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Decomposition and Transformation of Calcite-1 by Shearing at High Pressure

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Abstract – Transmission X-ray diffraction patterns were taken on imaging plates from calcite-1 slowly sheared at high pressure up to 16 GPa parallel to (101) plane and in the [2-1-1] direction at room temperature. They showed 22 broad diffused rings. Judging from the appearance of the rings, we may say that the formed substances are in an amorphous state. The patterns revealed that most of the rings do not correspond to calcite-1, but to high-pressure substances except graphite2H, CaO and CaC_2. They were thought to have formed through decomposition and transformation to its polymorphism. They remain at atmospheric pressure. Although the results mentioned above seem to be contrary to the common knowledge among scientists, phenomena that support the results are mentioned in the text.

Keywords**:** Calcite, Gigh pressure, Shearing, Decomposition, Transformation.

1. Introduction

The main purpose of this paper is to present the formation of high-pressure substances through decomposition and transformation to polymorphism by shearing calcite-1 at high pressure. These substances are in an amorphous state and remain at atmospheric pressure.

We may expect to form other amorphous substances by shearing solids at high pressure.

2. Experimental Procedure

A calcite-I plate, 0.5 mm thick, with the largest surfaces 1 mm x 1 mm parallel to (1 0 1) plane was put between two tungsten carbide rods (2 mm in diameter) with the face at π/4 rad from the normal to the axis at one end. All of them were inserted into a pierced hole right-angled to one of the paired surfaces of magnesia octahedron. The pressure around the octahedron was then increased at the rate of about 3.2 GPa /h to 16 GPa by using an uniaxial split-sphere apparatus in which the cubic assembly of eight tungsten carbide anvils is compressed with the aid of a 49 MN hydraulic press (Ito et al.,1984; Kawai et al.,1973). We performed pressure calibration by detecting the transitions of the following pressure fixed points: Bi I-II (2.55 GPa), Bi III-IV (7.7 GPa), ZnS semiconductor-metal (15.4 GPa). While the pressure was increasing, the specimen was sheared (Karato et al.,1988). The shearing direction was [2-1-1]. After keeping this pressure for 1h, it was lowered slowly (less than 2 GPa/h) to atmospheric pressure.

Transmission X-ray diffraction patterns were taken from the above specimen on imaging plates, after a lapse of about one year from the shearing to know the structure and state that remain at atmospheric pressure.

The target, the filter, the collimator aperture, the tube voltage, the tube current, the specimen-imaging plate distance and the exposure time were Mo, 0.1 mm thick Zr, 1.5 mm, 46 KV, 40mA, 70 mm and 3 min, respectively.

3. Results and Discussion

Fig.1 shows a transmission X-ray diffraction pattern taken from calcite-I sheared at high pressure.

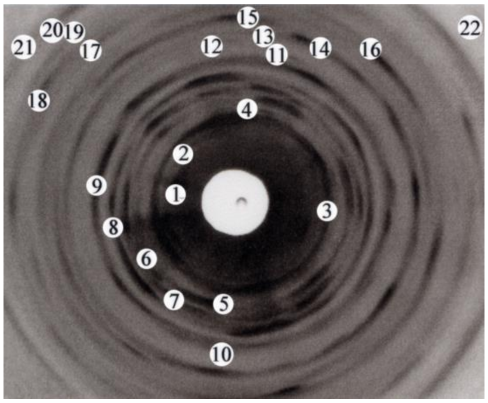

Fig.1. Transmission X-ray diffraction pattern with ring numbers in Table.

The rings are broad and highly diffused. This indicates that the state after the shearing is amorphous.

As shown in Table 1, not all rings correspond to calcite 1, but to its polymorphism and to simple substances and compounds formed as a result of decomposition of calcite-1.

Table1. Interplanar spacings (pm) corresponding to the rings in Fig. 1 and those of polymorphism of calcite-1 and its decomposed products by shearing at high pressure.

Ring		Calcite-I	Calcite-II	Calcite-III	Aragonite	Graphite2H	Ca	δ–O_2	β–CO	CO_2-III	CaO	CaC_2
No	d	[5-586]	**[29-305]**	**[17-163]**	[41-1475]	[41-1487]		[38-903]			[28-775]	[4-712]
1	368.3										368 (40)	
2	337.3				339.7 (100)	338 (100)		332.9 (20)			333 (100)	
3	299.0	303.5 (100)	299.8 (100)	302 (100)					293.4 (30)	298.9 (15.4)	300 (100)	332 (33)
4	274.1								273.3 (100)	279.8 (100)		274 (100)
5	249.8	249.5 (14)	247.0 (15)		248.1 (40)		251.7 (100)				252 (20)	
6	233.3				233.,0 (12) 234.2 (21) 237.3 (45)					232.8 (7.6)		
7	228.3	228.5 (18)	226.4 (20)	228 (10)				227.6 (100)			228 (60)	
8	210.5	209.5 (18)	211.3 (2)		210.8 (20)	213.9 (2)		210.9 (20)			209 (40)	208 (70)
9	187.3	187.5 (17)	188.6 (20) 186.9 (20)		188.21 (25) 187.75 (25)						191 (60) 188 (60)	186 (40)
10	181.0			181 (10)	181.49 (20)					183.7 (1.4)		
11	177.3		177.3 (2)				177.95 (14.38)		178.4 (10)	174.7 (2.3)		
12	168.5		169.6 (2)			168.1 (4)						167 (25) 166 (40)
13	162.5	162.6 (4)	160.4 (10)									
14	157.2	156.7 (3)				154.8 (1)						

15	150.0	1518 (4) 151.0 (3)	151.8 (10)				147.4 (30)	152.4 (2)	
16	141.8	144.0 (5) 144.2 (3)				145.30 (24.41)			
17	133.6	133.9 (2)							135 (33)
18	127.3	128.4 (1)				125.83 (6.47)			127 (25)
19	122.7	123.5 (2)			123.4 (3)				123 (40) 121 (25)
20	116.4	115.4 (3)			116.04 (3)				115 (33)
21	114.0	114.3 (1)		113.89 (1)		112.55 (8.18)			
22	104.3	104.5 (4)							105 (13)

[ ], **[ ]**:JCPDF FILE NNUMBER. [ ] TARGET Cu, **[ ]** TARGET Mo. ( ): RELATIVE SENSITIVITY.

Most of them are based on high-pressure structure: calcite-II (1.7 GPA-about 2GPa, Suito et al., 2001), calcite-III (above about 2GPa, Suito et al., 2001), aragonite (above about 0.3GPa, readout from a graph, Levin and McMurdie 1975), Ca (20-32 GPa, Olijnyk and Holzapfel 1984), δ-O_2 (9-10GPa, readout from a graph, solid, Akahama et al.,1995), β-CO (2.35–5 GPa, readout from a graph, solid, Mills et al.,1986), and CO_2-III (above12GPa, Aoki et al.,1994), except Graphite 2H (Web-1), CaO (William 2011) and CaC_2 (Knapp and Ruschewitz 2001). We cannot, however, say that all these substances exist because plural substances correspond to the same rings and the formation of some of these substances is considered to be difficult.

Considering the elapse of time after the shearing, we may say that the high-pressure state of the above substances remains at atmospheric pressure.

Although these results seem to be contrary to the common knowledge among scientists, they are consistent with previous experiments that shearing at high pressure not only transforms compounds to another polymorphism but also simple substances to allotropy: they remain at atmospheric pressure (Arndt and Stöffler 1969; Furuichi 2004, 2011; Furuichi et al., 2002, 2003, 2004, 2007).

Carbon acid gas emission by rubbing calcite-1 at atmospheric pressure has been reported (Martinelli and Plescia 2004).

It is widely known that high pressure arises when micro asperities on the specimen contact with those on the slide (Bowden and Tabor 1950). Severe discontinuous dry rubbing decomposes a compound to simple substances and compounds constituting of the elements of the original compound. They remain at atmospheric pressure (Furuichi 1993; Furuichi and Matsuura1997; Furuichi et al., 2000), e.g. in discontinuously rubbed zirconia, high-pressure state amorphous zirconium and other high-pressure state substances generated by decomposition.

4. Conclusions

Calcite-I sheared at high pressure not only transformed to its polymorphism but also decomposed to compounds and simple substances. Most of them are high-pressure substances and they remain at atmospheric pressure.

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