$^{18}O/^{16}O$ AND $^{13}C/^{12}C$ RATIO VARIATIONS IN KAJARHAT LIMESTONES

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ABSTRACT

Oxygen-18 and carbon-13 isotopic analyses of Kajarhat limestones from Bhawanathpur area of Palaman District have been carried out. The isotopic data for both carbon and oxygen are in the range of exchanged marine carbonates of Cambrian age. The irregular correlations between the δ values of the samples from the area have been attributed to different extent of dolomitization and post-depositional exchanges with fresh water and carbon dioxide.

INTRODUCTION

THE study of oxygen-18 and carbon-13 isotope distribution in limestones and carbonates have been used for the elucidation of the environmental conditions of formation (Sharma and Sharma, 1970; Pandey *et al.*, 1969; Pillai and Sharma, 1969; Singh *et al.* 1973). Usually the isotopic composition of limestones are dependent upon the temperature of deposition, source of formation and the postdepositional alterations. Limestones are usually deposited in the sedimentary environments at low temperature and their $\delta^{18}O$ and $\delta^{13}C$ values are higher compared to metamorphic and igneous rocks and minerals as suggested by Silverman (1951). The deposition of limestones in marine environment gives higher $\delta^{18}O$ compared to fresh water carbonates due to higher $\delta^{18}O$ value for marine water. The isotopic exchange of the carbonates of the limestone during and after the deposition with fresh water and atmospheric or biogenic carbon dioxide alters the original δ values of the limestones.

In the present work several limestone samples from different sections of Bhawanathpur area (latitude 24° 25', longitude 83° 35'–36' approx.) in the District of Palamau, Bihar, have been studied. The sample belongs to lower Vindhyan Kajarhat limestones of the Basal stage of the Semri series. The isotopic analyses of the samples have been carried out with a view to ascertain the extent of alteration and isotopic exchange.

EXPERIMENTAL

Carbon dioxide was extracted from the samples using 100% phosphoric acid (McCrea, 1950) according to the procedure suggested by Sharma and Sharma (1969). The mass spectrometric analyses were carried out on a 6"–60°–RMS–19 double collecting isotope ratio mass spectrometer in the Department of Chemistry, I.I.T., Kanpur. The isotopic data are reported in terms of δ terminology defined as:

$$\delta\%_0 = \left[\frac{R_{sample}}{R_{standard}} - 1\right] \times 1000$$

where $R = {^{18}O/^{16}O}$ or $^{13}C/^{12}C$ ratio. The δ values are corrected for instrumental effects (Craig, 1967) and are given in terms of SMOW and PDB for oxygen and carbon respectively.

The reaction of the limestones with phosphoric acid was found to be slow indicating the presence of dolomite. X-ray analysis of the samples were carried out on a G.E.C. X-ray diffractometer using a Cu-target and $d(112)$ reflections were recorded by scanning the chart between 28·5° and 32°. The samples showed the calcite and dolomite characteristic peaks around 29·5° and 31° respectively.

RESULTS AND DISCUSSION

The peak heights of the samples from the X-ray spectrum have been shown in Table I. The isotopic data of the limestones are shown in Table II. The $\delta^{18}O$ values of the limestone are lower than the average unaltered limestones (28 to 32‰). The lowering of the $\delta^{18}O$ is attributed to exchange with fresh water according to the reaction

$$\tfrac{1}{3}(C^{18}O_3)^{=} + H_2{^{16}O} = \tfrac{1}{3}(C^{16}O_3)^{=} + H_2{^{18}O}$$

Epstein *et al* (1964) have demonstrated that $\delta^{18}O$ values of limestones change with age due to exchange with fresh water. As the samples belong to lower Vindhyan, the lowering of $\delta^{18}O$ due to exchange with fresh water, is plausible.

The Z values calculated for the samples under investigation according to the equation of Keith and Waber (1964) are listed in Table III. The values are around 120 and thus are indicative of exchanged marine nature of the samples as

TABLE I

X-Ray data for limestone samples

Sample	Calcite peak	Dolomite peak	Ratio Cal./Dol.
A$_8$	35·0	7·5	4·66
B$_1$	59·5	20·0	2·43
B$_2$	21·5	7·0	3·71
B$_3$	8·0	23·5	0·35
B$_4$	3·5	53·5	0·06
B$_5$	11·0	43·0	0·28
C$_1$	35·5	5·25	6·17
C$_2$	33·0	14·0	2·35
C$_3$	32·5	27·5	1·18
C$_4$	25·0	20·5	1·22

TABLE II

Isotopic data for limestones

Sample	$\delta^{18}O$ (SMOW)	$\delta^{13}C$ (PDB)
A$_8$	19·42±0·06	− 0·62±0·05
B$_1$	17·62±0·14	− 1·36±0·04
B$_2$	21·08±0·06	− 1·32±0·12
B$_3$	21·14±0·05	− 1·77±0·08
B$_4$	21·46±0·13	− 0·23±0·06
B$_5$	22·97±0·06	− 0·32±0·02
C$_1$	17·92±0·06	− 1·04±0·05
C$_2$	19·62±0·17	− 0·86±0·14
C$_3$	23·44±0·17	− 0·52±0·16
C$_4$	21·06±0·11	−10·18±0·14

± Represents average deviation for three analyses.

TABLE III

Z values of the limestone samples

Sample	$\delta^{18}O$ (PDB)*	$\delta^{13}C$ (PDB)	Z†
A$_8$	− 9·78	−0·62	121·1
B$_1$	−11·58	−1·36	118·7
B$_2$	− 8·12	−1·32	120·6
B$_3$	− 8·06	−1·77	119·6
B$_4$	− 7·74	−0·23	123·0
B$_5$	− 6·23	−0·32	123·5
C$_1$	−11·28	−1·04	120·0
C$_2$	− 9·58	−0·86	120·8
C$_3$	− 8·14	−1·18	120·8
C$_4$	− 5·76	−0·52	123·4

$\delta^{18}O$ (PDB)* = $\delta^{18}O$(SMOW) − 29·2‰.

Z† = 2·048 ($\delta^{13}C$ + 50) + 0·498 ($\delta^{18}O$ + 50).

suggested in our previous communication (Singh et al., 1973).

The variation of $\delta^{18}O$ values may be explained on the basis of the extent of alteration, i.e., dolomitisation of the limestones. Different peak heights of the samples indicate different amount of dolo-mite and consequently different extent of dolo-mitisation. Calcite (calcium carbonate) exchanges faster with water as compared to dolomite and hence samples containing more dolomite should be heavier in ^{18}O. From the peak heights, ratio of calite and dolomite and $\delta^{18}O$ values no correlation is observed with the dolomite content. The absence of correla-tion may be attributed to the mixed processes operative in dolomitisation. If dolomitisation occurs by metasomatic cation exchange process there should be no difference in the $\delta^{18}O$ values for calcite and dolomite. Whereas in the event of formation of dolomite from the dissolution of calcite by solution process it should enrich the dolomite content by 4 to 6‰. Thus the correlation between $\delta^{18}O$ and dolomite content is likely to be lost due to the formation of dolomite by a combi-nation of the metasomatic and the hydrothermal processes.

There is no regular correlation between $\delta^{18}O$ and $\delta^{13}C$ values and some of the samples show very low value of $\delta^{13}C$ which may be attributed to the postdepositional exchange of the carbonate with biogenic carbon dioxide according to the equation:

$$(^{13}CO_3)^= + {}^{12}CO_2 = (^{12}CO_3)^= + {}^{13}CO_2.$$
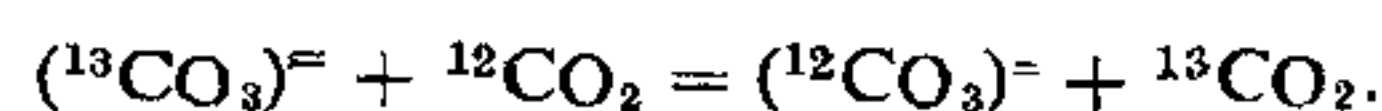
This type of exchange lowers the $\delta^{13}C$ whereas the $\delta^{18}O$ value is not appreciably affected.

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