

WARM TO COLD WATER CARBONATE FORMATION DURING THE ORDOVICIAN AND THE JURASSIC: EXAMPLES FROM IRAN, AUSTRALIA, AND ENGLAND

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Abstract

Isotope data from bulk carbonates, micrite, marine calcite cements, non-skeletal grains and brachiopods indicate deposition of a wide spectrum of warm to cold water carbonates during the Ordovician and the Jurassic. This isotopic interpretation is supported by warm to cold climatic models proposed for the Ordovician and the Jurassic. These carbonates formed during the Greenhouse mode (conditions similar to present day) and Icehouse mode. Isotopic equilibrium trends of carbonate minerals indicate an originally aragonite-calcite mixture during the late Ordovician of Tasmania and Late Jurassic of Iran (Kopet-Dagh Basin-Sarakhs area) corresponding to warm temperatures; whereas originally calcitic mineralogy deposited during the Mid Jurassic in England and Scotland, and the Late Jurassic at Mallorca Island, Spain, correspond to cool to cold water temperatures. Sedimentological features of these ancient limestones are similar to modern warm to cold water carbonates.

Keywords: Isotopes; Climatic models; Carbonates; Ordovician; Jurassic

Introduction

Extensive modern warm (tropical; $>25^{\circ}\text{C}$), cool (temperate; $<25^{\circ}\text{C}$ to 10°C) and cold (polar; $<10^{\circ}\text{C}$) water carbonates are now forming in many areas [e.g., 1]. By the principle of uniformitarianism, we should expect to find similar extensive warm to cold water carbonates in geologic past. However, surprisingly few ancient cool to cold carbonates have been documented.

In this study, we present examples of warm to cold water carbonates from the Ordovician (Tasmania, Australia) and the Jurassic (England and Iran) by considering sedimentological features, the O and C isotopes and paleotemperatures, climatic models (Icehouse and Greenhouse modes), isotopic equilibrium trends of carbonate minerals, carbonate mineralogy, isotopic trends preserved after meteoric and burial diagenesis.

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Method of Study

Various limestone components were separated for oxygen and carbon isotope analysis, employing a microscope with a dental drill to extract carbonate powders from polished slabs. Thick brachiopod shells were sampled for isotope analysis using needle and dental drills. For oxygen and carbon isotope analysis, 15 mg of the powders of 114 limestone samples of the Mozduran Formation, including: 28 micrites, 12 non-skeletal grains, 5 brachiopod shells, and 69 bulk carbonates were allowed to react with anhydrous phosphoric acid (H_3PO_4) in reaction tubes in a vacuum at 25°C for 24 h respectively. The CO_2 extracted from each sample was analyzed for $\delta^{18}O$ and $\delta^{13}C$ values, using Micromass 602 D gas mass spectrometry at the Central Science Laboratory, University of Tasmania.

These values are expressed in conventional per mil notation relative to PDB standard. The precision of data was established with duplicate analysis for both oxygen and carbon, and is $\pm 0.1\%$.

Sedimentological Features

Major features of Jurassic and Ordovician carbonates considered in this study are summarised in Table 1. These carbonates were deposited in high- to low-latitude regions and have been interpreted as warm to cool water carbonates. The Late Ordovician Carbonates of Tasmania contain tropical biota, diverse non-skeletal grains, abundant stromatolites, early diagenetic dolomites and originally aragonitic and high-Mg calcite mineralogy similar to modern tropical carbonates (Table 1; 2).

Table 1. Major features of the Late Ordovician carbonates of Tasmania [2, 14], the Late Jurassic carbonates of Iran [this study] and the Mid Jurassic carbonates of England [3].

Parameter	Late Ordovician <i>Tasmania</i>	Late Jurassic <i>Iran</i>	Middle Jurassic <i>England</i>
Major depositional environments	Peritidal	Peritidal	Barrier Island Complex
Paleolatitude	10°N	20°N	35°N
Inferred climatic zone	Subtropical	Subtropical	Temperate
Temperature (from $\delta^{18}O$ values):			
Heaviest value	24°C	16°C	8°C
Skeletal values	23-28°C (brachiopods)	26-30°C (brachiopods)	22-25°C (oysters)
Major Biota	Calcareous algae, corals, molluscs, stromatoporoids, crinoids and bryozoans	Bivalves, brachiopods, crinoids, gastropods, calcareous red algae, sponges and solitary corals	Bivalves (rich in oysters) and shell debris
Non-skeletal grains	Intraclasts, pellets, oolites, and aggregates	Oolites, intraclasts, minor pellets and aggregates	Oolites and pellets
Stromatolites	Abundant	Present	Absent
Evaporites	Rare	Abundant (beds and xtalls)	Absent
Dolomite (early diagenetic)	Abundant	Common	Absent
Mineralogy of Fauna	Aragonite>high-Mg calcite	Aragonite + high-Mg calcite	Calcite>aragonite
Mineralogy of non-skeletal grains and cements	Aragonite>high-Mg calcite	Aragonite + high-Mg calcite	High-Mg calcite> aragonite
Trace elements	Low Sr, moderate Na, and high Mn	Low Sr and Na, and high Mn	Low Sr
Isotopes:			
$\delta^{18}O\text{‰ PDB}$	Moderate negative up to -4.5‰	Low negative up to -1.2‰	Low negative up to -0.6‰
$\delta^{13}C\text{‰ PDB}$	Low negative to positive up to 1.5‰	Positive up to 4.4‰	Positive up to 3‰

The Mid Jurassic carbonates of England were originally calcitic with minor aragonite and no dolomite and evaporites (Table 1; 3). The occurrence of algal rich biota, diverse skeletal and non-skeletal grains, evaporites and early diagenetic dolomites (Table 1) in shallow marine carbonates of Iran are similar to those of modern subtropical shallow marine environment during the Late Jurassic. Petrographic evidence, such as fibrous and isopachous sparry calcite cements, abundant shattered micritic envelopes, deformed and spalled ooids, indicate an originally aragonite mineralogy [4]. Other samples from relatively deeper parts of the basin, contain predominately calcitic skeletons, such as crinoids, brachiopods, forams and bryozoans and bladed marine calcite cements. These indicate that the Iran carbonates are composed of mixtures of aragonite and calcite.

Oxygen and Carbon Isotopes

Wadleigh and Veizer [5] presented $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of a large number of Ordovician brachiopods from many localities around the world (Fig. 1). It is now well established that the Ordovician seawater ^{18}O values were around -5‰ [e.g., 6,7]. Determination of Ordovician paleotemperatures from oxygen thermometry, using the brachiopod values of Wadleigh and Veizer [5] and Ordovician seawater ^{18}O value of -5‰ , indicates cool to cold condition (23° to 3°C). The heaviest $\delta^{18}\text{O}$ values of micrite, marine calcite cement and non-luminescent brachiopods indicate tropical depositional temperatures of 23° to 28°C , assuming an enriched $\delta^{18}\text{O}$ value of seawater of -3‰ during the Late Ordovician due to glaciation (Fig. 1; 2).

The heaviest $\delta^{18}\text{O}$ value of the Middle Jurassic carbonates of England [3] give cold seawater temperatures of 8°C , when seawater ^{18}O values of -1.2‰ PDB are assumed [e.g., 8; Fig. 2]. Middle Jurassic oysters from the Castle Bytham quarry of England, indicate cool temperatures of 22° to 25°C (Fig. 2), corresponding to modern temperate seawater temperatures around 36°S latitudes of southern Australia [9]. The paleolatitude of England during the Middle Jurassic was about 35°N [3]. The heaviest $\delta^{18}\text{O}$ value of low-Mg calcite belemnite from the Late Mid Jurassic from Scotland, at a paleolatitude of 45°N , substituted in ^{18}O thermometry corresponds to 13°C [Fig. 2; 10]. This surface seawater temperature is similar to modern cool temperate surface seawater temperatures around Tasmania, Australia at a latitude of about 44°S [9]. Many Mid Jurassic limestones from other localities are cool water carbonates [8].

The heaviest $\delta^{18}\text{O}$ value of the Late Jurassic marine

micrite from Iran gives cool seawater temperature of 16°C , whereas the heaviest and least altered value of brachiopods correspond to a warm seawater temperature of 26°C (Fig. 3), using a seawater $\delta^{18}\text{O}$ value of -1.2‰ in the oxygen temperature equation. The heaviest isotopic values of marine calcite cements are believed to record original isotopic signature [11, 12]. The heaviest $\delta^{18}\text{O}$ value of calcite cement of the Late Jurassic of Iran gives an ambient seawater temperature of 21°C . In the Late Jurassic, the paleolatitude of Iran was about 20°N and thus it was in subtropical conditions. In contrast to Iran, the Late Jurassic belemnite $\delta^{18}\text{O}$ values of Mallorca Island in Spain, at paleolatitudes of 25° to 30°N , correspond to seawater temperature ranging from 13° to 16°C , using a seawater ^{18}O value of -1.2‰ in the oxygen temperature equation.

The $\delta^{18}\text{O}$ values of belemnite from Mid to Late Jurassic limestones from Mediterranean-Northern European region, from eleven localities including England, France, Switzerland, Germany and Russia, indicate average temperatures of 16°C [8]. A compilation of $\delta^{18}\text{O}$ values from the Mid to Late Jurassic belemnite guards from New Zealand, Australia, New Guinea and Russia indicate temperatures $<16^\circ\text{C}$ [13].

Climatic Models

Warm to cold climatic models are proposed for the Ordovician and the Jurassic. The relationship between $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in worldwide Ordovician marine calcites indicates that during the Middle and Late Ordovician, atmospheric CO_2 levels were similar to those of present day but were higher during Early Ordovician [14]. These levels indicate that climatic conditions changed progressively from "Greenhouse mode" during Early Ordovician, to a climate similar to present-day (with icecaps) during Middle Ordovician and ultimately to glacial climatic conditions during Late Ordovician [2]. World-wide cooling occurred even in low latitudes during Late Ordovician [15,16]. Distribution of reefs worldwide suggests cooling intervals were particularly dominant during the Ordovician in northern Europe [15]. These Ordovician carbonates are subpolar limestones; some are coeval with tillites and formed at temperatures $<8^\circ\text{C}$ [17]. Cool conditions have also been inferred for some Canadian [18] and American Ordovician carbonates [19-21].

Latitudinal positions of England (35°N) and Scotland (45°N) during Mid Jurassic, together with $\delta^{18}\text{O}$ thermometry, indicate cool water carbonate formation in these regions, similar to modern temperate carbonates

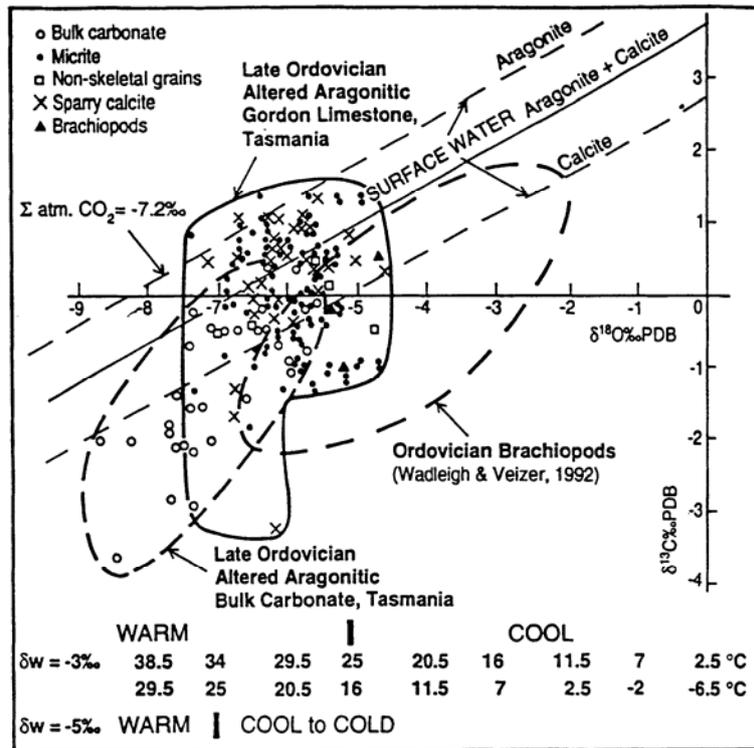


Figure 1. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ variations in Late Ordovician carbonate of Tasmania and brachiopods from different localities [5].

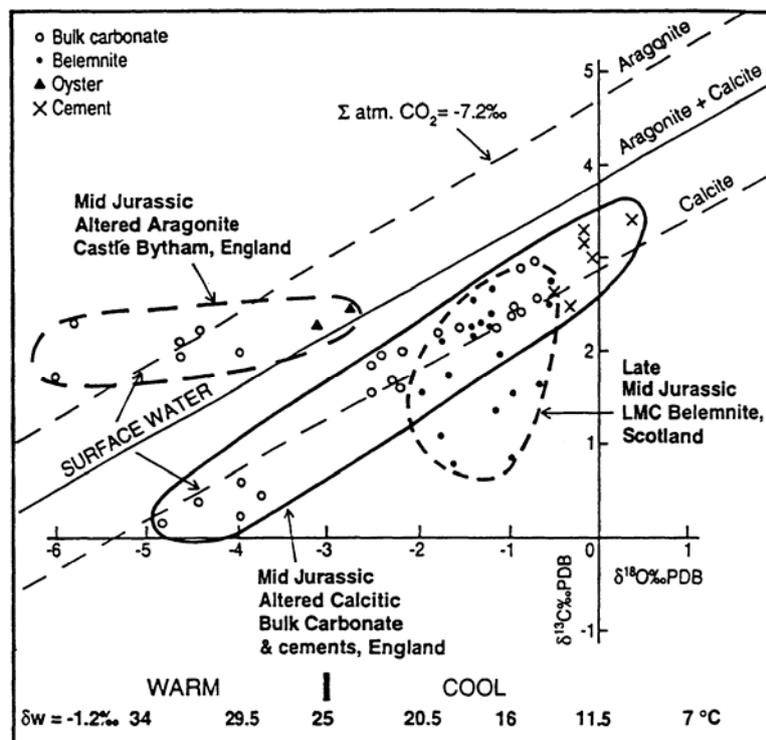


Figure 2. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ variations in carbonates from the Mid Jurassic of England [3] and belemnite of Scotland [10].

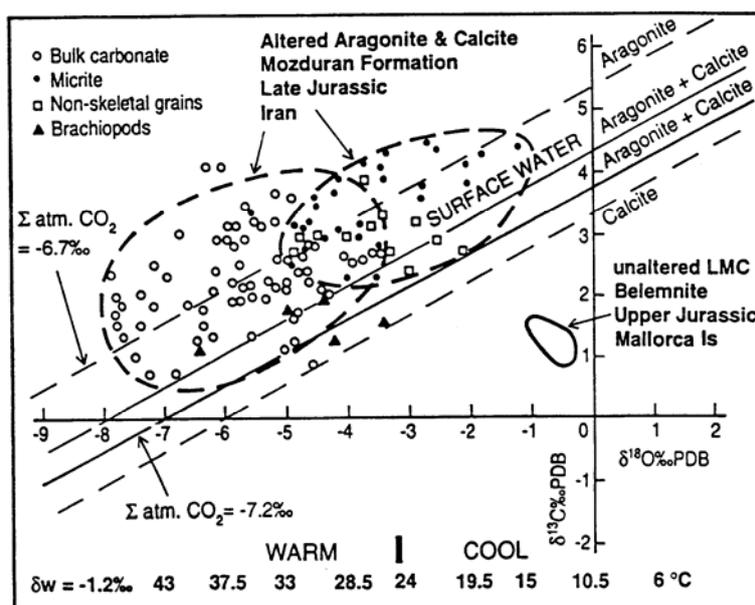


Figure 3. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ variations in bulk carbonates, micrites, non-skeletal grains and brachiopods from the Late Jurassic of Iran [this study] and belemnite from the Late Jurassic of Mallorca Island, Spain [8].

around southern Australia. Temperature of about 11°C prevailed at about 29°N latitude in Russia in the Mid Jurassic [13], is considered to be cool temperate. Although there is no evidence of glaciation during the Jurassic, Mid Jurassic seawater temperatures were cooler than at present [22].

During the Late Jurassic, CO_2 levels were about 4 times higher than present day values due to the occurrence of a "Greenhouse mode" [e.g., 23-25]. The area of study in Iran (Kopet-Dagh Basin, Sarakhs area) corresponds to an arid desert climate with moderately low rainfall [based on Global Circulation Models; 23,24]. The open seawater temperatures of the Upper Jurassic carbonates of Iran were relatively uniform $\sim 20^\circ\text{C}$, while in the coastal area temperatures fluctuated from 16° to 26°C . Thus, the Iranian shallow sea was similar to that of the subtropical Persian Gulf, where wide temperature fluctuations occur in the coastal areas from 40° in summer to 15°C in winter [26]. The Mallorcan average paleotemperature of 15°C (Fig. 3), calculated from $\delta^{18}\text{O}$ values of belemnite, are due to cooler sub-surface waters [8]. $\delta^{18}\text{O}$ values of Late Jurassic sedimentary rocks of Russia [13] correspond to a temperature of 16°C , similar to the temperature obtained from the heaviest $\delta^{18}\text{O}$ value of the Late Jurassic limestones of Iran, which we interpret to have been in close proximity to Russia during the Late Jurassic based on brachiopod studies [27].

Isotopic Equilibrium Trends of Carbonate Minerals

In Figures 1 to 3, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ temperature equilibrium lines [2] were drawn for aragonite, aragonite and calcite mixtures and calcite using temperature equations for $\delta^{18}\text{O}$ [28] and $\delta^{13}\text{C}$ [29], taking $\delta^{18}\text{O}$ of seawater as 0‰ , atmospheric $\delta^{13}\text{C}$ as -7.2‰ and mineralogical fractionations of $\delta^{13}\text{C}$ [30]. These $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ equilibrium lines shift downwards or upwards depending on an increase or decrease of atmospheric CO_2 levels respectively. The $\delta^{13}\text{C}$ values in seawater decrease with increasing water depth and thus $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ temperature equilibrium lines move downwards. If both $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of seawater shift, as occurs during evaporation [31] or dilution by fresh water, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values in carbonate minerals increase or decrease respectively.

The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ data from Ordovician, the Mid Jurassic and the Late Jurassic fall on $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ equilibrium lines due to their formation in shallow water ($<30\text{ m}$) and because they are in equilibrium with atmospheric CO_2 (Figs. 1 to 3). The heaviest $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the Ordovician carbonates fall on aragonite and aragonite-calcite mixture lines indicating that the original carbonate mineralogy during the Ordovician was aragonite and high-Mg calcite. This mineralogy is consistent with petrographic features and

elemental composition [2]. Similarly, the Mid Jurassic data from England and Scotland fall on the calcite line or the aragonite-calcite mixture line due mostly to calcite mineralogy during the Mid Jurassic. $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ data from the Late Jurassic of Iran fall above $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ equilibrium line with present day atmospheric CO_2 levels of -7.2‰ (Fig. 3). This is because of heavy CO_2 levels and Greenhouse mode during the Late Jurassic. The Late Jurassic PCO_2 levels calculated from $\delta^{13}\text{C}$ values, assuming the paleotemperatures calculated by $\delta^{18}\text{O}$ are correct, indicate that the Late Jurassic atmospheric $\delta^{13}\text{C}$ was -6.7‰ (Fig. 3). The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ equilibrium line of an aragonite-calcite mixture, using this $\delta^{13}\text{C}$ values of -6.7‰ , bisects the Iran carbonate data indicating that original mineralogy was aragonite and high-Mg calcite.

Meteoric and Burial Diagenesis

The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the ancient limestones studies have been affected by meteoric and burial diagenesis. The Ordovician carbonates of Tasmania show an "inverted J-trend" typical of meteoric diagenesis [32; Fig. 1]. The Mid Jurassic carbonates of England and Late Jurassic carbonates of Iran have been affected by burial diagenesis, which is characterised by a large shift in $\delta^{18}\text{O}$ values due to higher burial temperatures [33; Figs. 1, 2].

Discussion and Conclusions

Experimental studies indicate aragonite forms primarily at temperatures $>30^\circ\text{C}$; mixtures of aragonite and high-Mg calcite form between 30° and 17°C ; mixtures of high-Mg calcite and low-Mg calcite are precipitated from 17° to 5°C and only low-Mg calcite forms below 5°C [34,35]. Aragonite to calcite ratios in recent carbonates decrease from tropical, temperate to polar regions [e.g., 1,36]. In ancient carbonates, the original carbonate mineralogy could be aragonite and/or calcite. Calcite was the predominant mineral in Early and Middle Paleozoic and Jurassic to Cretaceous; while aragonite was the predominant mineral during other periods [37]. This variation in carbonate mineralogy during Phanerozoic carbonates has been attributed mainly to variations in atmospheric PCO_2 levels: low PCO_2 corresponding to aragonite with conditions similar to present day or that during the "Icehouse mode", and high CO_2 corresponding to calcite with conditions similar to that during the "Greenhouse mode" [37-39]. The occurrence of an aragonite and calcite mixture during the Late Ordovician from

Tasmania, corresponding to Icehouse mode and widespread glaciation elsewhere, is due to warm water and low CO_2 levels. However, the Jurassic examples from Iran, with aragonite and calcite mineralogy in warm water during Greenhouse mode, do not agree with the occurrence of aragonite during high CO_2 levels.

Aragonite or both aragonite and calcite can form at the same time in relatively similar tectonic settings. Examples include modern carbonate in Baffin Bay Texas [40], the Upper Jurassic Smackover carbonates of the Gulf Coast region of the USA [41], the Upper Jurassic Purebeck limestones of Swiss and French Jura [42] and the Upper Jurassic Mozduran Formation of Iran [4]. Thus, the original carbonate mineralogy through time varies with both temperature and atmospheric CO_2 levels, as illustrated in this study.

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