

Oxygen and Carbon Isotope Fractionation Study of Coexisting Limestones

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Investigation of limestone samples has been made with a view to study O^{18} and C^{13} fractionation. The isotopic fractionation between dolomite and calcite are in the range -0.23 to 0.95 for oxygen and -1.49 to 1.13 for carbon. The variation in ΔO^{18} and ΔC^{13} have been explained as due to the formation of dolomite from the calcite precursor by the combination of both solid state cation exchange (metasomatic) and dissolution processes under isotopic non-equilibrium.

MANY chemical and physical processes occurring in nature are accompanied by isotopic fractionations of the lighter elements. With the development of precise mass spectrometry^{1,2} and careful sample preparation procedures more clear picture of physical and chemical conditions for the deposition of rocks and minerals can be had. The formation of dolomite in natural assemblages is an important problem. Several postulates have been put forth regarding the formation of dolomite³⁻⁸. In case of primary dolomites, the dolomite is considered to be directly precipitated from the solution and the δO^{18} values of calcite and dolomite differ considerably. The secondary dolomites are formed either by metasomatic cation exchange process, in which δO^{18} of calcite and dolomite are same, or by the dissolution of calcite (wet process) in which calcite and dolomite differ by 4 to 6 per mil. at lower temperature. Thus isotopic analysis of coexisting dolomite and calcite should give information regarding the condition of formation of the dolomite.

In our previous communication⁸ the isotopic equilibrium in the limestones associated with crystallised calcite were studied and the variation in O^{18} and C^{13} were attributed to the dolomitization of the limestone. In X-ray analysis⁹ the sample shows presence of dolomite in the limestone base in considerable ratio. Therefore, isotopic analysis of dolomite and calcite fractions present in the limestone base were carried out with a view to examine the fractionation between dolomite and calcite and to find the mode of formation of dolomite.

Experimental

Carbon dioxide is liberated by reacting the carbonate samples with 100% phosphoric acid according to the method described by McCrea¹⁰.

The method has been further modified by Sharma and Sharma¹¹. The actual procedure followed for the extraction of carbon dioxide from calcite and dolomite fractions of the carbonate samples are the same as described in our earlier communication¹². The isotopic analyses were carried on a 6"-60°-RMS-19 double collecting isotope ratio mass spectrometer in the Department of Chemistry, I.I.T., Kanpur. The isotopic data have been reported in terms of δ (delta) defined as:

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

where R represents O^{18}/O^{16} or C^{13}/C^{12} ratios. The isotopic data are corrected for instrumental effects¹³ and reported with respect to SMOW and PDB for oxygen and carbon respectively. Further the δO^{18} and δC^{13} values of the carbonates have been calculated using fractionation factors reported by Sharma and Clayton¹⁴.

Results and Discussion

The isotopic data of calcite and dolomite are shown in Table 1. The variation of δO^{18} and δC^{13} of the limestone samples have been discussed earlier^{8,12}. The variations have been explained due to exchange with fresh water and different extent of dolomitization.

The isotopic fractionation ΔO^{18}_{D-C} for the samples are in the range -0.23 to 0.95 . The value is close to zero and hence it may be concluded that the dolomite has been formed by the metasomatic cation exchange process. If the dolomite had been formed by dissolution of calcium carbonate then the

TABLE 1—ISOTOPIC DATA FOR CALCITE AND DOLOMITE PRESENT IN LIMESTONE SAMPLES.

Sample	δO_D^{18}	δO_C^{18}	ΔO^{18}_{D-C}	δC_D^{13}	δC_C^{13}	ΔC^{13}_{D-C}
A1	18.75±0.13	18.18±0.12	+0.57	-1.58±0.13	-0.31±0.09	-1.27
A2	22.04±0.08	21.12±0.19	+0.92	-0.16±0.03	-0.97±0.19	+1.13
A3	20.56±0.19	20.39±0.19	+0.17	-1.06±0.09	+0.43±0.13	-1.49
A4	21.07±0.15	21.30±0.15	-0.23	-0.05±0.09	-1.10±0.17	+1.05
A5	21.41±0.07	21.30±0.12	+0.11	-0.18±0.06	-1.10±0.06	+0.82
A6	20.05±0.11	19.78±0.09	+0.27	+0.19±0.01	-1.10±0.07	+1.29
A7	20.63±0.12	19.68±0.05	+0.95	+0.18±0.08	+0.02±0.01	+0.16

± = average deviation for three analyses.

TABLE 2—ISOTOPIC DATA FOR CRYSTALLIZED CALCITE AND LIMESTONE.

Sample	Crystallized Calcite		Limestone Calcite		Limestone Dolomite	
	δO^{18}	δC^{13}	δO^{18}	δC^{13}	δO^{18}	δC^{13}
A1	19.8	-2.2	18.2	-0.3	18.8	-1.6
A2	20.3	-0.6	21.1	-1.0	22.0	0.2
A3	21.4	-0.8	20.4	0.4	20.6	-1.1
A4	20.5	-2.4	21.3	-1.1	21.1	-0.05
A5	21.4	0.2	21.3	-1.1	21.4	-0.2
A6	19.2	-0.2	19.8	-1.1	20.1	0.2
A7	19.7	-1.7	19.7	0.02	20.6	0.2

ΔO^{18}_{D-C} should have been around 3‰. The dolomites are not ordered ones as evidenced from the displacement of the X-ray peaks from the normal 31° peak⁹. The small variation in the ΔO^{18}_{D-C} may be explained due to formation of the dolomite under non-isotopic equilibrium. When this is the case then the metasomatic process alone is not sufficient to explain the process of formation of the dolomite. It seems plausible that after formation of the dolomite by the metasomatism, the limestones suffered some hydrothermal attack where by some of the calcites decomposed and got precipitated as dolomite. This is supported by the fact that the limestone samples are associated with crystallised calcite and bear significant marks of hydrothermal attack.

The δO^{18} values of the crystallised calcite and the calcite and dolomite present in the limestones are shown in Table 2. Inspection of the data indicates that δ values of the crystallised calcites are much closer to the dolomite specially in the case of δC^{13} values. Thus it is reasonable to assume that the dolomite in the limestone was formed, in part, due to the dissolution of calcite. Thus it may be concluded that the dolomites in the limestone were first formed by metasomatic process and at a later stage the limestone suffered hydrothermal attack due to which the calcite present in the limestone dissolved and part of which crystallised as calcite and another part remained in the bulk of the limestone and got converted to dolomite.

Further, if the formation occurred in equilibrium, then the ΔO^{18}_{D-C} should be around 1 to 3‰, but as the values are around zero, the formation during

the hydrothermal attack was under non-isotopic equilibrium which is in accordance with the result demonstrated by O'Neil and Epstein¹⁵ in the study of calcite-dolomite pairs. The above conclusion gets further support from the isotopic study of limestone samples from adjoining areas as in our previous communication^{12,16}.

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