Lower Permian brachiopods from Oman:
Their potential as climatic proxies

L. Angiolini¹, D. P. F. Darbyshire², M. H. Stephenson³, M. J. Leng²&⁴, T. S. Brewer⁵, F. Berra¹ and F. Jadoul¹

¹ Dipartimento di Scienze della Terra ‘A. Desio’, Università degli Studi di Milano, Via Mangiagalli 34, Milano, 20133, Italy.
E-mail: lucia.angiolini@unimi.it
² NERC Isotope Geosciences Laboratory, British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK.
³ British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK.
⁴ School of Geography, University of Nottingham, Nottingham NG7 2RD, UK.
⁵ Department of Geology, University of Leicester, University Road, Leicester, LE1 7RH, UK.

ABSTRACT: The Lower Permian of the Haushi basin, Interior Oman (Al Khlat Formation/lower Gharif member) records climate change from glaciation, through marine sedimentation in the Haushi sea, to subtropical desert. To investigate the palaeoclimatic evolution of the Haushi Sea we used δ18O, δ13C, and Sr isotopes from 31 brachiopod shells of eight species collected bed by bed within the type-section of the Saiwan Formation. We assessed diagenesis by scanning electron microscopy of ultrastructure, cathodoluminescence, and geochemistry, and rejected fifteen shells not meeting specific preservation criteria. Spiriferids and spiriferinids show better preservation of the fibrous secondary layer than do orthotetids and productids and are therefore more suitable for isotopic analysis. δ18O of −3.7 to −3.1‰ from brachiopods at the base of the Saiwan Formation are probably related to glacial meltwater. Above this, an increase in δ18O may indicate ice accumulation elsewhere in Gondwana or more probably that the Haushi sea was an evaporating embayment of the Neotethys Ocean. δ13C varies little and is within the range of published data: its trend towards heavier values is consistent with increasing aridity and oligotrophy. Saiwan Sr isotope signatures are less radiogenic than those of the Sakmarian LOWESS seawater curve, which is based on extrapolation between few data points. In the scenario of evaporation in a restricted Haushi basin, the variation in Sr isotope composition may reflect a fluviol component.

KEY WORDS: carbon, cathodoluminescence, geochemistry, Gondwana deglaciation, Haushi basin, late Sakmarian, oxygen, strontium isotopes, ultrastructure.

Articulated brachiopod shells (Subphylum Rhyynchonelliformea) are known to record the primary geochemical signal of ancient seawater, as the low-Mg-calcite (LMC) of their shell is generally resistant to diagenetic change (i.e., Compston 1960; Lowenstam 1961; Popp et al. 1986; Veizer et al. 1986, 1999; Korte et al. 2003, 2005). Articulated brachiopods secrete a two- or three-layered calcite shell below an outer proteinaceous periostracum. The primary layer is prismatic and generally has carbon and oxygen isotope ratios that are lower than expected for equilibrium, whilst the secondary layer is fibrous or laminar and is thought to precipitate in isotopic equilibrium with ambient seawater (Lowenstam 1961; Brand 1989; Grossman et al. 1991; Brand et al. 2003). The tertiary layer, when present, is prismatic and locally confined inside the shell. Vital effects are generally not recorded in the slow-growing secondary layer of brachiopod shells, though Carpenter & Lohmann (1995) found differences within individual specimens in the thin outer primary layer and in specialised areas of the secondary shell. Curry & Fallick (2002) recorded different δ18O values from the dorsal and ventral valves of a terebratulid species from the mouth of a narrow cave on the Otago Peninsula (New Zealand). Auclair et al. (2003) found deviations of several per mil from expected equilibrium values in the outer part of the secondary layer of one punctate intertidal brachiopod shell. Very recently, Parkinson et al. (2005) have shown that δ18O values from the fibrous secondary or prismatic tertiary shell layers of recent Terebratulida (including the same species already analysed by Curry & Fallick (2002) and Auclair et al. (2003) and Rhyynchellidae species were in oxygen isotopic equilibrium with ambient seawater and were relatively unaffected by shell specialisation. Also, Parkinson et al. (2005) found no significant difference in δ18O compositions between ventral and dorsal valves. However, carbon isotope composition can be highly variable and possibly subjected to a vital effect produced by metabolic prioritisation. Therefore it is the innermost and, when possible, non-specialised secondary layer of fossil brachiopod shells with similar ultrastructures to modern Terebratulida and Rhyynchellida that should be sampled for stable isotope ratios.

The isotopic composition of carbon (δ13C), oxygen (δ18O) and strontium (87Sr/86Sr) in ancient seawater has varied through time in response to palaeoenvironmental evolution. Brachiopods are among the best shells from which to obtain
limestones, previously informally named the Haushi limestone by Hudson & Sudbury (1959). The Saiwan Formation was deposited in the Haushi sea, south of the Neotethys Ocean rift shoulder (Fig. 2), and overlies both the glacigene diamicrite of the Al Khlat Formation and the basal sandstones of Osterloff et al. (2004). At its top, the Saiwan Formation is believed to be bounded by an unconformity, separating it from the overlying continental Gharif Formation sensu Dubreuilh et al. (1992). Angiolini et al. (2003a) showed the evolution of a pioneering cold-water brachiopod palaeocommunity (Pachycyrtella palaeocommunity) at the base of the formation, followed by a more mature secondary palaeocommunity of a more diversified marine biota above. The Pachycyrtella palaeocommunity is characterized by: (1) a random distribution pattern over a limited area; (2) clustering in groups; (3) numerical dominance (>85%) of P. omanensis; and (4) suspension feeding. Palaeoecological analyses (Angiolini et al. 2003a, 2006) suggested that these brachiopods thrived on a mobile arenitic substrate at shallow depths around or just below the fair weather wave base (10–20 m). The brachiopods also had rapid rates of reproduction and growth (r-strategy), reached maturity early and had high mortality rates in the juveniles (Angiolini et al. 2003a). The disappearance of this basal palaeocommunity is related to a drastic change in the physical environment, recording the interplay of final Gondwanan deglaciation and initial Neotethys opening (Angiolini et al. 2003a). The secondary palaeocommunity rapidly reached high diversity, testifying to a significant climatic amelioration and more stable environmental conditions. Both the Pachycyrtella palaeocommunity and the overlying secondary palaeocommunity are dominated by large spire-bearing brachiopods, suggesting a high nutrient setting (Perez-Huerta & Sheldon 2006). Eutrophic condition at the base of the Saiwan Formation evolved upward into more oligotrophic conditions.

Stephenson & Osterloff (2002) and Stephenson et al. (2005) studied equivalent beds in the subsurface of South Oman. In this region, the equivalent-aged rocks comprise clastic sandstones of terrestrial origin, suggesting that the Haushi sea did not transgress as far south as South Oman. However, the palynological succession allowed detailed metre-by-metre reconstruction of vegetational changes within the deglaciation period. In the lowest part of the South Oman lower Gharif member, a cold climate ‘fern’ wetland palaeocommunity was present, probably on lowland outwash alluvial plains, whilst on the surrounding uplands or better-drained ground, a primitive conifer community developed (Stephenson et al. 2005; Stephenson & Osterloff 2002). Later in the postglacial period these communities were replaced. In the lowland alluvial plains, a cycad-like and lycopsid vegetation developed, while in the uplands or better drained areas a taeniate- and non-taeniate bisaccate pollen producing glossopterid or other gymnospermous flora was established. Slightly later, restricted marine conditions occurred in parts of the sedimentary basin in South Oman. Within the bodies of brackish or salt water, an ephemeral microflora and fauna (indicated by rare acritarchs and microforaminiferal linings) developed. Evidence from the carbon isotope composition of bulk organic material from the Al Khlat and lower Gharif formations show a trend which is thought to reflect postglacial warming, since there is sedimentological and palaeontological evidence of deglaciation in the sequence (Stephenson et al. 2005).

The age of the limestones of the lower Gharif member, the subsurface equivalent of the Saiwan Formation, was established in subsurface borehole core sections of Wafra-6 and Hasirah-1 around 100 km to the west of the Saiwan Formation outcrop (Angiolini et al. 2006). Samples from two horizons contained the fusulinids Pseudofusulina inobservabilis Leven, the primary geochemical signal and environmental information. This present study assesses the degree of diagenetic alteration by scanning electron microscopy (SEM), cathodoluminescence (CL), and geochemistry from a suite of brachiopods from the Lower Permian Saiwan Formation, Interior Oman. It then investigates the evolution of the Haushi sea, the body of water in which the Saiwan Formation was deposited, using O, C, and Sr isotopes of brachiopod shells collected bed by bed from the Saiwan Formation.

1. Geological setting

In central Interior Oman, Lower Permian strata are represented by the Al Khlat and Saiwan formations in surface outcrop (Fig. 1) and by the Al Khlat Formation and the lower and middle Gharif members in the subsurface. Correlation of these units, particularly the Saiwan Formation and the lower Gharif member, has only recently been understood based on brachiopod and palynomorph biozones (Angiolini et al. 2006).

The surface Saiwan Formation was introduced by Dubreuilh et al. (1992) for the marine fossiliferous sandy

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**Figure 1** Geological sketch map of the Haushi surface outcrop area in central interior Oman, with location of the Saiwan type section (modified from Angiolini et al. 2003a).

2. Material and methods

Thirty four articulated brachiopod specimens from the *Pachycyrtella* palaeocommunity (bed OL14 Fig. 3) and the overlying secondary ecological palaeocommunities (beds OL15–OL18 Fig. 3) of the Saiwan Formation were selected for ultrastructural analysis. Of these, 31 underwent subsequent geochemical and isotope analyses and the data are shown in Table 1. The analysed brachiopods belong to seven species of the orders *Productida* (*Rideoconcha permixta*), *Orthotetida* (*Derbyia hardmani* Foord, 1890), *Spiriferida* (*Neospirifer* (*Quadrospira*) aff. *hardmani* Foord, 1890) and *Spiriferinida* (*Pachycyrtella omanensis* Angiolini, 2001, *Pachycyrtella* sp. A, *Punctocyrtella spinosa* Płodowski, 1968, *Subansiria cf. ananti* Singh, 1978). The systematic palaeontology of those brachiopods has already been published (Angiolini et al. 1997, 2003a; Angiolini 2001).

The specimens were embedded in resin, cut along longitudinal and transverse sections, then etched with 5% HCl for 20 s and metallic coated before being investigated using SEM to check the preservation of their shell fabric. In addition thin sections were made to allow cathodoluminescence microscopy along the same sections.

The brachiopods were sampled for geochemical and isotope analysis by drilling 6–8 mg along the longitudinal section of each shell using a diamond drill bit. The powder was split into two parts, one for geochemistry and Sr isotopes and the other for C and O isotopes. Only the diagenetically unaltered inner part of the thick secondary shell layer of both the ventral and dorsal valves was sampled for geochemical and isotope analyses (Table 1). Features such as the muscle attachment areas, articulation points, interareas and lophophore support were avoided, although Parkinson et al. (2005) showed there is a minimal risk when sampling specialised shell fragments.

Geochemical analyses were undertaken at the analytical geochemistry laboratories at the British Geological Survey and the Department of Geology, University of Leicester. Subsamples for geochemical analysis at the British Geological Survey and for Sr isotope analysis were dissolved in ultra-pure acetic acid. The acetic acid leached fraction reserved for geochemistry (see below) was evaporated to dryness and the residue taken up in 1% nitric acid. Geochemical data were obtained by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) on a Fison/ARL 3580 simultaneous/sequential spectrometer with Gilson auto sampler.

At the Department of Geology, University of Leicester, all the samples were digested in acetic acid and analysed using a Horiba Jobin Yvon Ultima ICP Optical Emission Spectrometer. The sample digestion was often incomplete, and residues composed of white, yellow or red material were found in some samples. A number of samples were analysed in both the British Geological Survey and University of Leicester
laboratories, and, given the partial dissolution that occurred for some samples, the data are consistent between the two laboratories. Although a direct one-to-one correlation is not observed between the two data sets, the positive covariance between individual elements indicates that the data sets are comparable and that any differences are the result of the partial dissolution and possible weighing errors, given the small sample sizes.

Approximately 5 mg of the powdered carbonate was used for the carbon and oxygen isotope analysis. The sample material was reacted with anhydrous phosphoric acid in vacuo overnight at a constant 25°C. The CO2 liberated was separated from water vapour under vacuum and collected for analysis. Measurements were made on a VG Optima mass spectrometer. Overall analytical reproducibility for these samples is normally better than 0.1% for δ13C and δ18O. Isotope values (δ13C, δ18O) are reported as per mil (%). Deviations of the isotopic ratios (13C/12C, 18O/16O) calculated to the VPDB scale using a within-run laboratory standard norm were 0.710248 for NBS 987. Replicate determinations (n=128) of the 0.0000097 (2σ) obtained for the NBS 987 international standard were made at three separate times and the relevant mean values were normalised to the accepted value n=11) and 0.7102486 (2σ). Analyses on the Triton were operated in static mode. Thirty analyses of the international standard for Sr isotopes were carried out at BGS, half of the solution retained for this purpose. The remaining solution was evaporated to dryness and the residue was taken up in 2.5 M HCl. Strontium was separated by conventional cation exchange techniques using BioRad AG 50W-X8 ion exchange resin. Sr samples were loaded on rhenium (Re) filaments together with a tantalum superimposed solid symbols indicate that the isotope values from two or more specimens from the same stratigraphic level (data highlighted in bold in Table 1); multiple superimposed solid symbols indicate that the isotope values from two or more specimens from the same stratigraphic level are identical. The solid line represents the average trend. The open symbols and the dotted line represent the data from four additional specimens (OM46-9, OL17-4, OL15-66, IS-4; data underlined in Table 1) which, despite showing a diagenetically altered and luminescent shell fabric, have acceptable contents of Fe, Mn and Sr.

The SEM study of the ultrastructure is a common technique to check the preservation of shell fabric. The classification of the shell ultrastructure has been carefully described byWilliams (1966, 1968, 1971), McKinnon (1974), and Williams in Williams et al. (1997). A recent paper by Samtleben et al. (2001) presents a classification of nine types of ultrastructure based on a combination of biological fabric and diagenetically altered structures. For present purposes, a classification that enhance the types of pristine shell fabric is preferred, in order to distinguish the original features of the shell from subsequent changes caused by diagenesis. Therefore, McKinnon (1974) and Williams in Williams et al. (1997) are followed for the description of the unaltered shell fabric, distinguishing specimens which show perfectly shaped or slightly imperfect and amalgamated fibres of the secondary layer from those where the secondary layer is laminar. When the shell fabric is obliterated by dissolution, amalgamation and reccrystallisation the specimens are considered as diagenetically altered.

Cathodoluminescence (CL) is a screening technique widely used to assess preservation of brachiopod shells (Popp et al. 1986; Grossman et al. 1993), as they commonly show no luminescence in absence of significant geochemical alteration. However, its reliability to distinguish altered from unaltered shells has been questioned, as modern unaltered brachiopod shells can sometimes display orange-coloured luminescence typical of altered carbonate, whereas some clearly altered fossil shells can, in fact, be non-luminescent (Korte et al. 2005). England et al. (2006) have recently shown that hyperspectral CL imaging can overcome the drawbacks of conventional optical CL and determine the real causes of luminescence. They showed that the direct comparison of optical CL analyses is hampered by the fact that beam current conditions vary in the different studies. To overcome this problem of comparison between the present data, all the samples were analysed with the same instrument operating under the same beam conditions. Furthermore, CL was integrated with the other two screening techniques, cross-checking the results before discarding isotope analyses.

The third screening technique was the determination of trace element contents of Ca, Mg, Fe, Mn and Sr in the calcite shell to assess if certain elements were in concentrations usually found in modern brachiopods. According to Brand et al. (2003) well-preserved modern brachiopods from a variety of depositional environments display Sr contents of 450–1928 ppm. Mn concentrations range from 1–199 ppm with the majority of specimens containing <80 ppm, and Fe contents are generally <140 ppm although values as high as 610 ppm were observed. Popp et al. (1986) reported Sr contents as high as 3400 ppm and Mn of 250 ppm in non-luminescent portions of Palaeozoic brachiopod shells. However, the majority of their samples, which were mainly Carboniferous and Permian in age, displayed Sr and Mn concentrations within the range reported for modern brachiopods. Korte et al. (2003) adopted the criteria of <250 ppm Mn and >400 ppm Sr for samples to be classified as well preserved. Bruckschen et al. (1999) accepted a more conservative cut-off limit of 200 ppm for Mn, which they considered to be a more reliable indicator of...
### Table 1: Table of results.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Valve</th>
<th>Species</th>
<th>Ultrastructure</th>
<th>Cathodolum</th>
<th>Ca (ppm)</th>
<th>Fe (ppm)</th>
<th>Mg (ppm)</th>
<th>Mn (ppm)</th>
<th>Sr (ppm)</th>
<th>δ13C</th>
<th>δ18O</th>
<th>87Sr/86Sr</th>
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<td>753</td>
<td>&lt;8</td>
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</table>

Key to ultrastructure: SL secondary layer; DA diagenetically altered.

Samples highlighted in bold are brachiopods thought to retain pristine carbonate based on ultrastructure, Mn<200ppm, Fe<120ppm Sr 400-800ppm. Samples underlined have a diagenetically altered secondary layer, but acceptable values in trace element contents. NL: non luminescent shell; L: luminescent shell; NL/L: non luminescent shell with luminescent areas.
diagenetic alteration than Sr content. High concentrations of both Mn and Fe can result from surface coatings of oxy-
hydroxides, and low Mn and Fe are not always reliable
indicators of pristine calcite as both elements are insoluble
under oxic conditions (McArthur et al. 2000). Therefore, the Sr
concentration and isotope composition of the calcite could be
altered during oxic diagenesis without raising the Mn and Fe
to levels of concern. Popp et al. (1986) ascribed the variability in Sr concentration as mainly due to taxonomic
differences among samples; however Joachimski et al. (2005)
observed the highest concentrations in Silurian brachiopods
(1211–1830 ppm) and much lower values (556–707 ppm) in
those which were Permian in age. Steuber & Veizer (2002)
explained the trend in Sr/Ca ratios measured in biogenic
low-Mg calcite from high values observed in the Silurian to
lower ratios for the Carboniferous and Permian by the change
in the predominant carbonate phase from Sr-rich calcite to
Sr-rich aragonite. Joachimski et al. (2005) therefore considered
that the low Sr concentrations in the Permian carbonates
resulted from precipitation of shell calcite from seawater with
low Sr/Ca ratios rather than from a diagenetic loss of Sr. Ca
and Mg concentrations were analysed to establish the bulk
compositions of the shells.

In the present study, limits of 200 ppm for Mn and 400–
800 ppm for Sr have been adopted, and samples with
Fe>120 ppm have been excluded.

4. Results

4.1. Ultrastructural analyses

The shell structure of thirty-four specimens (OL14-1, OL16-35,
OM48-14, in addition to those listed in Table 1) belonging to
eight different species of articulated brachiopods (Reedoconcha
permixta, Derbyia haroubi, Neospirifer (Quadrospira) aff. hard-
manti, Pachycyrtella omanensis, Pachycyrtella sp. A, Punctocyrtella
spinosa, Cyrtella sp. A, Subansiria cf. ananti) was
analysed using a SEM (Figs 4–6).

The outer primary layer is very rarely preserved and it was
only clearly detected in one specimen (Fig. 5 (4)), where it
shows an acicular fabric. The secondary layer is invariably
present with different degrees of preservation (Table 1) and
shows two kinds of fabric: (i) calcite fibres in the spiriferids and
spiriferinids (Fig. 4 (1–8), Fig. 5 (1–8)) as in the secondary
layer of recent Terebratulida and (ii) calcitic lamination in
productids and orthotetids (Fig. 6 (1–8), Fig. 7 (1)). The fabric
of fibrous secondary shell is the result of the elongation of
discrete patches of calcite into fibres within proteinaceous
sheaths (Williams 1966, 1968, 1971; Williams in Williams et al.
1997; McKinnon 1974). Fibres tend to grow differentially
forming spiral arcs with local modifications and re-orientation
(Fig. 5 (6)), but remaining strongly interlocked and orthodoxly
stacked (Fig. 4 (2–5), Fig. 5 (7)). The secondary layer increases
in thickness from the anterior margin to the umbo, where it
shows consistent variation in the orientation of the calcite
fibres producing shell strengthening (Alvarez 1990). In all the
investigated spire-bearing genera the transverse sections of
orthodoxly stacked fibres have a keel and saddle morphology,
9–16 μm wide and 2–5 μm thick (Fig. 4 (1, 6), Fig. 5 (1–2, 8)),
with Neospirifer (Quadrospira) aff. hardmani showing the larg-
est and thickest fibres. Its shell structure is consistent with that
observed by McKinnon (1974) for a Carboniferous species of
Neospirifer, whose secondary orthodoxly stacked fibres measured
up to 15 μm in width.

In Pachycyrtella omanensis, Pachycyrtella sp. A, Punctocyrtella
spinosa, Cyrtella sp. A and Subansiria cf. ananti the fibrous fabric is perforated by thin and sparse unbranched
punctae (16–27 μm in diameter) around which the fibres are
outwardly deflected (Fig. 5 (3, 5)), but no perforate canopies at
their distal end could be detected. These spiriferinid genera are
thus characterised by punctate shells with very thin and sparse
punctae, whose volume is negligible when compared with the
total volume of the shell. This imply that the calcitic fillings the
punctae are volumetrically negligible and do not affect the geochemical and isotopic analyses of the shells
(Table 1).

The secondary fabric of the orthotetid Derbyia haroubi and
of the productid Reedoconcha permixta is a cross-bladed
lamination, which is well preserved in the former (Fig. 6 (1–3))
and strongly altered in the latter (Fig. 6 (4–8)). Laminae are
about 1·5–3 μm thick in Derbyia haroubi, thus thicker than the
lamination observed by Williams (1968, p. 43) in another
Permian species of Derbyia. Pseudopunctae have been detected
in both of these taxa, but are usually rarer and consist of
rosettes of conical laminae (20–25 μm wide) in Derbyia haroubi
(Fig. 6 (2)), whereas they are coarser (50 μm wide), densely
distributed and with a rod of recrystallised calcite at the core
(taleola) in Reedoconcha permixta (Fig. 6 (7)). Hollow spines
communicating with canals to the shell interior and formed by
concentric banding of flat laminae (Williams 1968) have also
been detected in Reedoconcha permixta (Fig. 6 (8)). The strongly altered secondary fabric of Reedoconcha permixta
may be related to a higher organic content (proteinaceous
membranes), the porous fabric of in vivo taleolae (Williams
in Williams et al. 1997) and to the occurrence of hollow
bases of spines, which may have favoured dissolution and
recrystallisation.

A few specimens of Neospirifer (Quadrospira) aff. hardmani,
Pachycyrtella omanensis and Derbyia haroubi show local traces
of biocorrosion (Fig. 4 (7); Fig. 6 (3)) probably caused by
crusting bryozoans and barnacles. These traces differ from
the porosity caused by punctae by their larger dimensions,
their branched arrangement and by the absence of deflection
of the secondary layer fibres which surround them. Also they
develop from the outer shell surface towards the interior,
without reaching the innermost shell layer (Fig. 6 (3)). Their
number, shape and arrangement (Fig. 8 (6)) indicate they
are domicinial borings (Angiolini et al. 2003a) and not boreholes
caused by predation, which are usually few per shell, are drilled
perpendicular to shell surface and shoe site selectivity.

Based on the preservation of the secondary layer fabric, the
analysed brachiopods were subdivided into two categories
(Table 1): ‘preserved’ when all fibres/ laminae of the secondary
layer are intact (Fig. 4 (1–5), or when occasionally some
fibres/laminae are imperfectly shaped (Fig. 4 (6), Fig. 5 (8)); or
‘diagnostically altered’ when the fabric is obliterated by dis-
solution, amalgamation and recrystallisation (Fig. 6 (4, 6); Fig. 7
(3, 5)).

4.2. Cathodoluminescence

Following SEM analysis, CL investigation of brachio-
pod shells was performed using a Nuclide luminescope (ELM28)
operating at 10 KV. Neospirifer (Quadrospira) aff. hardmani,
Pachycyrtella sp. A, Punctocyrtella spinosa and Subansiria cf.
ananti appear mostly non luminescent with rare thin lines or
bright calcite punctae infillings (Fig. 8 (2, 4)). Generally there is
good correspondence to the shell ultrastructure, with preserved
specimens lacking any trace of luminescence indicating that the
shells have not been affected by diageneric alteration (Fig. 8 (2)). When the ultrastructure indicates dissolution, amalgamation and
recrystallisation of secondary layer fibres, the shell fabric is
luminescent (Fig. 7 (3–6), Fig. 8 (3, 5)). In some cases it is likely
that luminescence, where it occurs, has been caused by diagene-
netic diffusion of Mn from the matrix to the shell through

radial microfractures mainly produced by burial compaction (Fig. 7 (3–4), Fig. 8 (3)). However there are exceptions, for example a well-preserved secondary laminar fabric, is seen in *Derbyia haroubi* but these specimens are also characterised by a luminescent shell (Fig. 7 (1–2), Fig. 8 (1)). This may be related to a higher organic content (proteinaceous membranes, luminescent in CL) in the original in vivo laminar fabric, whose post-mortem decomposition may cause an intra-laminar porosity. The latter in turn controlled the diffusion of Mn during diagenesis along laminar boundaries producing the pattern observed in Fig. 8 (1).

The specimens of *Pachycyrtella omanensis* show a very peculiar rhythmic pattern of bright CL lines, running diagonally to the shell exterior. In most cases this microstructures are periodically spaced and uniformly wide, but in some specimens they widen and grade into the surrounding non-luminescent shell fabric (Fig. 7 (7–8), Fig. 8 (7)). Rhythmic CL lines are known to occur in modern brachiopods and some other marine invertebrates due to lower growth rates or growth disturbance (Barbin & Gaspard 1995), but they have been only very recently detected in fossil brachiopods (Tomášových & Farkáš 2005). These authors correlated the distribution pattern of CL lines to changes in growth rates caused by short-term environmental instability suggesting that species found in stable environmental settings are more likely to have a regular repetition of CL lines, whereas species of shallower water settings have an irregular CL line patterns. This is supported by this study as we see that in some shells, the width and spacing of CL lines is more irregular and especially in *Pachycyrtella omanensis* which inhabited a shallow-water, physically-stressed, high-energy, environment. However, CL lines may also be related to diagenetic processes (Tomášových & Farkáš 2005) and there is not enough data to solve this uncertainty. What is certain is that widening of CL lines into irregular fringed banding is due to diagenetic diffusion (Fig. 8 (7)).

The relationships between preservation and luminescence can be interpreted taking into account the characteristic of the bulk rock, which is generally characterised by different orange colours recording the major diagenetic events. Most of the bioclasts (bivalves, gastropods, echinoderms, byozoans) and coated grains are predominantly orange (Fig. 8 (8)), whereas the pristine fibrous secondary layer of brachiopods is usually black. CL analysis of microfacies suggests that diagenesis did not significantly affect the resistant original fibrous fabric of the brachiopod shells.

4.3. Elemental data

As stated in section 3, a limit of 200 ppm for Mn had been adopted in this study and samples with Fe>120 ppm have been excluded. Not all the samples with high levels of Mn have elevated Fe contents (Table 1) and in the case of OM46-16, high Fe is accompanied by very low Mn. Also, whilst some samples which exhibit diagenetic alteration have high Mn and Fe, some have contents which would be deemed acceptable (OM46-9, OL17-4, OL15-66; I5-4).

Sr concentrations in the analysed brachiopods range from 225 to 1335 ppm (Table 1), however all of the specimens with Sr<500 ppm display other indicators of poor preservation. Three samples have much higher concentrations than the norm and Mn and Fe above the adopted cut-off levels. Sr levels generally decrease during diagenetic alteration of low-Mg calcite; however if the fluid responsible for the alteration was Sr rich, then increased concentrations might be observed. Celestite occurrences are reported from the top of the Al Khlata Formation and in the clastic basal deposits of the Saiwan Formation (Angiolini et al. 2003a, Le Métour et al. 1994), possibly indicating migration of supersaline brines during diagenesis.

Sr/Ca ratios of the pristine brachiopods range from 0-60 to 0-87 mmol/mol and a Sr/Ca ratio for seawater may be calculated assuming a value for the molar distribution coefficient for Sr of 0-13 \(\left[\frac{\text{Sr}}{\text{Ca}}\right]_{\text{seawater}}\) as observed in modern brachiopods (Steuber & Veizer 2002). The resultant mean ratio of 5·35 ± 0·64 mmol/mol is comparable with values calculated by Steuber & Veizer (2002) for the Early Permian seas.

Interestingly, brachiopods with laminar secondary layer show trace element contents outside the acceptable values even when the ultrastructure is very well preserved (*D. haroubi* in OL15). This is in agreement with the data of Parkinson et al. (2005), who showed that extant brachiopods with laminar ultrastructure (i.e. craniids) do not record ambient seawater composition and are not recommended as climate proxies.

Brachiopods thought to retain pristine carbonate based on ultrastructure, CL and trace elements are highlighted in bold in Table 1. Their isotope values have been used to construct the solid curves in Figure 3. However, there are four additional specimens (OM46-9, OL17-4, OL15-66, I5-4; underlined in Table 1) which despite showing a diagenetically altered and luminescent shell fabric have acceptable contents of Fe, Mn and Sr. Those have been added using a dotted line in Figure 3 and are discussed in the following sections.

4.4. Stable isotope data

Carbon and oxygen data from 31 brachiopod shells which were analysed for stable isotopes range between +0·5 and +3·7 ‰, and are discussed in the following sections.

When plotted stratigraphically (solid symbols in Fig. 3), the pristine brachiopods show the lowest δ18O that is higher than 

-4·2 to -0·5 ‰, respectively. The lower δ18O occur in samples where there is other evidence for alteration. However, on the whole, the stable isotope data do not provide supporting evidence for alteration. The brachiopods which are thought to be comprised of pristine carbonate (samples highlighted in bold, Table 1) have δ13C between +3·3 to +5·4 ‰ and δ18O -3·7 to -0·5 ‰. The oxygen isotope data lies within the range that is generally thought to represent Permian seawater values (Korte et al. 2005).
the lowermost OL14. Plotting also the values of the four additional specimens which show a diagenetically altered and luminescent shell fabric, but have acceptable contents of Fe, Mn and Sr (samples underlined in Table 1 and represented by open symbols in Fig. 3), results in a very similar trend which is slightly smoothed especially in correspondence of the decrease in OM47. Data from the stratigraphic level OL14 are derived from the use of the single species *P. omanensis*, whereas the results from the overlying stratigraphic beds are obtained using a combination of different species (*N. (Q.) aff. hardmani, Cyrtella sp. A, Pachycyrtella sp. A, P. spinosa, S. ananti*); this could imply a taxonomic control on the trend. However, Parkinson *et al.* (2005) found no significant difference in δ18O values from the secondary layer of four terebratulid and one rhynchonellid co-existing species, thus excluding a taxonomic control on brachiopods with this standard ultrastructure. Also *Pachycyrtella* sp. A, the species control on brachiopods with this standard ultrastructure. Similarly, in the over-:

### 4.5. Strontium isotope data

The strontium isotope ratios of brachiopod specimens from bed OL14 are significantly higher than those from higher levels in the sequence. The three samples considered to be pristine (highlighted in bold in Table 1) yield a mean 87Sr/86Sr ratio of 0.7078021 ± 0.0000058 (2σ) and all of the less well-preserved samples have higher ratios. Sample OL14-400 has a Sr isotope composition which approaches that obtained for a sample of celestite from the base of the Saiwan Formation (0.7082904; D. P. F. Darbyshire, unpublished data) suggesting that it might be the source of the elevated Sr concentration. The mean ratio for the four pristine specimens from level OL15 is 0.7077915 ± 0.0000318 (2σ), and with the exception of OL15-66, the altered samples display higher ratios. However, specimen OL15-23 with a Sr concentration of 1040 ppm did not have the highest Sr isotope signature. Only one of the brachiopods from bed OL17/OM46 passed all the selection criteria for good preservation (OM46-17 87Sr/86Sr=0.7078169); surprisingly the mean ratio for all five samples is almost identical (0.7078167 ± 0.0000762), but the large error reflects the range in values. The values obtained by the two additional specimens OM46-9 and OL17-4 are very close to the value obtained by the only one of the brachiopods which passed all the selection criteria for good preservation (Fig. 3). Similarly, in the overlapping bed, only one sample was found to be pristine (OM47-23) and its Sr isotope signature (0.7077801) is close to the average value for all six specimens (0.7077845 ± 0.0000226). The best estimate of the external precision of a single measurement is given by the standard deviation of 128 analyses of north Atlantic seawater (± 0.0000096 2σ) over a 2-year period. So while the Sr isotope signatures of pristine brachiopods in beds OL15 and OL17/OM46 overlap within analytical error, a significant decrease in ratio is observed in bed OM47. The three well-preserved brachiopod specimens from OM48 display the widest range of 87Sr/86Sr ratios and the mean value is 0.7079715 ± 0.0000318 (2σ). Variations of up to 50 × 10^-6 have been observed in pristine brachiopods within the same stratigraphical level (e.g. Azmy *et al.* 1999). The diagenetically altered specimen (OM48-15) from this bed yielded a significantly higher ratio although the Sr content appeared to be unaffected lending credence to the suggestion that dense punctae may have diagenetically altered fillings.

### 5. Interpretation and discussion

There are relatively few studies using stable isotopes specific to the Early Permian. There are, however, low resolution isotope curves which record seawater composition for most of the Phanerozoic based on compilations of the carbon and oxygen isotope ratios of brachiopod shells (e.g. Veizer *et al.* 1999). Through the Phanerozoic, changes in marine δ18O are interpreted in terms of global changes in burial and re-oxidation of organic matter, although other processes such as release of low δ18O volcanic or mantle CO₂ into the atmosphere, discharges of oceanic methane and overturn of low δ18O anoxic bottom waters are all described (Korte *et al.* 2005). A recent study by Pufahl *et al.* (2006) on Miocene brachiopods from an epeiric sea (South Australia) shows that higher δ18O may be related to increased aridification and decreasing continent derived nutrients. Variation in δ18O in brachiopod shells is thought to be largely due to the growth and retreat of continental glaciers (e.g. Veizer *et al.* 1997). The Phanerozoic seawater curves show that in the Early Permian there was a rapid decline in δ18O, although the δ13C curve is rather flat (Veizer *et al.* 1999).

The only specific Permian isotope seawater curves are based on a compilation of brachiopod data from a series of discrete basins (Korte *et al.* 2005). This δ18O data shows a decline of 2.5% in the Early Permian (Asselian to Artinskian) (Korte *et al.* 2005, fig. 8). The main cause of the decline, which reached a minimum in the Artinskian (Korte *et al.* 2005), was the return of 18O-depleted glacial meltwater to the oceans after melting of Carboniferous-Permian glaciers at high latitudes. Closer inspection of Korte’s data set published online (doi: 10.1016/j.palaeo.2005.03.015) shows that this decline is not as smooth as the compiled data, notable is an excursion to higher δ18O values, within the overall trend towards lower values, in the Sakmarian. The Early Permian brachiopod isotope data given in Korte *et al.* (2005) are entirely derived from the Southern Urals (sections from Usolka, Sakmara and Dalnij Tyulikas,

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**Figure 5** Ultrastructure of *Pachycyrtella omanensis* (1–4), *Pachycyrtella sp. A* (5), *Subansoria cf. amonti* (6), *Punctocyrtella spinosa* (7–8): (1) Transverse section of well-preserved secondary layer fibres with keel and saddle outline, specimen OL14-19, ventral valve; (2) Transverse section of well-preserved secondary layer fibres with keel and saddle outline, specimen OL14-49, ventral valve; (3) Longitudinal section of well-preserved orthodoxy stacked secondary layer fibres showing a transverse section of a punctum, specimen I4, ventral valve; (4) Longitudinal section of well-preserved primary (arrow) and secondary layers showing a longitudinal section of a punctum, specimen OL14-1, ventral valve; (5) Longitudinal section of well-preserved orthodoxy stacked secondary layer fibres showing a longitudinal section of a punctum, specimen OL15-66, ventral valve; (6) Local modification and re-orientation in the growth of secondary layer fibres, specimen OM48-11, ventral valve; (7) Spatulate termination of well-preserved orthodoxy stacked secondary layer fibres, specimen OL15-48, ventral valve; (8) Transverse section of secondary layer showing some imperfectly shaped fibres (arrows), specimen OL15-63, ventral valve.
able limited circulation between the Haushi Sea and the Neotethys Ocean. In addition, postglacial warming, increasing aridity and northward drift of Arabia and Gondwana during this interval (Angiolini et al. 2003b, Stephenson et al. 2005) would contribute to higher evaporation. A similar scenario was envisaged for the Delaware Basin (Guadalupian Mountains), where brachiopods were found to have high δ18O in the Kungurian and Guadalupian (Korte et al. 2005). The general trend towards slightly heavier δ13C supports not only increasing aridity, but also decreasing nutrients, as shown for the epeiric Murray Basin in the Miocene by Puftahl et al. (2006).

The LOWESS δ87Sr/δ18O curve of McArthur & Howarth (2004) is relatively flat for Asselian and Sakmarian seawater with values around 0.7081, but at the beginning of the Artinskian there is a steep decline in the ratio to 0.7075. The seawater curve for the Cisuralian is based on data from Denison et al. (1994a) and Martin & McDougall (1995) and is defined by a relatively small number of data points, particularly in the Sakmarian. Denison et al. (1994a) measured isotope ratios of lime mudstones and wackestones from the USA whereas Martin & McDougall (1995) analysed conodonts from the USA and Pakistan. Denison et al. (1994a, b) considered that as limemud-supported rocks excluded foreign pore fluids more effectively, they were more likely to retain the original seawater isotope composition. They adopted a rejection criterion of Sr/Mn > 2 and Mn < 300 ppm; however McArthur & Howarth (2004) used only some of the data from this suite of samples.

There is some evidence (Ebneth et al. 2001) that conodonts yield more radiogenic signatures than brachiopods of comparable age because they are susceptible to isotopic exchange with the surrounding matrix. However, Martin & McDougall (1995) focused on the time interval from middle Permian (Kungurian) to early Triassic, so there is no overlap with the samples measured here.

All of the pristine brachiopods analysed in this study display Sr isotope signatures that are less radiogenic than indicated by the LOWESS seawater curve (McArthur & Howarth 2004) for the Sakmarian. It might be argued that given the proximal environment postulated for the surface Saiwan Formation (Angiolini et al. 2006), the seawater would be more likely to have a terrigenous contribution. However, this component would have an even lower Sr isotope ratio, which tends to rule out sedimentary sources. Volcanic lithics are abundant in the upper part of the Al Khleta Formation and granitoid rock fragments are common. However, the Pachycyrtella Bed at the base of the Saiwan Formation is arkosic in composition, with a reduction in the amount of quartz indicating widespread exposure of granitoid to gneissic basement (Angiolini et al.

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**Figure 6** Ultrastructure of *Derbyia haroubi* (1–3) and *Reedoconcha permixta* (4–8): (1) Well-preserved secondary layer lamina, specimen OL15-23, dorsal valve; (2) Calcitic cross-bladed lamination showing pseudopunctuation in the form of rosettes of conical laminae (arrow), specimen OL15-23, dorsal valve; (3) Well-preserved secondary layer lamina showing two traces of biocorrosion (arrows), specimen OL15-15, ventral valve; (4) Calcitic cross-bladed laminae strongly affected by diagenetic alteration, specimen OL16-35, ventral valve; (5) Calcitic cross-bladed lamina strongly deflected by pseudopunctuation, specimen OL16-35, ventral valve; (6) Calcitic cross-bladed lamina strongly affected by diagenetic alteration, specimen OL16-35, ventral valve; (7) Pseudopunctum with tecta, a rod of recrystallised calcite at the core (arrow), specimen OL16-35, ventral valve; (8) Section of the base of a hollow spine (arrow), showing concentric banding, specimen OL16-35, ventral valve.

**Figure 7** SEM and petrological microscope photographs of specimens showed in the left column of Figure 8: (1) SEM lamellar fabric, *Derbyia haroubi*, specimen OM48-15, dorsal valve; (2) Petrological microscope photograph in transmitted light, *Derbyia haroubi*, specimen OL15-23, dorsal valve; (3) SEM recrystallised fabric, *Neostrayer* (*Quadrospera*) aff *Hardmani*, specimen OL15-140, ventral valve; (4) Petrological microscope photograph in transmitted light, *Neostrayer* (*Quadrospera*) aff *Hardmani*, specimen OL15-140, ventral valve; (5) SEM shell fabric showing diagenetic alteration (left), *Cyrtrella* sp. A, specimen OM48-15, ventral valve; (6) Petrological microscope photograph in transmitted light, *Cyrtrella* sp. A, specimen OM48-15, ventral valve; (7) SEM shell fabric showing diagenetic alteration, *Pachycyrtella omanensis*, specimen OL14-401, ventral valve; (8) Petrological microscope photograph, *Pachycyrtella omanensis*, specimen OL14-401, ventral valve.
Figure 8  Caption overleaf.
we might expect to find higher ratios in those from the deeper riverine contribution to the seawater at the basin margin, then brachiopods from the surface Saiwan Formation reflected a decrease in nutrient availability (Angiolini et al., unpublished data) indicate similar or slightly more negative Sr isotope ratios. The brachiopod assemblage in the subsurface Haushi limestone is consistent with a deeper marine environment, more distant from the source of terrigenous input. If the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the brachiopods from the surface Saiwan Formation reflected a riverine contribution to the seawater at the basin margin, then we might expect to find higher ratios in those from the deeper waters of the basin, but this was not observed.

6. Conclusions
The Lower Permian (Sakmarian) succession of the Haushi basin, Interior Oman (Saiwan Formation/lower Ghariif member) records rapid climate change through glacial conditions to subtropical desert. This was caused by global warming following the Permo-Carboniferous glaciation, enhanced by northward continental drift during the Early Permian. Palynological, $\delta^{13}\text{C}_{\text{org}}$ and organic geochemical studies (Stephenson et al. 2005) show palaeoenvironmental change through the lower part of the succession in south Oman. The isotope record may have resulted from climate amelioration through increases in palaeoatmospheric CO$_2$. Studies of similar beds at outcrop show changes in the fauna including the development of a pioneer cold-water brachiopod community (OL14), followed by a more mature secondary ecological community of a more diversified marine biota (OL15-OL18), indicating significant climatic amelioration and concomitant decrease in nutrient availability (Angiolini et al. 2003a).

To investigate the palaeoclimatology and the evolution of the Haushi sea in Interior Oman a combination of O, C, and Sr isotopes was used on bed-by-bed-collected brachiopod shells within the Saiwan Formation. The degree of diagenetic alteration and rejected shells not meeting strict preservation criteria was assessed. Spiriferids and spiriferinids show better preservation of the fibrous secondary layer than do orthotetids and productids, whose laminar secondary layer is usually altered and/or luminescent. Spiriferids are the most suitable for isotopic analysis.

Three sets of isotope data (C, O and Sr) are consistent with two possible scenarios. In an open ocean setting, the carbon and oxygen would suggest maximum deglaciation within the base of the Saiwan and then a return to glacial conditions elsewhere in Gondwana, which however it is not generally supported by the sedimentology and palaeontology of Gondwanan regions (SE Australia) and by published smoothed curves. There is a suggestion in the data of Korte et al. (2005) that there are minor irregularities in the unsmoothed curve that may account for the upturn in the Sr isotope data does not conform to the published seawater curve for the Sakmarian, but as this is based on extrapolation between a few data points, it is possible that the Sr does reflect open ocean in this region. Alternatively, the upturn in the oxygen isotope data may reflect evaporation, implying a restricted Haushi basin south of the Neotethys rift shoulder, in which case the variation in Sr isotope composition may reflect a fluvial component. The Sr concentration would increase with evaporation, but the isotope ratio would not change. The trend towards higher $\delta^{13}\text{C}$ may indicate increasing aridity and oligotrophy. This second scenario sounds more logical and reasonable.

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8. References


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