# Geochemistry, and carbon, oxygen and strontium isotope composition of brachiopods from the Khuff Formation of Oman and Saudi Arabia

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## ABSTRACT

Brachiopods are abundant in the Oman Khuff Formation and similar brachiopod faunas are present at a few horizons in the same formation in Central Saudi Arabia. Following extensive systematic and biostratigraphic studies of these faunas, specimens from the base of the Midhnab Member of the Khuff Formation of Saudi Arabia (Buraydah Quadrangle), and from Member 3 of the Khuff Formation of the Huqf outcrop of Oman were assessed for isotope geochemistry (Sr, O and C). Dating using $^{87}Sr/^{86}Sr$ alone is not conclusive. Five pristine Oman brachiopods from biostratigraphically well-constrained early Wordian horizons record a range of $^{87}Sr/^{86}Sr$ values that form a separate cluster offset from the current Sr isotope sea water curve which defines the Early Permian and earliest Mid-Permian. The $^{87}Sr/^{86}Sr$ of the pristine Saudi Arabian brachiopod sits in an area which corresponds to a wide scatter of $^{87}Sr/^{86}Sr$ in the seawater curve data. However, the Saudi Arabian data does indicate that the Midhnab Member is likely younger than Member 3 of the Khuff Formation of the Huqf outcrop.

The well-preserved brachiopod carbonate allows deductions to be made about the palaeotemperature of the Oman Khuff Formation Member 3 seawater using its oxygen isotope composition ($\delta^{18}O$). Assuming $\delta^{18}O$ of seawater < –0.5‰, then

palaeotemperature derived from brachiopods in the Oman horizons would be +25°C, +22°C and +17°C respectively. This is consistent with the trend of shallowing within Member 3, suggested by facies.

## INTRODUCTION

The Khuff Formation (Steineke et al., 1958) comprises the Middle Permian to Lower Triassic carbonate rocks of the Arabian Peninsula and is a hydrocarbon-producing unit in Bahrain, Iran, Qatar, Saudi Arabia and the United Arab Emirates. Its deposition started in the Mid-Permian and accompanied the drifting of Cimmerian terranes from Gondwana (Konert et al. 2001). The Khuff Formation was mainly deposited as a post-rift carbonate succession (Maurer et al., 2009; Koehrer et al. 2010) on a passive continental margin of the newly forming Neo-Tethys Ocean during a period of relative tectonic quiescence and steady subsidence (Muttoni et al., 2009).

In the Haushi Outcrop area in Oman, the Khuff Formation reaches a maximum thickness of 30 to 40 m and is divided into three members (Figures 1, 2; Angiolini et al., 2003). Member 1 represents the onset of carbonate shelf sedimentation succeeding the organic-rich, marsh–alluvial to estuarine environments of the uppermost Unit B of the Gharif Formation (Stephenson, 2011; Berthelin et al., 2003, 2006; Broutin et al., 1995; Angiolini et al., 2004). The lower part of Member 1 (Unit C of Angiolini et al., 2003) consists of paralic to coastal sands interpreted as tidal sand-flat to barrier-beach deposits, variably reworked by waves and tidal currents in a lagoonal or bay environment (Angiolini et al., 2003). Carbonate sedimentation became progressively more common in Unit D (the upper part of Member 1) which consists of inner- to outer-shelf sediments deposited at water depths between fair weather wave-base and storm wave-base. Member 2 is characterized by limestones and marlstones with open-marine fauna, and records transition to outer-shelf conditions mostly below storm-wave-base. Abundance of bioclastic storm layers in the lower part of Member 3 suggest deposition around storm wave-base, but sedimentary features in the topmost beds of Member 3 suggest shallower waters, well above storm-wave-base (Angiolini et al., 2003).

In Central Saudi Arabia (Figures 1, 3), the terrigenous sediments of the lowest Khuff Formation Ash Shiqqah Member are succeeded by the Huqayl Member which consists of calcarenite, gypsiferous claystone, dolomite, and solution breccias related to subsurface evaporites (Angiolini et al., 2006). The succeeding Duhaysan Member is the first true calcareous subtidal to littoral unit of the Khuff Formation (Le Nindre et al., 1990b), and it is succeeded by the Midhnab Member which displays a succession ranging from marine fossiliferous limestones at the base, to gypsiferous and dolomitic rocks deposited in restricted palaeoenvironments, in the upper part. Locally, in north Central Saudi Arabia, the topmost continental facies of the Midhnab Member include lacustrine limestone, sandstone channels and claystone in meandering river systems and swamps. These facies contain drifted wood and plant remains (Vaslet et al., 2005).

The Khuff Formation throughout the Arabian Peninsula contains a rich fauna including brachiopods, bivalves, gastropods, conularids, bryozoans, echinoderms, barnacles, ostracods, fishes, asterozoans, nautiloids, conodonts, fusulinids, echinoderms, small foraminifers and ammonoids (Angiolini et al., 1998, 2003, 2004;

Angiolini and Bucher, 1999). However, only the lower part of the Khuff Formation in Oman has been dated with certainty using this fauna, as early Wordian (Angiolini et al., 2003, 2004).

The age of the lower part of the Khuff Formation in Central Saudi Arabia is in dispute. Vaslet et al. (2005) suggested that (1) the lowest part of the Ash Shiqqah Member is Capitanian in age; (2) the overlying Huqayl Member is Wuchiapingian in age; (3) the Duhaysan Member is Wuchiapingian to Changhsingian in age; and (4) the Midhnab Member is Changhsingian in age. However, the conodont '*Jinogondollella*' cf. *altaduensis* from the base of the Midhnab Member suggests an older, late Capitanian age (Nicora et al., 2006) and the ostracod species recorded in the lower Midhnab Member (*Hollinella herrickana* Girty) has an Early to Mid-Permian range (Crasquin-Soleau et al., 2005). The Midhnab Member was also dated as Changhsingian by Vachard et al. (2005) based on the occurrence of the foraminifer *Paradagmarita* and of a new species of *Glomospirella*? similar to a species from the early Changhsingian of South China. However, the genus *Paradagmarita* has a Wuchiapingian to Changhsingian distribution (Zaninetti et al., 1981; Pronina, 1999; Groves and Altiner, 2005; Maurer et al., 2009).

Brachiopods are abundant in the Oman Khuff Formation and similar brachiopod faunas are present at a few horizons in the same formation in central Saudi Arabia. Following collection of these faunas, it was suggested that the brachiopods may be useful in elucidating palaeoenvironment and age through their geochemistry. Articulate brachiopod shells (Subphylum Rhynchonelliformea) are known to record the primary geochemical signal of ancient seawater, as the low-Mg-calcite of their shell is generally resistant to diagenetic change (see Compston, 1960; Lowenstam, 1961; Popp et al., 1986; Veizer et al., 1986, 1999; Korte et al., 2003, 2005; Angiolini et al., 2009). Articulate brachiopods secrete a two- or three-layered calcite shell below an outer proteinaceous periostracum. The primary layer is granular/acicular and usually low in $\delta^{13}C$ and $\delta^{18}O$; 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; Parkinson et al., 2005); and the tertiary layer, when present, is coarse prismatic and locally confined inside the shell and is also thought to be in equilibrium with ambient seawater. No 'vital fractionation effects' leading to departure from isotopic equilibrium greater than ± 1‰ have been recorded in the slow-growing secondary and tertiary layers of modern articulate brachiopods (Carpenter and Lohmann, 1995; Curry and Fallick, 2002; Brand et al., 2003; Korte et al., 2005; Parkinson et al., 2005), and therefore it is these layers that are generally sampled for their stable isotope composition.

In this study, we assess the degree of diagenetic alteration in the brachiopod shells by scanning electron microscopy (SEM), cathodoluminescence (CL), and geochemistry. We therefore ascertain which brachiopods are most likely to record primary environmental information in the isotope ratios of their shells. We use these data to (1) test the possibility that $^{87}Sr/^{86}Sr$ can be used to date the Khuff Formation in the Arabian Peninsula (since the $^{87}Sr/^{86}Sr$ ratio gradient is very steep in the Mid-Permian (Korte et al., 2006, McArthur and Howarth, 2004); and (2) investigate the palaeotemperature of Khuff Formation seawater using $\delta^{18}O$.

## MATERIALS AND METHODS

### Brachiopod specimens

Twenty brachiopods belonging to the following six species were analysed: *Omanilasma husseinii* Angiolini and Zarbo in Angiolini et al. (2006), *O. desertica* Angiolini and Zarbo in Angiolini et al. (2006), *Juresania omanensis* Hudson and Sudbury (1959), *Derbyia* cf. D. *diversa* Reed (1944), *Callispirina* sp. ind., and *Kotlaia* cf. K. *bistriata* Reed (1944).

The brachiopod fauna from the Midhnab Member (Figure 1) was collected at outcrop by D. Vaslet and Y.-M. Le Nindre in 2002 (Angiolini et al., 2006). This fauna represents one of the few records of Permian brachiopods so far reported from Saudi Arabia (Vaslet et al., 1985; Le Nindre et al., 1990a, b; Al-Aswad, 1997). The fossiliferous locality is located in the Buraydah quadrangle (Vaslet et al., 1985) at 26°07′01″ N-44°02′26″ E, 5 km to the north of the town of Midhnab. The brachiopods occur in the lowest part of the subunit 2 of the Midhnab Member (Figure 3; Angiolini et al., 2006), in bioclastic limestones with marine fauna, alternating with marly limestones, which correspond to the maximum flooding surface (MFS PKm) of central Saudi Arabia (Le Nindre et al., 1990b; Sharland et al., 2001; Vaslet et al., 2005). This very rare brachiopod fauna includes *Kotlaia* sp. ind. of the order Orthida and *Omanilasma husseinii* of the order Terebratulida. *Kotlaia* is a long-ranging genus, spanning the Mid- to Late Permian time interval. *Omanilasma* is known from the early Wordian of Oman and from the Wordian Ruteh Limestone of north Iran

(Crippa and Angiolini, 2012). Seven specimens were analysed by CL, SEM and geochemistry, and for their isotope composition (Table 1).

The brachiopod fauna of the Khuff Formation of the Haushi Outcrop area of interior Oman was collected by L. Angiolini from 1995 to 2001 (Angiolini and Bucher, 1999, Angiolini et al., 2003, 2004). It is diverse, comprising more than 2000 specimens belonging to more than 30 species. Thirteen specimens were analyzed by cathodoluminescence, SEM and geochemistry, and for their isotope composition (Table 1) from section K7 at 21°02′30′′N-57°42′00′′E (Figure 2) in the *Acritosia* sp.-*Globosobucina* sp. Biozone and the *Grandaurispina ghabaensis* - *Kozlowskia tescorum* Biozone (Angiolini et al., 2003, 2004).

## Ultrastructural SEM analyses

Well preserved non-luminescent secondary layer fibres were observed in five out of seven specimens of *Omanilasma husseinii* from Saudi sample level KH0211 (Plates 1, 2). The secondary layer fibres have a keel and saddle profile with a thickness of 3-5 µm and are slightly deflected around very thin punctae (diameter 8-13 µm). Occasionally, secondary layer fibres show some dissolution and minor coalescence. The maximum measured thickness of the secondary layer is 202 µm.

Most of the thirteen specimens analyzed from the Khuff Formation of Oman were well-preserved in that all the secondary fibres were intact. In general the Oman specimens have a thicker secondary shell and are better preserved than those of Saudi Arabia. Diagenetic alteration appears not to be related to taxonomy or stratigraphic position as the three altered specimens belong to two species of different orders (*K.* cf. *K. bistriata* and *J. omanensis*), and occur in the same beds as other well-preserved specimens. However, specimens of *J. omanensis*, characterized by a secondary laminar shell, tend to be more easily altered externally around the hollow bases of spines (Plate 2) and appear luminescent.

A specimen of a different taxon, *Callispirina* sp. ind. (AO73-107, Table 1), was also analyzed. It has very well preserved secondary layer fibres, however these are deflected around coarse and dense punctae, which may have diagenetically-altered fillings.

The well-preserved non-luminescent secondary shell of the Oman specimens of *O. husseinii* is much thicker than the conspecific Saudi Arabia ones, reaching thicknesses of more than 500 µm. The secondary layer fibres have a keel and saddle profile with a thickness of 3-5 µm and are deflected around larger punctae (diameter 30-45 µm) (Plates 2, 3). The single specimen of *O. desertica* (AO210-153) has the same ultrastructure as *O. husseinii*. Punctae seem to have been filled soon after decomposition of the soft parts as the fibres surrounding them do not show any sign of dissolution.

## Cathodoluminescence

Cathodoluminescence analysis (CL) was performed using a cold cathode luminoscope (Nuclide ELM2) operating at 10KV voltage with a current beam of 5-7 MA. CL is a screening technique widely used to assess preservation of brachiopod shells (Popp et al., 1986), as they commonly show no luminescence in absence of significant geochemical alteration. To overcome one of the drawbacks of conventional optical CL (i.e. the fact that beam current conditions vary in the different studies), we analysed all the thin sections of the brachiopod shells with the same instrument operating under the same beam conditions.

## Geochemistry and isotopes

The brachiopods were sampled for trace element geochemistry and isotope analysis by drilling a portion of the longitudinal section of each shell, avoiding specialised areas such as the muscle attachment areas, articulation points and interareas. The powder was split into two parts, one for trace element geochemistry and $^{87}Sr/^{86}Sr$, and the other for $\delta^{13}C$ and $\delta^{18}O$ isotopes.

Subsamples for trace element geochemistry and $^{87}Sr/^{86}Sr$ were dissolved in ultrapure acetic acid. The reserved acetic acid leachate was evaporated to dryness and the residue taken up in 1% nitric acid. Trace element geochemistry was obtained by ICP-AES on a Fison/ARL 3580 simultaneous/sequential spectrometer with Gilson auto sampler.

For strontium isotopes, a subsample of ~1-3 milligrams was weighed into a Savillex© FEP beaker and the carbonate dissolved in ultrapure 1M acetic acid ($CH_3COOH$). After centrifuging, half of the $CH_3COOH$ solution was reserved for geochemical analysis and the other half evaporated to dryness. The residue was taken up in 2.5M HCl and 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 oxide (TaO) activator following the method of Birck (1986) and isotope ratios were measured on a Finnegan MAT Triton operated in static mode. Analyses were made at two separate times and the relevant mean values obtained for the international isotope standard NBS 987 were 0.710234 ± 0.000008 (2σ n=11) and 0.710237 ± 0.000007 (2σ n=19). For consistency all the measured ratios reported in Table 1 are normalised relative to the accepted value of 0.710248 for NBS 987. Replicate determinations (n = 100) of the north Atlantic seawater standard yielded 0.709175 ± 0.000011 (2σ), relative to 0.710248 for NBS 987.

The ratios are compared to the most recent $^{87}Sr/^{86}Sr$ curve for the Permian developed by Korte et al. (2006). The geochronological scale used here is that of ICS (http://www.stratigraphy.org/).

Carbon and oxygen isotope analysis was achieved using a GV IsoPrime mass spectrometer with multiprep device. Isotope values ($\delta^{13}C$, $\delta^{18}O$) are reported as per mil (‰) deviations of the isotopic ratios ($^{13}C/^{12}C$, $^{18}O/^{16}O$) calculated to the VPDB scale using a within-run laboratory standard (KMC) calibrated against the international NBS standards (NBS18 and 19). Analytical reproducibility for these analyses was better than 0.1‰ for $\delta^{13}C$ and $\delta^{18}O$.

## RESULTS

The results of the SEM, CL, geochemical and isotope analyses are presented in Table 1. Saudi specimens of *O. husseinii* have Mn concentrations between 67.3-112 ppm, which are well below the cut-off of 200-250 ppm suggested by Bruckschen et al. (1999) and Korte et al. (2003) for pristine brachiopods, and in the range of values measured in extant brachiopods (Brand et al. 2003). Sr however is rather depleted being >400 ppm only in specimen KH0211-2 and >300 in specimen KH0211-7A. According to Popp et al. (1986) Mn concentrations are a better indication of chemical diagenesis in brachiopods than Sr. High Fe and low Sr concentrations are present in sample KH 0211-3, although similar values are found in KH0211-9A where the SEM analysis indicated that the calcite is more pristine. However KH 0211-9A has the lowest Sr concentration and very similar $\delta^{18}O$ to the two samples deemed not well preserved after SEM analysis and is therefore excluded from the pristine data set.

The Oman specimens of *O. husseinii* and *O. desertica* from beds AO72, AO73 and AO210 (Table 1) have Mn concentrations between 105-431 ppm. Sr is less depleted than in the Saudi Arabian specimens of the same species, reaching 480-612 ppm in the most pristine samples and up to 1282 ppm in less well preserved specimens. All samples with Mn above 200 ppm are excluded from the pristine data set. The specimen of *Callispirina* sp. appears to be unaltered but its coarse and dense punctae indicate that the isotope data should be viewed with caution. The poorly preserved specimen of *Kotlaia* cf. *K. bistriata* from bed AO80 further down the sequence within the Oman Khuff Formation, was found to have a high Mn content.

The $\delta^{13}C$ and $\delta^{18}O$ data from the nine pristine brachiopods from both sections show relatively stable $\delta^{13}C$, and a range in $\delta^{18}O$ values. In the Saudi Arabian samples, $\delta^{18}O$ ranges between –4.5 to –2.7‰ (mean –3.8, SD=0.8), while the Oman values are –3.1 to –0.7‰ (mean –2.0, SD=1.0).

The $^{87}Sr/^{86}Sr$ of Saudi Arabian Khuff samples KH0211-3 and KH0211-10A (0.707198 and 0.707146 respectively) confirm that these samples have suffered some degree of diagenetic alteration. KH0211-9A also shows elevated $^{87}Sr/^{86}Sr$ (0.707069), which supports the decision to exclude this specimen from the pristine data set. The mean of $^{87}Sr/^{86}Sr$ yielded by the remaining samples is 0.707011 ± 0.000056 (2σ). However, the value obtained for the best-preserved specimen KH0211-2 (which met all the required conditions to be considered a pristine shell) is 0.706988 which is indistinguishable within error from the $^{87}Sr/^{86}Sr$ of 0.706988 for KH0211-11.

Samples from the five Oman pristine brachiopod range from 0.707217 to 0.707280 (Table 1, Figure 4). Poorly preserved samples have increasing $^{87}Sr/^{86}Sr$ ratios and higher Mn concentrations. Sample AO73-44 has high Sr, Mn, and $^{87}Sr/^{86}Sr$ of 0.707731 suggesting that the source of the diagenetic fluids is significantly radiogenic and Sr and Mn rich. The specimen of *Callispirina* sp. yielded a higher $^{87}Sr/^{86}Sr$ ratio (0.707381 AO73-107) than the pristine *O. husseinii* samples suggesting that the coarse and dense punctae may have diagenetically altered fillings.

## DISCUSSION

The $^{87}Sr/^{86}Sr$ data of the five pristine early Wordian brachiopods forms a separate cluster when plotted with the Sr seawater data of Korte et al. (2006, their appendix A; Figure 4). However, the seawater Sr data for the Early Permian and earliest Mid-Permian is sparse and scattered; the data also shows wide variation of $^{87}Sr/^{86}Sr$ from multiple brachiopods at single horizons or horizons that are close together. $^{87}Sr/^{86}Sr$ for the Oman brachiopod horizons in ascending stratigraphic order are: AO210 (0.707231 and 0.707217); AO73 (0.707280); and AO72 (0.707267 and 0.707243) (Figure 4). According to the general decreasing trend of Korte et al. (2006), the oldest (lowest) level, AO210, would most likely provide the highest $^{87}Sr/^{86}Sr$ ratio, while the converse should be true of AO72. However Korte et al. (2006) have no data within the Wordian, and therefore there could be an increasing trend (shown by the Oman data) within the overall general decreasing trend.

At present therefore, there is too much uncertainty in the distribution of $^{87}Sr/^{86}Sr$ over this period. Our firmly biostratigraphically-dated horizons suggest that the $^{87}Sr/^{86}Sr$ curve, at least in the early Wordian, requires refining. Despite this, a steep $^{87}Sr/^{86}Sr$ gradient seems to exist between the Asselian and the Capitanian (Figure 4; see also McArthur and Howarth, 2004), and if more data were available, brachiopod or other types of pristine carbonate would be a useful method for dating within this time period, independently of biostratigraphy. We recommend that further data be gathered which will allow a better constrained curve to be constructed.

$^{87}Sr/^{86}Sr$ for the most pristine Saudi specimens of *O. husseinii* would plot in a less steep part of the curve where there is a much greater spread of $^{87}Sr/^{86}Sr$ values in the Korte et al. (2006) data (Figure 4), making the curve harder to define. Thus the accuracy with which the Midnab Member horizon can be dated is lower than that of Oman Khuff Formation Member 3. The range that could be suggested by the value 0.706988 from the best-preserved Saudi specimen (KH0211-2) is Capitanian to Wuchiapingian which means that it is not possible to resolve the different ages suggested by foraminifera, conodonts and ostracods (see earlier discussion), however it does indicate that the Midnab Member is probably younger than Member 3 of the Khuff Formation of the Huqf outcrop of interior Oman.

The stable isotope data allows inferences to be made about palaeoclimate. The $\delta^{13}C$ data suggest an open marine environment, consistent with Permian brachiopods from elsewhere (Korte et al., 2006), while $\delta^{18}O$ allows deductions to be made about the palaeotemperature of the Khuff Formation sea (Figure 5). Using Leng and Marshall's (2004) rearrangement of the expression of Kim and O'Neil (1997): $T°C = 13.8 - 4.58(c - w) + 0.08 (c - w)^2$ and in the absence of ice caps where seawater $\delta^{18}O$ sw (w) is assumed to be < –0.5 ‰ (Craig, 1965), the palaeotemperature for the Oman beds AO72, AO73 and AO210 would be +25°C, +22°C and +17°C respectively (Figure 5). This is consistent with the trend envisaged for Member 3 by Angiolini et al. (2003), with a shallowing from the basal bed AO210, deposited at depth of some tens of metres, to the upper part of the member which was deposited in progressively shallower and thus warmer waters (AO72).

The Saudi Arabian brachiopod from bed KH02-11 gives a palaeotemperature of +29°C, using the $\delta^{18}O$ mean value of –3.6‰. However, if evaporation rates were higher than in Oman as suggested by evaporitic facies in close proximity to bed KH02-11, the isotopic composition of seawater could have been higher than the $\delta^{18}O$ value of seawater (–0.5‰) adopted here. Today, low latitude seawater has a more positive $\delta^{18}O$ than that of high latitudes, where the seawater is 0.25‰ more negative than the global average of 0‰ (Zachos et al., 1994). If seawater $\delta^{18}O$ was –0.25‰ or higher during the period when the Saudi Arabian brachiopod lived, then palaeotemperature would have been above 30°C in the KHO211 bed of the Midhnab Member.

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## FIGURE CAPTIONS

**Figure 1:** (a) Locations of areas discussed in Oman and Saudi Arabia; (b) stratigraphic context of the sampled sections and horizons, after Stephenson et al. (2003) and Melvin et al. (2010). Small red squares show the sampled sections and horizons.

**Figure 2:** Graphic log of the three members of the Khuff Formation in Interior Oman, section K7 at 21°02'30''N-57°42'00''E, showing the stratigraphic position of the brachiopod horizons in bold. [MIH: use figure 9 on page 166 of SP3]

**Figure 3:** Graphic log of the Khuff Formation in the Buraydah Quadrangle, northern Central Saudi Arabia, showing the location of the brachiopods collected in pebbly bioclastic calcarenite in the Midhnab Member (modified from Vaslet et al., 2005; Angiolini et al., 2006). [MIH: use figure 2 on page 47 of volume 11, number 4]

**Figure 4**: $^{87}Sr/^{86}Sr$ from Korte et al. (2006), blue diamonds; and Oman $^{87}Sr/^{86}Sr$ data, red crosses. Chan. = Changhsingian; Wuchia = Wuchiapingian; Cap. = Capitanian; Word. = Wordian; Ro. = Roadian; Kungur = Kungurian; Art. = Artinskian; Assel. = Asselian. Dates from ICS (http://www.stratigraphy.org/). The $^{87}Sr/^{86}Sr$ from Oman brachiopod horizons are plotted within the range of the early Wordian in accordance with their biostratigraphic age. [MIH: we will add stages and ages from ICS]

**Figure 5**. $\delta^{18}O$ and $\delta^{13}C$ data for Member 3 of the Khuff Formation in Interior Oman. [MIH: I think we can combine this figure with figure 2].

**Table 1.** Isotope, trace element and ultrastructure data.

## PLATE EXPLANATIONS

**Plate 1**: Khuff Formation brachiopods from Saudi Arabia showing well preserved non-luminescent secondary layer fibres in *Omanilasma husseinii* from sample level KH0211: (a) specimen KH0211-2; (b) specimen KH0211-7; (c) specimen KH0211-8; (d) specimen KH0211-8; (e) specimen KH0211-9; (f) specimen KH0211-11.

**Plate 2** (a) to (b): Khuff Formation brachiopods from Saudi Arabia showing well preserved non-luminescent secondary layer fibres in *Omanilasma husseinii* from sample level KH0211: (a) specimen KH0211-11; (b) specimen KH0211-11. Figures (c) to (d) Oman specimens of *Juresania omanensis* characterized by a secondary laminar shell. These tend to be more easily altered around the hollow base of a spine and appear cathodoluminescent: (c) specimen AO72-16; (d) specimen AO72-16. Figures (e) to (f) Well-preserved non-luminescent secondary shell of Oman specimens of *O. husseinii* which is much thicker than conspecific Saudi Arabia specimens, reaching thicknesses of more than 500 µm. The secondary layer fibres have a keel and saddle profile with a thickness of 3-5 µm and are deflected around larger punctae (diameter 30-45 µm): (e) specimen AO73-39. (f) specimen AO73-39.

**Plate 3**: Oman specimens of *O. husseinii*. (a) specimen AO73-44; (b) specimen AO73-44; (c) specimen AO210-3; (d) specimen AO210-9; (e) specimen AO210-25; (f) specimen AO210-25.

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Prof. Mike Stephenson is Head of Science (Energy) at the British Geological Survey (BGS). His education has included a BSc, MSc and PhD from the University of Sheffield and Imperial College, London as well as various postgraduate teaching qualifications. He began his career as a schoolteacher in rural Africa and stayed there for almost ten years, but returned to pursue research. Mike's scientific work is mainly concerned with the geology of Arabia, and he has published over 60 papers on this and other regions as well as working extensively as a consultant for oil companies. Mike now runs the Energy Programme at BGS including carbon capture and storage, hydrocarbons, renewables and unconventional energy. He sits on the boards of several journals and is Editor-in-Chief of an Elsevier geological journal. He

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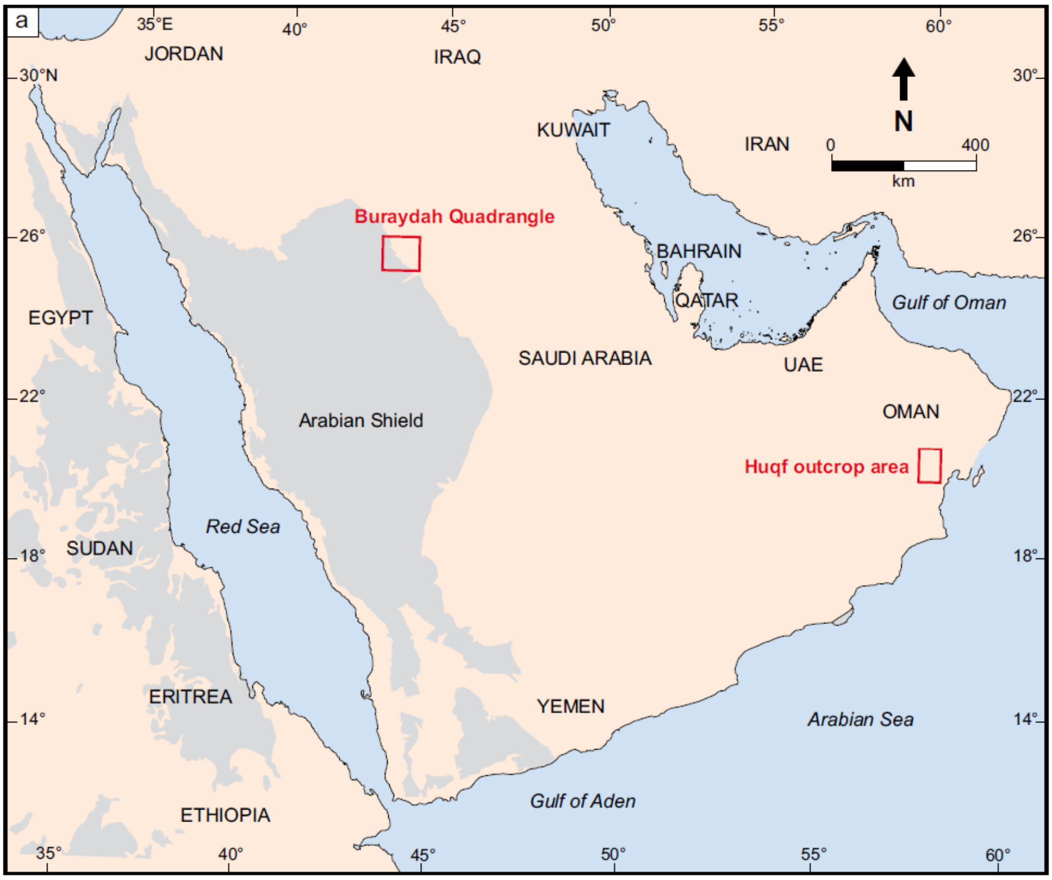


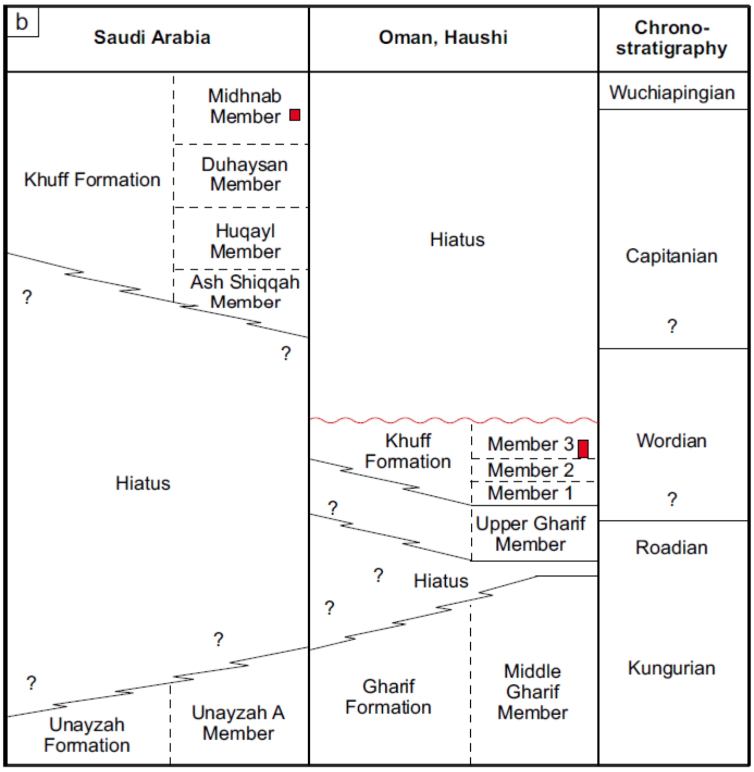
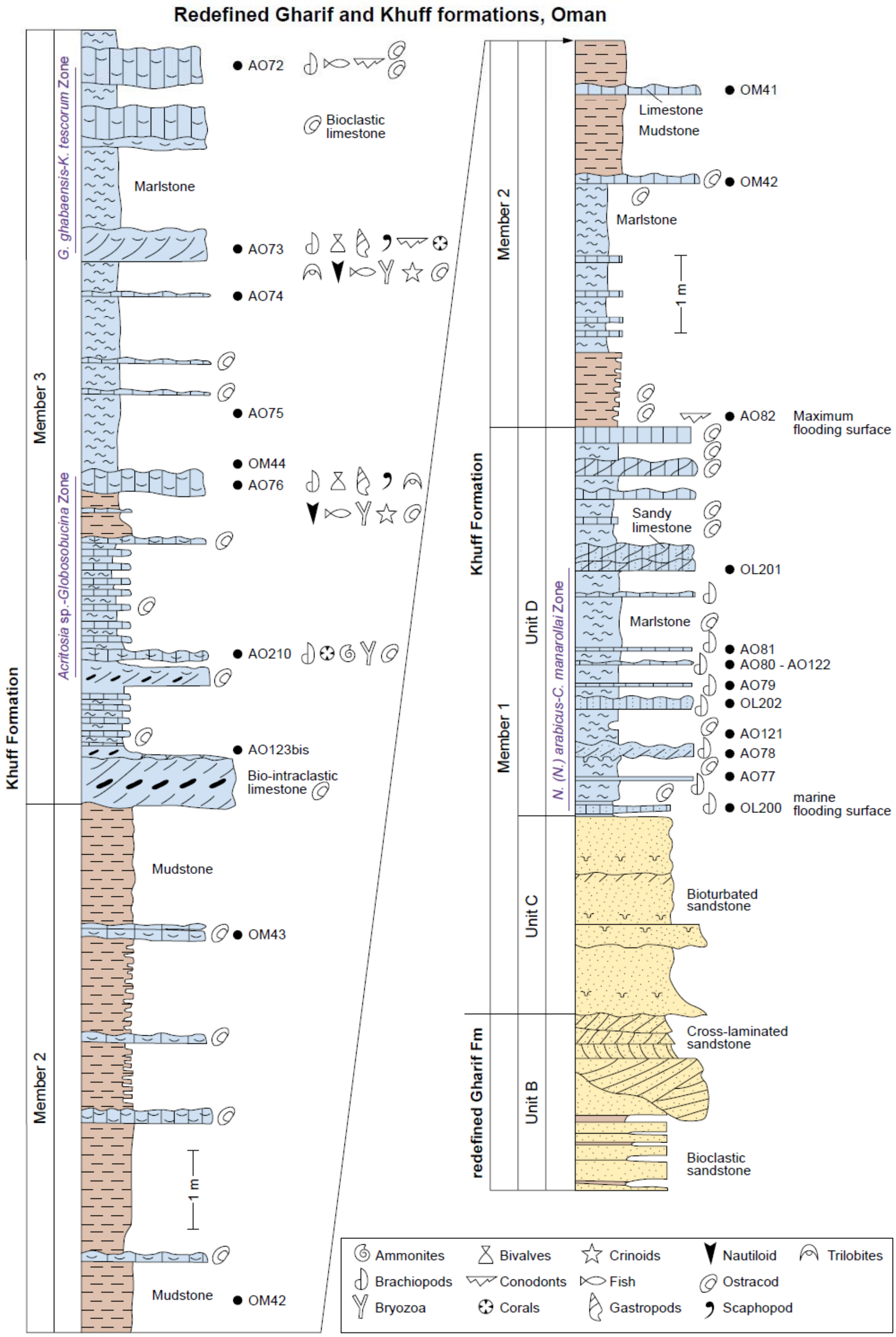




Figure 1: (a) Locations of areas discussed in Oman and Saudi Arabia; (b) stratigraphic context of the sampled sections and horizons, after Stephenson et al. (2003) and Melvin et al. (2010). Small red squares show the sampled sections and horizons.

Fig 1



Redefined Gharif and Khuff formations, Oman
Khuff Formation
Member 3
Member 2
G. ghabaensis-K. tescorum Zone
Acritosia sp.-Globosobucina Zone
AO72
Bioclastic limestone
Marlstone
AO73
AO74
AO75
OM44
AO76
AO210
AO123bis
Bio-intraclastic limestone
Mudstone
OM43
1 m
Mudstone
OM42
Khuff Formation
redefined Gharif Fm
Member 2
Member 1
Unit D
Unit C
Unit B
N. (N.) arabicus-C. manarollai Zone
OM41
Limestone
Mudstone
OM42
Marlstone
1 m
AO82
Maximum flooding surface
Sandy limestone
OL201
Marlstone
AO81
AO80 - AO122
AO79
OL202
AO121
AO78
AO77
OL200
marine flooding surface
Bioturbated sandstone
Cross-laminated sandstone
Bioclastic sandstone
Ammonites
Bivalves
Crinoids
Nautiloid
Trilobites
Brachiopods
Conodonts
Fish
Ostracod
Bryozoa
Corals
Gastropods
Scaphopod


Fig 2

## Khuff Formation, Buraydah quadrangle, Saudi Arabia

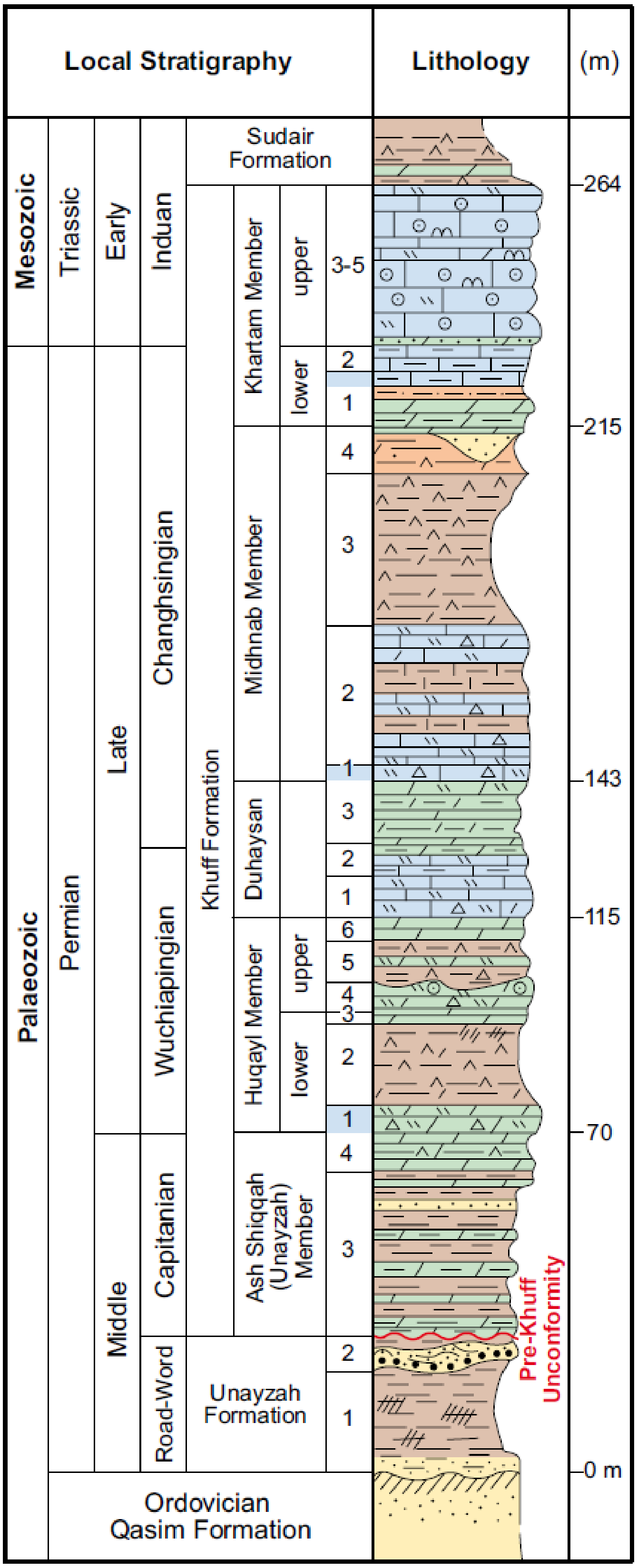
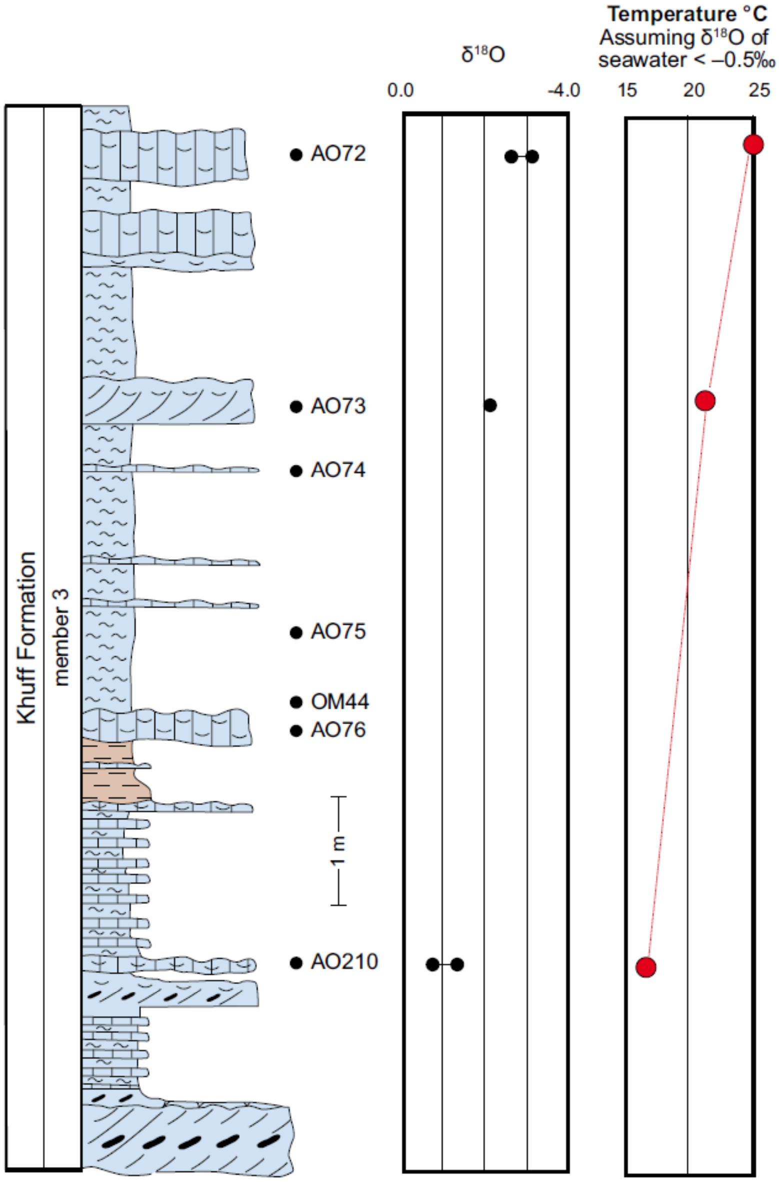



Fig 3



Temperature °C
Assuming δ18O of seawater < –0.5‰
δ18O
0.0
-4.0
15
20
25
Khuff Formation
member 3
AO72
AO73
AO74
AO75
OM44
AO76
AO210
1 m


Fig 5

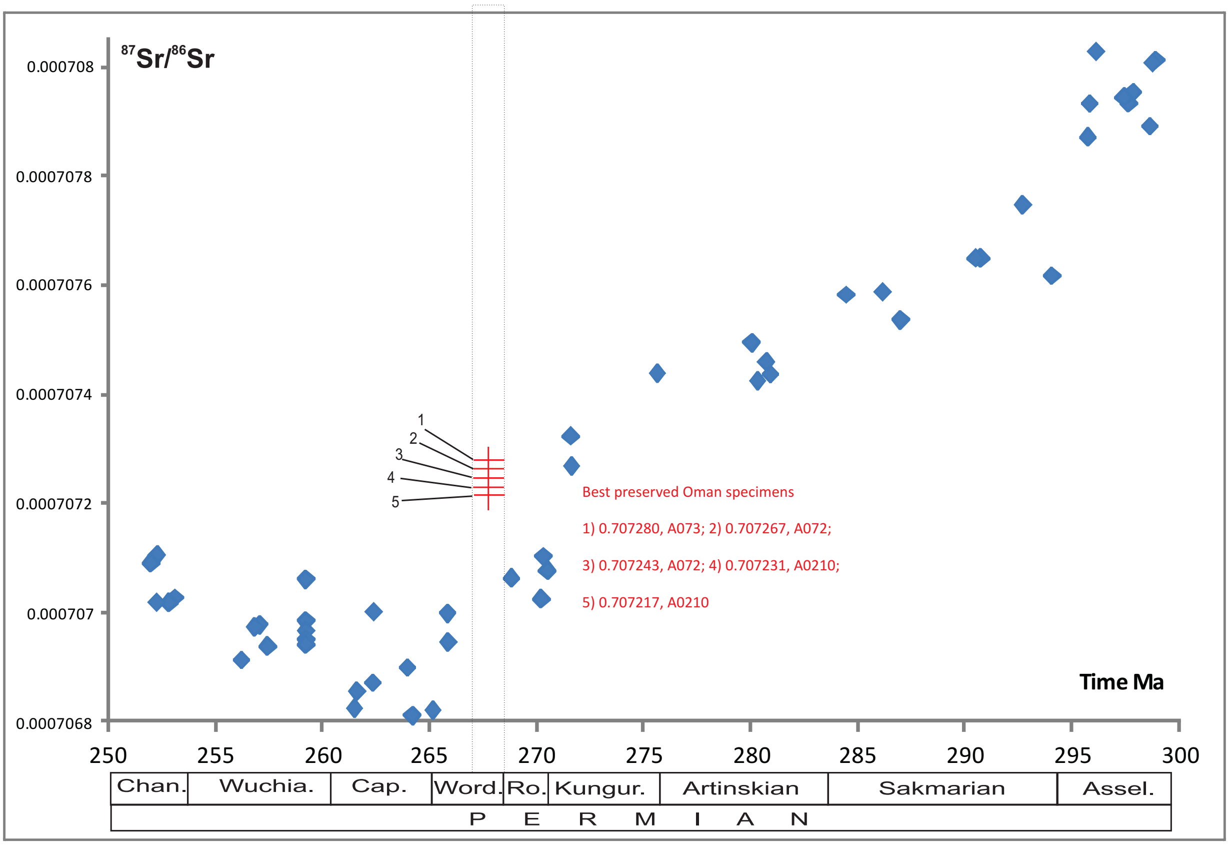

87Sr/86Sr
0.000708
0.0007078
0.0007076
0.0007074
0.0007072
0.000707
0.0007068
1
2
3
4
5
Best preserved Oman specimens
1) 0.707280, A073; 2) 0.707267, A072;
3) 0.707243, A072; 4) 0.707231, A0210;
5) 0.707217, A0210
Time Ma
250
255
260
265
270
275
280
285
290
295
300
Chan.
Wuchia.
Cap.
Word.
Ro.
Kungur.
Artinskian
Sakmarian
Assel.
P E R M I A N

Fig 4

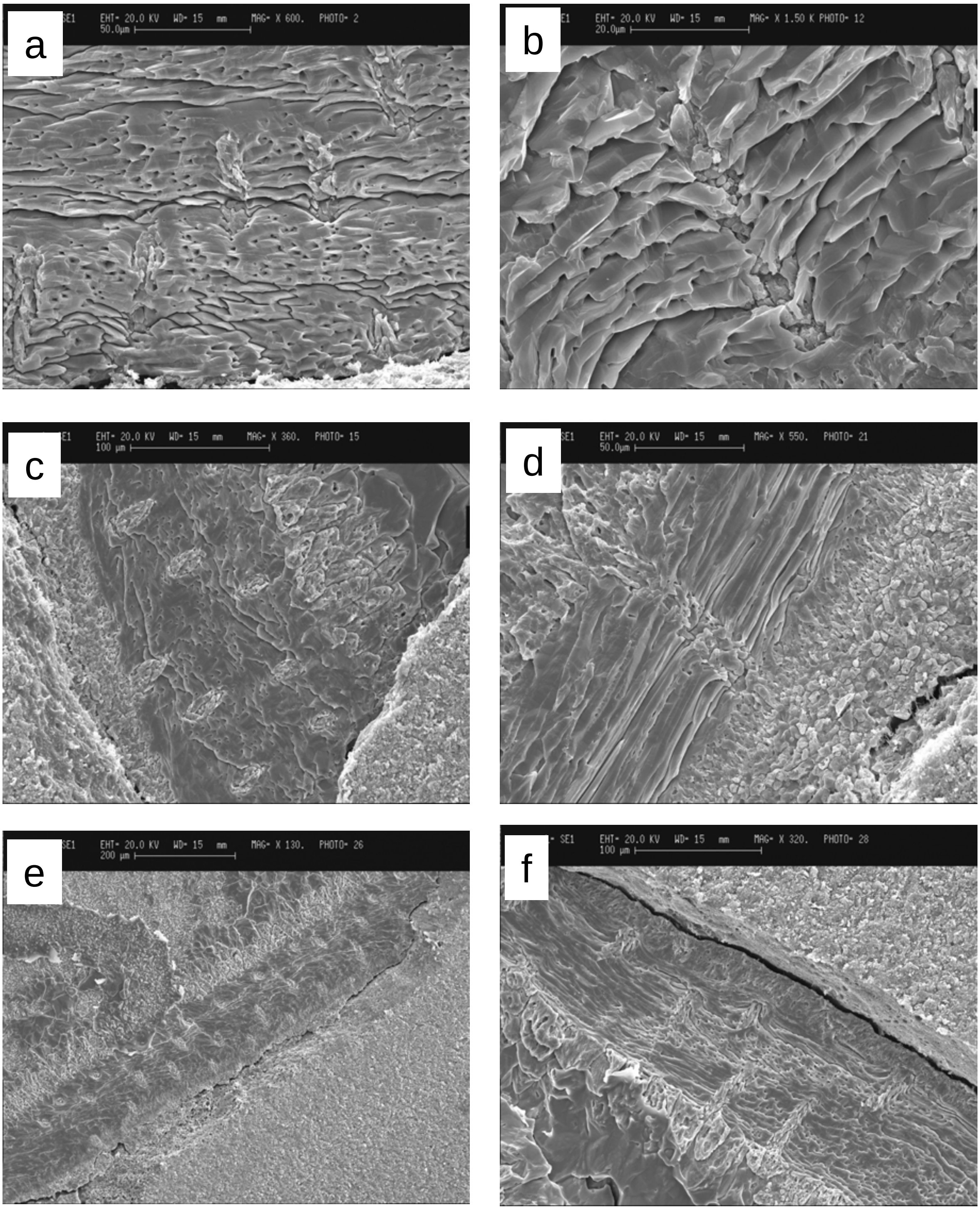

a
EHT= 20.0 KV WD= 15 mm MAG= X 600. PHOTO= 2
50.0µm
b
EHT= 20.0 KV WD= 15 mm MAG= X 1.50 K PHOTO= 12
20.0µm
c
EHT= 20.0 KV WD= 15 mm MAG= X 360. PHOTO= 15
100 µm
d
EHT= 20.0 KV WD= 15 mm MAG= X 550. PHOTO= 21
50.0µm
e
EHT= 20.0 KV WD= 15 mm MAG= X 130. PHOTO= 26
200 µm
f
EHT= 20.0 KV WD= 15 mm MAG= X 320. PHOTO= 28
100 µm

Plate 1

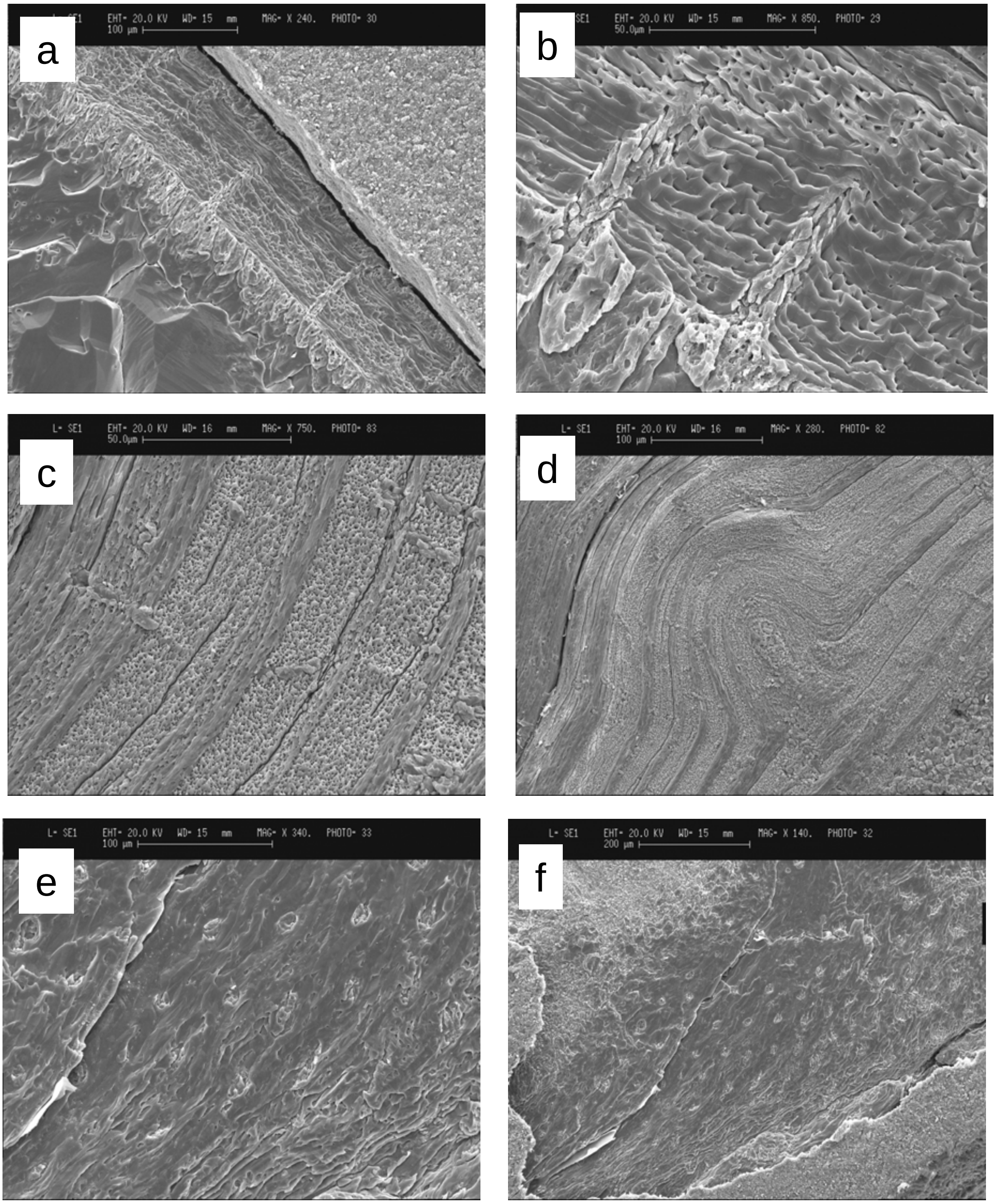



Plate 2

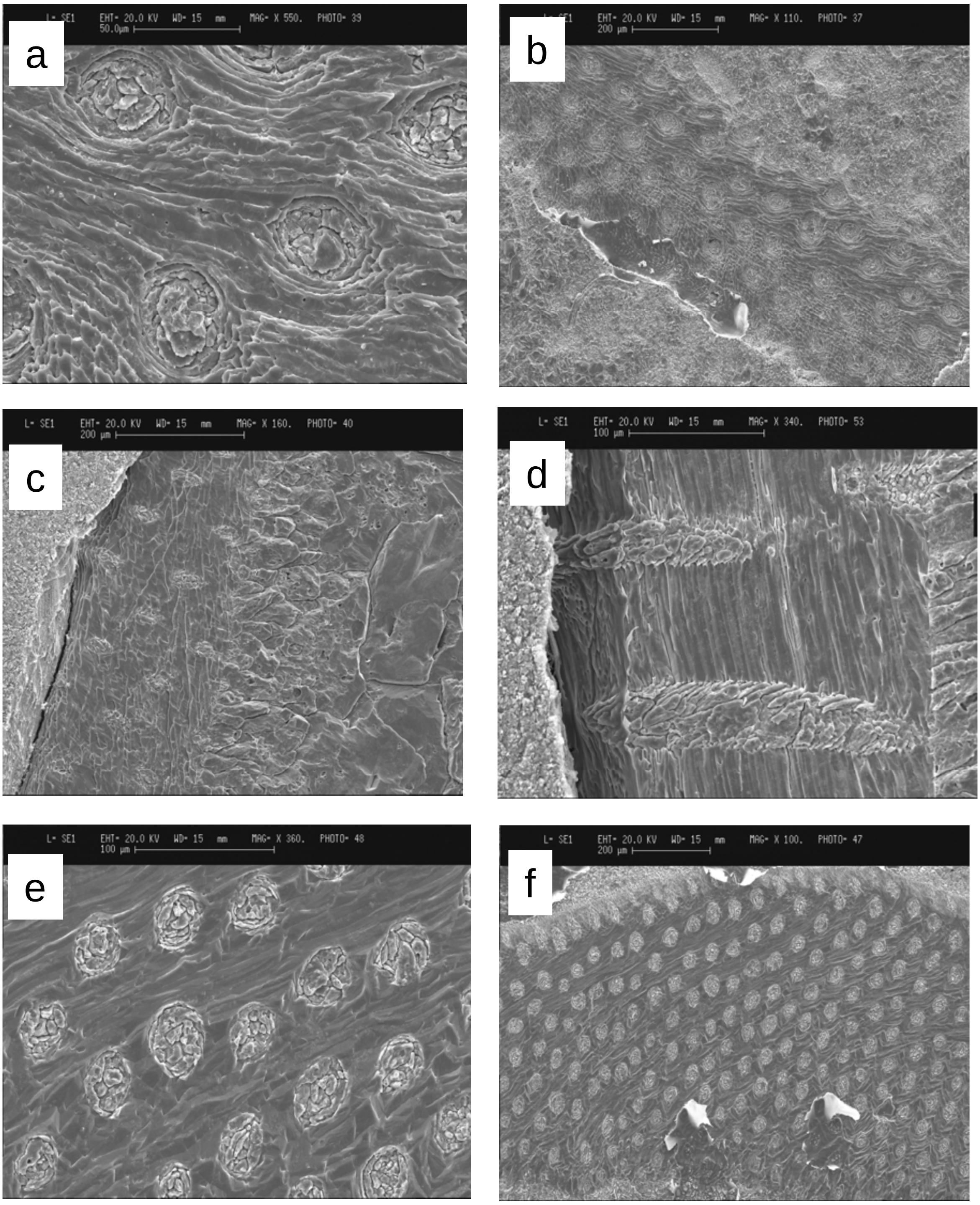



Plate 3

| Specimen | Species | Ultrastructure category | Ca (ppm) | Fe(ppm) | Mg(ppm) | Mn(ppm) | Sr(ppm) | δ$^{13}$C (‰) | δ$^{18}$O (‰) | $^{87}$Sr/$^{86}$Sr |
|---|---|---|---|---|---|---|---|---|---|---|
| Khuff Fm, SAUDI ARABIA 26°07'01" N/44°02'26" E, Buraydah quadrangle (Vaslet et al., 1985), 5 km north of Midhnab town | | | | | | | | | | |
| **KH0211-2 (bed: KH0211)** | ***Omanilasma husseinii*** | **VERY GOOD** | **358313** | **372** | **2787** | **95.9** | **432** | **+2.7** | **-2.7** | **0.706988** |
| KH0211-3 **(bed: KH0211)** | *Omanilasma husseinii* | NOT WELL PRESERVED | 406731 | 773 | 3219 | 97.1 | 207 | +3.7 | -5.2 | 0.707198 |
| **KH0211-7A (bed: KH0211)** | ***Omanilasma husseinii*** | **VERY GOOD** | **456364** | **343** | **3647** | **96.7** | **304** | **+3.7** | **-4.3** | **0.707045** |
| **KH0211-8A (bed: KH0211)** | ***Omanilasma husseinii*** | **GOOD** | **508405** | **415** | **3629** | **81.7** | **283** | **+3.6** | **-4.5** | **0.707022** |
| KH0211-9A **(bed: KH0211)** | *Omanilasma husseinii* | GOOD | 444305 | 699 | 3280 | 112 | 178 | +3.8 | -5.4 | 0.707069 |
| KH0211-10A **(bed: KH0211)** | *Omanilasma husseinii* | NOT WELL PRESERVED | 338882 | 435 | 2928 | 71.3 | 268 | +3.5 | -5.5 | 0.707146 |
| **KH0211-11 (bed: KH0211)** | ***Omanilasma husseinii*** | **VERY GOOD** | **394505** | **340** | **3349** | **67.3** | **283** | **+3.2** | **-3.8** | **0.706988** |
| Khuff Fm, OMAN 21º00'35''N/57º39'27''E, Section K7 | | | | | | | | | | |
| **AO72-3 (bed: AO72)** | ***Derbyia* cf. *diversa*** | **GOOD** | **284629** | **388** | **1330** | **105** | **480** | **+4.0** | **-3.1** | **0.707243** |
| AO72-6 (bed: AO72) | *Juresania omanensis* | NOT WELL PRESERVED | 396080 | 868 | 1978 | 236 | 630 | +3.8 | -4.1 | 0.707364 |
| AO72-16 (bed: AO72) | *Juresania omanensis* | GOOD | 418064 | 1086 | 2437 | 215 | 844 | +3.5 | -4.1 | 0.707314 |
| **AO72-21 (bed: AO72)** | ***Derbyia* cf. *diversa*** | **GOOD** | **419680** | **516** | **1959** | **155** | **712** | **+4.0** | **-2.6** | **0.707267** |
| **AO73-39 (bed: AO73)** | ***Omanilasma husseinii*** | **GOOD** | **360008** | **1037** | **2453** | **165** | **612** | **+4.9** | **-2.2** | **0.707280** |
| AO73-44 (bed: AO73) | *Omanilasma husseinii* | VERY GOOD | 391598 | 1612 | 2903 | 316 | 1282 | +4.4 | -3.8 | 0.707731 |
| AO73-107 (bed: AO73) | *Callispirina* sp. | VERY GOOD | 360501 | 943 | 3149 | 191 | 661 | +4.3 | -3.4 | 0.707381 |
| AO210-3 (bed: AO210) | *Omanilasma husseinii* | VERY GOOD | 364963 | 939 | 2617 | 264 | 505 | +3.8 | -0.7 | 0.707249 |
| AO210-9 (bed: AO210) | *Omanilasma husseinii* | GOOD | 444794 | 1558 | 4052 | 431 | 640 | +2.5 | -2.3 | 0.707287 |
| **AO210-25 (bed: AO210)** | ***Omanilasma husseinii*** | **VERY GOOD** | **375667** | **449** | **1517** | **128** | **482** | **+4.3** | **-0.7** | **0.707217** |
| **AO210-153 (bed: AO210)** | ***Omanilasma desertica*** | **GOOD** | **358587** | **610** | **2052** | **160** | **500** | **+4.8** | **-1.4** | **0.707231** |
| AO210-91 (bed: AO210) | *Juresania omanensis* | NOT WELL PRESERVED | 371194 | 1299 | 2261 | 505 | 667 | +2.0 | -4.2 | 0.707333 |
| AO80-17 (bed: AO80) | *Kotlaia* cf. *bistriata* | NOT WELL PRESERVED | 406506 | 713 | 3974 | 1529 | 837 | +2.3 | -4.3 | 0.707286 |

Key to preservation: 'Very good' – all secondary fibers are intact; 'Good' – secondary fibers are intact, but some imperfectly shaped; 'Not well preserved' – many fibers show imperfections. Fe >600ppm when accompanied by high Mn or poor preservation.

Samples highlighted in bold are brachiopods thought to retain pristine carbonate based on ultrastructure, cathodoluminescence and Mn<200ppm

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