

## RESEARCH NOTES

### Carbon and Oxygen isotopic study of limestones from the Triassic Lower Krol Formation of India

G. C. PANDEY

Jawaharlal University, New Delhi

#### Abstract

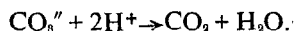
The  $O^{18}/O^{16}$  and  $C^{13}/C^{12}$  ratios of dolomite and calcite from Rajpur area on the Dehra Dun-Mussori road have been reported. The samples belong to the Lower Krol Formations of Triassic age. The isotopic composition data have been utilised to determine the conditions of formation. The data indicate that the precipitation occurred in warm waters and under isotopic equilibrium conditions.

#### Introduction

Studies of physical and chemical conditions of formation of rocks and minerals have received much attention in recent years. Measurements of the carbon and oxygen isotope ratios in minerals are of quite importance in this respect. Variations in the carbon and oxygen isotope ratios of natural carbonates have been studied by several workers, (Clayton *et al*, 1968; Pandey *et al*, 1969, 1970). These variations have been explained on the basis of different factors like temperature of deposition, source of deposition and subsequent isotopic exchange with the surroundings etc. In the present work samples from the Rajpur area on the Dehradun-Mussori road were studied to determine the conditions of deposition of dolomite and calcite.

#### Experimental procedure

The carbonates were decomposed with 100% phosphoric acid according to the reaction,



the carbon dioxide thus obtained was purified and collected for isotopic analysis by the method described by Epstein *et al*, (1964). The  $O^{18}/O^{16}$  ratio of the dolomite and calcite were calculated from that of the carbon dioxide using fractionation factor between dolomite and carbon dioxide and calcite and carbon dioxide respectively, reported in literature (Sharma *et al*, 1965, 1969). The isotopic composition is reported in terms of  $\delta$ -defined as:

$$\delta O^{18} = \left\{ \frac{(O^{18}/O^{16})_{\text{Sample}}}{(O^{18}/O^{16})_{\text{Standard}}} - 1 \right\} \times 1000$$
$$\text{and } \delta C^{13} = \left\{ \frac{(C^{13}/C^{12})_{\text{Sample}}}{(C^{13}/C^{12})_{\text{Standard}}} - 1 \right\} \times 1000$$

The  $\delta$ -values reported in this work have been corrected for instrumental factors (Craig, 1957) and reported with respect to SMOW (Standard Mean Ocean Water) and PDB (Chicago Standard) standards for oxygen and carbon isotopic ratios respectively (Craig, 1961).

#### Geologic background

The samples studied were collected from Rajpur area on the Dehra Dun-Mussori road. The limestones of this area belong to the Lower Krol Formation (Triassic).

These are described as marbles in literature and analytical data show that they are fairly pure rocks. The presence of some dolomitic limestones and dolomites particularly in the lower part of the formation have also been reported (Mehta *et al*).

### Results and Discussion

The isotopic data ( $O^{18}$  and  $C^{13}$  isotope ratios) of the calcite and dolomite under study are given in Table I. The  $\delta O^{18}$  value of the samples indicate that they belong to the marine limestones of Triassic age (Weber *et al*, 1964). This fact is consistent with the geological evidences. A comparison of the oxygen isotopic composition shows that dolomites have higher  $\delta O^{18}$  values than calcite. These isotopic data have been utilized to determine the isotopic fractionation between calcite and dolomite. Such a study would help in understanding the conditions of formation of dolomite and the extent of the isotopic equilibrium attained at the time of precipitation.

The isotopic fractionation factor ( $\alpha$ ) between any two phases (A and B) may be defined as:

$$\alpha_{A-B} = \left[ \frac{(R_2/R_1)_A}{(R_2/R_1)_B} \right]$$

Where  $R_2$  and  $R_1$  represent the heavier and lighter isotopic species. This fractionation factor is approximately equal to  $\sim \delta_A - \delta_B = \Delta_{A-B}$ . Thus, the isotopic fractionation between dolomite and calcite may be represented as:

$$\alpha_{D-C} \sim \Delta_{D-C} = \delta_D - \delta_C$$

Where  $\Delta_{D-C}$  = Isotopic fractionation factor between dolomite and calcite.

$\delta_D$  = ( $O^{18}/O^{16}$ ) or ( $C^{13}/C^{12}$ ) ratio of the dolomite

$\delta_C$  = ( $O^{18}/O^{16}$ ) or ( $C^{13}/C^{12}$ ) ratio of the calcite.

Thus a difference in the isotopic composition of dolomite and calcite gives the isotopic fractionation value. From the data (Table I) it may be observed that the oxygen isotope fractionation is about 2‰ for these samples. There is a considerable discussion in the literature (Schwarcz, 1966, Degens *et al*, 1962) about the fractionation of  $O^{18}$  in coexisting dolomite-calcite pairs. Under isotopic equilibrium conditions of precipitation, it is expected that the dolomite should be heavier (in  $O^{18}$  value) by about 8‰ than calcite. But for natural sedimentary dolomite-calcite pairs, it has been observed that the  $O^{18}$  fractionation should range between 0‰ to 2‰ for low temperature rocks and from 2‰ to 4‰ for the higher temperature rocks (Degens *et al*, 1962).

The  $\Delta_{D-C}^{O^{18}}$  - in this study, therefore, indicates that the samples belong to the low temperature group. Thus on the basis of  $O^{18}$  data, it may be concluded that the samples are of marine origin. The temperature at the time of deposition was slightly higher (i.e. samples deposited from warm waters).

The  $\delta C^{13}$  values are within the range found for marine limestones. These values are slightly lower than expected for Triassic carbonates (Weber *et al*, 1964). There is very little carbon isotopic fractionation between dolomite and calcite which suggests that the source of deposition was the same at the time of precipitation of both the calcite and dolomite. The enrichment of  $\delta C^{13}$  and  $\delta O^{18}$  in dolomite compared to calcite also indicates that the precipitation occurred under isotopic equilibrium conditions (Clayton *et al*, 1968, Pandey *et al*, 1970).

TABLE I

Oxygen and carbon isotopic composition of dolomite and calcite from the Lower Krol of Rajpur (Dehra-Dun)

Sl. No.	Sample Number	Sample	$\delta O^{18}$ (SMOW) in ‰	$\delta C^{18}$ (P.D.B.) in ‰
1	17F <sub>A</sub>	Calcite	20.00	-0.80
2	17F <sub>B</sub>	Calcite	20.15	-1.00
3	18F <sub>A</sub>	Calcite	21.90	0.00
4	18F <sub>B</sub>	Calcite	22.00	0.56
5	19F <sub>A</sub>	Dolomite	23.40	2.60
6	19F <sub>B</sub>	Dolomite	23.00	2.50
7	20F <sub>A</sub>	Dolomite	24.00	2.00
8	20F <sub>B</sub>	Dolomite	24.25	2.23

## References

- CRAIG, H., (1957) 'Isotopic Standards for carbon and oxygen and correction factors for mass spectrometric analysis of carbon dioxide.' *Geochim Cosmochim Acta*, v. 12, p. 133.
- (1961) 'Standards for reporting concentrations of deuterium and oxygen-18 in natural waters.' *Science*, v. 133, p. 1833.
- CLAYTON, R. N., SKINNER, H. C. W., BERNER, R. A. and RUBINSON, M., (1968) 'Isotopic compositions of recent South Australian lagoonal carbonates.' *Geochim Cosmochim Acta*, v. 32, p. 983.
- DEGENS, E. T. and EPSTEIN, S., (1962) 'Relationship between  $O^{18}/O^{16}$  in coexisting carbonates, cherts and diatomites.' *Bull. Amer. Assoc. Petrol. Geol.*, v. 46, p. 534.
- MEHTA, D. R. S., NARAYAN MURTHY, B. R. and NARASIMHAN, A. S., *Bull. Geol. Survey of India, Series A*, no. 16, p. 51.
- EPSTEIN, S., GRAFF, D. L. and DEGENS, E. T., (1964) 'Oxygen isotope studies on the origin of dolomites.' In *Isotopic and Cosmic Chemistry* (editors H. Craig, S. L. Miller and G. J. Wasserburg), pp. 169-180, North Holland.
- PANDEY, G. C., SHARMA, T. and MISRA, R. C., (1969) ' $O^{18}/O^{16}$  &  $C^{13}/C^{12}$  ratios of Limestones from caic-zone of Pithoragarh.' *Curr. Sci.* v. 38, p. 523.
- (1970) ' $O^{18}/O^{16}$  &  $C^{13}/C^{12}$  ratio variation in Limestones from Vindhyan range.' *Jour. Geol. Soc. India*, v. 11, p. 397.
- PANDEY, G. C. and SHARMA, T., (1970) 'Oxygen and carbon isotope fractionation between dolomite and calcite in Lesser Himalayan and Vindhyan Limestones.' *Geochim Cosmochim Acta*, v. 34, p. 625.
- SHARMA, T. and CLAYTON, R. N., (1965) 'Measurement of  $O^{18}/O^{16}$  ratios of total oxygen of carbonates.' *Geochim Cosmochim Acta*, v. 29, p. 1347.
- SHARMA, S. K. & SHARMA, T., (1969) 'Extraction of carbon dioxide from dolomite', *Ind. Jour. Chem.* v. 7, p. 295.
- SCHWARCZ, H. P., (1966) 'Oxygen and carbon isotopic fractionation between coexisting metamorphic calcite and dolomite.' *Jour. Geol.*, v. 74, p. 38.
- WEBER, J. N. and KEITH, M. L., (1964) 'Carbon and oxygen isotopic composition of selected limestones and fossils.' *Geochim. Cosmochim. Acta*, v. 28, p. 1787.