

4. Microcrystalline quartz, and magnetite textures and crystallite sizes indicate rapid cooling and growth by multiple nucleation.

5. This serpentinized ultramafic contains sufficient Mg, Fe, Cr, and Al to have been the source of the magnetite.

These points indicate that the glassy appearing magnetite originated from pre-existing iron-magnesium silicates by alteration and remobilization of a serpentinized ultramafic along the contact of a quartz pegmatite intrusion. Crystallization was rapid, producing microcrystalline quartz, crystallites of magnetite as small as a few thousand angstroms, and possibly a magnetite glass phase. The magnetite represents a complete recrystallization rather than simply alteration of a pre-existing spinel. Silicification by granitic pegmatite intrusion may be genetically related to similar granitic intrusives in this region commonly spatially associated with serpentinized ultramafics.

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DIFFERENTIAL THERMAL ANALYSIS OF EVAPORITES

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In view of the recent interest shown by petroleum geologists in the thermal history of evaporite minerals, a new development in the application of differential thermal analysis (D.T.A.) to this group may be of interest. Improved D.T.A. technique has made possible the analysis of minerals containing corrosive sulfur and arsenic (Kopp and Kerr, 1957, 1958) formerly beyond the scope of the method. More recently several evaporite minerals have been analyzed which contain elements of the halogen family, and the borate and nitrate radicals.

Difficulties ordinarily encountered in applying D.T.A. to a number of these minerals include the fluxing action of the molten material upon the metal thermocouples, corrosive gases released at some stage during the heating process, and the difficulty of sample removal upon cooling. Minerals for which difficulties have been reported include: cryolite,

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atacamite, borax, nitre, gypsum, polyhalite and others. Current procedure appears to consist of heating the mineral to a point somewhat below its melting point with no attempt to determine reactions above this temperature. For example, Kauffman and Dilling (1950) illustrate a differential thermal curve for cryolite and state, "The curve for cryolite shows the endothermic peak at 570° C. representing the change to the isometric modification. This reaction is reversible. The heating of this sample was stopped before the melting point was reached." Allen (1957), who analyzed thirteen borate minerals states, "Preliminary investigations confirmed these views and showed the inadvisability of heating borate minerals to temperatures approaching 1000° C." To avoid these difficulties runs were terminated at temperatures of 650° C. or less.

Apparatus previously described (Kopp and Kerr, 1957) involves protecting the metal head and thermocouples of the equipment with concentric alundum cylinders. This technique with some modification has been found suitable for examining evaporite minerals. Early in this investigation it became apparent that molten minerals would often percolate through the relatively coarse alumina filler and pass into the space between the inner alundum cylinder and the thermal head itself. This tended to contaminate the apparatus and made sample removal difficult. It was found necessary to prepare an impermeable base for the sample well.

This was done by placing the inner and outer alundum cylinders on a

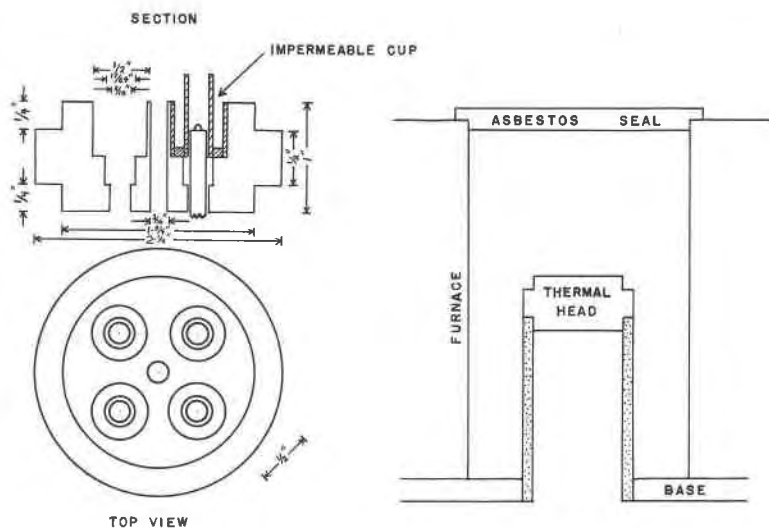


FIG. 1. Modified D.T.A. equipment for the analysis of evaporites.

suitable holder and pouring a base of alundum cement about $\frac{1}{8}$ inch thick. When dry, these cups are fired to 1000° C., hence they undergo no thermal reactions during the heating process. The cups are tested with water to be certain that they are completely sealed. Similar cups are used for both the sample and standard wells to avoid differences in heat flow characteristics. It is possible to salvage the sample cup if the reaction product is soluble, but ordinarily it is discarded after use. The apparatus is illustrated in Fig. 1.

Mineral samples were selected from the mineral collection at Columbia University and include halite, cryolite, borax, kernite, nitre, soda nitre, colemanite and sylvite. The samples were crushed and sieved and that portion passing a No. 100 sieve, but caught on a No. 120 sieve was analyzed. Samples were mixed with No. 60 alumina and tamped in the space between the inner and outer alundum cylinders. A heating rate from 12–14° C. per minute was employed. A preamplifier was used to amplify the curves 10X. Sample data are listed in Table 1 and the thermal curves obtained are presented in Fig. 2.

DISCUSSION

The reaction products obtained during the analysis have not as yet been studied. However, in the light of melting point data and the investigations of other workers, it is possible to briefly describe the nature of the reactions observed for each sample. It should be noted that the possibility of reaction between the molten material and the alumina filler exists, and that these reactions would be recorded in the D.T.A. curve. However, this does not eliminate the utility of the method since these reactions would be related to the composition of the mineral involved.

Halite—Only one reaction at 810° C. (endothermic) was observed for halite. This corresponds closely to the melting point given for pure NaCl (804° C.).

Cryolite—Two endothermic reactions at 565° C. and 972° C. respectively are noted in the curve for cryolite. The first corresponds to the inversion from monoclinic to isometric (570° C. according to Kauffman and Dilling, 1950). The second represents the melting point (about 1000° C.) and may also be related to the attack of the molten material upon the alumina present.

Borax—The borax used in this run has probably been converted to tinalconite by dehydration. Peaks are observed at 158° C., 343° C., 609° C. and 642° C. According to Allen (1957) tinalconite exhibits an endothermic peak at 160° C. The nature of the other peaks has not been determined.

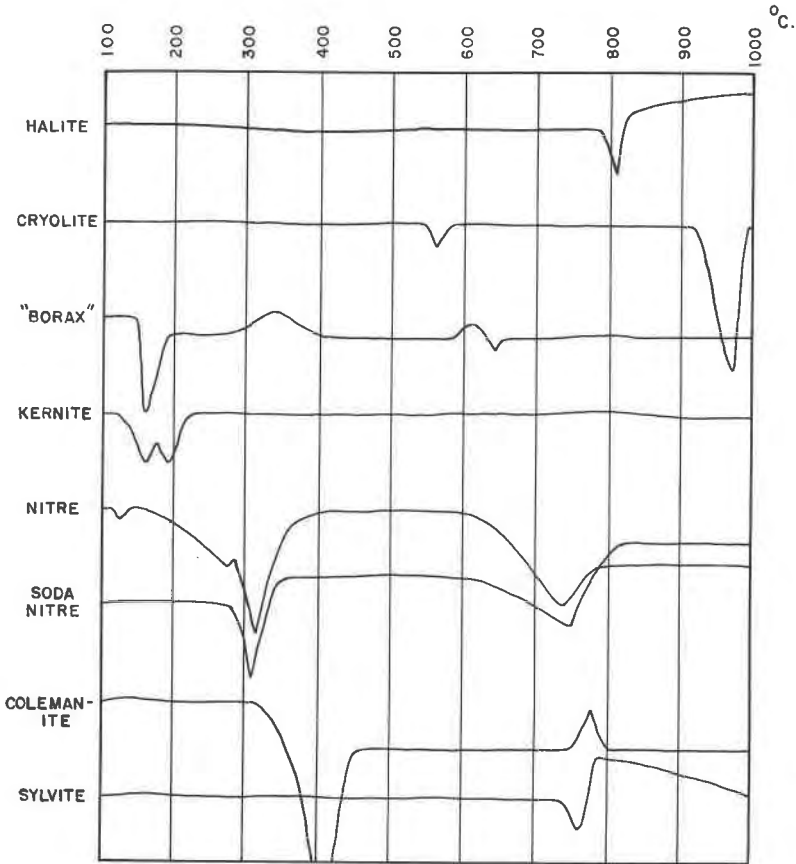


FIG. 2. D.T.A. curves for selected evaporite minerals.

Kernite—Two endothermic peaks, at 160° C. and 188° C. are observed. The endothermic peak temperature noted by Allen (1957) for kernite is 185° C. The peak at 160° C. probably reflects the presence of some tinalconite which may result from partial hydration of the kernite.

Nitre—The first endothermic reaction at 125° C. corresponds closely to the inversion temperature (129° C.) determined for nitre. The endothermic peak at 315° C. may represent the melting point (given as 334° C. in the Handbook of Chemistry and Physics, 35th edition). The other peaks are uncertain and the sample may be impure.

Soda Nitre—The initial endothermic peak at 308° C. agrees with the melting point of pure material which is also 308° C. The final endothermic peak at 754° C. is similar to the endothermic reaction recorded for nitre

TABLE 1. SAMPLE DATA

Mineral	Melting Temp. ° C. ¹	Locality	Weight (mg.)	Peaks (° C. ± 3° C.)
Halite NaCl	804	Minas de Zipaquira, Colombia, S. A.	50	810 ↓
Cryolite Na ₃ AlF ₆	~1000	Iviglut, Greenland	100	565 ↓ 972 ↓
Borax ² Na ₂ B ₄ O ₇ · 10H ₂ O	75	Tibet, China	50	158 ↓ 343 ↑ 609 ↑ 642 ↓
Kernite Na ₂ B ₄ O ₇ · 4H ₂ O	—	Kern Co., California	50	160 ↓ 188 ↓
Nitre KNO ₃	129 ³	Humboldt, Nevada	100	125 ↓ 275 ↓ 288 ↑ ? 315 ↓ 733 ↓
Soda Nitre NaNO ₃	308	Tarapaca, Chile	100	308 ↓ 754 ↓
Colemanite Ca ₂ B ₆ O ₁₁ · 5H ₂ O	decomp.	Mojave area, Cali- fornia	100	410 ↓ 782 ↑
Sylvite KCl	776	Kalusz, Poland	100	763 ↓

↓ Endothermic; ↑ Exothermic; (?) May result from the overlap of two consecutive peaks in the same direction.

¹ Melting point data obtained from International Critical Tables of Numerical Data, Physics, Chemistry and Technology, Vol. I, 1926.

² Probably tinalconite (Na₂B₄O₇ · 5H₂O); see discussion.

³ Inversion temperature (orthorhombic to trigonal).

at 733° C. While the nature of these peaks is uncertain they may represent the decomposition of the molten material or its boiling point.

Colemanite—Two reactions, one at 410° C. (endothermic), and a second at 782° C. (exothermic) are noted. Allen (1957) reports a peak temperature between 370–375° C. for colemanite from Death Valley, California. The value obtained for this sample shows the greatest divergence from reported values. The reactions are uncertain, but the initial endothermic reaction may represent the melting point of the mineral.

Sylvite—The melting point recorded at 763° C. is slightly lower than the melting point for the pure compound (776° C.) and may indicate that the mineral is not pure KCl.

CONCLUSION

It appears possible through the use of the method described to extend the observable D.T.A. range beyond the melting point of a mineral without encountering the difficulties noted for analyses made with unprotected thermocouples. This offers the possibility of widespread application of the D.T.A. method to a considerable group of minerals not previously amenable to the method. The few analyses mentioned constitute a small sample of the applications which are conceivable.

REFERENCES

- ALLEN, ROBERT D., 1957, "Differential Thermal Analysis of Selected Borate Minerals," *Geol. Surv. Bull.* **1036-K**.
- KAUFFMAN, A. J., JR. AND DILLING, E. D., 1950, "Differential Thermal Curves of Certain Hydrated and Anhydrous Minerals, With a Description of the Apparatus Used," *Econ. Geol.*, **45**, 222-244.
- KOPP, O. C. AND KERR, P. F., 1957, "Differential Thermal Analysis of Sulfides and Arsenides," *Am. Mineral.*, **42**, 445-454.
- , 1958, "Differential Thermal Analysis of Sphalerite," *Am. Mineral.*, **43**, 732-748.
- , 1958, "Differential Thermal Analysis of Pyrite and Marcasite," *Am. Mineral.*, **43**, 1079-1097.

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REFINEMENT OF THE CRYSTAL STRUCTURE OF DOLOMITE*

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The mineral dolomite was one of the early substances to be investigated by x-ray diffraction methods (Wyckoff and Merwin, 1924). Dolomite, $\text{CaMg}(\text{CO}_3)_2$, was considered by some to be a solid solution of the simple carbonates calcite and magnesite and by others as a definite compound, distinct from the two simpler carbonates. This early investigation established, with the use of Laue photographs, that the symmetry of the atomic arrangement of dolomite was lower than that of calcite and, therefore, it was a distinct chemical compound. It also established the unit cell dimensions and showed that four atomic parameters needed to be evaluated to determine the structure. At that time no attempt was made to determine the exact positions of the atoms of the carbonate group. The atomic parameters of dolomite were not investigated until Bradley *et al.* (1953) determined the four necessary parameters from powder data. Because the dolomite structure is of such importance in

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