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Title	Thermal Studies of Some Minerals, No. 2
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Citation	Geological report of the Hiroshima University , 14 : 25 - 41
Issue Date	1965-02-22
DOI	
Self DOI	10.15027/52836
URL	https://ir.lib.hiroshima-u.ac.jp/00052836
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Thermal Studies of Some Minerals, No. 2

By

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with 5 Tables and 6 Text-figures

(Received July, 30 1964)

ABSTRACT: For the purpose of discerning the inner structures of chlorite group from one another, thermal variations of the related specimens collected from a chromite deposit in serpentinite have been continuously traced during the heated states at various temperatures up to ca. 950°C kept respectively for long enough hours by means of X-ray diffractometer accompanying the specific heating apparatus and a few data obtained through infra-red absorption have been added to for reference.

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I. INTRODUCTION

In the previous work dealt with by UMEGAKI et al. (1963) under the same heading, some data indicative of röntgenographic traceability for variations in the inner structures of minerals during heat treatment (not quenched after heating) were presented to prove essential specifically for scrutiny of the layer silicates. In relation to this, the procedures nearly similar to those carried out in the preceding experiments have been repeated again in the present research, though with especial care to the holding manner of the specimen so as to reach the best condition for x-ray diffraction.

The specimens provided for this study have been obtained mainly from the Hirose mine producing the chromite ores pregnant in serpentinite intervening in the Sangun metamorphics and, in particular, confined merely to chlorite because of the authors' interest in its miscellaneous occurrence discerned hardly even under microscope and in its interrelation with ore genesis as well as with the origin of serpentinite, whereas dispute as to the structure of the mineral in question only will be subjected to hereunder.

As for chlorite, it is naturally inferable that the isomorphous substitution of

Mg with heavy metals mainly within the octahedron sheet of the mineral bearing a general formula: $R''_{6-x}R'''_x(Si_{4-x}R'_x)O_{10}(OH)_8$ (where $R''=Mg, Fe'', Mn$ and $R'''=Al, Fe''', Cr, Ti$) is to be reflected röntgenographically on each spacing, though to a slight extent, giving an useful clue to identification hardly achieved for this sort of mineral. The role and behavior of the substituting heavy elements comprised in the octahedron sheet were skilfully deduced from the relation of the diffraction intensity revealed on the basal planes of lower orders to the respective structure factors by BROWN (1955), BRINDLEY and GILLERY (1956), LAPHAM (1958), SCHOEN (1962) and PETRUCK (1964) etc.

On the other hand, tracing for thermal variation of diffraction patterns is, as was alluded to often, also surely considered effectively providable as an indirect means for distinguishing one from another in the inner structures of crystals with allied characteristics or simply for confirming their structural transformation. To be noted is that various changes coming out on heating are in an intimate connection with the chlorite structure composed mainly of the layers of mica (or talc) and brucite (cf. ENGELHARDT, (1961); WARSHAW and ROY, (1961)). In fact, such a view that thermal effects on the mineral concerned result at the first step in remarkable variation of the basal reflection ascribed to low-temperature dehydration of the brucite layer with emergence of the modified structure of chlorite and at the second stage in the destruction of the structure together with formation of olivine in company with furthermore dehydration was suggested by BRINDLEY and ALI (1950).

As another means seeking after the crystal structure or its variation, utility of the infra-red absorption for pursuit of the related elements and linkages is, though numerous works pertaining to this factor have already been presented (cf. STUBIČAN and ROY, (1961)), to be added to. Thus, a few reference to the data obtained for only the representative specimens preliminarily ascertained irreversible through quenching from the high-temperature states will also be outlined.

II. CONSIDERATIONS ON EXPERIMENTAL DATA

A. Specimen provided for experiments

The specimens were collected from a chromite deposit of the Hirose mine situating at Tari, Nichinan-chô, Hino-gun in Tottori Prefecture. Of all, those numbered 67, 19, 39, 98, 20, 84, 81, 74, 80-1 and 148 were sampled from several parts within the ore body, in its contact zone with the surrounding serpentinite and in its pinched zone appearing in the main galleries, and No. 30 only from the vein in the sheared zone of a fault cutting across the ore body in the 6-7 adit.

B. X-ray diffraction

(1) *Device for sample holding*

Considering that the highest accuracy in the intensity of diffraction be a requisite for calculating the structure factor combined intimately with the inner structure of crystal or with its variations through any treatments, the average (1) of five times experiments for diffraction of the pulverized specimen No. 74 filled in the frame, enlarged laterally up to 4.6 cm, with a thickness of 0.5 mm (permissible down to 80μ) on the glass plate and that (2) for the same specimen dispersed simply within the same area on the glass plate have been compared with each other though with 1° in angular aperture of divergent slit and in the similar conditions concerning the other factors. As a result, the first procedure has been successively followed throughout this research because of its superiority to the second specifically on (001) reflection.

(2) *Diffraction data*

The observed and calculated values of the respective spacings obtained for all the specimens without any treatments are given in Table 1 and the related cell parameters derived from these data are in Table 2.

Inspection of the tables points to the similarity in each pair of No. 98 with No. 20, of No. 84 with No. 81 and of No. 74 with No. 80-1, the decrease in the angle of β (ranging within the values given by BROWN and BAILEY, (1962)) and more significantly, the increase in the values of d_{001} from 14.16\AA (No. 67) to 14.30\AA (No. 148). With respect to this, ENGELHARDT (1942), BANISTER and WHITTARD (1952), HEY (1954), BRINDLEY and GILLERY (1956), SHIRÔZU (1958) and so on were of opinion that the d_{001} values intensely depend on the strength of the interlayer bondings in connection with replacement of Si with trivalent Al and Fe in the tetrahedron sheet and that of Al with Mg in the octahedron sheet. In consequence, the increase of d_{001} in the present data is, in reference to the researches achieved by BRINLEY and GILLERY, and SHIRÔZU, to be resulted from the decrease in the strength of the interlayer bondings or from Al contents decreasing from 1.25 to 0.75, assuming that $\text{Si} + [\text{Al}]^{4+}$ equals to 4.

That the substitution of Mg^{2+} with Fe^{2+} and Mn^{2+} in the octahedron sheet also gives the effects on the cell constants, a and b , is easily inferable from the equation:

$$a = 5.320 + 0.016 \text{ Fe(total)} + 0.027 \text{ Mn}$$

and

$$b = 9.202 + 0.028 \text{ Fe(total)} + 0.047 \text{ Mn}$$

given by HEY (1954) on the basis of regression analyses, while, on the other hand, RADOSLOVICH (1962) proposed for b another equation:

$$b = 9.23 + 0.03 \text{ Fe}^{3+} \pm 0.0285$$

Table 1. Data for x-ray diffraction

h k l		No. 67			No. 19			No. 39			No. 98		
monoclinic	ortho-hexagonal	d(Å) calc.	d(Å) obs.	I/I ₀	d(Å) calc.	d(Å) obs.	I/I ₀	d(Å) calc.	d(Å) obs.	I/I ₀	d(Å) calc.	d(Å) obs.	I/I ₀
001	001	14.16	14.1	89	14.18	14.2	100	14.20	14.2	100	14.22	14.3	85
002	002	7.08	7.08	100	7.09	7.08	100	7.10	7.11	100	7.11	7.13	100
003	003	4.720	4.72	60	4.727	4.72	68	4.733	4.73	66	4.740	4.74	60
020	020	4.600	4.60	9	4.605	4.60	8	4.610	4.61	6	4.605	4.60	8
004	004	3.540	3.539	70	3.545	3.545	77	3.555	3.551	68	3.555	3.556	68
005	005	2.832	2.831	20	2.836	2.836	21	2.844	2.840	18	2.844	2.845	16
	200				2.658	2.655	3				2.658	2.655	2
131, 20 $\bar{2}$		2.586	2.584	11	2.580	2.579	10	2.583	2.584	5	2.579	2.578	8
13 $\bar{2}$, 201		2.535	2.536	15	2.538	2.539	20	2.540	2.541	8	2.538	2.538	15
132, 20 $\bar{3}$		2.433	2.435	13	2.435	2.437	14	2.439	2.436	7	2.437	2.436	11
13 $\bar{3}$, 202		2.375	2.378	7	2.378	2.376	8	2.381	2.381	5	2.379	2.379	6
133, 20 $\bar{1}$		2.252	2.253	6	2.254	2.255	6	2.257	2.259	4	2.256	2.257	5
134, 20 $\bar{5}$					2.063	2.063	3	2.066	2.068	2	2.066	2.067	2
007	007	2.023	2.023	5	2.026	2.025	5	2.029	2.027	5	2.031	2.029	4
13 $\bar{5}$, 204		1.998	1.998	11	2.001	2.000	14	2.003	2.003	8	2.003	2.002	11
135, 20 $\bar{6}$		1.878	1.878	6	1.880	1.880	6	1.882	1.881	3	1.883	1.884	5
13 $\bar{6}$, 205		1.820	1.818	6				1.824	1.823	3	1.825	1.824	5
	240										1.740	1.738	2
136, 20 $\bar{7}$											1.715	1.716	1
13 $\bar{7}$, 206					1.661	1.660	3	1.663	1.661	2	1.664	1.664	3
137, 20 $\bar{8}$		1.562	1.563	9	1.564	1.564	9	1.566	1.567	6	1.567	1.567	8
060, 33 $\bar{1}$		1.533	1.534	9	1.535	1.536	13	1.537	1.537	6	1.535	1.535	12
062, 331, 33 $\bar{5}$		1.497	1.499	6	1.500	1.500	4	1.502	1.502	3	1.500	1.501	4
063, 332, 33 $\bar{1}$											1.460	1.461	2
0010	0010	1.416	1.418	5	1.418	1.418	3	1.420	1.420	2	1.422	1.421	3
064, 333, 33 $\bar{5}$											1.409	1.413	2
13 $\bar{8}$, 208		1.392	1.390	9	1.393	1.393	9	1.395	1.395	6	1.396	1.396	6
065, 334, 33 $\bar{6}$											1.351	1.352	2
400, 26 $\bar{2}$													
139, 2010					1.319	1.319	3	1.321	1.320	2	1.322	1.320	3
401, 26 $\bar{3}$													
066, 335, 33 $\bar{7}$					1.287	1.286	3	1.289	1.285	2	1.288	1.290	3
1310, 2011					1.219	1.220	3	1.221	1.220	2	1.222	1.222	2
26 $\bar{6}$, 404													
1311, 2010													
0012											1.185	1.185	2

It thus follows that content of Fe substituting the octahedral Mg is estimated at most 0.6~0.7 per 6 atoms from the equation relating to a and less than 1 per 6 atoms from the equations connecting with b and reveals the increase of its own

Table 1 (continued)

No. 20		No. 84			No. 81		No. 74			No. 80-1		No. 30		No. 148		
d(Å) obs.	I/I ₀	d(Å) calc.	d(Å) obs.	I/I ₀	d(Å) obs.	I/I ₀	d(Å) calc.	d(Å) obs.	I/I ₀	d(Å) obs.	I/I ₀	d(Å) obs.	I/I ₀	d(Å) calc.	d(Å) obs.	I/I ₀
14.2	97	14.27	14.3	98	14.3	91	14.28	14.3	100	14.3	100	14.3	99	14.30	14.3	72
7.12	100	7.14	7.14	100	7.14	100	7.14	7.14	100	7.14	88	7.14	100	7.15	7.16	100
4.74	73	4.757	4.76	77	4.75	54	4.760	4.76	69	4.67	60	4.76	76	4.767	4.77	49
4.61	4	4.610	4.60	7	4.60	10	4.610	4.60	5	4.60	8			4.610	4.60	16
3.555	73	3.568	3.567	68	3.565	58	3.570	3.570	63	3.570	54	3.570	66	3.575	3.579	63
2.843	20	2.854	2.854	19	2.854	12	2.856	2.856	17	2.856	15	2.858	19	2.860	2.860	11
2.656	1									2.661	1					
2.581	6	2.583	2.582	7	2.584	7	2.583	2.584	4	2.585	7	2.589	1	2.584	2.585	13
2.540	9	2.541	2.543	13	2.540	14	2.542	2.542	9	2.545	15	2.544	2	2.542	2.543	22
2.438	8	2.440	2.441	12	2.441	12	2.441	2.442	8	2.444	12	2.444	2	2.441	2.443	19
2.378	5	2.383	2.384	7	2.384	7	2.383	2.382	4	2.382	6	2.381	2	2.384	2.385	9
2.250	4	2.260	2.260	6	2.262	5	2.261	2.260	4	2.261	4	2.260	1	2.262	2.263	6
2.065	2	2.070	2.073	3	2.070	2	2.071	2.074	2	2.071	2					
2.030	5	2.039	2.038	5	2.037	3	2.040	2.041	4	2.040	4	2.042	5	2.043	2.040	5
2.003	10	2.008	2.006	13	2.008	12	2.008	2.008	9	2.008	11	2.009	1	2.009	2.009	13
1.881	3	1.887	1.886	4	1.886	4	1.888	1.888	3	1.888	5	1.891	1	1.888	1.889	3
1.822	3	1.829	1.828	4	1.828	5	1.830	1.829	3	1.830	4	1.828	1	1.831	1.828	4
1.737	1															
1.716	2						1.720	1.719	2	1.722	3					
1.665	2	1.668	1.665	2	1.670	2	1.669	1.669	3	1.669	3	1.668	1	1.670	1.669	3
1.565	7	1.571	1.570	9	1.570	8	1.572	1.572	7	1.572	6	1.572	4	1.573	1.572	8
1.535	5	1.537	1.537	8	1.537	13	1.537	1.537	7	1.537	11	1.537	2	1.537	1.537	21
1.500	2	1.502	1.502	4	1.502	5	1.502	1.502	3	1.502	3	1.503	1	1.502	1.503	8
1.421	2						1.428	1.429	2			1.429	3	1.430	1.430	3
														1.412	1.412	4
1.394	6	1.400	1.399	8	1.399	6	1.401	1.400	6	1.401	6	1.401	4	1.402	1.401	6
1.320	2	1.325	1.320	3	1.320	2				1.321	3			1.328	1.32	4
1.287	3	1.291	1.291	3	1.292	4	1.290	1.291	3	1.292	3	1.293	1	1.291	1.293	4
1.222	2	1.225	1.22	3			1.226	1.226	2			1.228	3			
1.184	3	1.189	1.189	2			1.190	1.190	2			1.191	2	1.192	1.192	1

from No. 67 to No. 148, whereas BRINDLEY and GILLERY pointed out the higher reliability of calculation based on the structure factor compared with that obtained from regression analyses. Numbers of the heavy atoms in the octahedron

Table 2. Parameters for unit cell

No.	67	19	39	98	20	84	81	74	80-1	30	148
$d_{001}(\text{\AA})$	14.16	14.18	14.20	14.22	14.22	14.27	14.27	14.28	14.28	14.29	14.30
$a(\text{\AA})$	5.31	5.32	5.32	5.32	5.32	5.32	5.32	5.32	5.32	5.32	5.32
$b(\text{\AA})$	9.20	9.21	9.22	9.21	9.21	9.22	9.22	9.22	9.22	9.22	9.22
$c(\text{\AA})$	14.27	14.29	14.31	14.33	14.33	14.38	14.38	14.39	14.39	14.40	14.41
$\beta(^{\circ})$	97.08	97.09	97.08	97.06	97.06	97.04	97.04	97.04	97.04	97.03	97.03

sheet calculated after the idea enlightened by Petruck from their relation to the specific ratio of the diffraction intensity are in the range from 0.3 to 0.8 with a few exceptions, as are referred to in Table 3, revealing a good harmony with the values mentioned above.

Table 3. Calculated data for the heavy atoms in the octahedron sheet

No. of specimen	$\frac{I_{002}+I_{004}}{I_{003}}$	$\frac{I_{002}+I_{004}}{I_{003} \text{ corrected}}$	Numbers of the heavy atoms
67	2.83	2.59	0.3
19	2.60	2.54	0.3
39	2.55	2.85	0.5
98	2.80	3.23	0.8
20	2.37	2.64	0.4
84	2.60	2.71	0.4
81	2.96	3.95	1.3
74	2.36	2.92	0.6
80-1	2.37	2.86	0.5
30	2.18	2.64	0.4
148	3.33	4.44	1.8

On the other hand, the structure factors for the reflection from the basal planes of lower order are practically found from Schoen's equation representing their intimacy with the intensity of diffraction and with LORENTZ-polarization factors, as are shown in Table 4. Here, it is worthy mentioning that Schoen combined the structure factor with the chemical composition concerning chlorite, Brown related the isomorphous substitution of Mg and Al with Fe to the basal reflection, BRINDLEY and GILLERY emphasized the effects of Fe, Cr and Mn contained in two octahedral positions on the basal reflection and PETRUCK demonstrated the allied conclusion though for the reason of scattering factors of the heavier atoms (Fe, Cr, Mn and Ti) twice those of the lighter ones (Mg, Si and Al).

Numbers of the heavy atoms and the ratios of the structure factors referring to F_{002} are, as are plotted in Fig. 1, characterized with a tendency of inverse proportion to each other. This may be resulted in certain sense from that with increase of the heavy atoms distributed symmetrically in the brucite layer and

Table 4. Relative values for structure factor

No. of specimen	67	19	39	98	20	84	81	74	80-1	30	148
F_{001}	37	38	38	35	38	38	36	38	38	38	32
F_{002}	77	78	77	77	77	77	77	77	72	77	77
F_{003}	91	97	95	91	100	103	86	97	90	102	82
F_{004}	133	140	131	131	136	130	121	125	116	129	125
F_{005}	91	93	86	81	91	88	70	83	78	88	67

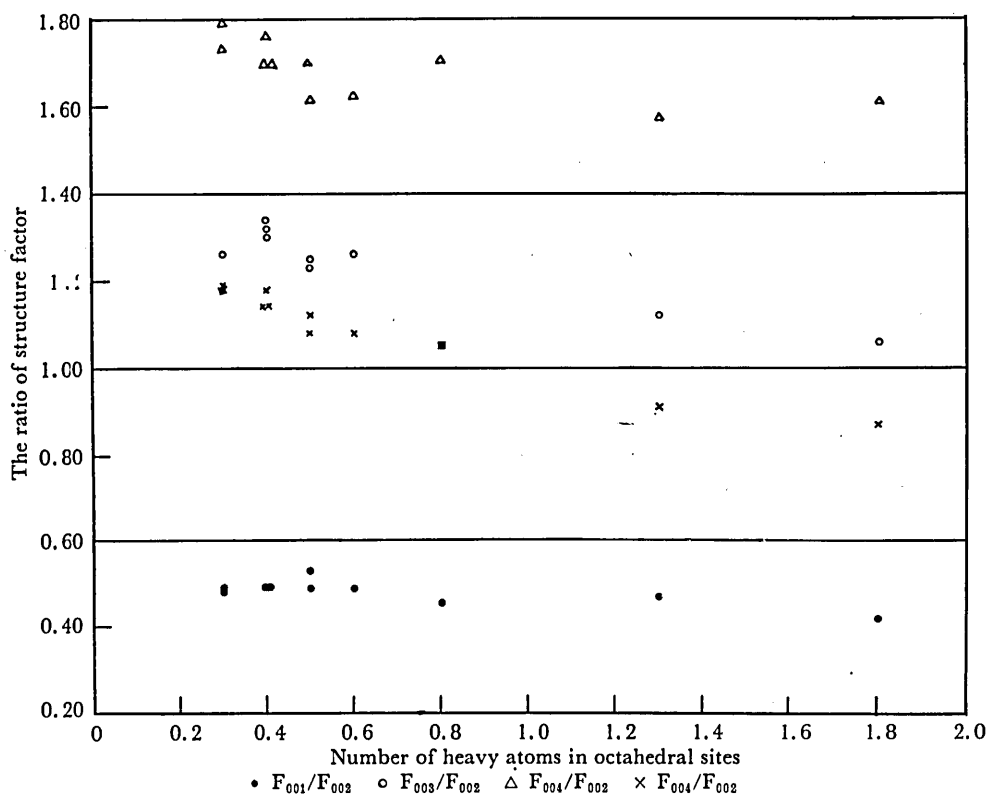


FIG. 1. Relation of the ratio of structure factor to number of the heavy atoms

in the mica layer theoretical values of the structure factor for the odd-order reflection are kept invariable even when those for the even-order reflection relatively increase.

(3) Thermal transformation

Variations or modifications emerging in the inner structures of the specimens during heat treatments have been continuously traced with lapse of time at

various temperatures lower than 950°C directly by means of x-ray diffractometer equipped with an electric furnace, the details of which were described already in the former report. In particular, heating conditions have been kept constant during long time at lower temperatures in order to find the lowest limit of the temperature requisite for transformation. In reality, the check for variations in several kinds of reflection from the basal planes, however, has been started at 500°C, when any changes were not recognized in the diffraction intensities through slow heating from the room temperature up to this temperature. The tests have been confined to two kinds of the specimens as the representative for such reasons that all the specimens are allied to one another in their inner structures and, into the bargain, long duration (at least several days) is necessary for one cycle of continuous heating.

The relative variations in the diffraction intensity for some basal planes of the specimens Nos. 20 and 74 enclosed in the heating apparatus, though of course different from those obtained very carefully in the case of the structure-factor calculation, are illustrated respectively in Figs. 2 and 3. Noticeable is that common tendencies in the declination of the initially appeared spacings and in the development of the new ones emerging on the way are recognizable in the figures. More detailedly describing, diminution of (002), (003) and (004) and coming-out of the new spacings on the higher-angle (2 θ) sides of (001) and (005) (probably representing a part of the *modified chlorite* and hereunder respectively designated (001)M and (005)M etc.) become more conspicuous at 550°C kept for some hours, when especially in the case of No. 20 the apparent increase of (001) seems ascribable to the overlapping of (001)M on itself in almost similar angle. Even at the same temperature, a trace of the talc structure begins to bring forth during heating for about 12 hours. The spacings of (002), (003), (004) and probably (005) diminishing markedly at 575°C kept for 2 hours after treated at 550°C for about 24 hours culminate in their disappearance at 625°C kept for 2.5 hours after heated at 575°C and 600° respectively for about 24 hours, while those of (001) together with (001)M, (005)M, and (004)M emerging at 600°C as well as that of talc, though different from one another in the relative intensity, maximize in these temperature-ranges, reveal the decay to a certain extent at 775°C, and become extinct completely at 900°~925°C, accompanying setting-up of the olivine structure.

On the whole, remarkable variations displayed in the related figures may be reasonably ascribed to the beginning of breaking-down of the brucite layer at 550°~575°C, its extinction at 600°~625°C and the disappearance of the whole structure at ca. 900°C. To be added to, however, is that the thermal effects in the furnace attached to the x-ray diffractometer specifically at higher temperature have brought an apparent shifting to the higher-temperature side compared with those obtainable in the large-scaled tubular furnace provided simply for heating: that is to say, the complete destruction of the chlorite structure as well

as the initial formation of forsterite (or enstatite) have been discernible already at 775°C kept for 5 hours in the air with use of the latter furnace concerning the specimens that were preliminarily verified irreversible for quenching after any heat treatments.

2θ variation for the basal planes of the same specimens are exhibited respectively in Figs. 4 and 5. As for No. 20, it runs that (001) is almost invariable up to 550°C but reveals a slight increase (implying contraction of the interlayer distance) when combined with (001) M at 575°~625°C, (002) and (003) show somewhat steep decrease (expansion) at 550°C and go on invariably up to 600°C, (004) very slowly diminishes up to 600°C while (004)M brings forth on the higher-angle side at 600°~825°C, and (005) is not convertible up to 575°C while (005)M increases gradually with lapse of some hours at this temperature to 600°C, diminishes slightly at 625°C and then indicates a little increment up to 900°C. In the case of No. 74, the fact is that (001) discloses a very little diminution up to 550°C while (001)M coming out at this temperature on the higher-angle side also diminishes up to 600°C, increases once up to 650°C and then declines again up to 875°C, (002), (003), and (004) trace the process nearly similar to those shown in No. 20, and (005) is almost constant up to 575°C while (005)M emerging at this temperature on far higher-temperature side increases gradually up to 875°C.

With reference to these results, worthy mentioning is the work given by WEISS and ROWLAND (1956) concerning clinocllore, according to which (001)M associated with (001) (2θ : 6.25) at 575°C indicates the variation from 6.29° to 6.39° in 2θ and disappear at 850°C, (002) and (003) begin to break down with shifting to the lower-angle side at 575°C and completely get lost at 640°C, (004) together with (005) accompanying (004)M and (005)M respectively on the higher-angle sides pick the ways same as the others, and the last is in connection with the olivine structure, as to which the present authors, however, have a suspicion to a considerable extent. The thermal study of BRINDLEY and ALI concerning penninite gave a suggestion for construction of the modified chlorite at 600°~700°C, destruction of the chlorite structure at 760°C and emergence of the olivine structure at 800°C and furthermore such an interpretation that two third parts of water contents in the brucite layer is set free after the reaction: $Mg_6(OH)_{12} \rightarrow 6MgO + 6H_2O$ at the first dehydration stage, new reflection connected with the modified chlorite then appears on the higher-angle side, and the water contents remained at the first reaction together with those included in the mica (talc) layer are lost at all at the second dehydration stage in association with breaking-down of the whole structure.

By the by, coming-out of the talc structure observed at 550°C kept for 12~16 hours in the present experiments is in a close relation to the relative increase of intensity attributable to destruction of the brucite layer or the first dehydration, the strengthening of (001), (004), and (005) reflections as well as the weakening

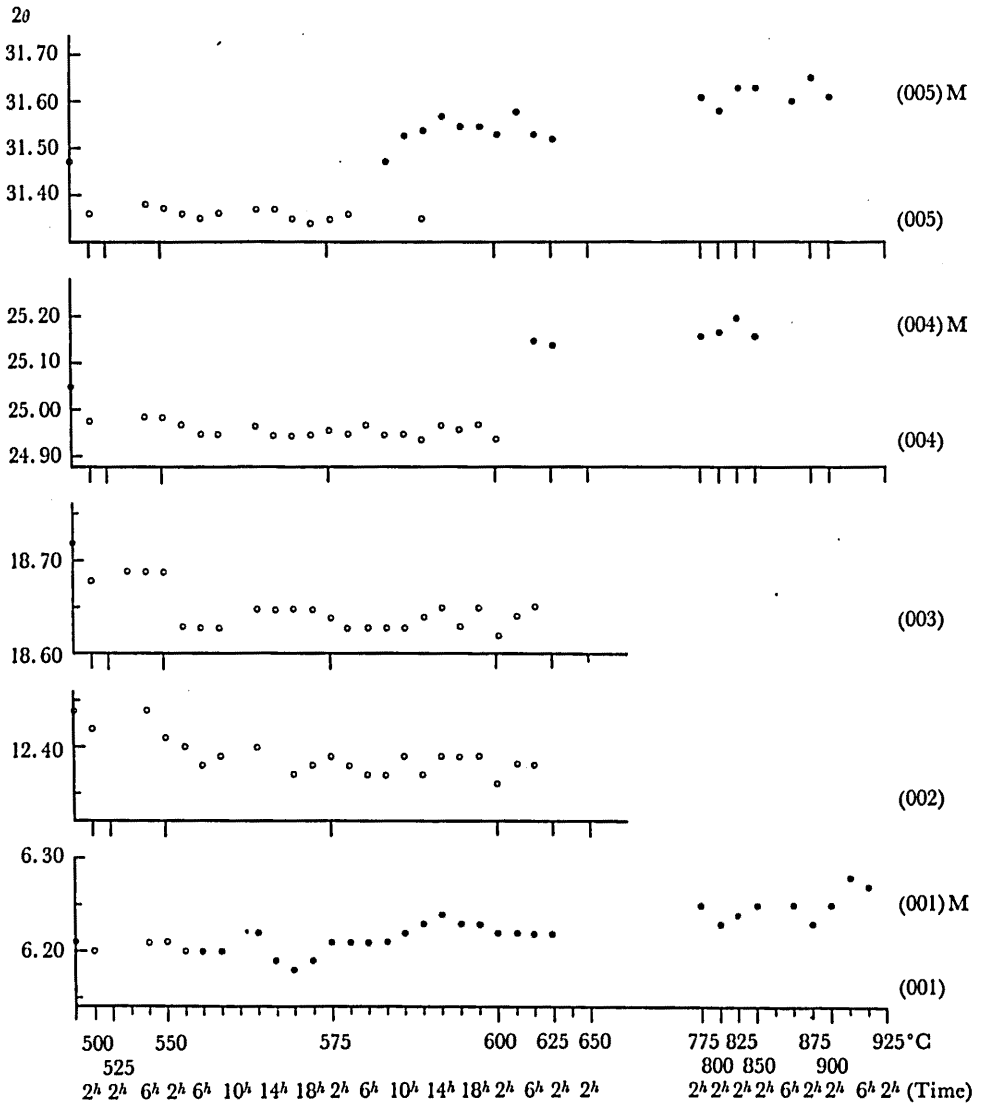


FIG. 4. Variation in the spacings of the specimen No. 20.

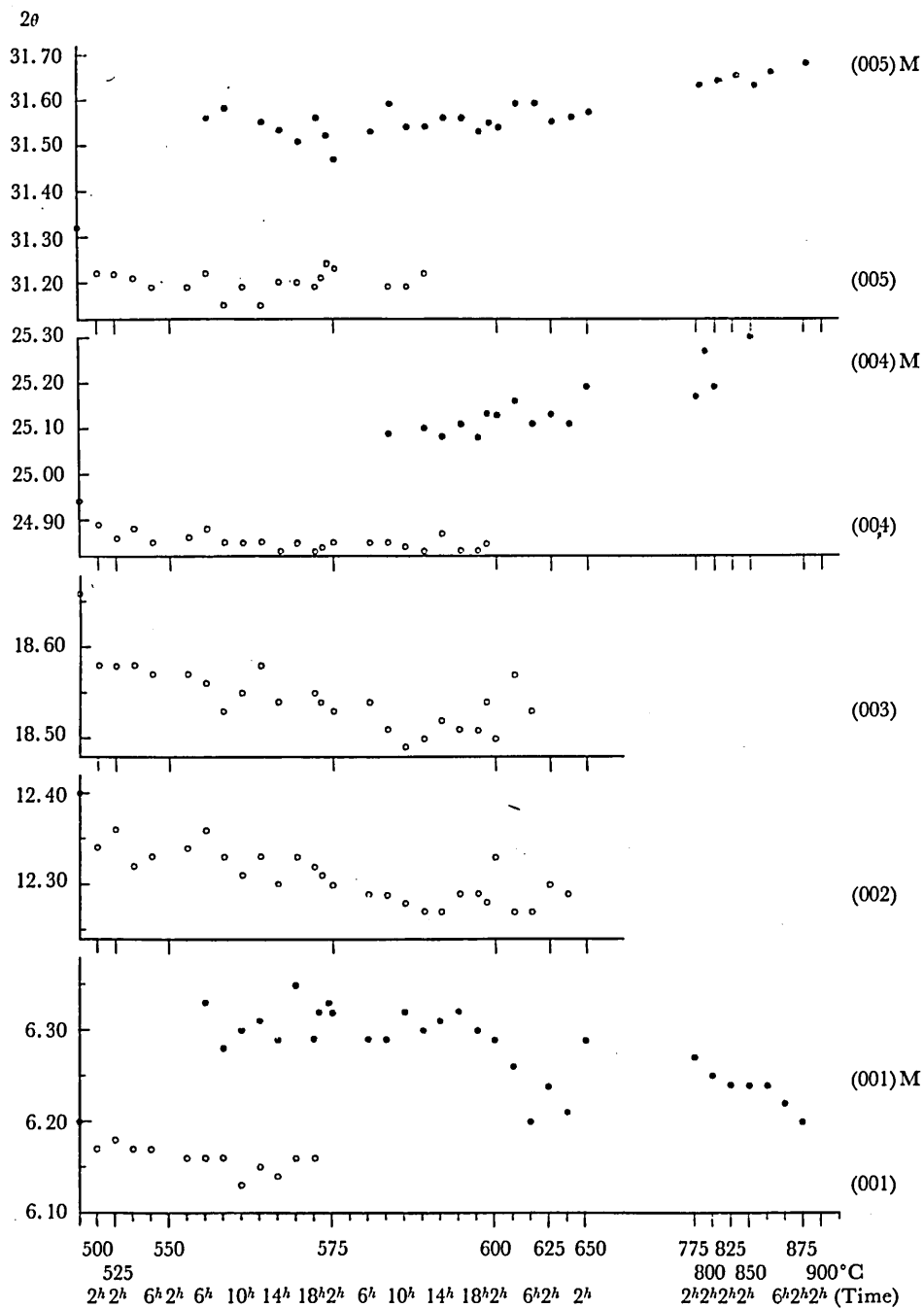


FIG. 5. Variation in the spacings of the specimen No. 74.

of (002) and (003) reflections are, though most of the specimens here provided for research are grouped into clinocllore and there still remains a difference in dealing with the modified chlorite, also in good harmony with a tendency in variation of the structure factors mentioned by BRINDLEY and ALI concerning penninite, as are, for reference, exhibited again in Table 5, and that nothing other than forsterite or enstatite was recognizable subsequent to destruction of the whole structure through heating up to 950°C even in the most effective furnace differs from the previous data suggesting the appearance of spinel (cf. BRINDLEY and ALI, (1950) and NELSON and ROY, (1958)).

Table 5. Structure factors of normal and modified penninite (BRINDLEY and ALI, 1950)

Basal plane	Normal penninite (obs)	Modified penninite (obs)
001	29	125
002	61	32
003	91	47
004	100	100
005	75	173

C. Infra-red absorption

Thermal variations of the chlorite specimens provided similarly for x-ray diffraction have, after their irreversibility from once heated to then quenched states was carefully verified, been checked through inspection of the respective infra-red absorption spectra taken at several temperatures kept constant for some hours. To examine how and to what extent these data might have been combined with those illustrated röntgenographically in the preceding was an immediate objective and hence no specimens other than Nos. 20 and 74 have been subjected to operation. Moreover, taking account of the similarity in infra-red absorption spectra ascertained only for Nos. 20 and 74 within the range of wavelength from 4000 cm^{-1} to ca. 600 cm^{-1} (the unit will be cut down hereafter), mere allusion to No. 20 will be offered as a representative.

Of all the data, those treated at 550°C kept for 24.5 hours, at 575°C kept for 2 hours, at 650°C kept for 2 hours, and at 850°C kept for 2 hours are recorded in Fig. 6. At the first state presumably just before the first dehydration, absorptions representing OH at 3580, 3440 and 1625, Si-O at 982, 658 and 642, and (Si, Al^{IV})-O at 820 and 758 are surely recognizable, as were already indicated by STUBIČAN and ROY (cf. LAUNER etc.). The state of the second stage is evidently characterized in that, owing to destruction of the brucite layer, absorptions for OH are considerably weakened though not to such an extent as have been ideally expected and those for Si-O and (Si, Al^{IV})-O probably attaching to the mica layer are comparatively strengthened. At the third state revealing the stability of the

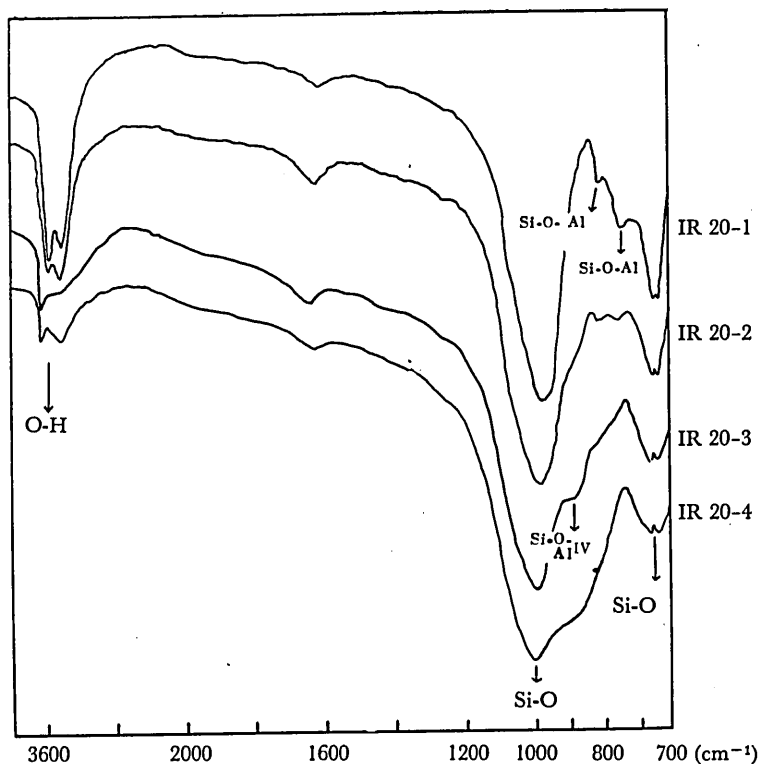


FIG. 6. Infra-red absorption spectra

modified chlorite, both decrease of OH absorption with addition of new one corresponding to another (Si, Al^{IV})-O at 900 more intensely reflect the stabilized presence of the tetrahedron sheet. At the last stage, conspicuous decrease of OH absorption as well as the relative increase of absorptions at 900 and 820 seem to imply the second dehydration somewhat prior to catastrophe of the whole structure.

III. SUMMARY

Basing on the unit cell parameters calculated from eleven species of the massive chlorite pregnant in a chromite deposit, it seems permissible as a rule that at the normal states of the specimens without any other effects both expansion of d_{001} and extension of b-axis are in proportion to Fe content but reversely to Al content and furthermore attribute to convergence of the axial angle β to 97° in degree.

Of due significant relation is the inverse proportion of the structure factor ratios: F_{001}/F_{002} , F_{003}/F_{002} , F_{004}/F_{002} and F_{005}/F_{002} to the numbers of heavy atoms, substituting Mg involved in the octahedron sheet (brucite layer), derived after

PETRUCK's law.

Scrutiny on thermal variations appearing in the inner structures of the specimens makes it possible to divide a series of the process under consideration into three parts such as: (1) the decrease of the diffraction intensities for the basal planes associating the emergence of new spacings representing the modified chlorite on the higher-angle sides in 2θ at 550°C kept for some hours (signifying the start of destruction of the brucite layer), (2) the decay of the main basal planes (002), (003), (004) and (005) together with the prosperity of (001)M, (004)M and (005)M of the modified chlorite and the faint growth of the talc layer at $600^\circ\sim 625^\circ\text{C}$ (corresponding to perfect destruction of the brucite layer) and (3) the entire ruin of the whole structures as chlorite at ca. 900°C (probably lowerable down to ca. 800°C).

The results revealing variations of the definite bondings such as OH, Si-O and (Si, Al^{IV})-O in the infra-red absorption spectra are considered surely helpful for elucidating these structural problems, although far more specimens than have been taken in this research are to be subjected to the procedure with use of the wave-length ranging at least to 400 cm^{-1} .

The data resulted from x-ray diffraction and infra-red absorption reasonably point to the identity of the specimens in question with clinocllore and their genetical relation to the other species of chlorite occurring in the similar surroundings however still remain to be researched in more details.

REFERENCES

- BRINDLEY, G. W. and ALI, S. Z. (1950): X-ray study of thermal transformation in some magnesian chlorite minerals, *Acta Cryst.*, **3**, 25-30.
- BRINDLEY, G. W. and GILLERY, F. H. (1956): X-ray identification of chlorite species, *Amer. Mineral.*, **41**, 169-186.
- BROWN, B. E. and BAILEY, S. W. (1962): Chlorite polytypism: I. regular and semi-Random one-layer structure, *ibid.*, **47**, 819-859.
- BROWN, G. (1955): The effect of isomorphous substitutions on the intensities of (001) reflections of mica- and chlorite-type structures, *Miner. Mag.*, **30**, 657-665.
- ENGELHARDT, W. v. (1961): Neuere Ergebnisse der Tonmineralienforschung, *Geol. Runds.*, **51** 457-477.
- HEY, M. H. (1954): A new review of the chlorites, *Miner. Mag.*, **30**, 277-292.
- LAPHAM, D. M. (1958): Structural and chemical variation in chromium chlorite, *Amer. Mineral.*, **43**, 921-956.
- LAUNER, P. J. (1952): Regularities in the infra-red spectra of silicate minerals, *ibid.*, **37**, 764-784.
- NELSON, B. W. and ROY, R. (1958): Synthesis of the chlorites and their structural and chemical constitution, *ibid.*, **43**, 707-725.
- PETRUCK, W. (1964): Determination of the heavy atom content in chlorite by means of the x-ray diffractometer, *ibid.*, **49**, 61-72.
- PHILLIPS, W. R. (1963): A differential thermal study of the chlorites *Miner. Mag.*, **33**, 404-414.
- RADOSLOVICH, E. W. (1962): The cell dimensions and symmetry of layer-lattice silicates, II. Regression Relations, *Amer. Mineral.*, **47**, 617-636.
- SCHOEN, R. (1962): Semi-quantitative analysis of chlorites by x-ray diffraction, *ibid.*, 1384-1392.

- SHIRÔZU, H. (1958): X-ray powder patterns and cell dimensions of some chlorites in Japan, with a note on their interference colors, *Miner. Jour., Japan*, **2**, 209-223.
- (1958): Aluminian serpentine and associated chlorite from Usagiyama, Fukuoka Prefecture, Japan, *ibid.*, 298-310.
- (1960): Isomorphous substitution in chlorites (in Japanese), *Advances in clay science*, **2**, 127-135.
- STUBIČAN, V. and ROY, R. (1961): Isomorphous substitution and infra-red spectra of the layer lattice silicates, *Amer. Mineral.*, **46**, 32-51.
- (1961): A new approach to assignment of infrared absorption bands in layer-structure silicates, *Z. Krist.*, **115**, 200-214.
- UMEGAKI, Y. and NAGATOMI, S. (1963): Thermal studies of some minerals, No. 1, *Geol. Rep. Hiroshima Univ.*, No. 12, 401-418.
- WARSHAW, C. M. and ROY, R. (1961): Classification and a scheme for the identification of layer silicates, *Geol. Soc. Amer. Bull.*, **72**, 1455-1492.
- WEISS, E. J. and ROWLAND, R. A. (1956): Oscillating-heating x-ray diffractometer studies of clay mineral dehydration, *Amer. Mineral.*, **41**, 117-126.
- ERRATUM: — o — o — (001) M //, the mark drawn in Fig. 2 (p 33), is to be corrected as — • — • — (001) M //.

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