

## MINERALOGICAL NOTES

## THERMAL STABILITY OF AZURITE AND MALACHITE

DALE R. SIMPSON, RICHARD FISHER AND KARL LIBSCH,  
*Department of Geology, Lehigh University, Bethlehem, Penna.*

Although azurite and malachite are the two most common secondary copper minerals, there is no agreement among the reported decomposition temperatures for the minerals. This paper presents the results of experiments conducted to establish the temperature of decomposition of azurite and malachite at one atmosphere of air pressure.

In 1851 Rose reported that malachite began to decompose at 220° C. and after long heating had lost only 0.76 per cent weight. However, at 250° C. the weight loss was 2.16 per cent and at 300° C. it was 27.71 per cent. Rose further states that the weight loss of azurite is insignificant at 250° C. but at 300° C. it changed to copper oxide. Kelley and De Noyer (1960) report that malachite shows tan spots when heated in a micro-coil from 220 to 262° C. and that fragments of the mineral turn brown when heated to 325° C.<sup>+</sup> They also report that azurite becomes deep blue to black in the temperature range of 240° C. to 295° C. and that grains fuse, sinter, and turn black at 415° C.<sup>+</sup> They state that the reactions proved sluggish and were visible only at temperatures above published equilibrium values. Beck (1950b) reports that the decomposition of azurite begins at 350° C. and ends at 495° C., and that malachite begins to decompose at 315° C. and ends at 420° C. These values were established by DTA using an average heating rate greater than 10° C. per minute (Beck, 1950a).

The apparent temperature of decomposition of azurite and malachite from the Dixie mine, Utah, and reagent  $\text{CuCO}_3$  (very finely divided malachite) was established by thermo-gravimetric analysis using a heating rate of 1.25° C. per minute (Fig. 1). Azurite begins to decompose at about 300° C. and reaches a maximum rate of decomposition at 400° C. All of volatiles are lost below 500° C. Malachite shows some weight loss at 275° C.; however, the maximum rate of decomposition is not reached until 440° C. Decomposition of malachite continued to a temperature greater than 600° C. In contrast, finely divided malachite begins to lose weight at less than 100° C. and at 300° C. its weight loss is more than 5 times that of azurite or malachite. At 400° C. the decomposition is complete.

At a heating rate of 0.15° C. per minute, azurite and malachite are completely decomposed at a temperature under 450° C., and they show the maximum rate of weight loss at a temperature under 380° C. (Fig. 1). At

this slow heating rate the decomposition curve for azurite is similar to that for malachite; however, at the fast heating rate, malachite appears to be stable to a higher temperature than azurite.

With a heating rate of  $0.01^{\circ}\text{C.}$  per minute, malachite is completely decomposed at  $340^{\circ}\text{C.}$ , and very finely divided malachite is completely decomposed at  $240^{\circ}\text{C.}$  (Fig. 1). Decomposition of malachite reaches its maximum rate of  $280^{\circ}\text{C.}$  when heated at  $0.01^{\circ}\text{C.}$  per minute.

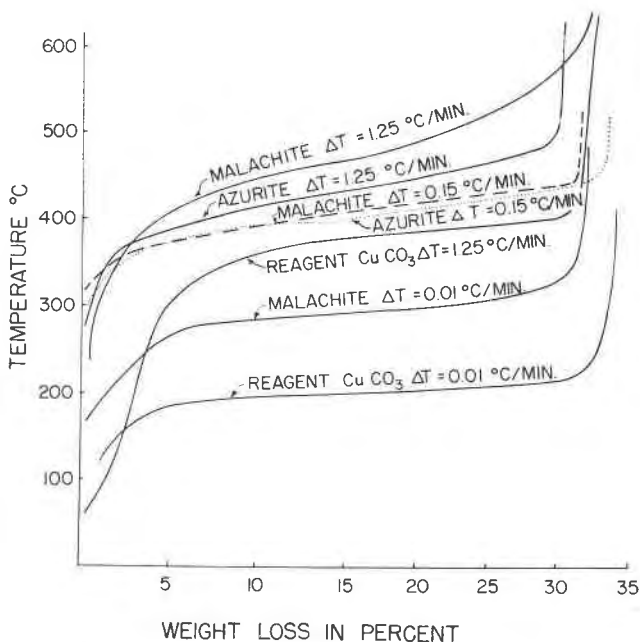


FIG. 1. Thermo-gravimetric analysis curves for malachite and azurite. Delta T indicates the heating rate.

A solid will decompose when the partial pressure of components of the solid becomes greater than the vapor pressure of the same components in the surrounding media. Because the vapor pressure of a solid is strongly temperature dependent, and because the rate of decomposition of a solid is dependent in part on the difference in vapor pressure of the solid and the surrounding media, an infinitely slow heating rate must be used if the true decomposition temperature of a solid is to be accurately determined.

When malachite is heated at 1.25, 0.15 and  $0.01^{\circ}\text{C.}$  per minute the maximum rate of weight loss begins at temperatures of 440, 375 and  $280^{\circ}\text{C.}$  respectively, and the log of these heating rates plotted against the temperatures gives a straight line (Fig. 2). This semi-log plot there-

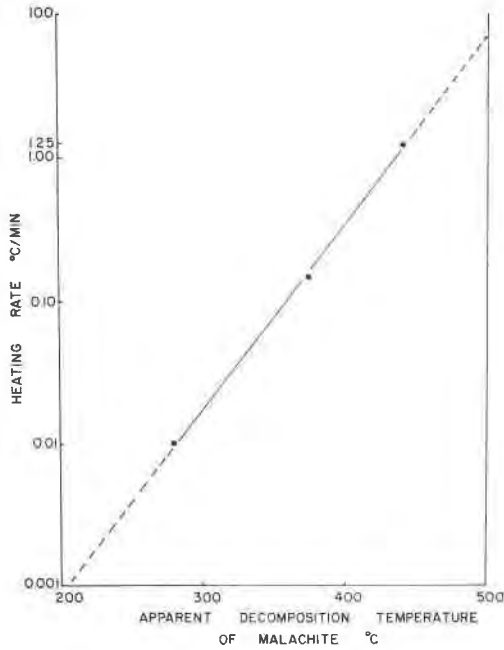


FIG. 2. Semi-log plot of heating rate vs. apparent decomposition temperature of malachite.

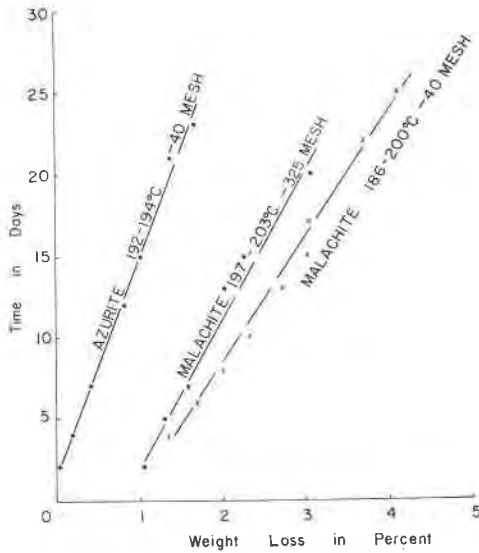


FIG. 3. Weight loss of azurite and malachite at about 200° C.

fore indicates the apparent temperature of decomposition of malachite with different heating rate, but it does not establish the minimum decomposition temperature of malachite. It does show, however, that if the decomposition of malachite is to be tested at, for example, 200° C., the heating rate can be no more than approximately 0.001° C. per minute.

To test whether decomposition of malachite proceeds at 200° C., samples were held at a constant temperature for 20 days. During this period of time there was more than 3 per cent weight loss with the products being CuO and malachite (Fig. 3). It would require about 200 days for the reaction to go to completion. Azurite was tested in a similar manner and found to decompose at 190° C. losing 2.76 per cent weight in 45 days. The temperature of decomposition of azurite and malachite is therefore less than 200° C.

In conclusion, the reported decomposition temperatures of azurite and malachite are largely explainable by the different heating rates used by the investigators. And further, the minimum possible heating rate should always be used for determinations of decomposition temperatures of any material.

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#### QUARTZ GLASS PRESSURE VESSELS FOR HYDROTHERMAL STUDIES

R. SPEED AND A. FILICE, *California Institute of Technology,  
Jet Propulsion Laboratory, Pasadena, California.*

#### INTRODUCTION

Sealed quartz glass tubes have proved useful as pressure vessels in low PT hydrothermal experiments in silica-saturated systems. These tubes provide an inexpensive means for making simultaneous runs along an