

MASTER

CARBON AND OXYGEN ISOTOPES IN APATITE CO₂
AND CO-EXISTING CALCITE¹

by

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Abstract

Carbon and oxygen isotopes were analyzed in carbonate apatite CO_2 and in co-existing calcite. Both C and O in apatite CO_2 are enriched in the respective light isotopes relative to calcite. These results confirm the proposition that carbonate is part of the apatite structure.

Introduction

Analyses of many natural apatites show them to contain appreciable quantities of CO_2 (up to 5 or 6 per cent), and specific names have been proposed for these species. Francolite has been used to describe carbonate-rich apatite which contains more than 1 per cent of fluorine, whereas dahlite applies to carbonate-rich apatite with low concentration of fluorine (1).

The structural nature of carbonate apatite has been a matter of controversy for thirty years (2,3,4). Sufficient evidence, based on x-ray, infra red spectroscopy and optical properties is now present to suggest that carbonate is part of the apatite structure (5,6,7,8).

Carbonate apatite can be formed in the laboratory by replacement of calcite. This was performed by Ames (3) who used C^{14} labelled CaCO_3 and formed carbonate apatite by reacting the calcite with a Na_3PO_4 aqueous solution. The carbonate apatite so formed is due to an incomplete replacement of CO_3^{-2} by PO_4^{-3} .

The purpose of the work reported here was to investigate the

location of CO_3 in sedimentary apatite by analyzing the isotopic composition of the carbon and oxygen in apatite CO_2 .

Infrared spectra of carbonate apatite (8, 9, 10, 11, 12, 13) indicate that the structural environment of carbonate in apatite differs from that in calcite. Therefore, the isotopic composition of carbon and oxygen in apatite derived CO_2 would be expected to differ from that of CO_2 obtained from co-existing calcite.

Experimental

A total of 29 samples were analyzed. These included ovulite phosphorites dredged from the sea off California and Agulhas Bank, phosphatized limestones from Chatham Rise, pellet-bone phosphorites and phosphatic limestones from the Campanian Mishash Formation in Israel. One sample of a living inarticulate brachiopod was analyzed-- a Lingula from the SE sector of Kaeohe Bay, Hawaii from 2m deep water, 26.5°C temperature and a salinity of 33.8‰ .

Dr. D.R. Simpson from Lehigh University kindly provided us with two synthetic carbonate-apatites he prepared. Both of them were made by reacting calcite with sodium phosphate (14). Sample SI-1 is one phosphate sample which was prepared from the calcite analyzed as SI-2. Sample SI-C6 contains unreacted calcite.

A flow sheet of the analytical procedure is shown on Figure 1. Calcite and apatite were separated chemically by dissolving calcite in triammonium citrate for 50 hours at 30°C . The technique was described in detail by Silverman and his co-workers (5). After treatment, the residue was x-rayed to ensure complete disappearance of calcite peaks. It was then assumed that all the CO_2 extracted

from the residue was derived from apatite-bound carbonate.

Carbon dioxide for isotopic analysis was extracted by reacting the samples (~ 0.04 g for calcite-rich samples, ~ 0.1 - 0.3 g for calcite-poor apatite) with phosphoric acid using the methods developed by McCrea (15).

The following tests were performed to ensure validity of the procedure:

a. Calcite-free apatite did not show any difference in the volume of CO_2 evolved before and after the triammonium citrate treatment. Neither did the treatment affect the δC^{13} value. Since δC^{13} of the citrate used (-24.9%) was isotopically much different from that of the samples studied the above result proves that no measurable exchange occurred.

b. No measurable CO_2 could be evolved by reacting citrate with phosphoric acid.

c. The 50 hours' reaction time with triammonium citrate was chosen after proving that this time is sufficient to dissolve all the calcite.

The isotope analyses are reported in terms of δ per-mil relative to the PDB standard.

All samples were run in duplicates: an average value for the duplicate analyses is reported. From repeated analyses of a single homogenized sample, as well as from a statistical analysis of the duplicate runs, the standard deviation of the overall procedure is estimated as 0.2 per mil. In all calculations where errors are reported, the aim was to achieve 95% confidence levels, hence an error of two standard deviations (0.4%) was assumed for the analyses.

From the volume of CO_2 evolved from the total sample and that evolved from apatite only, and from the δC^{13} or δO^{18} obtained on the total sample and apatite δO^{18} or δC^{18} of calcite was calculated using:

$$\delta_{\text{ap}} \cdot P_{\text{ap}} + \delta_{\text{cal}} \cdot P_{\text{cal}} = \delta_{\text{total}} \cdot 100 \quad (1)$$

where P_{ap} and P_{cal} are the percentages of apatite CO_2 and calcite CO_2 in total CO_2 evolved. Due to the structure of formula (1) the propagated error in values in calcite is large especially in cases where almost all the CO_2 was contributed by apatite. One must therefore view with caution all results where little calcite was present.

The fractionation between the two co-existing minerals is expressed by:

$$\Delta_{\text{CA}} = \delta_{\text{cal}} - \delta_{\text{ap}} \quad (\text{for } \text{O}^{18} \text{ or } \text{C}^{13}) \quad (2)$$

and

$$\alpha_{\text{CA}} = \frac{R_{\text{calcite}}}{R_{\text{apatite}}} \approx 1 + \frac{\Delta_{\text{CA}}}{1000} \quad (3)$$

where R is the ratio of abundance of $\text{O}^{18}/\text{O}^{16}$ and $\text{C}^{13}/\text{C}^{12}$ as recorded by the mass spectrometer. The error which applies to calculations of δ_{cal} is obviously propagated in calculating Δ_{CA} .

The reaction of carbonate with anhydrous H_3PO_4 involves the liberation of only two thirds of the oxygens. The isotopic fractionation for this reaction is constant at constant temperature. In this work α is assumed to be the same for calcite and carbonate apatite. This assumption is probably incorrect. It has been shown (16) that

whereas $\alpha_{\text{calcite}} = 1.01008$, $\alpha_{\text{dolomite}} = 1.01090$. α_{apatite} is not known at the present time, hence the δ values for apatite should be considered as a first approximation only. Once α_{apatite} will be determined, however, all the δ values reported here can be converted to true values.

Results

Tables 1, 2 and 3 summarize the results of calcite content, relative contribution of CO_2 by calcite and by apatite, and the isotopic composition of CO_2 from the total sample and from apatite after citrate dissolution. Calculated values for the isotopic composition of calcite CO_2 and for the difference Δ_{CA} are also included in the tables. Figures 2 and 3 summarize the analytical data graphically.

Attempts to interpret our analytical results are severely encumbered by several difficulties:

1. As the error in δ_{cal} is a propagated error, it becomes extremely large in samples which are very close to being monomineralic. This makes the comparison of δ_{cal} with δ_{apat} difficult in some cases.

2. If one is to use the isotope data in order to obtain information on the location of carbonate in the structure, one has to assume that all other factors determining the formation of apatite and calcite were identical. This is not necessarily the case, since there is a possibility that apatite and calcite in the studied rocks were not deposited contemporaneously. In several of the rocks from Israel, secondary calcite can be seen under the microscope so that one may claim here that differences in isotopic composition between calcite and apatite are actually differences in

the composition of the aqueous medium from which they were deposited.

3. In the francolite shell analysis of Lingula from Hawaii, the result is difficult to interpret. Although no calcitic shells of animals co-existing with the Lingula were available for analysis, the δO^{18} value in the apatite CO_2 is close to -6% , whereas calcite at equilibrium with sea water at the given temperature ($26.5^\circ C$) should have a δO^{18} value of $\approx -2\%$.

The following trends were, however, observed in the data:

a. Although the errors are large for the calcite values, the most probable value for calcite carbon almost always appears more enriched in C^{13} than the CO_2 in the apatite of the same sample (Fig. 2). Oxygen data are less regular (Fig. 3).

b. Several samples may be singled out for their importance in checking the significance of the results: (1) MK66Ca is an Israeli phosphorite with a calcitic matrix. This calcite seems to be enriched in heavy carbon and light oxygen as compared to the adjacent apatite-carbonate. MK66Si is a sample taken from the same hand-specimen, in which the matrix was silicified. No significant difference between two phases was observed here in either δC^{13} or δO^{18} . (2) Sample SI-C6 is a synthetic apatite prepared by Simpson, in which not all the calcite was reacted. There is no way in which later changes could have influenced this sample. Nevertheless, the relict calcite in SI-C6 is enriched in C^{13} and O^{18} as compared to the co-existing apatite (Figs. 2 and 3).

c. The most important result, is that in all but two samples in which both apatite and calcite are abundant, the isotopic composition of apatite CO_2 differs significantly from calcite CO_2 .

DISCUSSION

When examining Figs. 2 and 3, one has to bear in mind that the several populations represented differ from each other by more than their geographical location.

Whereas the California and Israel samples are textbook phosphorites (the former pelletal, the latter having a considerable bone component), the Chatham Rise samples and KP54 are phosphatized limestones. Thus, whereas the pellet phosphorites may have formed either as a direct precipitate from sea water or as a replacement product of calcite, the same does not apply to the Chatham Rise samples. They probably are the closest natural analogue of sample SI-C6, which was synthetically prepared by phosphatizing a calcite. One anomalous feature which should be noted, in the Israeli Mishash phosphorites, is the enrichment of the light isotopes (both in calcite and apatite), as compared to normal marine limestones (17).

Noting the above-mentioned characteristics the following generalizations can be made:

No significant differences are evident in most California phosphorites between the isotopic composition of calcite and apatite CO_2 . Exceptions are KP62 where the calcite carbon is significantly heavier than the apatite counterpart. The relation in samples KP33 and KP51 is interesting; whereas the black, organic matter-rich cores of these samples show no significant fractionation, there is a significant enrichment in O^{18} in the calcite of the outer parts of the nodules where organic matter is depleted. No simple explanation for this fact is offered. One possibility is that the calcite re-equilibrates with colder, O^{18} -enriched water after

deposition. It is impossible to determine whether the apparent similarity in isotopic composition of apatite and calcite in California phosphorites is a true phenomenon or whether it is caused by the very large errors in δ_{cal} (these samples having practically no calcite in them).

For almost all other samples, where there is a measurable amount of calcite, both oxygen and carbon are enriched in apatite CO_2 in their respective light isotopes. This holds true for the Chatham Rise samples, those from Israel and the synthetically prepared sample SI-C6. In the analyzed Lingula sample the reverse phenomenon is observed; calcite carbon is lighter than apatite carbon.

From plots of calcite content of the rock versus $\Delta_{\text{CA}}^{\text{C}^{13}}$ and $\Delta_{\text{CA}}^{\text{O}^{18}}$ ($=1000 \ln \alpha_{\text{CA}}$). As in Figs. 4 and 5 it appears that the fractionation of carbon between calcite and apatite increases with decreasing percentage of calcite in the rock.

This trend is even more evident for oxygen than it is for carbon (Fig. 5), where the linear correlation coefficient is significant $r = -84$.

In the process of phosphatization of limestone, the percentage of remaining calcite can serve as a good measure of how far the process has advanced. It seems therefore, that fractionation increases with increasing phosphatization, which suggests that isotopically light CO_2 is preferentially removed from the pre-existing calcite during this process, probably as bicarbonate.

Conclusions

The results of this study show that there is a difference in the isotopic composition between CO_2 extracted from apatite and that from co-existing calcite. It is concluded here that both oxygen

and carbon in apatite CO_2 are enriched in the light isotopes of each element as compared to the co-existing calcite. If the CO_2 which is associated with the apatite were just representing calcite which was not dissolved by the citrate treatment, one would expect its isotopic composition not to differ from the rest of the calcite in the rock. A quantitative estimate of calcite apatite fractionation is more difficult. Average values were calculated for $\Delta_{\text{CA}}\text{C}^{13}$ and $\Delta_{\text{CA}}\text{O}^{18}$ as 2.8 ‰ ($\delta = 1.0028$) and 2.1 ‰ ($\delta = 1.0021$) respectively for all significant data.

It is therefore concluded that the stable isotope data are in accord with other investigations, in particular with infrared spectroscopy, and indicate that carbonate does enter the apatite structure. There is no way to obtain further information on the location of CO_2 in apatite from the present isotopic analyses. Isotopic studies of apatites prepared at different temperatures and yielding different infrared spectra (13) may furnish further information.

The possibility of establishing a combined carbonate-phosphate geo- or paleo-thermometer on carbonate-apatites should be considered in the light of these results. A word of caution should be given, however, to workers presently studying δO^{18} in co-existing marine apatite-calcite suites. Unless the precaution of removal of apatite CO_2 is taken, the measured fractionation may be in error.

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Figure 1 Flow sheet for analysis of apatite and calcite CO₂.

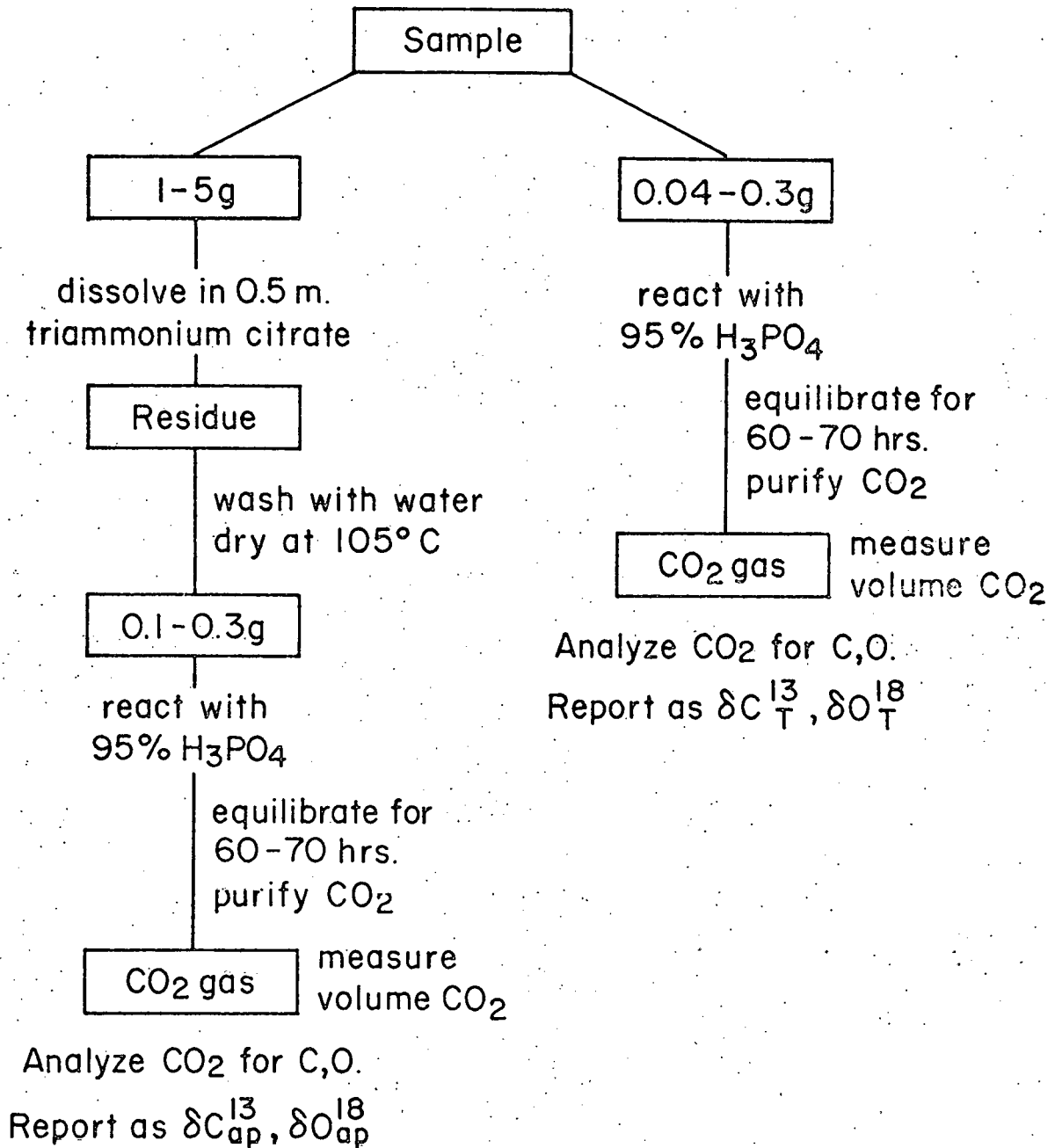


Figure 2 Isotopic composition of CC_2 carbon (δC^{13}) in co-existing apatite and calcite. Vertical lines show margin of error at 95% confidence level.

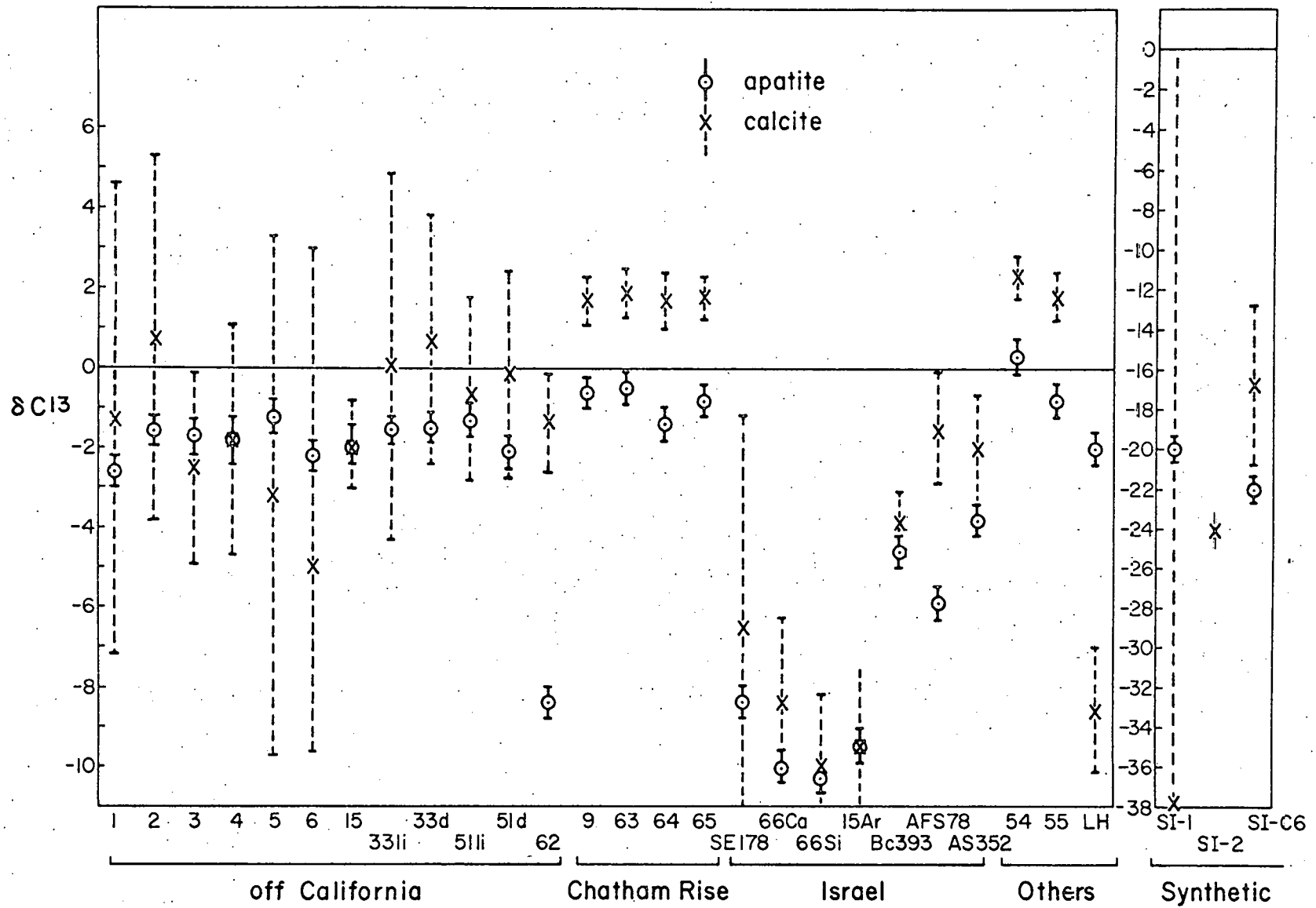


Figure 2

Figure 3 Isotopic composition of CO₂ oxygen (δ^{18}) in co-existing apatite and calcite. Vertical lines show margin of error at 95% confidence level.

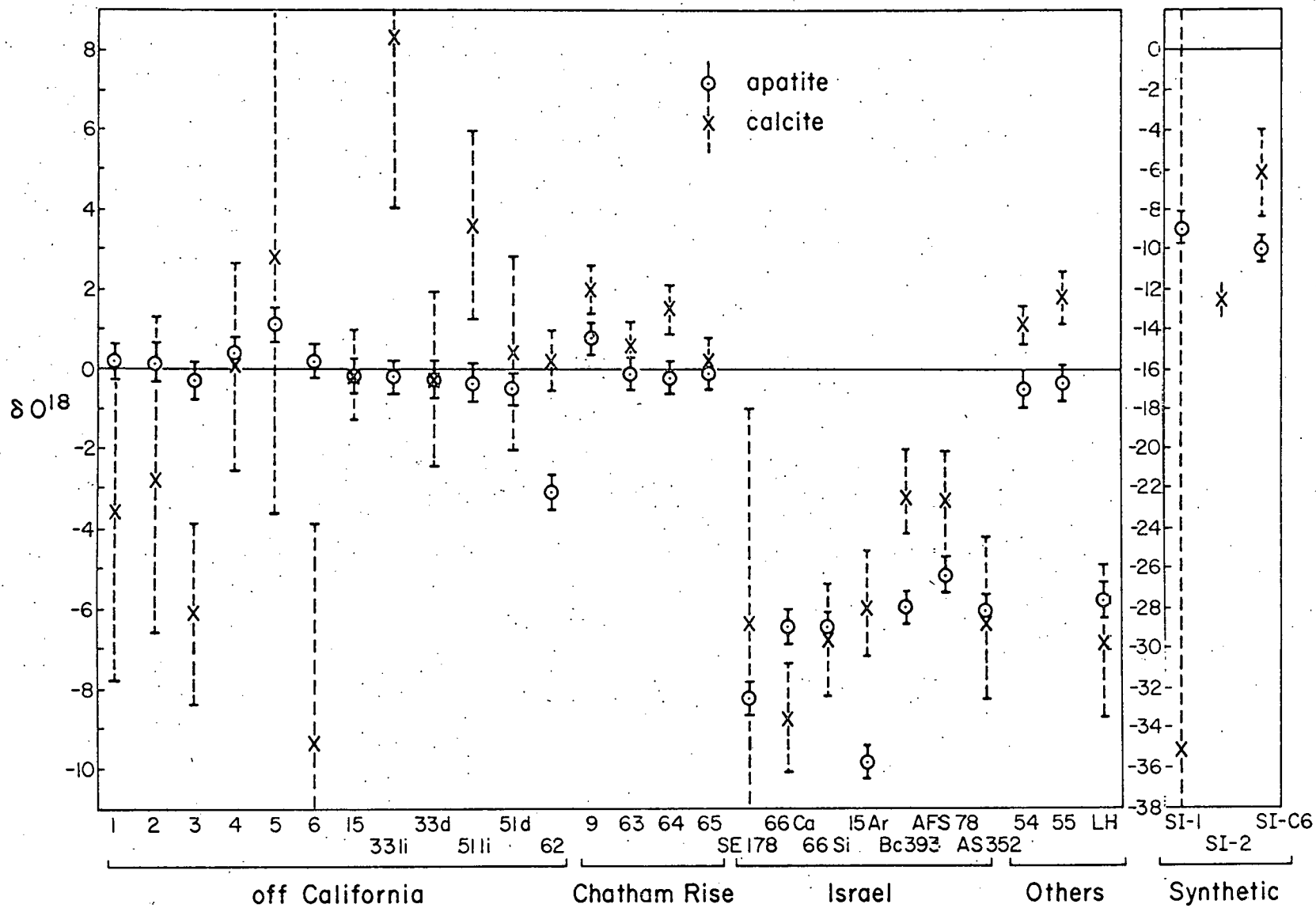


Figure 3

Figure 4

$\Delta_{CA}^{C^{13}}$ ($\delta^{C^{13}}_{cal} - \delta^{C^{13}}_{ap}$) versus the percentage of calcite in the sample. Only Δ_{CA} values which differ significantly from zero were plotted.

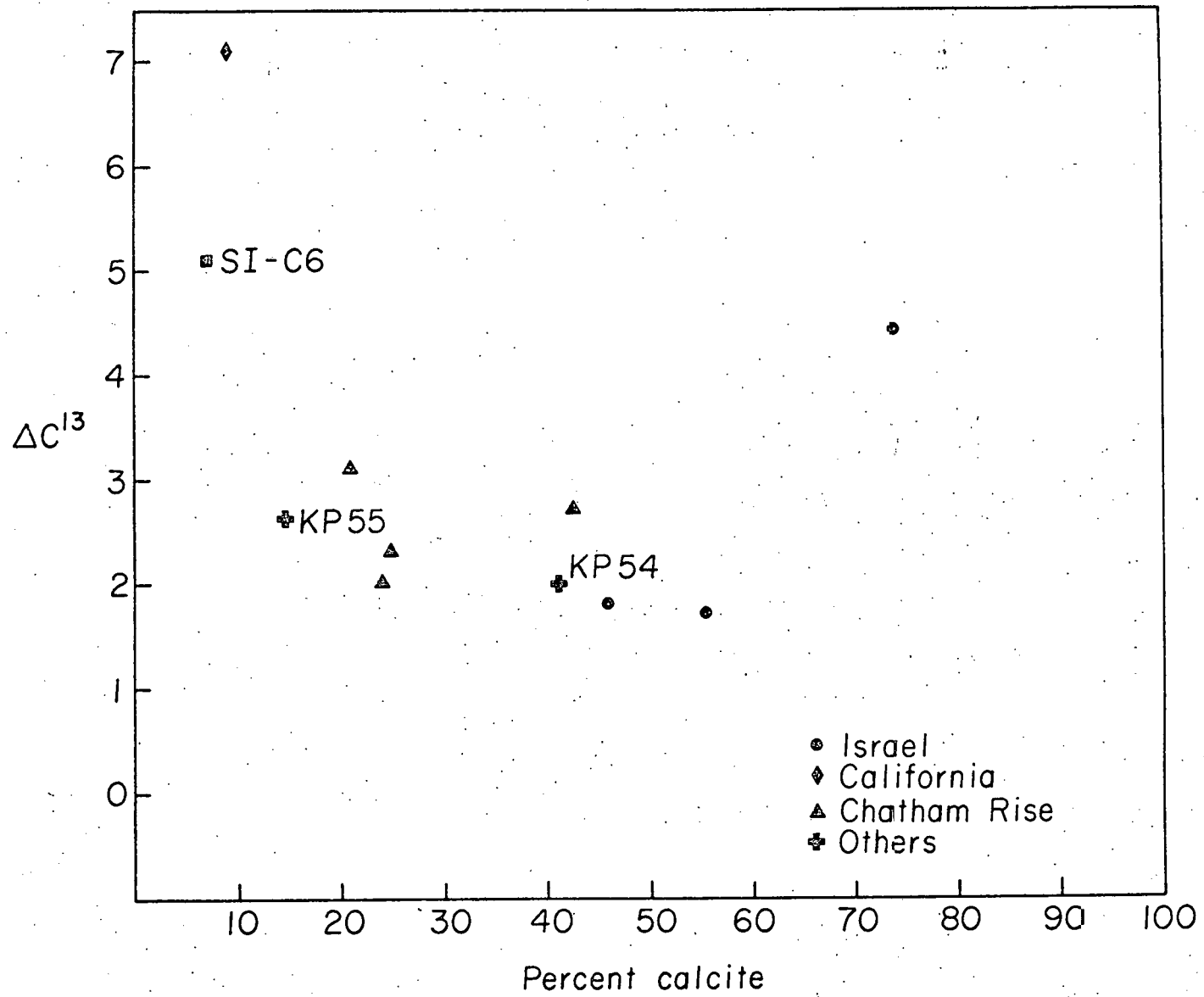


Figure 4

Figure 5 $\Delta_{CA}^{C^{18}}$ ($\delta^{18}_{cal} - \delta^{18}_{ap}$) versus the percentage of calcite in the sample. Only Δ values which differ significantly from zero were plotted. The linear regression line was drawn neglecting point AF S 78, and negative Δ values. The best linear fit is:

$$\Delta_{CA}^{C^{18}} = -0.09 (P_{cal} + 0.4)$$

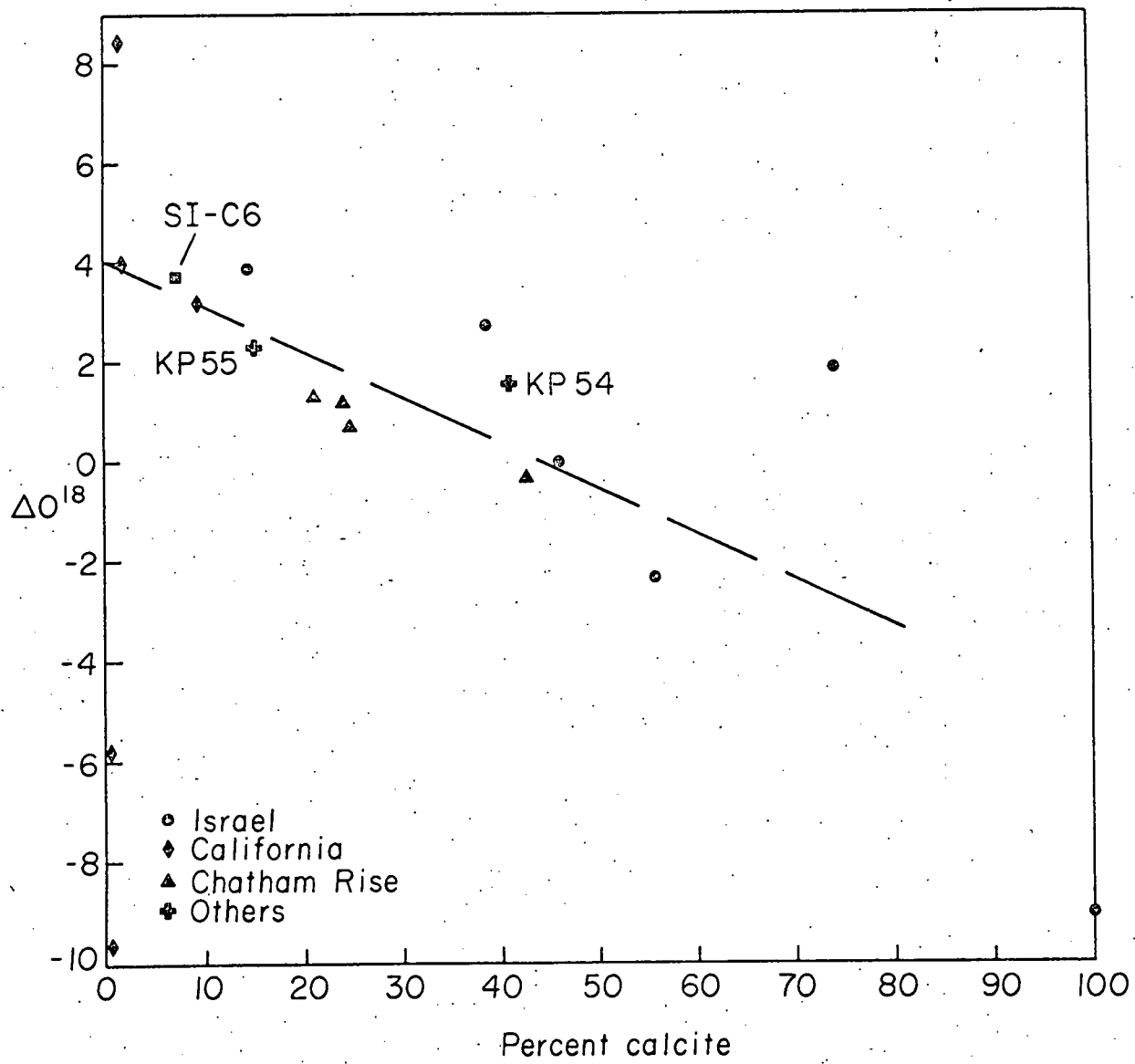


Figure 5

Table 1

Percent Calcite, Percent of CO₂ Contributed by Apatite, and Percent CO₂ in Residue

Sample No.	Sample description	% Calcite	% Apatite CO ₂ (Ap.)	% CO ₂ in Residue (R)
KP1.	Ovulitic phosphorite, off Calif.	1.3	87	3.7
KP2	Ovulitic phosphorite, off Calif.	1.5	86	4.2
KP3	Ovulitic phosphorite, off Calif.	2.2	77	3.2
KP4	Ovulitic phosphorite, off Calif.	1.9	80	3.5
KP5	Ovulitic phosphorite, off Calif.	1.1	90	4.5
KP6	Ovulitic phosphorite, off Calif.	1.3	90	4.9
KP15	Ovulitic phosphorite, off Calif.	3.5	59	2.3
KP33li	Ovulitic phosphorite, off Calif., Light margins of nodule	1.5	87	4.3
KP33d	Same as 33li, dark core of nodule	1.9	82	4.0
KP51li	Similar to 33li	2.0	78	3.2
KP51d	Similar to 33d	2.3	78	3.7
KP62	Phosphate sand, Baja, Calif.	9.3	16	0.8
KP55	Pelletal phosphorite, Agulhas Bank	15.1	32	3.2
KP9	Phosphatized limestone, Chatham Rise	23.9	30	4.4

KP63	Phosphatized limestone, Chatham Rise	24.8	31	4.8
KP64	Phosphatized limestone, Chatham Rise	20.9	33	4.6
KP65	Phosphatized limestone, Chatham Rise	42.4	20	4.7
KP54	Phosphatized limestone, Seamount NT5	41.0	23	5.4
MK66Ca	Pellet-Bone Phosphorite calcitic matrix, Israel	55.3	13	3.7
MK66Si	Same sample as MK66Ca, siliceous matrix	1.8	53	0.9
AR15	Pellet-Bone phosphorite, Israel	14.6	31	2.9
BC393	Pellet-Bone phosphorite, Israel	38.6	21	4.4
AFS78	Phosphatic chalk, Israel	73.9	10	3.8
AS352	Phosphatic chalk, Israel	45.8	6.7	1.5
SE178	Phosphatic limestone, Israel	84.8	3.3	1.3
LH	<u>Lingula</u> , Hawaii	2.0	63.5	1.5
SI-1	Synthetic apatite	1.3	89	4.4
SI-2	Calcite from which SI-1 was prepared	100		
SI-06	Synthetic apatite, not completely reacted	6.9	58	4.1

Table 3

 $\delta^{18}\text{O}$ Values in Total Sample, Apatite, Calculated Value for Calcite and Δ_{CA}

Sample No.	Sample description	$\delta^{18}\text{O}_{\text{total}}$	$\delta^{18}\text{O}_{\text{apat}}$	$\delta^{18}\text{O}_{\text{calc}}$	$\Delta_{\text{CA}}^{18\text{O}}$
KP1	Ovulitic phosphorite off Calif.	-0.3	0.2	-3.6 ± 4.1	I ³
KP2	Ovulitic phosphorite off Calif.	-0.3	0.1	-2.8 ± 3.8	I
KP3	Ovulitic phosphorite off Calif.	-1.7	-0.3	-6.1 ± 2.3	-5.8 ± 2.3
KP4	Ovulitic phosphorite off Calif.	0.3	0.4	0.1 ± 2.6	I
KP5	Ovulitic phosphorite off Calif.	1.3	1.1	2.8 ± 6.4	I
KP6	Ovulitic phosphorite off Calif.	-0.8	0.2	-9.4 ± 5.5	-9.6 ± 5.5
KP15	Ovulitic phosphorite off Calif.	-0.2	-0.2	-0.2 ± 1.1	I
KP33li	Ovulitic phosphorite off Calif. light margins of nodule	0.9	-0.2	8.3 ± 4.2	8.5 ± 4.2
KP33d	Same as 33li, dark core of nodule	-0.3	-0.3	-0.3 ± 2.1	I
KP51li	Similar to 33li	0.5	-0.4	3.6 ± 2.3	4.0 ± 2.3
KP51d	Similar to 33d	-0.3	-0.5	0.4 ± 2.4	I
KP62	Phosphate sand, Baja, Calif.	-0.4	-3.1	0.2 ± 0.7	3.3 ± 0.8
KP55	Pelletal phosphorite, Agulhas Bank	1.1	-0.4	1.8 ± 0.6	2.3 ± 0.7
KP9	Phosphatized limestone, Chatham Rise	1.7	0.8	2.0 ± 0.6	1.2 ± 0.7

	Rise	1.7	0.0	2.0±0.0	1.2±0.0
KP63	Phosphatized limestone, Chatham Rise	0.4	-0.1	0.6±0.6	0.7±0.6
KP64	Phosphatized limestone, Chatham Rise	1.1	0.2	1.5±0.6	1.3±0.8
KP65	Phosphatized limestone, Chatham Rise	-0.2	0.1	-0.2±0.5	I
KP54	Phosphatized limestone seamount NT5	0.7	-0.5	1.1±0.5	1.6±0.7
MK66Ca	Fellet-Bone phosphorite, calcitic matrix, Israel	-8.5	-6.5	-8.8±1.3	-2.3±1.3
MK66Si	Same sample as MK66Ca, siliceous matrix	-6.6	-6.5	-6.8±1.4	I
AR15	Fellet-Bone phosphorite, Israel	-7.2	-9.9	-6.0±1.2	3.9±1.3
BC393	Pellet-Bone phosphorite, Israel	-3.8	-6.0	-3.2±0.9	2.8±1.0
AFS78	Phosphatic chalk, Israel	-3.5	-5.2	-3.3±1.2	1.9±1.3
AS352	Phosphatic chalk, Israel	-6.4	-6.1	-6.4±2.0	I
SE178	Phosphatic limestone, Israel	-6.5	-8.3	-6.4±5.2	I
LH	<u>Lingula</u> , Hawaii	-6.2	-5.8	-6.9±1.9	I
SI-1	Synthetic apatite	-12.0	-9.0	-35.5±24	-26.5±24
SI-2	Calcite from which SI-1 was prepared	-12.5	-	-12.5	-
SI-C6	Synthetic apatite not completely reacted	-8.4	-10.0	-6.2±2.0	3.8±2.0

¹ The margin of error at the 95% confidence level is ± 0.4.

² Errors given at 95% confidence level.

³ $I - \delta^{18}\text{O}_{\text{calc}} - \delta^{18}\text{O}_{\text{apat}}$ does not significantly differ from zero.

Table 2

 $\delta^{13}\text{C}$ Values in Total Sample, Apatite, Calculated Value for Calcite and $\Delta_{\text{CA}}^{13\text{C}2}$

Sample No.	Sample description	$\delta^{13}\text{C}_{\text{total}}$	$\delta^{13}\text{C}_{\text{apat}}$	$\delta^{13}\text{C}_{\text{cal}}$	$\Delta_{\text{CA}}^{13\text{C}2}$
KP1	Ovulitic phosphorite off Calif.	-2.2	-2.6	-1.3 \pm 5.9	I ³
KP2	Ovulitic phosphorite off Calif.	-1.3	-1.6	0.7 \pm 4.5	I
KP3	Ovulitic phosphorite off Calif.	-1.9	-1.7	-2.5 \pm 2.4	I
KP4	Ovulitic phosphorite off Calif.	-1.8	-1.8	-1.8 \pm 2.9	I
KP5	Ovulitic phosphorite off Calif.	-1.4	-1.2	-3.2 \pm 6.5	I
KP6	Ovulitic phosphorite off Calif.	-2.5	-2.2	-5.0 \pm 8.2	I
KP15	Ovulitic phosphorite off Calif.	-2.0	-2.0	-2.0 \pm 1.2	I
KP33li	Ovulitic phosphorite off Calif., light margins of nodule	-1.3	-1.5	0.3 \pm 4.6	I
KP33d	Same as 33li, dark core of nodule	-1.1	-1.5	0.7 \pm 3.1	I
KP51li	Similar to 33li	-1.2	-1.3	-0.6 \pm 2.4	I
KP51d	Similar to 33d	-1.6	-2.1	-0.1 \pm 2.6	I
KP62	Phosphate sand, Baja, Calif.	-2.4	-8.4	-1.3 \pm 1.3	7.1 \pm 1.4
KP55	Pelletal phosphorite, Agulhas Bank	1.0	-0.8	1.8 \pm 0.6	2.6 \pm 0.7

KP9	Phosphatized limestone, Chatham Rise	1.1	-0.3	1.7±0.6	2.0±0.7
KP63	Phosphatized limestone, Chatham Rise	1.1	-0.5	1.9±0.6	2.3±0.7
KP64	Phosphatized limestone, Chatham Rise	0.7	-1.4	1.7±0.7	3.1±0.8
KP65	Phosphatized limestone, Chatham Rise	1.3	-0.9	1.8±0.5	2.7±0.7
KP54	Phosphatized limestone, Seamount NT5	1.9	0.3	2.3±0.5	2.0±0.7
MK66Ca	Pellet-Bone Phosphorite, calcitic matrix, Israel	-8.7	-10.1	-8.4±1.9	1.7±1.9
MK66Si	Same sample as MK66Ca siliceous matrix	-10.1	-10.3	-10.0±1.8	I
AR15	Pellet-Bone phosphorite, Israel	-9.6	-9.5	-9.6±1.2	I
BC393	Pellet-Bone phosphorite, Israel	-4.0	-4.6	-3.9±0.8	I
AFS78	Phosphatic chalk, Israel	-2.0	-5.9	-1.5±1.4	4.4±1.4
AS352	Phosphatic chalk, Israel	-2.2	-3.8	-2.0±1.3	1.8±1.4
SE178	Phosphatic limestone, Israel	-6.6	-8.4	-6.5±5.3	I
LH	<u>Lingula</u> , Hawaii	-4.4	-2.0	-8.6±1.5	-6.6±1.6
SI-1	Synthetic apatite	-22.3	-20.0	-40.3±4.7	I
SI-2	Calcite from which SI-1 was prepared	-24.0	-	-24.0±0.4	-
SI-C6	Synthetic apatite not completely reacted	-19.8	-22.0	-16.8±3.9	5.2±3.9

¹ The margin of error at the 95% confidence level is ± 0.4.

² Errors given at 95% confidence level.

³ $\delta^{13}C_{cal} - \delta^{13}C_{ap}$ does not significantly differ from zero.