

Study of Oxygen and Carbon Isotopic Equilibrium in Coexisting Limestone and Crystallised Calcite

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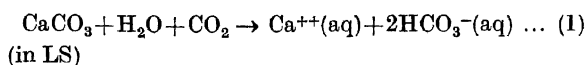
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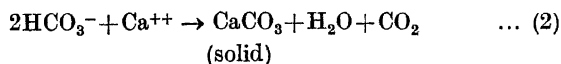
Limestone samples associated with crystallised calcite have been studied for O^{18}/O^{16} and C^{13}/C^{12} variations. The isotopic data are indicative of exchanged marine nature of the samples. The fractionation between the crystallised calcites and the limestones are in the range -1.41 to $+1.49$ for O^{18} and -0.80 to $+2.95$ for C^{13} . The ΔO^{18}_{LS-C} values have been found to be scattered and the scattering in data are indicative of slow processes involved in dissolution and crystallisation under non-isotopic equilibrium. The more positive ΔC^{13}_{LS-C} values are the consequences of the negative δ value of the calcite which may arise due to exchange of the HCO_3^- (from which calcite crystallised) with biogenic carbon dioxide.

THE isotopic species of molecules differ in their thermodynamic properties because the masses of the atoms that constitute them affect the energy states of the molecules. The thermodynamic properties of the isotopic substances, with special reference to the isotopic equilibria have been discussed in detail by Urey¹ and Bigeleisen and Mayer². With the development of precise mass spectrometry^{3,4} extensive work⁵⁻¹¹ has been carried out on the distribution of O^{18} and C^{13} isotopes in natural carbonates. The results have been useful in the study of conditions of formation of the natural carbonates.

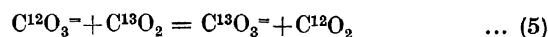
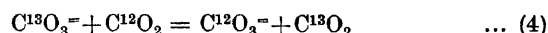
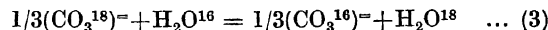
The dissolution and recrystallisation process in the formation of calcite from limestone undergoes several reactions. The dissolution may be represented by the equation :



When the conditions such as partial pressure of CO_2 or the temperature is altered, the $HCO_3^-(aq)$ is converted to $CO_3^{2-}(aq)$ and crystallises as calcium carbonate according to the equation :



Besides the dissolution and crystallisation processes, several isotope exchange reactions, as illustrated below, occur :



The extent of exchange reactions depend upon the nature of the dissolution and crystallisation processes. For slow dissolution and crystallisation, the exchange processes are effective and the isotopic composition of crystallised calcite and the undissolved limestone may show appreciable differences due to thermodynamical isotope effect involved in the exchange reactions. However, for fast reactions, there is no time for exchange and consequently the difference in the calcite and the undissolved limestone may be negligible.

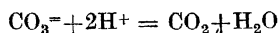
In the present work, several limestone samples associated with crystallised calcite have been analysed for O^{18} and C^{13} content. The samples under investigation are from Sheopahari Hills in Palamau district, Bihar and are of lower Vindhyan system. The analyses have been carried out with a view to ascertain the magnitude of the δO^{18} and δC^{13} , the extent of formation of the isotopic equilibrium in the samples and the mode of formation of the calcites from the limestones.

Experimental

Calcites were separated from the limestone base and both the phases were reacted separately with

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100% phosphoric acid¹². The carbon dioxide liberated according to the reaction :



was extracted and purified according to the procedure given by Sharma and Sharma^{13,14}. 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 of oxygen and carbon are reported in terms of δ values given by the following relations :

$$\delta \text{O}^{18}\text{‰} = \left[\frac{(\text{O}^{18}/\text{O}^{16})_{\text{sample}}}{(\text{O}^{18}/\text{O}^{16})_{\text{standard}}} - 1 \right] \times 1000$$

$$\delta \text{C}^{13}\text{‰} = \left[\frac{(\text{C}^{13}/\text{C}^{12})_{\text{sample}}}{(\text{C}^{13}/\text{C}^{12})_{\text{standard}}} - 1 \right] \times 1000$$

The δ values are corrected for instrumental effects⁶ and are with respect to SMOW and PDB for oxygen and carbon respectively.

Results and Discussion

The isotopic data of the crystallised calcite and the limestones together with the Δ_{LS-C} are listed in Table 1. The δO^{18} values of unaltered sedimentary limestones of recent deposition are around 28 to 32‰, whereas the δO^{18} values of the samples under investigation are in the range of 18 to 21‰. If the original limestone i.e., unaltered sample suffered dissolution, then δO^{18} value of the HCO_3^- should be around 29.5 to 27.5‰ as calculated from the material balance equation:

$$\delta \text{HCO}_3^- = \frac{3}{6} \delta \text{CO}_3^-(\text{LS}) + \frac{1}{6} \delta \text{H}_2\text{O} + \frac{2}{6} \delta \text{CO}_2 \dots (6)$$

where $\delta \text{CO}_3^-(\text{LS}) = 32$ to 28‰ , $\delta \text{H}_2\text{O} = -7\text{‰}$ and $\delta \text{CO}_2 = 44\text{‰}$. For fast crystallisation, δO^{18} of the calcite should be the same as that of the HCO_3^- and for slow process the δO^{18} of the calcite should be about 3‰ higher than the HCO_3^- . Thus the dissolution of the unaltered limestone should produce calcite of δO^{18} in the range of 29.5 to 27.5‰ for fast crystallisation and 32.5 to 30.5‰ for slow crystallisation.

The δO^{18} values of both limestones and calcites are much lower than the expected range and so it may be predicted that δO^{18} value of the limestone before dissolution was lower than the normal marine carbonates. The lowering of δO^{18} is caused due to exchange with fresh water according to equation (3). The Z values calculated for the limestone samples according to the equation given by Keith and Waber¹⁵ are listed in Table 2. The Z value gives the information regarding the origin of the carbonates. If the value of Z is above 120, the carbonate will be of marine origin, and if it is below 120, it will be of fresh water type. The Z values of the samples under investigation are around 120. Though the value is not decisive by itself regarding the classification of the carbonate, but the calculation supports the explanation given earlier that the samples have exchanged considerably with fresh water. The samples are from lower Vindhyan Kajarhat limestones (pre-cambrian age) and with passage of time considerable exchange with fresh water is evident as suggested by Epstein *et al.*¹⁶ for ancient limestones. The interaction with water here is also evident from the crystallised calcite veins occurring in the limestone samples. Because of this isotopic interaction with fresh water, marine limestone eventually loses δO^{18} values. And thus it becomes difficult to find isotopically preserved calcium carbonate in the older sedimentary formations. Therefore, the lowering of δ values, and hence the Z values, for the samples under study is obvious and it is quite reasonable to conclude that the carbonates are representative of exchanged marine limestones.

The $\Delta \text{O}^{18}_{LS-C}$ and $\Delta \text{C}^{13}_{LS-C}$ are in the range of -1.41 to +1.49 and -0.80 to +2.95 for oxygen and carbon respectively. The δO^{18} values of the undissolved limestone and the crystallised calcite are of the same order. The variation of about 1.5‰ in both directions, i.e., for some samples, the calcite is richer in O^{18} , while for others the limestone is richer in O^{18} indicate that slow dissolution and crystallisation must have occurred under non-isotopic equilibrium. Had the equilibrium been under isotopic equilibrium conditions, the variation in Δ values would have taken place only on one side and not scattered on both sides. This scattering of Δ values itself is indicative of isotopic disequilibrium. It

TABLE 1. OXYGEN AND CARBON ISOTOPIC DATA OF CRYSTALLISED CALCITE AND LIMESTONE (Samples of limestone associated with crystallised calcite from lower Vindhyan Kajarhat limestones)

Sample	δO^{18}_C	$\delta \text{O}^{18}_{LS}$	$\Delta \text{O}^{18}_{LS-C}$	δC^{13}_C	$\delta \text{C}^{13}_{LS}$	$\Delta \text{C}^{13}_{LS-C}$
A1	19.79 ± 0.04	18.38 ± 0.05	-1.41	-2.18 ± 0.05	-1.03 ± 0.03	+1.15
A2	20.29 ± 0.11	21.78 ± 0.19	+1.49	-0.57 ± 0.10	-0.96 ± 0.11	-0.39
A3	21.42 ± 0.20	20.45 ± 0.11	-0.97	-0.80 ± 0.11	-0.98 ± 0.11	-0.18
A4	20.53 ± 0.21	21.38 ± 0.17	+0.85	-2.43 ± 0.12	+0.52 ± 0.15	+2.95
A5	21.42 ± 0.08	21.33 ± 0.18	-0.09	+0.17 ± 0.01	-0.38 ± 0.05	-0.55
A6	19.17 ± 0.21	20.16 ± 0.11	+0.99	-0.23 ± 0.02	-1.03 ± 0.07	-0.80
A7	19.67 ± 0.09	20.16 ± 0.12	+0.49	-1.68 ± 0.10	+0.15 ± 0.02	+1.83

C = calcite, LS = limestone. ± = average deviation for three analyses.

may be also plausible that there must have been dolomitisation in the limestones and dolomite being slow in exchange reaction with water, the δO^{18} limestone is heavier, while due to exchange with

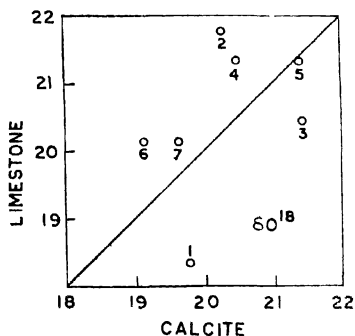


FIG 1

fresh water the calcite got depleted in δO^{18} . This seems evident from the δC^{13} and ΔC^{13}_{LS-C} values where the fractionation between calcite and limestone is much more positive. The δC^{13} calcite for the samples must have been lowered due to the exchange with biogenic carbon dioxide during and

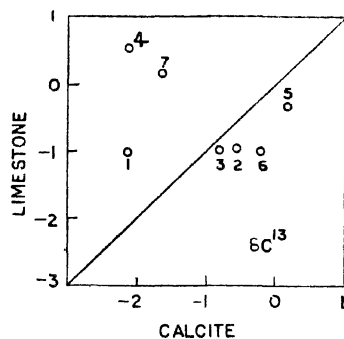


FIG. 2

after the crystallisation process. The plots of δO^{18} , δC^{13} , ΔO^{18}_{LS-C} and ΔC^{13}_{LS-C} are shown in figures 1 to 3. If the calcite is formed under isotopic equilibrium condition in a fast process, then all the points should have fallen on the line. As the points are scattered for all the plots, the scatterings are indicative of exchange and alterations in both the phases.

TABLE 2. Z VALUE FOR THE LIMESTONES

Sample	δO^{18} (PDB)*	δC^{13} (PDB)	Z**
A1	-10.8	-1.03	119.8
A2	-7.4	-0.96	121.6
A3	-8.7	-0.98	120.9
A4	-7.8	0.52	124.5
A5	-7.9	-0.38	122.6
A6	-9.0	-1.03	120.7
A7	-9.0	0.15	123.1

$$\delta O^{18} = \delta O^{18} - 29.2\%$$

$$^{(PDB)*}_{(SMOW)}$$

$$Z^{**} = 2.048 (OC^{13} + 50) + 0.498(OO^{18} + 50).$$

Finally, the evidences of X-ray analysis shows the presence of dolomite in the samples and in order to establish conditions of isotopic disequilibrium in

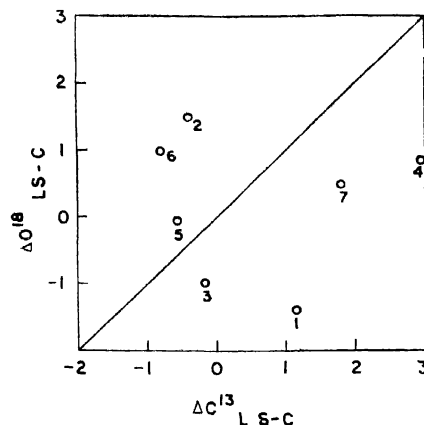


FIG. 3

limestone formations more samples are being studied for further communication.

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