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THE METAMICT STATE*

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ABSTRACT

The development of investigation of the metamict state is considered. Observations of the changes induced by heating metamict thorite are reported.

INTRODUCTION

The word "metamict" has been widely used in recent years. It appears several times in the first volume of the 7th edition of "Dana's System" and yet one will look in vain for a definition of it in dictionaries or encyclopedias and in most mineralogical textbooks.¹ Hence it may be of interest to refer briefly to the origin of this word.

"Metamict" was defined by Broegger in a publication not readily accessible to or generally known by mineralogists. The definition appears near the end of a thousand word article on "amorf" in the first edition of Salmonsens Konversationslexikon published in Danish in Copenhagen in 1893.² After pointing out the characteristic differences between crystalline and amorphous solid substances, Broegger referred to the fact that Breithaupt had long ago divided the latter into *porodine* amorphous substances, formed by slow hardening of gelatinous masses, for example opal, and *hyaline* amorphous substances, formed by rapid cooling from a molten state, for example obsidian. In addition to these two principal groups of amorphous substances Broegger recognized a third. Certain originally crystalline substances, he said, have in the course of time assumed the properties of amorphous substances. While

* Address of the retiring President of the Mineralogical Society of America given at the thirty-second meeting of the Society in Detroit, Michigan, Nov. 8, 1951.

¹ An exception is Klockmann's *Lehrbuch der Mineralogie* by Paul Ramdohr, 13th ed., 1948, where the word is defined by implication on page 227.

² Incidentally we may be reminded that another mineralogical matter of far greater importance was first developed in an encyclopedia. The first derivation of the 32 symmetry classes was given by J. F. C. Hessel in a 200 page article on "Krystal" in the fifth volume of Gehler's *Physikalisches Wörterbuch*, 1830, and it may well be that this obscure manner of publishing delayed the general recognition of the importance of the 32 classes until the work of Gadolin nearly 40 years later.

retaining their original crystalline form they have become lighter in specific gravity, assumed conchoidal fracture, have become optically isotropic and so on. He enumerated some of these materials, such as gadolinite, euxenite, fergusonite, thorite, zircon and others, many containing the rare earth elements and thorium or uranium. Some, for instance thorite, he said, are known only in the amorphous state.

Broegger's definition follows:

"For this third class of amorphous substances there is herewith proposed the name "metamict (from *μεταμικτυμ*, mix otherwise, that is by a molecular rearrangement to another molecular structure than the original crystalline) amorphous substances. The reason for the amorphous rearrangement of the molecules might perhaps be sought in the lesser stability which so complicated a crystal molecule as that of these minerals must have in the presence of outside influences."

STUDY OF THE METAMICT STATE

Broegger (1890) had been interested in isotropized materials for several years and had listed a large number in his monograph on the nepheline syenite pegmatites. Petersson (1890) did his work on gadolinite in part in Broegger's laboratory. He showed that isotropic and anisotropic gadolinite have essentially the same composition and that isotropic gadolinite could be made anisotropic at a certain temperature at which it shows the phenomenon of "glowing," this being a sudden incandescence which passes through the mineral when it is warmed to a moderate temperature and must be attributed to evolution of heat within the mineral itself.

This property of "glowing" which characterizes certain metamict substances was first reported by Berzelius (1815) who stated that his attention was called to it by Wollaston. Berzelius observed that gadolinites though differing in their behavior before the blowpipe all show the property of "glowing." He wrote:

"If a piece of gadolinite is slowly heated before the blowpipe to incipient incandescence so that the whole piece is warmed uniformly as far as possible, at a certain temperature it suddenly comes to ignition as though it took fire and this ignition will spread over the whole mass the more rapidly the more uniformly the piece has been heated."

The word "pyrognomic," meaning "readily becoming incandescent on heating," was coined by Scherrer (1840) to designate materials showing this behavior and it is still to be found in modern dictionaries although it is scarcely used by present day mineralogists.

Pyrognomic behavior was soon found in various minerals. For instance, Shepard (1851) recorded that a material he called rutherfordite, later shown to be fergusonite, "when heated in a glass tube by means of blowpipe—cracks to pieces, glows as if on fire, emits much moisture, and turns yellow."

In the course of time other changes produced by heat in the minerals which Broegger later classified as metamict were noted or investigated by mineralogists. Des Cloiseaux and Damour (1860) reported that optically isotropic gadolinite becomes birefringent after heating and made similar observations on a number of other substances. Damour (1864) recorded the increases in specific gravity produced by heating of zircons.

After Broegger various writers have tabulated the characteristics of metamict materials. In doing this they have usually proceeded from an acquaintance with only a few metamict materials and only a partial knowledge of the findings of other investigators. This has led to faulty and over-simplified summaries of the properties of metamict substances and especially to the attribution of the properties of particular species or even of particular specimens to metamict substances generally. Commenting on his recent summary Faessler (1942) says that not all of the properties he lists belong to all metamict materials but does not indicate just how this qualification is to be applied to the several items on his list. The following annotated list of the properties of metamict minerals has been compiled from many sources. It is valid only with the annotations.

PROPERTIES OF METAMICT MINERALS

1. Optically isotropic. Many metamict substances are heterogeneous being partly isotropic and partly anisotropic.
2. Pyrognomic, i.e., readily becoming incandescent on heating. In this regard there is great variation, Liebisch (1910), with no glowing observable in some cases. Even strongly pyrognomic minerals like gadolinite can be annealed below the temperature of glowing with complete loss of the pyrognomic quality, Faessler (1942). Prior (1894) had previously observed the restitution of birefringence in fergusonite by heating with no pyrognomic effect.
3. Lacking in cleavage, fracture conchoidal. Some, also, are particularly brittle.
4. Density increased by heating. This is commonly the case but the change is slight in some species and misleading reports have been given for a few on account of difficulties of accurate measurement, Scherrer (1840) and Rose (1843).
5. Crystalline structure reconstituted by heating. This conclusion was drawn from the optical changes noted by Des Cloiseaux and later workers. In some cases it is suggested that a single crystal is reformed (e.g. Ramdohr 1948). Reconstitution may be a very complex process and even where a single species results may not yield single crystals.
6. Resistance to attack by acid increased by heating. This curious effect of heating, just the opposite of heating to fusion in many instances, was found by Rose (1841), also noted by Petersson (1890) and investigated by Bauer (1939).

7. Contain U or Th. The content of U or Th may be low, e.g. 0.41% ThO₂ in gadolinite from Ytterby. The presence of rare earths and related elements has been emphasized by some workers.
8. Some minerals are known in both the crystalline and metamict states. In these cases little if any chemical difference can be found. There is evidence of hydration attending isotropization but no direct or general correlation has been established. Des Cloiseaux and Damour (1860) found allanites (orthites) might be anhydrous and either isotropic or birefringent or hydrated and either isotropic or birefringent.
9. X-ray amorphous. Vegard (1916) first reported the absence of x-ray diffraction in thorite. This has since been noted for many other metamict minerals. Some show traces of x-ray diffraction though optically isotropic.

Numerous causes have been assigned to metamictization or isotropization. Some early workers considered that the isotropic and birefringent forms correspond to dimorphs, Des Cloiseaux and Damour (1860). In recording the specific gravity increases on heating zircons, Damour (1864) referred to "l'allotropie des zircons." A little later the variation of density in zircons was even considered to be possibly due to the presence "instead of zirconium" of "another closely allied element," Stevanović (1902), Spencer (1904). Others have considered that the isotropic paramorphs arise "as a result of hydration" and this is expressly stated by Lacroix (1922-23) in the discussion of several metamict minerals.

Broegger attributed metamictization to unspecified "outside influences." He considered that the minerals which become metamict are especially susceptible to these influences because of the lesser stability of their "complicated crystal molecule." The notion of lesser stability has been elaborated upon by several later workers though it is no longer thought of as necessarily connected with complex composition. There are many materials that are of complex composition but not known to be metamict. On the other hand some metamict substances have a relatively simple composition.

The suggestion that the isotropization of metamict minerals might have been effected by radioactive emanations was first made by Hamberg (1914). He seems to have been led to this after considering the effects of alpha radiation in pleochroic halos. Even before the discovery of radioactivity, Michel-Lévy (1889) had observed that birefringence as well as color is affected in these halos. The reduction or loss of birefringence was the optical change most frequently noted by early students of metamict minerals, measurements of refractive indices being rarely made in those days before the introduction of the immersion method.

Recognition that alpha radiation might be involved in the process of metamictization did not solve the problem at all. It remained to explain why alpha bombardment is effective in some cases and not in others.

The condition for metamictization given by Broegger (1893), that minerals so affected must have a special predisposition thereto, was restated in phrases appropriate to a later era by Goldschmidt (1924). He enumerated three conditions required for metamictization: *A.* The original structure must be only weakly ionic and possibly susceptible to hydrolysis. *B.* The structure must contain one or more kinds of ions that are readily susceptible to changes in the state of ionization. *C.* In many cases it may additionally be necessary that the crystal is subjected to relatively *strong* radiation, either from radioactive material within the crystal itself or from outside sources. No one of these conditions is alone sufficient for isotropization. It may be noted that materials of strongly ionic binding are not known in the metamict state. This state is characteristic of isodesmic multiple oxides as recently pointed out by Holland and Kulp (1950). That natural irradiation, however strong, will not necessarily render a mineral metamict is shown by the existence of fully crystalline thorianite and pitchblende.

If the complicated composition of metamict minerals renders them unstable, as initially proposed by Broegger, one might suppose that this is due to the fact that extended isomorphous substitutions have a limited range of stability. Upon change of temperature and pressure from the conditions under which they formed these substances may become unstable. It was pointed out by Machatschki (1929) that this, however, leads to exsolution in many well-known cases. A few years later Machatschki (1941) suggested that for zircon the instability making it susceptible to metamictization might be sought in the eight coordination of its zirconium. This element has an ionic radius close to the limit of the ranges associated with eight- or six-fold coordination and is found in six coordination in many materials.

In a recent review of the "nature and cause of the metamict state" Hutton (1950) has emphasized the suggestion of Tomkiewf (1946) that changes in ionic radius attending oxidation of uranium will explain the metamictization of uraninite. This is considered to follow from Ellsworth's (1925) statement that "all minerals containing UO_2 automatically oxidize themselves at a rate depending on the rate of uranium and thorium disintegration." To me it seems that these authors have not considered the processes involved after a state of equilibrium has been reached, that is, when uranium is in equilibrium with its series of decomposition products and lead atoms are appearing at the same rate at which uranium atoms are disintegrating. Conybeare and Ferguson (1950) and Brooker and Nuffield (1951) have recently studied the correlation between the state of oxidation of uranium in pitchblendes and their degree of metamictness.

The characteristic behavior of pyrogonomic minerals may be con-

sidered to be caused by the liberation of heat as they change rapidly from the higher energy metamict state to a crystalline state, the energy released having been acquired in the process of isotropization. According to current views, the source of this energy is to be sought in the radioactive decay of constituents of the minerals themselves. Radioactive materials outside the affected minerals could hardly be expected to have the observed effect since the range of natural alpha particles in the materials concerned is of the order of 0.02 mm. (Stackelberg and Rottenbach, 1940).

The evolution of heat associated with the "glowing" of pyrognomic minerals was first demonstrated by Rose (1843). The first careful measurements were made by Liebisch (1910), who gave heating curves for a number of pyrognomic minerals and found that a rough correlation could be made between the generation of heat indicated by these curves and the visibility of the luminescence. He found, as might have been expected, that gadolinite, the first known pyrognomic mineral and the one showing the liveliest glow, gives the most pronounced break in the heating curve. The study of the heat effect was made quantitative by Faessler (1942) who managed to measure the heat of transformation by direct calorimetry on gadolinite from Ytterby which had been the subject of study by so many others. The heat of transformation was found to be of the same order of magnitude as the heat of crystallization of comparable materials. Incidentally Faessler carried out more precise and extensive measurements of the specific heats of reconstituted and of metamict gadolinite than had previously been made, and found that the relations of these specific heats are similar to those of crystalline silicates and their glassy equivalents.

Recently the heat effects shown by metamict minerals have been recorded by differential thermal curves (Kerr and Holland, 1951) and the use of these curves for purposes of identification has been suggested.

There has been some speculation as to the reasons for variations in degree of metamictness of different samples of the same mineral. Hutton (1950) has asked whether certain thorites might be not "old enough for the transformation to a metamict state to have taken place." Mügge (1922) noted that artificial U, Th and Ra salts show no metamictness, nor do such minerals in young rocks show it, e.g., it is not observed in zircons or allanites of young volcanics. A study of zircons from granitic rocks of various ages by Morgan and Auer (1941) showed that the degree of metamictness as indicated by change in optical properties could be correlated with radioactivity of the samples but this bears no simple relation to age.

The degree of metamictness has been estimated by Chudoba and

Lange (1949) from changes in density. Faessler (1942) considered time-temperature curves suitable for making such an estimate though his own observations do not seem to me to be in harmony with this opinion. Recently Holland and Kulp (1950) have suggested that an estimation of the degree of metamictness from differential thermal analysis might be used for age determination. They say:

"It seems plausible to assume with previous authors that these minerals were originally crystalline, and that destruction of the crystal lattice has taken place since their formation through alpha bombardment from the uranium and thorium in the lattice.

"If this is the true mechanism, it follows that the amount of destruction of the lattice is affected by (1) the inherent stability of the given mineral structure, (2) the total alpha activity of the mineral, and (3) the time elapsed since the formation of the mineral. If the first two variables can be specified and if the degree of destruction of the lattice can be quantitatively measured, then the age is uniquely determined.

"The amount of disorder created by alpha bombardment of the lattice can be measured by means of thermal analysis, since the area under the exothermic peak on the thermal record will be proportional to the amount of heat generated in the specimen upon returning to the crystalline state."

Little is known of the efficiency of alpha bombardment in the destruction of a crystal. The matter has recently been touched upon by Hurley (1951). He says:

"The exact nature of the structural disturbance caused by heavy ionizing particles is not known. It is well known . . . , that *x*-ray diffraction patterns are obliterated under heavy dosages of alpha particles. If the process in solids is at all similar to that in gases, an alpha particle will lose energy chiefly by interaction with electrons and not by nuclear reactions or scattering. According to classical theory, each alpha particle would initiate in the order of 10^6 secondary electrons of mean energy 100-200 ev. before coming to rest. This would leave a cylindrical volume along the track intensely irradiated by these electrons and those which they in turn displaced. In a non-conductor such as a silicate mineral the electrons might remain out of place, and the presence of the extra electrons as well as the disrupted bonds might displace the atoms or at least leave them in a weakly bound condition.

A calculation of the time required to make a given mineral metamict is possible if we make certain simplifying assumptions. Let us assume:

- A. That the entire energy from radioactive decay is spent in disruption of the crystal structure.
- B. That the "heat of transformation" of the metamict to the crystalline state is a correct measure of the energy differences of the two states, that is, of the energy which was required for disruption of the crystal structure.

We have the necessary data to make the calculation for gadolinite from Ytterby.

1. The heat of transformation of the gadolinite. This was determined by Faessler (1942) to be 89.1 calories per gram.
2. The concentration of thorium in the gadolinite. At 0.41% ThO_2 found by Petersson (1890) this is about 0.004 gram per gram.

3. The energy provided by thorium in equilibrium with its decay products. According to Evans and Goodman (1941) this is 0.203 calorie per gram per year.

Dividing 1 by the product of 2 and 3 we find that under the assumed conditions Ytterby gadolinite would become entirely metamict in about 110,000 years. If one makes a corresponding calculation for an hypothetical mineral having similar thermal properties to gadolinite and containing one per cent of uranium one finds that only 12,000 years would be required for complete metamictization.

Assumption *A* made above is probably not justified. No doubt only a part of the radioactive energy is effective in disruption of the crystal structure and this process takes much longer than the time calculated. On this point Hurley (1951) says:

“Differential thermographic measurements are being made to determine the amount of heat given off as zircon becomes ordered again at elevated temperature, as a part of a study of the proportion of alpha particle energy that goes into permanent disturbance of the structure.”

It is, however, not likely that all metamict materials will lend themselves so well to the determination of the heat of transformation as the markedly pyrogonomic gadolinite. The changes produced by heating metamict minerals may be very slow and in some cases do not lead to the simple reconstitution of the original structure.

Until the discovery of x -ray diffraction the best method for studying the changes effected in a metamict material by heat was observation under the polarizing microscope. Several investigators reported the reappearance of double refraction and some observed what was interpreted to be the reconstitution of a single crystalline edifice in proper orientation with the external form. As Mügge (1922) said “Es mutet das den Kristallographen an wie die Auferweckung eines Toten.” Mügge made very careful observations on the progressive changes in double refraction and showed that these indicated that intermediate stages may consist of a web- or sponge-like crystal whose meshes are filled with amorphous substances, the aggregate effect being that of a single crystal without fully restored birefringence.

X-RAY STUDIES

Vegard (1916) was the first to note the absence of x -ray diffraction in a metamict mineral (thorite). In later years many investigators have studied the reconstitution of metamict minerals by means of x -rays. Commonly powder methods only have been used and thus the possibility of recognizing fully what goes on within an apparent single crystal has been missed. Even such limited observations did yield interesting results. Goldschmidt (1924) found that fergusonite is recon-

stituted by heating whereas thorite is not reconstituted by "brief heating."

The use of single crystal patterns by v. Stackelberg and Chudoba (1937) and v. Stackelberg and Rottenbach (1940) showed that single crystals are indeed produced by the heating of some zircons that are partly metamict, but they also found that a fully amorphous zircon after suitable heat treatment may yield a ZrO_2 diffraction pattern and on further heating a zircon fiber pattern with a large measure of disorientation. The Ytterby gadolinite also yields but a fiber pattern after heating 10 hours at $950^\circ C$. according to Chudoba and Lange (1949) and the orientation is worsened by heating 16 hours at $1000^\circ C$. They further reported the complete reconstitution of both samarskite and euxenite at well below the pyrognomic temperature. Arnott (1950) speaking of metamict material which has presumably regained its original structure after heating says "the resultant material, however, is cryptocrystalline." It seems probable that single crystals can be reconstituted only when there are remnants of the original structure and even then only in certain cases.

OBSERVATIONS ON THORIUM SILICATE

Not long ago Professor Hutton discovered a monoclinic form of natural thorium silicate which I had the pleasure of naming huttonite. It is found in minute clear crystal fragments not in the least metamict, (Pabst and Hutton, 1951). Previously thorium silicate had been known naturally only as the tetragonal mineral thorite and only in the metamict state. Shortly after the discovery of natural monoclinic thorium silicate Hutton kindly gave me some minute single crystals of thorite containing 11.5% UO_2 and designated uranothorite. These proved to be not metamict, showing only a slight streaking in the single crystal pattern and last year I reported on the x -ray examination of this material showing that it has zircon type structure (Pabst, 1951). Since then Bonatti and Gallitelli (1951) have described a non-metamict thorite differing only in having slightly smaller cell dimensions.

Discovery of the dimorphism of thorium silicate suggested that a study of the effects of heat upon thorites might be of special interest. Accordingly heating experiments have been made on seven thorites, an artificial mixture of thorianite (ThO_2) and amorphous silica in one to one proportion, and on two partly metamict zircons. The results have shown that the effects of simple heating on metamict materials may be much more complex than has been previously reported, and that the differences between various samples of the same mineral may be great.

To obtain a maximum of information from a minimum of material

and observations the single crystal method was used in large part. Minute single crystals were repeatedly heated and set up for x -ray diffraction after each heating to allow the detection of the cumulative effects. Fragments of single crystals suitable for use on the Berman balance were employed in groups. By testing before and after heating it was, in some cases, possible to determine density, weight loss and shrinkage on the pieces used for x -ray study.

The only non-metamict thorium silicate available for study was the uranothorite from New Zealand reported on last year. At that time it was pointed out that heating to 850° C. has only the effect of slightly improving the x -ray "reflections." The same crystal heated stepwise to about 1400° C. and another crystal similarly treated showed no further changes. In each case a certain amount of disorientation remained. Attempts to use fluxes to promote a change on heating were unsuccessful due to the minuteness (less than 0.02 mg.) of the crystals.

Slightly larger single crystals of thorite from La Grange, California, described by George (1951), were found to be almost wholly metamict, yielding only a few faint powder halos with no suggestion of orientation. Heating to 760° for 15 hours entirely obliterated these traces of structure and produced no recrystallization. Further heating for similar periods at 1000° and at about 1400° C. brought first the beginning of crystallization of monoclinic ThSiO_4 and then the complete powder pattern of the same with no indication of other phases.

The two extreme cases just described, with no suggestion of any phases except tetragonal ThSiO_4 in one and only the monoclinic phase produced in the other, are the simplest found thus far. Five other metamict thorites have been examined. Essential data on the specimens are given in Table 1. Spectrographic examination showed that the minor constituents do not differ greatly and are very small in amount in most cases.

Table 2 collects some of the results obtained by heating. To the periods of heating indicated may be added the time required to heat up the furnaces, usually an hour or so, and a similar period of cooling. In all cases recorded in the table it seems certain that sufficient time was allowed to achieve essential completion of changes at a given temperature. Comparing the runs at 710, 715, 850 and 935° it is clear that shorter periods might in some cases suffice to bring about the recorded changes. It was, however, determined that changes are by no means instantaneous. Specimens *A* and *D* were heated to 850° C. for $\frac{1}{4}$ hour being placed in the fully heated furnace and air quenched at the end of the run. The results of these runs were very different from those obtained by longer heating at the same temperature. Both materials showed complete

TABLE 1. MATERIALS USED IN HEATING EXPERIMENTS

	A	B	C	D	E
<i>Name on label</i>	Thorite	Thorite	Orangeite	Thorite with 9% U	Thorite
<i>Locality</i>	"Brevig, Norway"*	Arøy, Langesundfjord, Norway*	Arø, near Langesund*	"Central Norway—Telemarken"†	Madagascar
<i>Dealer or collector</i>	R. M. Wilke	Minerals Unlimited	A. C. Lawson	received by A. C. Lawson from "Dahl" 1888	Minerals Unlimited
<i>Description</i>	loose resinous fragments	crystal embedded in nepheline syenite	amorphous fragment	waxy mass attached to orthoclase	loose crystal ca. 0.3 gram
<i>Initial density</i>	4.4	4.28	5.45	4.1	4.57
<i>Color</i>	dark brown	varying black to amber	deep orange with a few brown veinlets	uniform brown	orange, somewhat dull
<i>Refractive index</i>	1.705	1.664	variable 1.71-1.78	variable 1.72-1.78	1.695
<i>Results of spectrographic examination‡</i>					
<i>Large amount</i>	Th, Si	Th, Si	Th, Si	Th, Si	Th, Si
<i>Small amount</i>	—	Ca	—	Fe	—
<i>X%</i>					
<i>Very small</i>	Ca, Fe, Mn	Na, B, Fe	Ca, Fe	Ca, Mg, Mn	Ca, Fe
<i>0.X%</i>					
<i>Traces</i>	Li, Na, Mg, Al, B, Pb, Ti	Li, Mg, Al, Mn, Pb, Ti	Li, Na, Mg, Al, B, Mn, Pb, Ti	Li, Na, Ba, Al, B, Pb, Ti	Li, Na, Mg, Al, Pb, Ti
<i>0.0X-0.000X%</i>					

* Specimens A, B and C are all from the post-Devonian nepheline syenite pegmatite area around the Langesundfjord.

† The label of specimen D leaves some doubt as to its provenance. It is probably from the region of pre-Cambrian granite pegmatites near Arendal. This is within the province of Telemarken.

‡ Spectrographic examinations were made by Dr. T. G. Kennard of Kennard & Drake, Los Angeles. Uranium was tested for by fluorescence of a NaF bead. This showed specimen B to be lower in uranium content than the others.

but diffuse ThO_2 patterns with some lines of tetragonal ThSiO_4 being also present in the pattern of specimen A.

Only a small selection of optical observations is given in Table 2. In the main only aggregate effects are observable though inhomogeneity is easily recognizable under the microscope. In no case are crystals of sufficient size produced so that complete determination of the optical properties is possible. An increase in indices can be observed even after moderate heating. Some materials remain so fine-grained or so crowded with opaque inclusions even after indices have risen to 1.8 or more that no birefringence is discernible. Materials which are essentially tetragonal or monoclinic ThSiO_4 show average indices in the appropriate range. The

TABLE 2. RESULTS OF HEATING EXPERIMENTS

Initially After 40 h. at 640° C.	A Thorite, Brevig			B Thorite, Argy			C Orangette, Arö			D Thorite, 9% U, Telemarken			E Orangette, Madagascar			
	Iso. ThO ₂	Tel. ThSiO ₄	Monoc. ThSiO ₄	Iso. ThO ₂	Tel. ThSiO ₄	Monoc. ThSiO ₄	Iso. ThO ₂	Tel. ThSiO ₄	Monoc. ThSiO ₄	Iso. ThO ₂	Tel. ThSiO ₄	Monoc. ThSiO ₄	Iso. ThO ₂	Tel. ThSiO ₄	Monoc. ThSiO ₄	Other lines
	amorphous			amorphous			amorphous			amorphous			amorphous			
20	tr.	tr.+	halo 6.5 Å	tr.	—	—	—	—	—	—	—	—	—	—	—	—
710	l	(?)	halo 6.1 Å	tr.	tr.+	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	—
141	l	tr.	halo 6.3 Å fog	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	—
14	tr.	60%	40% 5.8 Å	tr.	80%	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	—
40	tr.	40	60 4.8 Å	tr.	95	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	—
14	tr.	15	85 5.8 Å	tr.	95	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	—
1 ca. 1200	tr.	95+	—	tr.+	8.6 Å	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	—
15 ca. 1400	tr.	95+	—	tr.+	8.6 Å	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	tr.	—
Density Before	4.4		(850°)*	4.28	(640°)	5.45	4.1	5.45	(850°)	4.1	4.1	4.1	4.57	4.1	4.1	—
After	5.1			4.2		5.58		5.58								—
R. I. Before	1.705		(850°)	1.664	(640°)	1.71-1.78	1.72-1.78	1.71-1.78	(850°)	1.72-1.78	1.72-1.78	1.72-1.78	1.695	1.72-1.78	1.695	—
After	1.80-1.81+			1.725		1.80	1.77-1.82+	1.80		1.77-1.82+	1.77-1.82+	1.739	1.77-1.82+	1.739	(640°)	—
Maximum observed Density	5.26	(935°)		5.6	(950°)†	7.23	5.33	7.23	(ca. 1400°)	5.33	5.33	6.69	6.69	5.33	(ca. 140°)	—
Weight loss	22%	(ca. 1400°)		14%	(930°)	9.8%	12.5%	9.8%	(ca. 1400°)	12.5%	12.5%	16%	16%	12.5%	(ca. 1400°)	—
Shrinkage	21½%	(635°)		33%	(950°)	32.6%	20.7%	32.6%	(ca. 1400°)	20.7%	20.7%	24%	24%	20.7%	(640°)	—

! Means that all lines of the indicated material were observed. d means lines diffuse.

Black slaggy mass stuck to crucible. After cleaning with K₂S₂O₈, yellow residue gave nearly pure monoclinic ThSiO₄ pattern.

* Figures in brackets indicate temperature of heating after which measurements were made.

† No data available for higher temperatures for specimen B.

lower indices of many materials are probably attributable to a large proportion of amorphous substance. These materials may also contain isometric ThO_2 but this is so fine-grained that it appears merely as a dust in the amorphous groundmass.

Though behavior of the several specimens varies widely there is one common feature. All are eventually converted to the monoclinic phase. This begins to appear after prolonged heating at 715° in two cases. It is the principal phase present after heating to 935 or 950° in most cases. The tetragonal phase does not persist at the highest temperature employed. Isometric ThO_2 always appears at intermediate stages, though in one case only in small amount, and may persist to high temperature. Its presence in abundance implies the presence of free silica. In no case is there any indication of the crystalline phases of silica. Some amorphous material must persist to fairly high temperatures. No other phases were found. The halos or weak extra lines near 6 \AA may be associated with the "amorphous" material.

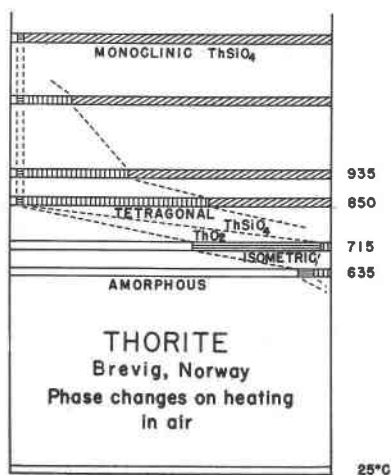


FIG. 1. Diagram of changes observed in specimen A.

The sequence of changes may be represented by a diagram such as Fig. 1 showing roughly the proportions of the several phases in the course of heating thorite from Brevig. A selection of the patterns indicating the phase changes for this material in four stages is shown in Fig. 2. It is apparent that the changes are very easily recognizable in this case.

These powder patterns, of course, do not allow us to see whether any single crystals or partly oriented aggregates have been present in the material. In Fig. 3 are shown two patterns of orangeites prepared from

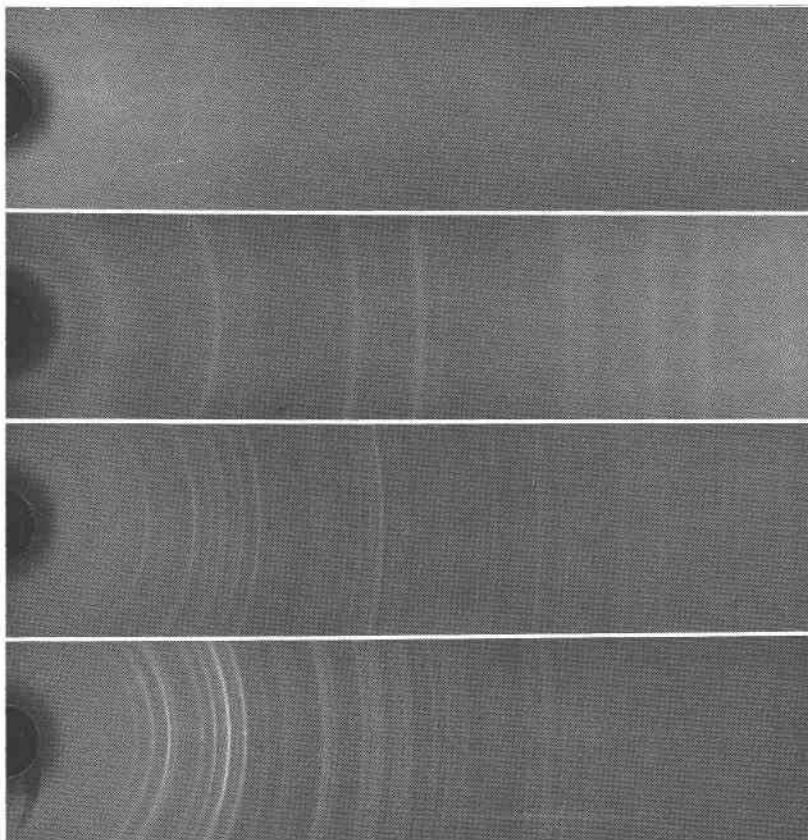


FIG. 2. Thorite, Brevig, Norway. 1. Unheated. Fully metamict. 2. Heated to 710° C. Isometric ThO_2 and amorphous. 3. Heated to 935° C. Mixture, mostly tetragonal ThSiO_4 . 4. Heated to about 1400° C. Almost entirely monoclinic ThSiO_4 .

single fragments. The Madagascar material yields a diffuse powder pattern even without heating. Apparently the single crystal has broken down to an aggregate or such an aggregate has formed by natural regeneration. In the Norwegian orangeite which is wholly amorphous as found there is no suggestion of orientation in the crystalline or partly crystalline material produced by heating.

Since several of the materials treated went through a stage in which they contained substantial quantities of ThO_2 with no crystalline SiO_2 , but all ended up as essentially ThSiO_4 , it seemed probable that one might synthesize ThSiO_4 by solid state reaction between crystalline ThO_2 and amorphous SiO_2 . This was tested by making a tablet of finely ground Ceylon thorianite and amorphous silica (Baker's "Acid Silicic") intimately mixed in suitable proportion and compressed at 10,000 lbs.



C



E

FIG. 3. C. Orängeite, Arö, near Langesund, Norway. Heated 40 hours at 650° C. "Single crystal" rotation pattern. Tetragonal ThSiO_4 only. E. Orangeite, Madagascar. Unheated. "Single crystal" rotation pattern. Tetragonal ThSiO_4 only.

per sq. in. This tablet was subjected to successive heatings. A selection of powder patterns of the products is shown in Fig. 4. The end product, as expected, is the monoclinic phase, but little of the tetragonal phase is formed at intermediate stages, possibly because reaction does not occur as readily in this artificial mixture as in metamict substances and is not extensive until the temperature range of formation of the monoclinic phase is reached.

Figure 5 shows that the monoclinic phases formed by heating thorite or by solid state reaction of thorianite and amorphous silica correspond to huttonite. The powder patterns agree in every detail.

Similar results upon heating thorites have been obtained by Mr. Kaiman (1951) of the Department of Mines and Technical Surveys, Ottawa, and by Mr. Berman (1951*a*) of the United States Geological

Survey. There remains another point to be considered. Bannister and Horne (1950) have shown that the results of heating a metamict mineral may differ with heating in air or in a neutral atmosphere. The material they examined contained ferrous iron and its oxidation might be presumed to affect the results. Significant changes due to oxidation do not seem likely in the heating of metamict thorites. Even so it would be

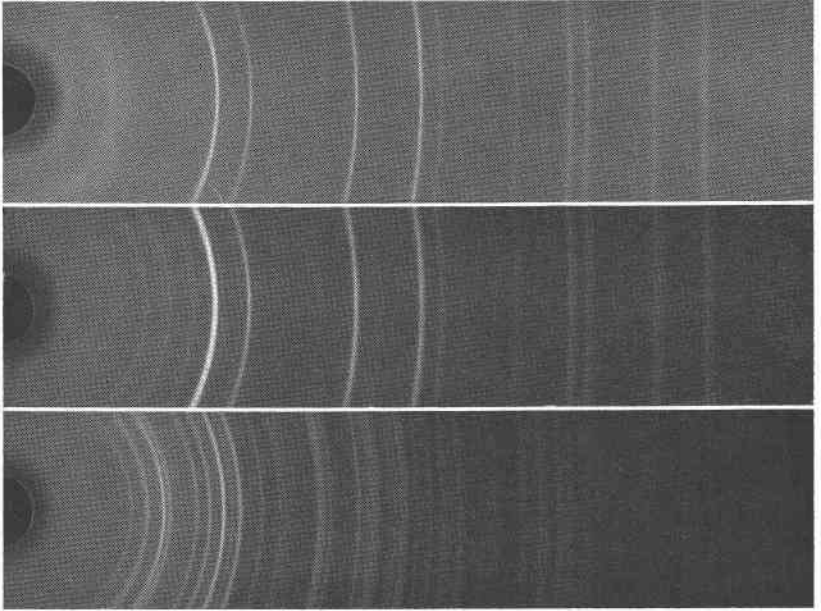


FIG. 4. Top: Thorianite, Ceylon. Middle: Thorianite and amorphous silica, after 40 hours near 1000° C. Bottom: Thorianite and amorphous silica, plus 15 hours near 1400° C.

desirable to make tests in a neutral atmosphere. This has been done by Mr. Berman (1951). As mentioned before, he also obtained the monoclinic phase by suitable heating in air but he states "when heated in a *water free* inert atmosphere they 'revert' to the tetragonal variety at a temperature around 1200° C. Likewise, crystalline thorite will form the monoclinic ThSiO_4 when heated high enough in air but does not appear to change when heated in the water free helium at our maximum temperature (1300° C.)." It will be recalled that the New Zealand uranorthorite in single crystals was unchanged upon prolonged heating even well above the maximum temperature employed by Mr. Berman so that it seems that other factors, for instance the perfection of the structure subjected to heating, will affect, at least, the rate of conversion.

Still another factor may influence the results of heating metamict minerals. The isotropization is in most cases attended by a certain

amount of hydration. Accompanying or superimposed upon this change there may be further chemical alteration. Examination of metamict brannerite from the type locality in Idaho has shown that heating produces two kinds of cryptocrystalline material the grains of which can be distinguished by external features. Presumably one kind corresponds to the heating product of simply metamict brannerite and the other to the

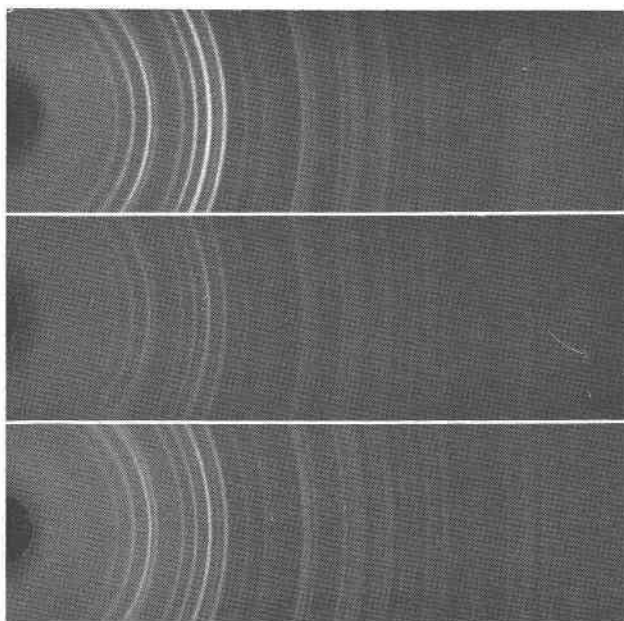


FIG. 5. Huttonite (top). Gillespie's Beach, South Westland, New Zealand. "Huttonite" (middle). Metamict thorite, Brevig, Norway, heated to about 1400° C. for 15 hours. "Huttonite" (bottom). Thorianite and amorphous silica heated to about 1400° C. for 15 hours.

heating product of brannerite that has in addition suffered some chemical change while remaining in the metamict state. The point will be further investigated.

OBSERVATIONS ON ZIRCON

That apparent single crystals may be a complex of phases was shown by Mügge (1922) who explained the changing optical properties of gadolinites as due to a web of crystalline material within the meshes of which is enclosed an amorphous phase. The complex of phases arising upon the heat treatment of metamict zircons has been studied with care by v. Stackelberg and Chudoba and coworkers. Following the experiments on thorite I have also made a few observations on zircon using cyrtolite from Norway and zircon from Indianahoma, Oklahoma. The

cyrtolite showed varying degrees of metamictness within a single crystal. At 950° C. both more and less metamict portions yielded a complete zircon pattern very diffuse at high angles with a few lines due to monoclinic ZrO_2 (baddeleyite) which persist even on heating to about 1400°, no indication of crystalline silica being found even though free silica must be presumed to be present.

The Oklahoma zircon occurs in large brown crystals that are mostly metamict. Enclosed within these are smaller crystals, some of which are fairly clear and give little suggestion of alteration. Figure 6 shows a set of rotation patterns made with such a crystal. Before heat treatment the pattern is almost that of a perfect single crystal showing little disorientation. After heating to 950° C. the same crystal yields a pattern with slightly more disorientation and showing diffraction from cubic ZrO_2 indicated by the powder arcs of this phase. After heating to about 1400° C. these powder arcs are lost but the disorientation of the parts of the crystal is even more pronounced. It is clear that here a disoriented foreign crystalline phase has arisen within the meshes of the slightly imperfect zircon host due to heating and upon further heating has disappeared while the host has become more imperfect.

ARTIFICIAL METAMICTIZATION

Since the metamict state is now generally agreed to arise from alpha particle bombardment it is surprising that so few attempts have been made to produce it artificially. Mügge (1922) was unsuccessful in attempting to alter the optical properties of orthite by exposure to radium emanation for one year. v. Stackelberg and Rottenbach (1940), on the other hand, claim to have "isotropized" a thin plate of zircon by one-sided exposure to radon for 4 months. After that period the plate cracked. This was attributed to differential expansion of the plate presumed to attend metamictization. No other indications of changes due to the irradiation were reported.

More powerful sources of radiation are now available. They might prove useful in the study of metamictization. A test case for examining the influence of structure is available in the dimorphous pair, tetragonal and monoclinic thorium silicate, which has been the principal subject of these notes. Both forms belong to well known structural types. Both have been synthesized in the laboratory of Professor Berry (1951) at Queen's University. If pure artificial preparations of these two forms were subjected to identical irradiation, using an artificial source, and differences could be established in their response, critical information would be gained on one factor in the process of metamictization.

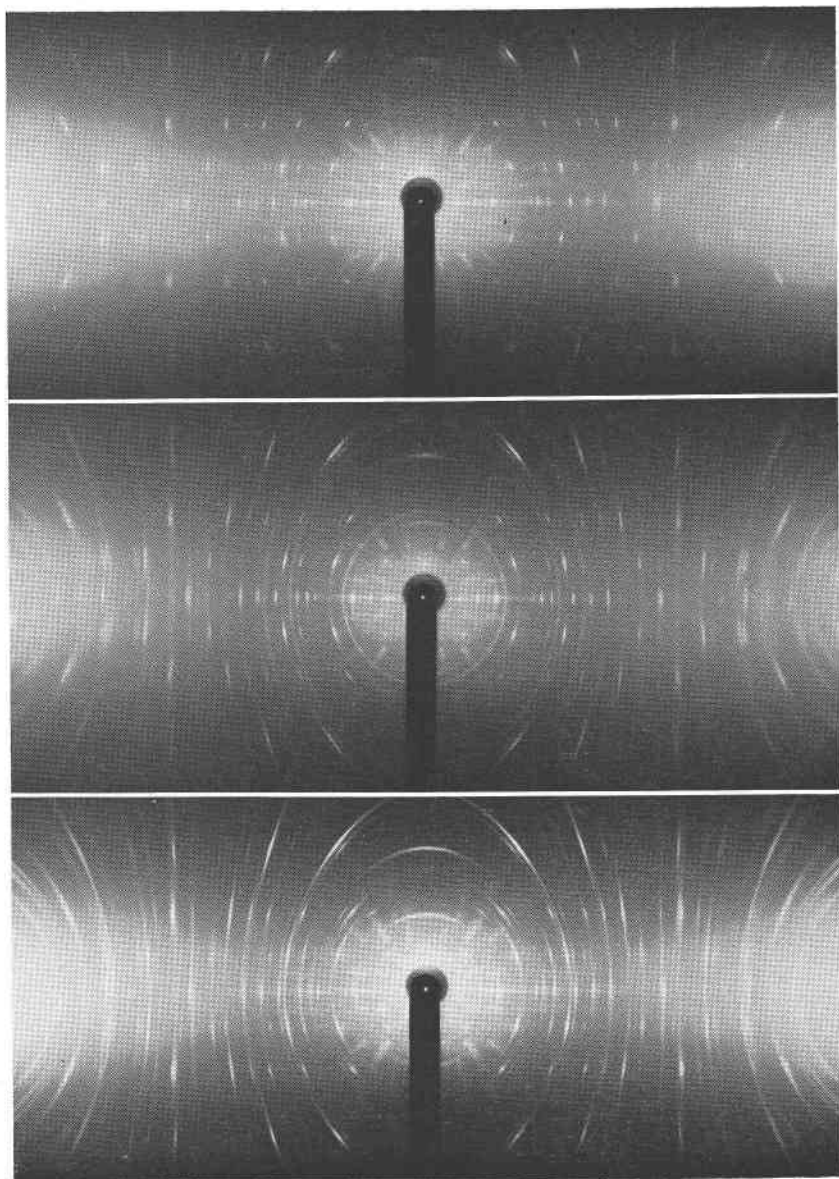


FIG. 6. Zircon, near Indiahoma, Oklahoma, *a*-axis rotation patterns. Top: Unheated. Middle: 15 hours at 950° C. Bottom: 15 hours at 950° plus 15 hours at ca. 1400° C.

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