

Bollettino della Società Paleontologica Italiana	37 (2-3), 1998	ISSN 0375-7633	507-514	–	Modena, Novembre 1999
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Sr isotopic variation in single conodont elements: implications for defining the Sr seawater curve

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KEY WORDS – Conodonts, Strontium, Isotopes, Isotope stratigraphy, Ordovician.

ABSTRACT – Sr isotopic compositions of single conodont elements were measured to investigate the potential usefulness of conodonts in defining the Sr isotope seawater curve. Analysed elements had very low colour alteration indices (CAI = 1) and were of the coniform species *Drepanodus arcuatus* (Pander, 1856), sampled from the Early Ordovician (early Bendigonian, ~490 – 492 Ma) Emanuel Formation in the Canning Basin of Western Australia.

$^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured from single whole conodont elements were compared to those from mechanically separated cusp tissue and from the element base with attachment cone, showing significant isotopic heterogeneity within single elements. Cusps are characterised by significantly lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.708949 – 0.709056) than their associated base and attachment cone (0.709503 – 0.709829), and are well within the boundaries of the seawater curve. Single whole elements have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.709097 – 0.709282) intermediate between cusp and basal tissue. Host-rock limestone from the same horizon yielded high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.709368, 0.709454). A few small, thin-shelled articulate brachiopods recovered from elsewhere in the section have also suffered significant diagenetic alteration; the $^{87}\text{Sr}/^{86}\text{Sr}$ measurements of secondary shell material range from 0.709027 to 0.709430.

These results indicate both carbonate and phosphate components have experienced significant diagenetic alteration, and that basal tissue appears to be a major source of secondary Sr in *D. arcuatus*. Despite the isotopic heterogeneity of conodont apatite, preliminary results suggest that the lowest, and perhaps primary, $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.708750) is retained near the 'core' of cusp tissue, at the growth axis.

RIASSUNTO – [Variazioni degli isotopi dello Stronzio in singoli conodonti: implicazioni per la definizione della curva isotopica dello Stronzio in acqua marina] – La composizione isotopica dello stronzio in singoli conodonti è stata misurata al fine di investigare la potenziale utilità di questi fossili nella definizione della curva isotopica dello Sr nell'acqua marina. Gli elementi analizzati hanno un indice di alterazione di colore molto basso (CAI=1) e appartengono alla specie coniforme *Drepanodus arcuatus* (Pander, 1856); provengono dall'Ordoviciano inferiore (Bendigoniano inf., ~490–492 Ma) della Emanuel Formation, nel Canning Basin, Australia occidentale.

I rapporti $^{87}\text{Sr}/^{86}\text{Sr}$ misurati negli elementi interi sono stati confrontati con quelli ottenuti nella cuspid e nella parte basale, dopo una rottura meccanica degli esemplari: è stata così osservata una significativa eterogeneità isotopica all'interno dei singoli esemplari. Le cuspidi sono caratterizzate da rapporti $^{87}\text{Sr}/^{86}\text{Sr}$ significativamente più bassi (0.708949 – 0.709056), rispetto alle loro parti basali (0.709503 – 0.709829) e sono ben all'interno dei limiti dell'oscillazione della curva dell'acqua marina. Gli elementi interi hanno rapporti $^{87}\text{Sr}/^{86}\text{Sr}$ intermedi tra le cuspidi e le parti basali (0.709097 – 0.709282). Nello stesso orizzonte la roccia calcarea ospitante ha valori del rapporto $^{87}\text{Sr}/^{86}\text{Sr}$ decisamente più alti (0.709368, 0.709454). Nella stessa sezione, ma in diversi livelli, sono stati rinvenuti alcuni piccoli brachiopodi articolati a conchiglia sottile, che hanno subito notevoli alterazioni diagenetiche: la misura del rapporto $^{87}\text{Sr}/^{86}\text{Sr}$ nel materiale conchigliare secondario varia tra 0.709027 e 0.709430.

Questi dati indicano che sia i componenti carbonatici che quelli fosfatici hanno subito significative alterazioni diagenetiche e che in *D. arcuatus* il tessuto basale sembra essere la principale sorgente di Sr secondario. Nonostante l'eterogeneità dell'apatite nei conodonti, risultati preliminari suggeriscono che il rapporto $^{87}\text{Sr}/^{86}\text{Sr}$ più basso (0.708750), probabilmente primario, sia nella parte centrale della cuspid, lungo l'asse di crescita.

INTRODUCTION

Strontium isotope stratigraphy relies on recognised variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater over time. Because of the combination of a relatively short mixing time with a much longer residence time, Sr in seawater is isotopically uniform. Long-term variations in the crustal and mantle-derived Sr entering the oceans, has resulted in a seawater Sr isotope evolution curve that has important scientific implications for understanding the evolution of the crust, but also significant practical applications in stratigraphic correlation (eg. Burke *et al.*, 1982; Veizer *et al.*, 1997).

In Cenozoic sequences, particularly in the mid to late Tertiary, Sr isotope stratigraphy is widely used for dating and correlation (eg. Hodell *et al.*, 1991; Oslick *et al.*, 1994; Eisenberg *et al.*, 1996; Whitford *et al.*, 1996), and may yield higher resolution in limited

stratigraphic intervals than more conventional biostratigraphic correlation techniques. In older sequences however, diagenetic alteration combined with greater uncertainties in estimating absolute ages leads to greater uncertainties in the exact shape of the Sr isotope seawater curve. Because of their abundance, fine-scale biostratigraphic resolution and high strontium content, conodonts have the potential to improve the curve. Their application to define the curve has been addressed by several workers (Kürschner *et al.*, 1992; Cummins & Elderfield, 1994; Martin & Macdougall, 1995; Diener *et al.*, 1996; Holmden *et al.*, 1996; Ruppel *et al.*, 1996; Ebner *et al.*, 1997), however, opinions vary as to their suitability, as conodonts have been shown to be susceptible to diagenetic alteration.

Because of their potential importance, we have revisited the question of the suitability of conodonts

for defining the Sr seawater curve. In particular, we have investigated the isotopic heterogeneity of single conodont elements to determine whether the effects of diagenetic alteration can be overcome, and whether primary isotopic signatures can be discerned within components of single elements.

The samples analysed in our investigations include conodont apatite along with whole-rock carbonate and calcareous brachiopods of Early Ordovician age (Bendigonian Be1 – Be2) which correlate with the *Prioniodus elegans* conodont Zone. Due to the uncertainties in correlating the biostratigraphy of the Emanuel Creek Section with absolute ages, age approximations of these samples will vary depending on the timescale used. Following the timescale of Harland *et al.* (1990), which is used to calibrate the $^{87}\text{Sr}/^{86}\text{Sr}$ seawater curve of Veizer *et al.* (1997), the early Bendigonian approximates 490 to 492 Ma with the Cambrian-Ordovician boundary at 510 Ma. However, the more recent AGSO Phanerozoic Timescale (Young & Laurie, 1995) places Be1 – Be2 at ~483 to 485 Ma with the Cambrian-Ordovician boundary at 490 Ma. Such variations are inherent problems when comparing different data sets and relating their $^{87}\text{Sr}/^{86}\text{Sr}$ values to positions on the seawater curve. The recent seawater curve compiled by Veizer *et al.* (1997) is based on data derived from phosphatic and well preserved low-Mg calcitic skeletal components, and is used in this study as a reference to recognise reliable, less diagenetically altered isotopic signatures. The portion of the seawater curve at the estimated age of the Emanuel Formation (~490 – 492 Ma) is defined by $^{87}\text{Sr}/^{86}\text{Sr}$ ratios ranging from ~0.7088 to ~0.7092 which are apparently derived from biogenic calcite samples.

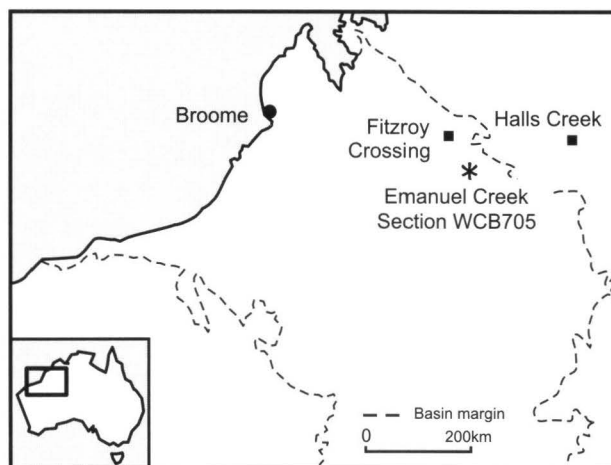
This investigation includes:

- characterisation of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of whole-rock limestone samples of the Emanuel Formation,
- evaluation of the Sr isotopic heterogeneity of single elements of *Drepanodus arcuatus*,
- comparisons of the whole-rock and conodont Sr isotopic results with brachiopods, and
- evaluation of the $^{87}\text{Sr}/^{86}\text{Sr}$ results in the context of seawater evolution.

Further work is currently underway to track the variation in Sr isotope composition within separated cusp tissue, by means of sequential dissolutions. However, this requires technical developments to improve analytical sensitivity.

GEOLOGICAL SETTING

The samples were collected from the type-section (WCB705) of the Emanuel Formation, which outcrops in the Emanuel Creek about 60 km southeast of Fitzroy Crossing, Canning Basin, in northern Western Australia (Text-fig. 1). The section comprises carbonates interbedded with shales and siltstones, and



Text-fig. 1 – Locality map showing location of the Canning Basin and the Emanuel Creek Section. Modified from Nicoll *et al.*, 1993.

provides well preserved, diverse and abundant faunas (Nicoll *et al.*, 1993). Conodonts and telephinid trilobite assemblages correlate with the *Prioniodus elegans* (Baltoscandia; Victoria, Australia) and *Acodus deltatus*-*Oneotodus costatus* (North America) conodont zones, and the G1 - G2 trilobite zones (Utah, USA) (Shergold *et al.*, 1995a). This indicates the Emanuel Formation fauna to be of Early Ordovician, early Bendigonian (Be1 - Be2), age (Shergold *et al.*, 1995b; Laurie & Shergold, 1996). The carbonate rocks throughout the section are variably weathered, however, the conodonts are well preserved and have a low colour alteration index (CAI = 1), indicating that they have not suffered significant thermal alteration (Epstein *et al.*, 1977).

BRACHIOPOD AND CONODONT ISOTOPE GEOCHEMISTRY

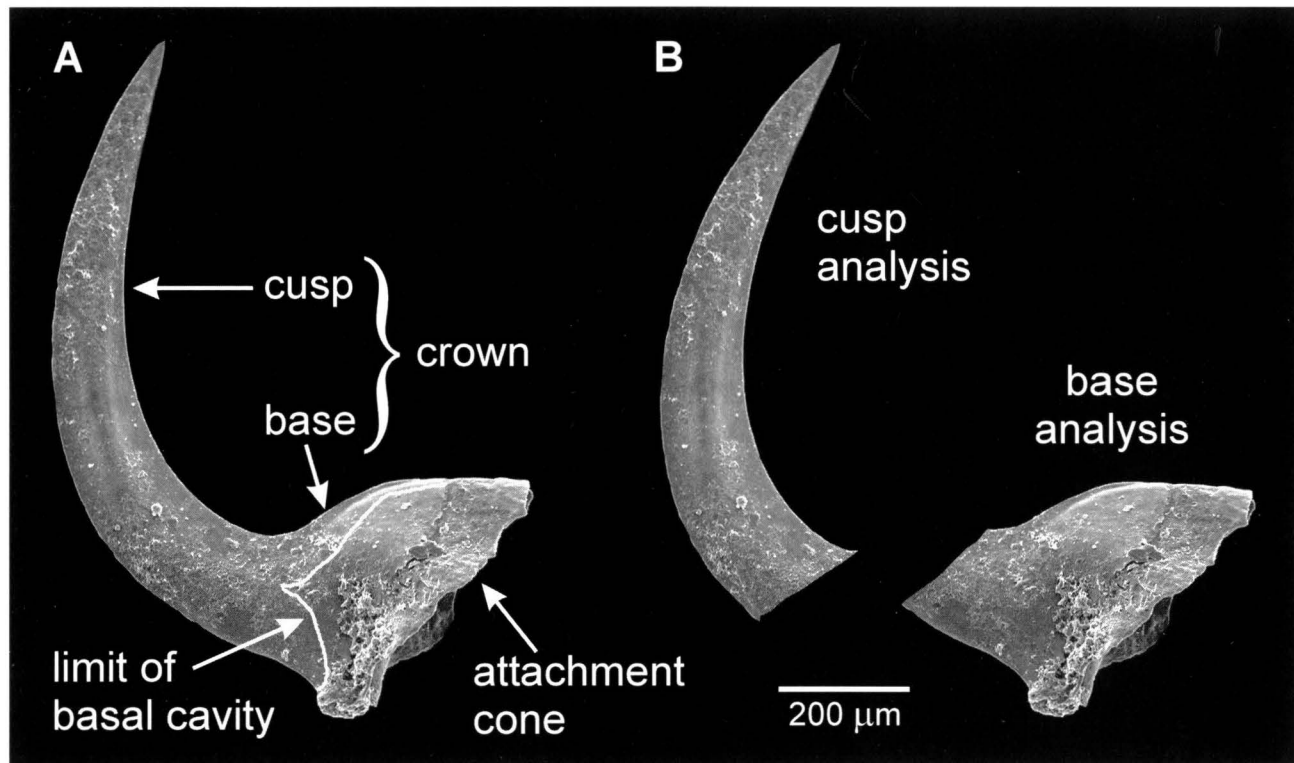
Brachiopods and conodonts have been widely studied in attempting to refine sections of the Phanerozoic Sr seawater curve. Studies of well preserved calcareous articulate brachiopods indicate that secondary shell material is least susceptible to alteration and may retain its original marine isotopic signature (Diener *et al.*, 1996; Ebner, 1997; Veizer *et al.*, 1997), but requires careful extraction and screening by both cathodoluminescence and scanning electron microscopy (Qing & Veizer, 1994). Comparisons of coeval brachiopod and conodont $^{87}\text{Sr}/^{86}\text{Sr}$ data in some studies have consistently shown the isotopic signatures of conodonts to be significantly altered by secondary Sr, suggesting that conodonts are less reliable indicators of seawater isotopic composition (Diener *et al.*, 1996; Ebner, 1997; Veizer *et al.*, 1997). However, calcareous brachiopods are comparatively uncommon and

therefore not particularly useful for broad-scale isotope stratigraphic correlations. Consequently, the attraction of analysing conodonts is due to their relative abundance and high stratigraphic resolution.

There are significant uncertainties with respect to the extent of the diagenetic alteration of conodonts. Alteration has been related to conodont CAI with a high CAI often characterised by a higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (Bertram *et al.*, 1992; Kürschner *et al.*, 1992), though conodonts with a low CAI (1.5 - 2.5) are also apparently affected by secondary Sr (Diener *et al.*, 1996; Ebner *et al.*, 1997). Previous studies have presented a number of techniques for Sr isotope analysis of low CAI conodont apatite, but yielded conflicting data and varied opinions as to their potential for retaining (near) primary isotopic signatures. The various approaches to sample preparation involved cleaning procedures such as sonication in distilled water (Kürschner *et al.*, 1992; Diener *et al.*, 1996; Qing *et al.*, 1998) or in ammonium chloride (Bertram *et al.*, 1992; Cummins & Elderfield, 1994) prior to the complete dissolution of specimens. Others employed a "leaching" process prior to dissolution of the residuum (Martin & Macdougall, 1995; Ruppel *et al.*, 1996). The latter "leaching", or partial dissolution, of conodont elements

was aimed at removing the outer apatite layers which are assumed to be most affected by secondary Sr (Ruppel *et al.*, 1996).

Conodont morphology is a significant variable as contaminants are readily contained within the attachment cone and/or basal cavity. Additionally, there are apparent compositional differences between the element base (with or without attachment cone) and the 'upper' crown material (Text-fig. 2), the latter being less prone to diagenetic alteration (Holmden *et al.*, 1996). Holmden *et al.* (1996) showed that conodonts with substantial bases (eg. multidenticulate elements), as well as phosphatic brachiopods and conulariids, are more susceptible to Sr exchange yielding significantly higher and more variable $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than conodonts with small bases and shallow cavities. They compared the distribution of Ca and P contents from the outer crown rim to the inner deep basal cavity of the coniform conodont *Panderodus gracilis* Branson & Mehl. The basal tissue yielded Ca/P ratios very similar to phosphatic brachiopod shell and conulariids suggesting a difference in composition to that of the 'outer' crown. They also showed that diagenetic Sr decreased in *P. gracilis* after the basal material had dissolved during successive acid leaches, suggesting that an unconta-



Text-fig. 2 – S element of *D. arcuatus*; A) the conodont element is composed of the crown and attachment cone. The crown is subdivided into the base and cusp at the level of the tip of the basal cavity. Note presence of attachment cone; B) shows the separation of cusp and base (with attachment cone) used for Sr isotope analyses in this study.

minated reservoir of Sr may reside within the deeper layers of the remaining crown tissue.

A quantitative approach to ascertain the degree of isotopic heterogeneity of conodont elements, within a species population, underlies our current investigations. In designing techniques to isolate potential primary Sr, sources of contamination are of major concern. The expectation that conodont basal tissue, attachment cones and contaminants within their cavities are the major sources of secondary Sr, was the reason for selecting the coniform element *Drepanodus arcuatus* (Pander). This species has a shallow basal cavity that does not extend into the cusp, thus allowing easy separation of the cusp from its base and attachment cone with a scalpel. Analyses of single whole elements (Text-fig. 2A) are used as a reference to compare the measured isotopic compositions of individual base (with attachment cone) and cusp separates (Text-fig. 2B). We anticipate that analysing different components of single conodont elements will lead to locating potential reservoirs of primary Sr.

METHODS

Samples were extracted from existing collections of R.S. Nicoll, having been collected previously for biostratigraphic correlation studies (Nicoll, 1992; Nicoll *et al.*, 1993; Shergold *et al.*, 1995b). Conodont extraction from the limestone matrix followed conventional acetic acid digestion procedures, and sodium polytungstate and magnetic separation techniques.

Conodont data detailed in this paper are from specimens extracted from one stratigraphical horizon (168) only. All conodont elements selected for Sr isotopic analysis were clean, with no adhering matrix or obvious secondary mineralisation, devoid of obvious microfractures, and thermally unaltered having a CAI of 1. All specimens were left overnight in high-purity water then the supernatant decanted prior to dissolution. A fine clean scalpel was used to separate cusp from base and attachment cone tissue. Each component was dissolved separately in a few drops of high-purity concentrated HNO_3 . Whole conodont elements were dissolved separately in a few drops of high-purity concentrated HNO_3 for comparative analysis. The sequential dissolution of a separated cusp was conducted for a total of 10 hours in 1.5M acetic acid, the leachate decanted then replaced by fresh acid at 2 hourly intervals.

Articulate brachiopods are rare in the Emanuel Formation, so secondary shell material from several orthids from three horizons (97, 105 and 175) only, were analysed. The small orthids were extracted from the enclosing limestone matrix using a dental drill, then lightly fractured in a mortar and pestle to separate and fragment the thin calcareous shell. Small shell fragments

(1 - 2 mm) of fibrous calcite were handpicked and cleaned in high-purity water in an ultrasonic bath, dried, then examined by cathodoluminescence microscopy.

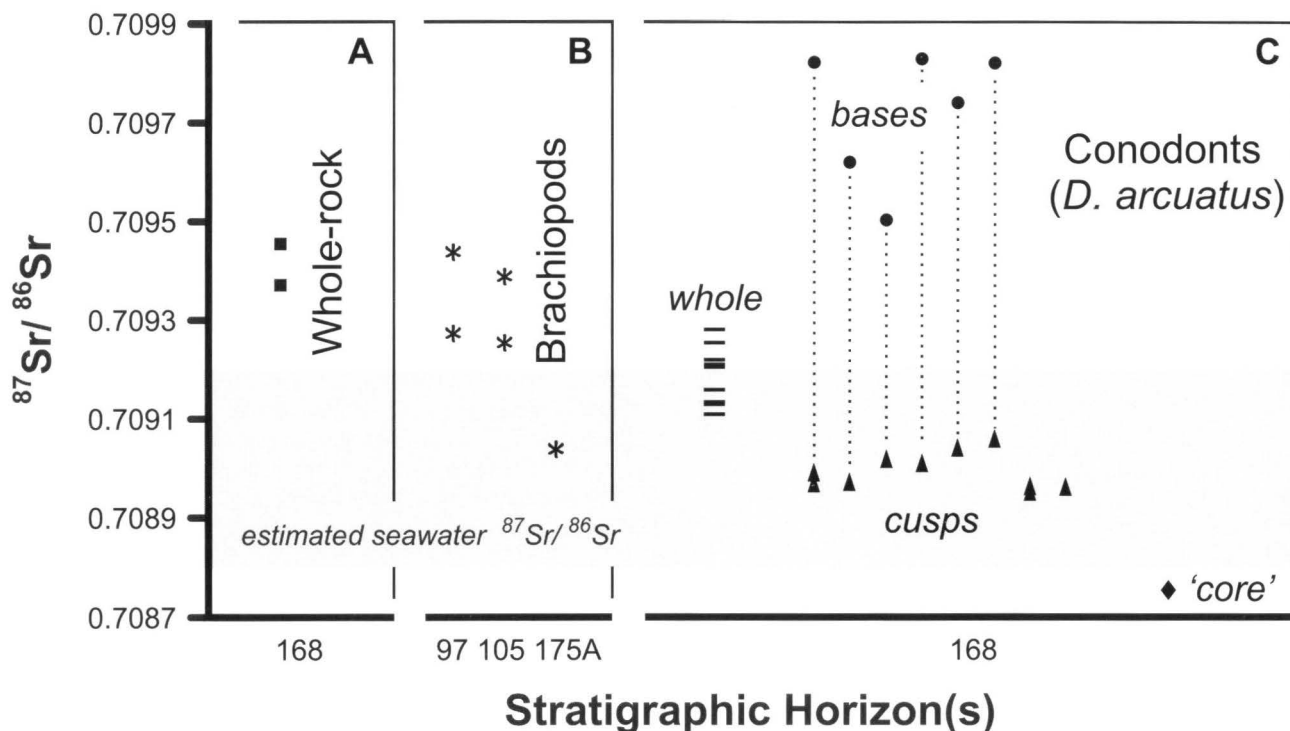
Samples of whole-rock limestone were fractured and the freshest pieces selected then crushed. The whole-rock (~50mg) and brachiopod secondary shell fragments selected for Sr analysis were dissolved in acetic acid then centrifuged. The supernatant was decanted, taken to dryness, then dissolved in HCl ready for Sr separation. All samples were loaded onto pre-conditioned cation exchange columns (Bio Rad Econo Columns), filled with -400 mesh AG50W-X8 resin, for Sr separation.

The Sr samples were loaded onto Ta single filaments with high-purity water and phosphoric acid and then oxidised. The isotopic compositions were measured on a VG 354 thermal ionisation mass spectrometer located at the CSIRO Radiogenic Isotope Facility, Mineral Research Laboratories, at North Ryde (Sydney). Samples were run in "dynamic" mode at 3V with an ion beam intensity of 3×10^{-11} A of ^{88}Sr . Six blocks of 9 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were measured totalling 54 ratio determinations per sample. The exception to this is the conodont 'core' sample that was measured at 2V with 5 blocks of 9 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, totalling 45 ratio determinations. All $^{87}\text{Sr}/^{86}\text{Sr}$ ratios were normalised to $^{86}\text{Sr}/^{88}\text{Sr} = 0.1194$. Samples were analysed in discrete batches over a period of 22 months and NBS987 standards were measured with each barrel of unknowns. Over this time interval measured $^{87}\text{Sr}/^{86}\text{Sr}$ values of NBS987 averaged 0.710241 ± 0.000017 ($n = 426$; 2σ external precision at 95% confidence limits). All data were normalised to NBS987 $^{87}\text{Sr}/^{86}\text{Sr} = 0.710235$ for interlaboratory comparison (Hodell *et al.*, 1991). Blanks have a negligible effect on measured ratios.

RESULTS

Initial experiments included isotopic analyses of whole-rock limestone matrix of a suite of samples ranging throughout the Emanuel Formation Section WCB705. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios yielded by whole-rock samples are variable, ranging from 0.709368 to 0.711422 (Tab. 1), and much higher than those defining the seawater curve (Text-fig. 3). Two sub-samples from horizon 168 yielded the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.709368, 0.709454) of the whole-rock data.

All conodont data are derived from specimens from horizon 168 due to the abundance of *Drepanodus arcuatus*. Measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios show significant isotopic heterogeneity within single conodont elements and, with the exception of separated basal tissue, are significantly lower than their whole-rock host. Ten whole elements of *D. arcuatus* (Text-fig. 2A) were individually analysed yielding $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.709097 and 0.709282 (Tab. 2; Text-fig. 3). Eight



Text-fig. 3 – Comparison of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios measured from A) whole-rock host, B) brachiopod secondary shell and C) conodont apatite. Components of the conodont *D. arcuatus* analysed are: single whole elements ('whole'), element bases with attachment cones ('bases'), cusps ('cusps'), and residuum of cusp tissue ('core') after 10hrs of chemical dissolution. Note that brachiopod data are derived from samples from different horizons than the conodonts and whole-rock limestone; analyses of separated conodont cusps are aligned with those of their basal counterparts; analytical error is within the limits of the symbols; grey band represents the estimated $^{87}\text{Sr}/^{86}\text{Sr}$ composition of seawater at -490 Ma, after Veizer *et al.*, 1997.

additional elements were selected for comparative analysis of cusp and basal tissue (Text-fig. 2B) which showed a systematic difference in their Sr isotopic compositions. Each separated cusp yielded a significantly lower ratio than its base and attachment cone (Text-fig. 3). The $^{87}\text{Sr}/^{86}\text{Sr}$ measurements of cusp tissue are more internally consistent, showing less dispersion, ranging from 0.708949 to 0.709056 (Tab. 3). The variability in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of basal material is high (0.709503 – 0.709829) and may be dependent, to some degree, upon the amount of cusp tissue included after physical separation. Preliminary results of the sequential dissolution of cusp tissue show that after 10 hours of dissolution (~30% of original cusp size), the residuum ('core') yielded the lowest ratio ($^{87}\text{Sr}/^{86}\text{Sr} = 0.708750$) (Tab. 3; Text-fig. 3).

Samples of brachiopod secondary shell material, extracted from several specimens from three different horizons (97, 105 and 175), showed varying degrees of luminescence during examination by cathodoluminescence microscopy indicating diagenetic alteration. The least altered shell sample exhibited luminescent streaks, while the bulk of the sample remained non-luminescent. This sample fraction

Bed Number	$^{87}\text{Sr}/^{86}\text{Sr}$	2sem%
41B	0.710455	0.0016
78	0.713028	0.0014
105	0.711422	0.0017
124B	0.710911	0.0018
155B	0.709924	0.0013
168 ¹	0.709368	0.0013
168 ²	0.709454	0.0017
177A	0.709605	0.0018
214	0.710580	0.0019
232	0.710075	0.0013
251A	0.709785	0.0014

2sem - 2 standard errors of the mean ($2\sigma/\sqrt{n}$) internal precision of Sr analyses
¹first subsample; ²second subsample

Tab. 1 - Sr isotopic composition of whole-rock limestone matrix from section WCB705, Emanuel Formation, Canning Basin, Western Australia.

yielded the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of all the analysed shell samples that ranged between 0.709027 and 0.709430 (Tab. 4).

Bed/Specimen	$^{87}\text{Sr}/^{86}\text{Sr}$	2sem%
168/specimen 1	0.709212	0.0017
168/specimen 2	0.709282	0.0021
168/specimen 3	0.709134	0.0018
168/specimen 4	0.709254	0.0026
168/specimen 5	0.709097	0.0017
168/specimen 6	0.709218	0.0021
168/specimen 7	0.709205	0.0026
168/specimen 8	0.709136	0.0016
168/specimen 9	0.709159	0.0014
168/specimen 10	0.709281	0.0013

2sem - 2 standard errors of the mean ($2\sigma/\sqrt{n}$) internal precision of Sr analyses

Tab. 2 - Sr isotopic composition of ten discrete whole elements of *D. arcuatus* from bed 168, section WCB705, Emanuel Formation, Canning Basin, Western Australia.

Bed/Sample	$^{87}\text{Sr}/^{86}\text{Sr}$	2sem%
168/base 1	0.709823	0.0016
168/cusp 1a ¹	0.708968	0.0017
168/cusp 1b ¹	0.708989	0.0020
168/base 2	0.709621	0.0016
168/cusp 2	0.708969	0.0018
168/base 3	0.709503	0.0017
168/cusp 3	0.709016	0.0014
168/base 4	0.709829	0.0013
168/cusp 4	0.709006	0.0017
168/base 5	0.709740	0.0022
168/cusp 5	0.709039	0.0020
168/base 6	0.709821	0.0025
168/cusp 6	0.709056	0.0024
168/cusp 7 ²	0.708965	0.0019
168/cusp 7 ³	0.708949	0.0015
168/cusp 8 ²	0.708959	0.0015
168/cusp 9 ('core')	0.708750	0.0027

2sem - 2 standard errors of the mean ($2\sigma/\sqrt{n}$) internal precision of Sr analyses

¹cusp halved a = oral half, b = aboral half; ²base of specimen not analysed

³repeat mass spectrometry run of original sample load

Tab. 3 - Sr isotopic compositions of separated components of elements of *D. arcuatus* from bed 168, section WCB705. Cusps have been physically separated from their base with attachment cone. 'Core' sample represents the residuum fraction of separated cusp tissue after 10 hours of chemical dissolution.

Bed/Sample	$^{87}\text{Sr}/^{86}\text{Sr}$	2sem%
97/fraction 1	0.709272	0.0012
97/fraction 2	0.709430	0.0011
105/fraction 1	0.709261	0.0014
105/fraction 2	0.709378	0.0016
175A/fraction 1	0.709027	0.0015
175A/fraction 2	0.709029	0.0016

2sem - 2 standard errors of the mean ($2\sigma/\sqrt{n}$) internal precision of Sr analyses

Tab. 4 - Sr isotopic compositions of brachiopod secondary shell from section WCB705, Emanuel Formation, Canning Basin, Western Australia.

DISCUSSION

The Emanuel Creek Section apparently spans a short time interval, approximately 2 my (~490 - 492Ma), so it is expected that variations in the primary isotopic signature throughout the section would be insignificant and well within the resolution of the current seawater curve. On this basis it is assumed that large isotopic compositional differences between samples reflect diagenetic effects rather than their stratigraphic position within the section.

Text-fig. 3 shows the distribution of $^{87}\text{Sr}/^{86}\text{Sr}$ values associated with each experiment. $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the whole-rock host are substantially higher than the range inferred for Early Ordovician seawater, suggesting significant diagenetic alteration. Isotopic heterogeneity of the conodont *D. arcuatus* indicates that conodont apatite has also been affected by alteration. High $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the element base and associated attachment cone clearly show they are a major source of secondary Sr thereby affecting data derived from single whole conodont elements which plot between values of the base and cusp tissue. Cusp tissue appears less altered, yielding more consistent and lower ratios which plot well within the boundaries defining the Sr seawater curve for the estimated age of the samples. These data also compare well with apparently coeval samples (491.5 Ma) of whole elements of *D. concavus* from Newfoundland that yielded $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between 0.70890 and 0.70895 (Qing *et al.*, 1998).

We are currently extending our work to assess the isotopic heterogeneity of separated cusp tissue. Preliminary results of the sequential dissolution of cusp tissue indicate alteration has occurred within the outer and middle layers, whereas the cusp 'core' yielded the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.708750, measuring lower than estimated seawater composition (Text-fig. 3). However, due to the considerable reduction in Sr contents of the leachates from each dissolution stage, technical developments are required to greatly improve the sensitivity of current mass spectrometry techniques in order to confirm this apparent trend. Denison *et al.* (1998) have also measured a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70875 from a sparry grainstone from Oil Creek, Oklahoma, USA, estimated to be 491 Ma using the timescale of Harland *et al.* (1990).

Brachiopods are rare in the Emanuel Formation and "pristine" shell material is lacking. This is a common problem and highlights the need to pursue investigations of the isotopic compositions of ubiquitous fossils such as conodonts. The few articulate brachiopods available for this study generally yielded $^{87}\text{Sr}/^{86}\text{Sr}$ ratios similar to or greater than single whole conodonts. The least altered samples (horizon 175) yielded the lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.709027, 0.709029) which are equivalent to some of the ratios derived from conodont cusp tissue (Text-fig. 3), and fall within the boundaries of the seawater curve.

Sample suitability is critical in the application of isotopic techniques and influencing factors may be location and/or age specific. These include quality of preservation, diagenetic history and sample morphology. The complexities of diagenetic alteration impose significant limitations because local geological and diagenetic histories are clearly responsible for differences in the isotopic compositions of geographically distinct yet apparently coeval samples. Results of this study also indicate that the susceptibility of conodonts to alteration is partly a function of morphology and is therefore a significant variable, complicating attempts to isolate primary Sr from conodont apatite. The physical separation of cusp tissue is a relatively simple and easily applied technique utilising routine mass spectrometry procedures. However, the routine use of conodonts in Sr isotope stratigraphy requires the development of techniques suitable for the wide range of morphologies that exist over different time intervals.

CONCLUSION

Results of our investigations of the Emanuel Formation to date show:

- $^{87}\text{Sr}/^{86}\text{Sr}$ of whole-rock limestone matrix suggest significant diagenetic alteration,
- there is significant Sr isotopic heterogeneity within 'pristine' ($\text{CAI} = 1$) single conodont elements,
- the element base with attachment cone of *Drepanodus arcuatus* are a major source of secondary Sr,
- $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of separated cusp tissue of *D. arcuatus* are less variable and plot within the boundaries of the seawater curve, and
- the 'core' of *D. arcuatus* cusp tissue yields lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios; our best estimate for the Sr isotopic composition of early Bendigonian seawater is 0.70875.

In the Emanuel Creek Section diagenetic alteration has significantly affected the carbonate rocks and their calcareous and phosphatic skeletal components. Despite this, diagenetic effects on conodont apatite may be limited as results of our experiments indicate that much of the secondary Sr can be avoided, thus obtaining lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios approaching primary seawater values. Further work measuring the $^{87}\text{Sr}/^{86}\text{Sr}$ variation in cusp tissue, as well as different compound conodont morphologies, will hopefully clarify the potential use of conodont apatite in Sr isotope stratigraphy and better define the boundaries of the seawater curve.

ACKNOWLEDGEMENTS

This work developed from a CSIRO initiative on Older and Deeper Basins led by Dr Joe Hamilton. The authors thank Drs A

Andrew, Steve Ruppel and an anonymous reviewer for helpful comments on the manuscript. We also thank Andrew Todd, Brad Macdonald and Alistair Law for providing technical assistance with mass spectrometry, and Andrew Kelman for help with some figure preparation.

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(manuscript received December 15, 1998
accepted June 7, 1999)

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