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Strontium-Isotope Stratigraphy of the CRP-1 Drillhole, Ross Sea, Antarctica

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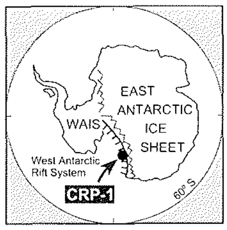
Abstract - Strontium isotope stratigraphy was used to date five discrete horizons within CRP-1. Early and late Quaternary (0.87-1.3 Ma and 0-0.67 Ma respectively) age sediments overlie a major sequence boundary at 43.15 meters below sea floor (mbsf). This hiatus is estimated to account for ~16 m.y. of missing section. Early Miocene (16.6-~20.8-25 Ma) age deposits below this boundary are in turn cut by multiple erosion surfaces representing hiatuses of between 0.2 and 1.2 m.y. Estimated minimum sedimentation rates range between 0.9 and 2.8 cm/k.y. in the Quaternary, and 1.5 and 6.4 cm/k.y. in the lower Miocene.



INTRODUCTION

Strontium isotope dating allows accurate age estimates to be obtained from *in situ*, unaltered marine carbonates. In the Antarctic, the technique has proven particularly useful in dating shallow-water sequences where little biostratigraphic control is available (*e.g.* Dingle & Lavelle, 1998; Dingle et al., 1997; Prentice et al., 1993). Before drilling commenced on CRP-1, Lavelle et al. (unpubl. data) re-evaluated the strontium isotope stratigraphy of the Miocene to Oligocene/Eocene Ross Sea succession preserved in the CIROS-1 drillhole (Barrera, 1989). This study confirmed that the upper Tertiary marine sediments of the Ross Sea were generally suitable for strontium isotope dating.

The 148 m-long CRP-1 core encountered a succession of Quaternary and early Miocene age marine sediments (Cape Roberts Science Team, 1998). The strontium isotope stratigraphy presented here is used to produce an age model for the cored sediments. Estimated age and duration of hiatuses, as well sedimentation rates, are also discussed.

ANALYTICAL METHODS

Post-drilling sampling at McMurdo Station identified biogenic carbonate potentially suitable for Sr-isotope dating from three depths within the working half of CRP-1. Examination of the archive core-half held in the Antarctic Geology Research Facility of the Florida State University at Tallahassee identified four additional horizons. A review of the strontium isotope dating technique, including diagenetic considerations, is presented in McArthur (1994) and Lavelle & Armstrong (1993). In summary, surficial contaminants were removed from the shell surface by a repeated 10-second ultrasound treatment in 1M acetic acid. Infilled foraminifera were gently crushed between glass plates and clean test fragments picked and treated as above. 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 to identify original shell ultrastructure at the sub-micron scale. Representative micrographs from each of the major faunal groups are shown in figure 1. For samples meeting the above criteria, the matching working halves were rinsed in distilled water in an ultrasonic tank and dissolved in quartz-distilled 1.75M HCl.

Strontium was extracted using standard ion-exchange techniques and 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. Values were normalised to NIST 987 = 0.710249 (n=29, SD=0.000015) measured during this study period, and $^{86}Sr/^{88}Sr = 0.1194$. Analytical blanks were typically <100 pg Sr. Corrected mean isotope measurements were converted to best-fit age using the LOWESS fit to the marine Sr isotope curve of Howarth and 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 is 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 attempt has been made to reduce sampling and analytical uncertainty below that of the long-term standard deviation value quoted above. The magnetochronology of Cande & Kent (1995) is used throughout this study.

RESULTS

Examples of carbonate preservation in CRP-1 are shown in figure 1. Interpreted SEM images of all analysed

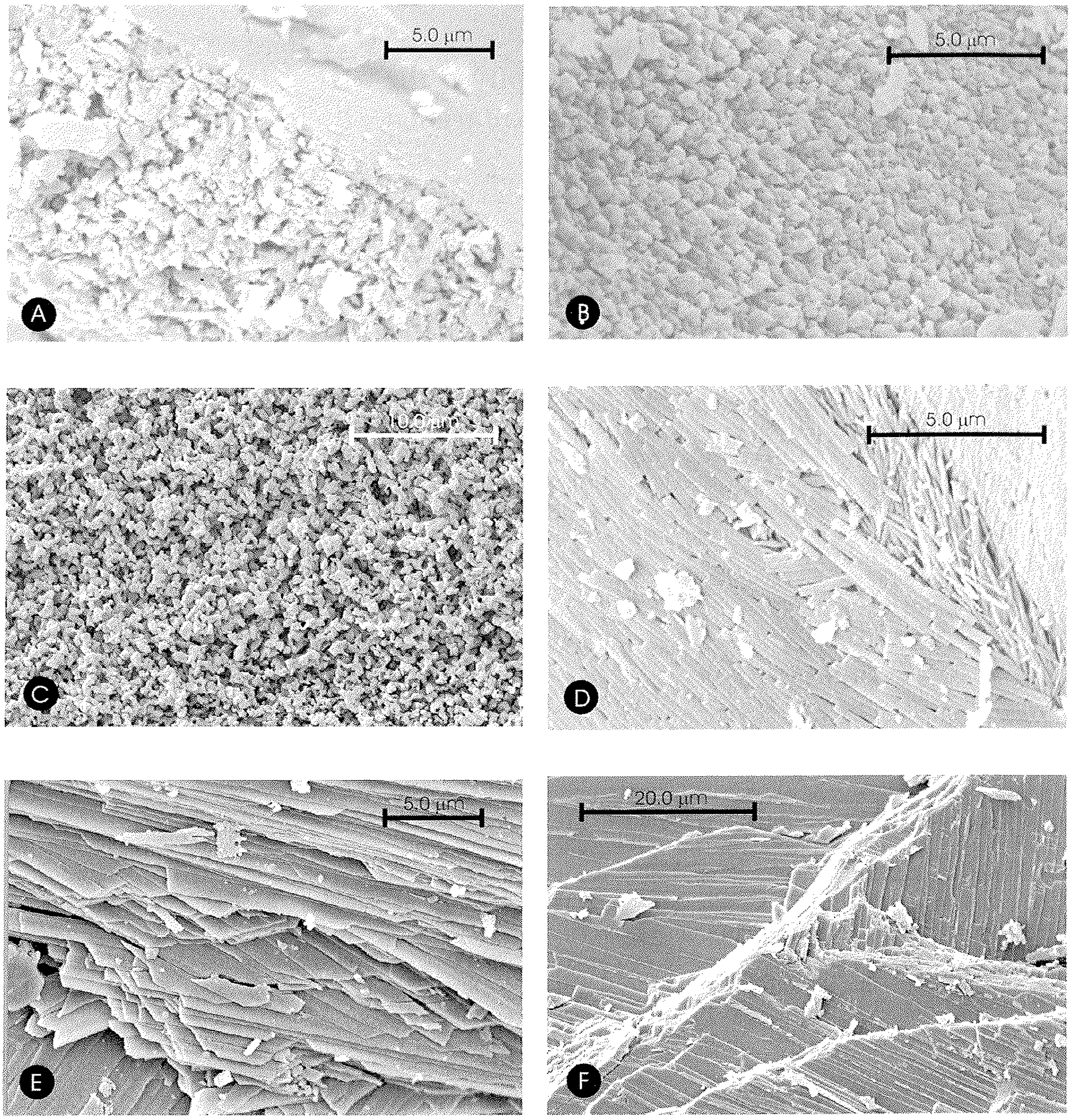


Fig. 1 - Examples of ultrastructure preservation in the groups analysed: *A)* Gastropoda (32.05 mbsf) vertical section through recrystallised outer shell margin showing no evidence of original aragonitic complex crossed lamellar ultrastructure. *B)* Bryozoan (32.05 mbsf) end-on view of primary granular calcite crystallites. *C)* Echinoidea (32.95-32.98 mbsf) outer surface of spine showing granular calcite ultrastructure. *D)* Foraminifera (32.05 mbsf) umbilical edge of porcelaneous miliolid showing original calcite laths. *E)* Bivalvia (32.95-32.98 mbsf) three first-order lamellae of crossed foliated calcite in vertical fracture surface of pectinid. *F)* Bivalvia (62.19 mbsf) two first-order lamellae of crossed foliated calcite in horizontal fracture of pectinid.

samples are available from the author. Strontium isotope results are summarised in table 1. Lithostratigraphic unit numbers refer to the summary core lithologies in Cape Roberts Science Team (1998). To maintain consistency between sedimentological and chronological techniques discussed in this study, all references to depth in CRP-1 are from core top to total depth.

QUATERNARY UNITS (Fig. 2)

Initial post-drilling biostratigraphy suggested the upper ~43 m of CRP-1 was of Pleistocene age (Cape Roberts Science Team, 1998). Eight biogenic carbonate samples from three depths between 27.75 – 32.97 mbsf were dated by Sr-isotope stratigraphy (Tab. 1). A taxonomic and taphonomic study of the macrofossil debris preserved in lithostratigraphic Unit 2.2 suggested that the material was likely to have been reworked from a lower unit in the core (Cape Roberts Science Team, 1998). Macrofossil material from the underlying carbonate-rich Unit 3.1 was considered to be *in situ*.

Two unidentified bryozoan fragments were analysed from 27.75 mbsf (Unit 2.2). The calculated mean age of 1.13 (+0.28/-0.34) Ma is within error of the value obtained for the underlying carbonate-rich Unit 3.1. Additional strontium-isotope measurements were undertaken at 32.05 and 32.97 mbsf within the carbonate rich Unit 3.1. At 32.05 mbsf four individual analyses of well preserved

Tab. 1 - Strontium isotope data.

Depth	Unit	Type	$^{87}Sr/^{86}Sr$	Error*	Age (Ma) (Best-fit)	Age (Ma) (UCL)	Age (Ma) (LCL)
27.75	2.2	Bryozoa #1	0.709135	16			
27.75	2.2	Bryozoa #2	0.709131	13			
		Mean	0.709133	16	1.13	1.41	0.79
32.05	3.1	Bryozoa	0.709123	14			
32.05	3.1	Miliolid	0.709132	14			
32.05	3.1	Bivalve	0.709132	13			
32.05	3.1	Echinoid	0.709134	14			
		Mean	0.709130	15	1.17	1.43	0.87
32.97	3.1	Echinoid	0.709129	12			
32.97	3.1	Bivalve	0.709138	14			
		Mean	0.709134	15	1.11	1.38	0.79
46.09	5.1	Serpulid #1	0.708711	17			
46.09	5.1	Serpulid #2	0.708696	22			
		Mean	0.708704	22	16.64	17.03	16.22
62.19	5.3	Bivalve #1a	0.708548	15			
62.19	5.3	Bivalve #1b	0.708554	14			
62.19	5.3	Bivalve #1c	0.708558	15			
62.19	5.3	Bivalve #2	0.708541	15			
		Mean	0.708550	15	18.69	18.91	18.48

Depth	Unit	Type	$^{87}Sr/^{86}Sr$	Error*	Remarks
32.05	3.1	Gastropod	0.709177	11	Recrystallised
91.39	5.7	Bivalve	0.709216	50	Recrystallised
138.86	6.3	Bivalve	0.710340	66	Recrystallised

Note: *internal 2SE quoted for individual measurements; external 2SD quoted for mean values; UCL / LCL: upper/lower confidence limit.

bryozoa, miliolid foraminifers, an unidentified bivalve fragment and several echinoid bosses suggest an early Pleistocene age [1.17 (+0.26/-0.30) Ma] for the unit. Two additional bivalve and echinoid samples from 32.97 mbsf indicate a similar early Pleistocene age of 1.11 (+0.27/-0.32) Ma.

MIOCENE UNITS (Fig. 2)

Initial post-drilling biostratigraphy suggested the lower ~100 m of CRP-1 were deposited between ~17.5 - 22.5 Ma. A further calibration of the measured CRP-1 polarity zonation to the geomagnetic polarity time scale indicated a possible age range of ~17 – 24 Ma (Cape Roberts Science Team, 1998). Six Sr-isotope analyses of two serpulid and two bivalve samples from 46.09 mbsf (Unit 5.1) and 62.19 mbsf (Unit 5.3) indicate ages of 16.64 (+0.39/-0.42) Ma and 18.69 (+0.22/-0.21) Ma respectively (Tab. 1).

DIAGENESIS

Three samples were identified as recrystallised based on visual criteria. A single juvenile eatoniellid gastropod from 32.05 mbsf within the carbonate-rich Unit 3.1 was observed to be partially pyritised. On further examination under the SEM, the test wall showed a simple granular pattern (Fig. 1A), with no evidence of the expected original complex crossed-lamellar ultrastructure. Strontium-isotope analysis of the specimen produced an $^{87}Sr/^{86}Sr$ ratio of 0.709177, within error of the modern day $^{87}Sr/^{86}Sr$ value of seawater. It is therefore suggested that the original specimen has undergone complete recrystallisation from circulating porewaters recently derived from modern seawater. If the diagenetic system was a truly open one (as suggested by the shallow burial depth and poorly consolidated nature of the overlying sediments - Cape Roberts Science Team, 1998), the upper confidence limit on the analysis indicates recrystallisation could have

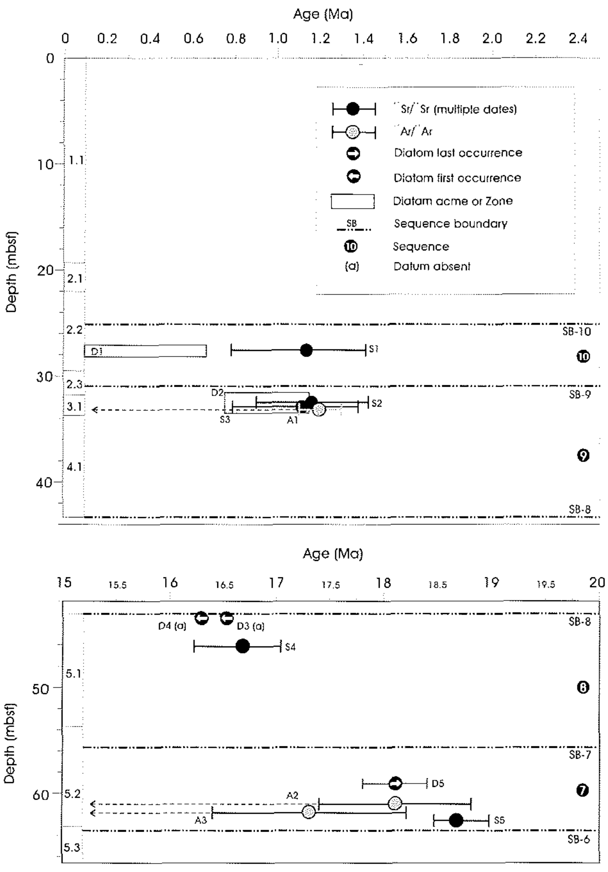


Fig. 2 - $^{87}Sr/^{86}Sr$, $^{40}Ar/^{39}Ar$ and diatom age data for the upper 65 m of CRP-1. Datum codes refer to table 2.

occurred at any point within the past 580 k.y. Theoretically, however, if the diagenetic system was partially closed, the mixing of ^{87}Sr enriched pore fluids and early Pleistocene seawater Sr from the original shell could also produce a similar value. As porewater Sr-isotope values were not measured in CRP-1, no further conclusions can be made.

A further two bivalves from 91.39 and 138.86 mbsf show $^{87}Sr/^{86}Sr$ values higher than modern seawater (Tab. 1). This down-core increase in Sr-isotope ratio is attributed to the replacement of circulating seawater by ^{87}Sr enriched porewaters within the deeper, more compacted part of the sediment column.

DISCUSSION AND AGE MODEL

Strontium-isotope stratigraphy allows the accurate dating of biogenic carbonates from five depths within CRP-1. While the rigorous treatment of specimens prior to analysis is believed to minimise the risk of error, there are two mechanisms by which the calculated ages may be inaccurate:

1 - Diagenesis: the simple diagenetic study above shows that unrecognised recrystallisation of biogenic carbonate (*e.g.* epitaxial replacement) in CRP-1 is likely to produce calculated ages that are younger than the true depositional age. There is no visual evidence of diagenetic resetting in any of the samples for which ages are quoted. The visual identification of three 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.

2 - Reworking: taphonomic analysis of preserved macrofossil remains suggests reworking has occurred at 27.75 mbsf (Cape Roberts Science Team, 1998). The bryozoa analysed were rare, highly worn, and separated from an underlying source of *in situ* bryozoa (bryomol-type sediment forming Unit 3.1) by a sequence boundary (Fielding et al., this volume). The identification of these potential maximum erosion surfaces allows the effects of reworking to be further minimised by comparing ages only within single sequences.

To minimise these potential influences, I have combined the Sr-isotope data with all available chronological data from CRP-1. All datums used in the generation of the age model are listed in table 2. Diatom datums are from Cape Roberts Science Team (1998), Bohaty et al. (this volume) and Harwood et al. (this volume). $^{40}Ar/^{39}Ar$ clast, feldspar and pumice dates are from McIntosh (this volume).

CALCULATION OF TOTAL AGE RANGE (TAR)

In order to take account of occasional discrepancies between different dating techniques, a Total Age Range (TAR) is defined. While $^{40}Ar/^{39}Ar$ dating is often the most precise of the three techniques applied, the clast and feldspar dates are considered to be maxima. Similarly, diatom stratigraphy of the high-latitude Cenozoic can be highly precise (*e.g.* Harwood & Maruyama, 1992), but becomes more problematic when applied to shallow water sections where barren lithologies and multiple erosion surfaces are common. The TAR takes into account the total potential age range of all datums (including confidence limits where available) from within narrowly defined depth ranges. Datums spanning an identified sequence

Tab. 2 - Datums used in calculating total age range.

Code	Depth (mbsf)	Age (Ma)	Remarks
STRONTIUM			
S1	27.75	1.13 (+0.28/-0.34)	Reworked from Unit 3.1
S2	32.05	1.17 (+0.26/-0.30)	Insitu faunas
S3	32.97	1.11 (+0.27/-0.32)	Insitu faunas
S4	46.09	16.64 (+0.39/-0.42)	Serpulid in carbonate concretion
S5	62.19	18.69 (+0.22/-0.21)	Disarticulated pectenid fragments
ARGON			
A1	33.20	1.2 (±0.1)	Clast: maximum age
A2	*c.* 61	18.1 (±0.7)	Clast: maximum age
A3	*c.* 61	17.3(±0.9)	Clast: maximum age
A4	*c.* 90	19.3 (±0.3)	Anorthoclase: maximum age
A5	*c.* 90	17.9 (±0.4)	Clast: maximum age
A6	*c.* 90	17.2 (±0.8)	Clast: maximum age
A7	*c.* 104	19.3 (±0.1)	Anorthoclase: maximum age
A8	*c.* 114	19.7 (±0.9)	Clast: maximum age
A9	*c.* 117	18.4 (±1.2)	Pumice: depositional age
DIATOMS			
D1	26.95 – 28.11	0.0 – 0.67	*T. lentiginosa* Zone
D2	31.70 – 33.75	0.75 – 1.15	Acme *T. elliptipora*
D3	43.55	>16.6	FAD (absent) *D. maccollumii*
D4	43.55	>16.3	FAD (absent) *A. ingens*
D5	58.75 – 59.68	17.8 – 18.4	LAD *T. praefraga*
D6	88.81 – 91.23	>18.5	LAD *A. symmetricus*
D7	102.2 – 103.4	<20.3	FCAD *T. praefraga*
D8	141.48 – 141.80	*c.* >20.8	LAD *S. spinossisima*
D9	*c.* 145	*c.* >20.5	LAD *C. rectus*
D10	*c.* 148	*c.* >25	LAD (absent) *K. carina*

boundary (see Fielding et al., this volume) are considered separately (*e.g.*, Sr dates at 27.75 mbsf and 32.05-32.97 mbsf fall within sequence stratigraphic Unit 10 and Unit 9 respectively). With the exception of the pumice depositional age at *c.* 117 mbsf, the $^{40}Ar/^{39}Ar$ ages are considered to be maxima. Where Sr, Ar and/or diatom ages overlap, the older (for lower confidence limits - LCL) and younger (for upper confidence limits - UCL) ranges are used to define the TAR (*e.g.* S2 and D2 overlap; the older S2 LCL defines the TAR-2 LCL, Tab. 3). Where Sr, Ar and/or diatom ages are mutually exclusive within a depth range, the younger LCL or older UCL is used to extend the TAR (*e.g.* D5 and S5 are exclusive; the younger D5 LCL defines the TAR-4 LCL, Tab. 3).

CALCULATION OF STRATIGRAPHIC TOTAL AGE RANGE (STAR)

In calculating a simple age model for the core, the Stratigraphic Total Age Range (STAR) may be used to further refine the Total Age Range (TAR). Assuming the calculated age ranges are robust, in a simple geological succession, such as CRP-1, the LCL of a dated horizon cannot exceed the LCL of an overlying dated horizon. Similarly, the UCL of a dated horizon may not exceed the UCL of an underlying dated horizon. Figure 3 illustrates the effect of this treatment in refining the age model.

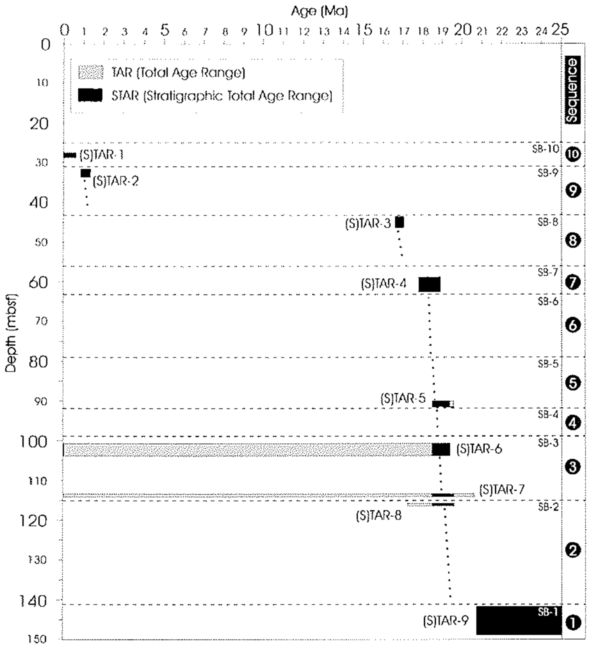


Fig. 3 - Age model for the CRP-1 drillhole. (S)TAR data from table 3. Sequence stratigraphy from Fielding et al. (this volume).

While TARs 1-4 are unaffected, TARs 5-8 are significantly improved. It is recognised that this technique may

Tab. 3 - Total/Stratigraphic Age Range (S)TAR data.

	TAR Total Age Range (Ma)	Depth range (mbsf)	STAR Stratigraphic Total Age Range (Ma)+
(S)TAR-1	0 – 0.67 [Diatom (D1) 0 – 0.67 Ma]	26.95 – 28.11 [26.95 – 28.11]	0 – 0.67 (D1 LCL – D1 UCL)
(S)TAR-2	0.87 – 1.3 [Diatom (D2) 0.75 – 1.15 Ma] [Strontium (S2) 0.87 – 1.43 Ma] [Strontium (S3) 0.79 – 1.38 Ma] [Argon (A1) 1.1 – 1.3 Ma (clast maximum age)]	31.70 – 33.75 [31.70 – 33.75] [32.05] [32.97] [33.20]	0.87 – 1.3 (S2 LCL – A1 UCL)
(S)TAR-3	16.6 – 17.03 [Diatom (D3) >16.6 Ma] [Diatom (D4) >16.3 Ma] [Strontium (S4) 16.22 – 17.03 Ma]	43.55 – 46.09 [43.55] [43.55] [46.09]	16.6 – 17.03 (D3 LCL – S4 UCL)
(S)TAR-4	17.8 – 18.91 [Diatom (D5) 17.8 – 18.4 Ma] [Argon (A2) 17.4 – 18.8 Ma (clast maximum age)] [Argon (A3) 16.4 – 18.2 (clast maximum age)] [Strontium (S5) 18.48 – 18.91]	58.75 – 62.19 [59.68 – 58.75] [*c.*61] [*c.* 61] [62.19]	17.8 – 18.91 (D5 LCL – S5 UCL)
(S)TAR-5	18.5* – 19.6 [Diatom (D6) >18.5 Ma [Argon (A4) 19.0 – 19.6 Ma (feldspar maximum age)] [Argon (A5) 17.5 – 18.3 Ma (clast maximum age)] [Argon (A6) 16.4 – 18.0 Ma (clast maximum age)]	*c.* 90 [88.81 – 91.23] [*c.* 90] [*c.* 90] [*c.* 90]	18.5 – 19.4 (D6 LCL – A7 UCL)
(S)TAR-6	<19.4** [Diatom (D7) <20.3 Ma] [Argon (A7) 19.2 – 19.4 Ma (feldspar maximum age)]	102.2 – *c.* 104 [102.2 – 103.4] [*c.* 104]	18.5 – 19.4 (D6 LCL – A7 UCL)
(S)TAR-7	<20.6 [Argon (A8) 18.8 – 20.6 Ma (clast maximum age)]	*c.* 114 [*c.* 114]	18.5 – 19.6 (D6 LCL – A9 UCL)
(S)TAR-8	17.2 – 19.6*** [Argon (A9) 17.2 – 19.6 Ma (pumice depositional age)]	*c.* 117 [*c.* 117]	18.5 – 19.6 (D6 LCL – A9 UCL)
(S)TAR-9	*c.* 20.8 – *c.* 25 [Diatom (D8) >20.8 Ma [Diatom (D9) >20.5 Ma [Diatom (D10) <25 Ma	141.48 – *c.* 148 [141.48 – 141.80] [*c.* 145] [*c.* 148]	*c.* 20.8 – *c.* 25 (D8 LCL – D10 UCL)

Note: + LCL/UCL: Lower/Upper confidence limit; *TAR-5 LCL restricts STAR-6,-7 and -8 LCL's; **TAR-6 UCL restricts STAR-5 UCL; ***TAR-8 UCL restricts STAR-7 UCL.

potentially perpetuate errors through the core. This uncertainty is minimised, however, by the robust method of generating the TAR, as outlined above.

CALIBRATION OF THE CRP-1 MAGNETIC POLARITY ZONATION

An attempt was also made to further refine the age model by tying the well-defined TAR points (*i.e.* excluding TAR 9) between ~60 mbsf and ~117 mbsf to the CRP-1 magnetic stratigraphy (Roberts et al., this volume). Comparison to the geomagnetic polarity timescale (Cande & Kent, 1995) between the LCL of TAR 4 (17.8 Ma) and the UCL of TAR 8 (19.6 Ma) identifies a possible range between Chron C5Dr and C6n. This equates to a maximum of two reverse (C5Dr/C5Er) and two normal (C5En/C6n) polarity intervals. The associated CRP-1 polarity zonation consists of three reverse and three normal polarity intervals (Roberts et al., this volume). Without adding extra uncertainty therefore, it is not possible to use the magnetic polarity zonation of the CRP-1 core to further refine the age model presented in this study.

AGE MODEL, SEDIMENTATION RATES AND EROSION

The vertical dashed line in figure 3 illustrates the first-order age model for CRP-1. The line is generated with a mean-fit slope, and assumes sediments within a single sequence stratigraphic unit are deposited within the confidence limits of the associated STAR value. Sedimentation rates calculated by this method (*i.e.* sequence stratigraphic unit minima), range between 0.9 and 2.8 cm/k.y. in the Quaternary, and 1.5 and 6.4 cm/k.y. in the lower Miocene. The mean minimum sedimentation rate for the ~85 m succession between sequence stratigraphic Unit 2 and Unit 7 (Fig. 3) is 2 cm/k.y. Both rates are relatively low for glacial environments, but are supported by other sedimentological studies (*e.g.* Fielding et al., this volume; Woolfe et al., this volume).

The dashed line in figure 3 highlights the erosion potential of the identified sequence boundaries (SB), interpreted by Fielding et al. (this volume) as ice grounding lines. Sequence boundary 8 at ~1.3 Ma represents the largest unconformity in the core, spanning a break of ~16 m.y. Sequence boundary 9 (31 mbsf), SB 7 (56 mbsf) and SB 1 (141 mbsf) are the next largest, representing minimum time breaks of 0.2, 0.8 and 1.2 m.y. respectively. The remaining erosion surfaces are all interpreted as representing minimal time breaks.

CONCLUSIONS

The following conclusions have been reached:

1 - strontium-isotope stratigraphy may be used to accurately date high-latitude, near-shore Cenozoic successions;

2 - in several instances, Sr-isotope ratios of biogenic carbonates in the Quaternary and Miocene sections of CRP-1 have been affected by recrystallisation in contact with pore waters enriched with radiogenic Sr;

3 - CRP-1 preserves a record of deposition and erosion from the Recent back to the earliest Miocene/latest Oligocene (*c.* 20.8 - *c.* 25 Ma);

4 - a major unconformity at 43.15 mbsf accounts for ~16 m.y. of missing section between 1.3-16.6 Ma (early Pleistocene-early Miocene);

5 - sedimentation rates throughout the core are low (minima range between 1.5 and 6.4 cm/k.y. for individual sequences).

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