Terra Antartica
2001, 8(4), 593-597

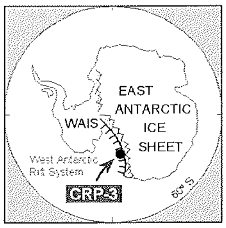
Strontium Isotope Stratigraphy for CRP-3, Victoria Land Basin, Antarctica

M. LAVELLE

British Antarctic Survey, High Cross, Madingley Road, Cambridge CB3 0ET and
Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ – UK (mlavelle@esc.cam.ac.uk)

Received 23 January 2001; *accepted in revised form* 19 November 2001

Abstract - Strontium isotope stratigraphy was used to date 5 discrete horizons within the CRP-3 drillhole. A single *in situ* modiolid bivalve fragment at 10.88 mbsf gives an age of 30.9 (±0.8) Ma for the associated sediment. The four remaining well preserved fragments recovered from 29.94-190.31 mbsf are within error of this age, indicating a high sedimentation rate and suggesting little time is missing in disconformities. The diagenetic alteration of carbonate macrofossils by continental fluids (and possibly seawater) is a common feature to 320 mbsf.



INTRODUCTION

Strontium isotope dating allows accurate age estimates to be obtained from *in situ*, unaltered marine carbonates. In Antarctica, the technique has proven particularly useful in dating shallow-water sequences where biostratigraphic control is restricted (*e.g.* Barrera, 1989; Prentice et al., 1993; Dingle et al., 1997; Dingle & Lavelle 1998; Lavelle, 1998, Lavelle, in press).

The 939-m-long CRP-3 core encountered: (1) a succession of glacially influenced marine sediments of early Oligocene age (3 - *c.* 330 mbsf), (2) a thick succession of undated marine sands and conglomerates (*c.* 330 - 790 mbsf), and (3) terminated in middle Devonian sandstones attributed to the Beacon Supergroup (Cape Roberts Science Team, 2000).

ANALYTICAL METHODS

Biogenic carbonate that is potentially suitable for Sr isotope dating was obtained from five horizons within the working half of the CRP-3 core. A review of the strontium isotope dating technique, including diagenetic considerations, is presented by Lavelle & Armstrong (1993) and McArthur (1994). In summary, surficial contaminants were removed from the shell surface by a repeated 10-second ultrasound treatment in 1M acetic acid and quartz-distilled water. All samples were visually inspected using a binocular microscope, and homogenous and well-preserved macrofossil specimens were divided into working and archive splits. The archive fractions were examined using a scanning electron microscope (SEM) to identify original shell ultrastructure at the sub-micron scale (Fig. 1). A further study of shell taphonomy (position in core, shell type, and preservation) was also carried out to assist in the identification of *in situ* and reworked specimens (see below). For archive samples that were identified as homogenous and well preserved, the matching working halves were rinsed in distilled water in an ultrasonic tank and dissolved in quartz-distilled 1.75 M HCl.

Strontium was extracted using standard ion-exchange techniques and was loaded onto a tantalum filament as a nitrate. Isotope measurements were carried out using a VG Sector 54 mass spectrometer in the Department of Earth Sciences, University of Cambridge. $^{87}Sr/^{86}Sr$ ratios were normalised to our long-term laboratory standard NIST-987 = 0.7210248 (n=59, 2SD=0.000020), and $^{86}Sr/^{88}Sr$ = 0.1194. Analytical blanks were typically <100 pg Sr. Corrected mean isotope measurements were converted to best-fit age and error using the LOWESS fit to the marine Sr curve of Howarth & McArthur (1997). As we have no long-term laboratory average $^{87}Sr/^{86}Sr$ value for modern biogenic carbonate, the long-term precision value for NIST-987 was used to calculate the 95% confidence limits on the best-fit age. Where internal within-run errors exceed this external value, the larger 2SE value is applied. No statistical attempt has been made to reduce sampling and analytical uncertainty below that of the long-term standard deviation value quoted above. The relatively large errors quoted for several of the samples are due to small sample size; in many cases, the cleaned $CaCO_3$ samples weighed < 1 mg (typically < 200 ng Sr for pectinid calcite) which makes it difficult to measure

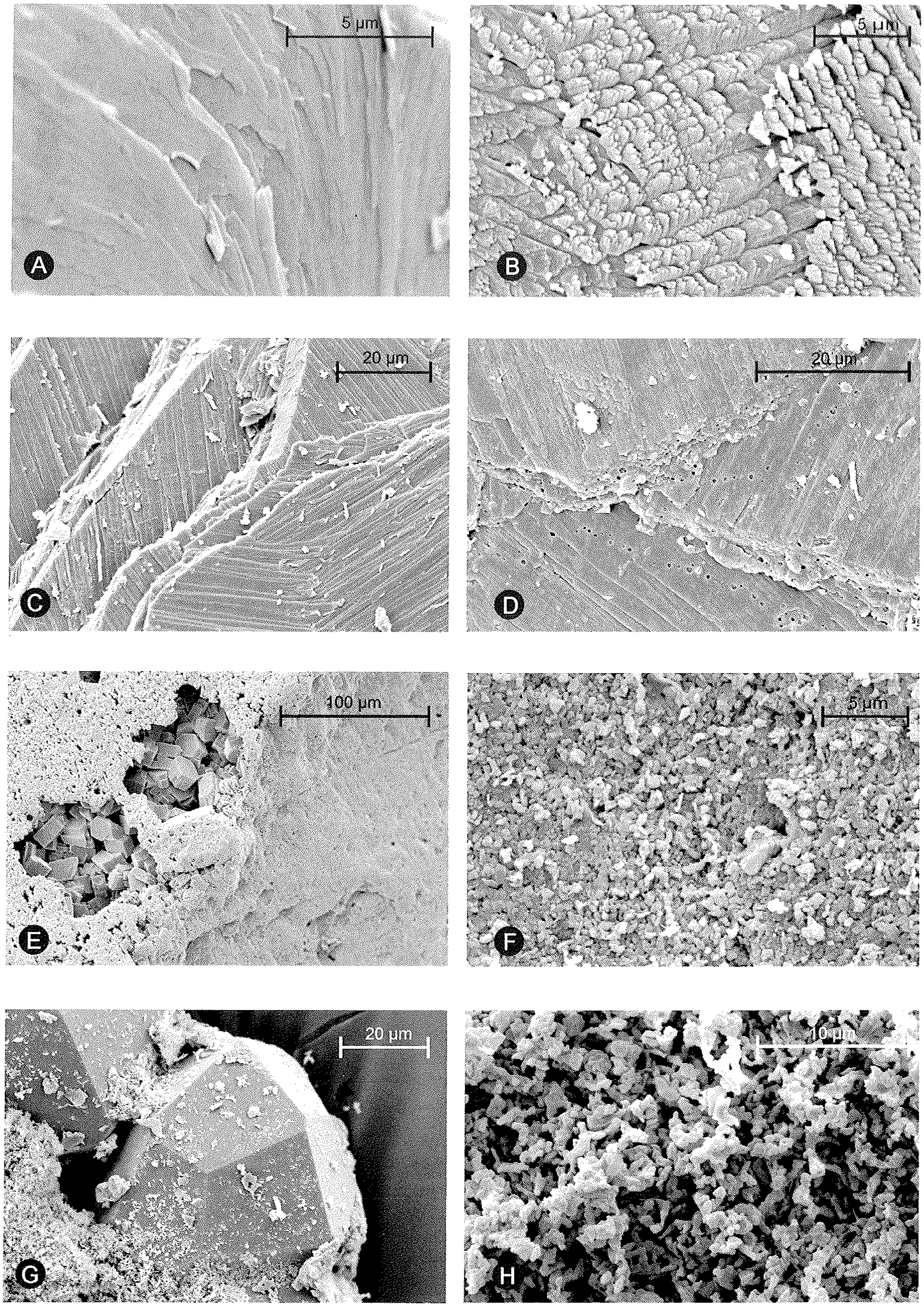


Fig. 1 - Scanning electron micrographs of preserved ultrastructures from selected representative CRP-3 carbonate samples: A) 10.88 mbsf, horizontal section through well-preserved aragonitic modiolid bivalve. B) 29.94 mbsf, oblique section through well-preserved pectinid bivalve fragment displaying three first-order lamellae of crossed foliated calcite. C) 47.55 mbsf, horizontal section through well-preserved pectinid bivalve displaying four first-order lamellae of crossed foliated calcite. D) 190.29 mbsf, horizontal section through well preserved pectinid bivalve displaying three first-order lamellae of crossed foliated calcite. E) 89.02 mbsf, poorly preserved unidentified bivalve showing localised sparry calcite precipitation overlying original aragonite. F) 127.48 mbsf, horizontal section through poorly preserved unidentified bivalve displaying fine-grained amorphous calcite texture. G) 190.50 mbsf, close-up of view of calcite overgrowth on unidentified bivalve. H) 320.36 mbsf, close up view of coarse-grained amorphous calcite from poorly preserved unidentified bivalve.

the *c.* 150 multicollector ratios often necessary for high precision dating.

Throughout this study, a cautious approach was taken to linking measured age and depositional age. All dated samples are identified as *in situ* or of unacertain provenance (tab. 1). Evidence for *in situ* faunas includes: disposition in the core (*e.g.* fauna are recovered in life position); for bivalves, the preservation of articulated valves; absence of abrasion features on internal, and to a lesser extent, external surfaces; absence of internal shell borings, *etc.* It should be noted that this is a cautious approach, and does not preclude the possibility that samples identified as reworked in this study may actually be *in situ* (*e.g.* many calcareous shallow marine faunas may exhibit both external surface abrasion and boring while alive). Well preserved fragmented shell material is labelled as of uncertain provenance in table 1, and is treated as potentially reworked in all further discussions.

Interstitial water analyses were performed on two 10 cm whole-round fine-grained sediment sections, which were cut, capped and sealed immediately after the core arrived in the processing laboratory. Interstitial water extraction took place *c.*8 weeks later utilising the geochemistry facilities aboard the Ocean Drilling Program vessel *Joides Resolution*. Before squeezing, the outside surface of each whole-round section was removed with a spatula to minimize potential contamination. Whole rounds were placed into a titanium and stainless steel squeezing device and squeezed at ambient temperature by applying pressure up to 40 000 lb (approximately 4150 psi) with a hydraulic press (Manheim and Sayles, 1974). Interstitial water was extruded through a pre-washed Whatman No.1 filter fitted above a titanium screen. All interstitial water samples were filtered through 0.45mm Gelman polysulfone disposable filters and collected into clean plastic syringes. After collection of *c.*10 ml of interstitial water, the syringe was removed, a fresh 0.45mm Gelman filter was attached and the water was dispensed into plastic vials for storage. A small aliquot (100 µl) of interstitial water (*c.* 800 ng of Sr), was loaded directly onto ion exchange columns. The analytical procedure then followed that outlined above for the carbonate samples.

To maintain consistency between sedimentological, palaeontological and chronological techniques discussed in this study, all references to depth in CRP-3 are given in metres below sea floor (mbsf). The timescale of Cande & Kent (1995) is used throughout this study.

RESULTS

Interpreted SEM images of a representative subset of the thirteen analysed carbonate samples are presented in figure 1. Multiple interpreted images of all analysed samples are available in digital format from the author. Additional example images of criteria used to define original and altered biogenic ultrastructure can be found in Lavelle (1998). Strontium isotope results are summarised in table 1 and are plotted in figure 2. Lithostratigraphic and sequence stratigraphic unit numbers refer to the summary of results in Cape Roberts Science Team (2000).

Biostratigraphic age control is available for the upper 200 mbsf of CRP-3 (Cape Roberts Science Team, 2000). Presence and absence datums of pelagic diatoms and calcareous nannofossils confine this upper sequence to 31-33 Ma (early Oligocene).

Five biogenic carbonate samples from four horizons between 10.88 and 190.31 mbsf have been dated using Sr isotope stratigraphy (Tab. 1). All showed the preservation of original carbonate ultrastructure at the sub-micron level (Fig. 1; see caption for detailed descriptions). A single articulated modiolid bivalve recovered from 10.88-10.89 mbsf is considered to be *in situ,* based on available

Tab. 1 - Strontium isotope data for marine carbonates from the CRP-3 drillhole. UCL/LCL (upper/lower confidence limit). Unit numbers refer to sedimentary units in Cape Roberts Science Team (1999). N/a = not applicable. For the definition of statistical terms used here, see «Analytical Methods» in the text. SEM datum codes refer to figure 1.

SEM datum	Depth range (mbsf) min	max	Unit	Sample	Shell type	Preservation	Taphonomy	$^{87}Sr/^{86}Sr$	Uncertainty 2SE ($\times10^{-6}$)	Age (Ma) (Best Fit)	Age (Ma) (UCL)	Age (Ma) (LCL)
Chronologic study												
A	10.88	10.89	1.1	Modiolid bivalve	Articulated	Well preserved	*In situ*	0.707949	20	30.9	31.7	30.1
B	29.94	29.96	1.2	Pectinid bivalve	Fragments	Well preserved	Uncertain	0.707946	12	31.0	31.7	30.2
C	47.55	47.57	1.2	Pectinid bivalve	Fragments	Well preserved	Uncertain	0.707949	17	30.9	31.7	30.1
D	190.29	190.31	6.1	Pectinid bivalve	Fragments	Well preserved	Uncertain	0.707946	18	31.0	31.7	30.2
D	190.29	190.31	6.1	Pectinid bivalve	Fragments	Well preserved	Uncertain	0.707934	24	31.3	32.1	30.5
Diagenetic study												
E	89.02	89.03	2.1	Unidentified bivalve	Fragments	Partially recrystallised	Uncertain	0.707988	17	n/a	n/a	n/a
n/a	124.96	125.01	3.1	Echinoid plates	Fragments	Partially recrystallised	Uncertain	0.708048	20	n/a	n/a	n/a
F	127.48	127.50	3.1	Unidentified bivalve	Fragments	Partially recrystallised	Uncertain	0.708328	20	n/a	n/a	n/a
G	190.50	190.52	6.1	Unidentified bivalve	Articulated	Partially recrystallised	In situ	0.708357	30	n/a	n/a	n/a
n/a	197.61	197.64	6.1	Unidentified bivalve	Fragments	Partially recrystallised	Uncertain	0.708249	21	n/a	n/a	n/a
n/a	198.79	198.81	6.1	Unidentified shell	Fragments	Partially recrystallised	Uncertain	0.708224	20	n/a	n/a	n/a
n/a	247.27	247.31	7.2	Unidentified shell	Fragments	Partially recrystallised	Uncertain	0.710497	21	n/a	n/a	n/a
H	320.36	320.38	8.1	Unidentified bivalve	Fragments	Partially recrystallised	Uncertain	0.708072	24	n/a	n/a	n/a
Interstitial water study												
n/a	81.29	81.39	1.4	Sandy mudstone	Water	n/a	n/a	0.711362	16	n/a	n/a	n/a
n/a	225.47	225.57	7.2	Sandy mudstone	Water	n/a	n/a	0.711073	20	n/a	n/a	n/a

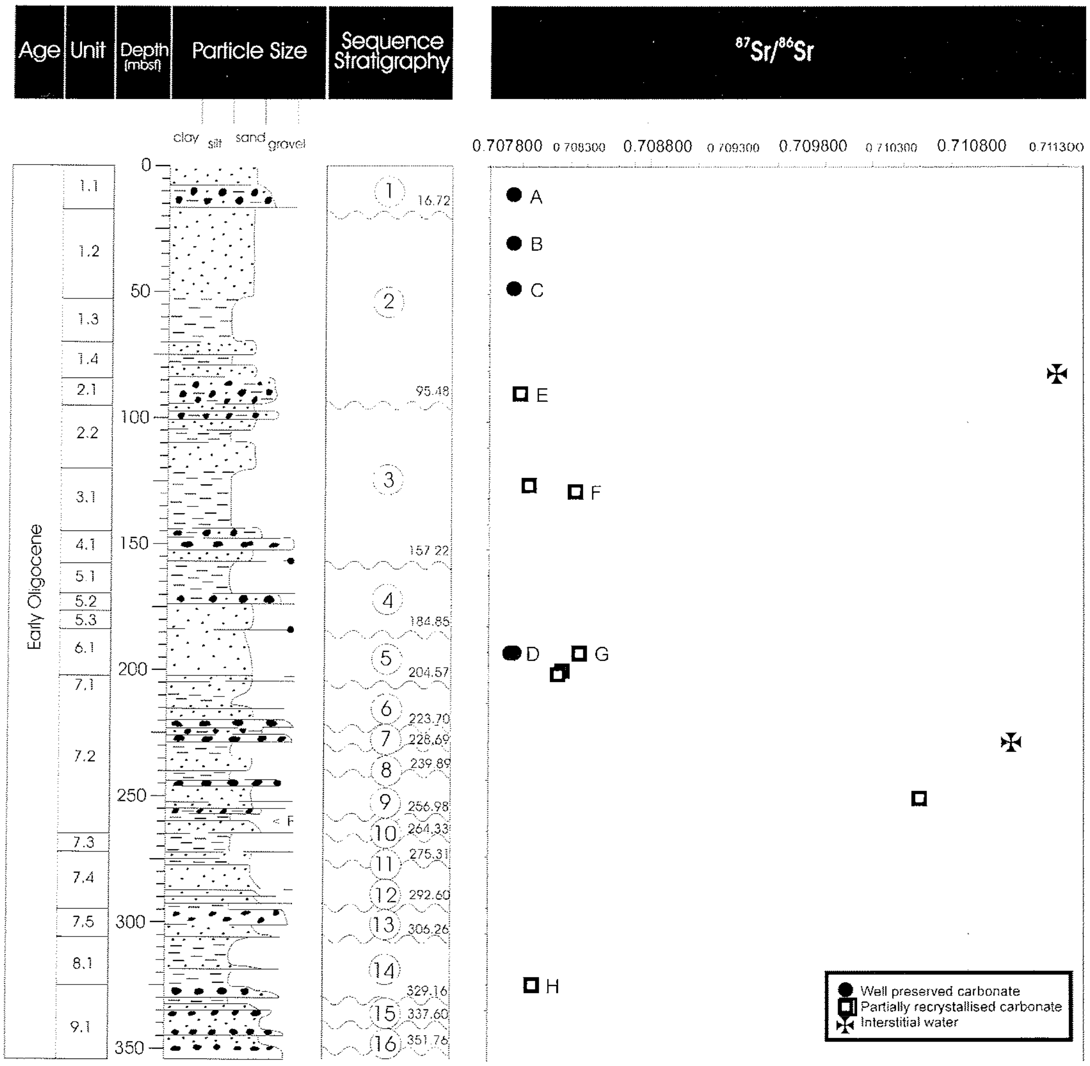


Fig. 2 - Strontium isotope results from well-preserved bivalve fragments, recrystallised bivalve and echinoid fragments, and interstitial waters for the upper 350 mbsf of CRP-3. 2SE error bars fall within the individual symbols. Also shown are lithological units, a simplified sedimentary log and sequence stratigraphy. Sequence boundaries are annotated with their exact depths (mbsf).

taphonomic data. The remaining four well-preserved pectinid bivalve samples are fragmented and are treated as of uncertain provenance. The five samples have a mean age range of 30.9–31.3 Ma, with a total error range (2SE: 95% confidence limit) of 30.1-32.1 Ma (Tab. 1).

One *in situ* and seven fragmented bivalve specimens from 89.02-320.36 mbsf were identified as recrystallised, based on visual criteria (Tab. 1). The replacement of characteristic molluscan ultrastructure with chemically precipitated amorphous carbonate (*e.g.* Fig. 1F) and rare sparry calcite (*e.g.* Fig. 1E) was used as a guide in rejecting samples from the chronologic study. All eight partially recrystallised samples yielded Sr-isotope signatures more ^{87}Sr enriched (43 ppm to 2.6 ‰) than the true depositional seawater Sr-isotope signature derived from the associated well-preserved specimens (0.707945; 31.0 Ma). Seven of these values are lower than modern day seawater (0.709175). A single small bivalve fragment recovered from 247.27-247.31 mbsf yielded a relatively radiogenic $^{87}Sr/^{86}Sr$ value of 0.710497.

Interstitial waters recovered from 81.29-81.39 mbsf and 225.47-225.57 mbsf yielded $^{87}Sr/^{86}Sr$ values of 0.711362 and 0.711073, respectively.

DISCUSSION

The first appearance datum (FAD) at *c.* 49 mbsf of the marine diatom Cavitatus jouseanus indicates an age of *c.* 31 Ma (Cape Roberts Science Team, 2000) for the associated sediments. This is in agreement with the three Sr isotope dates on co-occurring modiolid and pectinid bivalves above 47.57 mbsf (ξ=30.9 Ma). Between 49-195 mbsf, biostratigraphic age control is poor and indicates an age of <33 Ma. The two Sr isotope dated pectinid fragments at 190 mbsf indicate a mean age of 31.2 Ma, well within error of the overlying dates. This does not necessarily imply that the fragments are physically *in* *situ*. The very high sedimentation rates resulting from the Cape Roberts proximal glacio-marine setting (100-200 m/m.y., Cape Roberts Science Team, 1999), means that stratigraphic reworking over tens of metres will fall within the measurement and age calibration errors for the early Oligocene Sr isotope curve (*e.g.* Howarth and McArthur, 1997).

There are two possible origins for the fluid that has altered the Sr isotope signatures of the eight recrystallised samples analysed between 89-320 mbsf.

1 - *Seawater*: the strontium isotope value of global seawater has been growing progressively more radiogenic (^{87}Sr-enriched) from the middle Eocene to the present day (*e.g.* Howarth & McArthur, 1997). The Cape Roberts region has clearly experienced many relative sea level variations since the early Oligocene, as indicated by the multiple sequence boundaries present in all three cores (Fig.2 and Cape Roberts Science Team, 1998, 1999, 2000). Re-exposure of the original macrofossil and its subsequent total/partial re-crystallisation in the presence of relatively ^{87}Sr-enriched younger seawater will produce ^{87}Sr/^{86}Sr values between 0.707945 (early Oligocene seawater) and 0.709175 (modern seawater). The final value is a function of both degree and timing of alteration. All but one of the recrystallised samples, recovered from 247 mbsf, show values that may be the result of this process (but see below).

2 - *Continental fluids*: interstitial waters extracted from the CRP-3 core are highly radiogenic relative to Cenozoic seawater (Tab. 1). The sample at 247 mbsf clearly shows the fluid involved in the diagenetic reaction at this depth was of continental rather than marine origin. The remaining seven samples may also reflect a very small degree of alteration in the presence of these continentally derived fluids.

Since it has proved impossible to estimate the degree of alteration within each sample, no further diagenetic conclusions can be made. In all cases, unrecognised post-depositional recrystallisation of biogenic carbonate (*e.g.* epitaxial replacement) will produce calculated ages that are younger than the true depositional age. The visual identification of eight altered specimens, which subsequently showed reset Sr-isotope values, confirms that detailed diagenetic evaluation of crystal structure at the sub-micron level is a powerful tool in proofing samples for dating.

CONCLUSIONS

Strontium isotope stratigraphy may be used to accurately date high-latitude, near-shore Cenozoic successions. However, care must be taken during sample selection and preparation, to ensure that samples are well-preserved and identified as either *in situ*, reworked or of uncertain provenance. Four erosional sequence boundaries divide the upper 200 m of CRP-3 core into five sedimentary sequences (Fig 2). Five strontium isotope dates from 11-190 mbsf indicate a depositional age of 31.0 (±0.8) Ma, indicating a high sedimentation rate, and suggesting little time is missing in individual disconformities. The dates are in good agreement with the available biostratigraphic datums above 195 mbsf.

The diagenetic alteration of macrofossils by continental fluids (and possibly seawater) is a common feature within the carbonate preservation zone (0-320 mbsf).

ACKNOWLEDGEMENTS - The author thanks M. Greaves and A. Pimmel for laboratory assistance, and M. Taviani, T. Janecek and M. Curren for sampling and curatorial support. The manuscript was improved by constructive reviews from Isabel Montañez and an anonymous reviewer.

REFERENCES

Barrera E., 1989. Strontium isotope ages. In: Barrett P.J. (ed). Antarctic Cenozoic history from the CIROS-1 drillhole, McMurdo Sound. *DSIR Bulletin*, **245**, 151-152.

Cande S.C. & Kent D.V., 1995. Revised calibration of the geomagnetic polarity timescale for the Late Cretaceous and Cenozoic. *J. Geophys. Res.*, **100**, 6093-6095.

Cape Roberts Science Team, 1998. Initial Report on CRP-1, Cape Roberts Project, Antarctica. *Terra Antartica*, **5**, 1-187.

Cape Roberts Science Team, 1999. Studies from the Cape Roberts Project, Ross Sea, Antarctica. Initial Report on CRP-2/2A. *Terra Antartica*, **6**, 1-173.

Cape Roberts Science Team, 2000. Studies from the Cape Roberts Project. Ross Sea, Antarctica. Initial Report on CRP-3. *Terra Antartica*, **7**, 1-209.

Dingle R.V. & Lavelle M., 1998. Antarctic Peninsula cryosphere: early Oligocene (c. 30 Ma) initiation and a revised glacial chronology. *J. Geol. Soc. Lond.*, **155**, 433-437.

Dingle R.V., McArthur J.M. & Vroon P., 1997. Oligocene and Pliocene interglacial events in the Antarctic Peninsula dated using strontium isotope stratigraphy. *J. Geol. Soc. Lond.*, **154**, 257-264.

Howarth R.J. & McArthur J.M., 1997. Statistics for strontium isotope stratigraphy: a robust LOWESS fit to the marine Sr-isotope curve for 0 to 206 Ma, with look-up table for derivation of numeric age. *J. Geology*, **105**, 441-456.

Lavelle M., 1998. Strontium isotope stratigraphy of the CRP-1 drillhole, Ross Sea, Antarctica. *Terra Antartica*, **5**, 691-696.

Lavelle M., 2000. Strontium isotope stratigraphy and age model for CRP-2/2A, Victoria Land Basin, Antarctica. *Terra Antartica*, **7**, 611-619.

Lavelle M. & Armstrong R.A., 1993. Strontium isotope ratios in modern marine biogenic and chemical marine precipitates from southern Africa. *S. Afr. J. Sci.*, **89**, 553-536.

Manheim F.T. & Sayles F.L., 1974. Composition and origin of interstitial water of marine sediments based on deep sea drilled cores. In: Goldberg E.D. (Ed.), *The Sea* (Vol. 5): New York (Wiley Interscience), 527-568.

McArthur J.M., 1994. Recent trends in strontium isotope stratigraphy. *Terra Nova*, **6**, 331-358.

Prentice M.L., Bockheim J.G., Wilson S.C., Burckle L.H., Hodell D.A., Schluchter C. & Kellogg D.E., 1993. Late Neogene Antarctic glacial history: evidence from central Wright Valley. In: Kennett J.P. & Warnke D.A. (eds.), The Antarctic palaeoenvironment: a perspective on global change, 2, AGU, *Antarctic Res. Ser.*, **60**, 207-250.