

Atypical diagenetic effects on strontium-isotope composition of Early Jurassic belemnites, Queen Charlotte Islands, British Columbia, Canada

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Abstract: In this study, strontium-, carbon- and oxygen-isotope data are reported from Early Jurassic belemnites from Yakoun River, Queen Charlotte Islands (QCI), British Columbia. Assuming that the established ammonite correlations between Canada and Europe are accurate, the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve between Europe and QCI should be similar. However, the *Rarenodia planulata* and *Phymatoceras crassicostra* ammonite biozones from Yakoun River record $^{87}\text{Sr}/^{86}\text{Sr}$ values that are lower than expected. This shift is interpreted to be a result of diagenetic alteration by later hydrothermal fluid (^{87}Sr -depleted). In general, the diagenetic samples have more negative $\delta^{13}\text{C}_{\text{bel}}$ and $\delta^{18}\text{O}_{\text{bel}}$ values, and higher Mn concentrations, but show no difference in Fe concentration. A $\delta^{13}\text{C}_{\text{bel}}$ curve from diagenetically screened samples exhibits only slightly depleted values with respect to a similar curve generated from Europe. A similar curve for $\delta^{18}\text{O}_{\text{bel}}$ shows a striking similarity with that generated from Europe. This study illustrates that diagenetic effects on Sr-isotope composition can lower values from the expected seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve, thus potentially producing erroneous correlations between ammonite biostratigraphic schemes. Traditional screening methods for diagenesis, such as cathodoluminescence and trace-element abundances, were inadequate for evaluating diagenesis in the Yakoun River sections. Other such studies must also consider alternative and (or) a combination of methods in evaluating geochemical data from belemnites.

Résumé : Dans la présente étude, les données des isotopes du strontium, du carbone et de l'oxygène sont rapportées de bélemnites de la rivière Yakoun (Jurassique précoce), aux îles de la Reine-Charlotte, Colombie-Britannique. En assumant que les corrélations établies pour les ammonites entre le Canada et l'Europe soient précises, les courbes $^{87}\text{Sr}/^{86}\text{Sr}$ de l'eau de mer pour l'Europe et les îles de la Reine-Charlotte devraient être similaires. Toutefois, les biozones à ammonite *Rarenodia planulata* et à *Phymatoceras crassicostra* de la rivière Yakoun enregistrent des valeurs $^{87}\text{Sr}/^{86}\text{Sr}$ inférieures à celles attendues. Ce décalage serait le résultat d'une altération diagénétique par des fluides hydrothermaux plus tardifs (appauvris en ^{87}Sr). En général, les échantillons diagénétiques ont des valeurs $\delta^{13}\text{C}_{\text{bel}}$ et $\delta^{18}\text{O}_{\text{bel}}$ plus négatives et des concentrations en Mn plus élevées mais ils ne montrent pas de différence en ce qui concerne la concentration en Fe. Une courbe $\delta^{13}\text{C}_{\text{bel}}$ provenant d'échantillons tamisés de manière diagénétique ne montre que des valeurs légèrement appauvries par rapport à une courbe similaire générée à partir de données européennes. Une courbe semblable pour $\delta^{18}\text{O}_{\text{bel}}$ montre une similarité remarquable à celle générée à partir des données européennes. La présente étude démontre que des effets diagénétiques sur la composition en isotopes du Sr peuvent abaisser les valeurs attendues de la courbe $^{87}\text{Sr}/^{86}\text{Sr}$ pour l'eau de mer, donnant potentiellement des corrélations erronées entre les modèles biostratigraphiques des ammonites. Les méthodes de tri traditionnelles pour la diagenèse, telles que la cathodoluminescence et l'abondance des éléments traces, étaient inadéquates pour évaluer la diagenèse dans les sections de la rivière Yakoun. D'autres études du même genre doivent aussi considérer d'autres méthodes et (ou) des combinaisons de méthodes pour évaluer les données géochimiques provenant des bélemnites.

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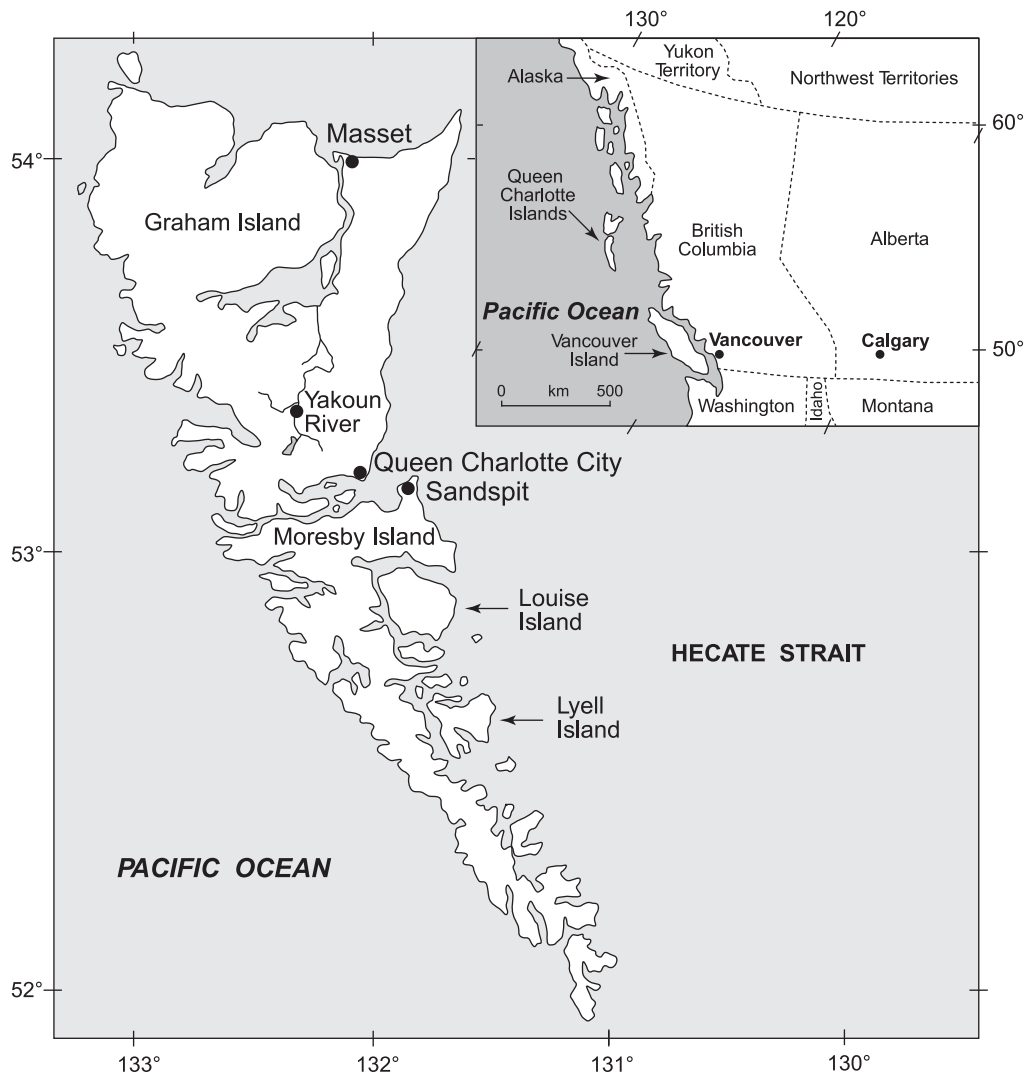
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Introduction

The seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve for the Paleozoic is well established from the analysis of various sites and materials. Veizer et al. (1999) have constructed a seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve using data from sources including conodonts, brachiopods, foraminifera, and micritic matrix. More recently, $^{87}\text{Sr}/^{86}\text{Sr}$ data from Jurassic belemnites have been compiled to produce a curve that can allow correlations to be made at the scale of individual ammonite biozones and biosubzones (Jenkyns et al. 2002).

There are several important factors that must be considered when constructing a seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve and using

Fig. 1. Locality map of the Queen Charlotte Islands off the coast of western Canada (inset) and the geographic position of the Yakoun River in Graham Island.

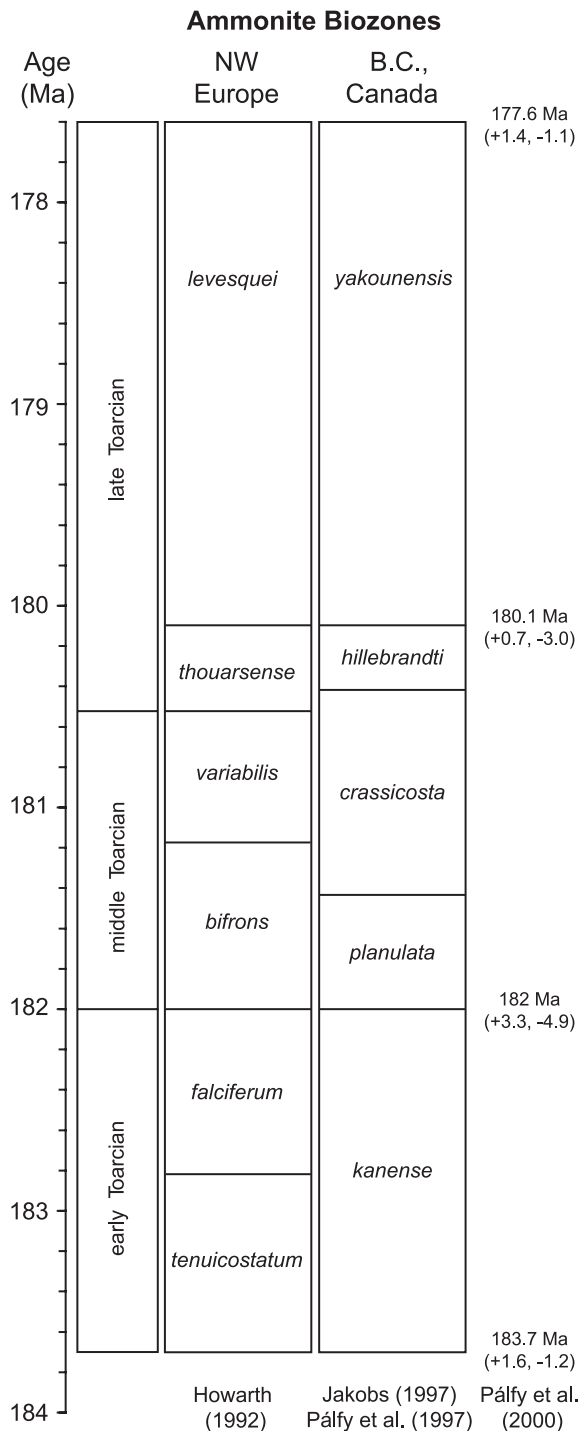


it for correlation. To begin with, it is necessary to assume that the $^{87}\text{Sr}/^{86}\text{Sr}$ value of seawater is homogeneous at any time, as a result of the relatively long residence time of Sr (~2.5 million years; Hodell et al. 1990) in the ocean compared with the mixing time (Goldberg 1965). To be useful for correlation, it must also be the case that the $^{87}\text{Sr}/^{86}\text{Sr}$ value of the oceans has varied through geological time, this occurring as a result of the interplay between hydrothermal activity supplying fluids depleted in ^{87}Sr and weathering of continental crust, supplying material enriched in ^{87}Sr . Peterman et al. (1970) first indicated that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of carbonate has varied through geological time, and this was later corroborated by the more widely cited study of Burke et al. (1982) that showed major variation in Sr-isotope ratios through the Phanerozoic Eon. The construction of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ requires that the ratio is accurately recorded in calcium-bearing minerals precipitated directly from seawater. McArthur (1994) and Reinhardt et al. (1999) showed that the $^{87}\text{Sr}/^{86}\text{Sr}$ value of calcium carbonate from modern marine organisms is within 0.000004 of the $^{87}\text{Sr}/^{86}\text{Sr}$ value of seawater, which is well within analytical error. In addition,

the Sr-isotope signature of ancient seawater must become locked into skeletal carbonate through geologic time. Hence, samples that are used in the construction of a seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve must be screened for diagenesis, and it was Burke et al. (1982) who first indicated that more elevated $^{87}\text{Sr}/^{86}\text{Sr}$ values above the curve were related to diagenetic alteration.

The most widely adopted method to screen for diagenetic alteration in belemnites was developed following Brand and Veizer (1980) and discussed in detail by Jones (1992) and Jones et al. (1994). This method used trace-element chemistry of the belemnite rostra, in particular the abundance of iron and manganese. Jones (1992) found that British belemnites with Fe and Mn values ≥ 150 ppm and ≥ 75 ppm, respectively, also had elevated $^{87}\text{Sr}/^{86}\text{Sr}$ values. In contrast, Jones (1992) found little correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{13}\text{C}_{\text{bel}}$ or $\delta^{18}\text{O}_{\text{bel}}$, and thus only used trace-element abundances for evaluating diagenesis. Jones et al. (1994) adopted the procedure that any sample with an Fe and (or) Mn value below these cut-off levels was well enough preserved to be used in the construction of a seawater $^{87}\text{Sr}/^{86}\text{Sr}$ curve. The

Fig. 2. Correlation between ammonite biostratigraphy of north-western Europe and that of British Columbia, Canada. Ammonite biozones are correlated based on the work of Jakobs et al. (1994) and Jakobs (1997) and using the ammonite biozonations for northwestern Europe as outlined in Howarth (1992). Correlation of boundaries to absolute time was accomplished using the time scale of Pálfy et al. (2000), which is based on the western Canada ammonite biozonation scheme by Jakobs et al. (1994) and Jakobs (1997). A date just above the *R. planulata* – *P. crassica* biozone boundary was taken from section 7.



cut-off levels adopted by some authors (e.g., Jones et al. 1994; Gröcke 2001; Jenkyns et al. 2002) are lower than those employed by others (e.g., McArthur et al. 2000).

The primary aim of the present study was originally to conduct strontium-isotope analyses of Early Jurassic belemnites from the Queen Charlotte Islands (QCI), British Columbia, to test previous ammonite biostratigraphic correlations between faunal provinces (Jakobs et al. 1994; Pálfy et al. 1997). A radiometric age has also been obtained from the Toarcian strata of QCI, making the succession important for calibration of the geological time scale (Pálfy et al. 1997). However, in the course of this study, it became apparent that many of the belemnite Sr-isotope values had been altered in an atypical manner and this led to a switch in focus to one of deciphering diagenetic alteration.

Geological setting

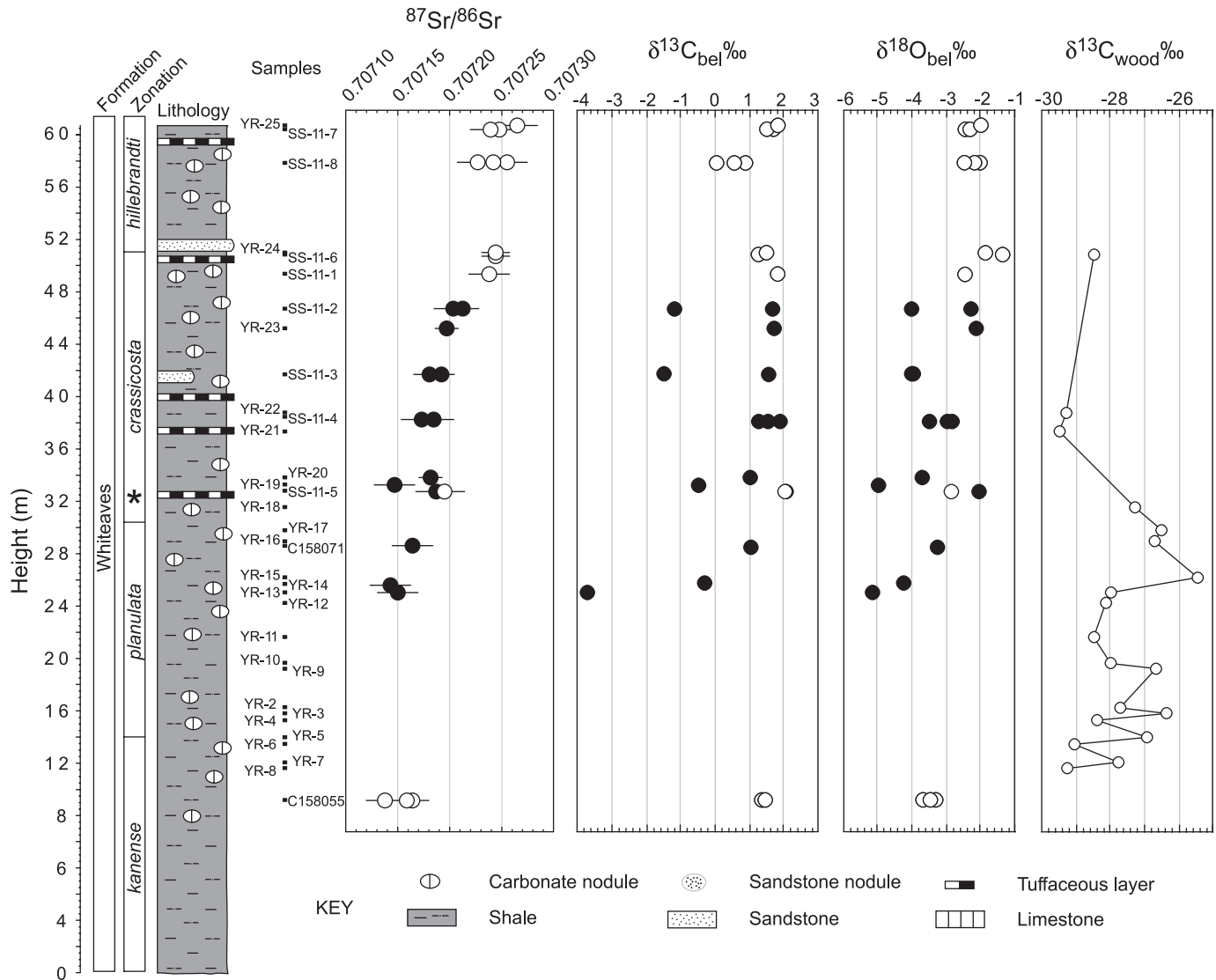
The Queen Charlotte Islands are located off the west coast of British Columbia, western Canada, between 52°N and 55°N (Fig. 1). The islands' geology comprises Paleozoic, Mesozoic, and Tertiary granites; Mesozoic and Tertiary volcanic rocks and sedimentary sequences; and Quaternary deposits (a detailed account of bedrock geology of QCI can be found in Lewis et al. 1991). Part of the Wrangellia terrane of the Insular Belt of western North America, the Mesozoic sedimentary sequences, have excellent preservation of many fossils including foraminifera, bivalves, ammonites, and belemnites (e.g., Jakobs et al. 1994; Kottachchi et al. 2002; Ward et al. 2004). During the Triassic, the islands were located near the equator and through the Mesozoic migrated up to 3000 km northwards (Kottachchi et al. 2002), although it has been suggested that the QCI were located between 35°N and 40°N during the Early Jurassic (Aberhan 1998).

This study uses belemnites collected by Giselle Jakobs and Charlie Jones from stratigraphic sections 7 and 12, representing a well-exposed Toarcian sequence along the Yakoun River, Graham Island, Queen Charlotte Islands (Jakobs et al. 1994). A detailed lithostratigraphic and biostratigraphic summary can be found in Cameron and Tipper (1985) and Jakobs et al. (1994).

The Yakoun River sections discussed here are surrounded by the Masset Formation of Tertiary igneous rocks, which dominate the northern part of Graham Island and unconformably overlie Mesozoic strata (Hamilton and Dostal 2001). Sedimentary deposits from throughout the Mesozoic can be found on these islands, which have received more attention recently with the recognition of a complete marine Triassic–Jurassic boundary section (e.g., Ward et al. 2004). The Jurassic strata also contain tuffs that have provided the basis for geochronological studies (see Pálfy et al. 2000), as well as abundant ammonites with both Boreal and Tethyan affinities, thus providing the basis for correlation with European ammonite biozones (Jakobs et al. 1994).

Western North American ammonite biozones lack several key taxa for comparison to northwestern European biozones, and vice versa. The correlation used here is based on the occurrences of a small number of genera occurring in both regions (Jakobs 1997; Pálfy et al. 1997). The *Dactylioceras kanense* biozone, for example, is defined in western North America on the basis of the first occurrence of *Dactylioceras*

Fig. 3. Section 7 from near Yakoun River (see Jakobs 1997, fig. 37, p. 32) Queen Charlotte Islands, Canada. Ammonite biozonation based on Jakobs et al. (1994) and Jakobs (1997). The tuff horizon marked with an asterisk has been dated by Pálffy et al. (1997) at 181.4 ± 1.2 Ma. $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{13}\text{C}_{\text{bel}}$, and $\delta^{18}\text{O}_{\text{bel}}$ values that are deemed diagenetic based on Sr-isotope curve offsets, are represented as filled symbols.



above the last occurrence of *Amaltheus* and *Fanninoceras* (Smith et al. 1988). *Dactylioceras* is a rare genus in North America, but it is present in small numbers in the QCI sections (Jakobs et al. 1994). The *D. kanense* biozone of western North America correlates with the combined *Dactylioceras tenuicostatum* and *Harpoceras falciferum* biozones from northwestern Europe based on the occurrence of the genera *Cleviceras*, *Dactylioceras*, *Tiloniceras*, and *Hildaites* on both continents (Jakobs 1997). Long-distance correlation of the middle and late Toarcian biozones based upon ammonites is discussed in detail in Jakobs (1997) and Pálffy et al. (1997).

In combination with this, U–Pb dating of tuffs within sedimentary sections from British Columbia has provided numerical dates against well-defined ammonite biostratigraphic zones (Pálffy et al. 2000: Fig. 2). One of the dates for the Pálffy et al. (2000) Jurassic time scale includes a tuff deposit from section 7 (181.4 ± 1.2 Ma; Fig. 3), providing an age of the western North American *Rarenodia planulata* –

Phymatoceras crassicoستا biozone boundary. This boundary corresponds to the upper *Hildoceras bifrons* biozone from northwestern Europe. Isotopic $^{187}\text{Re}/^{188}\text{Os}$ dating of the Jet Rock Formation, Yorkshire, England, provides an age of 181 ± 13 Ma for the *Cleviceras exaratum* biosubzone of the *H. falciferum* biozone (Cohen et al. 1999), and more recently Cohen et al. (2004) have determined an age for the *H. falciferum* biosubzone at 178.2 ± 5.6 Ma. Both $^{187}\text{Re}/^{188}\text{Os}$ dates have large uncertainties, and therefore they provide only an indication of the broad accuracy of the ammonite correlations. A graphical representation of the biostratigraphical–geochronological sequence used in this study is provided in Fig. 2.

Methods

Prior to isotopic analysis, samples were pre-treated to remove any secondary calcite from the outer surfaces of the

Table 1. Belemnite isotopic and trace-element data from section 7, Yakoun River, QCI, Canada.

Sample ID	$\delta^{13}\text{C}_{\text{bel}}$	$\delta^{18}\text{O}_{\text{bel}}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm 2\text{se}$	Fe (ppm)	Mn (ppm)
C158055	1.498	-3.349	0.707164	0.000014	97	655
C158055A	1.384	-3.684	0.707138	0.000019	56	164
C158055D	1.425	-3.467	0.707159	0.000024	491	335
YR-13B	-3.707	-5.189	0.707150	0.000020	362	623
YR-14	-0.310	-4.218	0.707143	0.000019	201	626
C158071	1.002	-3.273	0.707164	0.000019	102	835
SS-11-5A	2.027	-2.874	0.707199	0.000019	74	108
SS-11-5B	2.345	-2.076	0.707187	0.000023	78	91
YR-19	-0.547	-5.024	0.707147	0.000020	263	678
YR-20	1.023	-3.725	0.707181	0.000011	196	370
SS-11-4A	1.880	-3.052	0.707184	0.000021	474	614
SS-11-4B	1.448	-3.555	0.707173	0.000020	285	521
SS-11-4C	1.219	-2.482	0.707182	0.000021	965	511
SS-11-3	-1.491	-4.109	0.707180	0.000018	176	664
SS-11-3A	1.567	-3.978	0.707191	0.000019	1024	415
YR-23	1.691	-2.177	0.707196	0.000012	99	79
SS-11-2A	1.657	-2.291	0.707214	0.000019	217	149
SS-11-2B	-1.222	-4.058	0.707202	0.000018	202	967
SS-11-1	1.809	-2.448	0.707239	0.000027	609	164
SS-11-6	1.448	-1.865	0.707244	0.000014	35	41
YR-24A	1.224	-1.395	0.707244	0.000014	134	12
SS-11-8A	0.135	-2.216	0.707241	0.000016	1021	173
SS-11-8B	0.894	-2.024	0.707255	0.000016	22	59
SS-11-8C	0.580	-2.535	0.707228	0.000019	530	149
SS-11-7	1.687	-2.372	0.707247	0.000020	156	139
SS-11-7A	1.456	-2.487	0.707239	0.000020	338	100
YR-25	1.902	-1.977	0.707265	0.000020	58	26

Note: Detection limits for Fe (18 ppm) and Mn (14 ppm). bel, belemnite; se, standard error of analysis. Stable-isotopes ratios expressed against VPDB. Sr-isotope ratios against NBS 987. Section 7 (Jakobs 1997) was originally described as section 11 in Cameron and Tipper (1985), and thus sample numbers are labelled as SS-11-X. Bold samples are deemed diagenetic.

belemnites as these regions are commonly affected by diagenesis. The belemnites were then thoroughly cleaned using deionized water and dried at room temperature. The subsequent chemical treatment was described in Jones et al. (1994), although it is repeated here with the modifications described in Gröcke (2001).

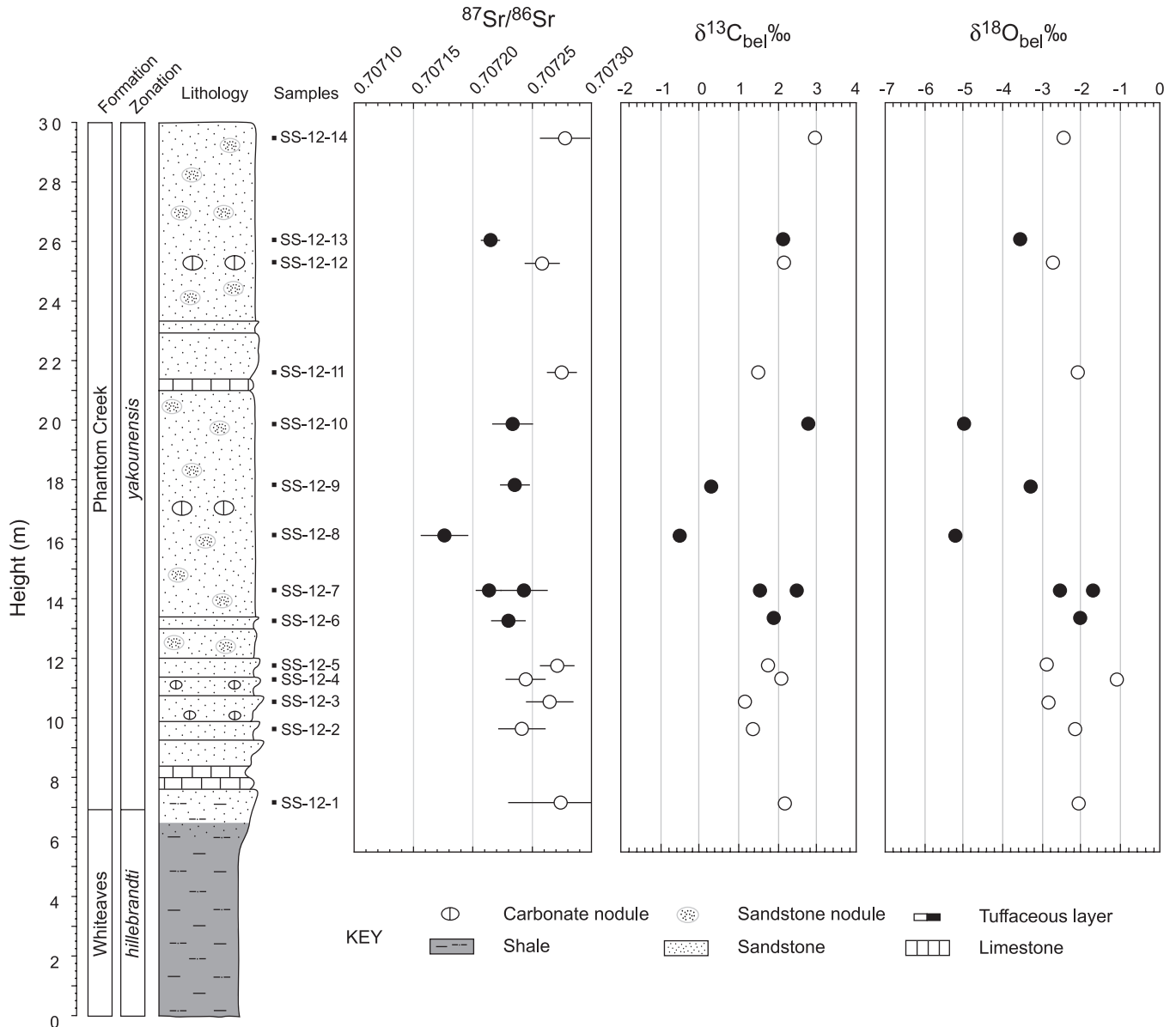
Strontium-isotope analysis

After physically removing the external coating from the belemnites and reducing them in size to <5 mm, samples were treated with 0.6 mol/L HCl in clean beakers and excited in an ultrasonic bath for ~10 min. Samples were then rinsed with water, dried, and broken into <2 mm sized fragments. Finally, after etching with 0.3 mol/L HCl for ~10 min (sustaining the reaction by dropwise additions of 6 mol/L HCl), samples were rinsed with water and dried. About 60 mg of sample was placed in a FEP beaker, dissolved in 1–2 mL of ~6 mol/L HCl, and the solution evaporated to incipient dryness. After dissolving the residue in 4 mL of 3 mol/L HCl, the solution was transferred to a 15 mL centrifuge tube and centrifuged. A 2 mL quantity of

the sample solution was loaded into a calibrated cation-exchange column (AG 50W X12, 200–400 mesh resin to form a resin bed 0.7 cm × 8.5 cm in water) equilibrated with 5 mL of 3 mol/L HCl. After washing the column with a total of 19 mL of 3 mol/L HCl, the Sr was eluted in 8 mL of 3 mol/L HCl, collected in a FEP beaker and evaporated to dryness. Any remaining organic matter at this stage was destroyed using a few drops of aqua regia. High purity reagents were used throughout.

A 0.5 μL quantity of 1.2 mol/L H_3PO_4 was then placed in the centre of an outgassed single tantalum filament, followed by the sample Sr in 1 μL water, and the solution dried onto the filament by passing a current of ~1 A through the filament. Finally, the current was increased momentarily until the filament became dull red to remove excess phosphoric acid and then turned off. Sr-isotope measurements were performed on a modified VG Isomass 54E thermal ionization mass spectrometer at the Age and Isotope Laboratory at the University of Oxford. All $^{87}\text{Sr}/^{86}\text{Sr}$ values were internally normalized to an $^{86}\text{Sr}/^{88}\text{Sr}$ ratio of 0.1194 and the data were then adjusted using a National Bureau of Standards (NBS)

Fig. 4. Section 12 from near Yakoun River (see Cameron and Tipper 1985, p. 27, GSC 190995), Queen Charlotte Islands, Canada. Ammonite biozonation based on Jakobs et al. (1994) and Jakobs (1997). $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{13}\text{C}_{\text{bel}}$, and $\delta^{18}\text{O}_{\text{bel}}$ values that are deemed diagenetic based on Sr-isotope curve offsets, are represented as filled symbols.



987 value of 0.710250. The Sr-isotope value obtained for NBS 987 at the Age and Isotope Laboratory during this study was 0.710255 ± 0.000013 ($n = 54$).

Carbon- and oxygen-isotope analysis

Powdered carbonate samples were measured into thimbles and cleaned of organic matter using 10% H_2O_2 for ~20 min, after which time acetone was added to extract water, and then dried in an oven set at 60 °C. The samples were then loaded into a carousel with four standards (Carrara marble) at the start and end of a run (eight standards and 36 samples). Calcium carbonate was generated using a common-orthophosphoric acid bath system connected to a VG Series II Prism mass spectrometer. All results are reported in standard delta (δ) notation in per mil (‰) against Vienna Pee Dee Belemnite (VPDB). The VG Series II Prism at the Uni-

versity of Oxford is calibrated to VPDB using the internal standard, Carrara Marble, which is calibrated against the standard NBS 19. Analytical reproducibility of replicate samples using this method was better than 0.1‰ for both carbon and oxygen.

Fossil wood samples were powdered to <0.7 mm and a sample of ~30 mg was placed in a 50 mL polypropylene centrifuge tube and reacted with 3 mol/L HCl for ~1 h, after which time the solution was brought to the boil for 1 min to remove any pyritic compounds. Samples were then rinsed with deionized water, centrifuged, and rinsed again until neutrality was reached. Samples were sealed in 8 mm × 6 mm steel-foil cups and placed in a Europa Scientific Limited CN biological sample converter connected to a 20–20 isotope-ratio mass spectrometer at the Archaeology Research Laboratory, University of Oxford. Carbon-isotope

Table 2. Belemnite isotopic and trace-element data from section 12, Yakoun River, QCI, Canada.

Sample ID	$\delta^{13}\text{C}_{\text{bel}}$	$\delta^{18}\text{O}_{\text{bel}}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm 2\text{se}$	Fe (ppm)	Mn (ppm)
SS-12-1A	2.177	-2.069	0.707274	0.000047	268	84
SS-12-2	1.315	-2.154	0.707241	0.000020	401	303
SS-12-3	1.189	-2.848	0.707264	0.000020	94	283
SS-12-4	2.056	-1.150	0.707244	0.000018	59	372
SS-12-5A	1.781	-2.922	0.707271	0.000016	335	197
SS-12-6	1.859	-2.014	0.707230	0.000015	431	209
SS-12-7A	1.563	-1.720	0.707213	0.000010	146	24
SS-12-7B	2.430	-2.569	0.707243	0.000020	180	52
SS-12-8	-0.575	-5.277	0.707176	0.000020	83	240
SS-12-9	0.332	-3.371	0.707235	0.000013	330	295
SS-12-10	2.779	-4.979	0.707233	0.000018	98	473
SS-12-11	1.302	-2.105	0.707275	0.000013	196	57
SS-12-12	2.148	-2.760	0.707255	0.000015	322	104
SS-12-13	2.127	-3.565	0.707215	0.000007	997	664
SS-12-14A	2.978	-2.495	0.707278	0.000021	194	88

Note: Detection limits for Fe (18 ppm) and Mn (14 ppm). bel, belemnite; se, standard error of analysis. Stable-isotope ratios expressed against VPDB. Sr-isotope ratios against NBS 987. Bold samples are deemed diagenetic.

ratios were measured against an internal standard ($\delta^{13}\text{C}_{\text{nylon}} = -26.2\text{‰} \pm 0.2\text{‰}$), and analytical reproducibility of replicate samples was better than 0.2‰ for carbon.

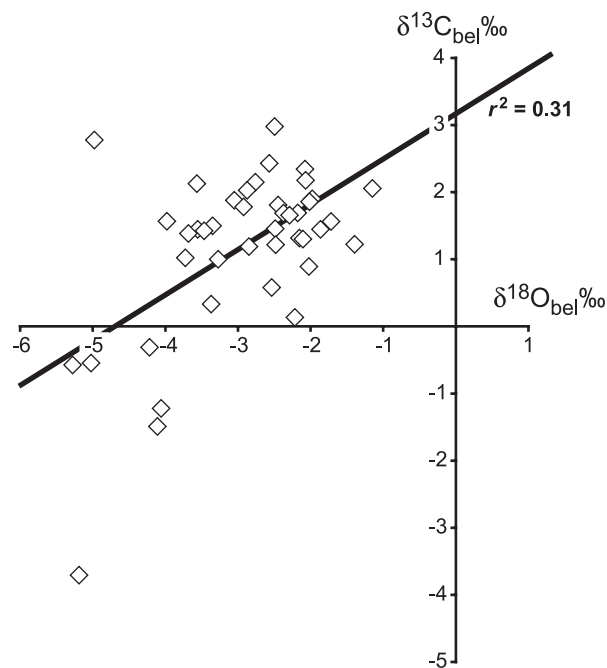
Trace-element analysis

Belemnites used for construction of the Sr-isotope curve were also analyzed for trace-element composition. The details of cleaning the belemnites are outlined in the Sr-isotope analysis section. Two mL of ~3 mol/L HCl was added to the remaining 2 mL of dissolved belemnite solution. Trace-element analysis was conducted at Royal Holloway, University of London (London, UK), using inductively coupled plasma – atomic emission spectrometry (ICP–AES) with an ultra-pure calcium standard (referred to as Ca-high). Every nine samples were separated by an internal standard (KC11) and were drift corrected at the end of the run. At the start of a run, blank concentrations were determined and subsequently subtracted from the sample measurements prior to drift correction. The Ca-high standard was analyzed at the start and end of a run, which normally consisted of ~200 samples. Blanks were also run to monitor background levels and memory effects. Reproducibility, based on replicate analysis, was calculated at 18 ppm for Fe and 14 ppm for Mn.

Results

Section 7

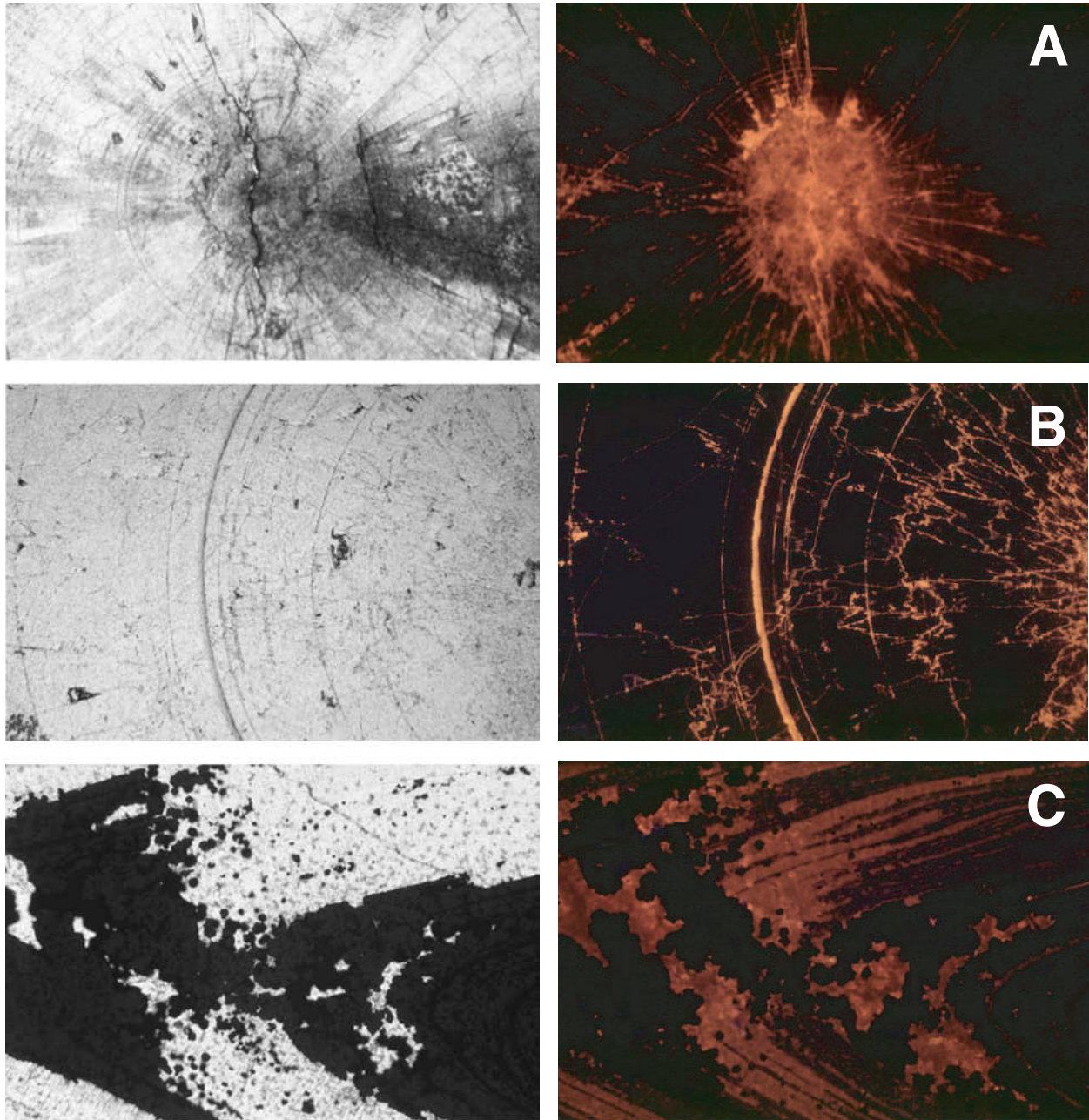
Section 7 (Fig. 3; Table 1) includes the *Dactylioceras kanense* biozone at its base and ranges through to the lower portion of the *Phymatoceras hillebrandti* biozone. This interval correlates approximately to the *D. tenuicostatum* to *Grammoceras thouarsense* biozones in Europe (Pálffy et al. 2000). The $^{87}\text{Sr}/^{86}\text{Sr}$ curve for section 7 displays a general rise through the section, starting at ~0.70715 in the high *D. kanense* to mid *Rarenodia planulata* biozones. In the upper

Fig. 5. Cross-plot of the $\delta^{13}\text{C}_{\text{bel}}$ and $\delta^{18}\text{O}_{\text{bel}}$ data from this study. r , correlation coefficient.

R. planulata and lower *P. crassica* biozones, the $^{87}\text{Sr}/^{86}\text{Sr}$ values increase to ~0.70719, showing only a slight rise to 0.70720 near the top of the *P. crassica* biozone. Above this, there is a sharp rise in the upper *P. crassica* biozone to ~0.70729 and a gradual rise through the *P. hillebrandti* biozone to a maximum of 0.70732.

The $\delta^{13}\text{C}_{\text{bel}}$ values range between -4‰ and +2‰, but most lie between +1‰ and +2‰ throughout section 7, except for several pronounced negative excursions: -3.8‰ in the upper *R. planulata* biozone; -0.6‰ in the lower *P. crassica*

Fig. 6. Normal light (left) and cathodoluminescent (right) images of belemnites from the Yakoun River, Queen Charlotte Islands. (A) Near tip of phragmocone in SS-11-8C. (B) Luminescent ring and fractures in SS-12-3. (C) Oil-filled longitudinal section of SS-11-4A. All images represent a view 1 cm wide and 0.5 cm high.



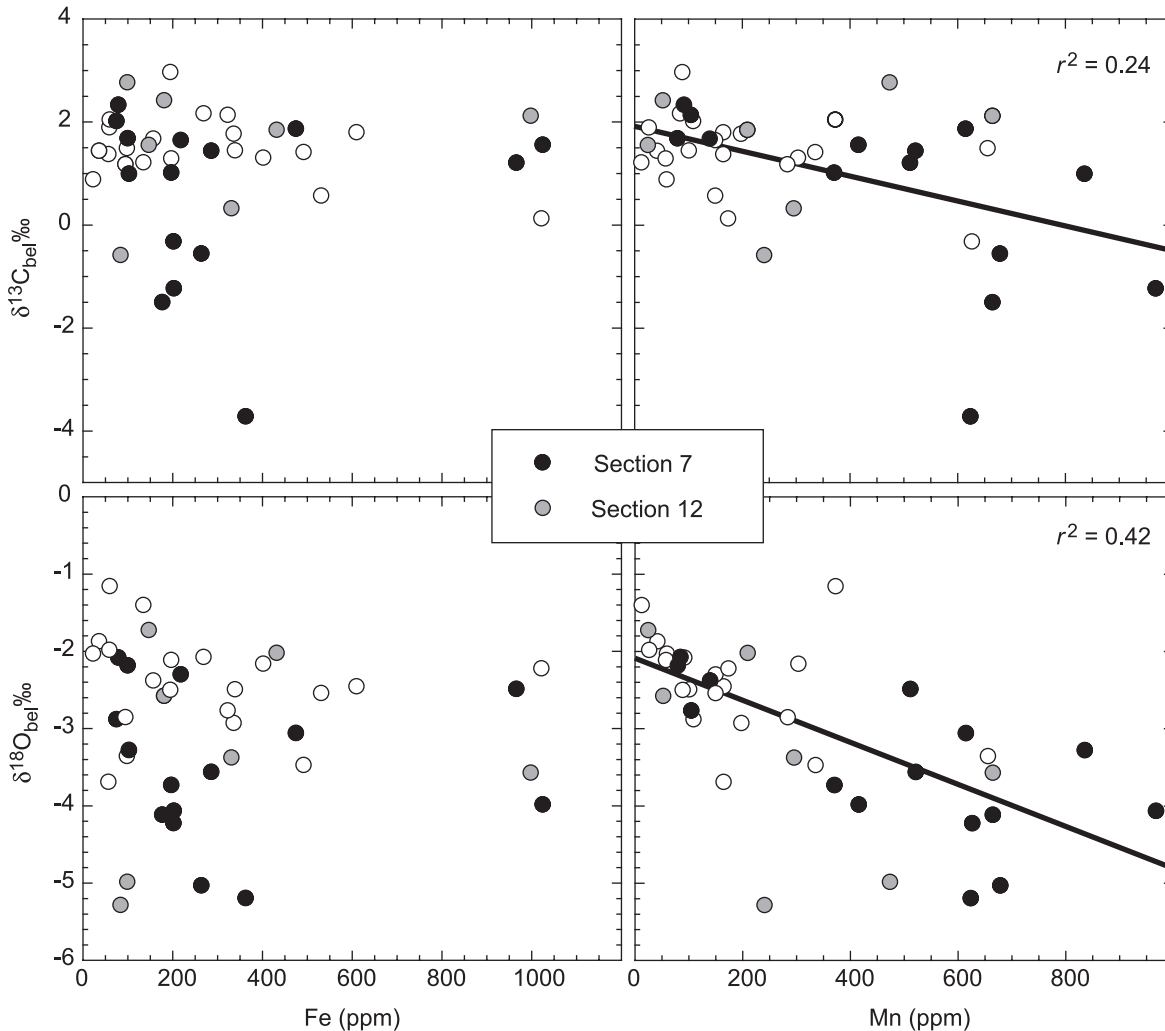
biozone; and two reaching $\sim -1.4\text{‰}$ in the middle *P. crassicosta* biozone.

The $\delta^{18}\text{O}_{\text{bel}}$ values show a general rise up through section 7, starting at $\sim -3.5\text{‰}$ at the base and finishing at $\sim -2\text{‰}$ at the top. The range in $\delta^{18}\text{O}_{\text{bel}}$ is somewhat narrower than that for carbon, ranging between -5‰ and -1.4‰ , although several negative excursions are also recorded at similar levels as recorded for carbon.

Carbon-isotope data from fossil wood are also shown, and range from -25.5‰ to -29.5‰ (Fig. 3). The lightest of these values are comparable with those that characterize negative

excursions at oceanic anoxic events in the Jurassic and Cretaceous from northwestern Europe (Jenkyns and Clayton 1997; Gröcke et al. 1999; Hesselbo et al. 2000, 2003). It may be argued that the wood isotope data show an upward trend to heavier values through the upper *D. kanense* and the *R. planulata* biozones, and then return to isotopically light values in the *P. crassicosta* biozone. This signature is similar to that from some *D. tenuicostatum* and *H. falciferum* biozone (or *D. polymorphum* and *H. levisoni* biozone) sections in Europe (e.g., see Jenkyns et al. 2002), but the established correlations do not allow us to make direct comparisons. It

Fig. 7. Comparison of $\delta^{13}\text{C}_{\text{bel}}$ and $\delta^{18}\text{O}_{\text{bel}}$ with trace-element abundances of Fe and Mn from sections 7 and 12, Yakoun River, Queen Charlotte Islands. The filled symbols correspond to samples that have been deemed diagenetically altered based on Sr-isotope curve offsets (see Fig. 10) and their corresponding sections. r , correlation coefficient.



would, therefore, appear more likely that in this case $\delta^{13}\text{C}_{\text{wood}}$ values were produced by trees whose “background” isotopic composition was slightly lighter than plants hitherto analyzed; possibly related to environmental factors, such as ample water availability (Gröcke 2002).

Section 12

Section 12 ranges from the *P. hillebrandti* biozone to the *Yakounia yakounensis* biozone (Fig. 4; Table 2) and is dominated by sandstones. The $^{87}\text{Sr}/^{86}\text{Sr}$ value at the *P. hillebrandti* – *Y. yakounensis* biozonal boundary is ~ 0.70728 , with a gradual fall to 0.70718 in the middle of the *Y. yakounensis* biozone. This is followed by a sharp increase to 0.70728, above which the values remain relatively stable for the remainder of the section.

The $\delta^{13}\text{C}_{\text{bel}}$ values for section 12 vary from -0.6‰ to $+3\text{‰}$, but for the most part fluctuate around $+2\text{‰}$. Carbon-isotope values remain relatively stable in the lower *Y. yakounensis* biozone, but shift to more negative values in the middle *Y. yakounensis* biozone, followed by a gradual rise to $\sim +3\text{‰}$ the top of the section.

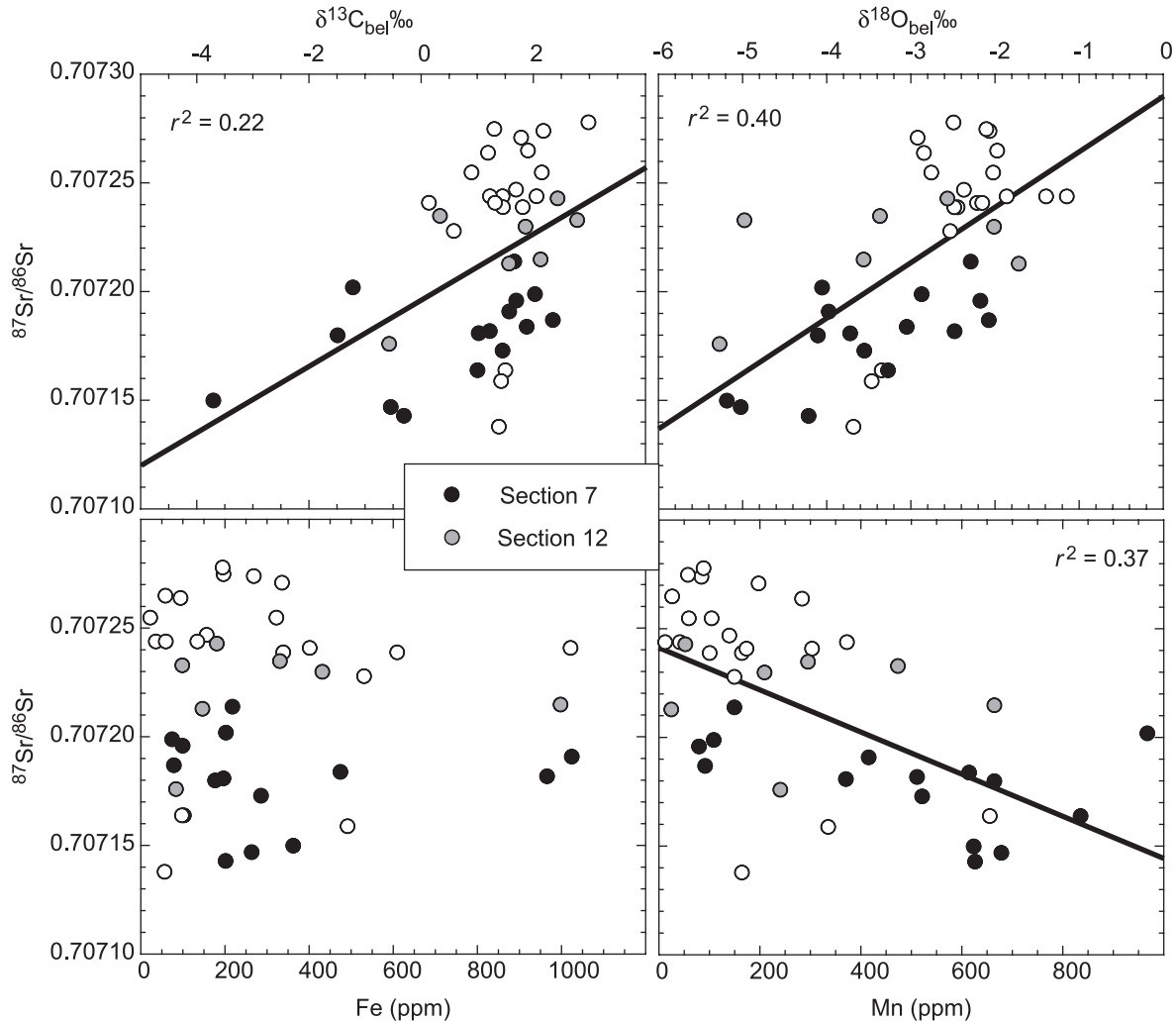
The $\delta^{18}\text{O}_{\text{bel}}$ values for section 12 vary from -5.2‰ to -1.1‰ , although most values are recorded between -2‰ and -3‰ . At the base of the section, $\delta^{18}\text{O}_{\text{bel}}$ values fluctuate around -1.9‰ before shifting to -5‰ in the middle *Y. yakounensis* biozone, followed by relatively constant values of $\sim -2.5\text{‰}$ for the remainder of the section.

A cross-plot between $\delta^{13}\text{C}_{\text{bel}}$ and $\delta^{18}\text{O}_{\text{bel}}$ values from sections 7 and 12 shows no clear correlation ($r^2 = 0.31$). Although the $\delta^{18}\text{O}_{\text{bel}}$ values are generally quite negative, the lack of a correlation with more depleted $\delta^{13}\text{C}_{\text{bel}}$ values suggests limited diagenetic alteration (Fig. 5).

Trace-element abundances

Trace-element ratios for sections 7 and 12 far exceed the preservation boundaries used for European belemnites defined by Jones et al. (1994). Fe and Mn concentrations reach up to ~ 1000 ppm (Tables 1, 2), which would suggest, based on the criteria of Jones et al. (1994), that the belemnites from the QCI are all diagenetically altered. However, cathodoluminescence images apparently indicate that little or minimal alteration has occurred in the calcite (Fig. 6). No

Fig. 8. Comparison of $\delta^{13}\text{C}_{\text{bel}}$ and $\delta^{18}\text{O}_{\text{bel}}$ with $^{87}\text{Sr}/^{86}\text{Sr}$ values, and $^{87}\text{Sr}/^{86}\text{Sr}$ values compared with trace-element abundances of Fe and Mn from sections 7 and 12, Yakoun River, Queen Charlotte Islands. The filled symbols correspond to samples that have been deemed diagenetically altered based on Sr-isotope curve offsets (see Fig. 10 and their corresponding sections). r , correlation coefficient.



correlation with Fe nor any of the isotopic systems investigated in this study have been found. However, a poorly correlated trend between Mn and $\delta^{13}\text{C}_{\text{bel}}$, and similarly between Mn and $\delta^{18}\text{O}_{\text{bel}}$, was noted (Fig. 7). A similar relationship was also found with Mn and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and between $\delta^{13}\text{C}_{\text{bel}}$ and $\delta^{18}\text{O}_{\text{bel}}$ with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Fig. 8).

Discussion

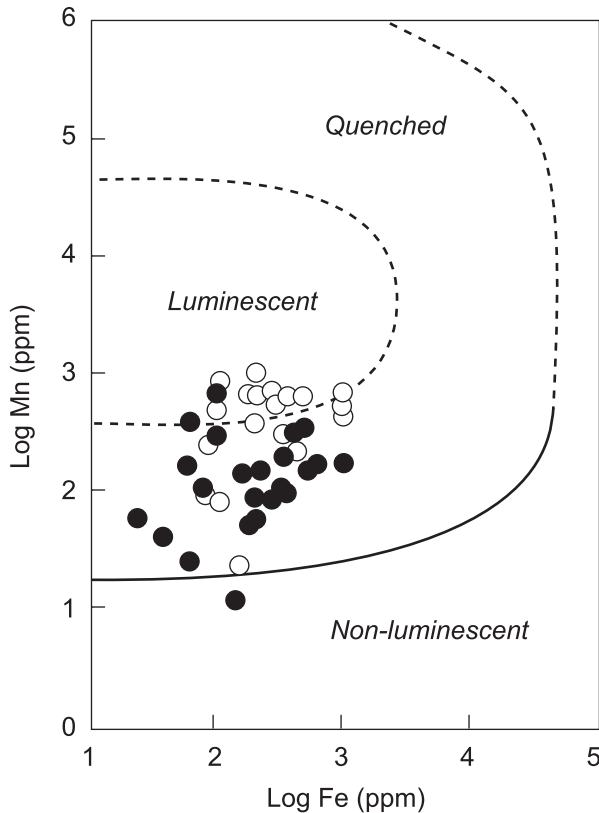
High concentrations were observed for Fe and Mn in the belemnites from the Queen Charlotte Islands. This is a common trait for belemnites analyzed so far from the British Columbia and Alberta regions (Gröcke 2001). Enrichment in these two elements relative to samples from Europe may, in fact, reflect differences in burial history that have not necessarily led to diagenetic alteration of the isotopic archives and (or) a difference in paleoceanographic concentrations of these elements. A cross-plot of the logarithm of Mn versus the logarithm of Fe (Fig. 9) indicates that the majority of samples from QCI actually plot in the quenched region, as defined by Machel and Burton (1991). This may explain

why cathodoluminescence was not a useful indicator of diagenesis, since high Fe levels will quench an activator, such as Mn (Machel 2000; Fig. 9). Therefore, rather than using the concentration levels of Fe and Mn in these belemnites (which can be influenced by additional factors) as a record of diagenesis, a method comparing the data generated in this study with the established $^{87}\text{Sr}/^{86}\text{Sr}$ curve from northwestern Europe is used to determine which belemnites have undergone diagenetic alteration.

Strontium-isotope ratios as a diagenetic indicator

The seawater Sr-isotope curve has been successfully used for the correlation of Jurassic strata. However, in the present case, ammonite data conflict with a straightforward correlation of the QCI strata to the standard seawater Sr-isotope curve. Figure 10 graphically represents the $^{87}\text{Sr}/^{86}\text{Sr}$ curve from England and Scotland (Jenkyns et al. 2002; Waltham and Gröcke 2006) together with the data generated in this study from Canada set against the correlation of ammonite zones based on Fig. 2. Note that the biozone and biosubzone divisions for northwestern Europe provided in Jenkyns et al.

Fig. 9. Logarithm Mn versus logarithm Fe plot for calcite for data from the Queen Charlotte Islands belemnites. The filled symbols correspond to samples that have been deemed diagenetically altered based on Sr-isotope curve offsets (see Fig. 10). Note that most of the diagenetic samples fall within the quenched range as defined by Machel and Burton (1991).



(2002) have been adopted in the compiled figures. The data exhibit a similar, if somewhat exaggerated, curve to the standard for the early Toarcian, but if interpreted as unaltered the QCI data would indicate a correlation of the *R. planulata* and lower *P. crassica* biozones with the upper *H. falciferum* to lower *Hildoceras bifrons* biozones of northwestern Europe (Fig. 10). This would imply a miscorrelation that is not tenable even taking the least likely possible correlations assessed on the basis of a “unitary association” quantitative stratigraphic method (Pálffy et al. 1997).

In detail, the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ values from the uppermost *D. kanense* biozone are concordant with their European counterparts, but from the *R. planulata* to *crassica* biozones, the ratios become depleted by as much as 0.00006 relative to the European curve, if one accepts the ammonite correlations as correct. Most of the $^{87}\text{Sr}/^{86}\text{Sr}$ values from the *P. hillebrandti* and *Y. yakounensis* biozones plot concordantly with the European data; however, the data show a high degree of scatter (Fig. 10). Although one might suppose that some of the belemnites are reworked samples from lower in the section (e.g., from the *R. planulata* and (or) *P. crassica* biozones), reworked fossils usually show signs of significant abrasion, corrosion, or encrustation, and these features were absent from the samples within this study.

Due to the large number of analyses and diversity of locations used for the composite European Sr-isotope record, its

integrity is beyond question, and therefore unlikely to be a source of error. The problem then likely lies in the preservation of the QCI belemnite Sr-isotope record. Diagenesis has commonly been reported to elevate $^{87}\text{Sr}/^{86}\text{Sr}$ values (e.g., McArthur 1994; MacLeod et al. 2001), although extremely low carbonate Sr-isotope values have been recorded, which are generally associated with young igneous rocks and hydrothermal activity. The resultant seawater Sr-isotope curve is formed through the interplay among sources with relatively non-radiogenic Sr (i.e., mantle origin) and those enriched in radiogenic Sr (i.e., from the continental crust). Hence, an alternative explanation for low $^{87}\text{Sr}/^{86}\text{Sr}$ values from QCI belemnites (i.e., older Toarcian ages) is that they have undergone diagenetic alteration from recrystallization with fluids of hydrothermal origin associated with basic igneous intrusions.

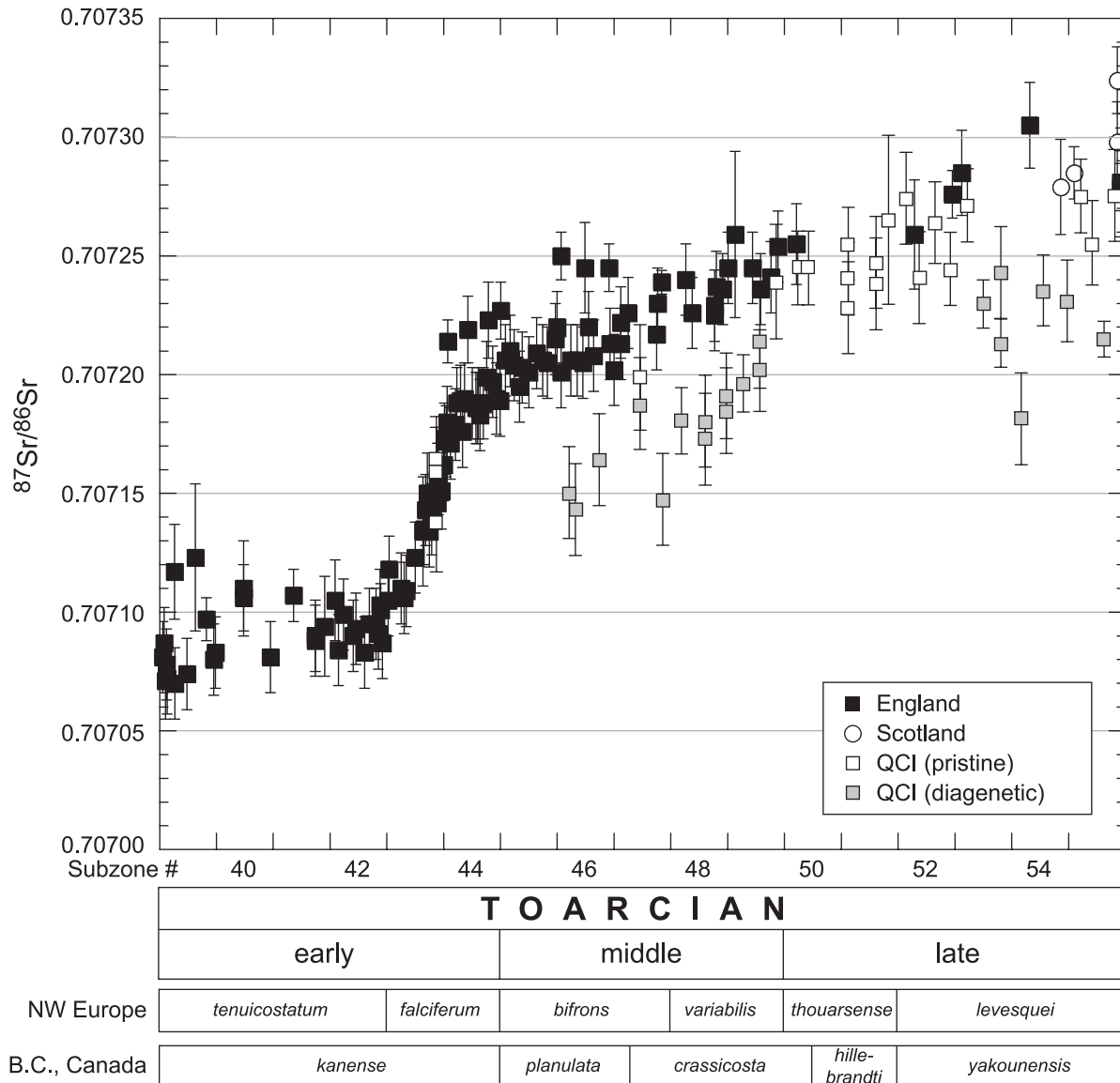
The sections investigated in this study are overlain stratigraphically by Eocene igneous rocks of the Masset Formation, which led to the intrusion of dykes through the Yakoun River sections (Hamilton and Dostal 2001). The dykes within the Yakoun River region have Sr-isotope ratios between 0.7030 and 0.7040 (Hamilton and Dostal 2001), which is significantly lower than that observed in the belemnites from the Yakoun River sections (0.7071–0.7073). Using a simple mixing model, the offset in $^{87}\text{Sr}/^{86}\text{Sr}$ values for the *R. planulata* biozone (~0.70714) in the QCI compared with Europe (~0.70721) can be accounted for by exchange of only 2% of the Sr in the belemnite calcite from a fluid with a $^{86}\text{S}/^{87}\text{Sr}$ value of 0.7035. However, what is not clear is why alteration is limited to certain parts of the succession or to some belemnites within single horizons and not others.

As shown in Fig. 3, the majority of the diagenetic $^{87}\text{Sr}/^{86}\text{Sr}$ values occur stratigraphically near to tuffaceous layers in the *P. crassica* biozone, suggesting that these volcanic sediments may be an alternative source of magmatic–hydrothermal $^{87}\text{Sr}/^{86}\text{Sr}$ values. In contrast, the diagenetic $^{87}\text{Sr}/^{86}\text{Sr}$ values from the *Y. yakounensis* biozone (Fig. 4) are contained within a major sandstone unit of section 12. These belemnites are likely affected by the sandstone acting as a conduit for pore fluids and (or) the weakly radiogenic strontium component of the tuffaceous horizons, or fluids generated during Eocene magmatism. Whatever the detailed mechanism, the data from the QCI highlight the possibility that hydrothermal pore fluids can affect $^{87}\text{Sr}/^{86}\text{Sr}$ values preserved in low-Mg calcite and that this diagenetic process (recrystallization) can lower $^{87}\text{Sr}/^{86}\text{Sr}$ values rather than elevate them, as it is typically reported. Altered Sr-isotope values, both with more- and less-radiogenic values, have been reported for fossil fish debris (composed of hydroxyfluorapatite) for the Cenozoic (Martin and Scher 2004), hence, demonstrating exchange with local pore fluid values.

Belemnites that can be categorized as diagenetically altered have been selected on the grounds of depleted $^{87}\text{Sr}/^{86}\text{Sr}$ values, as indicated in Fig. 10. At present, the slightly elevated $^{87}\text{Sr}/^{86}\text{Sr}$ values associated with the *P. hillebrandti* and *Y. yakounensis* biozone belemnites have not been dismissed, as this part of the Sr curve from Europe is not well defined.

To confirm our use of Sr-isotope values as a method for screening, a few belemnite sample fragments that were not cleaned or used during this study were investigated using a Philips 515 scanning electron microscope (SEM) at the

Fig. 10. The seawater Sr-isotope curve for the Toarcian, compared with data from Yakoun River, Queen Charlotte Islands (QCI). European ammonite biostratigraphy is from Howarth (1992), and western Canadian ammonite biostratigraphy from Jakobs et al. (1994) and Jakobs (1997). Grey-filled symbols from QCI represent diagenetic samples.



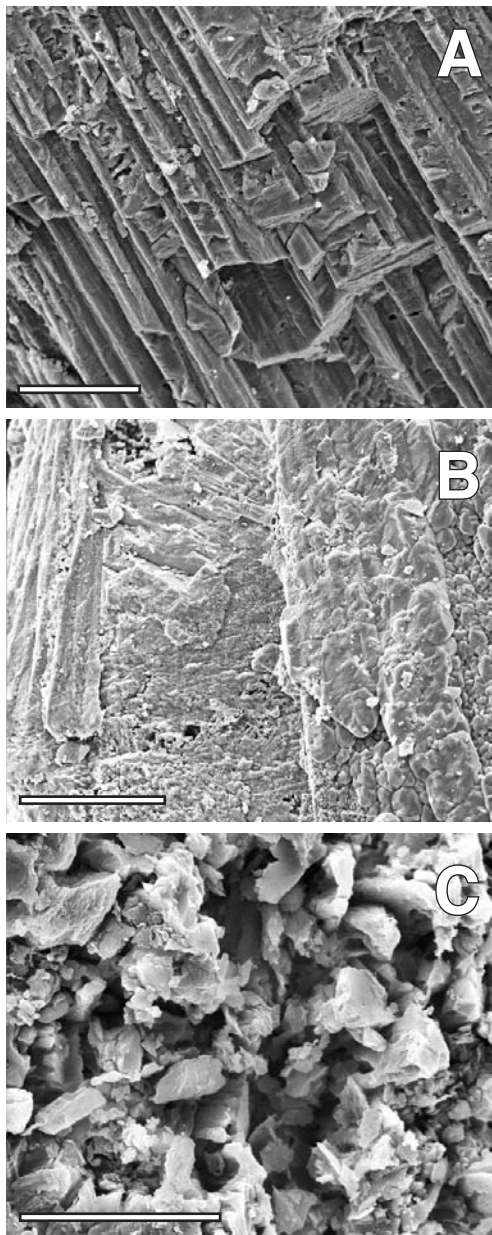
Brockhouse Institute for Materials Research at McMaster University. This type of method has been used extensively for monitoring diagenetic alteration of brachiopods and bivalves in the geologic record (see references in Veizer et al. 1999), although its application in determining belemnite diagenesis has been minimal (Podlaha 1995; Podlaha et al. 1998). Sample SS-12-5 records a concordant Sr-isotope value with that from Europe for the same biozone, and thus is deemed not to be diagenetic, produces excellent crystalline prismatic structures that are indicative of pristine preservation (Fig. 11A). However, samples SS-12-8 and SS-12-9, which are deemed diagenetic based on an $^{87}\text{Sr}/^{86}\text{Sr}$ value that is offset from the European Sr-isotope curve, clearly show recrystallization in the form of globular and more massive structures (Figs. 11B, 11C). Such structures have been recorded in trilobite cuticle and proposed to be indicative of diagenetic alteration (McAllister and Brand 1989).

Strontium-isotope ratios versus carbon- and oxygen-isotope ratios

On an initial evaluation of the geochemical data, a correlation, although relatively poor, was recorded among $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{13}\text{C}_{\text{bel}}$, $\delta^{18}\text{O}_{\text{bel}}$, and Mn (Figs. 7, 8). As $^{87}\text{Sr}/^{86}\text{Sr}$ values become lower, $\delta^{13}\text{C}_{\text{bel}}$ and $\delta^{18}\text{O}_{\text{bel}}$ values generally become more negative. However, with lower $^{87}\text{Sr}/^{86}\text{Sr}$ values, Mn concentrations generally increase, although no similar relationship is observed for Fe. Based on our evaluation of the Sr-isotope curves generated from Europe and this study (see the preceding section and Fig. 10), the majority of the belemnites from Yakoun River are diagenetically altered (Figs. 3, 4). By removing these diagenetic samples, the apparent relationship of $^{87}\text{Sr}/^{86}\text{Sr}$ with $\delta^{13}\text{C}_{\text{bel}}$ and with $\delta^{18}\text{O}_{\text{bel}}$ is removed (Figs. 7, 8).

By excluding the diagenetic belemnites, $\delta^{13}\text{C}_{\text{bel}}$ values are more closely grouped between 0‰ and +3‰, while $\delta^{18}\text{O}_{\text{bel}}$

Fig. 11. SEM images of belemnites from the Yakoun River, Queen Charlotte Islands. (A) Pristine prismatic structure in SS-12-5A. Scale bar = 50 μm . (B) Globular, massive structure indicative of recrystallization in SS-12-8. Scale bar = 10 μm . (C) Recrystallized calcite with no regular shape in SS-12-9. Scale bar = 20 μm . Based on Sr-isotope ratios (A) is considered pristine, while (B) and (C) are diagenetic.



values are between -3.6‰ and -1‰ ; such values are reasonable primary values from a paleoceanographic viewpoint (see discussion below). The lack of association of elevated $^{87}\text{Sr}/^{86}\text{Sr}$ values with elevated Fe and Mn in the present study contrasts with observations made by Jones et al. (1994). If a cut-off value for Mn of 300 ppm is used to indicate diagenetic alteration, this would remove $\sim 65\%$ of the belemnite Sr-isotope values in this study and include only 12% that have $^{87}\text{Sr}/^{86}\text{Sr}$ values that fit on the strontium-isotope seawater curve from Europe. Such a result highlights the

need to look at multiple geochemical proxies when screening belemnites for diagenesis, since many belemnites that have elevated trace-element contents (e.g., Mn) may in fact be recording a primary signal. This can be seen in the study by Jones et al. (1994), illustrating both diagenetically screened and pristine belemnite $^{87}\text{Sr}/^{86}\text{Sr}$ values, and where many samples that were classified as diagenetic did record reliable primary isotopic values (see figs. 4, 5, 7 in Jones et al. 1994).

The Toarcian $\delta^{13}\text{C}_{\text{bel}}$ curve

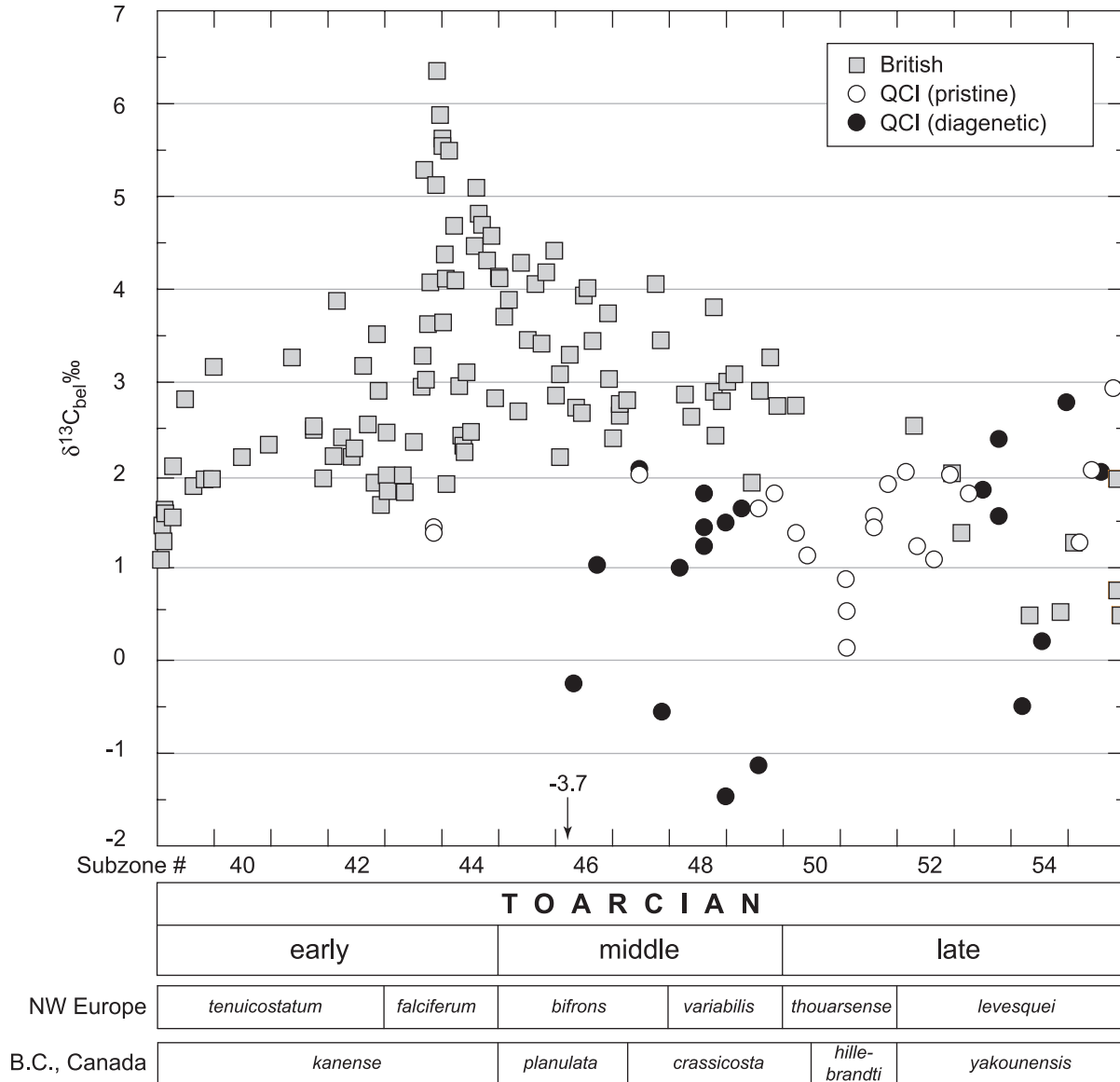
Stable-isotope ratios in belemnites have been used as a paleoenvironmental proxy for seawater chemistry, although it is well known that belemnites show a high degree of scatter from individual horizons (Jenkyns et al. 2002). Stratigraphic variation in $\delta^{13}\text{C}_{\text{bel}}$ values are shown in Fig. 12, which includes data only from those European samples that have been used to generate the $^{87}\text{Sr}/^{86}\text{Sr}$ seawater curve generated in Fig. 10. A major positive $\delta^{13}\text{C}_{\text{bel}}$ excursion is recorded in the *H. falciferum* biozone that is attributed to a major organic carbon burial episode associated with the Toarcian oceanic anoxic event (Hesselbo et al. 2000). In the *H. falciferum* biozone (= uppermost *D. kanense* biozone), the positive excursion recorded in belemnites from Europe is followed by a gradual decline to pre-excursion values in the *Dumortieria levesquei* (\approx *Y. yakounensis*) biozone. Samples from the upper *D. kanense* biozone do not exhibit the very positive $\delta^{13}\text{C}_{\text{bel}}$ values found in Europe, but are comparable with the lightest values obtained (Fig. 12). Although the QCI $\delta^{13}\text{C}_{\text{bel}}$ data do not show the positive excursion, this may be, in part, due to a lack of belemnites in the section covering the uppermost *D. kanense* (\approx upper *H. falciferum*) and lower *R. planulata* (\approx *Hildoceras bifrons*) biozones.

Belemnite samples from the upper *R. planulata* and lower *P. crassicosta* biozones have depleted $\delta^{13}\text{C}_{\text{bel}}$ values and thus are very different from the European equivalents (Fig. 12). Based on their Sr-isotope ratios these samples are considered as diagenetically altered and so removed from discussion. The $\delta^{13}\text{C}_{\text{bel}}$ values that are considered pristine by our diagenetic screening process from the *P. crassicosta* and *P. hillebrandti* biozones are generally more depleted than age-equivalent samples from Europe, although the latter has a sparse record and so a direct comparison and interpretation is not feasible at present.

The Toarcian $\delta^{18}\text{O}_{\text{bel}}$ curve and paleotemperatures

For $\delta^{18}\text{O}$ values to be interpreted confidently in terms of paleotemperature, several variables need to be assessed, particularly vital effects and local variation in seawater $\delta^{18}\text{O}$. If belemnites are assumed to secrete their calcite in equilibrium with the surrounding seawater, $\delta^{18}\text{O}_{\text{bel}}$ values may be used to reconstruct oceanic paleotemperatures (Wierbowski 2002). The $\delta^{18}\text{O}$ of seawater is controlled largely through freshwater contributions and continental ice volume. During the Jurassic, the world is assumed to have been largely ice-free, and a seawater $\delta^{18}\text{O}$ value of -1‰ is commonly used for paleotemperature calculations (Shackleton and Kennett 1975). However, the assumption that the Jurassic was continuously ice-free has been challenged (e.g., Price 1999; Gröcke et al. 2003; Shaviv and Veizer 2003). Notwithstand-

Fig. 12. $\delta^{13}\text{C}_{\text{bel}}$ data for the Toarcian compared with data from Yakoun River, Queen Charlotte Islands (QCI). The filled symbols correspond to samples that have been deemed diagenetically altered based on Sr curve offsets (see Fig. 10). Note that one sample from QCI falls outside the graph and is represented by the value and arrow in Subzone #46.



ing this, paleotemperatures may be obtained from $\delta^{18}\text{O}_{\text{bel}}$ values using the equation by Anderson and Arthur (1983):

$$T (^{\circ}\text{C}) = 16 - 4.14 (\delta_{\text{c}} - \delta_{\text{w}}) + 0.13 (\delta_{\text{c}} - \delta_{\text{w}})^2$$

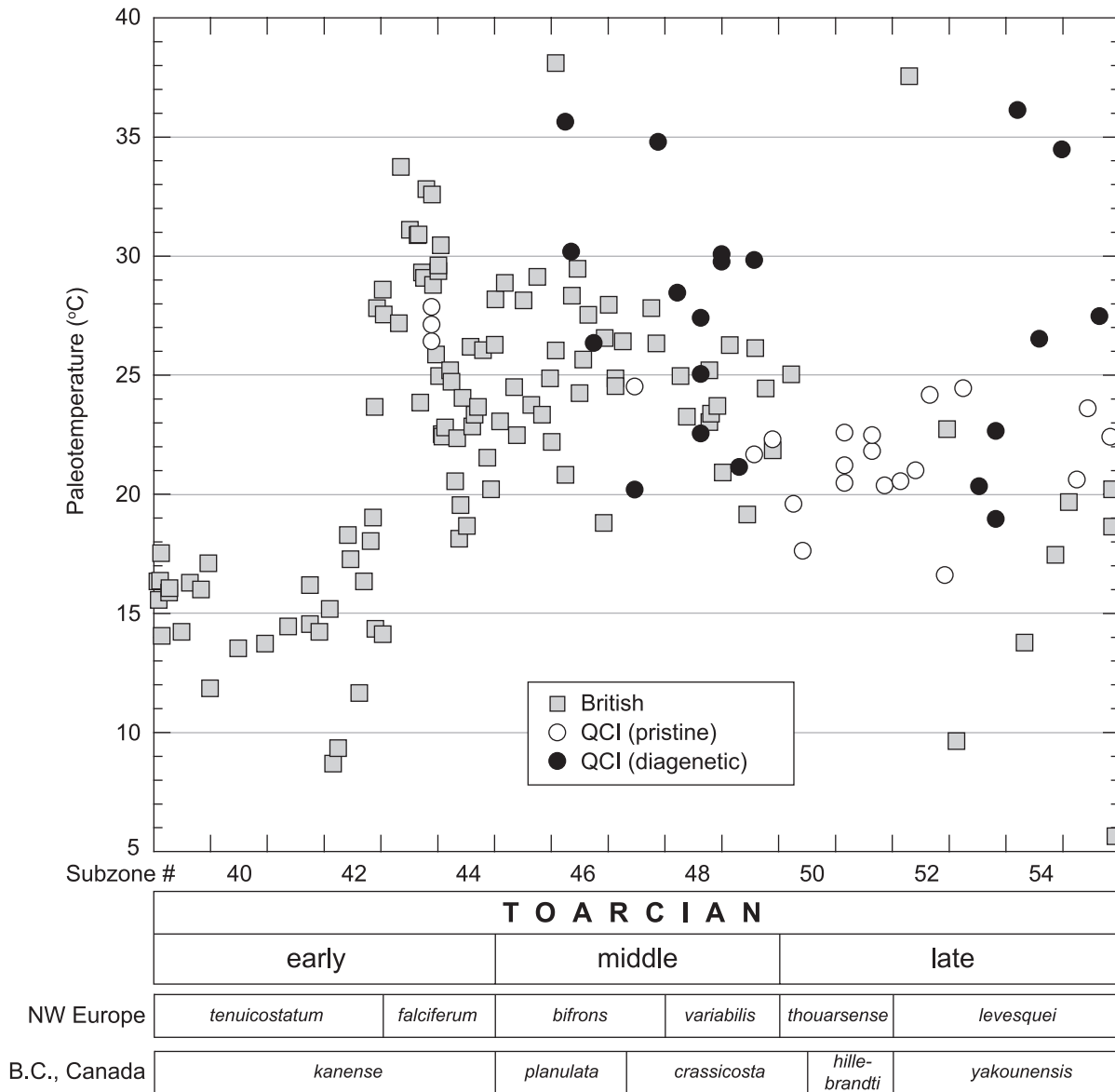
where δ_{c} represents the $\delta^{18}\text{O}$ of the measured calcite, and δ_{w} represents the $\delta^{18}\text{O}$ of ancient seawater relative to SMOW. Using a δ_{w} value of -1‰ also assumes a homogeneous ocean and does not take into account local or regional effects and variation.

Paleotemperatures calculated from $\delta^{18}\text{O}_{\text{bel}}$ values throughout sections 7 and 12 in the QCI range between $\sim+16^{\circ}\text{C}$ and $\sim+36^{\circ}\text{C}$ (Fig. 13), although a high degree of scatter is observed. Those belemnites deemed pristine only show a paleotemperature variation between $\sim+16$ and $\sim+28^{\circ}\text{C}$. The paleolatitude of the QCI during the Toarcian interval is estimated to be $\sim 40^{\circ}\text{N}$ (Aberhan 1998; P.L. Smith, personal

communication, 2005), which is similar to the European localities used to construct the seawater Sr-isotope curve (Fig. 10). Therefore, in Fig. 13 the QCI data are plotted directly against the European belemnite data without any latitudinal correction. The correspondence between the QCI and European paleotemperature curve for the Toarcian is noteworthy (Fig. 13).

Paleotemperatures for the upper *D. kanense* biozone are moderately high at $\sim 27^{\circ}\text{C}$, but are comparable with those observed in the Europe dataset. The upper *P. crassicosta* and *P. hillebrandti* biozone paleotemperatures fluctuate between $\sim+17$ and $+23^{\circ}\text{C}$. As was the case for $\delta^{13}\text{C}_{\text{bel}}$ records, $\delta^{18}\text{O}_{\text{bel}}$ based paleotemperatures for the *P. hillebrandti* and *Y. yakounensis* biozones are comparable with those obtained from Europe, although the latter has a very sparse record. It should be noted that the cold paleotemperatures ($\sim+8$ to

Fig. 13. Oxygen-isotope-based paleotemperatures for the Toarcian compared with data from Yakoun River, Queen Charlotte Islands (QCI). The filled symbols correspond to samples that have been deemed diagenetically altered based on Sr-isotope curve offsets (see Fig. 10).



+18 °C) from the earliest Toarcian are only recorded in a few samples after the Toarcian oceanic anoxic event (OAE) (*H. falciferum* biozone) (Fig. 13). Late Toarcian paleotemperatures remain elevated (typically above +20 °C), thus the Toarcian represents a time in the Early Jurassic during which the global paleoclimate had shifted from a cooler to warmer environment, which is also supported by other climatic proxies (e.g., Kemp et al. 2005; McElwain et al. 2005): alternatively, a shift in seaway dynamics and thermohaline circulation (Bjerrum et al. 2001).

Conclusions

An investigation of Sr-isotope ratios from the Toarcian interval from the QCI was conducted to help refine the correlation between northwestern Europe and British Columbia

based upon biostratigraphy. However the $^{87}\text{Sr}/^{86}\text{Sr}$ values from the QCI, if unaltered, would indicate a mismatch between biostratigraphic and chemostratigraphic correlation. It is, therefore, likely that diagenesis has substantially affected some belemnite isotopic and elemental values. Trace-element abundances are typically used to screen belemnites for diagenesis, but the majority of QCI belemnite samples so far analyzed suggest that the low cut-off values may not be applicable (see also Hall et al. 2004). Cathodoluminescence was employed to determine diagenetic alteration, but through the process of elemental quenching, this was not a useful technique for these belemnite samples. Anomalous $^{87}\text{Sr}/^{86}\text{Sr}$ values from Yakoun River compared with those generated from European results have been used to assign samples as diagenetic. The less-radiogenic signature of these samples suggests that they were altered involving hydrothermal fluids.

This procedure removed a significant portion of the data set, but also removed apparent diagenetic correlations among Mn, $\delta^{13}\text{C}_{\text{bel}}$, $\delta^{18}\text{O}_{\text{bel}}$, and $^{87}\text{Sr}/^{86}\text{Sr}$. SEM analysis of several specimens also revealed that our method of using offset Sr-isotope values from QCI showed that the belemnite calcite had recrystallized. The positive $\delta^{13}\text{C}_{\text{bel}}$ excursion recorded in the early Toarcian of Europe is not recorded from QCI, but this may be due, in part, to the sparse belemnite record from the upper *D. kanense* biozone. The $\delta^{18}\text{O}_{\text{bel}}$ values from the QCI are comparable with those from European belemnites. Environmental differences between Europe and the QCI may have also resulted in the minor disparity between the $\delta^{13}\text{C}_{\text{bel}}$ and $\delta^{18}\text{O}_{\text{bel}}$ records. It is suggested that future Sr-isotope investigations of belemnite calcite should not only use cathodoluminescence and trace-element abundances to screen diagenetically altered samples from the data set, but also use the disparity between Sr-isotope curves and SEM results. In addition, using only trace-element abundances and cathodoluminescence may be inadvertently removing samples that record an original isotopic signal that could be used in reconstructing paleoceanographic conditions in the geologic record.

Acknowledgments

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