Dynamic Temperature X-ray Diffraction (DTXRD) Studies on Dolomite ($MgCO_3CaCO_3$) of Balochistan (Pakistan).

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Summary: Dolomite ($MgCO_3CaCO_3$) is identified as the crystalline phase in the low temperature range, i.e. at temperatures less than 816 K. At 816 K, the high temperature compound periclase (MgO) is produced, as a consequence of, phase transition. This is confirmed from iso-intensity plot of DTXRD. For MgO at 1273 K, the cubic unit cell parameter is estimated to be about 4.26 A°. We observe certain microscopic changes on dolomite at temperatures less than 816 K as is evidenced from diffraction patterns.

Introduction

Deposits of dolomite are found at a distance of about 11 km south of Wadh village in the vicinity of Khuzdar, a city in Balochistan.

The ionic bond breaking occurs at 723 K [5]. With sudden drop at 728 K, in thermogrevimetry analysis (TGA) of dolomite, we observed inverted peaks at 816 K and 835 K [5]. The stretching of ionic bonds in a cubic structure of $MgCO_3$ is confirmed at 427 K on TGA [5]. All these observations are in conformity with DTXRD.

Results and Discussion

Our interpretations are in conformity with previous study [5]. An iso-intensity plot of the long measurement is shown in Fig. 1 and 2. It can be clearly seen that only one phase transition occurs.

Analysis has been made for the datasets before Fig. 3 and after Fig. 4 of the phase transition. In the low temperature range, magnesite $MgCO_3$ could be identified as the crystalline phase. The high temperature compound is periclase MgO, which is the decomposition product of $MgCO_3$. The 'cell tune' tool of EVA was used to determine the change of the lattice parameter due to the thermal expansion. For MgO at 1273 K, the cubic unit cell parameter is estimated to be about 4.26A° whereas the room temperature value is 4.21 A° according to the corresponding PDF-2 card.

A measurement at room temperature after the heating experiment indicated that the MgO was maintained upon cooling. An overview of the second experiment can be found in Fig. 5 for completeness. Our interpretations agree with our previous study [1-5].

Experimental

We used DX Advance diffractometer with Vantec detector. The radial soller was used to minimize diffuse air scattering. The measurements and evaluations were carried out with the software DIFFRAC® plus BASIC on the PC platform Windows XP. The analysis of the data was done with the EVA software, in combination with the PDF-2 database.

The sample has been prepared as a suspension in isopropanol in order to facilitate the deposition of a homogeneous sample layer on the heating strip of the high temperature chamber. The heating chamber was an MRI Basic with a PtRh heating strip. The high temperature experiments were done in static air.

Locked coupled measurements were made from 283 K to 353 K (2θ) with a step size of 0.021°C (2θ) and 0.15s per step. This results in a total measurement time of only 10 minutes for one scan. This measurement was repeated every 293 K from room temperature up to 1273 K. A delay time of 60s

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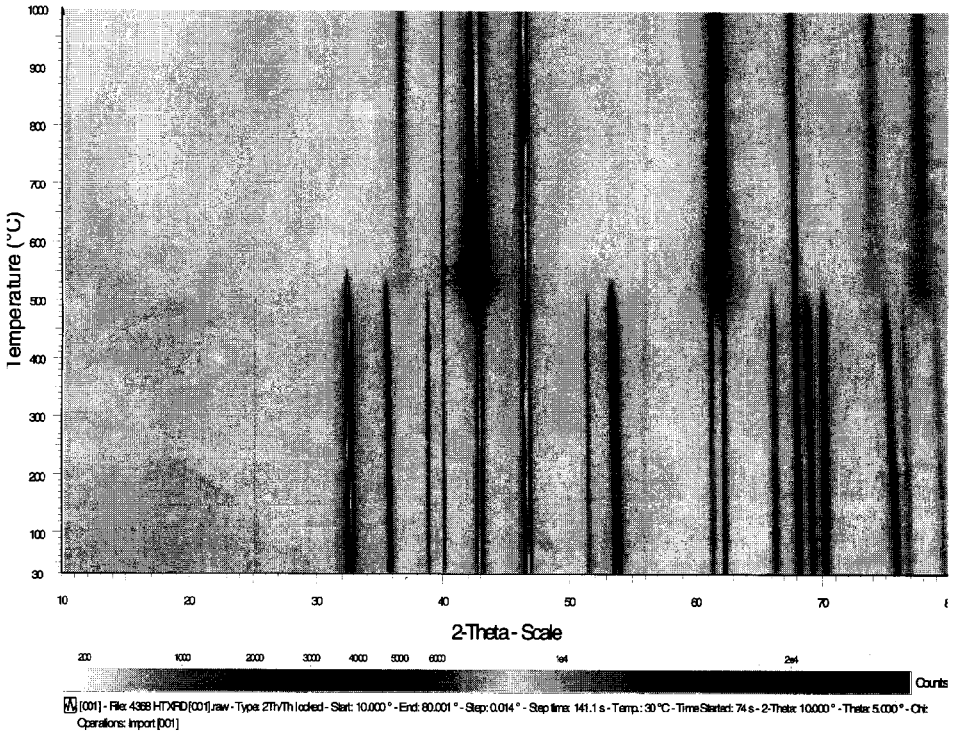

Fig. 1: Iso-intensity plot (overview). Diffraction peaks from the heating strip are indicated by Pt. One phase transition can be clearly seen and is indicated by the dotted line. Pt. One phase Transition can be clearly seen is indicated by the dotted line at 816 K.

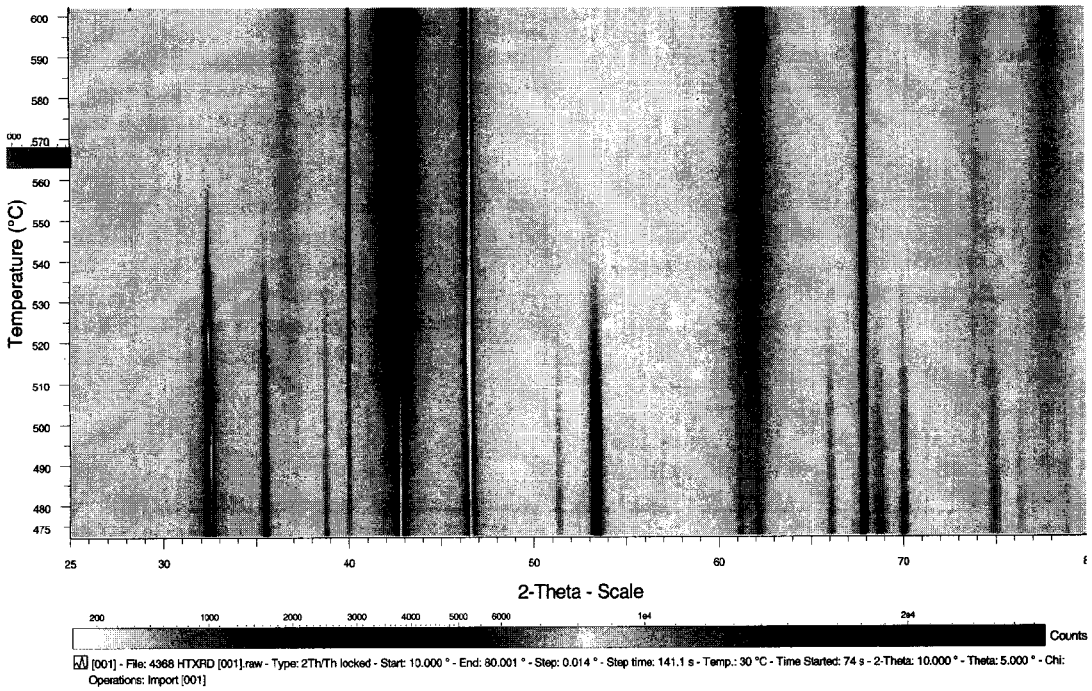

Fig. 2: Iso-intensity plot (zoomed). Diffraction peaks from the heating strip are indicated by Pt.

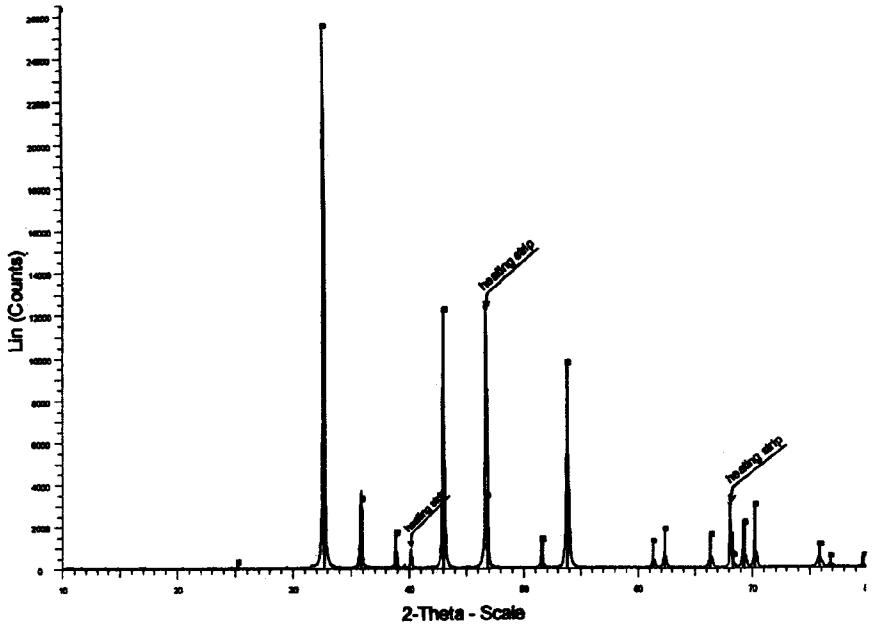

Fig. 3: Phase identification of the low temperature compound: measured data at 303K (background subtracted scan, black), theoretical peak positions of $MgCO_3$ (PDF-2 C86-2344). The diffraction peaks of the heating strip are indicated.

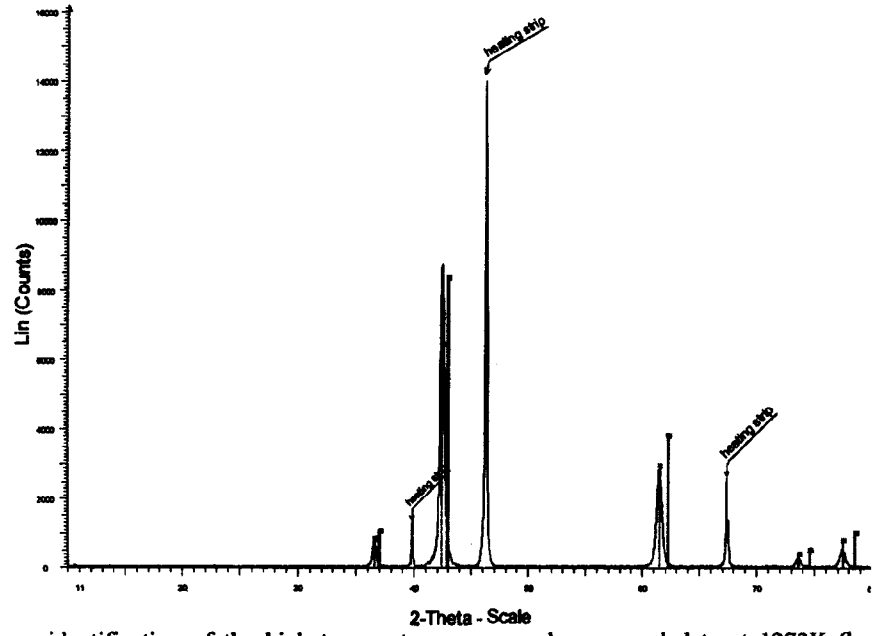

Fig. 4: Phase identification of the high temperature compound: measured data at 1273K (background subtracted scan, black), theoretical peak positions of MgO at room temperature (PDF-2 C78-0430). Diffraction peaks of MgO corrected for thermal expansion at 1273K. The diffraction peaks of the heating strip are indicated.

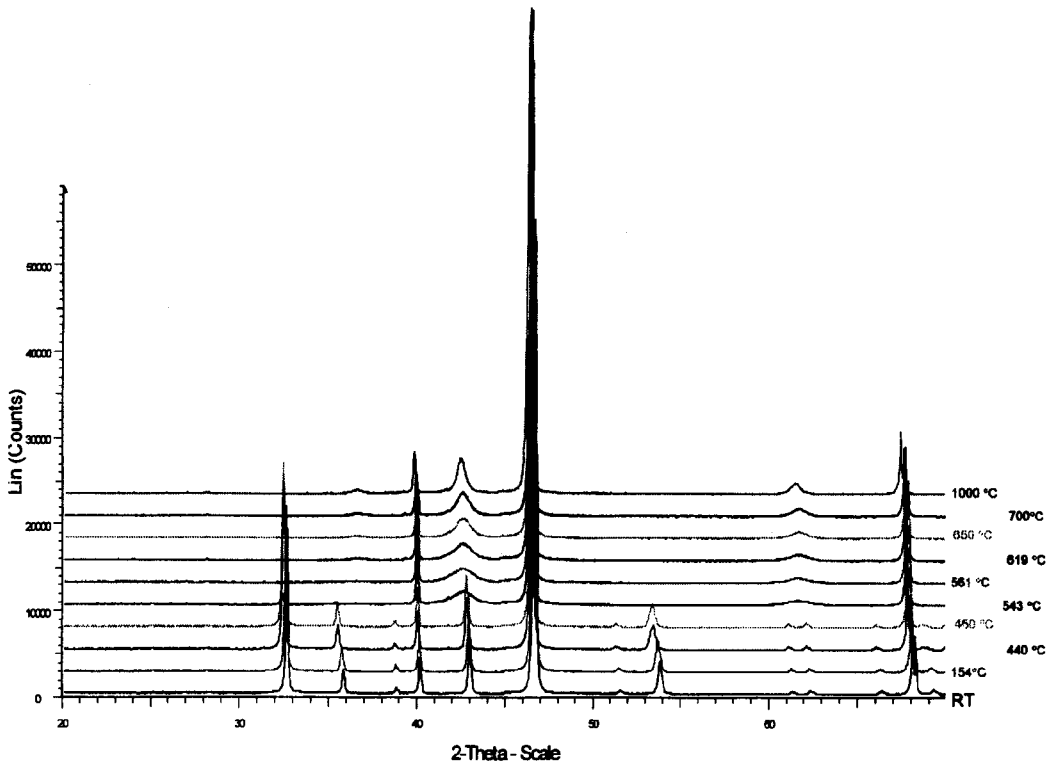

Fig. 5: Diffraction patterns at the requested temperatures, shifted in Y.

was inserted before starting the measurement at a selected temperature, in order to allow completion of a possible phase transition. The whole temperature profile was set up with a few mouse clicks using the non-ambient module of the XRD Wizard. The total experiment took about 9 hrs.

A second experiment was done with measurements only at the requested temperatures (RT, 427 K, 713 K, 816 K, 834 K, 892 K, 923 K, 973 K and 1273 K). Also the 2θ-interval was limited to 293 K – 363 K (2θ) since no significant diffraction peaks were observed outside this interval.

Conclusions

1. For MgO at 1273 K, the cubic unit cell parameter is estimated to be about 4.26 A° whereas the room temperature value is 4.21 A°.
2. The high temperature compound is periclase MgO, which is the decomposition product of $MgCO_3$.

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