涂光炽学术文集

涂光炽 ◎ 著

科学出版社

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北京

内 容 简 介

本文集收集了中国科学院院士涂光炽先生自20世纪50年代以来发表在不同杂志上的部分文章117篇，包括科研论文、学科回顾与展望等。

涂光炽先生一生致力于矿床学和地球化学研究。这是一本侧重于矿床形成机制、时空展布、找矿思路及矿床地球化学的文集。文集收录的内容主要包括了矿物学与实验、成矿作用及理论、铁矿与稀土矿、花岗岩类与成矿、层控矿床与铅锌矿床、低温地球化学与分散元素成矿作用、金矿、超大型矿床及在新疆地区找矿、地球化学的回顾与展望、环境及地学思维等内容。

本文集可供矿产地质调查人员、地质院校师生和矿床、地球化学专业科研人员和相关专业的有关人员参考使用。

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出 版 说 明

本文集收集了中国科学院院士涂光炽先生自20世纪50年代以来发表的部分文章，包括科研论文、学科回顾与展望等。以涂光炽先生为主编的许多专著及已在《成矿与找矿》文集（2003）中收录的内容未在其中，涂光炽先生的许多咨询建议、治学思想及人生感想等文章也未收录其中。

涂光炽先生一生致力于矿床学和地球化学研究。不言而喻，这是一本侧重于矿床形成机制、时空展布、找矿思路及矿床地球化学的文集。文集的收录基本是以矿物与实验、成矿作用及理论、铁矿与稀土矿、花岗岩类与成矿、层控矿床与铅锌矿床、低温地球化学与分散元素成矿作用、金矿、超大型矿床及在新疆地区找矿、地球化学的回顾与展望、环境及地学思维等内容为主，并基本按时间先后为顺序排列。因时间跨度大，物理量单位、符号等均保留原貌，体例各篇统一，外文论著亦保持原文种不变。

目前我国正在建设创新型社会，知识的创新与积累已经成为经济发展、社会进步最具革命性的推动力。中国科学院地球化学研究所策划出版《涂光炽学术文集》是为了汇编整理涂光炽先生的重要科技成果及学术思想，既指导当前矿床及地球化学的科研工作，为加速成矿与找矿的科技进步服务，积累珍贵科技史料，又为了弘扬涂光炽先生“献身、创新、求实、协作”的科学精神和高尚情操，鞭策后来者为我国地学事业再创辉煌。

诚愿以此纪念涂光炽先生诞辰九十周年。

本文集由张兴春具体负责涂光炽先生文稿的收集、整理和初步编辑工作，冷成彪、糜梅、黄万才、任涛等同志做了大量文字打印、图件清绘等工作。在此一并向他们表示诚挚的谢意。

中国科学院地球化学研究所

2010年2月28日

目　　录

A Preliminary Study of the Phase Transitions in the System $TiO_2$①

摘要：地质产状、热力计算及高温高压试验之综合结果，可以证明在二氧化钛系中，金红石（Rutile）为高温度下唯一稳定之矿物。在低温下，金红石与锐钛矿（Anatase）之自由能相近，但金红石或较稳定。板钛矿（Brookite）在此系中之位置尚无法测知。试验室中所证明之不结晶性：TiO_2→锐钛矿→金红石之变化与地质上白榍石（Leucoxene）→锐钛矿→金红石之变化可视为同一作用。试验证明，金红石至少可在 250℃左右制成。若时间加长，可能使其于更低温度出现。

1. Introduction

Anatase, brookite, and rutile are the three polymorphic forms of TiO_2. Despite their wide geological occurrences as accessory minerals in numerous types of rocks, their phase relationships have remained largely unsolved. Very little agreement has been reached on the inversion temperature between anatase and rutile while brookite has never been authentically synthesized.

As most of the previous works were done under atmospheric conditions, it was thought that the application of pressure might shed some light on the transformation of TiO_2. This was considered feasible as new vessels had been developed which could stand relatively high pressure at temperatures below 1 000℃. The results, while still preliminary in nature, may prove helpful in geological interpretations.

2. Previous Work

The more important work done in the last two decades on the transformation of the different modifications of TiO_2 is summarized in Table 1. For earlier work, the readers are referred to Clark (1924) and Pascal and Baud (1932).

Several general statements can be made from the literature survey:

1) There is no definite transition temperature between either the anatase-rutile or the brookie-rutile pair; the transition is a sluggish one.

① 此文原载于《清华大学科学报告》第三种，地质地理气象，1950，2 (1)：72～87.

Table 1 Summary of Previous Work on the Transformation of TiO_2 Polymorphs

1. Anatase→Rutile transition (Atmospheric pressure)

Temperature/℃	Investigators
Above 400[a)]	Bunting (1933)
600～1200	Schossberger (1942)
750～1050[b)]	Ricker (1949)
800～1000	Pamfilov & Ivancheva (1940)
800～1000	Barblan et al. (1944)
915	Schroder (1928)
Room Temp.[c)]	Thienchi (1946)

a) In the presence of mineralizers; b) Personal communication; c) Under pressure of 7 t/cm^2.

2. Brookite→Rutile transition (Atmospheric pressure)

Temperature/℃	Investigators
700～800	Barblan et al. (1944)
650	Schroder (1928)

2) Brookite has not been made authentically.

3) While both anatase and brookite can be converted to rutile, the reverse never takes place.

4) The inversion depends a great deal on rate of heating, chemical environment and pressure.

3. Methods of Investigation

3.1 Equipment and Experimental Procedures

Experiments in which only hydrostatic pressure was applied were performed in "test-tube" bombs. These are made of stainless steel or high-cobalt or-nickel alloy having an adequate yield strength at high temperatures. The bomb was placed vertically in a furnace and was connected to a pressure pump by the cone-and-cone seal and the pressure tubing. Samples, wrapped in gold or platinum, were placed directly opposite the thermo-couple well. At the end of a run, the furnace was quickly withdrawn and the bomb quenched in a stream of water, reaching room temperature in about 20～30 seconds.

When mineralizers were present, closed bombs, similar to that described by Morey and Ingerson (1937), were used. A small muffle furnace was on hand in studying reactions under atmospheric pressure.

3.2 Starting Materials

Starting materials used were synthetic pure chemicals, except in the case of brookite, in which case only natural minerals could be used. These are listed below.

(a) TiO_2 gel—One mole of TiO_2 C. P. was fused with one mole of Na_2CO_3. The product was dissolved in concentrated HCl, followed by neutralizing with concentrated NH_4OH to Phenol Red. The final product was white, and was amorphous as indicated by X-ray. The wet gel was used in most cases. After aging for two months at room temperature, the gel remains amorphous. If boiled in water, it gives an anatase pattern with broad peaks in 4 hours.

(b) TiO_2 C. P.—Anatase pattern, white.

(c) "Spectroscopically pure" TiO_2— X-ray pattern shows 90%～95% rutile and 5%～10% anatase, white.

(d) TiO_2 3 TG — Technical grad, about 95% anatase and 5% rutile, cream-colored.

(e) Brookite — Single crystals from Magnet Cove, Arkansas, USA. Only those crystals that do not show rutile lines in X-ray patterns were used. Crystals were crushed and passed through 325 mesh; black.

3.3 Identification of Phases

Identification of phases was done almost exclusively by X-ray methods. A Norelco X-ray spectrometer with Cu $K\alpha$ radiation with Ni-filter was used. Due to the extreme fineness of the product and its very high refractive indices, microscopic methods were difficult to apply.

ASTM① X-ray standard patterns were used for comparison. While the standard patterns for anatase and rutile correspond satisfactorily with those of natural or synthetic minerals, the standard pattern for brookite contains definitely lines of rutile, and hence, was not used for identification. Several single crystals of brookite from different localities were X-rayed, and when found to be free from rutile, were used as standard. The spacings and intensities of these brookite minerals are given in Table 2, together with ASTM patterns of anatase and rutile.

4. Discussion of Experiments

4.1 Studies of TiO_2 under Pressure

About 100 runs were made, ranging in temperatures between 250～800℃, pressures be-

① ASTM = American Society for Testing Materials.

tween the atmospheric and 30 000 lbs/in^2 and in time from a few hours to 2 weeks. The more significant runs are tabulated in Table 3.

Table 2 X-ray Diffraction Data for Anatase, Brookite and Rutile

Anatase ASTMII No. 876		Rutile ASTM II No. 1089		Brookite ASTM II No. 1116		Brookite Genth Col. 253. 8 Magnet Cove, Ark. USA		Brookite Switzerland	
d	I	d	I	d	I	d	I	d	I
3. 508	1. 00	3. 24	1. 00	3. 46	0. 60	3. 48	1. 00	3. 49	1. 00
2. 425	0. 10	2. 49	0. 70	3. 22	1. 00*	3. 23	0. 30*		
2. 372	0. 50	2. 31	0. 20	2. 87	0. 60	2. 88	0. 70	2. 90	0. 80
2. 333	0. 10	2. 26	0. 30	2. 45	0. 80	2. 46	0. 30	2. 46	0. 30
1. 887	0. 90	2. 19	0. 40	2. 39	0. 05	2. 37	0. 20		
1. 696	0. 70	2. 05	0. 30	2. 29	0. 05	2. 29	0. 10		
1. 662	0. 70	2. 01	0. 20	2. 24	0. 05				
1. 447	0. 70	1. 877	0. 40	2. 17	0. 40			2. 14	0. 10
1. 361	0. 60	1. 779	0. 20	2. 12	0. 05	2. 13	0. 20		
1. 335	0. 60	1. 682	1. 00	2. 04	0. 30				
1. 261	0. 70	1. 622	0. 60	1. 953	0. 30	1. 95	0. 40		
1. 247	0. 20	1. 500	0. 20	1. 881	0. 40	1. 89	0. 70		
1. 163	0. 60	1. 470	0. 20	1. 842	0. 20	1. 845	0. 30		
1. 158	0. 10	1. 450	0. 40	1. 681	1. 00*	1. 685	0. 40*		
1. 054	0. 10	1. 357	0. 80	1. 654	0. 20	1. 655	0. 40	1. 660	0. 30
1. 049	0. 50	1. 338	0. 70	1. 619	0. 60			1. 610	0. 20
1. 041	0. 50	1. 306	0. 20	1. 601	0. 20				
1. 016	0. 50	1. 238	0. 40	1. 531	0. 20	1. 535	0. 20		
		1. 194	0. 20	1. 476	0. 20				
		1. 163	0. 50	1. 450	0. 40	1. 440	0. 20	1. 466	0. 30
		1. 141	0. 40	1. 429	0. 20				
				1. 414	0. 20				
				1. 356	0. 80*				
				1. 341	0. 20	1. 337	0. 30		
				1. 307	0. 10				
				1. 236	0. 10				
				1. 166	0. 20				
				1. 146	0. 30				
				1. 116	0. 30				
				1. 090	0. 40				

* indicate rutile lines in brookite patterns; d=spacings in Å; I=relative intensity.

In the TiO_2 system, where the transition is very sluggish, there is difficulty in proving that equilibrium has been reached. However, if only one phase appears in a run lasting 4 to 10 days at a fairly high temperature, say 600℃ and 15 000 lbs/in^2, one may be safe to conclude that at least a metastable equilibrium has been reached, especially when different starting substances give essentially the same result. Under this condition, a true equilibrium may not be reached at all, even if much longer time is consumed. Such a metastable equilibrium, while of little value from the thermodynamic viewpoint, may prove of interest in geologic interpretations, as shown later.

Bearing this metastable equilibrium relationship in mind, one can see from Fig. 1, which is a graphic presentation of data contained in Table 3, that the curve separating the anatase and the rutile fields is the limit above which neither anatase nor brookite is stable. To the left of the curve, anatase remained unchanged in the duration of the experiment. Rutile was never converted to anatase in the metastable region of the latter.

The curve was drawn from data using TiO_2 C. P. as the starting material. Slight shift was observed if other material, such as TiO_2 gel or TiO_2 3 TG was used. For brookite, the transition to rutile took place at somewhat lower temperatures than for anatase for the same time duration.

The curve slopes toward the anatase region as pressure is raised. This is in accord with the density relationship of the minerals concerned. The slope is rather steep at pressures higher than 5 000 lbs/in^2, but levels off gradually at lower pressures.

The reason why only anatase and rutile, but not brookite are present, as shown in the diagram, is explained as follows. It is true that both anatase and brookite change to rutile to the right of the curve and that the reaction is irreversible. However, if one starts with TiO_2 gel, the transition always takes place in the direction amorphous TiO_2→anatase→rutile. Brookite never appears as even a transient phase.

4.2 Studies of TiO_2 in the presence of mineralizers

In order to activate the anatase→rutile transition, mineralizers were used, in most cases with TiO_2 gel as the starting material. Mineralizers included alkali fluorides, aluminum chloride, sodium borate and other salts. The experiments were carried out exclusively in closed bombs. Water was present in all cases. Results of experiments are tabulated in Table 4.

The data show that, ①the direction of phase transition is always amorphous TiO_2→anatase→rutile, ②rutile forms at much lower temperatures than if mineralizers are absent, and ③different mineralizers give essentially the same results. The lowest temperature at which rutile was found to be present is 250℃.

Table 3 Studies of TiO_2 under Water Vapor Pressure

Ser. No.	Temp. /℃	Pressure/(lbs/in^2)	Time/d	Products	Remarks
Starting Material = TiO_2 C. P. (Anatase)					
185	565	25 000	3	anatase	
197	565	30 000	3 1/2	rutile	
202	580	20 000	4	rutile	
249	585	15 000	5	anatase	
225	590	12 000	3 1/2	anatase	
173	590	30 000	3	rutile	
208	600	17 000	3 1/2	rutile	
255	605	13 000	6	anatase	
159	615	6 000	3	anatase	
213	615	13 000	2	rutile	
199	620	10 000	3 1/2	anatase	
229	630	5 000	3 1/2	anatase +rutile	
243	650	4 000	5	anatase	
258	670	3 000	4	anatase	
261	700	2 000	4	anatase	
77	660	atm.	10	anatase	
55	715	atm.	5	anatase	
Starting Material = "Spetroscopically Pure TiO_2" (95% rutile & 5% anatase)					
186	565	25 000	3	rutile + anatase	
198	565	30 000	3 1/2	rutile	
203	580	20 000	4	rutile	
174	590	20 000	2 1/2	rutile	
224	600	5 000	12	rutile + anatase	
209	600	17 000	3 1/2	rutile	
Starting Material = TiO_2 Gel					
329	545	20 000	5	anatase	
323	575	14 000	6	anatase + rutile	
326	606	10 000	5 1/2	anatase + rutile	
332	635	8 000	6	rutile	
78	660	atm.	10	anatase + rutile	
57	715	atm.	5	rutile + anatase	
Starting Material = TiO_2, 3 TG (95% anatase & 5% rutile)					
310	530	30 000	9	rutile	grayish blue
301	570	20 000	7	anatase + rutile	
298	575	21 000	7	rutile	grayish blue
269	580	15 000	5	rutile	grayish blue
275	655	5 000	4 1/2	anatase + rutile	gray
58	715	atm.	5	anatase + rutile	white

Table 3 (cont.)

Ser. No.	Temp. /℃	Pressure/(lbs/in^2)	Time/d	Products	Remarks
Starting Material = Brookite, Magnet Cove, Ark., U. S. A.					
309	530	30 000	9	rutile	
300	570	20 000	7	brookite	
324	575	14 000	6	brookite + rutile (little)	
268	580	15 000	5	rutile	
327	605	10 000	5 1/2	brookite + rutile (little)	
303	610	12 000	6	rutile	
333	635	8 000	6	rutile + brookite (little)	
274	655	5 000	4 1/2	brookite	
79	660	atm.	10	brookite + rutile (little)	yellowish white
278	700	5 000	4 1/2	rutile + brookite	
56	715	atm	5	rutile	yellowish white
Starting Material = Brookite + TiO_2 C. P.					
250	585	15 000	5	anatase + brookite	
256	605	13 000	6	anatase + brookite	
244	650	5 000	5	anatase + brookite	
247	650	15 000	5	rutile	
253	690	3 000	5	rutile	
262	700	2 000	4	anatase + brookite	

Table 4 Studies of TiO_2 in the Presence of Mineralizers

Ser. No.	Temp. /℃	Time/h	Product	Remarks
Starting Material TiO_2 gel + BeF_2—LiF glass*				
91	240	264	anatase + rutile (trace)	grayish
16	320	160	anatase + rutile	bluish
2	360	56	rutile + anatase (trace)	bluish
Starting Material TiO_2 gel + BeF_2—NaF glass*				
85	170	360	anatase	
89	255	96	anatase + rutile	
20	285	170	rutile	bluish
32	430	87	rutile	bluish
1	430	16	anatase + rutile	bluish
Starting Material TiO_2 gel+ BeF_2—KF glass*				
83	165	360	anatase	
87	270	96	anatase + rutile (little ?)	grayish
40	310	42	anatase	
99	340	56	anatase + rutile	bluish
24	360	136	rutile	bluish
28	480	90	rutile	bluish

Table 4 (cont.)

Ser. No.	Temp. /℃	Time/h	Product	Remarks
Starting Material TiO_2 gel + $AlCl_3$				
60	155	312	anatase	
51	165	77	anatase	
67	235	132	anatase	
44	310	44	rutile	bluish
49	320	20	anatase	
Starting Material TiO_2 gel + Na-borate				
61	120	312	anatase	
69	235	132	anatase + rutile (little ?)	
48	455	43	rutile	bluish
Starting Material TiO_2 C. P. + BeF_2—LiF glass				
13	320	160	anatase	
10	465	42	rutile	grayish blue
Starting Material TiO_2 C. P. + BeF_2—NaF glass				
17	285	170	anatase	
29	430	87	anatase + rutile (trace)	
Starting Material TiO_2 C. P. + BeF_2— KF glass				
21	360	136	anatase	
25	480	90	rutile	bluish
Starting Material Brookite+ BeF_2—LiF glass				
14	320	160	brookite	
11	465	42	rutile	
Starting Material Brookite + BeF_2—NaF glass				
18	285	170	brookite	
31	430	87	brookite	
Starting Material Brookite + BeF_2—KF glass				
22	360	136	brookite	
26	480	90	rutile + brookite	
Starting Material TiO_2 3 TG+BeF_2—KF glass				
12	465	42	rutile + anatase	grayish blue
6	545	41	rutile	grayish blue

* BeF_2—LiF glass (60% BeF_2 and 40% LiF); BeF_2—NaF glass (60% BeF_2 and 40% NaF); BeF_2—KF glass (60% BeF_2 and 40% KF).

One may argue that rutile may have formed metastably in the low temperature region due to the presence of mineralizers. Such a possibility, however, seems unlikely, as, with the same mineralizer and at similar temperatures, runs of shorter duration yielded anatase while those of longer duration gave rutile. If rutile could have formed only metastably thus implying anatase to be the stable phase at lower temperature, anatase could not possibly form first and then disappear and give place to rutile.

While runs at temperatures lower than 250℃ yielded anatase, there was indication that rutile may have formed in longer time. In the following sections, geologic and thermodynamic evidences will be presented, which are in favor of this inference.

5. Geological Considerations

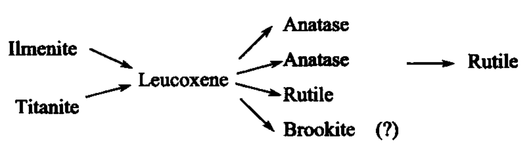
Rutile, brookite and anatase occur in nature in decreasing order of abundance. Rutile is found in almost all types of rocks. It is an important accessory mineral in igneous, contact and regional metamorphic rocks. It may form the major constituent in the heavy mineral fraction of sediments. Occasionally it may be found in large crystals in pegmatites and hydrothermal veins.

Brookite and anatase are much less common than rutile and rarely, if ever, form primary minerals in igneous rocks. However, they are observed under a great variety of conditions, and, in sediments, they may be as abundant as rutile. For a more detailed description, the readers are referred to Dana (1944) and Pettijohn (1949).

In this report, a few examples will be singled out in which the three or two of the TiO_2 polymorphs occur together. By studying these occurrences some indication of phase relationships can be found.

In his recent paper on the geology of Switzerland, Niggli (1948) states that the paragenesis of minerals in the fissure veins of the Alpine regions is as follows: quartz, adularia, albite, calcite, brookite, anatase, rutile, apatite, ilmenite, pyrite, sphene, and monazite. Anatase and brookite "frequently show the phenomenon known as differentiation in the fissures. That is to say, they either appear on different walls of the same fissures, or else appear separately in adjoining fissures. Cases are, however, frequent, in which both occur in close association, and are even joined by rutile" . He goes on to say that "both anatase and brookite may be wholly or partially changed into aggregates of fine acicular crystals of rutile" . Many examples of paramorphism of rutile after anatase or brookite appear in the literature. Such a phenomenon cannot be satisfactorily explained by a simple reheating process.

From the study of Ti-bearing minerals in sediments, Krynine[①] concludes that the sequence of decomposition and rebuilding can be shown as follows:



The frequency of occurrences of leucoxene→ anatase and leucoxene→rutile pairs is larger than that of the leucoxene→ anatase→ rutile combination. Allen (1950) recently reports a sim-

① Personal Communication.