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THE EFFECTS OF THE CONTROLLABLE VARIABLES ON DIFFERENTIAL THERMAL ANALYSIS

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Differential thermal analyses are markedly influenced by variations in the heating rate, furnace atmosphere, composition and design of the sample holder, sample quantity, dilution ratio with inert material, degree of packing and particle size of the sample.

A slow heating rate is advantageous in producing peaks of greater definition as suggested by Stross and Abrams (1951), at lower temperatures, although the reaction intensity suffers reduction. These features are illustrated by Warne and Bayliss (1962) for the mineral cerussite. Arens (1951) shows that the recorded temperature is nearer the temperature at which the reaction occurs under equilibrium conditions, when measured in the sample rather than in the inert material, and this recorded temperature is less dependent on the heating rate.

A continually changing or dynamic furnace atmosphere produces sharper peaks on the differential thermal analysis curve for change in weight reactions. The reason is that a gaseous decomposition product is removed more rapidly in a dynamic atmosphere than in a static atmosphere, which causes an increase in the reaction rate.

The amount and availability of oxygen in the furnace atmosphere controls the oxidation rate. Thus the intensity of the oxidation reaction decreases with progressive reduction of the available oxygen as the furnace atmosphere is changed, for example from oxygen to air and then to nitrogen.

Each constituent gas in the furnace atmosphere exerts a partial pressure upon the solid sample under analysis. An increase in the partial pressure of a particular gas causes a shift to the left in the equation of any reaction which liberates this gas from the sample. Thus the peak occurs at a higher temperature, which in turn significantly increases the reaction intensity as shown by the curves for magnesite and calcite in carbon dioxide by Rowland and Lewis (1951). Similarly this partial pressure effect is observed with oxygen and water vapor atmospheres, on reduction and water evolution reactions respectively.

Curves obtained from traditional differential thermal analyses, (in which samples decompose in a static air furnace atmosphere), are difficult to interpret for the following reasons.

- (1) A static atmosphere inhibits to some extent the production of clearly defined peaks as the gaseous decomposition products disperse slowly.

- (2) The oxygen content of the air is usually not sufficient to ensure that any oxidation reaction occurs immediately and continues to completion.
- (3) The partial pressures exerted by the oxygen and carbon dioxide contents cause minor distortions to the portions of the curve representing reduction and carbonate decomposition reactions.

It is therefore considered that a "standard" differential thermal curve is best produced either in a dynamic atmosphere of an inert gas such as nitrogen, or in a vacuum. Comparison of the standard curve with those obtained in other atmospheres will produce further data. For example oxygen, carbon dioxide and water vapor atmospheres will give additional information on oxidation, carbonate decomposition and water evolution reactions respectively.

A sample holder of low thermal conductivity such as alundum gives differential thermal analysis curves with endothermic peaks of greater definition (Arens 1951) and intensity with lower peak temperatures (Gérard-Hirne and Lamy 1951), and exothermic peaks of poorer definition and greater intensity with higher peak temperatures, than do holders of high thermal conductivity such as nickel. Since most differential thermal analysis reactions are endothermic, a sample holder of low thermal conductivity is generally the most suitable.

A sample holder cover induces an internal static atmosphere, and hence the deleterious effects mentioned above.

A sample holder having circular holes with rounded bottoms as suggested by Lehmann *et al.* (1954) provides the nearest approach to a spherical arrangement so that the thermal effects from all parts of the sample arrive "in phase" at the centrally situated thermocouple junction. Therefore only one dimension, the radius, is variable to control the quantity of sample.

A larger sample increases both the intensity of reactions and the temperature at which they occur; but decreases the peak definition because the sample approaches reaction equilibrium more slowly due to the necessity for the heat to traverse a longer distance to the central thermocouple through the sample. In a fluidised bed differential thermal analysis, this time lag does not occur (Basden 1960).

Sample dilution with calcined alumina decreases the intensity and peak temperature of the reactions but the peak definition is not increased. This dilution technique is useful for comparing a sample which only contains a small percentage of a given mineral, and for obtaining an "on scale" curve of substances exhibiting high reaction intensities. In addition, dilution gives some protection to the thermocouple from the deleterious effects of the sample. Examples of sample dilution are given for siderite by Rowland and Jonas (1949) and for calcite by Kulp, Kent and Kerr (1951).

Tight packing increases the intensity and temperature of a reaction but decreases the peak definition. Loose packing obtained by gently tapping the side of the container as suggested by Clegg (1955), gives reproducible results. By altering the degree of packing of the inert material relative to the sample, the difference in heat conductivity between them can usually be eliminated, and so reduces to a minimum the undesirable effect of a curved baseline.

Uniform sizing of the sample improves the peak definition for each change in weight reaction, since the reaction is accelerated due to the more rapid diffusion of gases through the sample.

The particle size should be chosen to give the highest rate of reaction. This is a compromise between large particles which aid the reaction by the more rapid diffusion of gaseous products from the sample, and small particles which possess a greater surface area on which the reaction may occur. Large particles are reduced to the optimum size by crushing while as smaller particles cannot be enlarged to this size they may be removed. Inversion type reactions are not affected by these factors (Arens 1951).

The variables of heating rate, quantity and particle size of sample are not independent and should be adjusted for each mineral to give the best peak definition whilst still retaining a reasonable reaction intensity. An example is given for cerussite by Warne and Bayliss (1961), who found that a heating rate of 2° C. per minute with a half cubic centimeter sample of a 200 micron particle size gave excellent peak definition with sufficient reaction intensity. A method for increasing the reaction intensity without affecting the definition or temperature of the peaks is to use multiple thermocouples as suggested by Lodding and Strum (1957).

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PARAMELACONITE AND ASSOCIATED MINERALS FROM THE ALGOMAH MINE, ONTONAGON COUNTY, MICHIGAN

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Since the first description of paramelaconite from the Copper Queen mine, Bisbee, Arizona, by Koenig in 1891, only two specimens have been known to exist. During the present study a third specimen from the type locality, donated by Koenig to the A. E. Seaman Museum at the Michigan College of Mining and Technology, was found and used for purposes of comparison. The specimen is a small, superb group of crystals associated with connellite and malachite.

Several other specimens were found in the museum with the locality given as the Algomah mine, Ontonagon County, Michigan. Examination of these specimens revealed that all contain paramelaconite crystals, some reaching a length of eight mm. The crystals are rough and pitted and of pseudocubical habit, although a few individuals are pseudo-octahedral. A few cavernous crystals were found which contained small, highly perfect paramelaconite crystals in parallel orientation with the outer individual. Four of these crystals were examined on the goniometer and the following forms noted: {001}, {010}, {110}, {013}, {011}, {113} and {112}. All of these forms but {001}, {010} and {011} are new for the species. Two crystals exhibited {013} and {113} together and {110} and {112} were found once, on each of the other two crystals respectively. The appearance of all of these four crystals resembles the habit illustrated by Frondel (1941). The specific gravity of this material is 6.11 (average of four determinations on the microbalance).

The crystals occur in thin seams which are coated with poorly crystallized malachite and scattered small diopside prisms. The matrix of the specimens contains small blebs of cuprite which are ringed by tenorite and then chrysocolla. Blades of atacamite may be found embedded in the chrysocolla. Veinlets of granular paramelaconite transect all of the minerals in these blebs. Diopside is earlier than the paramelaconite but malachite is later; crystals of malachite commonly line skeletal paramelaconite crystals.

Professor K. Spiroff of the Department of Geology loaned the writer several specimens from the departmental collection which were obtained