Thermal Studies of Some Minerals. No. 1.

By

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With 6 Tables and 10 Text-figures

ABSTRACT: Thermal effects on the inner structures of some minerals were researched with use of special apparatus, a sort of thermal increment diffractometer, through which variations of the interplaner spacings in question were pursued not only at ordinary states, as were so far often carried out, recovered from high-temperature condition but also during continuously heated state at elevated temperature up to 1000°C. The results thus obtained have been found considerably different from those referred to in the previous works.

CONTENTS

I. INTRODUCTION

Most of the previous researches under the heading seem to have been accustomed to comparing the modifications revealed by the inner structures of certain minerals at ordinary state with those restored through cooling after thermal treatments. It however is difficult to trace the actual variations in the inner structures, even though remarkable differences in modifications be discernible at the final state recovered from heating at given temperatures, by ordinary means of X-ray (*cf.* UMEGAKI *et al.*, 1957; LIMA-DE-FARIA, 1958), infra-red absorption (*cf.* STUBIČAN, 1959; DACHILLE *et al.*, 1959; STUBIČAN *et al.*, 1961; TETTENHORST, 1962) and so forth, inasmuch as either reversible or irreversible variations, if any or all, are to be anticipated in the course of treatments. On the other hand, *DTA* methods (*cf.* KULBICHI *et al.*, 1959; SCHMIDT *et al.*, 1959) widely adopted may also be useful for pursuing conversions appeared in the modifications of materials bearing small heat contents and as a scheme for rapid, if not complete, identification of the specimens. At the same time, it is to be remembered that in such case the heating or cooling, for instance, in the rate of some degrees per minute, was too speedy, and duration of time at given state was too short, to cause the real and perfect conver-

sion for the comparatively stable structures, resulting in that seeming variations have been liable to occurring almost always on the sides of temperatures higher than are really necessiated. In view of this, some experiments have been carefully carried into effect concerning some of specific minerals with layer- and metamict structures.

II. EQUIPMENTS AND CONDITIONS FOR EXPERIMENTS

In pursuit of variations emerging in the inner structures, thermal effects on the pulverized specimens under consideration have been continuously traced during heated state at respective temperatures. The equipments used and the conditions settled in series of the experiments are outlined in the following:

(*1*) *X-ray apparatus.*

X-ray diffractometer provided for the research is that of GX-2B type, manufactured by Shimazu Man. Co. Ltd., to which the auto-scaler, recorder, powerful transformer putting out 60 *KV* in maximum and so on are attached.

(*2*) *Heating apparatus.*

The goniometer, on which the supporter for the sample-holder is placed, is enclosed in a cylindrical metallic case with the windows covered with double foils of nickel and special metal, through which both incident and diffractive X-ray can be penetrated. The holder is made of nickel, and platy in shape (80 mm in length, 9 mm in width, and 3 mm in thickness), in the central part of which a rectangular space (20 mm in length and 6.2 mm in width) is bored and bridged across by six Pt wires. The metallic case mentioned above is devised to be kept in air-tight condition and aspiratable strongly through a hole combined with a vacuum pump.

The paste of the pulverized specimen (finer than 250 mesh in grain-size) kneaded with nitrocellose diluted in amyl acetate as well as, if necessary, a little amount of quartz powder as a sort of indicator standardizing the spacings are filled closely in the space of the holder, flattened on the glass plate and allowed to be dried up in the air.

The holder containing the sample thus prepared is inserted in a cylindrical electric furnace (60 mm in length and 15 mm in inner diameter) connected with a current regulator and heated at any given temperatures, the variations of which are continuously measurable on the reading of millivoltmeter combined with Pt-PtRh thermo-couple held in the sample. Both the supporter of the holder and the metallic case are cooled with running water so as to be insulated from unnecessary thermal effects.

(*3*) *X-ray conditions.*

In accordance with necessity, 25–35 *KV* and 15–25 *mA* were yielded on the X-ray tube with Cu target and increase of some *KV* as well as of some *mA* was re-

quisite for putting out the sufficient intensity of diffraction from the specimens protected within the metallic case during thermal treatment, compared with in case of ordinary experiments in the air. Taking into account of counting miss ascribed to the electronic cirquit of *G. M.* counter, probable errors in numbers of pulses, opening angle of the slit, effect of duration of diffractive rays into the counter and the characteristics of the apparatus used, conditions suitable for the experiments were kept constant as follows:

X-ray: CuKα, time constant: 1.25 sec for 1000 cps (excepting the special cases), scanning speed: 1° (2θ)/min, rotating speed of chart: 1 cm/min, divergent slit: 1.5 mm in width, and receiving slit: 0.2 mm in width.

III. Preliminary Tests

Referring to the data given by Bassett and Lapham (1957), the specimens of low quartz (a_0: 4.91 Å and c_0: 5.39 Å at room temperature) collected from a small pocket of pegmatite in biotite granite occurring at Kuritani, Ôtake City, Hiroshima Prefecture were preliminarily provided for thermal treatments, as are briefly presented in the following:

(*1*) *Heating for an hour at several temperatures.*

X-ray diffraction figures revealed between 17° and 52° in 2θ were respectively recorded on charts in such way that the specimens were held at a given temperature and then successively at the temperature higher than the precedings for an hour plus time necessary for recording. A part of the data obtained are listed in Table 1, showing simply the expansion in each spacing, diminution of (110) and (102), and vanishing of (111), compared with those recognized at 25°C.

Table 1. Röntgenometric Data for Quartz

	Specimen from Kuritani, Ôtake City, Hiroshima Prefecture						Beta-quartz from Arkansas (Bassett & Lapham)	
Condition	at 25°C		heated for 1 hr. at 600°C.		heated for 1 hr. at 900°C.		heated at 625°C.	
hkl	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
100	4.255	26	4.332	28	4.332	30	4.340	22.8
101	3.342	>100	3.390	>100	3.390	>100	3.399	109.4
110	2.456	14	2.498	7	2.500	9	2.500	2.3
102	2.281	12	2.307	3	2.308		2.310	1.9
111	2.236	11		1		0		
200	2.127	9	2.165	7	2.165	7	2.166	3.2
201	1.980	7	2.010	8	2.012	8	2.013	3.9
112	1.818	26	1.842	29	1.842	28	1.837	10.3

(2) *Continuous heating*

To find out whether variations of the inner structures may or not depend on the conditions in heat treatment, the pulverized specimens of quartz were heated continuously in the rate of 5°C per minute from room temperature to 1000°C. The results obtained together with those remained not included in Table 1 are illustrat-

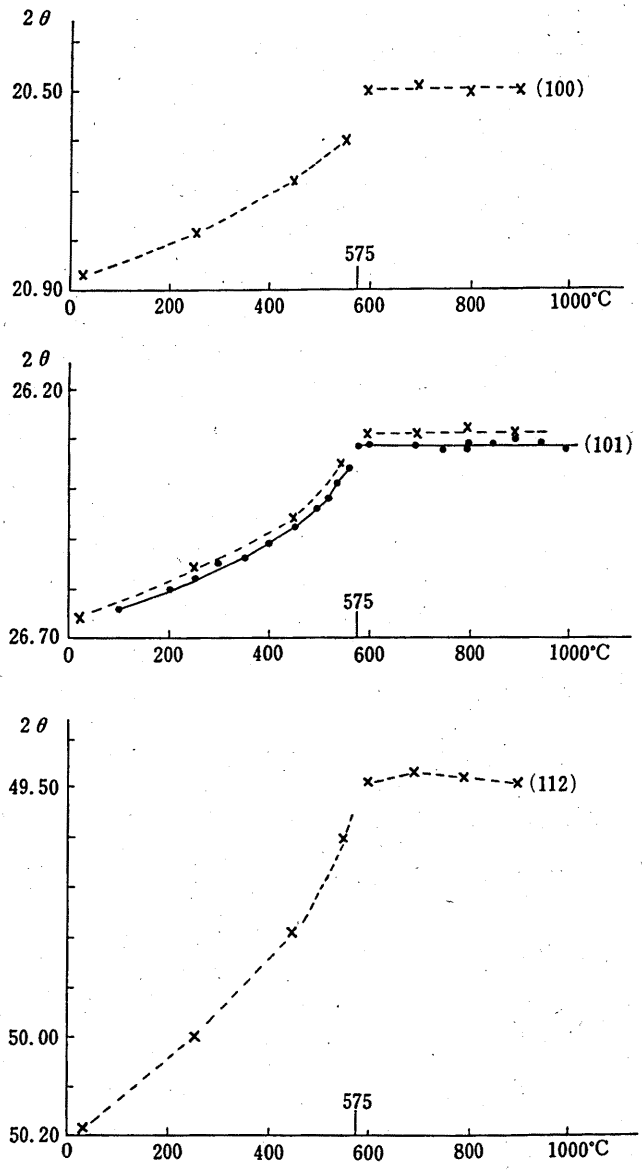

FIG. 1. Variation of spacings quartz
× kept constant for 1 hr. at each temperature checked
• heated continuously

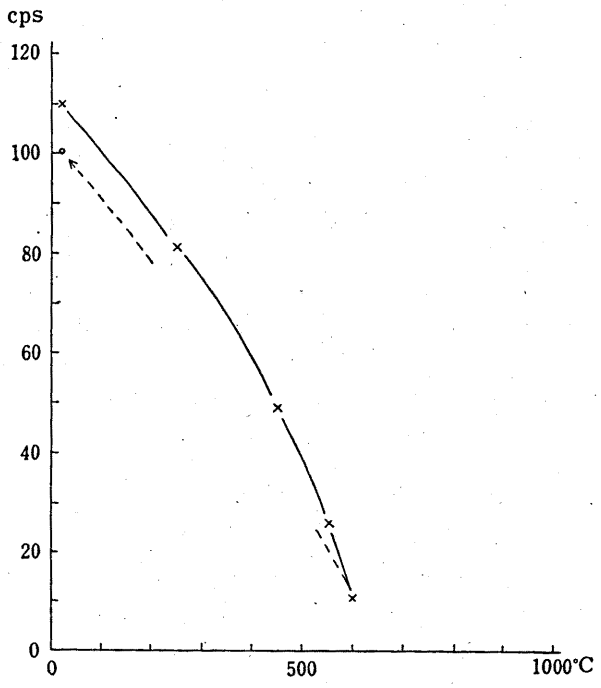

Fig. 2. Intensity variation revealed by (111) of quartz.
× kept constant for 1 hr. at each temperature checked.
o allowed to cooling.

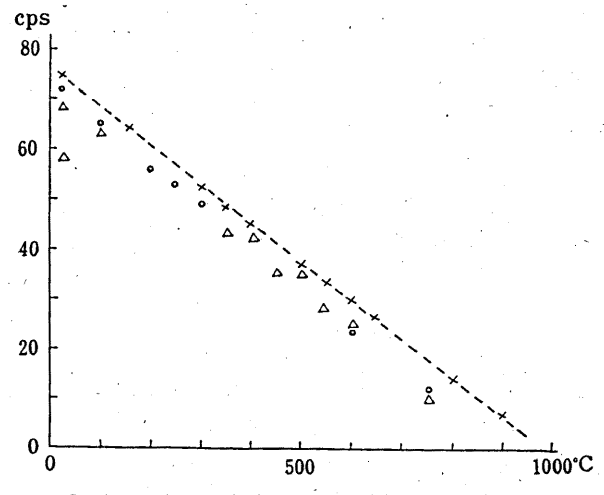

Fig. 3. Intensity variation revealed by (111) of quartz.
× heated continuously (5°C/min).
o cooled continuously.
△ allowed to cooling.

ed in Figs. 1, 2, and 3.

Inspection of these figures illustrates that certain spacings shown by pure quartz evidently reveal thermal expansion at the temperatures up to 575°C± and thenceforth invariable values or no trace of conversion into tridymite or others up to 1000°C indifferent to heat treatment. To be noticed is however that this is, as will later be alluded to, not the case with other kinds of minerals and, furthermore, that the intensity of diffraction relating to certain spacings is liable to be intensely controled by the heating speed. As is deducible easily from comparison of Fig. 2(a) with 2(b), rapid heating, for example, in the rate of 5°C/min seems not suitable for complete transition from low-temperature modification to higher one, and duration of heating for an hour at respective temperature is likely to making it easier even at the temperature fairly lower than that so far determined.

III. EXPERIMENTS

In the light of the results mentioned above, similar experiments were put into operation in order to clarify the essence of variations in the inner structures of some layer-structured and metamict minerals in comparison with the previous works (*cf.* TAKUBO *et al.*, 1953; WHITE, 1958; CARROLL, 1959; ERNST *et al.*, 1961; WARSHAW *et al.*, 1961).

(*1*) *Tests for pyrophyllite*

The specimens collected from Shôkôzan, Shôbara City, Hiroshima Prefecture were provided for thermal treatments. The main spacings obtained both at room temperature and at 1000°C are listed in Table 2.

TABLE 2 RÖNTGENOMETRIC DATA FOR PYROPHYLLITE FROM SHÔKÔZAN

	Room temp.		Kept const. at 1000°C for 1 hr.		A S T M	
hkl	d	I	d	I	d	I/I_1
002	9.18	56	9.41	31	9.14	40
004	4.596	40	4.713	35	4.57	50
111, 112	4.186	10	4.418	19	4.15	20
					3.87	5
113	3.389	3	3.486	4	3.34	20—40
006	3.064	79	3.145	78	3.04	100
	2.567	6	2.607	3		
	2.548	7	2.574	3		
$\bar{1}32$, 200	2.529	9	2.539	5	2.52	20
$\bar{2}04$, 132	2.414	12	2.430	4	2.40	40
008	2.300	4	⋮	⋮	2.29	20
	⋮	⋮			⋮	⋮

Of all the spacings, certain ones relating to the principal structure, such as (002), (004) and (006), were carefully traced at the state kept constant for an hour at various temperatures respectively. For reference, a part of the basic röntgenographs obtained in the experiments, though be omitted in the cases of other minerals scrutinized on the basis of the similar graphs, are presented in Figs. 4 and 5, and the results derived from these data are in Fig. 6.

It is clear from Fig. 6 that the spacing of (002) manifests a continuous variation both in 2θ and in cps representing the intensity without regard to the heating rate, and specific temperature, whereat transition between either modifications is to be appeared, can not so much obviously be recognized, while that of (004) is a little more discontinuous in cps at a temperature between 500°C and 700°C and that of (006) most distinctly points to a discontinuity at ca. 600°C. For inspection of the state prevailed at 600°C± more precisely, variation of (006) as well as that of one developed near the former (ca. 0.15° smaller in 2θ) were more detailedly traced at the state during being kept constant for some hours at each temperature, as has already been referred to in Fig. 5. The reality is that (006) becomes more and more faded with duration of heating but is not completely vanished and another one appeared by the former shows a gradual development, both being coincided with each other after certain hours. This should be of due significance in relation to

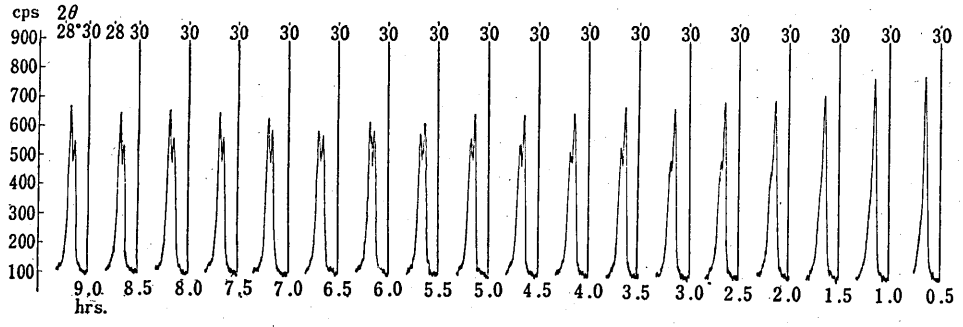

Fig. 4(a) Röntgenographs illustrating intensity variation in (006) of pyrophyllite kept constant at 580°C for long hours.

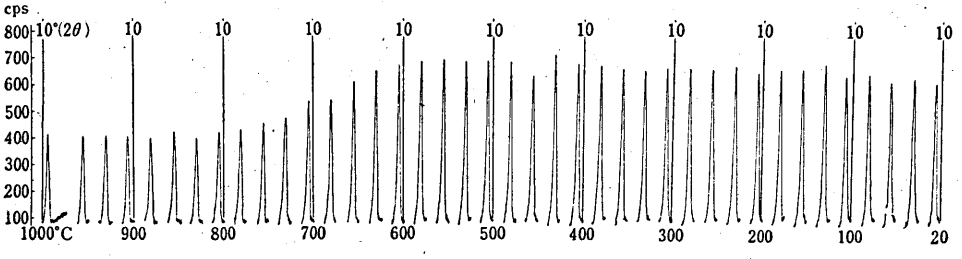

Fig. 4(b) Röntgenographs illustrating intensity variation in (002) of pyrophyllite heated continuously in the rate of 10°C/min. at each temperature.

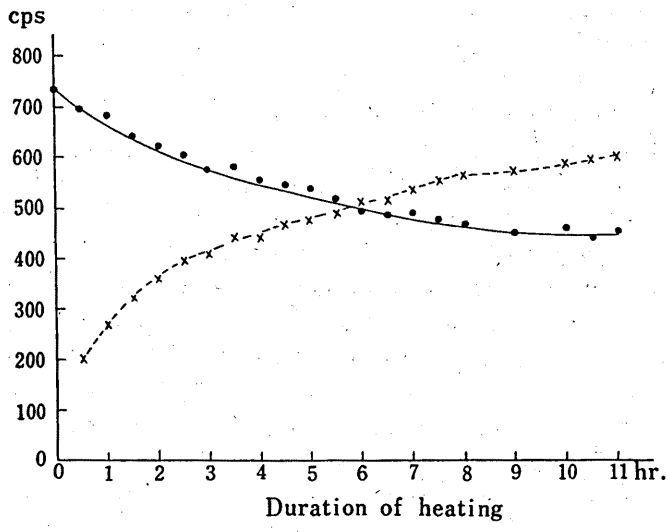

FIG. 5(a) Intensity variations resulted from Fig. 4(a) indicating splitting of (006) of pyrophyllite with duration of heating at 580°C.

• (006)

× Spacing splitted from the former.

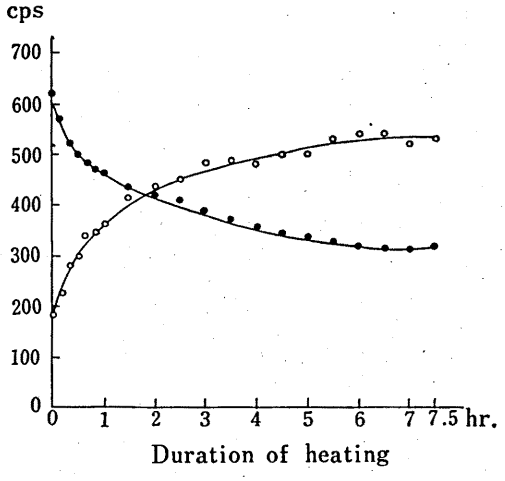

Fig. 5(b) Intensity variations indicating splitting of (006) of pyrophyllite with duration of heating at 600°C.

• (006)

× Spacing splitted from the former.

the structural variation of mineral.

On the other hand, a sort of endothermal peak of pyrophyllite, ascribed to setting-free of [OH], observed on *DTA* curve has commonly been believed to be

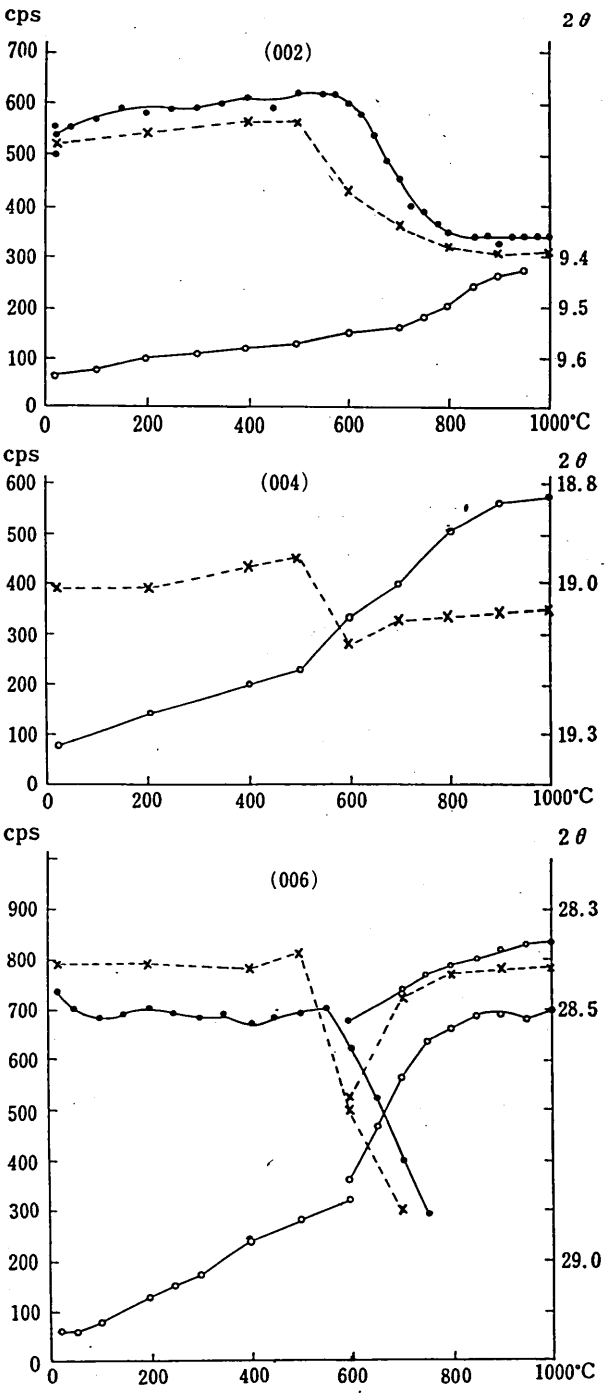

FIG. 6 Variation of spacings of pyrophyllite

× (cps) kept constant for 1 hr. at each temperature. • (cps) heated continuously.
o (2θ) kept constant for 1 hr. at each temperature.

completed at a temperature between 650° and 680°C, whereas the real variation is to be taken place in the representative layer spacings with duration of heating at the temperature lower than that generally expected through *DTA* and thenceforth becomes more complicated not simply because of disappearance of [OH] but rather on account of evolution of new spacing. This may also be the case with (004) to a certain extent.

(2) *Tests for muscovite*

Pure specimens sampled from Nako, Abu-gun, Yamaguchi Prefecture were subjected to the similar procedures excepting that *EMF* and current intensity of the X-ray tube were raised respectively to 35 *KV* and 20 *mA*. Most of the main spacings recognized both at room temperature and at 1000°C are listed in Table 3.

TABLE 3 RÖNTGENOMETRIC DATA FOR MUSCOVITE FROM NAKO

	Room temp.		Kept const. at 1000°C for 1 hr.		A S T M	
hkl	d	I	d	I	d	I/I_1
002	10.02	49	10.19	26	9.95	95
004	5.01	30	5.11	36	4.97	31
110					4.47	21
111	4.47	6	4.511	10	4.30	4
022					4.14	4
11$\bar{2}$					3.95	6
11$\bar{3}$					3.882	14
023					3.731	17
11$\bar{4}$					3.489	22
024					3.342	23
006	3.340	65	3.413	68	3.220	100
11$\bar{4}$	3.198	7	3.262	6	3.199	28
11$\bar{5}$					3.122	2
025	2.991	8	3.059	5	2.987	34
11$\bar{5}$	2.858	7	2.921	5	2.859	24
11$\bar{6}$	2.793	6	2.840	4	2.789	21
13$\bar{1}$					2.596	16
20$\bar{2}$	2.560	7			2.566	54
008	2.503	8	2.560	20	2.505	7
13$\bar{2}$					2.491	14
13$\bar{3}$					2.465	8
20$\bar{2}$					2.450	7
20$\bar{4}$					2.398	10
133					2.384	27
13$\bar{4}$					2.254	9
13$\bar{5}$					2.236	4
22$\bar{1}$, 204					2.208	7
22$\bar{3}$					2.189	4
20$\bar{6}$					2.149	15
135					2.132	21
223	2.127	4			2.070	4
044					2.053	6
00, 10	2.002	28	2.049	15	1.993	46

With specific regard to (002), (004) and (006), variations were continuously pursued during being held for an hour at each temperature. The data concerned are plotted in Fig. 7.

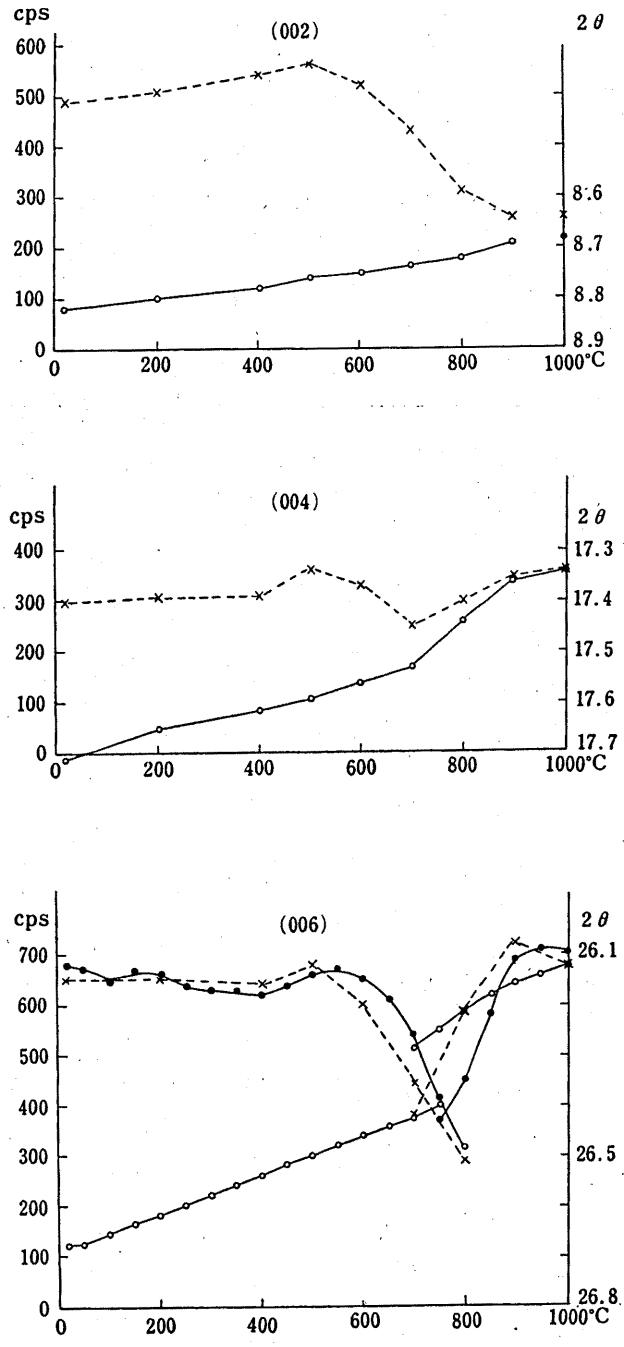

FIG. 7. Variation of spacings of muscovite
× (cps) kept constant for 1 hr. at each temperature
• (cps) heated continuously
○ (2θ) kept constant for 1 hr. at each temperature or heated continuously

The figure shows that the spacings of (002) and (004) reveal gradual variations without conspicuous discontinuity and that of (006) as well as its intensity illustrate a striking gap at 700°C, although the continuous heating in the rate of 8°C/min without staying at each temperature seems to cause deviation of more than 50°C toward higher-temperature side.

(*3*) *Tests for dickite*

The specimens taken from Shôkôzan were thermally treated in the conditions quite similar to in the preceding cases. Most parts of the principal spacings are tabulated in Table 4.

TABLE 4 RÖNTGENOMETRIC DATA FOR DICKITE FROM SHÔKÔZAN

	Room temp.		Kept const. at 1100°C for 1 hr.		A S T M	
hkl	d	I	d	I	d	I/I_1
002	7.16	69	8.12	4	7.153	90
020, 110	4.447	5	6.17	3	4.451	70
$11\bar{1}$	4.380	6	5.42	3	4.366	70
021	4.270	4	5.19	3	4.254	40
111	4.137	6	5.13	3	4.118	80
$11\bar{2}$	3.960	3	4.191	4	3.953	40
022	3.802	4	3.460	3	3.790	70
004, 112	3.579	72	3.391	3	3.578	100
$11\bar{3}$	3.430	4	2.543	5	3.428	50
023					3.262	30
113					3.094	40
$11\bar{4}$					2.936	40
024					2.794	40
114					2.650	10
$13\bar{1}$, 200	2.560	5			2.558	70
$11\bar{5}$					2.524	5
131, $20\bar{2}$	2.507	6			2.503	80
006, 132	2.386	10			2.383	50
$13\bar{3}$, 202	2.326	11			2.322	90
⋮	⋮	⋮			⋮	⋮

Date for the layer spacings such as (002) and (004) are plotted in Fig. 8, indicating that both are simply expanded up to ca. 800°C, while an abrupt diminution in their intensity seems to take place at ca. 500°C in the case of being kept at respective temperatures for an hour and at ca. 550°C in the case of being continuously heated with higher speed.

Remarkable is that both spacings corresponding to (002) and (004) are almost perfectly disappeared at the temperature above 700°C with very slow heating and

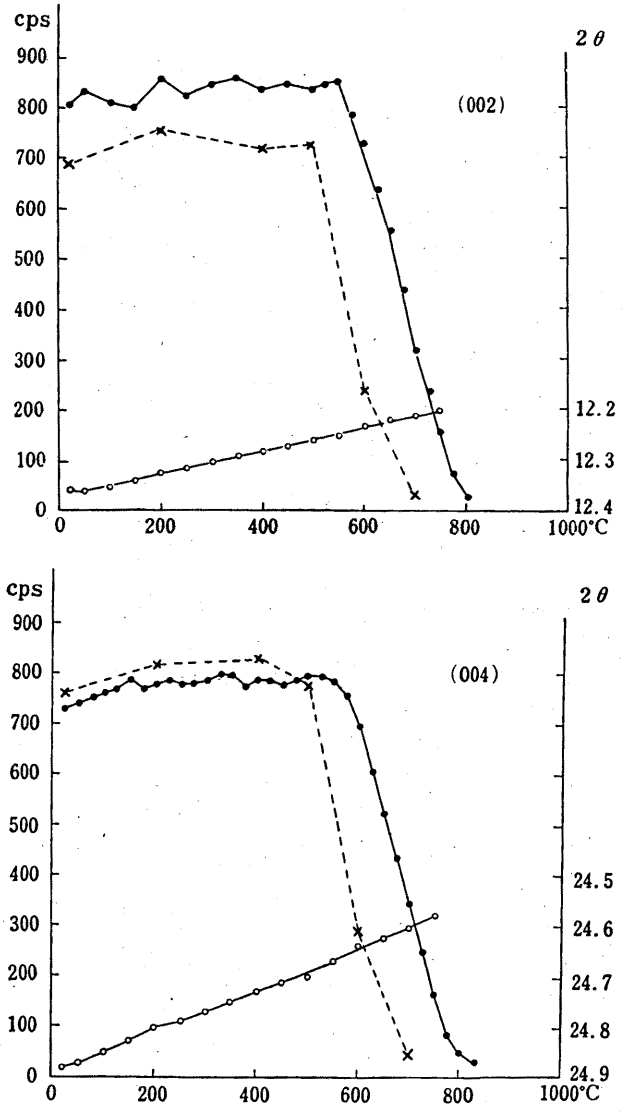

FIG. 8. Variation of spacings of dickite
× (cps) kept constant for 1 hr. at each temperature.
• (cps) heated continuously.
○ (2θ) heated continuously.

above 800°C with rapid treatment, and then quite different spacings assumed to represent the growth of a sort of meta-kaolin, though be yet remained to be researched in more details, are appeared.

(*4*) *Tests for fergusonite*

Blackish grey-colored specimens selected out from the coastal placer at Hagata-

chô, Ochi-gun, Ehime Prefecture were examined. The grains, some mm in maximum length, are seemingly well-crystallized but essentially amorphus in habit, bearing a considerably radioactive characteristic. Why this mineral was preferred for scrutiny lies mainly in that it is still now remained as a pending question how the metamict state may be transitional into the crystallized one and whether the previous data concerning the recrystallization of metamict minerals through thermal treatment might have been of reality or nothing but assumption, and that the data hitherto given were commonly referred to the results obtained at room temperature after thermal procedure, making light of that variation of the inner structures in the course of process might have been either reversible or irreversible though to more or less extent. Taking this circumstance into account, the results yielded during being treated thermally at high temperatures for several hours are given in Table 5.

TABLE 5 RÖNTGENOMETRIC DATA FOR FERGUSOMITE FROM HAGATA

Room temp.		Kept const. at 700°C for 1 hr.		Kept const. at 700°C for 10 hrs.		Kept const. at 700°C for 24 hrs.		Kept const. at 800°C for 1 hr.		Kept const. at 1000°C for 1 hr.		allowed to cooling down to room temp.		A S T M (heated at 1200°C)	
d	I	d	I	d	I	d	I	d	I	d	I	d	I	d	I/I_1
														5.47	3
														4.58	3
														4.02	3
												3.117B	25	3.29	3
		3.055	13	3.054	22	3.058	24	3.062	27	3.073	56	3.048	45	3.12	100
												2.991B	25	3.01	20
														2.86	90
		2.757	4	2.757	5	2.760	6	2.759	6	2.772	10	2.743	15	2.74	40
														2.64	20
		2.600	4	2.600B	5	2.600B	6	2.607B	6	2.610	12	2.589	15	2.59B	3
										2.543	3			2.53B	10
												2.521	5	2.52	10
metamict state														2.22	3
														2.06	5
		1.890	5	1.890		1.892	8	1.893B	9	1.899	17	1.901	15	1.901	50
										1.895		1.882	20		
												1.863B	10	1.855	30
						1.841	5	1.842	6	1.845	10	1.832B	10	1.754	10
						1.645	4	1.647	4m	1.652	9	1.634B	10	1.646	10
														1.627B	15
														1.620	15
						1.577	5	1.575	5	1.581	13	1.567	15	1.569	10
														1.563B	15
														⋮	⋮

Inspection of the table surely reveals that simple expansion of certain spacings is, in general, observable with heating of the specimens, while splitting of certain ones into some parts becomes more conspicuous with elevation of temperature and is almost completely remained even after cooling down to room temperature. This surely represents irreversibility of the process at least at the temperature lower than 1000°C. Similar relation is also deducible from the data presented in ASTM card, although the latter be of course connected with those obtained at the temperature 200°C higher than in the case of this experiment and, in consequence, splitting of the spacings be therein more obvious.

(*5*) *Tests for thorogummite*

Earthy matters picked up from pegmatite deposit occurring in the Tateiwa mine, Hôjô-chô, Onsen-gun, Ehime Prefecture were provided for the experiments. The specimens, faint brownish in color, are sporadically enclosed mainly in allanite and characterized with considerably intense radioactivity (ca. 50 cps/g). On the basis of the same reason as in the case of fergusonite, thermal effects on the mineral in question were pursued at each temperature above 600°C during being kept constant respectively for 10 hours, resulting in overlapping of the heating at higher temperatures. The results are listed in Table 6, wherein the spacings with asterices in the column of 1000°C are considered to be corresponding to those for thorite produced through thermal effects.

In this case, the fact is that the mineral under consideration is originally well-crystallized at ordinary state in spite of its earthy appearance, and nevertheless, it was accountably difficult to determine the positions of diffractive peaks drawn on the recorder because of their severe fluctuation and higher background ascribed to radioactivity of the elements contained. At any rate, scattering of almost all spacings seems to taken place already at ca. 600°C and to reach its culmination at ca. 900°C, whereas crystallinity recognized at 1000°C is apparently of the highest grade if merely based on numerous spacings but this is to be ascribed to a quite different condition due to production of thorite. On cooling down to room temperature, all the spacings appeared during thermal manipulation indicate a nearly complete recovery to the initial state without remainders of variation either in 2θ or in intensity, suggesting evidently a sort of reversible process. As has already been anticipated, the data obtained in these experiments are believed more accurate and useful for confirming the real variation appeared in the inner structures of certain minerals through thermal effects than the previous ones given at ordinary state simply after heating and, at the same time, more essential for enlightening the relation of secondarily produced minerals to the original one, metamictization of certain minerals and so on than those so far presented only on the basis of chemical connection with any other resembling minerals.

TABLE 6 RÖNTGENOMETRIC DATA FOR THOROGUMMITE

hkl	Room temp.		at 600°C		at 700°C		at 800°C		at 900°C		at 1000°C		allowed to cooling down to room temp.		A S T M	
	d	I/I_1	d	I/I_1	d	I/I_1	d	I/I_1	d	I/I_1	d	I/I_1	d	I/I_1	d	I/I_1
											5.28	40				
011	4.690	100	4.690	100	4.70	100	4.70B	100	(4.76 4.70)	90	(4.77 4.68)	100	4.720	100	4.695	90
											4.48	80				
											4.24	70				
			4.150	50	4.14	60	4.15B	60	4.15B	60	4.15	70				
200	3.539	90	(3.531 3.500)	70	(3.537 3.507)	80	(3.537 3.490)	80 70	(3.555 3.520)	100	(3.572 3.541*)	100	3.548	90	3.537	100
121	3.267	60	3.267	60	3.273	70			3.270	60	3.275	50				
											3.226*	60				
											3.172*	60	3.175	60		
112	2.821	50	2.823B	50	2.820	60					(2.858 2.831)	40	2.840	50	2.821	40
							(2.720	50					2.694	60	2.653	60
220	2.671	60	2.671	60	2.675	50	2.680B)	50	2.675B	60	2.679*	60	2.663	70	2.499	30
022	2.644	50									2.546*	40	2.522	40	2.336	5
031	2.205	30	(2.195 2.186)	40	(2.201B 2.187B)	40	(2.212 2.191)	40	2.212B	40	(2.227 2.219*)	30	2.206	40	2.203	40
											2.006	30			2.000	40
013	2.002	30	2.002	30							1.979	40				
							1.947	40	1.945B	50	(1.955* 1.938)	30 40				
321	1.868	40	1.866	40	1.871	50			1.859	50	(1.879 1.866)	40	1.878	40	1.869	30
312	1.819	50	1.821	50	1.817	50	1.824	50	(1.829 1.817)	70 60	(1.843* 1.833B*)	50				
							1.801	50	1.794	50	1.812	50	1.826	70	1.818	60
400	1.768	40	1.794	40			1.786	50	1.768	40	1.765B	30	1.763	30	1.767	10
123											1.689	30			1.740	10
411							1.697	40	1.656	50	1.661*	40	1.650	40	1.653	10
															.....	.....

* Probably thorite

V. Conclusion

(1) Thermal variations of certain minerals bearing the layer-structures are considered to be taken place more easily in their sub- or inter-layers than in the main ones and in the case of other manipulations such as *DTA* used to resulting in the apparent transition appeared generally at the temperature higher than be really so. In other words, conversion of one modification into the other is apt to being observed during being kept constant for long hours at the temperature considerably lower than in the case of continuous rapid heating, exclusive of the transition from low- to high-quartz.

(2) In spite of simple expansion revealed by the spacings with elevation of temperature, it often happens that the intensity corresponding to the same ones independently indicates the remarkable discontinuity at the related temperature. This may also be reflected on the data obtained through rapid heating as a sort of discontinuity even though at the temperature considerably higher than that necessary for real transition of the inner structure.

(3) In the layer-structures, thermal variations of the spacings other than those of basal planes are not so much distinct as be expected in other manipulations and accordingly useless for inspection.

(4) Special cares must be taken on researching the metamict structures, inasmuch as their variations are more complicated than were presented in the previous views that the metamict state should be 'irreversibly' converted into the crystalline one through simple heating regardless of difference of the process in that both reversible and irreversible variations are possible in accordance with respective characteristics attached to the structures concerned.

(6) It seems necessary to allude to that conspicuous fluctuation of the positions of the spacings recorded in the structures containing radioactive elements in more or less amount and the increment of the spacings in number through thermal effects are attributed either to raising of crystallinity of the related structure or to the formation of new modification, necessiating the re-inspection of the previous works on one hand and furthermore scrutiny concerning the inner structures of various minerals on the other.

(7) It has become clear that duration of heating at each temperature and detailed pursuit of the crystal structures both at the state during heated or cooled at respective temperatures and in ordinary condition recovered from the preceding state are considered most indispensable for this kind of study, and it is to be added to that deduction derived merely from chemical analyses is liable to falling into false understanding in relation to mineralogenesis.

Literatures

Bassett, W. A. and Lapham, D. M. (1957): A thermal increment diffractometer, Amer. Miner., **42**,

548–555.

CARROLL, D. (1959): Ion exchange in clays and other minerals, Geol. Soc. Amer. Bull., **71**, 749–780.

DACHILLE, F. and ROY, R. (1959): The use of infra-red absorption and molar refractivities to check coordination, Z. f. Krist., **111**, 462–470.

ERNST, E., FORKEL, W, and GEHLEN, K. v. (1961): A system of nomenclature for clays and similar ceramic raw materials, Amer. Ceram. Soc. Bull., **40**, (8), 479–483.

KULBICHI, G. and GRIM, R. E. (1959): A new method for thermal dehydration studies of clay minerals, Miner. Mag., **32**, 53–61.

LIMA-DE-FARIA, J. (1958): Heat treatment of metamict euxenites, polymignites, yttrotantalites, samarskites, pyrochlores, and allanites, Miner. Mag., **31**, 937–942.

SCHMIDT, E. R. and HECKROODT, B. O. (1959): A dickite with an elongated crystal habit and its dehydroxylation, ibid, 314–323.

STUBIČAN, V. (1959): Residual hydroxyl groups in the metakaolin range, Miner. Mag., **32**, 38–52.

STUBIČAN, V. and ROY, R. (1961): A new approach to assignment of infra-red absorption bands in layer-structure silicates, Z. f. Krist., **115**, 200–214.

TAKUBO, J., UEDA, T., NISHIMURA, S. and MASUTOMI, H. (1953): Studies on the minerals containing rare elements, Part 15, (in Japanese), Jour. Geol. Soc. Japan, **59**, 47–58.

TETTENHORST, R. (1962): Cation migration in montmorillonites, Amer. Miner., **47**, (5 and 6), 769–773.

UMEGAKI, Y., HABARA, T. and SOEDA, A. (1957): Über die pegmatitischen Mineralien, usw. Nr. 2, Jour. Sci. Hiroshima Univ., Ser. C, **2**, (1), 29–52.

WARSHAW, C. M. and ROY, R. (1961): Classification and a scheme for the identification of layer silicates, Geol. Soc. Amer. Bull., **72**, 1455–1492.

WHITE, W. A. (1958): Water sorption properties of homoionic clay minerals, Illinois State Geol. Surv. Rep. Invest., (208).

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