

Dolomitization by penesaline sea water in Early Jurassic peritidal platform carbonates, Gibraltar, western Mediterranean

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ABSTRACT

Peritidal carbonates of the Lower Jurassic (Liassic) Gibraltar Limestone Formation, which form the main mass of the Rock of Gibraltar, are replaced by fine and medium crystalline dolomites. Replacement occurs as massive bedded or laminated dolomites in the lower 100 m of an ≈460-m-thick platform succession. The fine crystalline dolomite has $\delta^{18}\text{O}$ values either similar to, or slightly higher than, those expected from Early Jurassic marine dolomite, and $\delta^{13}\text{C}$ values together with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that overlap with sea-water values for that time, indicating that the dolomitizing fluid was Early Jurassic sea water. Absence of massive evaporitic minerals and/or evaporite solution-collapse breccias in these carbonate rocks indicates that the salinity of sea water during dolomitization was below that of gypsum precipitation. The occurrence of peritidal facies, a restricted microbiota and rare gypsum pseudomorphs are also consistent with penesaline conditions (salinity 72–199‰). The medium crystalline dolomite has some $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios similar to those of Early Jurassic marine dolomites, which indicates that ambient sea water was again a likely dolomitizing fluid. However, the spread of $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ values indicates that dolomitization occurred at slightly increased temperatures as a result of shallow (≈500 m) burial or that dolomitization was multistage. These data support the hypothesis that penesaline sea water can produce massive dolomitization in thick peritidal carbonates in the absence of evaporite precipitation. Taking earlier models into consideration, it appears that replacement dolomites can be produced by sea water or modified sea water with a wide range of salinities (normal, penesaline to hypersaline), provided that there is a driving mechanism for fluid migration. The Gibraltar dolomites confirm other reports of significant Early Jurassic dolomitization in the western Tethys carbonate platforms.

Keywords Carbonate platform, C-O-Sr isotopes, dolomitization, Early Jurassic, Gibraltar, western Tethys.

INTRODUCTION

The origin of massive replacement dolomite has long been an enigma to geologists, and many models have been presented to account for it (e.g.

Land, 1985; Purser *et al.*, 1994). Current understanding is that dolomite can be produced by various fluids in different environments, e.g. evaporitic marine brines in sabkhas, evaporative brines during basinal evaporite drawdown, normal sea water in subtidal environments, freshwater/sea water in mixing zones and deep basinal fluids during burial. Such different dolomites can be recognized from their spatial distribution, facies associations and petrography and in their

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geochemical and isotopic signatures, which are controlled by variations in the temperature, salinity and composition of the dolomitizing fluids.

Classic examples of hypersaline dolomitization (e.g. Adams & Rhodes, 1960; McKenzie *et al.*, 1980) require the generation of saline brines by the evaporation of sea water to the point at which gypsum/anhydrite is precipitated, necessarily increasing the Mg/Ca ratio of the residual brine. The lateral and vertical movement of such brines can result in dolomitization of supratidal and underlying intertidal and subtidal carbonates. However, this model cannot be applied directly to extensive dolomitization of carbonates that are not associated with extensive gypsum/anhydrite deposits. In a recent review of the global, temporal and sedimentological settings of early dolomitization, Sun (1994) hypothesized that, in greenhouse (i.e. ice-cap free) periods of Earth history, dolomitization of extensive, cyclic peritidal carbonates could occur from the flooding and reflux of sea water of slightly increased salinities. As indicated by preliminary studies (Qing *et al.*, 1998), the dolomites from the Rock of Gibraltar provide petrographic and isotopic data in support of Sun's hypothesis. It is proposed that such dolomites be called penesaline dolomites using Adams & Rhodes's (1960) term for evaporated sea water with salinities varying from 72‰ to 199‰. Such salinities are indicated by the presence of restricted marine carbonate facies and marine biota and the absence of associated evaporites. Early Jurassic dolomites are common within Tethyan carbonate platforms (e.g. Colacicchi *et al.*, 1975; Martín, 1979; Flügel, 1983; Crevello, 1991; Soussi & M'Rabet, 1994; Barattolo & Bigozzi, 1996; Rey, 1997; Ronchi *et al.*, 2000; Scherreiks, 2000), and this is consistent with the high global abundance of dolomite in carbonate rocks of this time (Given & Wilkinson, 1987).

GEOLOGICAL SETTING

The Rock of Gibraltar dominates a narrow peninsula that juts south from Spain at the western entrance to the Mediterranean Sea (Fig. 1). Two topographic regions can be distinguished: the Main Ridge, which forms a north–south scarp with peaks over 400 m high; and the Southern Plateaux, where the Rock is truncated to the south by two Quaternary wave-cut platforms. Inverted and westward-dipping carbonate strata in the Main Ridge have recently been distinguished

from eastward-dipping, right-way-up strata in the Southern Plateaux (Fig. 1). The ≈460-m-thick Gibraltar Limestone Formation, which forms the main mass of the Rock, has been subdivided into four members on the basis of colour, bedding characteristics and degree of dolomitization (Rose & Rosenbaum, 1990, 1991a,b; Rose, 2000; Fig. 2). An Early Jurassic (Sinemurian) age for the upper part of the Gibraltar Limestone Formation has been verified on the basis of rare brachiopods (Owen & Rose, 1997) and from strontium isotope values from these same brachiopods (Bosence *et al.*, 2000).

Recent facies analysis by Bosence *et al.* (2000) shows that the Gibraltar Limestone Formation consists of restricted, shallow-marine peritidal carbonate facies, arranged in high-frequency metre-scale, shallowing-up cycles of restricted inner platform facies with subtidal and intertidal–supratidal components. These cycles are superimposed on low-order (third?) cycles of relative sea-level change. The subtidal sediments are characterized by peloidal mudstones–packstones–grainstones, peloidal–skeletal grainstones and intraformational intraclastic rudstones. Periodic subaerial exposure is indicated by laminar calcretes, fenestrae, shrinkage cracks, tepee structures and pisoids. Normal marine bioclasts are absent for most of the succession, but restricted-marine biota of dasycladacean algae and benthic foraminifera occur locally in the Keightley and Buffadero member limestones (Bosence *et al.*, 2000; Boudagher-Fadel *et al.*, 2001). The ubiquitous presence of restricted, inner-platform peritidal carbonates and the absence of massive evaporitic minerals (e.g. gypsum/anhydrite) and/or evaporite solution-collapse breccias suggest a slightly restricted evaporitic environment, i.e. penesaline sea water, with a maximum salinity that only rarely reached gypsum saturation, as indicated by the presence of very rare gypsum pseudomorphs in the Main Ridge succession (Bosence *et al.*, 2000).

METHODS

The petrographic and isotopic data are derived from samples collected during detailed logging of two composite sections (Figs 1 and 2) through the accessible lower and middle parts of the Formation: a 217-m right-way-up sequence through the Southern Plateaux, and a 314-m inverted sequence through the Main Ridge (Fig. 2), as described by Bosence *et al.* (2000). Approxi-

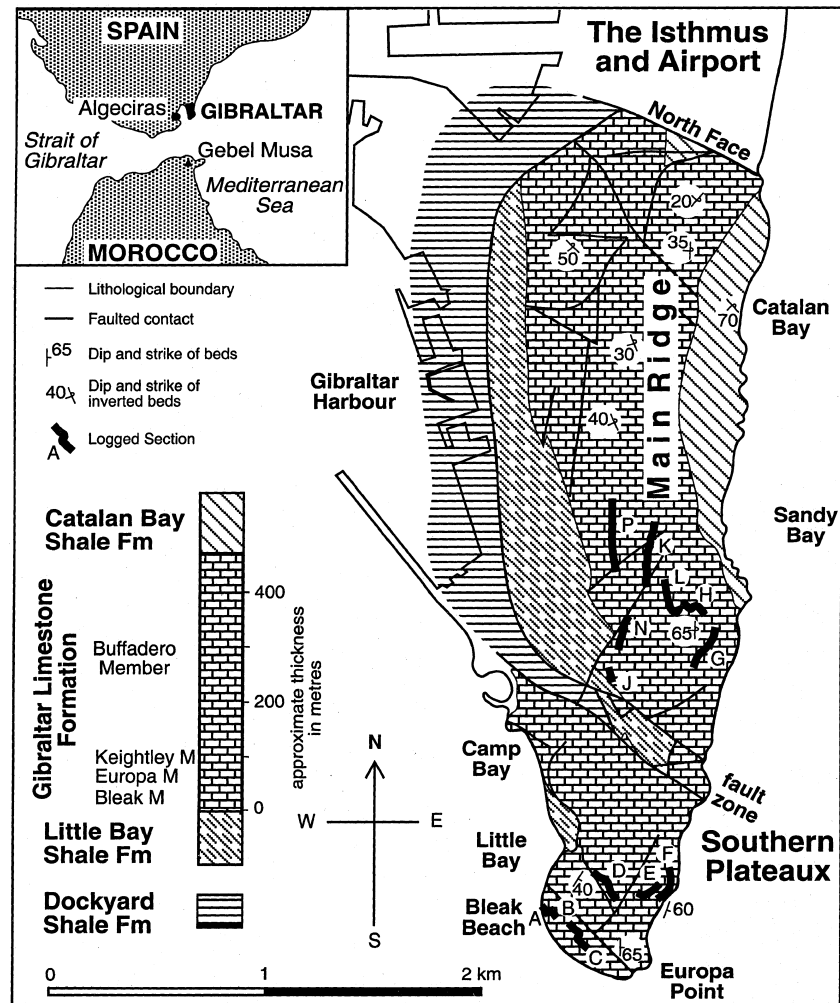


Fig. 1. Pre-Quaternary geological map of Gibraltar, with stratigraphic column showing the position of the Bleak, Europa, Keightley and Buffadero members and the location of logged sections in Fig. 2. (Map simplified after Rose & Rosenbaum, 1990, 1991a,b; logged sections after Bosence *et al.*, 2000).

mately 300 thin sections and peels were studied. All thin sections were stained with Alizarin-Red S and potassium ferricyanide (Dickson, 1965). Forty-six thin sections were also examined using a cathodoluminescence (CL) microscope.

Forty-one samples from the logged sequences of the two sections were analysed for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$, and 14 for $^{87}\text{Sr}/^{86}\text{Sr}$ (Table 1). These samples were obtained from limestones and dolomites using a dental drill after petrographic study. Stable O and C isotopes were analysed in the VG Prism mass spectrometer laboratory, and the strontium isotopes in the Thermal Ionization Mass Spectrometer (TIMS) laboratory, both in the Department of Geology at Royal Holloway, University of London. The precision of carbon and oxygen isotope values from replicate analysis of standards (NBS 19 and internal standards) is within 0.1‰ for C and 0.2‰ for O. Strontium isotope results are standardized to SRM 987 values of 0.710248.

DOLOMITE PETROGRAPHY AND STRATIGRAPHIC DISTRIBUTION

Two types of massive replacement dolomite can be recognized in the Gibraltar Limestone Formation:

1 Fine crystalline dolomite (Fig. 3A). This is either brown or grey in hand specimen with well-preserved fossil and sedimentary features. Microscopically, it consists of subhedral to anhedral dolomite crystals with a size range from 20 to 100 μm (mean 50 μm). These have a planar-S texture (cf. Gregg & Sibley, 1984) and lack undulatory extinction. Fine crystalline dolomite is generally non-luminescent under CL.

2 Medium crystalline dolomite (Fig. 3B). This is also brown or grey in hand specimen. However, precursor fossils and/or fine-scale sedimentary textures are partially to completely obliterated (Fig. 3B and D). This fabric is composed of

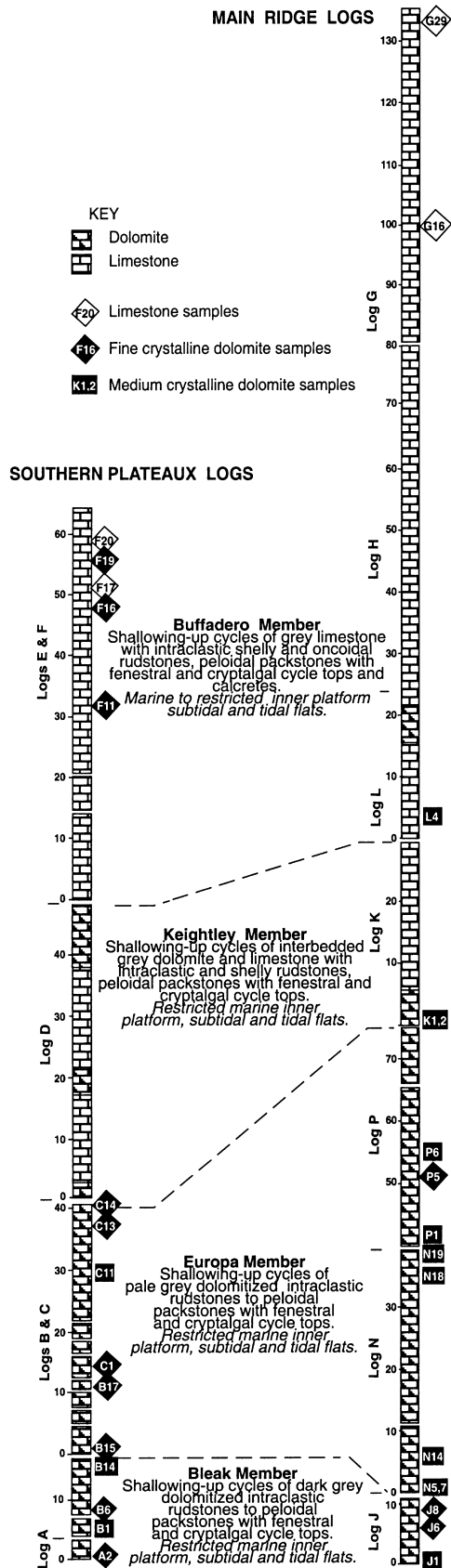


Fig. 2. Summary logged sections of Gibraltar Limestone Formation from the Main Ridge and Southern Plateaux regions of the Rock of Gibraltar indicating members, lithologies, dolomite occurrence and horizons sampled for analyses in Table 1 and corresponding micrographs in Fig. 3. Scale in metres. (For stratigraphic database, see Bosence *et al.*, 2000).

Table 1. $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ values for Gibraltar carbonates.

Sample	Lithology	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$^{87}\text{Sr}/^{86}\text{Sr}$
G29-2	LS	-2.44	2.35	0.70856
G29-1	LS	-2.31	2.33	
G16-2	LS	-3.97	2.30	0.70850
G16-1	LS	-3.63	2.40	
F20-2	LS	-2.31	1.93	
F20-1	LS	-2.05	2.32	
F17-3	LS	-2.92	2.20	
F17-2	LS	-2.98	2.15	
F17-1	LS	-2.92	2.21	0.70787
Mean		-2.84	2.2433	0.70831
P5	FCD	1.26	1.63	0.70777
J8-1	FCD	1.59	2.64	0.70798
J6-1	FCD	2.35	2.09	0.70776
F19-2	FCD	1.59	1.98	
F19-1	FCD	2.70	1.98	
F16-3	FCD	1.92	2.35	
F16-2	FCD	1.15	2.57	
F16-1	FCD	1.35	2.35	0.70809
C14-5	FCD	1.87	1.89	0.70759
C14-4	FCD	1.67	2.50	
C14-1	FCD	0.71	2.92	
C13-2	FCD	0.40	1.99	
C1-4	FCD	0.09	2.54	
B17	FCD	0.56	2.75	0.70794
B15	FCD	0.49	2.51	0.70782
B6	FCD	0.64	1.59	
A2-2	FCD	0.80	1.83	0.70804
A2-1	FCD	1.35	1.69	
A2-1	FCD	1.14	1.63	
Mean		1.24	2.1805	0.70787
K2-1	MCD	-1.22	2.08	0.70950
K1-1	MCD	-1.90	1.90	
P6	MCD	-0.31	-0.79	
P1	MCD	-2.42	1.89	
N19-1	MCD	-0.43	3.38	
N18-2	MCD	-1.67	0.63	
N14-1	MCD	0.05	3.57	
N7-1	MCD	-1.65	2.20	
N5-1	MCD	0.27	3.70	0.70787
J1-1	MCD	0.10	-0.62	
C11	MCD	-0.71	1.72	
B14	MCD	0.99	2.24	
B1	MCD	1.54	2.28	0.70775
Mean		-0.57	1.86	0.70837

Sample letter numbers refer to locations on logs in Fig. 2. LS, limestones; FCD, fine crystalline dolomite; MCD, medium crystalline dolomite.

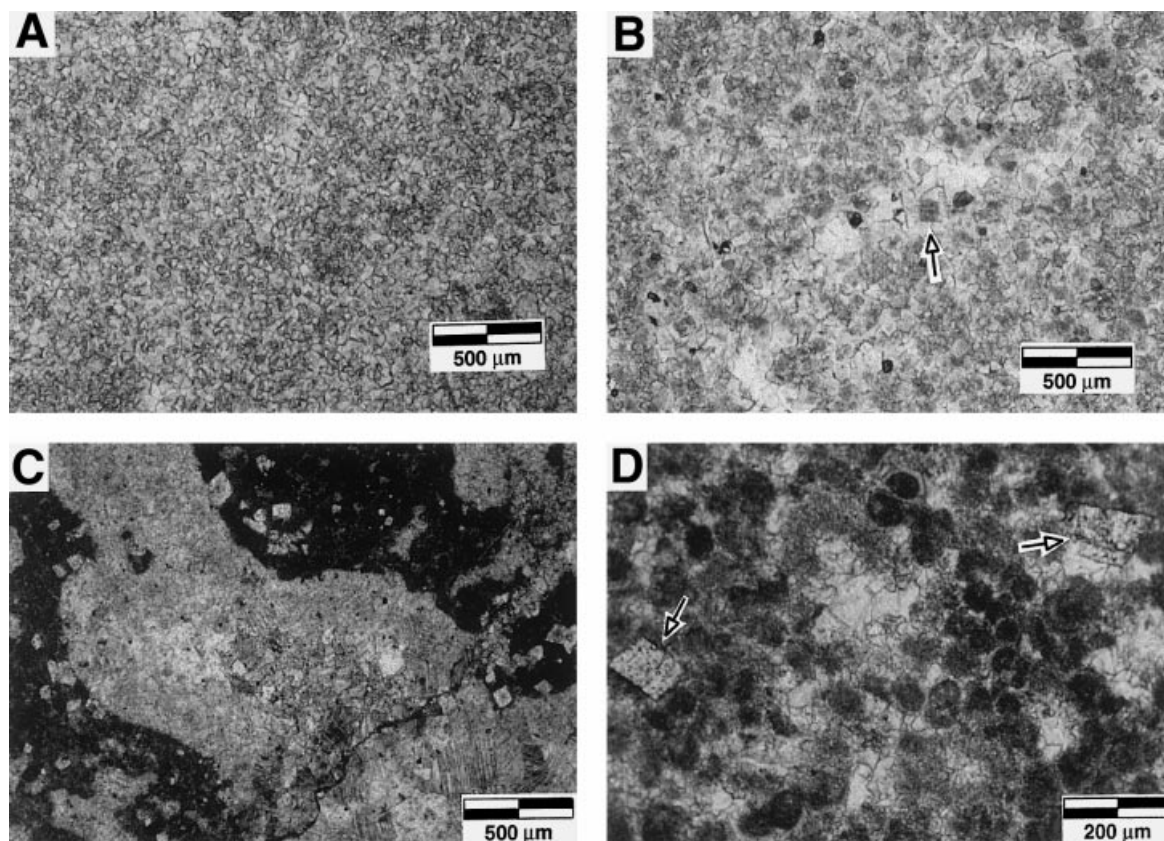


Fig. 3. Thin-section photomicrographs (in plain polarized light) of dolomite from the Gibraltar Limestone Formation. (A) Fine crystalline dolomite comprising subhedral to anhedral dolomite crystals ranging in size from 20 to 100 μm (mean 50 μm) and a planar-S texture (sample no. J8). (B) Medium crystalline dolomite composed of anhedral to subhedral dolomite crystals ranging in size from 100 to 300 μm (mean 150 μm). Some crystals have a cloudy centre and a clear rim (arrow) (sample no. C11). (C) Fine crystalline dolomite precipitated in the centre of bird's eye fenestra following radiaxial calcite cement. Crystal rhombs of the dolomite also replace the fenestrate peloidal packstone-wackestone. Dolomitization has therefore post-dated radiaxial and fine equant calcite cements (sample no. F11). (D) Peloidal grainstone cemented by fine equant calcite cement, both replaced (and therefore post-dated) by medium crystalline dolomite (sample no. L4).

anhedral to subhedral dolomite crystals, ranging from 100 to 300 μm (mean 150 μm) that either replace precursor grains and cements or infill pores after marine radiaxial calcite (Fig. 3C). Like the fine crystalline dolomite, crystals have a planar-S texture and lack undulatory extinction. Some medium crystalline dolomites have a cloudy centre and a clear rim (Fig. 3B). Although medium crystalline dolomite is generally non-luminescent under CL, some samples show blotches of dull-orange luminescence, suggesting possible neomorphism by later diagenetic fluids and/or two-stage dolomitization.

Massive replacement dolomites have the same stratigraphic occurrence in both the Southern Plateaux and the Main Ridge regions of the Rock (Fig. 2), although these are separated by a major NW–SE fault zone and the Main Ridge succession

is inverted. Both fine and medium crystalline types are abundant in the lower part of the Formation and decrease stratigraphically upwards (Figs 1 and 2). The lowest two members, Bleak and Europa, are completely dolomitized and consist of thick to thin-bedded and/or laminated dolomites. The overlying Keightley Member has massive replacement dolomites in the lower part, but these are succeeded stratigraphically by increasing amounts of limestone. The uppermost and thickest member, the Buffadero, consists mainly of limestone with scattered dolomite rhombs, patches and beds. The dolomitization clearly predated tectonic overturning of the Main Ridge strata, because the dolomite occurs in the stratigraphically lower levels both in the right-way-up Southern Plateaux section and in the inverted Main Ridge section (Fig. 2; Bosence *et al.*, 2000).

A recent study of cyclicity within the succession (Bosence *et al.*, 2000) indicates that the dolomitized portion of the succession relates to thinner than average high-frequency cycles interpreted to have formed during the falling stage and lowstand period of a low-frequency cycle (Bleak and Europa members). Thicker than average high-frequency cycles, which formed during a low-frequency transgressive phase, correlate with the up-section reduction in degree of dolomitization and the arrival of marine biota (Keightley and lower Buffadero members).

Diagenetic cements in the Gibraltar Limestone Formation include micrite, microspar, fibrous and radial fibrous calcite cements (Fig. 3C), which are inferred to have precipitated from sea water in a submarine environment (cf. Tucker & Wright, 1990). Fine and medium crystalline dolomites post-date these marine cements, filling the centres of pore spaces (Fig. 3C) or occurring as detrital internal sediments in geopetal structures, suggesting that dolomitization was also relatively early but post-dated marine CaCO₃ cements. The fine and medium replacement dolomites are cross-cut by stylolites (Fig. 3C) and by fractures that are filled with later stage calcite and dolomite cements that have not been investigated.

ISOTOPIC SIGNATURE OF EARLY JURASSIC SEA WATER

Because sea water shows secular variation in oxygen, carbon and strontium isotopic composition through geologic time (e.g. Burke *et al.*, 1982; Veizer *et al.*, 1997), it is critical to establish the isotopic signatures for Early Jurassic sea water before interpreting isotopic data from the Gibraltar dolomites. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of calcites precipitated from Early Jurassic sea water range from -3‰ to -1‰ PDB and 1‰ – 4‰ PDB, respectively (Fig. 4), according to analyses of pristine brachiopod shells and other calcitic fossils (Veizer *et al.*, 1997). Major *et al.* (1992) suggested that the oxygen isotopic fractionation between calcite and dolomite varies from 1.5‰ to 3.5‰ PDB. Taking a mean of 2.5‰ as the fractionation between dolomite and calcite, dolomites precipitated from normal Early Jurassic sea water should have $\delta^{18}\text{O}$ values from -0.5‰ to 1.5‰ PDB (Fig. 4). Dolomites formed by slightly evaporated Early Jurassic sea water before gypsum precipitation should therefore have $\delta^{18}\text{O}$ values slightly higher than 1.5‰ PDB (Figs 4 and 5). Dolomites

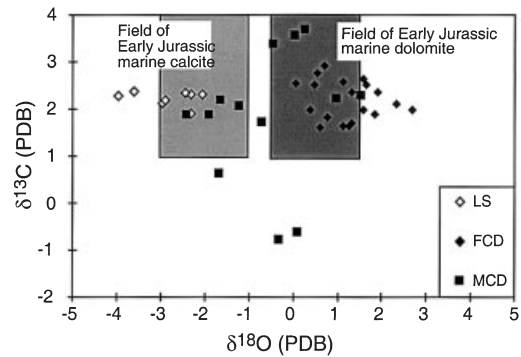


Fig. 4. A cross-plot of $\delta^{13}\text{C}$ against $\delta^{18}\text{O}$ for Gibraltar limestones and fine/medium crystalline dolomites, shown relative to fields plotted from the literature for Early Jurassic marine calcite (Veizer *et al.*, 1997) and calculated (cf. Major *et al.*, 1992) for Early Jurassic marine dolomite.

associated with present-day sabkha evaporites in Abu Dhabi have $\delta^{18}\text{O}$ values ranging from 1.4‰ to 4.0‰ (McKenzie, 1981).

Based on the analyses of whole carbonate rocks (Burke *et al.*, 1982) and belemnites (Jones *et al.*, 1994), the estimated $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Early Jurassic sea water range from 0.7071 to 0.7078 (Fig. 5). Diagenetically unaltered brachiopods collected from the upper parts of the Gibraltar Limestone Formation have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.707504–0.707570 (Fig. 5; Bosence *et al.*, 2000). This equates to the Sinemurian stage of the Early Jurassic (197.9–199.7 Ma).

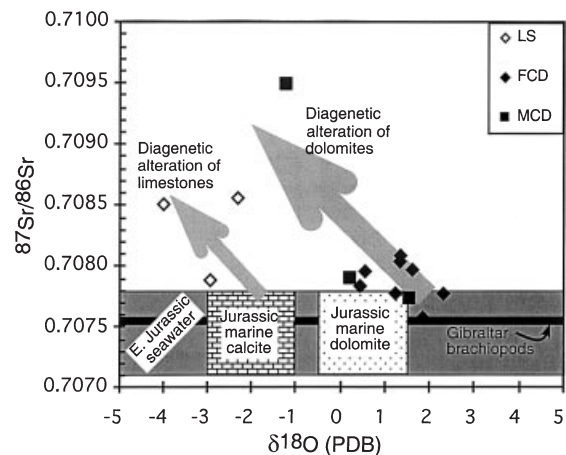


Fig. 5. A cross-plot of $^{87}\text{Sr}/^{86}\text{Sr}$ against $\delta^{18}\text{O}$ for Gibraltar limestones and fine/medium dolomites, shown relative to the range of $^{87}\text{Sr}/^{86}\text{Sr}$ values from Gibraltar brachiopod shells (Bosence *et al.*, 2000) and for Early Jurassic sea water (Jones *et al.*, 1994), with indication of apparent trends resulting from diagenetic alteration.

ISOTOPE GEOCHEMISTRY OF GIBRALTAR DOLOMITES

The $\delta^{18}\text{O}$ values display a gradual increase from the limestones to the medium crystalline to the fine crystalline dolomite (Fig. 4). The fine crystalline dolomite has the highest $\delta^{18}\text{O}$ values, ranging from 0.1‰ to 2.7‰ PDB (mean 1.2‰ PDB), which are either similar to or slightly higher than the expected values for dolomites formed by Early Jurassic sea water (Fig. 4). The $\delta^{18}\text{O}$ values of the medium crystalline dolomite vary from -2.4‰ to 1.5‰ PDB (mean -0.57‰ PDB; Fig. 4). Some of these values are slightly lower than those expected from dolomites formed by Early Jurassic sea water, whereas others are similar to the expected values and overlap with those of fine crystalline dolomites (Fig. 4). The $\delta^{18}\text{O}$ values for the limestones range from -4.0‰ to -2.1‰ PDB (mean -2.8‰ PDB), falling in the field of Early Jurassic marine calcite, except for two slightly lower values (Fig. 4).

The $\delta^{13}\text{C}$ values range from 1.6‰ to 2.9‰ PDB (mean 2.2‰ PDB) for fine crystalline dolomites, and from -0.8‰ to 3.6‰ PDB (mean 1.9‰ PDB) for medium crystalline dolomites. These fall within the range of published values for precipitates from Early Jurassic sea water except for three slightly lower values for medium crystalline dolomites (Fig. 4).

Five strontium isotope analyses taken from non-luminescent, matrix-free brachiopod valves from the upper part of the Buffadero Member vary from 0.707504 to 0.707570 (Bosence *et al.*, 2000; Fig. 5). Bulk strontium values from drilled limestone samples are higher and range from 0.70787 to 0.70856 (Fig. 5). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of eight fine crystalline dolomites range from 0.7076 to 0.7081 (mean 0.7079). Four of these ratios are similar to the estimated values of Early Jurassic sea water (0.7071–0.7078), and the remainder are slightly higher (Fig. 5). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of three medium crystalline dolomites are highly variable, ranging from 0.7077 to 0.7095 (mean 0.7084): one falls within the range of Early Jurassic sea water, one is close to but slightly higher than that range, and one is significantly more radiogenic.

DOLOMITIZATION MODEL

Petrographic evidence

The lack of normal marine biota from the lower dolomitized portion of the succession, the com-

mon occurrence there of restricted-marine, but moderate-energy peritidal carbonate facies, and the appearance of a restricted-marine biota of calcified green algae and agglutinated benthic foraminifera at horizons only where dolomite abundance decreases (i.e. at the top of the Keightley Member; Bosence *et al.*, 2000), all suggest waters of variable or elevated salinity during the deposition of the lower part of the succession. However, the absence of massive gypsum/anhydrite and/or evaporite solution-collapse breccias suggests that evaporated sea water did not reach the salinity required for abundant gypsum precipitation.

Isotopic evidence

The oxygen isotopes of the replacement fine crystalline dolomites are either similar to or slightly higher than those expected from Early Jurassic marine dolomite (Fig. 4). The highest $\delta^{18}\text{O}$ value is 2.7‰ PDB, about 1.2 to 3.2‰ higher than the estimated values for Early Jurassic marine dolomite (-0.5 to 1.5‰ PDB), indicating that the dolomitizing fluids were slightly evaporated Early Jurassic sea water. In addition, the $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of some fine crystalline dolomites fall within the range of expected values for Early Jurassic sea water (Figs 4 and 5), supporting the inference that this was the fluid responsible for dolomitization. The presence of a restricted marine biota and the rare gypsum pseudomorphs within parts of the Main Ridge succession is consistent with the penesaline rather than the normal marine salinity range for formation of the Gibraltar dolomites (Fig. 6).

The spread of $\delta^{18}\text{O}$ values from 0.1‰ to 2.7‰ (PDB) seen in the fine crystalline dolomites might result from factors such as: (1) mixing of evaporated sea water with fresh water; (2) variation in salinity resulting from different degrees of evaporation; and (3) diagenetic alteration during burial. The lack of negative $\delta^{13}\text{C}$ values and the absence of positive co-variation of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, typical of dolomites formed by mixed evaporative brines and fresh water (Meyers *et al.*, 1997), make the first possibility unlikely. Although dolomitizing fluids that originated from Early Jurassic sea water may have been subject to different degrees of evaporation and produced variable $\delta^{18}\text{O}$ values, the decrease in $\delta^{18}\text{O}$ values with a corresponding increase in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Fig. 5) is better explained by diagenetic alteration during burial. On this assumption, the primary composition of the fine crystalline dolomite was origin-

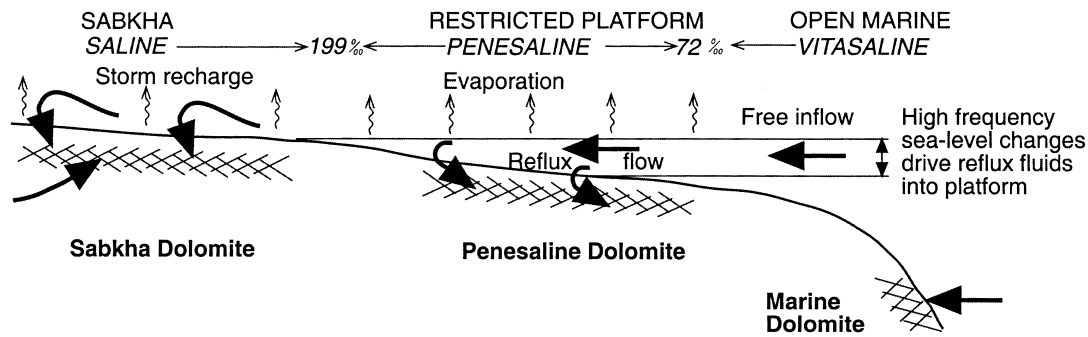


Fig. 6. Diagram indicating model for dolomitization of peritidal carbonates by slightly evaporated (penesaline) sea water in a restricted platform setting driven by high-frequency sea-level changes (after Adams & Rhodes, 1960; Tucker & Wright, 1990.).

ally in the range for dolomite formed by penesaline sea water (Fig. 5). Diagenetic alteration has produced a trend of decreasing $\delta^{18}\text{O}$ values with a corresponding increase in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, a trend also suggested by the limestone samples and the predicted Jurassic marine calcite field (Fig. 5).

Although some medium crystalline dolomites have oxygen, carbon and strontium isotopic values overlapping with those predicted for Early Jurassic marine dolomites, the remainder have lower $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ but higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Figs 4 and 5). The wider range of $\delta^{18}\text{O}$, $\delta^{13}\text{C}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ in the medium crystalline dolomite, compared with those of the fine crystalline dolomite, might be interpreted as the result of: (1) dolomitization at slightly higher temperatures during shallow burial; or (2) multistage dolomitization. A 1.8‰ (PDB) difference between the average $\delta^{18}\text{O}$ values of fine and medium crystalline dolomites indicates that the temperature of dolomitizing fluids was about 8 °C higher for medium crystalline dolomite if the $\delta^{18}\text{O}$ values of dolomitizing fluids were the same (equation of Land, 1985). The estimated thickness of the Gibraltar Limestone Formation is at least 460 m (Bosence *et al.*, 2000) with the younger Catalan Bay Shale of unknown thickness. Burial at ≈ 500 m depth would have been enough to raise the temperature of pore waters sufficiently to effect dolomitization of at least the lower parts of the formation (i.e. the Bleak and Europa members). For the second interpretation to be true, measured isotopic values should represent a mixture of early-stage fine crystalline dolomite with a later stage dolomite. This is supported by the cloudy centres with clearer rims and blotches of dull-orange luminescence seen under CL in some medium crystalline dolomite crystals (Fig. 3B). In both interpretations, Early Jurassic sea water is the presumed dolomitizing fluid.

Hydrology of dolomitizing fluids

The hydrological system of dolomitizing fluids with a slightly elevated marine (i.e. penesaline) salinity in a marginal marine setting is most similar to the reflux model described by McKenzie *et al.* (1980), i.e. a flow of denser saline waters from an inner platform outwards towards a less saline marine basin (Fig. 6). A revision to this classic reflux model has recently been proposed by Sun (1994) to explain the metre-scale, dolomitized, peritidal cyclic carbonates without associated evaporites that characterize greenhouse periods of Earth history. He proposed that dolomitization could occur in laterally extensive platform-top environments from repeated flooding and reflux of marine waters of slightly increased salinity. The combination of high-frequency, metre-scale cyclicity superimposed on low-frequency (third-order?) cycles within the Gibraltar Limestone indicates an additional mechanism whereby marine or elevated marine pore waters may be driven through the peritidal carbonates during high-frequency sea-level changes during low-frequency falling stages. Petrographic and isotopic data from this study, therefore, provide evidence for the validity of Sun's model. The volumetric flow model proposed by Shields & Brady (1995) also suggests that regional-scale reflux is a viable mechanism for regional-scale dolomitization during shallow burial (<500 m). On the Great Bahamas Bank, sea water of elevated salinity develops on the platform interior (e.g. Simms, 1984) and can be refluxed into the platform, resulting in massive dolomitization (Whitaker & Smart, 1990). Work undertaken on the Cretaceous of Israel (Sass & Katz, 1982) interprets massive dolomitization of evaporite-free, shallow-water carbonates with stable isotope values similar to those estimated

for Cretaceous sea water ($\delta^{18}\text{O}$ -2.5 to $+0.7$ and $\delta^{13}\text{C}$ -0.9 to $+2.5$).

Reflux of penesaline sea water driven by high-frequency sea-level changes could therefore produce a large-scale flow system that affects thousands of square kilometres on ancient carbonate platforms during periods of hydrographic restriction and climatic aridity, resulting in massive dolomitization.

The maximum abundance of replacement dolomite is within the first falling and lowstand phase of low-frequency (third-order?) cycles that affected the stratigraphically lowest portion of the Gibraltar Limestone (Bosence *et al.*, 2000) in the Bleak and Europa members. Reflux dolomitization has previously been argued to characterize sea-level falls in arid climate settings (Purser *et al.*, 1994) as brines are driven into previously deposited limestones. However, a second phase of falling and lowstand conditions in the uppermost part of the Gibraltar Limestone (Buffadero Member) is not affected by dolomitization. The Little Bay Shale Formation that underlies the Gibraltar Limestone Formation (Fig. 1) would probably have acted as a basal aquitard constraining fluid flow to within the overlying peritidal carbonates and thereby promoting dolomitization. Higher in the sequence, the Buffadero Member carbonates have coarser textures and are not underlain by an aquiclude, and the falling stage and lowstand carbonates are not dolomitized.

Global and regional comparisons

Dolomites are common in the Early Jurassic of western Tethys, and this is consistent with their recorded global abundance (60–65%) for this period (Given & Wilkinson, 1987).

Early Jurassic dolomites from western Tethys are reported from the Betic Mountains of Spain (e.g. Martín, 1979; Rey, 1997), the Atlas Mountains of Morocco (e.g. Crevello, 1991), central Tunisia (e.g. Soussi & M'Rabet, 1994), Greece (e.g. Flügel, 1983; Scherreiks, 2000), the Apennines (e.g. Colacicchi *et al.*, 1975; Barattolo & Bigozzi, 1996) and the Iblean Plateau (Ronchi *et al.*, 2000) of Italy. Few of these studies include detailed geochemical analyses for the dolomite enabling environments of dolomitization to be established. Exceptions are Soussi & M'Rabet (1994) and Ronchi *et al.* (2000) who both interpret a deep burial environment for dolomitization of cyclic peritidal carbonates. This is in contrast to the shallow post-depositional environment proposed here for the dolomites of the Gibraltar Limestone.

Clearly, these widespread Early Jurassic dolomites formed in different geological environments, and more studies are required before a regional model for dolomitization can be proposed.

SUMMARY AND CONCLUSIONS

Peritidal carbonates of the lower part of the Lower Jurassic Gibraltar Limestone Formation have been replaced by fine and medium crystalline dolomites. The dolomitizing fluid responsible for the fine crystalline dolomite is inferred to have been penesaline Early Jurassic sea water that refluxed through the primary carbonate sediments during high- and low-frequency sea-level changes. This is supported by $\delta^{18}\text{O}$ values that are either similar to, or slightly higher than, those expected for Early Jurassic marine dolomite, and $\delta^{13}\text{C}$ values and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that overlap those of Early Jurassic sea water. The absence of massive evaporitic minerals and/or solution-collapse breccias in these inner-platform carbonates indicates that evaporation of sea water during dolomitization did not attain the concentration at which massive deposits of gypsum would precipitate.

Some of the medium crystalline replacement dolomite has oxygen, carbon and strontium isotopic values similar to those of Early Jurassic marine dolomites, whereas others have lower $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ but higher $^{87}\text{Sr}/^{86}\text{Sr}$. Early Jurassic sea water is interpreted as the possible dolomitizing fluid for the medium as well as the fine crystalline dolomite. The wider ranges of oxygen, carbon and strontium isotopes of the medium crystalline replacement dolomite, however, might indicate:

1 dolomitization during shallow (≈ 500 m) burial and consequently slightly higher temperature; or

2 multistage dolomite generation, as suggested by cloudy centres with clear rims and blotches of dull-orange luminescence in some medium crystalline dolomite.

Contrary to some classic models of dolomite formation, which infer the action of hypersaline brines, isotopic data from this study indicate that massive dolomitization may also occur in peritidal carbonates through the reflux of penesaline sea water driven by a combination of high- and low-frequency sea-level changes. This study, together with previously published dolomitization models, indicates that replacement dolomites

can be produced by sea water or modified sea water with a wide range of salinities, including normal, penesaline to hypersaline, provided that there is a driving mechanism for fluid flow.

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