

Thermal Investigation of Mineral by means of Dielectric Behaviours

By

Yasuo UKAI

Geological and Mineralogical Institute, University of Kyoto

(Received Sept. 30, 1955)

Abstract

The author could demonstrate the various changes of mineral in the thermal alteration process which were often beyond the scope of other investigation methods by studying the dielectric behaviours of mineral. The dehydration temperature of hydrous mineral was determined by the abnormal change of dielectric constant derived from the polarization of isolated water which escapes from the mineral at dehydration temperature. The author investigated these phenomena on hydrous iron minerals and ascertained that the dehydration temperatures of these minerals are influenced remarkably by their crystal states.

The dissociation temperature of mineral could also be measured by means of dielectric behaviour using several kinds of carbonate minerals. Furthermore, minute changes in crystal structure could be detected by studying the dielectric behaviours especially dielectric loss. The actual states of some metamict minerals in the course of crystallization were demonstrated by this method and they were classified into four groups, namely samarskite-, euxenite-, fergusonite- and allanite-groups.

Thus the author proposes that the investigation of dielectric behaviour is one of the most useful method for studying the thermal alteration process of mineral.

Introduction

The dielectric constant of mineral changes its value according to the variation of chemical composition or crystal structure.¹⁾ So if these components of mineral change by heating, the dielectric constant must undergo various changes accompanied by the maximum peak of dielectric loss.²⁾ If the weight of mineral changes by heating, the increasing or decreasing degree can be quantitatively determined by thermobalance. The transition phenomena which accompany no change of weight but transform the crystal structure can be ascertained by means of differential thermal analysis (D. T. A) or dielectric constant method described here. If the difference in lattice energies before and after the transition is relatively small, the transition of crystal structure can not be determined by the above methods, but the remarkable change of dielectric loss may point out its structural transition. Some investigations were attempted to explain the alteration

process of mineral by the variation diagrams which show the relation between dielectric behaviour and temperature. The results obtained from the dielectric behaviour were confirmed with other investigation methods such as D. T. A., thermobalance and X-ray study.

A. Dehydration phenomena

The dehydration phenomena of hydrous mineral have been studied with numerous investigation methods. The author has revealed these phenomena from the dielectric behaviour.

Dehydration of hydrous iron mineral³⁾

Descriptions of the naturally occurring hydrous iron minerals have resulted in a sizeable list of mineral names. The typical members of this group include limonite, goethite, lepidocrocite, hydrogoethite, xanthosiderite and turgite.

E. Posujk and H. E. Merwin⁴⁾ have demonstrated that no series of hydrous oxide exists, and their results have been proved by other investigators. Above all, it was concluded that the natural hydrous ferric oxide exists only as monohydrated mineral that is called goethite and its polymorphic lepidocrocite. Other members such as limonite, hydrogoethite and xanthosiderite which contain water in higher molecular ratio than $\text{H}_2\text{O} : \text{Fe}_2\text{O}_3 = 1$, contain their excess water as hygroscopic water. Members such as turgite which contains its water in lower than $\text{H}_2\text{O} : \text{Fe}_2\text{O}_3 = 1$, are considered to be mixed crystals of nonhydrated hematite and monohydrated goethite or lepidocrocite, or solid solution of hematite and water. Therefore only goethite (HFeO_2) and lepidocrocite $\text{FeO}(\text{OH})$ have been accepted as minerals of the hydrous iron oxides. In the physical properties, especially in optical character, there are remarkable differences between goethite and lepidocrocite. But these minerals are crystallized in so fine grains from the colloidal hydrogel^{5,6)} that the determination of these minerals by the microscopic observation is very difficult. J. L. Kulp^{7,8)} distinguished these minerals by the difference of their dehydration temperature by means of D. T. A.

Sample

Seven specimens were used in this experiment. The nominated name, chemical composition and specific gravity are indicated in the following table. One portion of each specimen ground in agate mortar was analysed chemically and residual portion was investigated by various thermal investigation methods. The results of chemical analyses⁹⁾ show that lepidocrocite (No. 1) contains considerable amount of MnO_2 , SiO_2 and that the impurities in goethite and limonite are relatively negligible. The molecular ratio of $\text{H}_2\text{O} : \text{Fe}_2\text{O}_3$ in these minerals

falls within the range of 0.989–1.101 and corresponds to monohydrate. Bog irons (No. 6), (No. 7) include such a large amount of Al_2O_3 , SiO_2 , negative water and humus substance that the ratio of $\text{H}_2\text{O} : \text{Fe}_2\text{O}_3$ can not directly be calculated from the above results.

The mean specific gravity of limonite is 3.936, that of goethite (No. 3) which is a relatively pure specimen is 4.077. Lepidocrocite not only contains various impurities but goethite components, so this value does not represent its characteristic specific gravity but shows the smallest value in these three minerals.

X-ray investigation⁽¹⁰⁾⁽¹¹⁾

The powder photographs (camera radius 57.3 mm., Cr $K\alpha$ radiations) of above specimens were compared with one another. The spacings and intensities are listed in table 2. Lepidocrocite (No. 1) shows several characteristic very strong patterns (6.24Å, 3.279Å, 1.935 Å) besides some moderately strong patterns (4.17Å, 2.695Å) as compared with those of goethite. Furthermore it has a few weak patterns corresponding to goethite. This mineral not only agrees well with typical lepidocrocite but also contains some goethites.

Goethites (No. 2) (No. 3) have many characteristic patterns of typical goethite and especially the crystal state of specimen (No. 3) is more perfect than that of the former. Limonites (No. 4) (No. 5) also indicate the diffraction rings belonging to goethite in relatively diffused state. Bog irons (No. 6) (No. 7) diminish still more in the intensity and number of pattern which corresponds to goethite, and have several other quartz's patterns.

Variation of dielectric constant with temperature

The variation of the electric capacity of powder sample equipped in the electric furnace was measured continuously under the ultra short wave length. The obtained results are indicated in the following figure.

Lepidocrocite (No. 1) shows the dehydration of hygroscopic water at about 110°C. and that of goethite at 350°C. besides the characteristic dehydration at 310°C. On the specimens of goethite (No. 2), (No. 3),

Table 1

Nominated name	Spe. Gr.	Fe_2O_3	Al_2O_3	MnO_2	CaO	MgO	SiO_2	H_2O^-	H_2O^+	Ig-loss	Total	$\text{H}_2\text{O}/\text{Fe}_2\text{O}_3$
(1) Lepidocrocite	3.619	68.84	1.18	6.20	—	0.09	14.68	0.58	8.20	—	99.77	1.004
(2) Goethite	4.035	89.90	0.52	—	—	—	0.34	0.24	9.74	—	100.74	0.997
(3) Goethite	4.077	89.68	0.82	—	—	—	0.34	0.15	9.64	—	100.63	0.989
(4) Limonite	3.910	86.57	0.26	—	—	—	2.10	0.73	10.35	—	100.01	1.101
(5) Limonite	3.961	88.17	0.27	—	0.27	—	1.79	0.36	10.04	—	100.90	1.048
(6) Bog iron	2.271	38.05	11.14	—	0.34	0.16	34.03	5.89	9.39	2.06	101.11	—
(7) Bog iron	2.582	39.04	17.28	—	0.37	0.32	31.38	3.33	8.56	0.53	100.81	—

Table 2 X-ray powder pattern of hydrated iron mineral.

No. 1		No. 2		No. 3		No. 4		No. 5		No. 6		No. 7	
I	d	I	d	I	d	I	d	I	d	I	d	I	d
10	6.24	5	4.96	3	4.96	3	4.96	2	4.96				
5	4.17	4	4.56	3	4.59	4	4.58	3	4.58	8	4.20	3	4.27
4	3.695	10	4.155	10	4.155	10	4.17	10	4.19	2	3.688	3	3.649
9	3.279	3	3.386	2	3.366	1	3.39	2	3.38	10	3.349	10	3.333
5	2.695	2	2.947	2	3.298	2	2.962	2	2.95				
8	2.468			1	2.839			2	2.832				
3	2.438	9	2.680	9	2.685	9	2.685	9	2.695	5	2.68	2	2.68
2	2.357	3	2.576	4	2.580	3	2.585	3	2.580	3	2.567	1	2.553
1	2.298	2	2.481	1	2.483	1	2.490						
1	2.241	8	2.436	8	2.444	8	2.452	9	2.448	9	2.436	4	2.436
1	2.186			1	2.412								
2	2.128	3	2.247	2	2.252	4	2.253	4	2.250			1	2.281
1	2.086	6	2.185	5	2.189	5	2.192	5	2.192				
8	1.935			1	2.009								
2	1.847			1	1.978								
1	1.795	2	1.916	2	1.919	1	1.926	2	1.924			2	1.958
3	1.734	2	1.886	2	1.887	1	1.893	2	1.888	3	1.814	2	1.818
2	1.716	3	1.799	3	1.801	1	1.802	2	1.801				
3	1.564	1	1.769					1	1.775				
4	1.523	9	1.717	7	1.717	7	1.719	8	1.721	5	1.712		
2	1.453	3	1.683	4	1.689	1	1.694						
2	1.435	2	1.657	4	1.653	2	1.661	2	1.661	1	1.632	1	1.637
3	1.390	2	1.600	4	1.601	2	1.604	2	1.603			1	1.593
1	1.370	8	1.560	6	1.565	6	1.567	6	1.565	3	1.547	1	1.539
2	1.212	6	1.508	4	1.509	6	1.513	5	1.510	2	1.499	1	1.496
2	1.203			1	1.475								
1	1.198	5	1.454	5	1.455	5	1.455	4	1.455	2	1.450	2	1.452
		4	1.420	3	1.422	3	1.425	2	1.421				
		3	1.390	3	1.394	1	1.393	1	1.395				
		2	1.366	2	1.369					2	1.375	2	1.379
		4	1.357	4	1.360	2	1.361	2	1.360			3	1.371
		2	1.347	2	1.347								
		5	1.317	5	1.319	3	1.320	3	1.319				
		3	1.291	2	1.294			1	1.291	1	1.286	1	1.299
		2	1.264	2	1.266			1	1.266	1	1.278	1	1.287
		2	1.243	2	1.244			1	1.243			1	1.256
		5	1.201	3	1.199								

they show a remarkable dehydration peak of goethite at 345°C. Limonites (No. 4), (No. 5) show a peak at 300°C. excepting that the specimen No. 4 indicates an indistinct dehydration at 340°C. Bog iron (No. 6), (No. 7) show only the dehydration peak at 300°C. The remarkable change of dielectric constant between 100–200°C. may indicate the dehydration of hygroscopic water, and the change of dielectric constant at 560°C. in specimen (No. 6) may indicate the transition of quartz which is contained over 30%.

Results of D. T. A. and thermobalance method¹²⁾

By the loss in weight and D. T. A., the dehydration phenomena of hydrous iron oxides were examined and compared with the above results obtained by

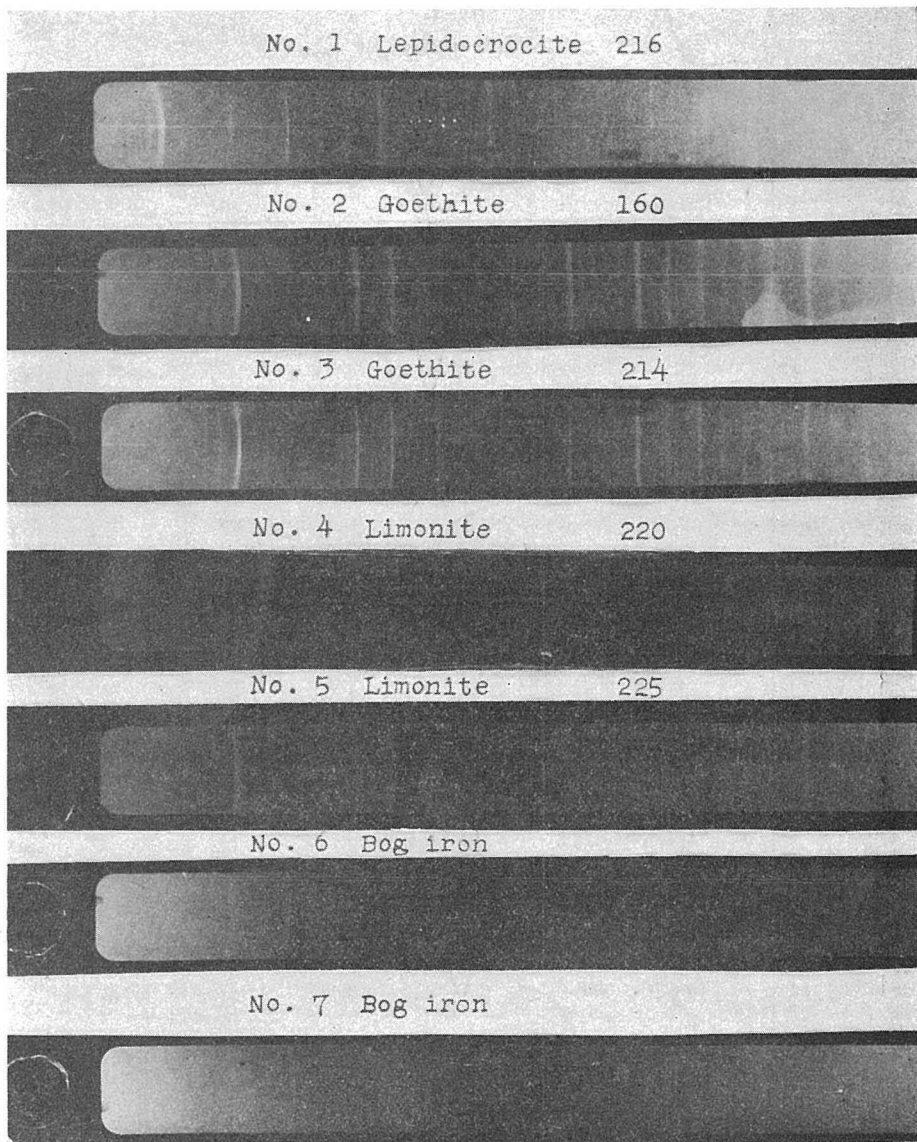


Fig. 1. Powder photographs of hydrated iron minerals

dielectric constant method.

The measuring apparatus for loss in weight is Oshima-Fukuda's thermobalance. About 0.3 gr. of each sample ground to fine powder was used. The samples were heated by raising the temperature 20°C. step by step after the weight of

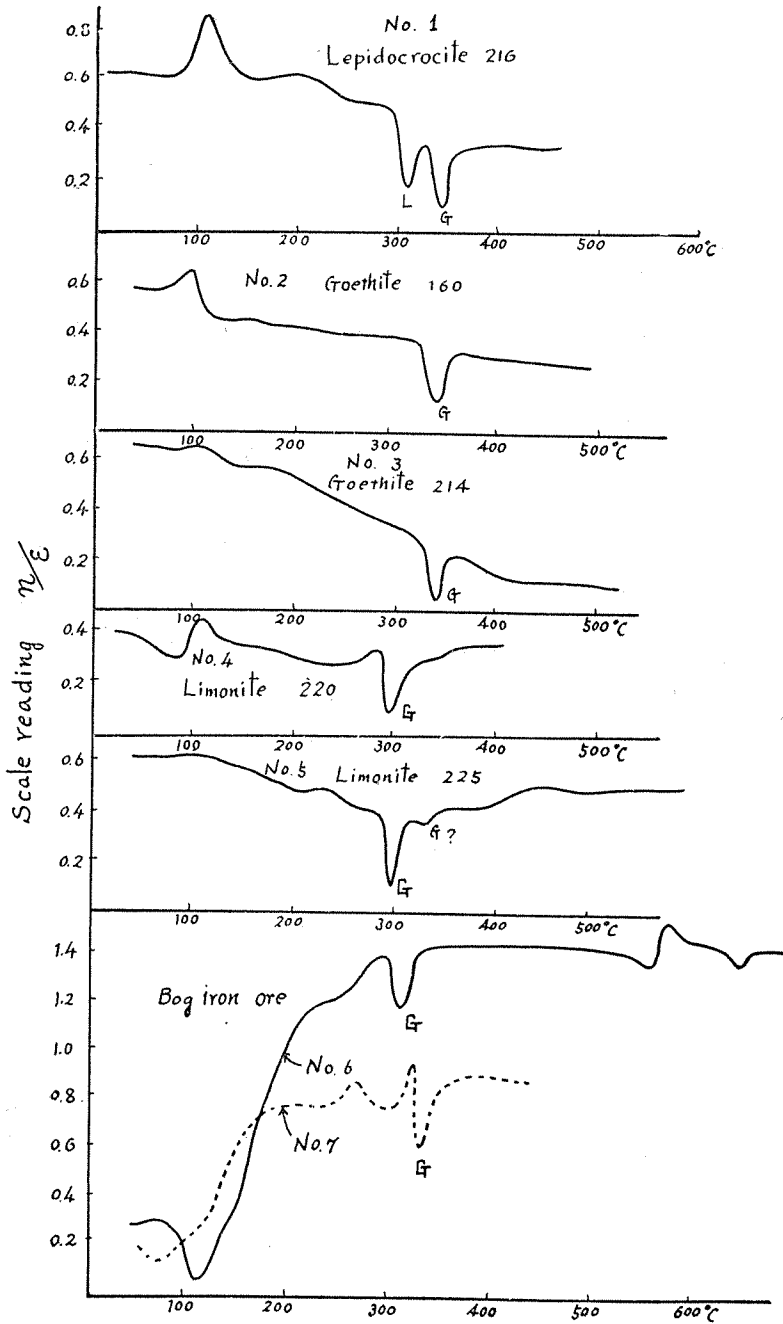


Fig. 2 Variation diagrams of dielectric constant

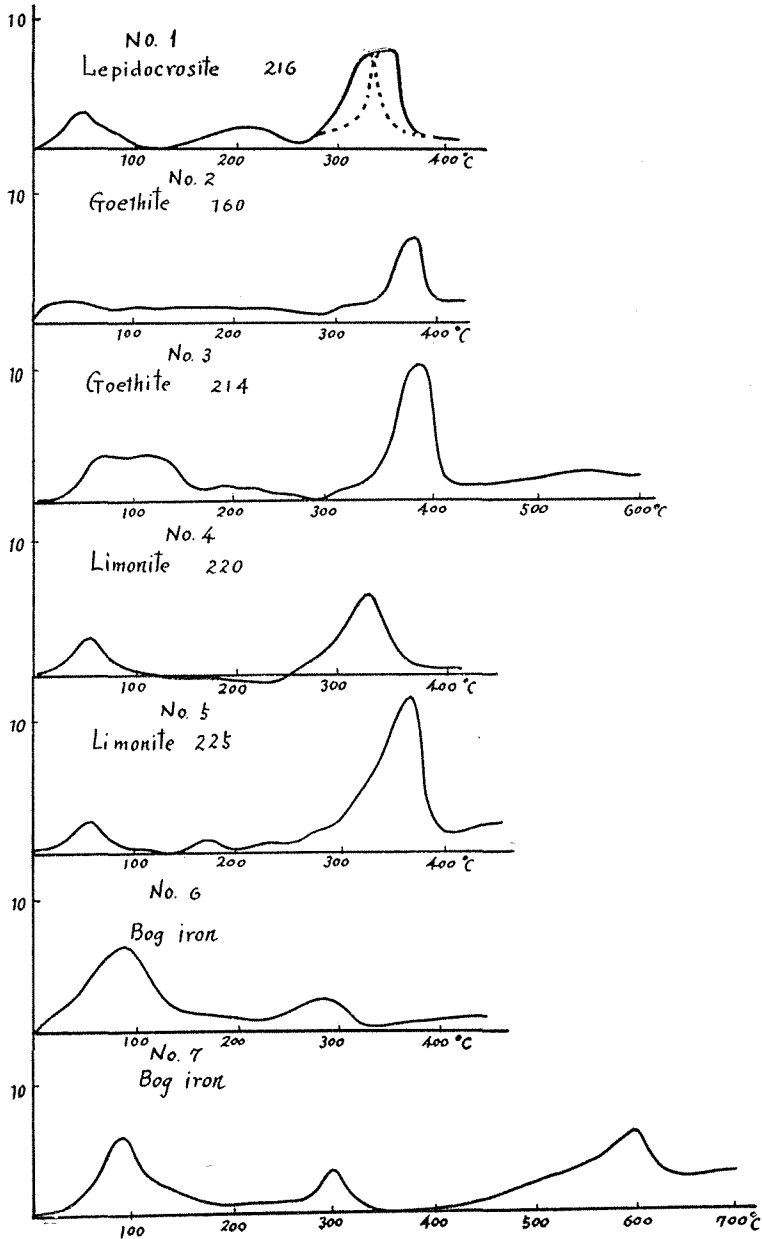


Fig. 3 Differential thermal analyses

specimen had become constant.

In D. T. A., the rate of heating was 3-4°C. per minute. The experimental results are represented in fig. 3 and 4.

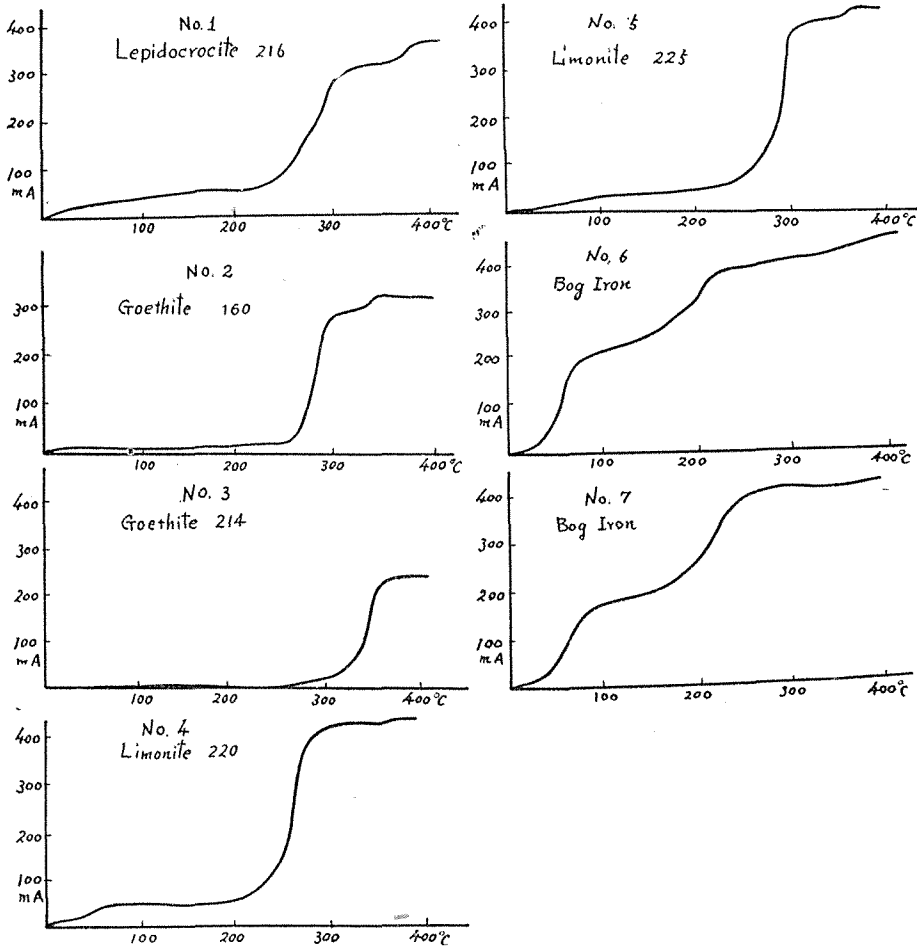


Fig. 4 Loss in weight by thermobalance

Lepidocrocite (No. 1) shows two remarkable endothermic peaks at 290°C. and 370°C. corresponding to lepidocrocite and goethite. Loss of weight begins at 250°C., occurs most vigorously at 290°C. and slightly at 360°C.

These results indicate that this mineral is composed of two members and are in a good agreement with that of dielectric constant method. Goethites (No. 2), (No. 3) show only the endothermic peak between 350°C. and 400°C. which corresponds to the dehydration of goethite, and the loss of weight corresponding to goethite was also observed.

Limonites (No. 4), (No. 5) represent the endothermic peak beginning at

290°C. and remarkable loss in weight similar to the results obtained by dielectric constant. Bog irons (No. 6), (No. 7) represent the endothermic reactions between 50–100°C. and 300°C. which correspond to the dehydration of absorbed water and goethite as in the case of the other methods.

Consideration

The following consideration may be summarized from the above investigation. The main components of hydrous iron minerals excepting specimen No. 1 are goethites which have different crystallization degrees. It was demonstrated by various thermal investigation methods that the dehydration temperature is not always constant but is influenced remarkably by its crystal state. Goethites having relatively perfect crystal structure dehydrate their water at higher temperature and those in poor crystallinity such as in limonite and bog iron dehydrate at lower temperature. So crystallinity must be taken into consideration in order to identify the mineral species by the dehydration temperature.

B. Dissociation of mineral

The dissociation temperature of mineral can be measured by several investigation methods. The dielectric constants of semi-conductive minerals generally change their values at the dissociation temperatures. Naturally, the changes of chemical compositions and crystal structures have great influence on the dielectric constants, but if the dissociated substances have any dipole moment, the dielectric constant may show a remarkable change while the dissociation reaction continues.

Dissociation of carbonate mineral

The carbonate minerals change their dielectric constants abruptly at the dissociation temperatures. The dielectric constants of carbonate minerals were measured with thin plates. The following results show a good agreement with those obtained by D. T. A.⁽¹³⁾⁻⁽¹⁹⁾ On the variation diagram of cerussite, the remarkable change of dielectric constant at 450°C. may be due to the oxidation of $\text{PbO} \rightarrow \text{PbO}_2$.

Some specimens such as siderite and rhodochrosite show two distinct peaks which correspond to the dissociation of each mineral. For the comparison of above results, data of differential thermal analyses of carbonate minerals determined by R. A. Rowland were referred to.

C. Crystallization of metamict mineral

The metamictization of mineral has been studied from various standpoints⁽²⁰⁾ and the explanations for respective results were related to one another by

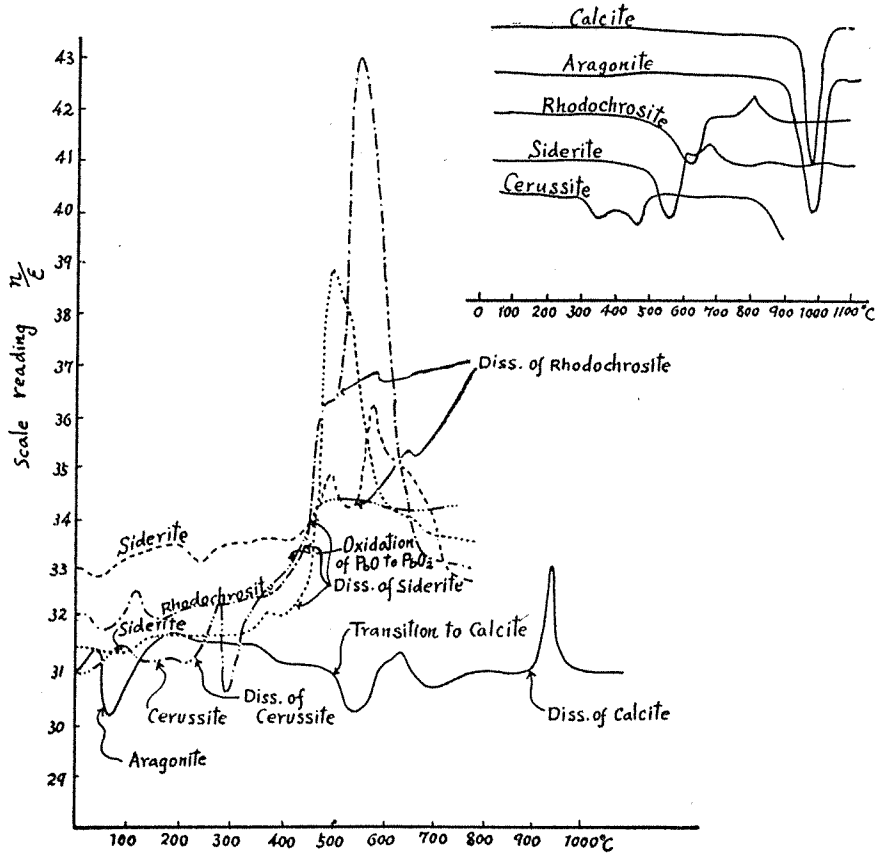


Fig. 5 Variation diagrams of dielectric constant and differential thermal analyses of carbonate minerals

investigating the dielectric behaviours of metamict minerals.

The types of crystallization by heating may be classified into four groups, namely one step change in samarskite type, two step changes in euxenite and fergusonite type and complicated change in allanite type. The two endothermic peaks at 300–400°C. and at about 700°C. determined by D. T. A. were also demonstrated by the investigation of dielectric behaviour. The structural change at low temperature of fergusonite which had been ignored in D. T. A. was detected distinctly by the dielectric behaviour, especially by the change of dielectric loss.

To inquire into the crystal state, the diffraction figures of raw specimens and of those heated at required temperatures were examined by Geiger-counter spectrometer.

Measuring method of dielectric behaviour

The specimen which was polished into a thin square plate, 1 mm. in thickness, and 5 mm. in one side was heated for twenty minutes at required temperature and cooled to room temperature. The dielectric constant of each specimen was determined accurately at 500 kc. wave and dielectric loss of 500 kc., 1 mc., 2 mc., 4 mc., 10 mc., etc. was measured by Q-meter. The details of measuring apparatus and methods were described in previous studies.²²⁾²³⁾ According to the variation

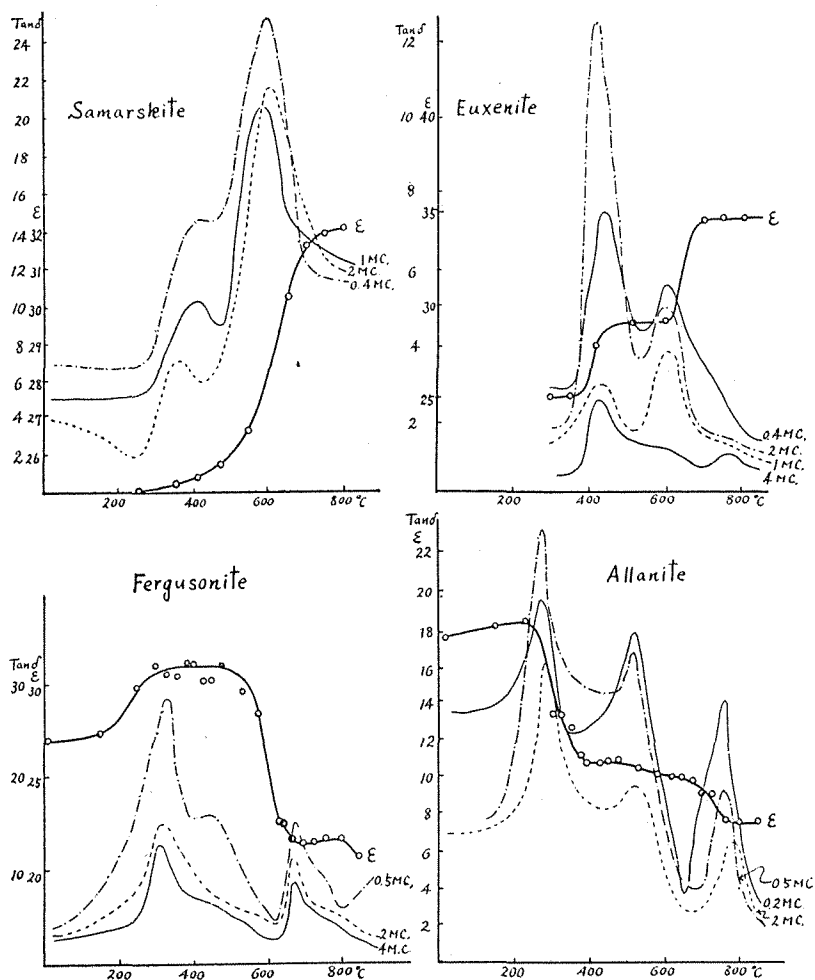


Fig. 6 Dielectric behaviours of metamict minerals

diagram of dielectric behaviour, the dielectric constant changes its value abruptly at a certain temperature accompanying the maximum peak of dielectric loss.

The intensity of maximum loss peak is naturally related to the frequency, that is, the intensity diminishes according as the increase of frequency. The discrepancies in some instances may be ascribed to the measuring conditions, especially to the contact condition of sample with platinum plates.

Samarskite. Samarskite shows a remarkable loss peak and change of dielectric constant (at 600°C.) These phenomena agree to the results of D. T. A.

Euxenite. Two remarkable loss peaks at 420°C. and 730°C. show good agreement with the results of dielectric constant and D. T. A.

Fergusonite. The dielectric constant of fergusonite enlarges its value remarkably at 300°C. and diminishes at 600°C. accompanied by two loss peaks at respective temperatures. The thermal analysis indicates an exothermic change at 600°C. but change at 300°C. was not observed.

Allanite. The degree of metamictization of allanite is varied according to its locality. The specimen under consideration is one from South Manchuria and is almost completely damaged in crystal structure. The dielectric constant diminishes its value at two temperatures, 200°C. and 700°C., but no exothermic peak was found by D. T. A.

X-ray study

Some portions of each specimen heated at 200°C., 400°C., 600°C. and 800°C. were investigated with Geiger-counter spectrometer.

Samarskite. The X-ray diffraction figures of samarskite heated at 800°C. are weak in intensity as compared with other members. This fact suggests that the crystallization should originate at higher temperature, and coincides with the results of dielectric property.

Euxenite. No diffraction pattern was found on the raw and 200°C. specimen but others heated at 400°C. and 600°C. dispose numerous strong spectra. There was almost no difference in intensity or number of spectra between these heated specimens but specimen heated at 800°C. differs in its diffraction character from the above two specimens. The results obtained from the specimen heated at 800°C. show a good agreement to the experimental data by R. J. Arnett.²⁴⁾ According to the X-ray study, euxenite crystallizes at 400°C. and undergoes some change in crystal structure at 700°C. accompanied by a more regular arrangement of atomic lattice and by some partial diffusion from atomic plane arranged in regular position already. Above all, euxenite may be considered to recover its original crystal structure by heating.

Fergusonite. Fergusonite from Suishozan, Fukushima Prefecture suffers from weak metamictization and retains the skeleton of original crystal structure. So the diffraction spectra of each specimen heated at different temperatures have similar appearances to one another excepting that the members heated at higher

temperature enlarge the glancing angle to some extent.

On the other hand, fergusonite from South Manchuria is almost completely broken down. The general course of recovering its crystal structure resembles the case of euxenite.

In this experiment, specimens were heated in open air condition. Therefore some of them should suffer from oxidation to some extent. Furthermore, the contamination of impure material is inevitable, since a relatively large specimen is required in order to study the dielectric property. The inaccuracy derived from the above reasons must be taken into consideration.

In short, it was concluded that the crystallizations of some metamict minerals begin at a low temperature and proceed rapidly accompanied by secondary crystallization at high temperature.

Conclusion

The thermal investigations of minerals have been executed by various methods but it was very difficult to demonstrate the actual state of minerals substantially. The minute change in crystal structure which was often beyond the scope of other investigation methods could be detected by studying the dielectric behaviours of minerals. Thus one of the most useful investigation method for studying the thermal alteration process of mineral is to study the dielectric behaviour of mineral.

Acknowledgments

The writer wishes to express his acknowledgments to Kenichi Fukuo of the Ceramic Institute, Nagoya Technical College for his valuable help and advice in carrying out the X-ray study. The author is also indebted to Mr. Masaaki Korekawa and Yutaka Mochida for their help in the investigations of metamict minerals. The writer also expresses his sincere thanks to the late Prof. Jitsutaro Takubo for his helpful suggestions.

References

- (1) J. TAKUBO and Y. UKAI: *Memoir. Coll. Sci. Kyoto Univ., Ser. B*, Vol. XX, No. 2, p. 119 (1952)
- (2) J. TAKUBO and Y. UKAI: *Jap. Jour. Geol Geogr.*, Vol. 24, p. 145 (1954)
- (3) T. TAKEUCHI and M. NAMBU: *Jour. Miner. Soc. Japan*, Vol. 2, No. 3, p. 145, (1955) in Japanese
- (4) E. PCSUJK and H. E. MERWIN: *Am. Jour. Sci.*, Vol. 47, p. 331 (1919)
- (5) E. S. MOOR and J. E. MAYNARD: *Econ. Geol.*, Vol. 24, p. 273, 365, 506 (1929)
- (6) H. J. ALLING: *Geol. Soc. Am. Bull.*, Vol. 58, p. 991 (1947)
- (7) J. I. KULP and A. F. TRITES: *Am. Mineral.*, Vol. 36, p. 23 (1951)

- (8) P. F. KERR and J. L. KULP: *Am. Mineral.*, Vol. 33, p. 387 (1948)
- (9) B. ROLAND: *Am. Mineral.*, Vol. 29, p. 111 (1944)
- (10) H. P. ROOKSBY: X-ray identification and structures of clay mineral, 256, 264 (1951)
- (11) A. F. WELLS: *Structural inorganic chemistry*, 412, 422 (1950)
- (12) R. E. GRIM and R. A. ROWLAND: *Am. Mineral.*, Vol. 27, p. 746, 801 (1942)
- (13) J. L. Kulp, P. Kent and P. F. Kerr: *Am. Mineral.*, Vol. 36, p. 643 (1951)
- (14) C. W. Beck: *Am. Mineral.*, Vol. 35, p. 985 (1950)
- (15) P. F. Kerr and J. L. Kulp: *Am. Mineral.*, Vol. 32, 678 (1947)
- (16) J. L. KULP, H. D. WRIGHT and R. J. HOLMES: *Am. Mineral.*, Vol. 34, P. 839 (1949)
- (17) R. A. Rowland and E. C. James: *Am. Mineral.*, Vol. 34, p. 550 (1949)
- (18) A. D. Fredrickson: *Am. Mineral.* Vol. 33, p. 372 (1948)
- (19) G. T. Faust: *Am. Mineral.*, Vol. 35, p. 207 (1950)
- (20) J. TAKUBO: *Jour. Miner. Soc. Japan*, Vol. 1, No. 1, p. 1 (1952)
- (21) A. PABST: *Am. Mineral.*, Vol. 37, p. 1 (1952)
- (22) J. TAKUBO, Y. UKAI and S. KAKIDANI: *Miner. Jour.*, Vol. 1, No. 1, p. 3 (1953)
- (23) J. TAKUBO and Y. UKAI: *Jour. Miner. Soc. Japan*, Vol. 1, No. 5, p. 258 (1954)
- (24) R. J. Arnett: *Am. Mineral.*, Vol. 35, p. 386 (1950)