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# PRELIMINARY AGE DETERMINATIONS OF CROWN OF THORNS STARFISH SPICULES BY ACCELERATOR MASS SPECTROMETRY

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# PRELIMINARY AGE DETERMINATIONS OF CROWN OF THORNS STARFISH SPICULES BY ACCELERATOR MASS SPECTROMETRY

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**ABSTRACT**

The INS accelerator mass spectrometry system has been used to determine the ages of selection of spicules from Crown of Thorns starfish, collected at The Great Barrier Reef, Queensland. The measurements constitute a pilot study to determine the feasibility of using the technique to establish whether or not there is a periodicity in the invasion of The Great Barrier Reef by Crown of Thorns starfish.

**KEY WORDS**

TAMS; RADIOCARBON DATING; C-14; ACANTHASTER PLANCI; STARFISH; GREAT BARRIER REEF; AUSTRALIA

## 1. Introduction

The object of this report is to examine the feasibility of using the accelerator mass spectrometry (AMS) facility recently installed at the Institute of Nuclear Sciences (INS) to provide radiocarbon ages for small (a few milligrams) spicules from Crown of Thorns (COT) starfish, collected from the Great Barrier Reef, Queensland. The spicules have been isolated from core samples taken from the Great Barrier Reef, and the horizons where the spicules were found have been independently dated at the Australian National University (ANU). The aim of this study is to determine whether or not a correlation can be established between the ages of the COT spicules and the core horizons in which they are found, whilst the main aim is to test for periodicity in COT invasions of The Great Barrier Reef.

Because the AMS system is still under development it is necessary to establish that it is capable of providing sufficiently reliable data for the main study to proceed. Also, these preliminary measurements have been able to point up more clearly the requirements to be placed on the original sample material to be dated.

## 2. General procedure

Ten samples of COT spicules, averaging 11 ±1 mg, were supplied from ANU, and were converted to graphite targets for insertion into the sputter ion source as described below. In addition, 600 mg of modern COT material was supplied as a comparison standard. This material has been determined at ANU as having a $^{14}C$ content 15% above "modern" carbon, defined as .95 times the $^{14}C$ content of NBS oxalic acid standard. Targets prepared from the modern COT were compared with the oxalic acid standard using the AMS system, to check the reproducibility of this ratio.

## 3. Sample preparation

The COT spicules were cleaned at ANU in demineralised water in an ultrasonic bath for 30 minutes. At INS each sample was dissolved in 2 ml of phosphoric acid at 100° under vacuum in a miniature Erlenmeyer flask. The samples dissolved readily, in less than 10 minutes, and after half an hour the evolved $CO_2$ was vacuum distilled into a calibrated reaction vessel fitted with a pressure transducer. Equivalent carbon yields were calculated by weight and are listed on page 7. The $CO_2$ was converted into a graphite target for AMS dating, using a catalytic method [1].

## 4. Measurement procedure

The tandem accelerator was operated with a terminal voltage of 3 MV. Carbon ions from the ion source were injected into the accelerator and stripped at the terminal by a 5 microgram/cm$^2$ carbon foil. The analysing magnet following the accelerator was set to transmit the $3^+$ charge state ions, these forming about 45% of the total accelerator output.

The carbon isotopes were pulsed sequentially through the accelerator, each cycle comprising 2 msec $^{12}C$, 19 msec $^{13}C$ and 400 msec $^{14}C$. The $^{12}C$ and $^{13}C$ currents were measured in shielded Faraday cups at the analysing magnet exit. The current signals were digitised and sent to the controlling computer. The $^{14}C$ ions were counted by a silicon surface barrier detector located at the exit of an electrostatic analyser. The computer generated an energy spectrum of the detector output, with a counting window set over the $^{14}C$ peak. The spectrum was displayed continuously during the measurements, providing a visual check that background counts did not contribute to the $^{14}C$ rate.

For the measurements on the COT spicules, 5 targets prepared from the COT samples were placed in the sample changer at a time, together with targets prepared from the modern COT material and NBS oxalic acid. For the measurements to cross-check the relation between modern COT and oxalic acid, three separate COT targets were prepared and one oxalic.

The procedure followed in all cases was the same. The measurement on each unknown sample was preceded and followed by a 5 minute count on the standard. This way, drifts which occurred in the equipment could be spread evenly over standards and unknowns, and allowed for.

The quantities determined during a counting run were :

1. The $^{14}C$ count rate, $N_{14}$ (counts per minute)
2. The $^{12}C$ current, $I_{12}$
3. The $^{13}C$ current, $I_{13}$ (both in nano-amps)

These quantities were used to obtain the ratios $R_{13} = I_{13}/I_{12}$ and $R_{14} = N_{14}/I_{12}$. Following Litherland et al. [2] we use the corrected ratio R* for comparing the $^{14}C$ rates of different samples, where

$$R^* = R_{14}/(R_{13})^2$$

$$= (N_{14}/I_{13})x(I_{12}/I_{13})$$

With NBS oxalic used as the comparison standard, the sample $^{14}C$ depletion with respect to "modern" carbon is then given by

$$D^{14}C = 1000(1.040 \times R^*_{sample}/R^*_{standard} - 1)°/_{oo}$$

The $D^{14}C$ value obtained includes the correction for the different $\delta^{13}C$ values between the sample and standard, and is the $D^{14}C$ of Stuiver and Polach [3].

## 5. Modern Crown of Thorns

Three graphite targets were prepared from the modern COT material, and inserted in the ion source, together with a target made from NBS oxalic acid and two targets prepared from shell fragments that are not relevant to the present discussion. The results are shown in figure 1, in which are plotted the corrected $^{14}C$ ratios R* for each target in the order in which they were measured, together with $R_{13}$ for each target. The $R_{13}$ ratios show excellent stability for all measurements. The R* values, which are more sensitive to small changes in conditions, show a gradual downward drift. However, all three COT targets and the oxalic standard show a uniform drift at the same rate, so the data were analysed by fitting a straight line to the oxalic points and using this line to infer the appropriate R* for the standard at each COT point.

The results are shown in the following table :

| Target | $D^{14}C$°/$_{oo}$ |
|---|---|
| COT #1 | 153 ± 36 |
| COT #2 | 171 ± 28 |
| COT #3 | 126 ± 33 |
| COT #1 | 137 ± 35 (repeat) |
| Weighted Mean | 149 ± 16 |
| ANU value | 145 ± 10 |

The errors in these results are dominated by counting statistics. The ANU value was obtained by radioactive decay counting.

## 6. Crown of Thorns Spicules

The ten COT spicules were counted in two groups of five, in each case with an NBS oxalic acid target and a modern COT target. A problem encountered in these measurements was the low current output obtained from the samples. This can be attributed in part to the fact that some of the spicules yielded about half the amount of carbon expected on the basis that the spicules were pure carbonate. The consequence was that counting statistics severely limited the precision of the results. The first set of samples were measured against the modern COT standard. In the second set, the output from the modern COT target was relatively low, so the measurements were referred to the oxalic standard, which gave a good output. The measured ratios were later related to NBS oxalic by means of the measured relation between oxalic and modern COT described in Section 5 above. The results are shown in figures 2 and 3, in which are plotted the R* values for each sample in the order in which they were measured. The ratios for the standards, which were repeatedly measured during the run, show variations larger than can be attributed to statistics, and which reflect instrumental drifts. The variations occur on a time scale that is long compared to the duration of a single measurement so the data were analysed by comparing the R* for each sample with the mean of the standard values on each side of it.

The results are summarised in the following table :

| JCU No. | Core No. | Depth Range | ANU Bulk Analysis $D^{14}C$ | Age | AMS $D^{14}C$ | Age | $CO_2$ Yield |
|---|---|---|---|---|---|---|---|
| 8 | JB8b | 42.0 - 52.0 | -80.6±7.7 | 680±70 | -62±60 | 518±514 | 6.3% |
| 9 | JB8b | 113.0 - 121.0 | -97.9±7.6 | 830±70 | -59±43 | 489±371 | 9.9% |
| 10 | JB8b | 251.5 - 259.0 | -196.3±6.9 | 1760±70 | -277±31 | 2604±346 | 11.6% |
| 1 | GI2c | 405.0 - 420.0 | -291.4±6.5 | 2770±80 | -213±28 | 1932±285 | 10.2% |
| 2 | GI5b | 343.0 - 350.5 | -309.5±6.4 | 2970±80 | -287±65 | 2727±727 | 4.2% |
| 3 | GI5b | 421.5 - 429.5 | -343.8±6.2 | 3380±80 | -356±35 | 3545±439 | 5.4% |
| 4 | GI6b | 217.0 - 224.5 | -154.4±7.4 | 1350±70 | -191±38 | 1704±376 | 10.2% |
| 5 | GI6b | 280.0 - 289.5 | -220.3±7.0 | 2000±80 | -50±54 | 416±455 | 8.8% |
| 6 | GI6c | 251.5 - 260.0 | -190.1±7.2 | 1690±70 | -122±90 | 1050±820 | 8.5% |
| 7 | GI6c | 310.0 - 321.0 | -238.3±6.9 | 2190±80 | -302±42 | 2889±479 | 8.9% |

The ANU data were obtained by radioactive decay counting, and are based on single 1000 minute counting periods.

The column labelled "$CO_2$ Yield" lists the fractional weight of each spicule that was converted to $CO_2$. Note that the maximum yield that can be obtained from pure carbonate is 12%.

Ages are based on the Libby ½-life, 5570 years. Figure 4 shows a plot of spicule (AMS) ages vs. bulk carbonate ages.

## 7. Discussion

The first conclusion to be drawn from the AMS data is that counting statistics form the main limitation. This originates in the low source output for many of the COT samples, caused in part by the relatively low carbon yield from some of the spicules. Other contributing factors, involving target preparation and source alignment, can be improved, which should lead to higher transmission efficiency.

The capability of the AMS system to run in a stable manner and give reproducible results is shown by the measurements comparing the modern

COT standard with NBS oxalic (Fig. 1, sect. 5 above). The value of $D^{14}C$ = 149 ± 16°/₀₀ compares well with the ANU figure of 145 ± 10°/₀₀.

Comparison of the ANU bulk carbonate ages with the AMS ages for individual spicules shows that there is a clear tendency for the spicule ages to follow the carbonate ages, with some notable exceptions at JCU #5, (Core #GI6b, depth 280 cm) and JCU #1, (Core GI2c, 405 cm). Marginal agreement can be seen at JCU #10, (Core #JB8b, 250 cm) and JCU #7, (Core #GI6c, 310 cm). Inspection of the AMS data shows no obvious reason to conclude that these deviations are not real, in spite of the large errors. They suggest that taking a bulk carbonate age estimate as representative of the age of all spicules at a given depth could be misleading. What is required is a number of measurements on individual spicules at the same level in order to determine the actual spread of ages encountered. This way, it might be possible to determine whether or not bio-turbation or other causes have smeared out the age-depth relation to the extent that no useful information can be obtained.

An alternative approach could be to measure a large number of spicules along a core and see if the ages obtained fall into clear-cut periods. This would have the advantage of making bio-turbation effects irrelevant, although the use of AMS would be necessary for the entire exercise.

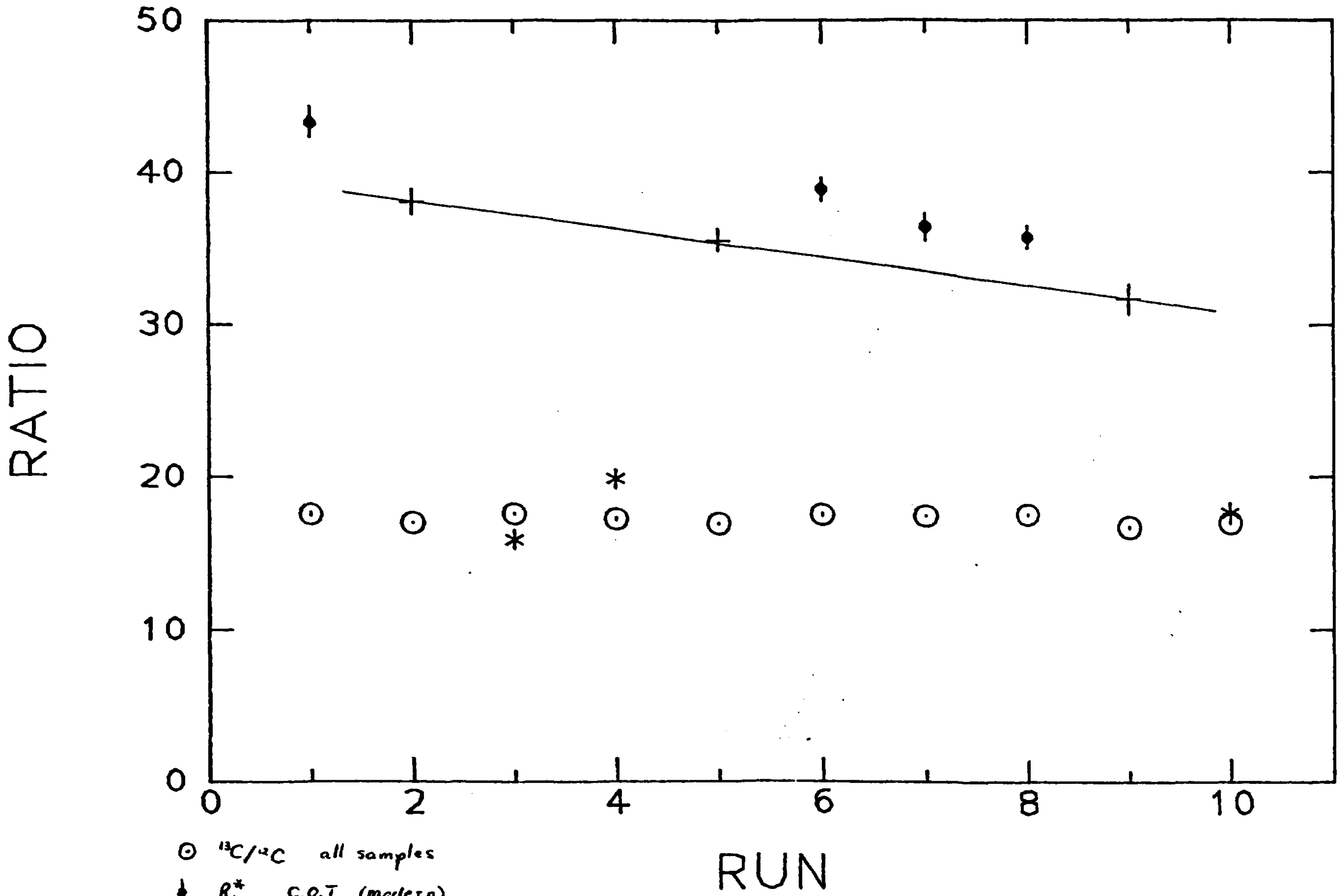
## REFERENCES

[1] D.C. Lowe and W.J. Judd, in preparation.

[2] A.E. Litherland, R.P. Beukens, W.E. Kieser, L.R. Kilius, H.W. Lee, Nucl. Instri. and Meth. B13 (1986), 663

[3] M. Stuiver and H.A. Polach, Radiocarbon 19 (1977), 355.

# C.O.T. STANDARD 14C RATIOS




⊙ $^{13}C/^{12}C$ all samples

ɸ $R^*_{14}$ C.O.T. (modern)

+ $R^*_{14}$ Oxalic standard

* $R^*_{14}$ shells.

Figure 1

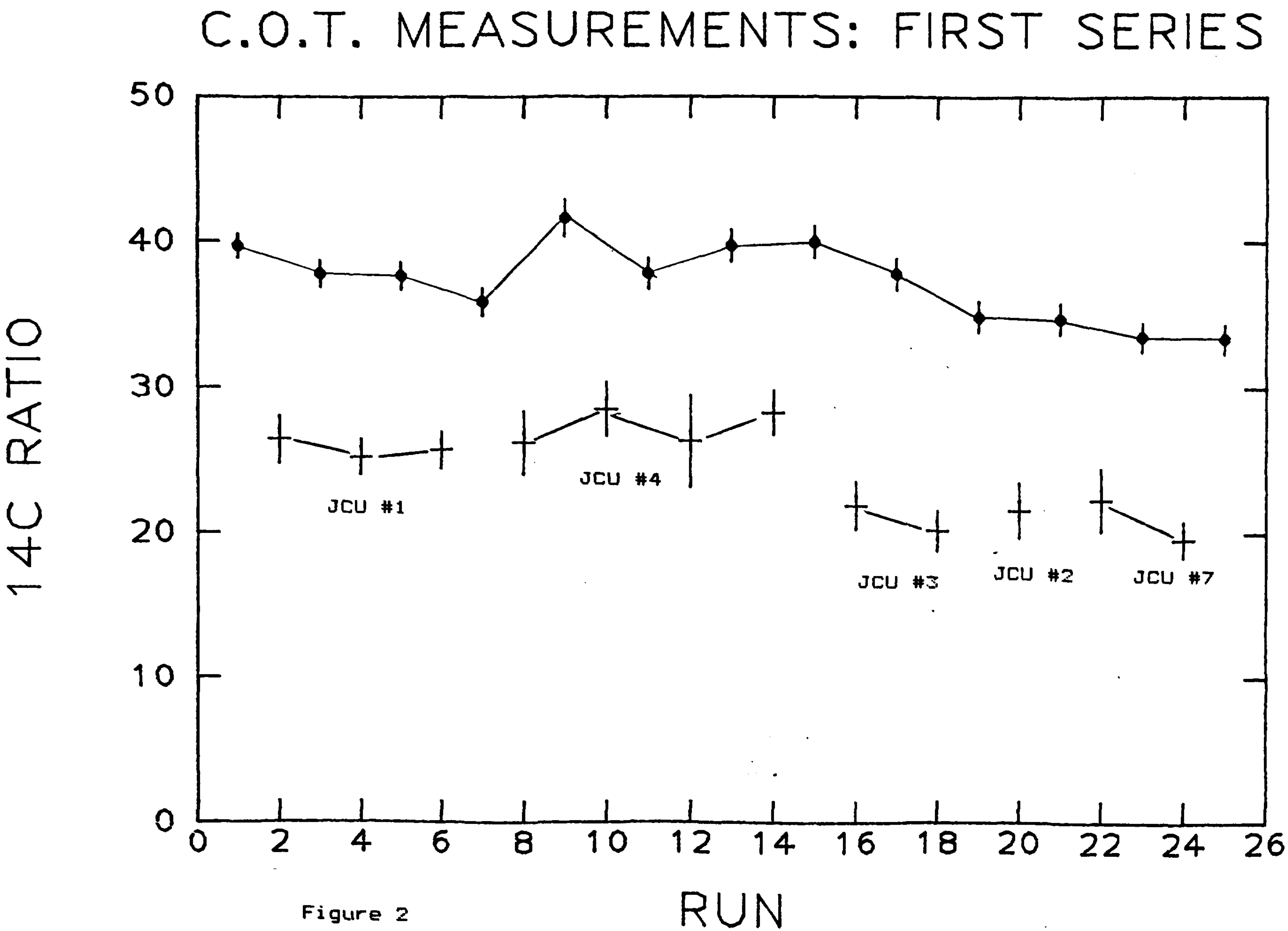

C.O.T. MEASUREMENTS: FIRST SERIES
50
40
30
20
10
0
14C RATIO
JCU #1
JCU #4
JCU #3
JCU #2
JCU #7
0
2
4
6
8
10
12
14
16
18
20
22
24
26
RUN

Figure 2

# C.O.T.: AMS AGES VS. BULK AGES

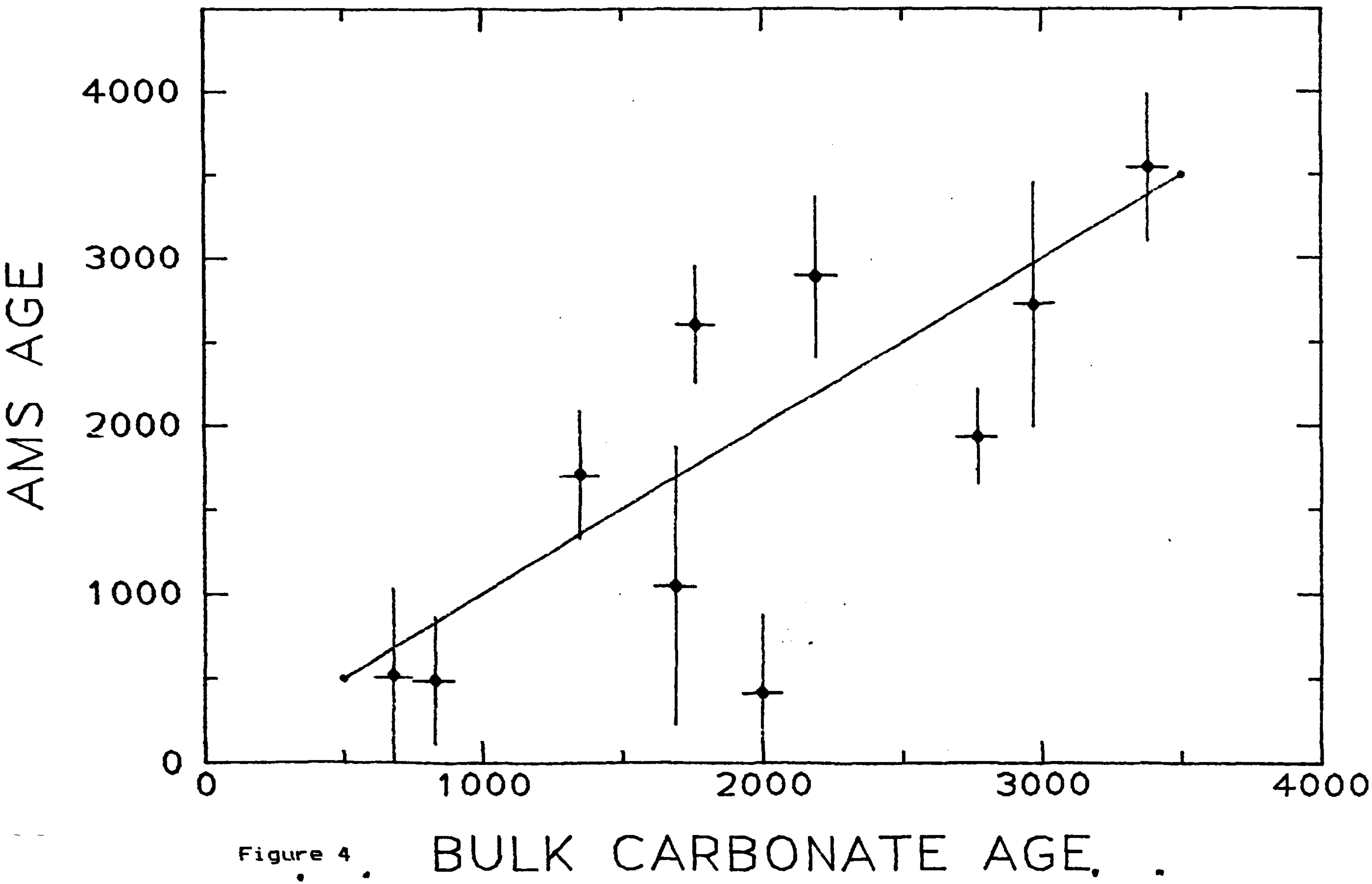



Figure 4