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IMPROVEMENTS AND COMMENTS ON THE METHOD OF "QUANTITATIVE ESTIMATION OF MAGNESITE BY DIFFERENTIAL THERMAL ANALYSIS"

S. St. J. WARNE

Department of Geology, The University of Newcastle, N. S. W. 2308, Australia

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The evaluation of magnesite contents in mixtures with other minerals is much improved by variable atmosphere DTA, using flowing CO_2 gas. Greatly increased identification accuracy and detection limits result.

Whilst in no way wishing to question the general findings of the paper "Quantitative Estimation of Magnesite by Differential Thermal Analysis" by Jehan *et al.* [1], it now appears that variable atmosphere DTA using flowing CO_2 gas, instead of air, yields improved curves for the evaluation of magnesite contents.

Although a detailed study applying this technique to the detection of carbonates in Entisols has been published [2], it is felt that additional documentation of the advantages to magnesites would be of considerable value in other fields of applied mineralogy.

Details of the equipment and experimental conditions used herein were as published previously [3] whilst a 2 l min^{-1} CO_2 flow rate was maintained over one gram samples.

Follow-up work, using the Bolton and Du Pont DTA units described [2, 4], gave similar results from 250 and 50 mg samples respectively, using 100 ml min^{-1} CO_2 flow rates, i.e. detection limits of approximately 0.25% from samples diluted with calcined alumina.

In flowing CO_2 the endothermic decomposition peak of magnesite becomes narrower, and more sharply defined with increased peak height. Furthermore, the complete peak moves up-scale to occur at a considerably higher temperature (Fig. 1. cf. curves a and b with c and d). The actual amount of this peak displacement and attenuation is dependent upon the partial pressure of CO_2 in the furnace atmosphere. These features may be further increased if DTA is carried out under greater (above ambient) CO_2 pressures, if further accuracy is required.

Jehan *et al.* [1] record (without comment) that content evaluations of magnesite are spuriously low in the presence of organic matter.

Various types of organic matter, e.g. in peat, coal, oil shales, soils and phytoclasts, when determined *in air* show large *exothermic* DTA effects in the range 400 to 700° [5–10]. In this range lies the diagnostic *endotherm* of magnesite (cf. curves a and b, Fig. 2). The superposition of these opposed thermal effects is negating, with the resultant magnesite peak being smaller than expected and its content evaluation is low. Similar determinations in flowing N_2 [3] or CO_2 [11] result in the almost complete suppression of the exothermic effects of moderate contents of organic matter, to yield a virtually featureless curve (Fig. 2, curve c).

Thus DTA in flowing CO_2 has the additional advantage of suppressing these deleterious oxidation effects so that the magnesite peak appears (a) without interference, (b) with its true size and (c) with greater peak resolution and height. Even with high proportions of organic matter magnesite is still clearly detected (Fig. 2, curves d and e).

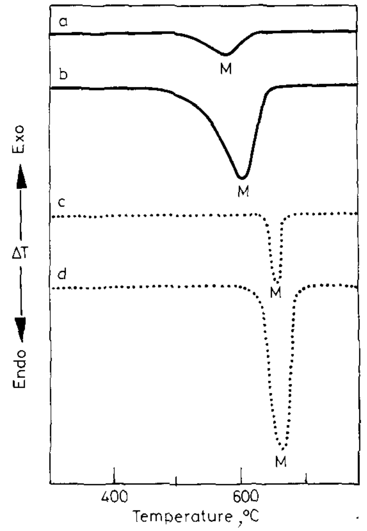

Fig. 1. DTA curves of artificial mixtures of the following compositions. Curves a and c, 2% magnesite with 98% Al_2O_3 and curves b and c, 10% magnesite with 90% Al_2O_3. ——— samples determined in air; .... samples determined in flowing CO_2. Magnesite peaks are marked M

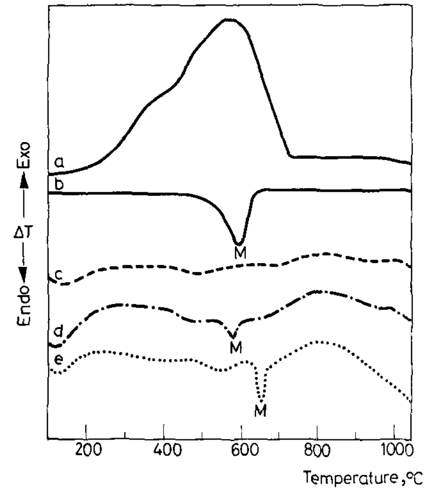

Fig. 2. DTA curves of artificial mixtures of a — 10% coal with 90% Al_2O_3; b — 10% magnesite with 90% Al_2O_3; c — 50% coal with 50% Al_2O_3; and d and e — 2% magnesite with 98% coal. ——— samples determined in air, —·—·—·— samples determined in flowing N_2 and .... samples determined in flowing CO_2. Magnesite peaks are marked M

The methodological improvements described herein are equally applicable to the more accurate detection and evaluation of calcite or dolomite, present as major components or as minor impurities [12], and to smithsonite ($ZnCO_3$), siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$). For the latter two minerals it suppresses associated oxidation reactions so that the single endothermic decomposition peak results without modification. This again greatly improves the accuracy of content evaluation.

In the context of the original work [1] the validity of the substitution of quartz (SiO_2) for opal (SiO_2nH_2O) in mixtures with magnesite, is supported by independent work [3]. However, a potential problem will occur should this DTA technique be used in the inverse way, i.e. to evaluate the silica content of natural magnesites. This is pertinent because with modern equipment the presence of *quartz* may be detected from its $\alpha-\beta$ inversion peak for contents down to 1% [13, 14].

In *air* the endothermic peak for lower contents of magnesite occurs within the same temperature range as the 573° endothermic $\alpha-\beta$ inversion peak of quartz. Here peak superposition occurs and the smaller quartz peak may be completely masked on the heating curve and the magnesite peak is a little enlarged. However, as the decomposition reaction of magnesite is not reversible, but β to α quartz is, the cooling curve will show only an exothermic peak for quartz and hence establish its presence.

By contrast, in *flowing CO_2* quartz may be detected from the heating curve because the up scale movement of the magnesite peak separates it completely from the $\alpha-\beta$ quartz peak which remains at 573°. (Crystallographic inversions are unaffected by changes in furnace atmosphere.)

The form of the SiO_2 is however critical, as the size of the $\alpha-\beta$ inversion peak for identical amounts of agate or chalcedony is much smaller than for quartz, and non-existent for opal. Thus opal will be missed and agate or chalcedony considerably under-estimated by the DTA method, regardless of atmosphere type.

Finally, "Proben-Abhängigkeit" curves (curves of sample amount dependence) as put forward by Smykatz-Kloss [15] cannot be used with the flowing CO_2 method, because, due to the much higher and constant partial pressure of CO_2, the magnesite peak temperatures are influenced very little by the amount of magnesite present in the samples.

It is concluded that magnesite DTA in flowing CO_2 results in peak; attenuation, correct size, up-scale movement and increased detection limits. In air the thermal effects of organic matter, being opposed to those of magnesite, are negating and result in reduced magnesite peak size. Quartz may be missed on the heating curve but shows clearly on the cooling curve, while the forms in which the SiO_2 minerals are present result in content evaluation variations.

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