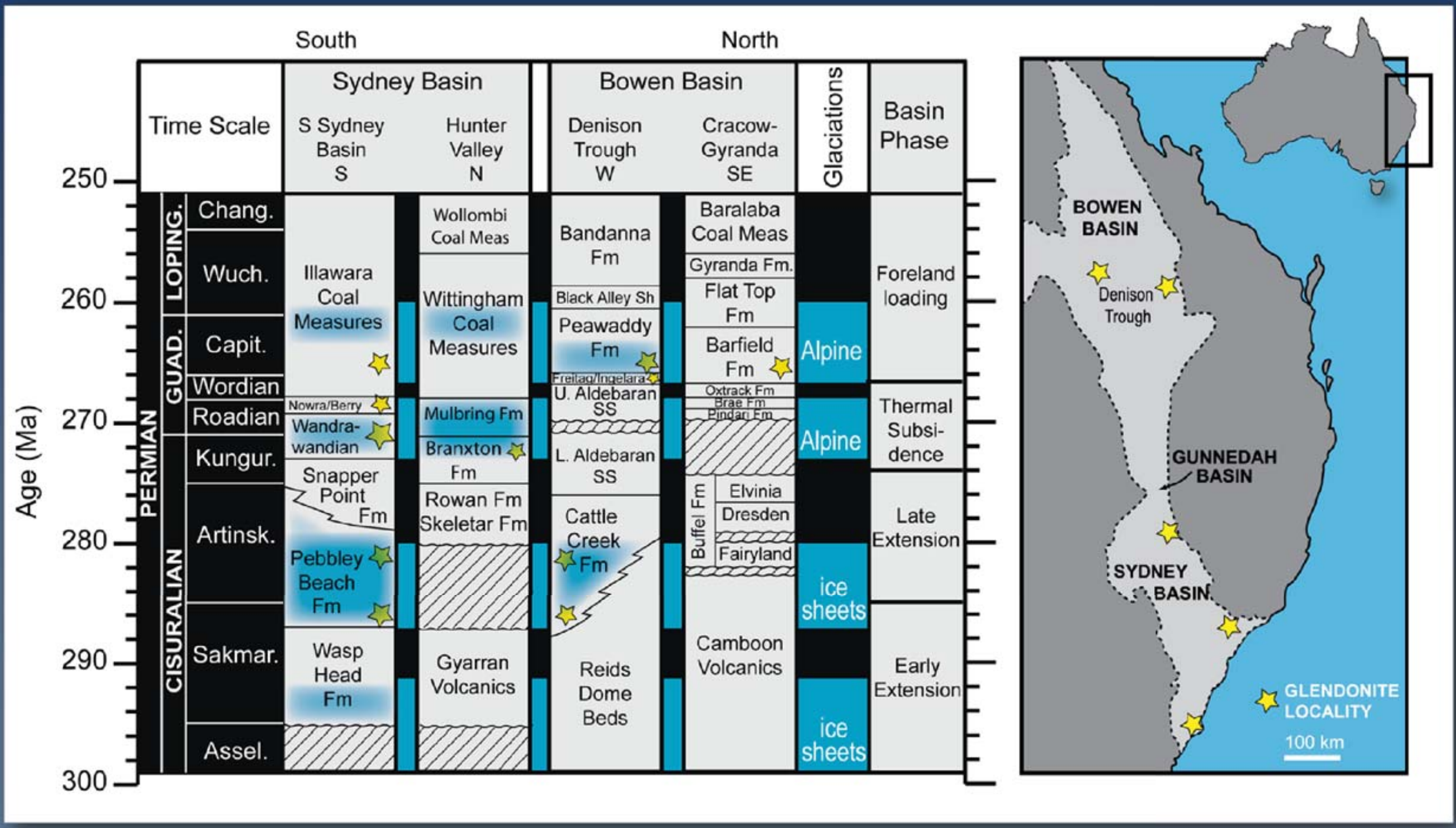
What can isotopic data tell us about seafloor temperature, seawater composition, depositional setting?

Notes by Presenter: Glendonites can be the most prominent form of carbonate in high-lat shelf deposits - this is the case in the Permian System of eastern Australia.

Given this, the purpose of this study is to explore the significance of carbon and oxygen isotopic data from glendonites in terms of seafloor temperature, seawater composition, and depositional setting.

The Permian system of eastern Australia contains abundant large glendonites and provide an ideal test case.

Permian System, eastern Australia



Eastern Australian glaciations from Fielding et al. (2008)

Notes by Presenter: This is a generalized stratigraphy for NSW and QLD.

The blue smudgy bars indicate formations that are glacially influenced.

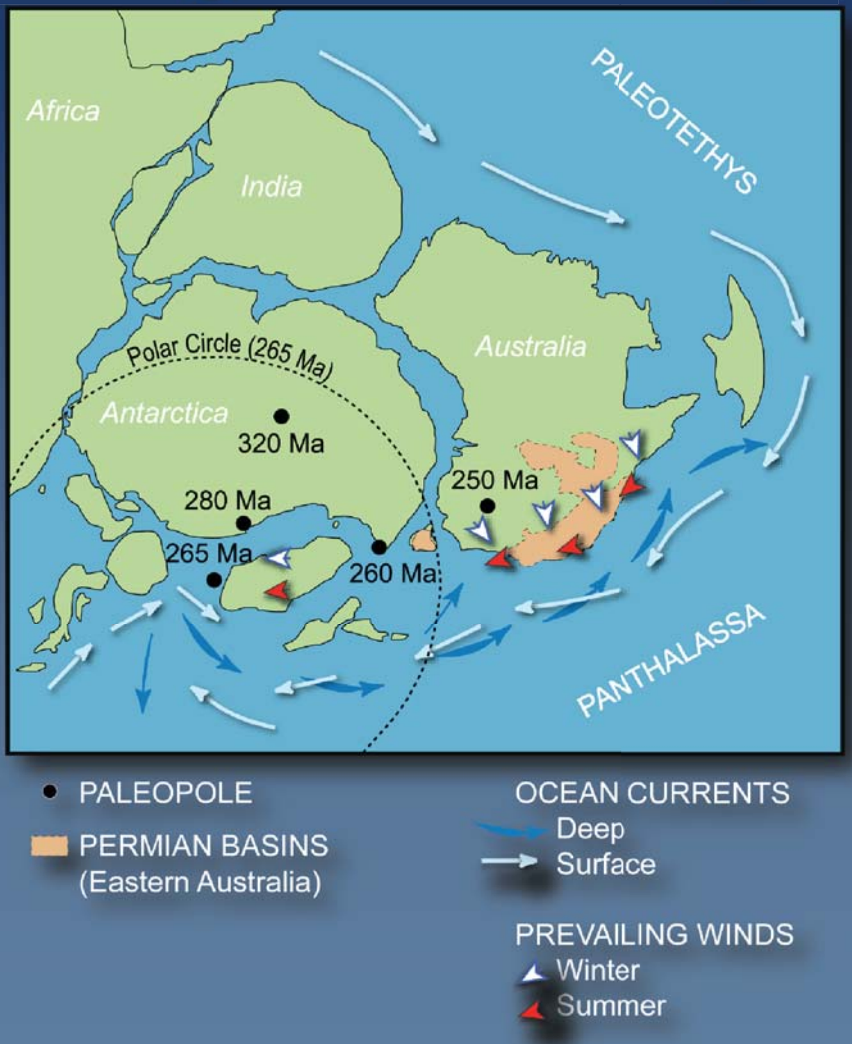
The stars indicate glendonites - note these occur in glacially-influenced deposits, as also indicated by outsized clasts, etc. Note P1-P4 glacials and inferred glaciation style. Intervening "non-glacial" intervals show no evidence of glaciation (warmer conditions inferred).

Acme of LPIA is in early Permian, with evidence for widespread ice. Glaciation wanes in P3 and P4 to alpine-style.

Glendonites occur in glacial units and are often associated with ice-rafted debris.

The glendonites are largest and most abundant in the south, and become smaller and less abundant toward the north (toward paleoequator). IRD shows the same trend.

Regional setting



Notes by Presenter: Glendonite-bearing strata accumulated throughout the BGSBS, which formed in temperate to polar latitudes along the southeast margin of Gondwana.

Depositional environment was an open marine shelf that faced the Panthallassan Ocean.

The margin was subject to upwelling, as indicated by high OM contents and the presence of phosphate. Upwelling was likely maintained year-round by offshore wind systems.

Wind and current systems are based on paleoclimate models of Winguth et al. (2002) for ocean currents and Gibbs et al. (2002) for winds.

Glendonites occur mainly in dark, fine-grained, offshore-shelfal facies

- Sparse open marine fauna
- *Zoophycos* ichnofacies
- Ice-rafted debris
- Organic C
  2.6 ± 2.1 wt%
  (n=85)

**Notes by Presenter: OM data are from Birgenheier (2007) – her thesis. Outcrop locality is Cabbage Tree Pt; this is a vertical cliff face.
Open marine fauna include brachiopods, crinoids, and corals.**

Three distinct morphologies

Mudstone
Silty fine sandstone

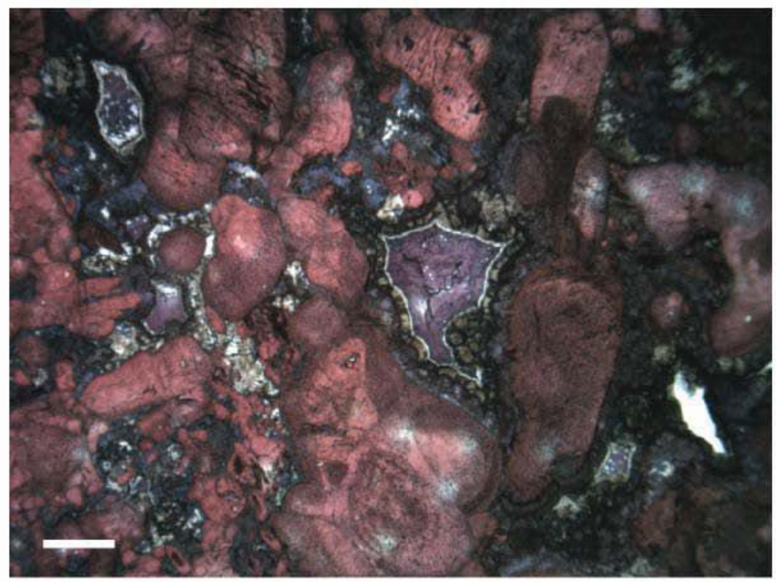
Sandy mudstone
Fine sandstone

Notes by Presenter: The rosette and blade are from the Wandrawandian; the stellate form is from the Pebbley Beach.

In thin section, glendonites possess granular texture

Inclusion-zoned, equant to bladed calcite grains enclosed by cements

Plane-polarized, transmitted light
Scale = 500 μm



Plane-polarized, transmitted light
Stained
Scale = 500 μm

Wandrawandian Siltstone (NSW)

Notes by Presenter: Glendonites are characterized by a granular texture, consisting of inclusion-zoned, equant to bladed calcite that “float” in a matrix of radiaxial fibrous, spherulitic, blocky, and poikilotopic calcite. Some samples contain minor chalcedony and pyrite cements.

Staining at right is Alizarin Red S and potassium ferricyanide.

Inclusion-zoned, equant to bladed calcite common to all samples

Plane-polarized, transmitted light
Scale = 250 μm

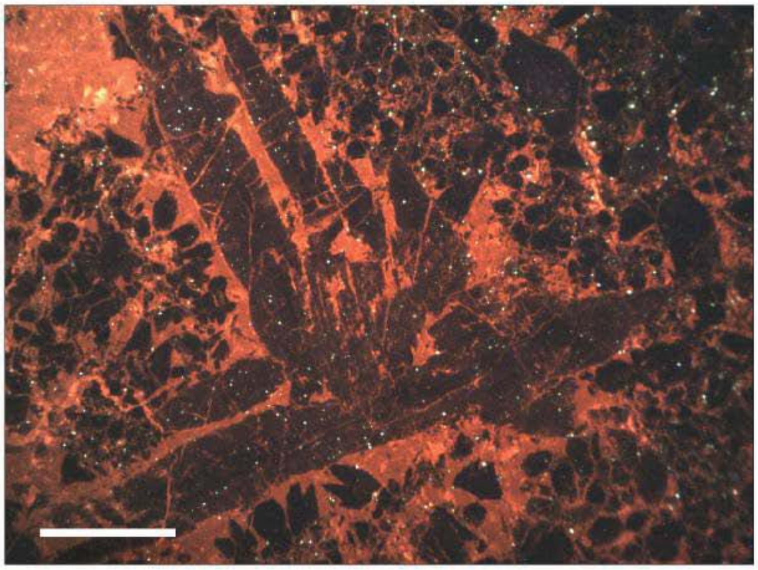
Barfield Formation (QLD)

Notes by Presenter: Among the Permian examples studied here, the light brown, equant to bladed, inclusion-zoned calcite is common to all samples. The characteristics of the enclosing cement phases vary locally.

A literature search shows that light brown, inclusion zoned calcite is commonly found in glendonites from numerous localities, both modern and ancient.

Inclusion-zoned, equant to bladed calcite is nonluminescent

Plane-polarized, transmitted light
Scale = 500 μm

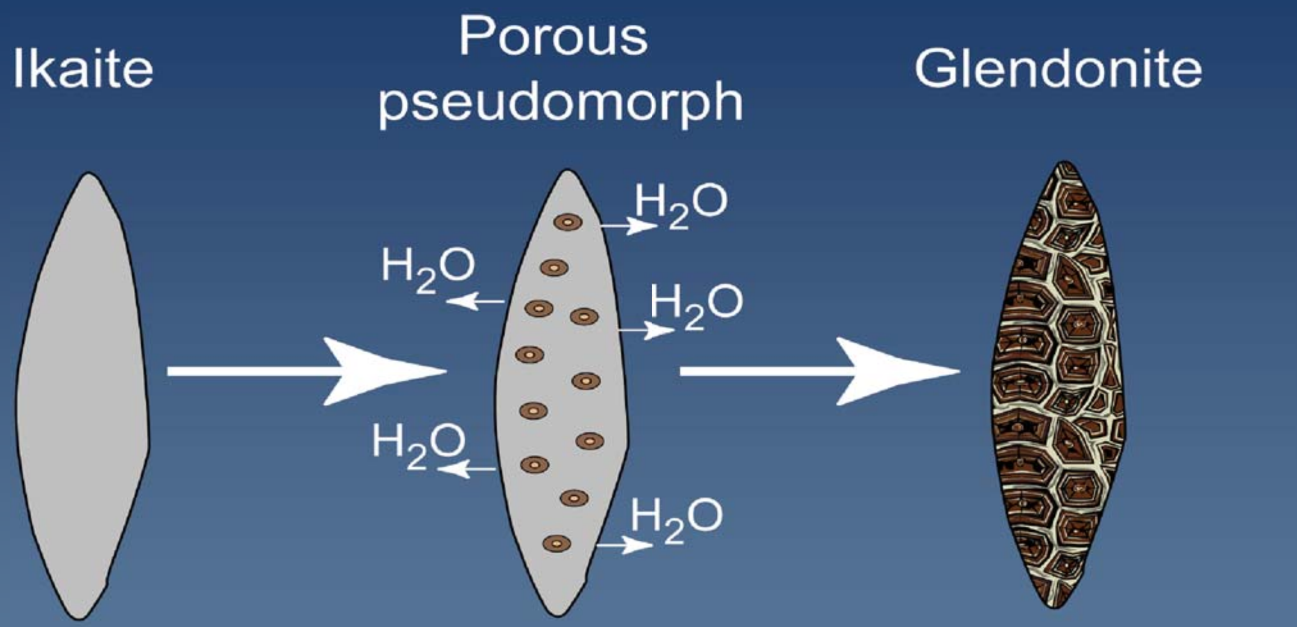


Cathodoluminescence
Scale = 500 μm

Branxton Formation (NSW)

Notes by Presenter: The inclusion-zoned, equant to bladed calcite is nonluminescent; enclosing cements tend to be dully to brightly luminescent.

Inclusion-zoned grains represent ikaite decomposition product



Equant to bladed, inclusion-zoned grains form

Cement phases over-grow inclusion-zoned grains, fill remaining pore space

Notes by Presenter: The point of this diagram is to explain that we think the bladed to equant inclusion zoned grains are the ikaite decomposition product. Why do we think this? this type of phase is common in glendonites from various settings and parts of the geologic record, and (2) enclosing cements occur as overgrowths on the inclusion-zoned grains, suggesting that the grains represent the first stage in glendonite paragenesis. To explain the preservation of the pseudomorph morphology in the sediment column despite the loss of solid framework during the transition process, Larsen (1994; his figure 12) proposed a model in which water released from the decomposing ikaite creates a positive pressure that keeps the void from collapsing. The end result of the transformation process is a porous pseudomorph supported by an open latticework of the ikaite replacement phase; namely, inclusion-rich equant to bladed calcite crystals. The porosity is subsequently filled with cement phases that overgrow the replacement phase to form the sparry matrix observed in ancient glendonites. The petrography and timing of emplacement of the enclosing cements are expected to vary locally as a function of the burial history of the host strata and the composition of fluids that pass through the rocks. This interpretation explains why the petrography of the cement matrix in which the inclusion-zoned calcite crystals “float” differs significantly from site to site.

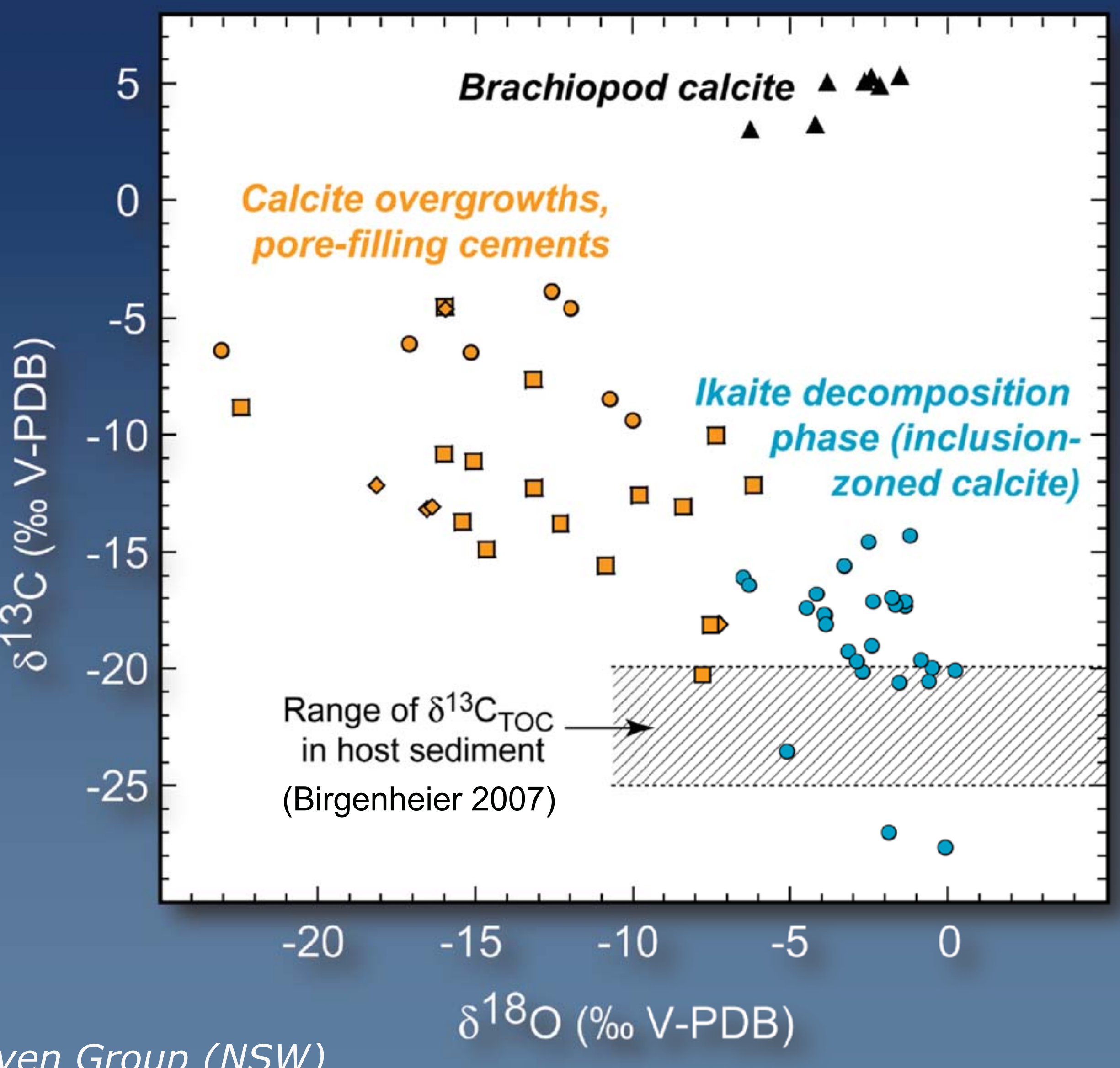
Approach

- Microscope-mounted drilling system (500 micron bits)
- Microsampling done on billets of thin sections used in petrographic analysis
  - Ikaite decomposition phase
  - Enclosing cements
  - Nonluminescent brachiopod calcite
- Some physical mixing unavoidable

Notes by Presenter: These are some notes on the sampling approach. The idea here is to explain that the sampling was done on billets of thin sections used in petrographic analysis. This allowed us to cross-check and determine exactly what we sampled.

We targeted - ikaite decomposition phase, the various enclosing cements, and nonluminescent brachiopod calcite. All are from the Shoalhaven Group, which contains the best examples of glendonites.

Some physical mixing was unavoidable due to the small size of individual phases.



Shoalhaven Group (NSW)

Notes by Presenter: The isotopic results.

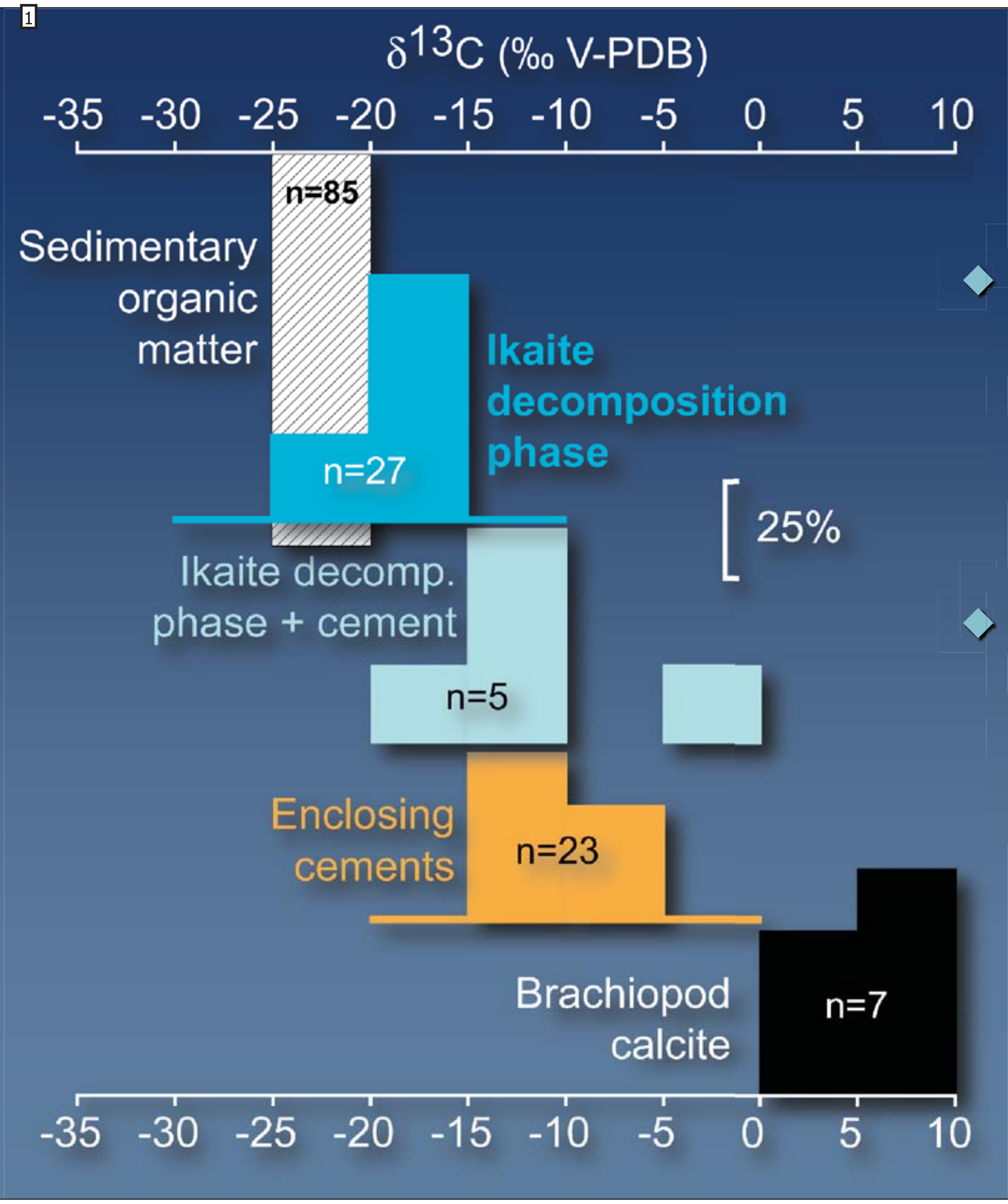
Note that best preserved brachs have d18O value of around -1, d13C values of around +5.

Note range of d13C and d18O values in ALL glendonite phases (orange + blue).

Note that ikaite decomposition phase has the highest d18O and lowest d13C values.

d18O values consistent with precipitation from colder or 18O-enriched waters (seawater) – compare to brachs (a bit higher, so at least 5°C lower) d13C values overlap with values for bulk organic matter in host sediment (data from Lauren's thesis).

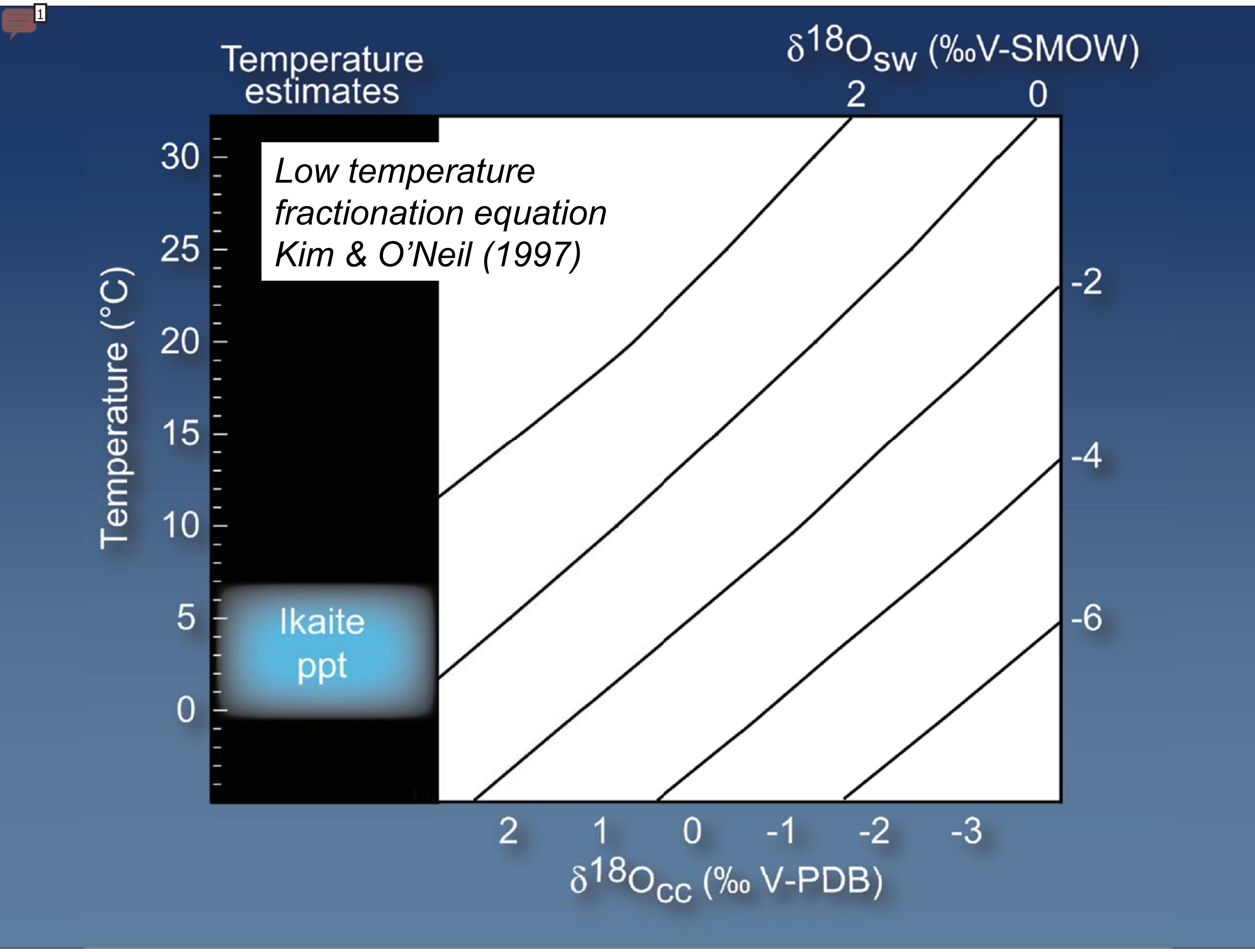
Lower d18O values of overgrowths consistent with emplacement during later phases of diagenesis at higher temperatures and/or from fluids depleted in 18O.



- Main carbon source is sedimentary organic matter
- Early diagenetic formation in zone of suboxic-anoxic diagenesis

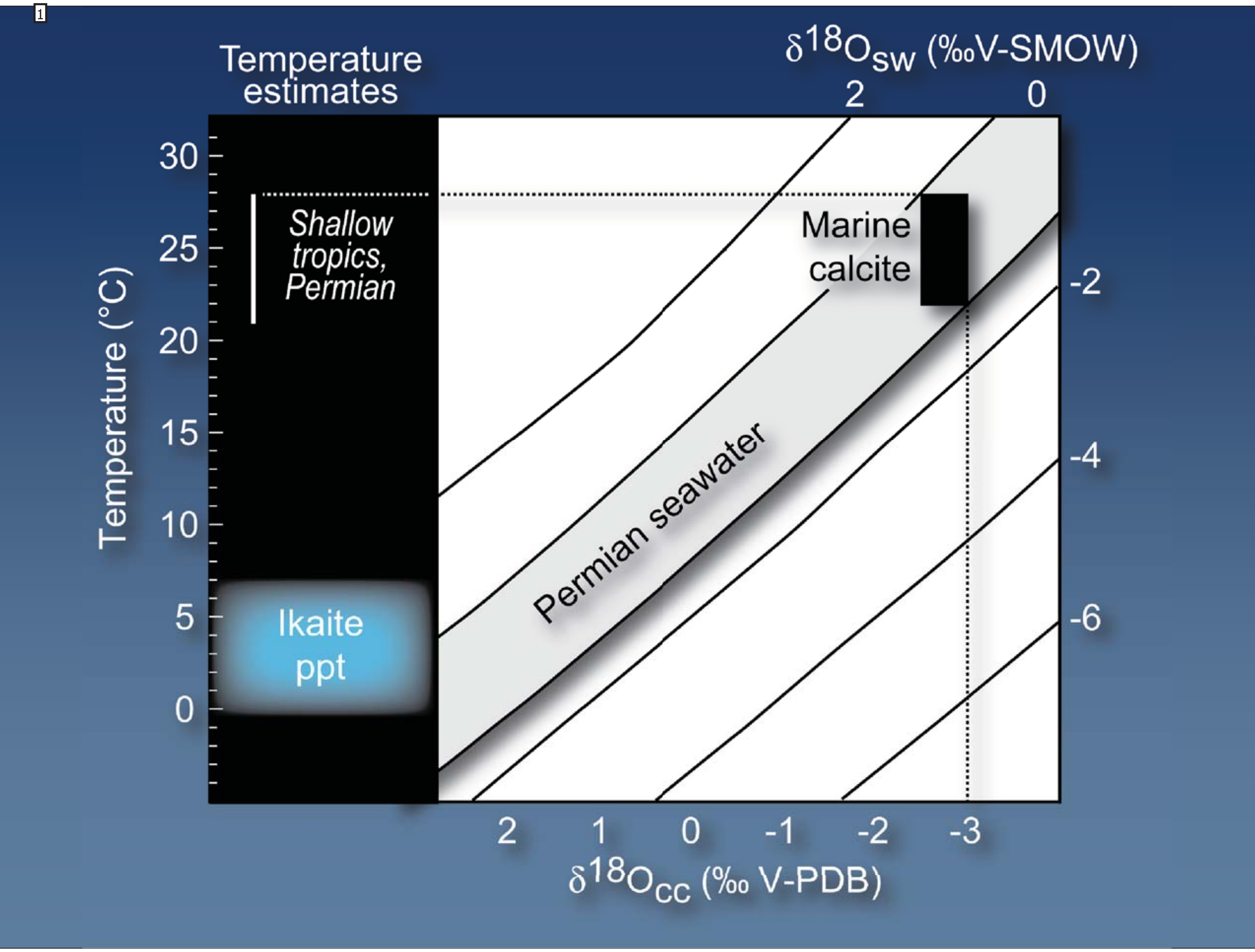
Notes by Presenter: Histogram summary of d13C data. The main points are that the d13C values of the ikaite decomposition phase are similar to compositions of sedimentary OM, and very different from d13C value of marine carbonate (brach data). This implicates OM as the main carbon source.

We suggest formation during early diagenesis in the zone of suboxic-to-anoxic diagenesis, where alkalinity and orthophosphate necessary for ikaite stability are released during microbial OM degradation.


Temperature estimates
δ18Osw (‰V-SMOW)
2
0
-2
-4
-6
Low temperature fractionation equation Kim & O'Neil (1997)
Temperature (°C)
30
25
20
15
10
5
0
Ikaite ppt
2
1
0
-1
-2
-3
δ18Occ (‰ V-PDB)

Notes by Presenter: Equilibrium d18O values for calcite and water between –1 and 32°C, calculated using the low-temperature calcite-water oxygen isotope fractionation equation of Kim and O’Neil (1997).

Temperature estimates at left, shown here the range of temperatures under which natural ikaite has been found forming.



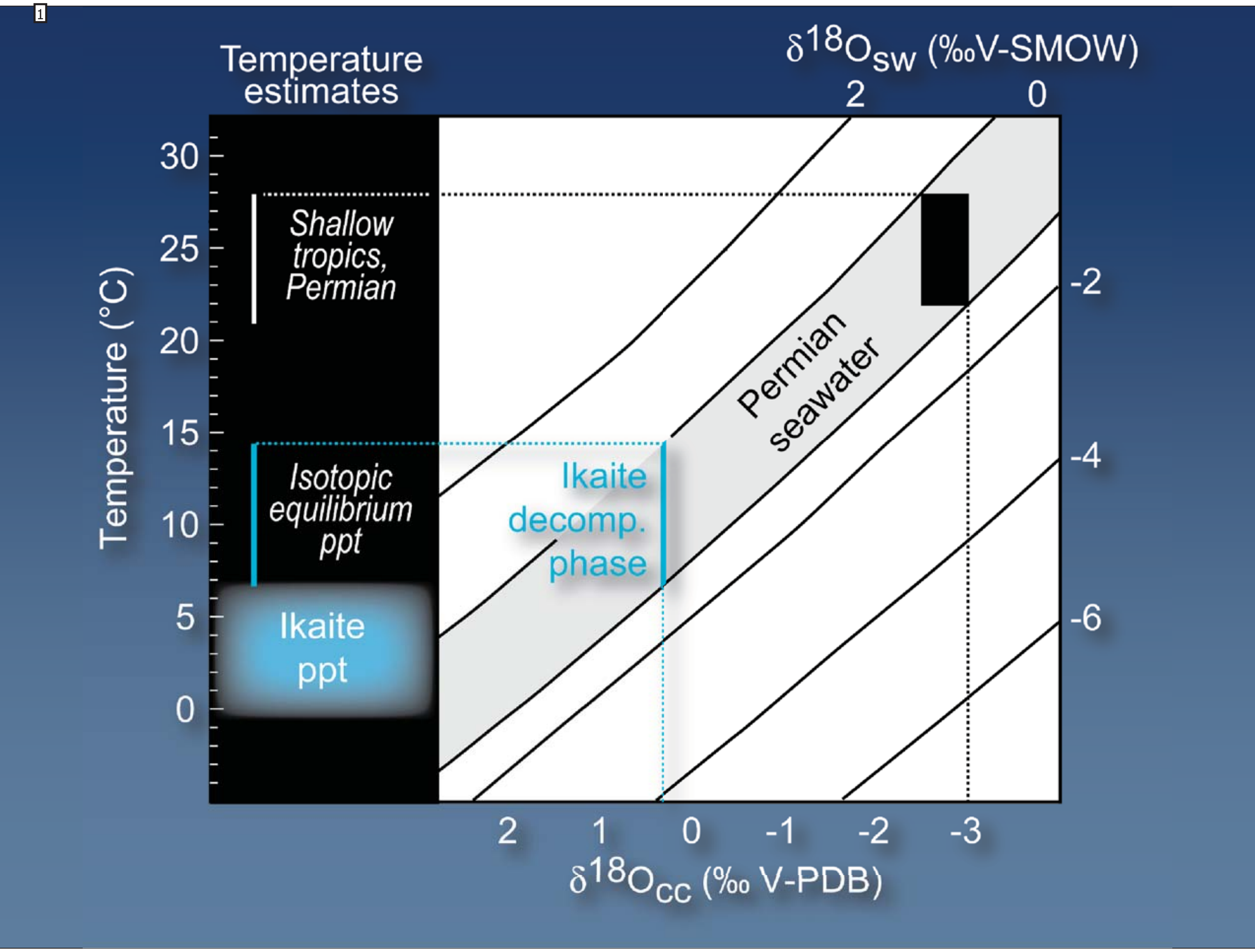
Temperature estimates
δ18Osw (‰V-SMOW)
2
0
30
25
20
15
10
5
0
Temperature (°C)
Shallow tropics, Permian
Marine calcite
Permian seawater
Ikaite ppt
-2
-4
-6
2
1
0
-1
-2
-3
δ18Occ (‰ V-PDB)

Notes by Presenter: We assume that ikaite formed and decomposed in the presence of seawater; so the next step is to estimate the composition of Permian seawater.

Field (black rectangle) representing Permian marine calcite based on data from well-preserved tropical Permian brachiopods (Korte et al. 2005) and reef cavity cements (Given and Lohmann 1985).

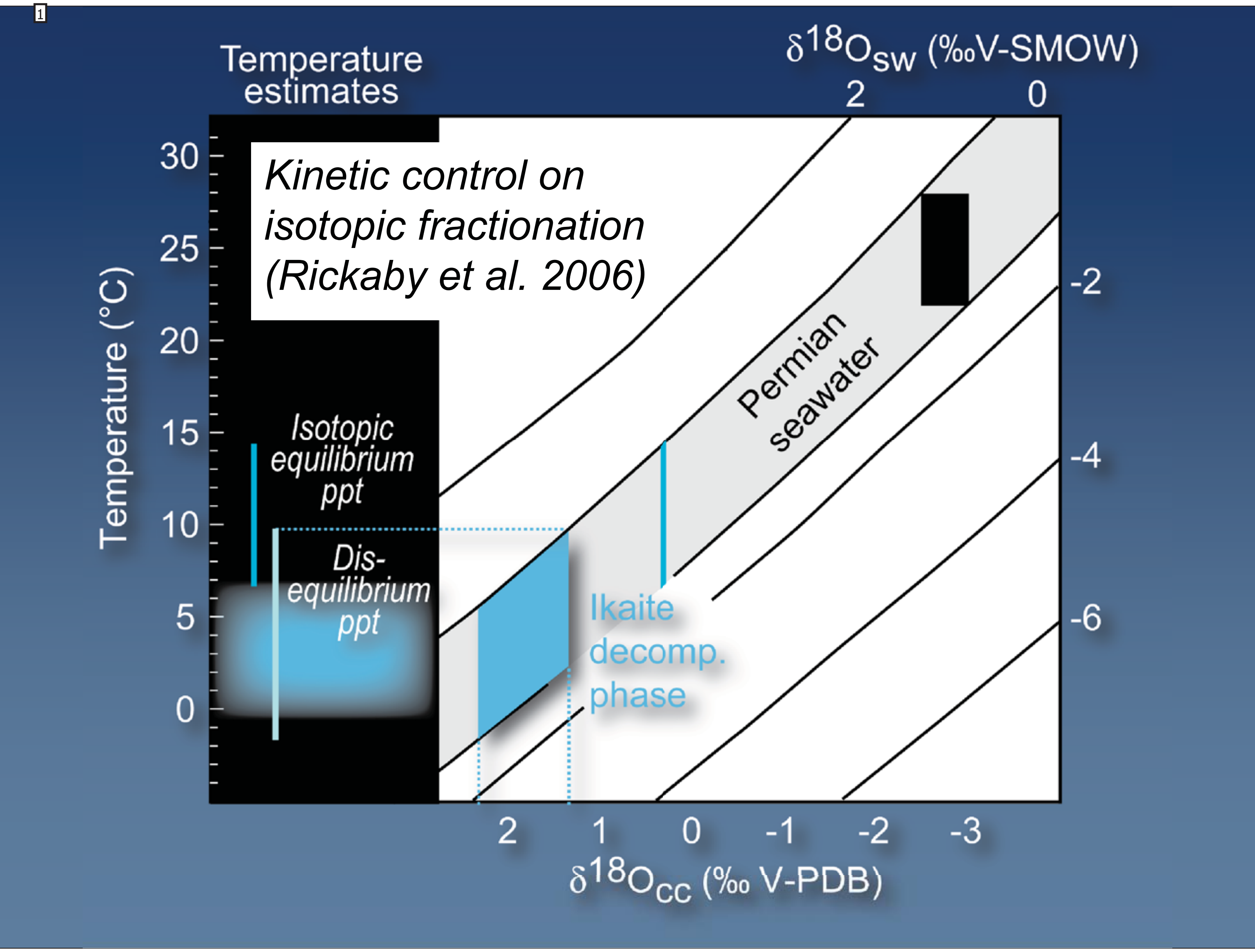
We assume these tropical carbonates formed between 22 and 28°C (Gonzalez and Lohmann 1985) (temperature range shown at left).

This yields d18O values for Permian seawater that range from –1.2 to +0.5‰ V-SMOW, as depicted by grey field extending across diagram from upper right to lower left.



Temperature estimates
$\delta^{18}O_{sw}$ (‰V-SMOW)
2
0
30
25
20
15
10
5
0
Temperature (°C)
Shallow tropics, Permian
Isotopic equilibrium ppt
Ikaite ppt
Ikaite decomp. phase
Permian seawater
-2
-4
-6
2
1
0
-1
-2
-3
$\delta^{18}O_{cc}$ (‰ V-PDB)

Notes by Presenter: Here we estimate temperature of precipitation fo the ikaite decomposition phase, based on the following:
Highest d18O value from this phase (+0.3‰) is least altered;
Precipitation took place under isotopic equilibrium with normal seawater
Temperature estimates indicated by blue bar at left.
Temperatures lie outside the ikaite stability range. Could this reflect the decomposition temperature?



Temperature estimates
$\delta^{18}O_{sw}$ (‰V-SMOW)
2
0
-2
-4
-6
Kinetic control on isotopic fractionation (Rickaby et al. 2006)
Temperature (°C)
30
25
20
15
10
5
0
Isotopic equilibrium ppt
Dis-equilibrium ppt
Permian seawater
Ikaite decomp. phase
2
1
0
-1
-2
-3
$\delta^{18}O_{cc}$ (‰ V-PDB)

Notes by Presenter: Here we utilize information from a recent study by Rickaby et al. (2006) of the oxygen isotopic composition of ikaite, the lattice-bound water, and the decomposition product (calcite).

Their experimental data shows that there is a kinetic control on the decomposition process, which imparts a 1 to 2‰ shift on the decomposition product, such that measured d18O values for the ikaite replacement phase are 1 to 2‰ lower than expected.

If this is the case, then the reaction occurred at temperatures that lie within the stability field of ikaite. If this holds true, then it is possible to use the d18O values of the ikaite decomposition phase to estimate seawater composition and temperature.

Conclusions - 1: **PETROGRAPHY**

- Glendonites posses granular fabric – *sand-sized, equant-bladed, inclusion-zoned calcite that "floats" in a matrix of enclosing cements*
- Ikaite decomposition phase identified based on paragenesis and ubiquitous presence in glendonites from multiple localities, modern & ancient
- Enclosing cements vary locally, reflect later diagenetic processes

Conclusions - 2:

STABLE ISOTOPE GEOCHEMISTRY

- Physical intermingling of heterogeneous phases requires precise sampling & cautious interpretation
- $\delta^{13}C$ values consistent with ikaite formation/ decomposition in zone of suboxic to anoxic diagenesis
- $\delta^{18}O$ values do not correspond to formation at near-freezing temperatures unless isotopic disequilibrium assumed

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