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On the Metamictization

By

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Abstract

The metamictization is the phenomenon that a mineral turns finally into an aggregate composed of various sorts of phases or minerals which are, in general, extremely minute. The process of the metamictization is the repetition of expansion and quenching. The expansion may be caused by the energy connected with radioactivity and not by direct heat energy. New phases are precipitated during such process.

Introduction

In recent years there has been an increasing interest in the study of the metamict minerals with regard to their origin, effects of the heat treatment and possible use as geologic age indicators. In attempting to study their origin as well as to use them in geologic age determination, it is of importance to look closely into the process of the metamictization. First of all, it is necessary to inquire whether the degree of the metamictization is possible to be measured quantitatively. BAUER[1], in 1939, on a number of zircons correlated density, hardness, optical properties, solubility, effects of the heat treatment and he concluded that solubility in certain acids was the best to measure the degree of the metamictization. MORGAN and AUER[2], in 1941, studied on zircons found in granitic rocks of various ages and reported that the degree of the metamictization was possible to be indicated by the changes in optical properties. CHUDOBA and LANGE[3], in 1949, estimated the degree of the metamictization on gadolinites, samarskites and euxenites by the changes in density. HOLLAND and KULP[4], in 1950, suggested the possibility to estimate the degree of the metamictization by the differential thermal analysis and at the same time they first pointed out that the metamict minerals might be useful as age indicators. HURLEY[5], in 1952, measured the contents of helium and radioactive elements on a number of zircons of different ages, and reported that helium leakage increased progressively with the disordering of the crystal structure. The total amount of helium increased within the mineral at the beginning, reached a maximum and then decreased again in a function involving time and alpha activity. KULP, VOLCHOK and HOLLAND[6], in 1952, carried out differential thermal analysis mainly on zircons and samarskites. They reported that the ratio of the area under the thermal curve peak to the alpha activity increased with the age of the mineral. HURLEY and FAIRBAIRN[7], in 1953, studied on a number of zircons of different ages. They reported that the metamictization was functional to the total alpha particle irradiation. The total irradiation was represented by the geological age times alpha activity, and the degree of the metamictization was determined by the changes of the X-ray diffraction angle of (112) plane measured by X-ray spectrometer. The angle is 35.635° (2θ) for non-metamict and it approaches 35.1° (2θ) asymptotically as zircon becomes more metamict. On this result they discussed that the process of the metamictization was possible to be used for age determination.

Recently, the writers have been engaged in X-ray spectrometry on a number of allanites which were all found in East Asia. The writers have found that the spacings of the lattice planes of allanite increase as the metamictization goes on and that the specimens which are completely in a metamict state are composed of various sorts of phases or minerals. Based on these results the writers have discussed with regard to the metamictization.

Experimental

Specimens subjected to this X-ray spectrometry are as follows.

Locality		Occurence
Daimonji-yama,	Kyoto Prefecture, Japan.	in biotite granite.
Mie-mura,	Kyoto Prefecture, Japan.	in pegmatite.
Ôyama-mura,	Toyama Prefecture, Japan.	in pegmatite.
Kido-mura,	Shiga Prefecture, Japan.	in pegmatite.
Hagata-mura,	Ehime Prfeecture, Japan.	in pegmatite.
Nogizawa-mura,	Fukushima Prefecture, Japan.	in pegmatite,
Kojima-mura,	Fukushima Prefecture, Japan.	in pegmatite.
Anak-ub,	Howangheto, Korea.	in pegmatite.
Hakson-myon,	Hamkyonpekto, Korea.	in pegmatite.
Santaikou,	South Manchuria.	in pegmatite.
Tafangshen,	South Manchuria.	in pegmatite.
Tungwenchungtan,	North China.	in pegmatite.

In X-ray spectrometry *Cu-Kα* radiation with *Ni*-filter was used. Diffraction curve of every specimen was drawn up in two ways. One is under the condition of scan speed 1° per minute, scaler 4, time constant 8 and chart speed 1/2 inch per minute, while the other is of 1/4°, 4, 8 and 1/2 inch respectively. Over the range of 45° (2θ), only small diffraction peaks were observed. Examples of the diffraction curves of several specimens are shown in Fig. 1 and 2. As will be seen in these figures, the diffraction curves are widely variable in peakedness. Since it is expectative that in the case of the ordered state the peakedness of the diffraction curve will be very great and it will gradually reduce to almost unrecognizable grade as the metamictization or the lattice destruction goes on, it is considered that the peakedness represents the degree of the metamictization. Moreover, it will be seen in these figures that the more peakedness decreases or the metamictization proceeds the more the shape of the peaks becomes asymmetry. Trials to measure the heights of the peaks or to calculate the areas under the peaks are given up on account of the difficulty, in the cases of the bitterly metamict specimens, to determine where the base line should be. Attempts to calculate the spacings from the means of the peaks or to find standard deviations

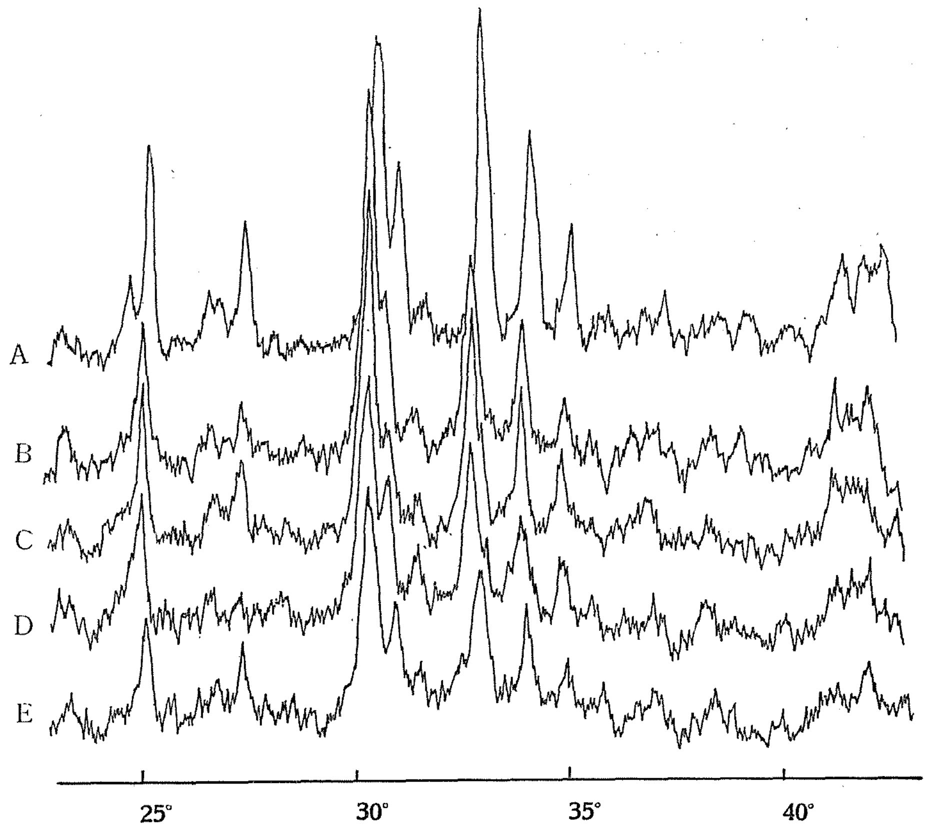

Fig. 1-a. The diffraction curves of allanites; scan speed 1° per min., scaler 4, time constant 8, chart speed 1/2 inch per min.
A. Anak-ub B. Ôyama-mura C. Hakson-myon
D. Kido-mura E. Daimonji-yama

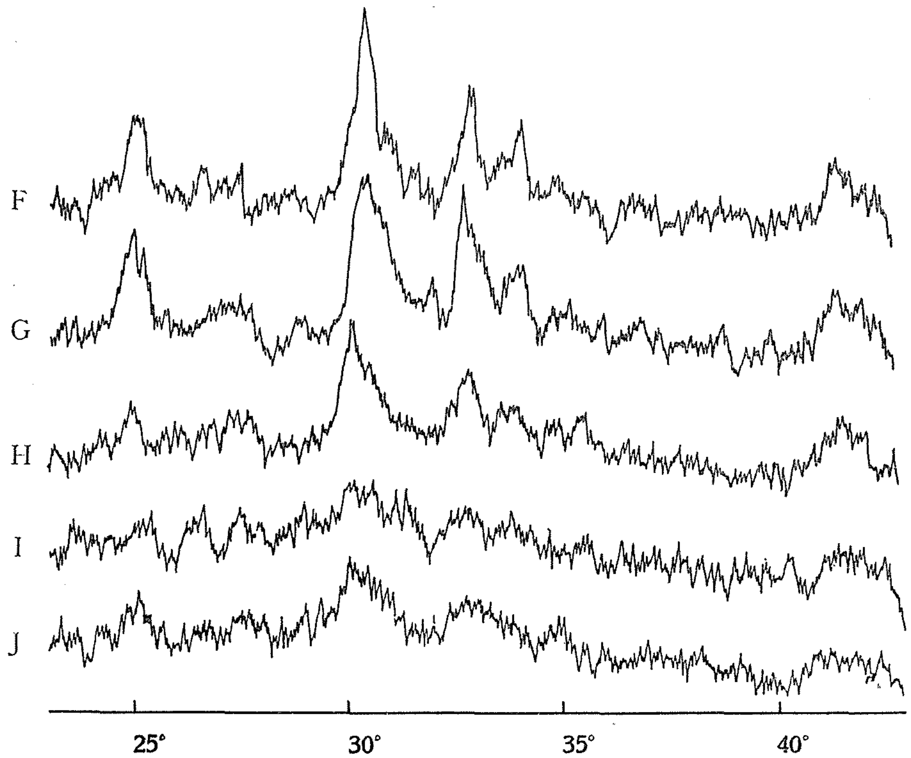

Fig. 1-b. The diffraction curves of allanites; scan speed 1° per min., scaler 4, time constant 8, chart speed 1/2 inch per min.
F. Mie-mura G. Hagata-mura H. Tungwenchungtan
I. Santaikou J. Tafangshen

of the peaks are also given up on account of the same reason.

Spacings calculated from the modes (maxima) of the peaks are as shown in Table 1. The values were corrected by silicon diffraction curve. The numbers at the last column in Table 1 denote the sequence of the peakedness of the diffraction curves estimated visually. From this result it is recognized that the spacings become larger as the peakedness of the diffraction curve decreases; in other words, spacings become larger as the metamictization goes on. For, the peakedness of the diffraction curve represents the degree of metamictization as stated above. The maximum differences between the spacings of the same lattice plane are 0.044Å, 0.034Å, 0.049Å, 0.042Å, 0.028Å, 0.025Å, 0.025Å and 0.026Å respectively. The percentages of the maximum differences to the minimum spacings in the same lattice planes are 1.2, 1.0, 1.7, 1.5, 1.0, 0.9, 1.0 and 1.0 respectively. Thus, the rate of increase of the spacings

Table 1. Spacings calculated from the modes of the peaks of the diffraction curves

Locality \ hkl	$\bar{2}11$	201	$\bar{1}13$ (or $\bar{3}02$)	020	211	013 (or 300)	$\bar{3}11$	202	
Anak-ub	3.525Å	3.239Å	2.916Å	2.872Å	2.816Å	2.709Å	2.619Å	2.554Å	1
Daimonji-yama	3.545	3.252	2.940	2.887	2.828	2.717	2.635	2.566	5
Mie-mura	3.557	3.251	2.933	2.892	2.831	2.722	2.635	2.572	6
Ôyama-mura	3.557	3.255	2.933	2.902	2.838	2.728	2.636	2.566	2
Hakson-myon	3.553	3.258	2.943	2.902	2.837	2.733	2.639	2.573	3
Kido-mura	3.557	3.258	2.943	2.900	2.837	2.733	2.642	2.573	4
Hagata-mura	3.566	3.267	—	2.907	2.837	2.734	2.639	2.576	7
Tungwenchungtan	3.569	3.273	2.965	2.914	2.844	—	2.644	2.580	8
Santaikou	—	—	—	—	—	—	—	—	9
Tafangshen	—	—	—	—	—	—	—	—	
Nogizawa-mura	—	—	—	—	—	—	—	—	10
Kojima-mura	—	—	—	—	—	—	—	—	

is directional. This may be related to the original structure.

Entering into details, however, the correspondence of the increase of the spacings to the degree of the metamictization is not necessarily satisfactory. The degrees of the metamictization of the specimens found at Daimonji-yama and Mie-mura are greater than of those found at Ôyama-mura, Hakson-myon and Kido-mura, though they were estimated from the peakedness of the diffraction curves. Nevertheless, the formers are smaller than the latters in the spacings. This may be due to that the spacings were calculated from the modes of the peaks of the diffraction curves; however, it seems to be probable that there is any other reason to exist. The writers will discuss it later.

The indices which will be seen at the 1st line in Table 1 are calculated with following lattice constants.

$$a = 8.98 \pm 0.01 \text{ Å}$$
$$b = 5.75 \pm 0.00 \text{ Å}$$
$$c = 10.23 \pm 0.01 \text{ Å}$$
$$\beta = 115°00' \pm 04'$$
$$\text{space group} : C_{2h}^{2}—P2_1/m$$

The writers have obtained these lattice constants of allanite by means of X-ray rotation photographing. The crystal used for this photographing was found at

Daimonji-yama and it was about 3mm in length and about 0.6 mm in diameter. The writers have assigned indices of $\bar{2}11$, 201, $\bar{1}13$ (or $\bar{3}02$), 020, 211, 013 (or 300), $\bar{3}11$ and 202 to the peaks of the diffraction curve of the specimen found at Daimonji-yama whose spacings are 3.545Å, 3.252Å, 2.940Å, 2.887Å, 2.828Å, 2.717Å, 2.635Å and 2.566Å respectively. The indices of the peaks whose

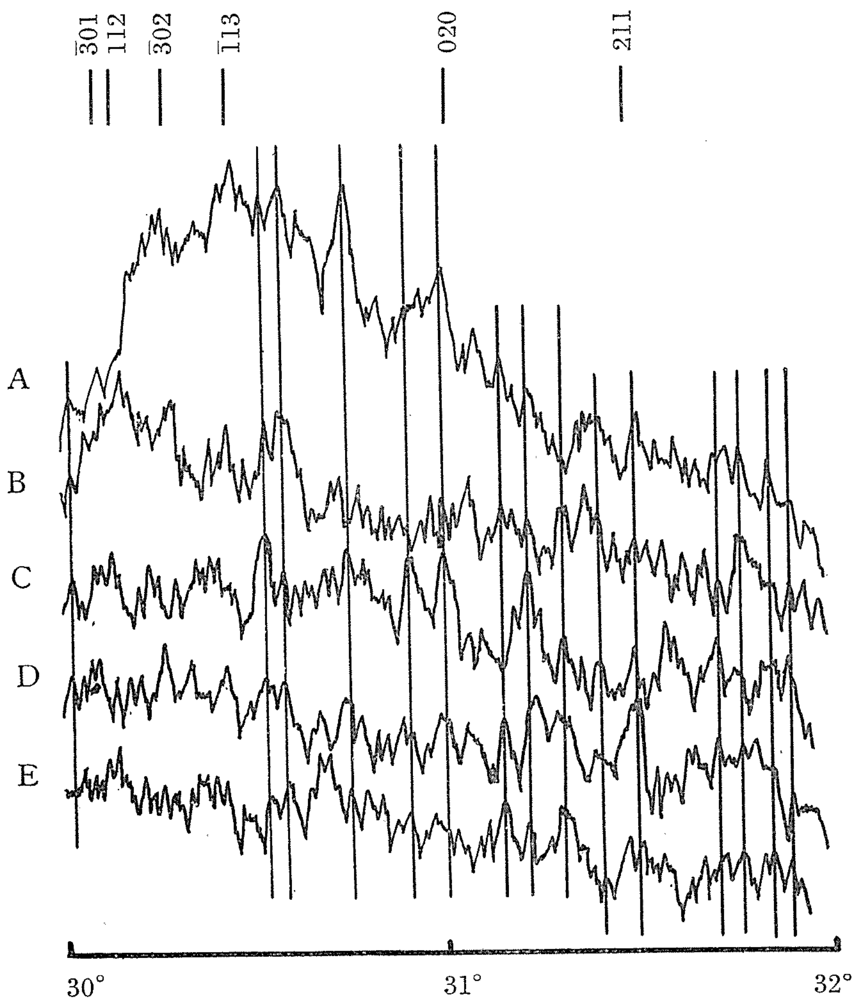

Fig. 2. The diffraction curves of allanites; scan speed 1/4° per min., scaler 4, time constant 8, chart speed 1/2 inch per min.
A. Hagata-mura B. Tafangshen C. Kojima-mura
D. Santaikou E. Nogizawa-mura

Table 2. The diffraction angles of the lattice planes of allanite

hkl	$1/d^2$	θ	*hkl*	$1/d^2$	θ	*hkl*	$1/d^2$	θ
200	.0604	10.92°	$\bar{2}13$	.1282	16.02°	301	.1811	19.15°
$\bar{2}02$	.0621	11.08	021	.1326	16.30	220	.1814	19.17
111	.0682	11.61	013	.1350	16.45	212	.1820	19.20
$\bar{1}12$	.0695	11.72	300	.1359	16.51	$\bar{2}22$	.1831	19.26
012	.0768	12.34	120	.1361	16.52	113	.1837	19.29
$\bar{2}11$	.0799	12.59	$\bar{1}21$	.1365	16.55	004	.1861	19.42
102	.0840	12.91	$\bar{3}03$	.1398	16.75	$\bar{1}14$	.1867	19.45
$\bar{1}03$	.0862	13.08	$\bar{3}11$	.1442	17.02	$\bar{2}14$	.1872	19.48
210	.0907	13.43	$\bar{3}12$	.1455	17.10	$\bar{3}04$	.1876	19.50
$\bar{2}12$	.0924	13.56	202	.1517	17.47	$\bar{4}02$	.1985	20.09
201	.0944	13.70	103	.1534	17.57	122	.2050	20.43
$\bar{2}03$	.0979	13.95	$\bar{1}04$	.1564	17.75	$\bar{1}23$	.2072	20.55
003	.1047	14.44	$\bar{2}04$	.1569	17.78	$\bar{4}01$	.2084	20 61
$\bar{3}01$	.1139	15.08	121	.1589	17.90	311	.2114	20.76
112	.1143	15.10	$\bar{1}22$	.1602	17.97	$\bar{4}03$	.2119	20.78
$\bar{3}02$	.1152	15.17	310	.1662	18.32	221	.2154	20.96
$\bar{1}13$	.1165	15.25	022	.1675	18.39	014	.2164	21.01
020	.1210	15.55	$\bar{3}13$	.1701	18.54	$\bar{3}14$	.2179	21.09
211	.1247	15.80	$\bar{2}21$	.1706	18.56	$\bar{2}23$	.2189	21.14

spacings are 2.940Å and 2.717Å are not decided, as the parameters of the atoms are not yet determined. The indices of the peaks of the diffraction curves of the specimens found at other localities have been assigned, correlating to the peaks of the diffraction curve of the specimen found at Daimonji-yama.

Looking at the diffraction curves into detail, drawn under the condition of scan speed 1/4° per minute, scaler 4, time constant 8 and chart speed 1/2 inch per minute, as shown in Fig. 2, it is noticed that there are many small peaks not due to the reflexions of the lattice planes of allan'te. At the upper part in Fig. 2, the positions of the possible reflexions due to the lattice planes of allanite are shown correspondently to the abscissa with rods. These are all the reflexions due to the lattice planes of allanite in the range from 30° (2θ) to 32°

(2θ). The diffraction angles of the lattice planes of allanite are shown in Table 2.

It is remarkable that these small peaks are in better agreement with regard to their positions as the degree of the metamictization becomes greater. The perpendicular lines between the diffraction curves shown in Fig. 2 denote the correspondence of the positions of these small peaks. These facts indicate that various sorts of crystalline phases are precipitated during the process of the metamictization.

Discussion

Many authors have hitherto discussed the cause of the metamictization. The suggestion that the metamictization might have been effected by radioactive emanations was first made by HAMBERG[8] in 1914. SLATER[9], in 1951, reported that the structure damage might be caused by the energy of alpha particles as well as of the recoil of the parent atoms. It is a current view that the cause of the metamictization is connented directly or indirectly with the disintegration of radioactive elements. HURLEY and FAIRBAIRN[10] reported that during the process of the metamictization of zircon the spacings of the lattice planes increase. During the process of the metamictization of allanite, this fact is also true. The increase of the spacing will be discussed later.

The asymmetry of the peaks of the diffraction curves, rising sharply at the high angle side and going down gently towards the low angle side, is considered to be due to the heterogeneity of the effects of the radioactivity. The asymmetry of the peaks is also observed by HURLEY and FAIRBAIRN[11] in the diffraction curves of zircon. They attributed it to the heterogenuous distribution of the radioactive elements or radioactive minerals included. The writers are, however, of the opinion that even if the radioactive elements are dispersed homogeneously, in the case of the low concentration asymmetrical peaks will probably appear. In Fig. 3 the changes of the diffraction curve, as the metamictization goes on to its saturation, are illustrated schematically. If the effects of the radioactivity were homogeneous, the peak would change in spacing and shape as in A, and if heterogeneous, it would as in B. Even if two specimens should be equal in the lapsed time and the content of the radioactive elements, the peak should not always be equal in spacing and shape owing to that whether the effect of the radioactivity is homogeneous or not. Consequently, to attempt to apply these changes of the spacing for age determination is, in general, quite difficult. It is reasonable that HURLEY and FAIRBAIRN[12] have given up asymmetrical peaks in such attempt.

It is very interesting that during the process of the metamictization the spacings of the lattice planes increase and various sorts of phases precipitate. On these points the writers now enter into discussion. The writers are of the opinion that the process of the metamictization is the repetition of the expansion and quenching of the lattice. The expansion may be caused not by the direct heat energy, but by the energy connected with radioactivity. As the expansion is, however, carried out in a rock, the lattice will be quenched immediately after expansion. The diffraction curves which are shown in Fig. 1 will represent respectively one of these stages of this repetition of the expansion and quenching. During the

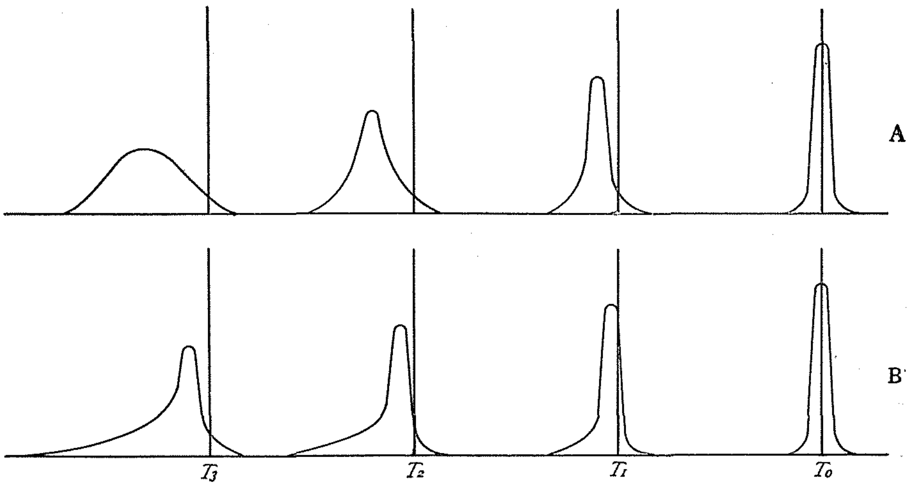

Fig. 3. The changes of the peak as the metamictization goes on to its saturation. A. The effect of the radiactivity is homogeneous, B. heterogeneous.

process of the repetition of the expansion and quenching, if the original phase acquires sufficient energy to jump over the potential barriers, other phases will be precipitated. The precipitation which can be surmised from the diffraction curves of the bittery metamict specimens is considered to be caused in such process. The writers are convinced that whether the mineral is in a final stage of metamictization or in a intermediate stage, it consists of various sorts of phases, where some are in a crystalline state and others are in amorphous state. The assortment of the phases will differ widely even in the specimens of the same kind of mineral, depending on the original chemical compositions, which means not only macro-compositions but also micro-compositions, and those acquired *posteriori*. In consequence, the substance in a metamict state, whether its degree is great or not, is considered to be an aggregate of various phases, which differs even in the specimens of the same kind of mineral. In the formations of the new phases, if original crystalline phase is most liable to precipitate, the metamictization will not go on. For, in this case, as the atom arrangement of the new phase is probably under the strong control of the surrounding original structure, the orientation of the new phase will be the same as that of the original one.

Many authors have hitherto observed the effects of the heat treatment on the metamict stage. GOLDSCHMIDT[13], in 1924, observed that fergusonite was recrystallized by heating whereas thorite was not recrystallized by brief heating. In 1937, v. STACKELBERG and CHUDOBA[14] and in 1940, v. STACKELBERG and ROTTENBACH[15] observed that single crystal pattern was indeed produced by the heating of some zircon that was partly metamict, but they also observed that a fully metamict zircon after suitable heat treatment yielded a ZrO_2 diffraction pattern and on further heating a zircon fiber pattern. CHUDOBA and LANGE[16], in 1949, observed that gadolinite found at Ytterby yielded a fiber pattern after heating for 10 hours at 950°C and the orientation was worsened by heating for 16 hours at 1000°C. They further observed the complete reconstitution of both samarskite and euxenite at well below the pyrognomic temperature. ARNOTT[17], in 1950, reported that euxenite recrystallized in its original structure after heating at 1000°C, however, only in cryptocrystalline. PABST[18], in 1952, studied carefully the effects of the heat treatment on some thorite and zircon. He reported that in the heat treatment on almost wholly metamict tetragonal $ThSiO_4$, there yielded at about 640°C isometric ThO_2 only in a very small quantity, at about 715°C to 1200°C tetragonal $ThSiO_4$ as well as monoclinic $ThSiO_4$ and that at about 1400°C all eventually converted into the monoclinic phase. He also reported that monoclinic $ThSiO_4$ was synthesized by solid state reaction between crystalline ThO_2 and amorphous SiO_2 at about 1400°C. He reported, however, that during the process of this reaction the tetragonal phase was formed at intermediate stages. In the heat treatment on zircon showing various degrees of metamictization within a single crystal, he observed that both more and less metamict portions yielded at 950°C zircon and monoclinic ZrO_2 (baddeleyite) which persisted even on heating to about 1400°C. According to these results, the effects of the heat treatment on the metamict minerals are more complex than those previously considered.

The writers are of the opinion that the recovery of the metamict mineral to the original phase by heat treatment is an exceptional case and, in general, the process during the heat treatment on the metamict mineral is no more than a reaction between solid states, which have precipitated during the process of the metamictization. In consequence, the metamictization is not, in general, likely to be reversible by the heat treatment only. The writers are doubtful of the possibility of age determination by means of thermal differential analysis which was first pointed out by HOLLAND and KULP[19], and shortly after was tried to prove by KULP, VOLCHOK and HOLLAND[20].

Summary

1. Twelve specimens of allanite found in East Asia were subjected to X-ray spectrometry. The diffraction curves of these specimens are widely variable in the peakedness. The peakedness was considered to represent the degree of the metamictization.

2. As the metamictization goes on, spacings become larger and the shape of the peaks of the diffraction curve becomes more asymmetrical. The former means that the lattice is expanded and the latter may be due to the heterogeneity of the effect of the radioactivity.
3. There are many small peaks in the diffraction curves which are not due to the reflexions of the lattice planes of allanite. These small peaks are in better agreement with regard to their positions as the degree of the metamictization becomes more great. These facts mean that various sorts of crystalline phases are precipitated during the process of the metamictization. Consequently, the mineral in the metamict state, whether it is in a final stage or not, is considered to be composed of many sorts of phases, where some are in a crystalline state and others may be in an amorphous state. The assortment of the phases will differ widely even in the specimens of the same kind of mineral, owing to their original chemical compositions and those acquired *posteriori*.
4. The attempt to use the changes of the spacings for age determination is, in general, considered to be difficult. The peak will not always be equal in spacing and shape owing to that whether the effect of radioactivity is homogeneous or not, even if two specimens are equal in the lapsed time and the content of the radioactive elements.
5. The lattice expansion may be caused by the energy connected with radioactivity. As the expansion is carried out in a rock, the lattice will be quenched immediately after expansion. It is the writers' opinion that the process of the metamictization is the repetition of the expansion and quenching of the lattice.
6. In the formations of the new phases, if original crystalline phase is most liable to precipitate the metamictization will not go on. For, in this case, as the atom arrangement of the new phase is probably under the strong control of the surrounding original structure, the orientation of the new phase will be the same as that of the original one.
7. The process during the heat treatment are considered to be no more than a reaction between solid states which, in general, will be irreversible. The writers are doubtful of the possibility of age determination by means of the differential thermal analysis.

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