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On Minerals Associated with Ultrabasic Rocks, Found in the Vicinity of Common Boundaries of Shimane, Tottori, Okayama and Hiroshima Prefectures (X)

—— Oxidized reddish orthohexagonal chlorite from the Wakamatsu mine, Tottori Prefecture ——

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Abstract

Reddish chlorite as alteration product from lizardite occurs in the south level of Wakamatsu mine, Tottori prefecture. The reddish mineral was studied by X-ray, differential thermal and chemical analyses. Their experimental data are presented in the paper. It was proved that the mineral is oxidized orthohexagonal chlorite.

Introduction

The mineral was found in the 8th chromite body of south level of Wakamatsu mine. The specimen shows reddish to reddish brown, and has soft, brittle characters. The reddish chlorite occurs as alteration product of lizardite intruded by gabbroic rock in the south level. The O^{2-} content in the lizardite analyzed by the writer (1970) is calculated as 9.24 (4.62×2), but it in the reddish chlorite altered from the lizardite shows value of 10.10. This indicates the fact that the conversion of OH^- to O^{2-} is necessary the changing of Fe^{2+} to Fe^{3+}. Under certain condition, serpentine may be intermediate phase and chlorite a more stable and product of what is regarded as the serpentinization process. Low-high iron chlorite division is based on ferric iron so that a low iron chlorite may contain considerable iron in the ferrous state. The specimen (8.92% Fe_2O_3) is high iron chlorite ($>4\%$ Fe_2O_3), which has been accounted for about 1/4 of all occurrences.

Structure of Chlorite

The structure of chlorites has been discussed as the following descriptions by some crystallographers.

Chlorite consists of talc brucite layers that stacked in various ways to form polytypes. The unit cell is slightly variable according to the chlorite type. b varies with the number of Fe^{+2} in the octahedral layer, and c with the number of Al^{3+} ions replacing Si^{4+} in the tetrahedral layer. It should be noted that Fe^{3+} is a necessary ion in many chlorite. Most of the remaining chlorites except IIb polytype of monoclinic unit cell are the Ib polytype based on an orthohexagonal unit cell. The formation of polytypes is due to equilibrium conditions as related to the energy available in the environment. Diagenetic chlorites are orthohexagonal Ib polytype or sometimes monoclinic IIb polytype. The hk spacings are the a and b directions of the unit cell in all minerals except those of the triclinic class. These spacings do not vary appreciably with treatment. The basal spacing gives periodicts normal to the plane along c, this dimension may vary with density, dehydration, glycollation, cations in interlayer positions, acid treatment, etc.. All chlorites have replacement of Si by Al which affords the tetrahedral sheets negative charge. This charge is balanced by the substitution of Al and Fe^{3+} for Mg and Fe^{2+} in the two octahedral sheets. A certain minimum amount of R^{3+} substitution is necessary in order to provide sufficient layer charge to bind the various layers. The chlorite structure is not stable with more than one-third of the octahedral positions filled with Al. Brown and Bailey (1962) found that the orthohexagonal and monoclinic Ib types were the ones most likely to be considered diagenetic chlorites. These are the chlorites with the lowest amount of tetrahedral Al and these polytypes are most apt to be stable with a small amount of tetrahedral Al. The Ib types readily convert to the more stable IIb types during metamorphism. The bonding force is a function of the amount of charge in the tetrahedral and octahedral sheets (particularly the hydroxide sheet) and is therefore proportional to the amount of Al substitution in the tetrahedral sheet (Brindley, 1961).

X-Ray and Thermal Identification

It is apparent that fine grinding gives the best results for X-ray diffraction. The X-ray powder diffraction patterns of the natural and heated specimens were taken by Shimazu X-ray diffractometer, and the observed intensities and measured spacings from those diffractometer charts are listed in Table 1. The ferric oxide rich chlorite gives moderately weak reflections for 001 and 003 basal planes and comparatively strong peaks for 002 and 004 ones. Each chlorite type has a distinct set of basal reflection related intensities, helpful in identifying the chlorite type. The $I_{(003)}/I_{(002)}$ ratio for the chlorite specimen is calculated as 1/7. The ratios for Fe-chlorite, Fe-rich chlorite and Mg-chlorite are generally given as 1/10—2/10, 6/10 and 1/1 respectively, then the specimen may be also denoted as Fe-chlorite from the X-ray analysis. The diffraction peak intensities were affected for more by chlorite type than sieve used. In unoriented mount, many hkl spacings are observable. The 060 reflection for the specimen was partially obscured by the 330 reflection. The 060 reflections of trioctahedral chlorite are from 1.53—1.55 Å and vary linearly with compositional variation in the octahedral sheet. The specimen shows d(060) 1.53—1.54 Å, so it can be said trioctahedral chlorite.

It is considered that Fe^3 in the specimen is mainly due to oxidation, and diagenetic chlorite is the orthohexagonal Ib polytype as before mentioned. The chlorite in which the proportion of octahedral positions is occupied by Fe^3 0.45, Fe^2 0.04 as showed in the later chemical analysis, gives no intensities at the five and six order positions. The ferric iron content of the sample was apparently factor governing the basal spacing. Fe^3 and Al contents in tetrahedral coordination are small amounts, so the basal spacing shows long value of 14.8 Å.

Table 1. X-ray data of oxidized orthohexagonal chlorite and its heated specimens.

	Room temp.		300°C	
hkl	d(Å)	*I*	d(Å)	*I*
001	14.8	12	14.7	3
002	7.38	75	7.38	100
003	4.81	11	4.82	9
020	4.62	20	4.61	2
004	3.67	79	3.67	51
202	2.504	41 B	2.508	13 B
025	2.458	9		
204	2.151	1		
007	(2.106)	1		
206			(1.833)	4
060	1.537	14 B	1.535	6 B
062	1.512	1	1.510	2 B
063 208	1.503	1	1.503	1
064	1.420	1	1.425	1

Table 1. *(continued)*

	450°C		500°C		800°C		1200°C	
hkl	d(Å)	*I*	d(Å)	*I*	d(Å)	*I*	d(Å)	*I*
002*	9.72 9.51	10	9.56	1				
020			5.16	3	5.14	3	5.14	3
020^{+}					4.46 4.42	5	4.40	1
021	3.90	4	3.90	12	3.91	7	3.91	9
101			3.746	4	3.746	2	3.746	4
111	3.520	3	3.520	3	3.507	4	3.520	6
211					3.302	3		
(420,221)$^{+}$			3.187	6	3.187	10	3.187	41
006*	3.15	5						
002			3.003	5			3.089	1
310$^{\cdot}$							2.908	33
610^{+}			2.903	15	2.885	23	2.894	24
130	2.776	5	2.776	11	2.780	9	2.780	6
421^{+}			2.710	4	2.698	5	2.734	5
(132,204)*	2.552	8						
131 311^{+}	2.511	4	2.512	33	2.522	39	2.525	34
112	2.462	7	2.462	18	2.468	8	2.468	13
200							2.395	1
041							2.356	1
210							2.321	2
122	2.276	3	2.279	3	2.270	7	2.276	4
140	2.265	2	2.268	7			2.257	2
220,211			2.171	3	2.154	3	2.166	2
630^{+}							2.115	2
531^{+}							2.101	2
132							2.062	8
222	1.752	4	1.751	15	1.752	11	1.751	10
061							1.647 1.642	3
133 023^{+}			1.622	2	1.614	7	1.616	5
004			1.497	7			1.501	6
062			1.481	12	1.481	7B	1.483	7
170					1.397	2	1.399	3

no symbol : Olivine, * : Talc, $^{+}$: Enstatite, : Clinoenstatite.

The Ib chlorite polytype, apart from the poor crystallinity, is difficult to distinguish from IIb polytype, except in X-ray analyses. The two principal chlorite polytypes, IIb and Ib, are recognizable by X-ray diffraction. Brown and Bailey (1962) gave the following d spacings for $20\bar{2}$, 202, $20\bar{1}$, and $20\bar{3}$ of the common polytypes of chlorite.

Polytype	Cell	hkl	d(Å)
IIb	Monoclinic	$20\bar{2}$	2.59
IIb	Do.	201	2.54
Ib	Do.	$20\bar{2}$	2.61
Ib	Do.	201	2.55
Ib	Orthohexagonal	202	2.50
Ib	Do.	203	2.33

The reflection from 202 net plane with d = 2.50 Å is characteristic for orthohexagonal chlorite, then it is clear that the specimen belongs to orthohexagonal chlorite.

The lattice type of the specimen is centered C-face (001) showing $h+k = 2n$. The specimen give reflection of an ortorhombic crystal that are hkl : $h+k = 2n$, okl : ($k = 2n$), hol : ($h = 2n$), okl : ($k = 2n$), 001 : no conditions, so the space group may be explained as C 2/m 2/m 2/m.

The chlorite consists of "talc and brucite" layers that stacked in a way to form Ib polytype. The talc and brucite layers are composed of $[Mg_{2.37}, Fe^{3}_{0.28}, (Ti, Ni, Ca, Na, K)_{0.06}]_{2.71} (OH)_{5.88}$ and $(Mg_{2.96}, Fe^{2}_{0.04})_{3.0}(Al_{0.07}, Fe^{3}_{0.15}, Si_{3.78})_{4.00}O_{10.10} (OH)_{2.02}$ respectively from the chemical composition describing in the following paragraph.

The unit cell is slightly variable according to the chlorite polytype. The reciprocal cell dimensions of the mineral calculated from Q_{004}, Q_{202}, Q_{060}, and Q_{204} are $a^* = 0.1858$, $b^* = 0.1084$, $c^* = 0.068$ and $\beta^* \doteqdot 90°$, then the unit parameters may be obtained from the transformation as follows : $a = 5.382$, $b = 9.223$, $c = 14.677$ Å, $\beta = 90°$.

Each specimen of the fine powder was heated in an electric furnace, and kept successive temperatures from 300° to 1.200°C at interval of 50° or 100°C. After cooling, the diffractometer patterns of each of the heated specimens were obtained by means of the X-ray apparatus. The specimen does not exhibit a shrinkage parallel to c, and considerable changes are observed in the reflective intensities for the 001 and the other net planes at 300°C. At the temperature, the intensity of 002 is increased and shows the strongest value, and on the contrary the intensities of 001, 003, and 004 are decreased. The intensities of 020 and 060 are also decreased at the temperature. On heating, the chlorite behavior is different from monoclinic chlorite that show marked increase in the intensity of the 001 reflection. If chlorite is heated for 1 hour at 450°C, the chlorite structure is destroyed and the order can not entirely observed, and talc and olivine begin to appear. The peaks of enstatite are perceived at 500°C, and the patterns composed of olivine and enstatite from 500° to 800°C show almost similar intensities except 002 reflection of talc at 500°C. The molecular percent of olivine generated from the specimen is calculated as 80.6% from the d(130) = 2.7757 Å, and the cell dimensions are a = 4.71, b = 10.31, c = 6.08 Å. The cell parameters of the enstatite recrystallized from the specimen are a = 18.37, b = 8.85, c = 5.33 Å. The 210 peak of clinoenstatite is noticed at 1.200°C in addition to the patterns of olivine and enstatite.

Differential Thermal Analysis

The D. T. A. curve (Fig. 1) for the specimen was achieved under thermocouple of C-A, sensitivity of ± 250μV, heating rate of 20°C/min., and chart speed of 4 mm/min.. Peak positions all may vary by heating rates, sample particle size and density, and procedures for recording. The endothermic peak on low temperature side at about 150°C is due to loss of absorbed water. Chlorite may have some interlayer water providing small initial endothermic reaction.

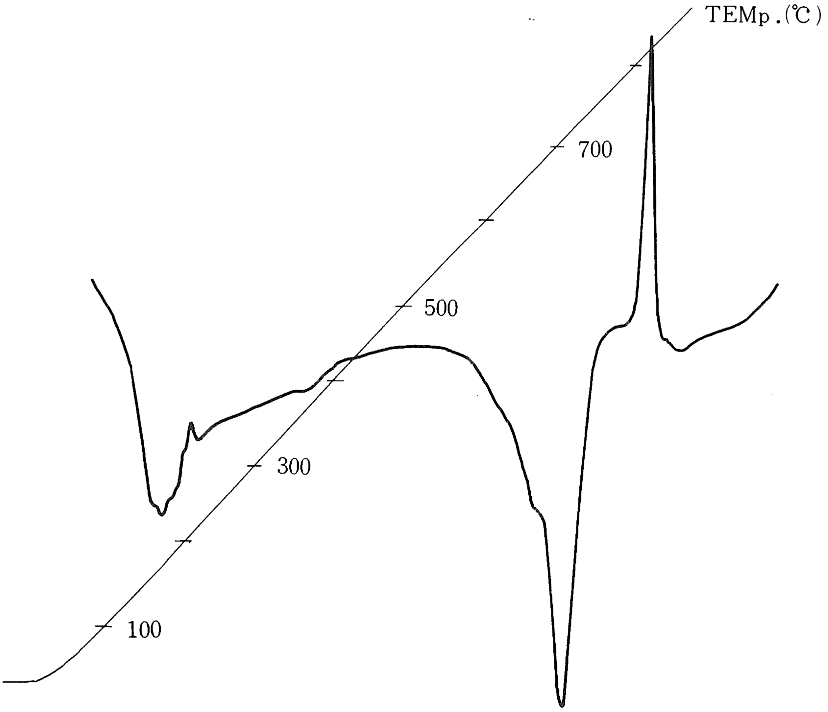

Fig. 1. D. T. A. curve of oxidized reddish orthohexagonal chlorite from the Wakamatsu mine.

It is regarded that the small endothermic peak at about 192°C is due to get out of water from interlayer. The detailed dehydration characteristics vary with particle size as mentioned above as well as composition. Chlorites have been found to dehydrate in two separate stages which dehydration curves and X-ray date indicate as being well separated, but by D. T. A. the second dehydration stage is not always observed. The principal well-marked endothermic peak at about 705°C is caused by the dehydration from brucite layer (dehydration of chlorite), and major structural changes occur. The peak of decomposition of the talc layer (silicate layer) is not detected in the figure. This may be because oxidation of F^{2+} and/or recrystallization proceeds simultaneously with the second dehydration stage. It is said that OH ions associated with Mg^{2+} ions more tightly bond than OH ions associated with Al^{3+}. The peak temperature on the thermograph of the specimen, higher than for most other chlorites, can be explained by a high magnesium content, a low aluminum content, and a low ferrous iron content. The sharp exothermic peak at about 806°C is generated by the crystallization of forsterite. The exothermic peak is occurred at lower temperature than those of monoclinic chlorites. The lower temperature of the exothermic peak is attributed to the iron contents of the sample, which strains the original structure, causing it to break down at a lower temperature, and large amount of iron probably means that the product of recrystallization is different from that obtained with low iron chlorite. It has been found that chlorites high in ferrous iron lost most often hydroxyl water at a lower temperature than do the magnesium chlorites. The dehydration brucite sheet reacts with external SiO_4 groups on the talc (mica) sheet and yields an exothermic peak.

Chemistry

The chemical analysis of the specimen was carried out in the laboratory of Dep. of Geol. and Min. of the Fac. of Lit. and Sci., Shimane Univ.. The chemical composition and atomic ratios calculated on the basis of (O, OH) = 18 are shown in Table 2. On the basis of the analytical data, the crystallochemical formula of the specimen was calculated, i. e. calculation of the chlorite formula was carried out as the following description on the basis of 10 oxygens with determination of the quantitative role of (OH) in the structure or on the foundation of 18 (O, OH) per formula unit according to the general formula $Y_6Z_4O_{10}(OH)_8$, where Y represents octahedrally coordination cations and Z tetrahedrally coordinated cations. $[(Mg_{5.33}, Fe^{3}_{0.50}, Fe^{2}_{0.04}, Ti_{0.01}, Ni_{0.01}, Ca_{0.01}, Na_{0.01}, K_{0.01})_{5.93}]^{VI}$

$[(Si_{3.78}, Fe^{3}_{0.15}, Al_{0.07})_{4.0}]^{IV}O_{10.10}(OH)_{7.90}$. It is considered that the reddish color of the specimen is due to high content (8.92% Wt.) of Fe_2O_3. A part of Fe^3 ions occupy tetrahedral coordination as shown in the table.

In most of the analyses reported, octahedral Al is dominant over octahedral Fe^{3+} although in the specimen the reverse is noted. Fe^{3+} is generally high in those sample where Fe^{2+} is abundant, but in the sample Fe^3 is comparatively high and Fe^2 is low content. In many chlorites much of the Fe^{3+} was necessary for the conversion of Fe^{2+} to Fe^{3+}. Fe_2O_3 is a normal constituent of many chlorites, this would be particularly true of low temperature chlorites. Hey (1954) divided the chlorites on the basis of more or less than 4% Fe_2O_3. Those with the smaller values, which are the most common, were assumed to

Table 2. Chemical analysis of oxidized orthohexagonl chlorite.

	Wt. %		Atom. ratios when O(OH) = 18
SiO_2	39.38	Si	3.779
TiO_2	0.05	Ti	0.006
Al_2O_3	0.56	Al	0.069
Fe_2O_3	8.92	Fe^3	0.645
FeO	0.53	Fe^2	0.040
NiO	0.05	Ni	0.006
MnO	0.06	Mn	0.006
MgO	37.04	Mg	5.334
CaO	0.10	Ca	0.012
Na_2O	0.07	Na	0.012
K_2O	0.04	K	0.006
H_2O^+	12.35	OH	7.903
H_2O^-	1.08	O	10.098
	100.23		

Tetrahedral ions

Si	3.78
Al	0.07
Fe^3	0.15
	4.00

$\sum$ Charges on cations 28.12

$\sum$ Charges on anions 28.10

Octahedral ions

Al	0
Fe^3	0.50
Ti	0.01
Fe^2	0.04
Ni	0.01
Mn	0.01
Mg	5.33
Ca	0.01
Na	0.01
K	0.01
	5.93

(Analyst : J. kitahara)

be unoxidized. (Taylor et al., 1968, showed by use of Mössbauer spectroscopy that some Fe^{3+} can be present in the tetrahedral sheet).

The ratios RO/SiO_2 and R_2O_3/SiO_2 are 1.43 and 0.014 respectively, and also the values of a (Fe^3/R^3) and f (Fe^2/R^2) are 0.90 and 0.007 severally. The chlorite does not fall within the field of the monoclinic chlorites. Judging from the coefficients a and f, the chlorite may be classified as an oxidized iron type.

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