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PHYSICO-CHEMICAL BEHAVIOUR OF THE CARBONATE ROCKS OF WESTERN SON VALLEY REGION, INDIA

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The techniques of DTA and TG were employed to study the thermal characteristics of unfossiliferous carbonate litho-units, viz. Fawn dolomitic limestone (microdolsparite) and Rohtas limestone (micrite) belonging to the Vindhyan Supergroup (Pre-Cambrian) of India. The DTA of Fawn dolomitic limestone displayed two successive endothermic peaks at 725° and 860° whereas only one endothermic change at 910° was recorded in the DTA curve of Rohtas limestone. It was confirmed by chemical analyses, TG, IR and X-ray diffraction studies that the two peaks in the first case are due to dissociation of CO_2 from magnesium and calcium lattice positions, while the sole peak in the second case is due to complete decarbonation. A tentative correlation between the thermal characteristics and structural changes of these carbonate rocks at various transition temperatures is presented.

In view of the great industrial importance of the carbonate rocks in various basic industries viz. cement, lime, iron and steel, paper, glass and sugar, etc., the thermal characteristics of the carbonate rocks of Western Son Valley Region of India have been studied in detail. The main techniques adopted were Differential Thermal Analysis (DTA), Thermogravimetric Analysis (TG) and the results of thermal analyses have been verified by the Chemical Analysis, Infrared Spectroscopy (IR) and X-Ray Diffraction studies. Excellent correlations have been obtained in the study of structural properties of these carbonate rocks by these techniques.

The two carbonate litho-units studied here are Fawn dolomitic limestone and Rohtas limestone, both belonging to the Semri Group of the Vindhyan Supergroup (Pre-Cambrian) of India. Petrographically, the Fawn dolomitic limestone and the Rohtas limestone are unfossiliferous microdolsparite and micrite [1], respectively.

Various field evidences support a warm shallow marine environment for the deposition of these rocks. The Rohtas limestone is considered as a marine inorganic precipitate of calcium carbonate in the warm shallow seas while the Fawn dolomitic limestone was formed as a result of diagenetic replacement of the lime mud. The dolomitization is considered to have taken place during the diagenetic stage [2].

Experimental

Chemical analysis

All the chemicals employed in chemical analysis were of Analar quality. A number of samples of Fawn Dolomitic limestone and Rohtas Limestone were chemically analysed by rapid methods of silicate analysis [3].

Differential thermal analysis (DTA)

Differential Thermal Analyses were carried out in air atmosphere using a manually operated DTA apparatus [4, 5], with a little modification, i.e. by using Chromel-Alumel thermocouple instead of the Platinum-Rhodium. In all the experiments, material crushed to 150 mesh (ASTM) were used.

Thermogravimetric analysis (TG)

Thermogravimetric analyses of the carbonate rock samples of both the units were carried out in a manually operated TG unit in air atmosphere.

Infrared spectroscopic studies (IR)

The infrared absorption spectra of both the original carbonate rock samples and samples preheated to 1000° have been recorded using nujol technique by Perkin-Elmer Infrared Spectrophotometer. The IR spectrum was scanned in the region $4000-625\ cm^{-1}$.

X-ray diffraction studies

X-ray diffraction studies of original carbonate rock samples and the samples preheated to different transition temperatures have been made by Philips X-ray diffraction unit, using nickel filtered CuK_{α} radiation.

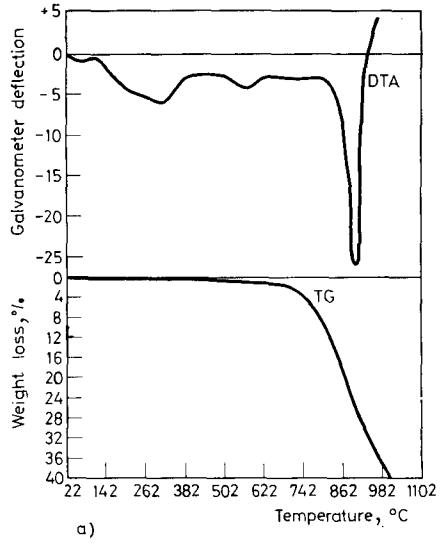
Results and discussion

Fawn dolomitic limestone

The results of the chemical analyses of Fawn dolomitic limestone are given in Table 1. From Table 1, it is apparent that the Fawn unit is essentially a dolomitic rock (MgO 17.50%) with some other minor impurities.

The DTA and TG curves of Fawn dolomitic limestone are shown in Fig. 1b. There is a slow downward base-line drift in the DTA curve within the temperature range 100°–680° followed by the two successive endothermic peaks at 725° (range 690–770°) and 860° (range 840–900°). The endothermic peak at 725° is almost similar in magnitude as that of at 860°.

The TG curve in Fig. 1 shows a gradual weight-loss up to 1000° and two well defined plateaux suggesting the presence of two or more intermediate stages during thermal treatment. The total weight-loss was calculated and found to be 39.25 percent. From chemical analysis it appears that the original rock sample is having 0.57 percent water and that much of weight-loss has been registered in the TG curve within the temperature range 50–200°. So the flat peak around this



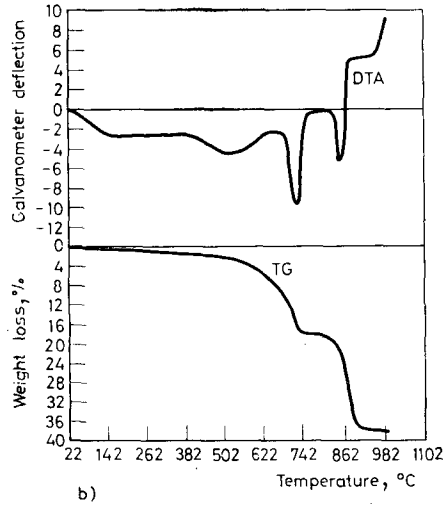


Fig. 1/a. DTA and TG curves of Rohtas limestone
Fig. 1/b. DTA and TG curves of Fawn dolomitic limestone

temperature is due to complete dehydration and can be expressed by the following sequence:

$$CaMg(CO_3)_2 \cdot XH_2O \text{ (plus traces)} \xrightarrow{-XH_2O} CaMg(CO_3)_2 \text{ (plus traces)}.$$

The TG curve shows a continuous weight-loss starting from 600° and ending at 800°. The weight-loss was found to be 18.58% which corresponds to the removal of one CO_2 molecule from one molecule of $CaMg(CO_3)_2$ (plus traces). So the endothermic peak at 725° is due to the following reaction course:

$$CaMg(CO_3)_2 \text{ (plus traces)} \xrightarrow{-CO_2} CaCO_3 + MgO \text{ (plus traces)}$$

The TG curve again represents a continuous weight-loss starting from 800°and ending at 1000°. The weight-loss was calculated and found to be 20.67 percent (total 39.25%) which corresponds to the removal of another CO_2 molecule from one molecule of ($CaCO_3$ + MgO) and therefore it is clear that the last endothermic peak at 860° is due to the following reaction:

$$(CaCO_3 + MgO) \xrightarrow{-CO_2} CaO + MgO$$

The sequences have been also verified by chemical analyses.

The IR spectrum of the original Fawn dolomitic limestone sample is shown in Fig. 2b, and the characteristic frequencies are given in Table 2. The spectra exhibit sharp absorption bands at 725 cm^{-1} and 874 cm^{-1} similar to those of dolomite and calcite [6, 7]. The IR spectrum of the sample preheated to 1000° is also shown

Table 1

Chemical composition of Fawn dolomitic limestone and Rohtas limestone (wt. percent oxides)

Oxides	Fawn dolomitic limestone	Rohtas limestone
CaO	24.24	50.42
MgO	17.50	2.03
CO_2	38.26	38.65
SiO_2	11.44	4.12
Al_2O_3	2.85	1.24
FeO	0.78	0.16
Fe_2O_3	1.15	0.92
P_2O_5	0.45	0.36
TiO_2	0.33	0.22
MnO	0.39	0.30
Na_2O	1.26	0.84
K_2O	0.86	0.67
H_2O	0.55	0.77
Total	100.06	100.70

in Fig. 2. This spectrum does not exhibit those characteristic bands as obtained earlier. It reveals that the decarbonation is complete when the sample is heated to 1000°.

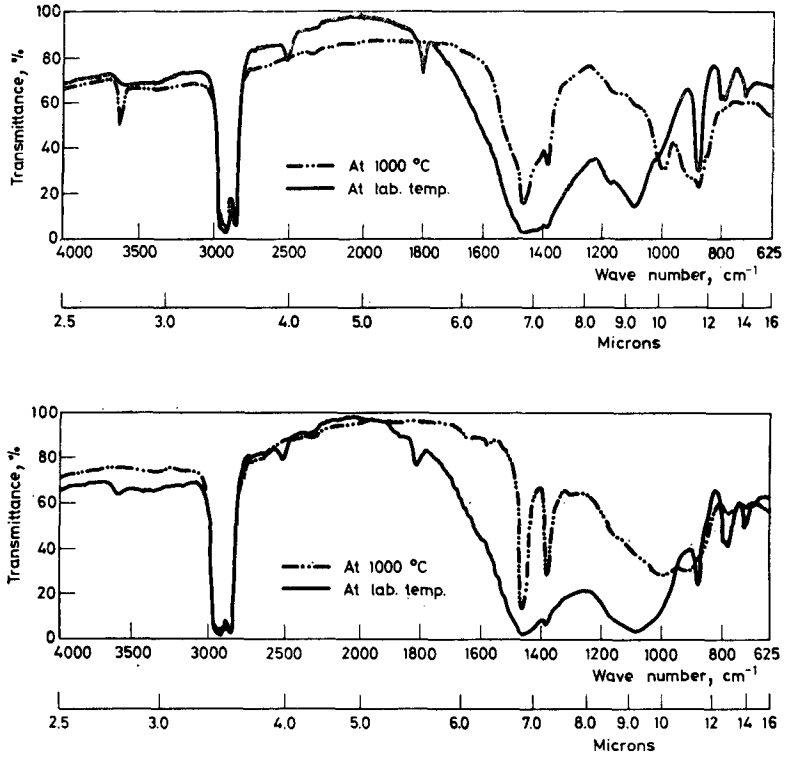


Fig. 2/a. Infrared spectrum of Rohtas limestone
Fig. 2/b. Infrared spectrum of Fawn dolomitic limestone

Table 2

Characteristic IR absorption bands of Fawn dolomitic limestone and Rohtas limestene

Constituents	Fawn dolomitic lst.	Rohtas lst.
	(wave number cm^{-1})	
Dolomite	725	—
Calcite	874	872
CO_3 i.p. deformation	725	710
CO_3 o.p. deformation	874	872
CO_3 group	1380	1380
CO group	1462	1463

X-ray analysis of the original Fawn dolomitic limestone sample showed in its diffraction pattern a number of lines of weak and moderate intensities. The most characteristic line was found to be at $d = 1.910$ Å. The various d-values obtained by this analysis have been compared with those given in ASTM chart for standard patterns and the d-values were found to resemble to those given for dolomite. X-ray diffraction pattern of the sample heated at 700° showed a number of lines of different intensities which are not identical to those obtained in the case of original sample. The strongest lines were at 3.149 Å, (most characteristic) and 1.649 Å. It indicates that the crystal structure of the original sample has been changed to more crystalline phase and a number of lines which are characteristic of dolomite are absent. But few lines which correspond to those of calcite ($CaCO_3$) are found to be present which indicates that the carbonate matrix has not suffered considerable distortion in the thermal treatment up to 700°. Therefore, it can be suggested that the change in crystal structure up to 700° may be due to the dissociation of CO_2 from the ions of magnesium lattice position.

X-ray analysis of the sample heated at 1000° showed a number of lines of moderate intensities which indicates that the crystal structure at this stage is entirely different than that of the original one. No lines corresponding to those of $MgCO_3$ or $CaCO_3$ have been found in the pattern which indicates that the $CaCO_3$ matrix which was present even after 700° has suffered distortion and the dissociation of CO_2 ions from calcium lattice position has taken place. Therefore, the thermal changes in Fawn dolomitic limestone can be expressed as follows:

$$CaMg(CO_3)_2 \cdot H_2O \text{ (plus traces)} \xrightarrow[-X\ H_2O]{50-200^\circ} CaMg(CO_3)_2 \text{ (plus traces)}$$

$$\xrightarrow[-\ CO_2]{200-800^\circ} CaCO_3 + MgO \xrightarrow[-\ CO_2]{800-1000^\circ} CaO + MgO.$$

Rohtas limestone

The results of the chemical analyses of Rohtas limestone are given in Table 1. From Table 1, it is clear that the Rohtas limestone is essentially a calcium carbonate rock (CaO 50.42%) with some other minor impurities.

The DTA and TG curves of Rohtas limestone are shown in Fig. 1a. The DTA curve shows that Rohtas limestone undergoes only one endothermal change on heating it up to 1000°. The endothermic decomposition begins at 800°, reaches a peak at 910° and ends rapidly at 940°.

The TG curve represents a gradual weight-loss up to 1000°. The total weight-loss was calculated and found to be 39.1 percent. The TG curve shows 0.75 percent weight-loss up to 600° which represents the complete removal of water molecules from the rock sample at this temperature. A continuous weight-loss is registered in the TG curve starting from 800° and ending at 1000°. The weight-loss was found to be 38.43 percent (total wt. loss 39.1 percent) which represents the

removal of one CO_2 molecule from one molecule of $CaCO_3$ (plus traces). Therefore, the endothermic peak at 910° may be due to the following reaction:

$$CaCO_3 \text{ (plus traces)} \xrightarrow[CO_2]{800-1000^\circ} CaO \text{ (plus traces)}.$$

The IR spectra of original Rohtas limestone sample is shown in Fig. 2 and the characteristic frequencies are given in Table 2. It exhibits a sharp absorption band at 872 cm^{-1} similar to those of calcite [6, 7]. The IR spectra of the sample preheated to 1000° is also shown in Fig. 2. The I.R. spectra exhibit the absence of those characteristic bands as obtained in the first case. It reveals that decarbonation is completed before 1000°.

X-ray analysis of the original Rohtas limestone sample showed a number of lines of different intensities. The relevant lines were at *d* 3.04 Å (most characteristic), 2.30 Å, 2.95 Å, 1.586 Å. These lines correspond to calcite.

The X-ray diffraction pattern of the sample preheated to 1000° were found to be entirely different than the one obtained for the original sample. All the characteristic lines which were obtained earlier, are found to be absent except a few lines of weak intensities. This clearly reveals that in the thermal treatment up to 1000°, the $CaCO_3$ matrix has suffered a considerable distortion followed by dissociation of CO_2 ions from the calcium lattice position. Therefore, the thermal changes in the Rohtas limestone can be summed up as follows:

$$CaCO_3 \cdot X\,H_2O \text{ (plus traces)} \xrightarrow[-X\,H_2O]{\text{upto } 600^\circ} CaCO_3 \text{ (plus traces)} \rightarrow$$

$$\rightarrow CaCO_3 \xrightarrow[-CO_2]{800-1000^\circ} CaO.$$

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RÉSUMÉ — On a utilisé les techniques ATD et TG pour étudier les caractéristiques thermiques de carbonates non-fossilifères appartenant au groupe précambrien de l'Inde. La courbe ATD du calcaire dolomitique de Fawn présente deux pics endothermiques successifs à 725 et 860°C tandis qu'un seul effet endothermique est observé à 910° sur la courbe ATD du calcaire de Rohtas. Des études effectuées par analyse chimique, TG, IR et diffraction des rayons X ont confirmé que, dans le premier cas, les deux pics sonst dus à l'élimination du CO_2 correspondant au magnésium et au calcium; le pic unique obtenu dans le second cas est dû à la décarbonatation complète. On présente un essai de corrélation entre les caractéristiques thermiques et les changements structuraux de ces roches carbonatées, à diverses températures de transition.

ZUSAMMENFASSUNG — Die DTA- bzw. TG-Techniken wurden zur Untersuchung der nichtfossilen Carbonate von Litho-Einheiten, d. h. braunem Dolomitkalkstein (Mikrodolsparit und Rohtas-Kalkstein (Mikrit), welche zur (pre-cambrischen) Vindhy Supergruppe von Indien gehören, eingesetzt. Die DTA-Kurve des braunen Dolomitkalksteins wies zwei aufeinanderfolgende endotherme Peaks bei 185 und 860° auf, während an der DTA-Kurve von Rohtas-Kalkstein nur eine endotherme Veränderung bei 910° zu beobachten war. Durch chemische Analyse, TG, IR und Röntgendiffraktion wurde bestätigt, daß die beiden Peaks im ersten Falle der Dissoziation von CO_2 von Magnesium und Calcium Gitterpositionen zuzuschreiben sind und der einzige Peak des zweiten Falles durch vollständige Decarbonierung entsteht. Eine versuchsweise Korrelation zwischen den thermischen Eigenschaften und den strukturellen Veränderungen dieser Karbonatgesteine bei verschiedenen Übergangstemperaturen wird gegeben.

Резюме — Для изучения термических характеристик не горнорудных карбонатов железа, а именно фавнокого доломитового известняка (микродолепарит) и рохтаского известняка (микрит), относящихся к Виндхьянской супергруппе (предкэмбрийской) Индии была использована техника *DTA* и *DTG*. Для фавнского доломитового известняка *DTA* показал два последовательные эндотермические пики при 725° и 860°, в то время как для рохтаского известняка кривые *DTA* показали наличие только одного эндотермического изменения при 910°. С помощью химического анализа, *TG*, инфракрасной спектроскопии и рентгеноструктурных исследований было установлено, что два пика в первом случае обусловлены диссоциацией CO_2 из решеточных положений магния и кальция, в то время как единственный пик во втором случае обусловлен полным обезуглероживанием. Представлена экспериментальная корреляция между термическими характеристиками и структруными изменениями этих карбонатных минералов при различных температурных переходах.