The Sydney Basin and frozen prawns - the cool mineral connection

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THE SYDNEY BASIN AND FROZEN PRAWNS - THE COOL MINERAL CONNECTION

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ABSTRACT
Calcite pseudomorphs after ikaite (glendonite) are common in the Permian marine sequences of the Sydney Basin and have been recorded from more than 30 localities representing six major glendonite-forming intervals. Recognition of glendonites in Sydney Basin strata provides unequivocal evidence for coldwater deposition. Stable isotope signatures of modern ikaite suggest carbonate precipitation in equilibrium with ambient seawater and are consistent with derivation of carbonate from methane oxidation. Review of published data suggests that while Holocene glendonite may provide reliable isotopic records of the conditions of ikaite crystallisation, precipitation of later calcite cement within the glendonite structure reduces the significance of the isotopic signature as an indicator of primary depositional conditions. Stable isotope data from Sydney Basin glendonites indicate that diagenetic processes have obscured whatever primary carbonate isotope signal might have been preserved.

INTRODUCTION
Glendonite is but one of several names used for a group of pseudomorphs that have been recorded from a wide range of geographic locations and in strata ranging from Precambrian to Recent in age. Samples from the original locality at Glendon in the northern Sydney Basin were presented to James Dwight Dana, the eminent American mineralogist, during his visit to Australia in 1839-40 and were later described and figured in his report on the geology of New South Wales (Dana 1849). The name “glendonite”, however, was not proposed until more than fifty years later when David et al. (1905) published a detailed description of the occurrence, morphology and significance of glendonites from Glendon and three other localities in the Sydney Basin. The aim of the current paper is to describe the occurrence and distribution of glendonites in the Sydney Basin, and to assess their significance for palaeoclimatic reconstructions and as a proxy for Permian seawater isotopic compositions.

PRECURSOR MINERAL
The identity of the precursor mineral to glendonites has been the subject of considerable debate throughout the last century with the majority of studies relying on crystallographic data for mineral identification. Several minerals including anhydrite (CaSO₄), aragonite (CaCO₃), celestite (SrSO₄), gaylussite (CaCO₃•Na₂CO₃•5H₂O), glauberite (Na₂SO₄•CaSO₄), gypsum (CaSO₄•2H₂O), sulphur (S) and thenardite (Na₂SO₄) have been suggested as possible precursors, with glauberite and thenardite probably being the most favoured choices. The lack of agreement between the early investigators about the identity of the precursor mineral for glendonites and other similar pseudomorphs is not surprising due to the ambiguity of the crystallographic data and because the most likely forerunner was not discovered in nature.
until relatively recently.

Synthetically produced calcium carbonate hexahydrate (CaCO₃•6H₂O) had been known to chemists before James Dana visited the Hunter Valley and described the original glendonites, but it was not found in nature until the mineral ikaite was discovered in the very cold waters of Ikka Fjord, southern Greenland (Pauly 1963). This discovery provided the first indication of the identity of the elusive precursor mineral and also vindicated the suspicions held by at least some mineralogists more than a century ago. According to Edward Dana (1884), who investigated the thinolites (i.e. glendonites) from Lake Lahontan, Nevada, "the original mineral was one which does not appear thus far to have been observed in its natural condition, although, as will be shown later, it probably has occurred abundantly at numerous other localities." Following the discovery of ikaite it took nearly another two decades before Kaplan (1979) recognized that the composition, morphology and distribution of this new mineral matched those required for the precursor for glendonites. Ikaite has now received widespread acceptance as the precursor mineral for glendonites and related pseudomorphs (e.g. Suess et al. 1982; Carr et al. 1989; Swainson & Hammond 2001).

IKAI TE OCCURRENCES
In the last two decades ikaite has been recognized in a wide range of facies ranging from lakes to estuaries, shallow-marine shelves and deep oceanic basins. All occurrences, however, are characterized by cold, alkaline conditions and, for at least some occurrences, elevated phosphate concentrations in precipitating waters. These elevated phosphate levels apparently suppress precipitation of other calcium carbonate polymorphs (Buchardt et al. 2001). Ikaite crystals rapidly degrade to calcite plus water when warmed above 4°C (Bischoff et al. 1993) and may result in the generation of calcite aggregates whose external form pseudomorphs the ikaite crystal morphology. The limited stability of ikaite makes it a robust indicator of coldwater conditions and thus the recognition of its pseudomorphs in the geological record is of great paleoclimatic significance.

The restricted temperature stability and rapid conversion of ikaite to pseudomorphic calcite aggregates (i.e. glendonites) provides the potential for using the stable isotopic characteristics of glendonite calcite as a proxy for water isotope chemistry in the depositional or early burial setting. The current model for the stable isotopic evolution of Phanerozoic seawater is based on biogenic carbonate records and the availability of another proxy for seawater chemistry would be of considerable value in validating the long-term trends (Veizer et al. 1999). Conversion of ikaite to calcite, however, involves a significant volume decrease resulting in development of high porosity and the potential for later precipitation of void-filling calcite under physical and chemical conditions that may be very different from the original depositional setting. This limits the reliability of stable isotopic results unless the primary calcite phase that was formed from ikaite conversion can be recognized and analyzed.

FROZEN PRAWN CONNECTION
Ikaite appears to be a rare mineral but its occurrence is probably much more common than generally realized. A common, albeit anthropogenic, example is the white spots that develop in the shell of frozen prawns during storage. X-ray diffraction analysis indicates that the mineral component of these white spots is ikaite (Mikkelsen et al. 1999).
SYDNEY BASIN GLENDONITES
Glendonites are common in the Sydney Basin and have been recorded from more than 30 separate geographic localities (Carr et al. 1989) representing six major glendonite-forming intervals – the Allandale Formation, upper Pebble Beach Formation, Wandawangan Siltstone-Branxton Formation, Berry-Mulbring Siltstones, Broughton Formation, and Kuhnara Marine Tongue in the lower Illawarra Coal Measures. All glendonite occurrences in the Sydney Basin have several features in common. In particular, all occur in dark grey, carbonaceous, Permian marine strata. The glendonites are restricted to particular stratigraphic intervals within each formation and tend to occur in several glendonite-bearing horizons within a stratigraphic interval several 10s of metres thick. These horizons are composed of mudstone, siltstone, or rarely, very fine-grained sandstone that is commonly bioturbated. The glendonites are prismatic or stellate with randomly-oriented long axes, and may partially or completely enclose fossils or pebbles. Glendonite-bearing beds are commonly overlain by sandy and/or fossiliferous beds that contain abundant rounded and less common subangular dropstones.

Glendonites in the Sydney Basin consist of brown to amber, blocky calcite crystals, 2-50 microns across, that form diffuse agglomerations and more regular dendritic arrays. This amber to brown calcite is interpreted as the calcite that formed during the early conversion of ikaite to calcite (cf. Greinert & Dekker 2004). Pore space within the brown to amber calcite network is filled with clear, millimeter- to micron-scale, secondary calcite. Brachiopods associated with glendonites in the Sydney Basin are well-preserved, with apparently minimal recrystallization and loss of primary microfabric. Joints within the glendonite-bearing units are mineralized with calcite and rare quartz that are probably related to later tectonic or burial phenomena, but some may be related to hydrothermal fluid systems developed near basalt flows coeval with sediment deposition.

STABLE ISOTOPIC DATA
Stable isotope analyses were carried out on hand-picked separates and bulk glendonite samples, together with samples of biogenic calcite (brachiopods), calcite spar from mineralized joints, and samples of coalified wood from the Sydney Basin. Samples of glendonites and associated biogenic carbonate from elsewhere were also analysed and the new data were integrated with published data to assess the reliability of glendonites as climate proxies and as records of stable isotopic chemistry of waters in the depositional setting.

The stable isotope signatures of modern (transformed) ikaite define distinctive trends. Most ikaite samples have a narrow range of δ^{18}O_{PDB} (+1 to +4.5‰) consistent with precipitation from normal marine waters at temperatures within the mineral’s stability field. The broader range of δ^{13}C_{PDB} (-19 to -32‰) reflects mixing of relatively depleted carbonate from methane oxidation with relatively enriched seawater carbonate. Data for samples from the type locality in Ikka Fjord define a different array resulting in precipitation from waters formed by mixing of meteoric, submarine spring water with seawater (Buchardt et al. 2001).

Stable isotope data for Sydney Basin brachiopods have a restricted range well within the range of Permian biogenic low-magnesium calcite reported in numerous studies as summarized by Veizer et al. (1999). The modest spread of the Sydney Basin data may suggest some recrystallization or filling of brachiopod shell punctae by later diagenetic cement.
Sydney Basin glendonite bulk samples and hand-picked separates form a broad array, particularly in terms of \( \delta^{18}O_{PDH} \) (-5.2 to -21.4\%). The lack of any glendonite \( \delta^{18}O_{PDH} \) values more enriched than -5\% may indicate initial precipitation from relatively depleted waters from mixed meteoric-seawater sources. Alternatively, the relative depletion in \( \delta^{18}O_{PDH} \) of glendonites compared to the brachiopod samples, may reflect physical mixing of a more depleted phase analogous to the late spar cement in mineralized joints. The separated amber calcite, which is presumed to represent the primary calcite from the transformation of ikaite during early burial, shows no significant difference from the bulk glendonite samples or the white/clear spar. This suggests that the scale of intergrowth of primary calcite and later spar is much finer than the mm-scale fragments that were separated by hand-picking.

**IMPLICATIONS OF GLENDONITE OCCURRENCES**

Glendonites are robust indicators of cold conditions but not reliable indicators of palaeolatitude. The glendonite-bearing formations in the Sydney Basin are predominantly very fine-grained and represent periods of slow deposition where water depths were below storm wave base on an open continental shelf (lower three intervals) or in a protected seaway (upper three intervals). Between the glendonite-bearing formations coarser sand-dominated successions represent shallower water offshore and shoreface facies (e.g. Le Roux & Jones 1994; Herbert 1995; Tye et al. 1996). The presence of glendonites in the Pebbley Beach Formation (and possibly the Allandale Formation) may represent deposition under icehouse conditions during the last major phase of Gondwanan glaciation (Fielding et al. 2006). The relatively common occurrence of glendonites through the upper part of the Sydney Basin marine succession, however, indicates that cold conditions (<4\°C) must have persisted at least periodically through most of the mid to Late Permian to allow the growth of ikaite crystals. Cold conditions with seasonal ice are also indicated throughout this succession by the presence of rounded erratic dropstones. Most of the formations (including the icehouse Pebbley Beach Formation) also contain wood fragments that have been washed into, and preserved in, the cold marine waters, thus indicating that the adjacent landmass supported a woody flora and the climate must have been only seasonally cold. The occurrence of glendonites in the deeper water phases of Sydney Basin deposition is probably the result of tectonic downwarping of the basin rather than glacio-eustatic sea level changes that would suggest they formed during interglacial periods.

**REFERENCES**


