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DIFFERENTIAL THERMAL ANALYSIS OF SHATTUCKITE

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ABSTRACT

The DTA curve of shattuckite from Ajo, Arizona, is characterized by a prominent endothermal peak with a false peak temperature at 774° C., and a small exothermal peak with a peak temperature of 980° C. Within the dehydration temperature range, shattuckite is decomposed gradually into cryptocrystalline tenorite, some cryptocrystalline α-quartz, and an unknown phase. The exothermal reaction is caused by the crystallization of α-cristobalite. All phases are identified by the *x*-ray powder diffraction.

Crystallization of tenorite begins at 675° C. and ends at 780° C. This is a strong exothermal reaction. However, an exothermal peak is obliterated completely by the endothermal dehydration reaction. At the same time, the shape of the dehydration endothermal peak is strongly skewed, and only a false endothermal peak is recorded on the graph. Some tenorite in the sample begins to decompose into cuprite at about 900° C. According to the total water content, the formula of shattuckite should be $3CuSiO_3 \cdot H_2O$. The accepted formula, $2CuSiO_3 \cdot H_2O$, is incorrect, because of an erroneous interpretation of loss of weight of the shattuckite sample by ignition.

INTRODUCTION

The occurrence of hydrated copper silicate minerals in the Southwest is fairly common. The identity of some of these minerals, however, is rather doubtful. Positive identification is often difficult, because the exact nature of these minerals has not been well defined. Therefore, studies have been initiated by the writer in order to learn more about hydrated copper silicate minerals. This paper is the first report on such study.

Dark-blue radiated and spherulitic shattuckite from Ajo, Arizona, has been used in this study. Green ajoite, quartz, and some opal are associated intimately with the shattuckite. The irregular shattuckite spherulites are about 2 mm. in diameter; the individual fibers or acicular crystals are about 2×.02 mm.; and the irregular quartz blebs or grains are about 1.5 mm. across. Samples have been crushed and handpicked with tweezers under a binocular microscope. The green ajoite and most of the quartz and opal may be removed from the sample. However, a small amount of quartz and possibly some opal, which occur between the individual shattuckite crystals, are difficult to remove. The presence of about 3% of quartz in the handpicked shattuckite sample is shown by an *x*-ray powder diffraction pattern.

DEHYDRATION OF SHATTUCKITE

A handpicked sample of shattuckite, when heated in a cylindrical electric furnace to 1,000° C., loses 3.87% of its weight, 3.71% being caused by loss of water and 0.16% by the decomposition of some tenorite into cuprite. The amount of cuprite formed from tenorite differs in different samples and under different heating conditions. A minus 100 mesh sample was heated to 200° C., and heating was continued at this temperature for 5 minutes. The sample was removed from the furnace, cooled in a desiccator, and weighed. Heating of the same sample was continued to 300° C., 400° C., and so on. The changes of color and the loss of weight at various temperatures are noted in Table 1. Figure 1D shows a fairly smooth dehydration curve for shattuckite.

TABLE 1. PERCENTAGE LOSS OF WEIGHT OF SHATTUCKITE UPON HEATING

Intermediate temperature	Loss of weight, per cent	Remarks
200° C.	—	Original pale-blue color of shattuckite powder below 100 mesh. (5B 6/2)
300° C.	—	No change in color
400° C.	—	No change in color
500° C.	0.16	Slightly dull blue
600° C.	0.71	Grayish blue-green
700° C.	1.74	Black with greenish hue
800° C.	3.71	Black (N2); maximum loss of water
900° C.	3.87	Black; maximum loss of weight; slightly brownish black streak
1,000° C.	3.87	Grayish black; part of the sample is fused

Because the water content is 3.71 per cent, the chemical formula of shattuckite was first suspected to be $3CuSiO_3 \cdot H_2O$, instead of $2CuSiO_3 \cdot H_2O$ (Shaller, 1915). This will be discussed further with the chemical analysis.

CHEMICAL ANALYSIS

In order to check the chemical composition of shattuckite, about 1 gm. of a handpicked sample was prepared for a complete silicate analysis. The result of the analysis is listed in Table 2. The percentage of H_2O^- was determined from the loss of weight of the sample when dried in an electric oven at 120° C. The percentage of H_2O^+ was determined from the loss of weight of the sample when ignited for 10 minutes in a covered upright platinum crucible, with a Meker burner. The burner temperature was about 1,100° C. to 1,250° C. The total loss of weight by ignition was 6.31 per cent. Usually it is taken for granted that this total loss of weight is caused by the removal of H_2O^+ from the sample. Accordingly, the H_2O^+

content of shattuckite would be recorded to be 6.31 per cent. Based on this analysis, the chemical formula of shattuckite would be calculated approximately as $2CuSiO_3 \cdot H_2O$. Complete chemical analyses by Shaller (see page 72, Ford, 1915) shows that shattuckite contains SiO_2 37.91–39.92%, CuO 53.20–55.51%, H_2O 5.83–6.41%, and minor amounts of FeO, CaO, and ZnO. According to the average of these analyses, the molecular ratio of $CuSiO_3$ and H_2O of shattuckite is 1.99 to 1. The accepted formula $2CuSiO_3 \cdot H_2O$, however, is erroneous, because the loss of weight by ignition is caused partly by the removal of H_2O^+ and partly by the decomposition of some CuO into Cu_2O. At high temperature, CuO tends to decompose into Cu_2O. Cryptocrystalline cuprite was identified in some shattuckite samples fired to 900 °C. At 1,935° C., Cu_2O will be decomposed into metallic copper under ordinary pressure of oxygen in the air. The entire CuO content of shattuckite may be decomposed completely into Cu_2O if the shattuckite is ignited long enough under favorable conditions. Table 3 shows the loss of weight of shattuckite under different ignition conditions.

TABLE 2. CHEMICAL ANALYSIS OF SHATTUCKITE, AJO, ARIZONA
Analyst: Dr. H. B. Wiik, Helsinki, Finland

Wt. per cent		Molecular number	Molecular ratio
SiO_2	35.90	.597	
TiO_2	0.0	.000	
Al_2O_3	0.79	.008	$SiO_2:CuO:H_2O=1.71:1.98:1$
Fe_2O_3 (total Fe)	0.31	.002	
CaO	0.00	.000	
CuO	55.27	.695	$CuSiO_3:H_2O=1.86:1$
H_2O^+	6.31	.350	
H_2O^- (120° C.)	0.08	.000	
CO_2	0.00	.000	
Total	98.66		

In the dehydration curve (Fig. 1D), it is shown that the total water content of the handpicked shattuckite sample is 3.71 per cent. Loss of weight by ignition, in excess of this percentage, is caused by the decomposition of some CuO into Cu_2O. The theoretical maximum loss of weight of shattuckite caused by decomposition of CuO into Cu_2O is 5.49 per cent.

Gaining weight upon heating is also possible. For instance, the oxidation of ferrous iron to ferric iron in stilpnomelane at about 450° C. will produce a gain in weight. The endothermal peak of stilpnomelane occurs

TABLE 3. LOSS OF WEIGHT OF SHATTUCKITE UNDER DIFFERENT IGNITION CONDITIONS

Ignition condition			Per cent loss of weight	*X*-ray identification
Sample container	Meker burner temperature	Time (minutes)		
Upright, covered porcelain crucible	725° to 900° C.	10	3.07	Tenorite, shattuckite
Platinum crucible, with access of air	1,100° to 1,250° C.	10	3.90	Tenorite, α-quartz
Upright, covered platinum crucible	1,100° to 1,250° C.	10	7.73	Tenorite, cuprite α-quartz, α-cristobalite
Upright, covered platinum crucible	1,100° to 1,250° C.	20	8.13	Tenorite, cuprite α-quartz, α-cristobalite
Upright, covered platinum crucible	1,100° to 1,250° C.	30	8.47	Cuprite, tenorite, α-quartz, α-cristobalite
Upright, covered platinum crucible	1,100° to 1,250° C.	40	8.73	Cuprite, tenorite, α-quartz, α-cristobalite
Upright, covered platinum crucible	1,100° to 1,250° C.	50	9.07	Cuprite, α-quartz, α-cristobalite, trace of tenorite
Upright, covered platinum crucible	1,100° to 1,250° C.	60 (or longer)	9.07 (maximum)	Cuprite, α-quartz, α-cristobalite, trace of tenorite

at about 350° C., but may be as high as 500° C. for some samples (Nagy, 1954). If a sample of stilpnomelane is ignited with access to air, the resultant loss of weight will be the loss of weight caused by the removal of water, minus the gain in weight caused by oxidation of ferrous iron into ferric iron.

Analysts who are not aware of this may report an incorrect molecular ratio between water and other constituents of a hydrated substance containing CuO or FeO.

Table 4 lists the impurities that were determined in the shattuckite analyzed. As indicated in the table, barium and aluminum are the chief minor constituents.

According to the chemical and spectrographic analyses, 2.52% of the handpicked shattuckite sample consists of impurities, including mainly Al_2O_3, Fe_2O_3, and BaO. According to *x*-ray powder diffraction analysis, about 3% of the handpicked sample is quartz. Thus, only about 94.48% of the handpicked sample is shattuckite. Dehydration shows that the

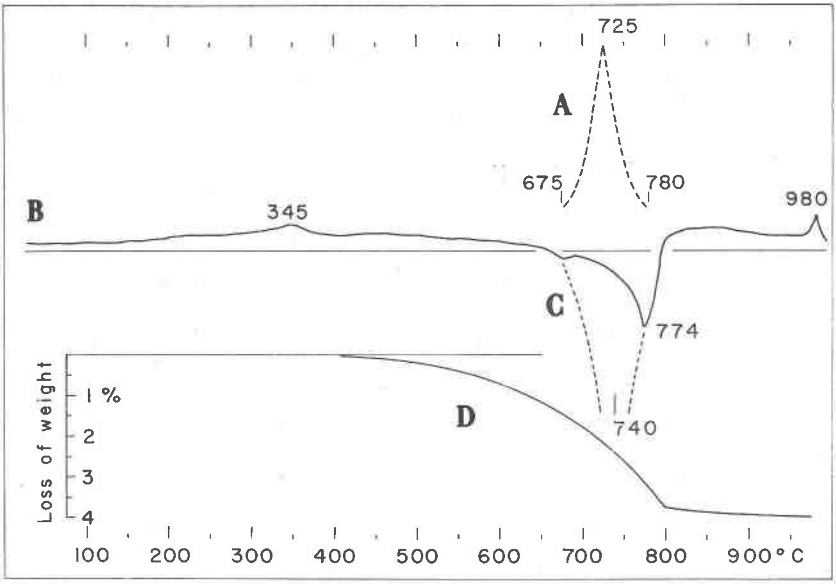

FIG. 1. A. The obliterated exothermal peak of the crystallization of tenorite. B. DTA thermal curve of shattuckite. C. The true endothermal peak of dehydration of shattuckite. D. Dehydration curve of shattuckite, (the sample contains 5.52 per cent impurities.)

handpicked sample contains 3.71% water. Thus, approximately 90.77% of the handpicked sample is $CuSiO_3$. The molecular ratio of $CuSiO_3$ and H_2O^+ of the handpicked sample is .650 to .206, or 3.16 to 1. Therefore, the chemical formula of shattuckite is $3CuSiO_3 \cdot H_2O$.

TABLE 4. SEMI-QUANTITATIVE SPECTROGRAPHIC ANALYSIS OF SHATTUCKITE, AJO, ARIZONA

Spectrographer: A. Davis Odom, Houston, Texas

Element	Per cent	Element	Per cent
Cu	22.	Ti	0.01
Fe	0.03	Mo	0.02
Si	32.	Na	looked for, not detected
Mn	0.06	Ba	0.9
Cr	looked for, not detected	K	looked for, not detected
V	0.02	Sr	trace
Al	1.	Zr	looked for, not detected
B	0.005		
Mg	0.08		
Ca	0.1	S and Se are not looked for	

Table 5. *X*-Ray Powder Diffraction Data of Shattuckite

CuKα = 1.54178 Å

d(Å) obs	I	*d*(Å) obs	I	*d*(Å) obs	I
12.48	3	1.791	7	1.006	3
9.91	4	1.760	1	.990	2
4.95	7	1.730	1	.972	4
4.43	10	1.683	<1	.949	<1
3.63	3	1.625	7	.943 *w*, *b*	2
3.50	7	1.596	4	.885 *b*	1
3.40	2	1.566	6	.847	1
3.31	8	1.506	<1	.823 *b*	2
3.11	2	1.480 *b*	2	.314 *b*	1
2.93	4	1.435	6	.789	<1
2.77 *w*, *b*	5	1.398 *b*	5	.773 *b*, halo	
2.69	2	1.357	3		
2.59 *b*	3	1.344	3		
2.46	3	1.297 *w*, *b*	5		
2.40	4	1.239	5		
2.36	6	1.227	3	Note:	
2.30	4	1.202	5		
2.22 *b*	1	1.181 *b*	1	*b* means blurred	
2.13	1	1.168 *b*	1	*w* means wide band	
2.09	1	1.150	<1		
2.04	1	1.118	1		
1.991 *b*	1	1.097 *b*	<1		
1.931 *w*, *b*	5	1.073	4		
1.853	<1	1.060	3		
1.821	4	1.036	3		

X-RAY POWDER DIFFRACTION DATA

A total of 61 powder reflections of shattuckite are recorded (Table 5). Several faint reflections of quartz, 4.26 Å, 1.54 Å, and 1.375 Å also appear on the shattuckite picture. Quartz lines of 3.34 Å and 1.817 Å are superimposed on 3.31 Å and 1.821 Å lines of shattuckite, respectively. The three strongest lines of shattuckite are 4.95 Å, 4.43 Å, and 3.31 Å. Some of the low-angle lines of shattuckite may be mistaken for lines of ajoite. The mistake can be avoided by observing a strong line of ajoite (6.19 Å) which does not appear in the shattuckite pattern, and a strong line of shattuckite (4.43 Å) which does not appear in a pattern of ajoite.

DIFFERENTIAL THERMAL ANALYSIS

The thermal curve (Fig. 1B) was traced on a Leeds and Northrup micromax recorder. The heating rate is 12° C. per minute. The scale factor is X20, which corresponds to 10 microvolts per division of the graph paper. The sample was crushed and ground to below 100 mesh.

In order to fit the characteristics of the thermal curve, samples were fired to selected temperatures. The fired samples were examined under a petrographic microscope, and the phases developed at different temperatures were identified by *x*-ray powder diffraction.

Thermal curve. The thermal curve (Fig. 1B) is fairly persistent for different samples, with slight variation in peak temperature. A minor broad exothermal peak occurs at 345° C., with a peak height of 20 microvolts. Another sample shows a peak temperature of 330° C., with a peak height of 20 microvolts. The cause of this exothermal peak is not known. A major endothermal reaction begins at about 440° C. and increases rather rapidly at 660° C. This endothermal reaction is caused by dehydration of shattuckite. A small false endothermal peak at 675° C. and a minor broad false exothermal peak at 690° C. are recorded on the graph. A major false endothermal peak at 774° C., with a peak height of 210 microvolts, is the most prominent peak of the thermal curve. This endothermal dehydration is greatly affected by an exothermal reaction of the crystallization of tenorite. Therefore, the true endothermal peak of dehydration does not show on the graph, whereas two minor and one prominent false peaks are recorded on the graph. A sharp exothermal peak (Fig. 1A) is obliterated completely by the endothermal dehydration reaction. At about 850° C. the thermal curve begins to show a weak and gradual endothermal reaction. A small and fairly sharp exothermal peak occurs at 980° C. The thermal curve was discontinued at about 995° C. It seems that the exothermal peak at 980° C. is followed closely by a strong endothermal peak beyond 995° C. This has not been verified experimentally because of the limitations of the DTA equipment used.

The obliterated exothermal peak. Because the major false endothermal peak is conspicuously skewed toward the high-temperature end of the thermal curve, an interfering exothermal reaction is suspected. The change of phase of shattuckite upon heating is fairly analogous to that of chrysocolla. (The nature of selected chrysocolla samples will be discussed in another paper.) From an illustration of this analogy, the obliterated exothermal peak of shattuckite will be evident.

(A) Chrysocolla (Tyrone, New Mexico). The DTA curve of a chrysocolla sample from Tyrone, N. Mex., derived under the same condition as the shattuckite sample, consists of (1) an endothermal peak at 154° C.;

peak height 760 microvolts; peak range 60 to 216° C., (2) an exothermal peak at 705° C.; peak height 440 microvolts; peak range 685 to 730° C., (3) an exothermal peak at 950° C.; peak height 130 microvolts; peak range 920 to 980° C. A similar DTA curve of chrysocolla was published by Kauffman and Dilling (1950). When fired to 500° C., all the constituents of the sample become amorphous, as shown by an *x*-ray powder diffraction pattern. When heated to 685° C., the beginning of the exothermal reaction, the sample becomes dull olive green, and two faint and blurred tenorite powder lines appear at about 2.32 Å and 2.52 Å in the *x*-ray diffraction pattern. There is also a broad halo at 4.5 Å to 5.5 Å. This halo indicates an incipient crystallization of silica, as in the case of some opal. When fired to the exothermal peak temperature of 705° C., cryptocrystalline tenorite, some cryptocrystalline α-quartz, and an unknown phase appear in the sample. When fired to 730° C., the end of the sharp exothermal peak, crystalline tenorite, some α-quartz, and an unknown phase appear in the sample. The exothermal reaction of chrysocolla is caused by the crystallization of tenorite from amorphous CuO. The exothermal peak of chrysocolla is distinctive and without distortion, because there is no endothermal or other thermal reaction at about 700° C.

(B) Shattuckite (Ajo, Arizona). When fired to 500° C., the sample changes from pale blue to grayish, bluish, green. The fired sample shows a clear *x*-ray powder diffraction pattern of shattuckite. When fired to 690° C., the sample becomes greenish black. The clear shattuckite *x*-ray powder diffraction pattern seems unchanged. Two faint, yet discernible, bands of tenorite appear at about 2.40 Å to 2.30 Å, and 2.59 Å to 2.46 Å. There is also a faint broad band at 4 Å to 5 Å. A sample fired to 705° C., the exothermal peak temperature of chrysocolla, shows that the shattuckite *x*-ray powder diffraction pattern has begun to fade away. Two faint tenorite bands and the faint broad band at 4 Å to 5 Å remain the same as those of the sample fired to 690° C. A sample fired to 715° C. shows that many shattuckite powder lines disappear. Tenorite powder lines at about 2.32 Å and 2.52 Å become darker, but no other tenorite powder lines appear. A sample fired to 740° C. shows a complete disappearance of crystalline shattuckite. Several blurred tenorite powder lines appear; also, a few faint powder lines of an unknown phase appear. A sample fired to 780° C. contains cryptocrystalline tenorite, some cryptocrystalline α-quartz, and an unknown phase. The halo at 4 Å to 5 Å becomes dark; also, a halo at 14 Å appears. The strong endothermal reaction of shattuckite ends at 800° C. A sample fired to 800° C. shows fairly sharp *x*-ray powder diffraction lines of tenorite, as well as some powder lines of alpha-quartz and an unknown phase.

Because the crystallization of tenorite in fired samples of shattuckite is analogous to the crystallization of tenorite in fired samples of chrysocolla, the existence of a strong exothermal reaction in the DTA of shattuckite becomes evident.

(C) Range and peak temperature of the obliterated exothermal peak. The range of the exothermal peak is 675 to 780° C., and the peak temperature is estimated to be 725° C. The small false peak at 675° C. indicates the beginning of the exothermal reaction. The exothermal peak range of chrysocolla is narrow, from 685 to 730° C. All of the CuO content of chrysocolla is amorphous when the sample is heated to 500° C. Only a narrow temperature range is required for the amorphous CuO to change into tenorite; on the other hand, a wide temperature range is necessary from 675° C. to about 780° C. for the CuO to shake itself loose gradually from the shattuckite structure. Therefore, the crystallization of tenorite is also a gradual process over this wide temperature range. The estimated obliterated exothermal peak of shattuckite is shown in Fig. 1A. The minor broad exothermal peak at 690° C. may be considered as a remainder of the obliterated true exothermal peak.

The true endothermal peak temperature. By projecting from the false endothermal peaks, one at 675° C. and the other at 774° C., the true endothermal peak temperature is estimated to be 740° C. Figure 1C shows the true endothermal peak. According to the dehydration curve, shattuckite loses 65% of its total water content by dehydration at 740° C. The loss of water at a dehydration endothermal peak temperature varies a great deal for different minerals. For instance, a goethite sample from Socorro, New Mexico, loses 87.6% of its water at its dehydration endothermal peak temperature of 395° C. A gypsum sample from Lake Lucero, New Mexico, loses 75% at its first endothermal peak temperature of 180° C., and loses all of its water at the second endothermal peak temperature of 215° C. A chrysocolla sample from Tyrone, New Mexico, loses 66.6% of its water at its dehydration endothermal peak temperature of 154° C. If the dehydration endothermal peak is strong and its range is narrow, the percentage of loss of water at the endothermal peak temperature is large; on the other hand, the percentage is small if the peak range is broad. Because shattuckite has a wide true endothermal peak range, the estimation of 65% loss of its water content at its endothermal peak temperature is reasonable. As interpolated from the dehydration curve, the loss of 65% of water occurs at 740° C. Therefore, the true endothermal peak temperature of dehydration is estimated to be 740° C.

The exothermal peak at 980° C. A sample fired to 950° C. contains tenorite, cryptocrystalline cuprite, and some cryptocrystalline α-quartz; the unknown phase that occurs in a sample fired to 800° C. disappears. A sample fired to 1,000° C. contains tenorite, cuprite, α-quartz, and α-cristobalite. One fired sample shows that the powder line 4.07 Å of α-cristobalite is darker than the powder line 4.29 Å of α-quartz, whereas the powder line 2.47 Å of cuprite is twice as dark as the powder line 2.54 Å of tenorite. The reverse is shown by another sample. Both samples were fired separately in the same cylindrical electric furnace. Thus, it appears that the decomposition of tenorite into cuprite may be accelerated by the crystallization of α-cristobalite, or vice versa.

The crystallization of α-cristobalite is an exothermal reaction. Alpha-cristobalite is formed in some clays fired to 1,000° C., such as montmorillonite from Chambers, Arizona (Bradley and Grim, 1951). The crystallization of α-cristobalite is usually indicated by a small but sharp exothermal peak at about 950° C. to 1,000° C. It seems likely that the exothermal peak at 980° C. in the DTA curve of shattuckite is caused by the crystallization of α-cristobalite.

Decomposition of tenorite into cuprite. The thermal curve begins to show a weak and gradual endothermal reaction at about 850° C. A sample fired to 900° C. contains a small amount of cryptocrystalline cuprite. The decomposition of tenorite into cuprite is a strong endothermal reaction. The weak and gradual endothermal reaction beginning at 850° C. represents only a gradual decomposition of a small amount of tenorite into cuprite. This decomposition increases rather vigorously above 995° C., the maximum temperature of the DTA. The thermal curve appears to show that the exothermal peak at 980° C. is followed closely by a strong endothermal reaction above 995° C. Heating was continued at 995° C. for a few minutes, and the thermal curve continued to show a strong endothermal reaction. Generally speaking, high temperature and low partial pressure of oxygen in the furnace will favor the decomposition of tenorite into cuprite.

The unknown phase. The unknown phase in shattuckite fired to 800° C. mentioned previously is represented by the following powder lines: 6.81 Å (2), 6.21 Å (2), 4.70 Å (3), 2.68 Å (1.5). The intensity of the tenorite powder line 2.53 Å is (10). These are not powder lines of paramelaconite ($Cu_2O \cdot 6CuO$); possibly they represent a copper silicate of some sort.

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