

VARIATIONS IN THE RATIO $^{48}\text{Ca}/(\text{TOTAL Ca})$ IN THE NATURAL ENVIRONMENT

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INTRODUCTION

The study of variations in the abundances of stable isotopes in the natural environment has been a fruitful one. Natural variations in the abundances of the stable isotopes of the elements of carbon, oxygen and sulphur have been useful tools in elucidating many geochemical and biochemical processes. Prompted by these results an investigation was undertaken to determine whether the stable isotopes of calcium fractionate in nature.

Calcium possesses six stable isotopes (*Table 1*) ranging in mass from ^{40}Ca to ^{48}Ca . The 20 per cent mass difference between these two nuclides compares favourably with the isotopic mass differences exhibited by carbon, oxygen and sulphur which have already been shown to undergo appreciable fractionation in the natural environment.

Table 1. Abundances of the isotopes of calcium (White and Cameron⁴)

<i>Isotope</i>	^{40}Ca	^{42}Ca	^{43}Ca	^{44}Ca	^{46}Ca	^{48}Ca
<i>Abundance (%)</i>	96.92	0.64	0.132	2.13	0.0032	0.179

Several earlier workers¹⁻⁵ studied the isotopic composition of calcium by solid-source mass spectrometry. The results obtained by these authors suggested that variations might exist, but, except for the Bikita lepidolite determination by Backus⁵ where the sample contained a large percentage of radiogenic ^{40}Ca and the cosmic-ray-induced anomalies in iron meteorites reported by Stauffer and Honda⁶§, it has never been entirely clear that the differences in the calcium isotopic abundances reported by these various workers were due to actual sample variations and not to inherent difficulties of solid-source spectrometry.

This investigation was carried out in two phases. The first phase was concerned with developing a technique of precision neutron activation analysis which would be sufficiently sensitive and accurate to reliably determine small variations (0.5 per cent or greater) in the relative abundance of ^{48}Ca and of devising an analytical method of determining total calcium with a precision of 0.1 per cent. The second phase consisted of using these methods to determine the extent and locale of any calcium isotopic fractionation. The experimentally-determined quantity in this study has been

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§ These isotopic differences result from nuclear phenomena and neither the Bikita lepidolite nor the meteoritic anomalies constitute a case of isotopic fractionation.

the $^{48}\text{Ca}/(\text{total Ca})$ ratio. By referring to *Table 1*, it can be seen that this ratio approximates the $^{48}\text{Ca}/^{40}\text{Ca}$ ratio.

RESUMÉ OF THE METHOD

The analytical method for this isotopic study is based upon independent determinations of the ^{48}Ca and total calcium contents of the sample. An amount of sampling containing approximately 40 mg of calcium is dissolved and taken through several purification steps with the result being a solution of calcium nitrate acidified to a pH of 1 with nitric acid (*Figure 1*). This solution is divided into carefully-weighed portions for the ^{48}Ca and total calcium determinations.

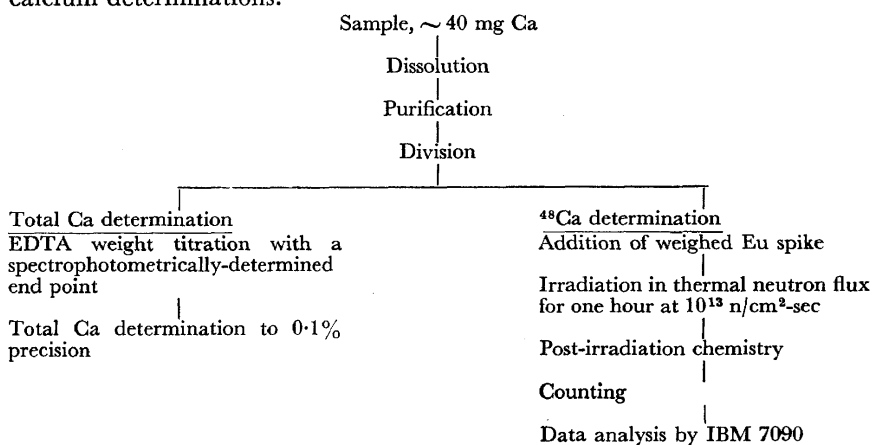
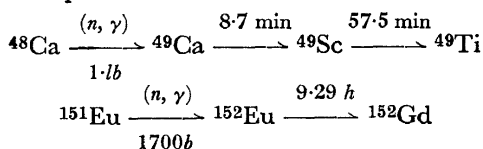


Figure 1. Outline of the method

The total calcium content of the sample is determined by an EDTA weight titration with a spectrophotometrically-determined end point. After approximately 97 per cent of the titrant has been added from a weight burette, the sample is placed in the cell compartment of a Beckman DU spectrophotometer and the remaining 3 per cent of the titrant added with a microburette. The absorbance is monitored at a wavelength of 510 μ until the end point is reached. The precision attainable in the total calcium determination is routinely better than 0.1 per cent. This method is an adaptation of the one reported by Carpenter⁷.

The ^{48}Ca content of the sample is determined by precision neutron activation analysis. The portion of the sample for this determination is spiked with approximately 5×10^{-2} μg of europium which acts as an internal standard. This calcium-europium solution is then packaged, irradiated, put through a post-irradiation chemistry step and counted using an end-window beta proportional counter equipped with an automatic sample changer and a print-out timer. The pertinent nuclear reactions are:



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The beta particles emitted by ⁴⁹Sc and ¹⁵²Eu are counted. The counting data are punched onto cards and the decay curve is resolved using Rogers'⁸ "Frantic" programme for IBM computers. The uncertainty introduced by the counting statistics is the major source of error in the ⁴⁸Ca determination. The uncertainty in the measurement of the ⁴⁸Ca content of a single sample is normally between 0.2 and 0.4 per cent. A detailed presentation of the entire analytical procedure is given by Corless⁹.

The method itself is a relative one in that all sample ⁴⁸Ca/(total Ca) ratios are compared to that of a standard. One or two reference standards are included in each irradiation. Some further comments are made in a later paragraph concerning reference standards.

EXPERIMENTAL RESULTS

Samples

Samples representing the geologic, oceanographic and biological environments were collected and analysed for their ⁴⁸Ca/(total Ca) ratios. The sample selection for this survey study was carried out with the aim of choosing samples or sets of samples which represented diverse origins and environments in order to maximize the possibility of finding any existing isotopic fractionation.

Definition of terms

All data are reported in terms of the quantity δ :

$$\delta = \left(\frac{R_s}{R_r} - 1 \right) 10^3$$

where R_s is the ⁴⁸Ca/(total Ca) ratio of the sample and R_r is that of the reference standard. The term δ is thus the deviation per mil in the ⁴⁸Ca/(total Ca) ratio of the sample from that of an arbitrary standard. The standard used in this work was a reagent-grade CaCO₃ designated as reference standard R_2 .

Results

Table 2 presents a tabulation of the δ values of the samples analysed in this preliminary study and brief sample descriptions. The uncertainties assigned to these δ values are the combined uncertainties of the sample and reference standard for that run. It should be born in mind, however, that the majority of the data reported in Table 2 is single determinations. The authors are of the opinion that the δ values for samples 19, 66, 68 and 69 are particularly to be regarded as suspect until redetermined. The best estimate of the reliability of this new analytical procedure and of the magnitude of the isotopic fractionation detected thus far in this investigation can be made from Figure 2.

Table 2. Sample tabulation

Sample no.	Description	δ
3	Calcite, var. Iceland spar Chihuahua, Mexico	-11.0 \pm 5.0

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Table 2—continued

<i>Sample no.</i>	<i>Description</i>	δ	
4	Human tooth	-33.0	5.0
9	Snail shell Gay Head, Martha's Vine- yard, Massachusetts	-5.5	7.0
19	Human tooth	-80.0	11.0
29	Pegmatitic apatite Kola Peninsula, U.S.S.R.	-11.0	5.0
36	Same as 3	-7.5	4.5
37	Snail shell Atlantic City, N.J.	-2.5	4.5
38	Pegmatitic apatite Renfrew Co., Ontario, Canada	-8.0	9.0
39	Same as 38	-16.0	9.0
41	Oyster shell Atlantic City, N.J.	6.5	7.0
42	Sea water Atlantic City, N.J.	15.5	6.0
43	Clam shell Atlantic City, N.J.	8.0	6.0
44	Groundhog tooth	-9.0	5.5
45	Groundhog rib	-4.5	6.5
50	Human tooth	-23.5	9.0
53	Carbonatite Oka Complex Oka, Quebec, Canada	7.5	3.5
54	Fibrous apatite Oka Complex Oka, Quebec, Canada	21.0	3.0
55	Grenville limestone near Hull, Ontario, Canada	4.0	3.0
65	Same as 42	13.0	4.5
66	Sea water Hypersaline water west of Andros Is. in the Bahamas 24° 50'N, 79° 55'W	50.0	5.5
67	Sea water Open ocean off the Bahamas 25° 20'N, 77° 50'W	25.0	5.0
68	Oolites Brown's Cay, Bahama Is. 25° 27'N, 79° 09'W	48.0	5.0

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Table 2—continued

Sample no.	Description	δ	
69	Aragonitic mud West of Andros Is. in the Bahamas 24° 48'N, 78° 25'W	54.0	4.5
77	Homestead meteorite	8.5	5.0
78	Same as 77	6.5	4.0

In *Figure 2* are presented in graphic form the replications of samples and reference standards. The plotted value is the $^{48}\text{Ca}/(\text{total Ca})$ ratio of the sample or reference standard (standards denoted by *R*) plus and minus the uncertainty for that particular determination. The horizontal scale is in terms of the quantity δ . The vertical scale has no significance. In Runs 1 and 3 the duplicate standards do not agree within the calculated uncertainties. A careful scrutiny of the procedure revealed that the counter was undergoing sensitivity variations of the order of 1 per cent over the counting period of a run. The subsequent introduction of a counting standard against which the samples and reference standards were normalized corrected this deficiency as is evidenced by the agreement between the reference standards in Runs 8, 10, 14 and 23. In Run 13, the reference standard was lost due to a mishap. Therefore, for the purpose of comparing Runs 13 and 17, sample 42 in Run 13 was drawn directly under sample 42 in Run 17. The descriptions of the samples presented in *Figure 2* are given in *Table 2*. Run 23 exemplifies the precision and sensitivity of the procedure at its present stage of development.

THE REFERENCE STANDARD

The supply of the reference standard employed in this initial study designated as standard R_2 , is nearly exhausted. A large quantity of a new reference standard, R_3 , has been obtained and will be used by the authors in subsequent studies. A quantity of R_3 will be made available to any interested investigator in order to facilitate the exchange and comparison of data.

CONCLUSION

Based on the results of this initial study the authors have concluded that the isotopes of calcium do undergo significant fractionation in nature. While it is true that the analytical method requires further development and that a considerable amount of additional data must be gathered to verify the variations detected in this investigation, the procedure does bear promise of developing into a useful tool for investigating geochemical and biochemical systems.

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