Differential reaction analysis (DRA)—a technique for obtaining differential thermal analysis data from inert substances

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Abstract

Many substances, including some common minerals, do not undergo thermal reactions of sufficient magnitude to provide useful differential thermal analyis data. The purpose of this study was to consider possible new techniques by which differential thermal data could be obtained from such relatively inert substances. The technique explored was to react two substances (the non-reactive material with some chemical agent) and to determine the thermal effects that occur as the mixture is heated. Several reactants were considered including alkali hydroxides, carbonates, and fluorides, microcosmic salt, V_2O_5, and Li_2WO_4. Of the reactants considered, Li_2WO_4 was found to be most satisfactory. Heating curves were obtained using heating rates of approximately 14°C per minute. Cooling curves were obtained by turning off the furnace power and the cooling rates were nonlinear.

Eight silicate minerals, wollastonite, grossular, bytownite, albite, microcline, enstatite, olivine, and zircon were studied. Differential curves for wollastonite, grossular, bytownite, albite, and microcline showed detectable reactions and characteristic differences. The reaction temperatures for enstatite, olivine, and zircon were apparently too high for the furnaces used (1000°C limit) to detect any reactions. X-ray and optical examination revealed the presence of $CaWO_4$, Na_2WO_4, and $LiAlSiO_4$ in the reaction end products. It was concluded that this method is feasible and if further developed might broaden the scope of presently existing differential thermal techniques. It is proposed that this method be called differential reaction analysis (DRA).

Introduction

Differential thermal analysis (DTA) is one of the most widely used of the thermal techniques and, at present, is probably the most useful thermoanalytical method. In this technique, the sample temperature is continuously compared with the temperature of a reference material, such as alundum (Al_2O_3) or quartz (SiO_2), and the temperature difference is recorded as a function of furnace temperature or time.

Differential thermal analysis techniques have generally been applied to substances which have transitions involving sufficiently large ΔH and rapid reaction rates (i.e., kinetics) to be detected and recorded. The purpose of this study was to investigate a possible technique by which DTA data can be obtained from substances which have kinetics sufficiently slow or which do not have any transitions below the melting point and therefore appear "inert" in a routine DTA experiment. The method considered here involves the reaction of two substances (the non-reac-

tive, "inert" material plus some chemical reagent) and the measurement of any thermal effects that may occur as the mixture is heated and cooled. This technique, in effect, consists of making and studying thermal reactions in (pseudo-) binary systems. We propose that this method be called differential reaction analysis (DRA) to distinguish the resulting data from those obtained by ordinary DTA. [A reviewer of this paper brought to our attention an article by Ramachandran and Sereda (1971) which describes a technique for the indirect determination of some calcium compounds in cement. In this technique, $AgNO_3$ is reacted with the phases, and the amount of unreacted $AgNO_3$ is determined by DTA. However, the technique and its applicability to "inert" substances appear to be quite different from the technique described here.]

The present study involves the investigation of reactions which occurred in effectively closed systems. Although the "characteristic temperature" (Murray and Fisher, 1951) would be the best parameter by

which to study DRA curves, it was found to be difficult to determine with any degree of precision because of amplifier noise as well as the small chart recorder used. Therefore, the peak temperature (at maximum displacement from the baseline) was determined. It is realized that this latter temperature has no real significance for the systems studied; however, it was felt that the peak temperatures would suffice for this preliminary investigation. In the future, it might be desirable to determine and report characteristic temperatures for DRA, since in many respects this method of analysis involves the determination of eutectic temperatures, peritectic temperatures, etc.

Experimental method

Equipment

The techniques involved in DRA are basically the same as those of DTA with respect to instrumentation and results. The instrument used in this investigation was modified from a DTA unit originally designed and assembled in this department by Kopp and Coker (1963). The furnaces could reach 1000°C. The reaction and temperature curves were recorded using a Yellow Springs Instrument Company Model 81 two-channel recorder. The differential signal was am-

FIG. 1. Schematic view of thermal head for DRA (temperature thermocouple not shown)

plified using a DC preamplifier (Keithley Instrument, Inc. Model 151R null detector-microvoltmeter).

The typical well-type thermal head could not be used for DRA because the sample holders must be cleaned or replaced after each run. Platinum cups were found to give most satisfactory results. The cups could be reused and were easy to clean. One cup housed both the temperature and reference thermocouples, and the third thermocouple was placed in the sample cup (Fig. 1). A protective platinum sleeve kept the thermocouple isolated from the reactive substances but was sensitive enough to detect thermal changes that occur in the cup. (In the present design the thermocouples had to enter from above, but the thermal head and cups could be designed so that the thermocouples enter from below. This would further protect thermocouples from accidental spillage and leakage of the reacting substances in the cup).

Quartz was used as a reference material in the standard cup because its peak at 573°C (α-β inversion) provided a built-in calibration point that could be used to correct for thermal lag in the system.

Factors affecting DRA curves

The factors that affect ordinary DTA curves will also affect DRA curves. The peak temperatures, general shape and direction of the curves, magnitudes of peaks, and peak areas are all dependent on the various instrumental and sample parameters such as sample holder material and geometry, amount of sample, packing density, etc. (Wendlandt, 1964). In addition, the following factors may also affect the reproducibility of DRA curves: (1) volatility of the reactive substance, (2) the previous thermal history of the reactive substance, and (3) sample homogeneity.

Criteria for the Selection of a Reactant

The selection of a reactant for the purpose of producing DRA curves was based on the following criteria: (1) It should react with the sample at a reasonable rate and produce detectable thermal change(s) with the material being studied. Unless detectable reactions occur between the sample and the reactant, DRA will not be possible. (2) Its melting and solidification points should be well within the instrumental limits. The melting point should be at least a few hundred degrees below the upper limit of the furnace used so that the molten reactant will have ample time to react with the sample. (3) The reactant should have sufficiently low volatility so that it does not leave the
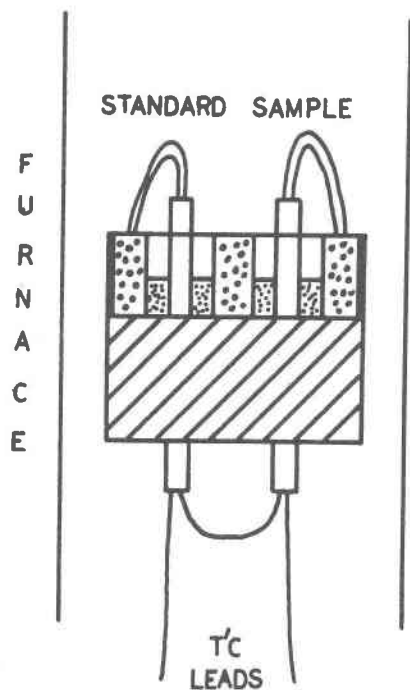
"scene of reaction" at higher temperatures when it is actually needed. (4) The reactant should have minimal thermal reactions of its own. A reactant that shows few reactions of its own keeps the resultant DRA curve simpler and easier to interpret. (5) It should be essentially non-reactive with sample cups. Chemicals that react with sample cups should be avoided since they may produce unwanted effects on the DRA curve and may damage the cups. (6) It should be easy to handle. The hygroscopic nature of some reagents causes problems in their handling. Reagents that are poisonous or require lengthy pretreatment should also be avoided. (7) Reactants that are readily available and are relatively inexpensive are preferable.

On the basis of these criteria several potential reactants were considered for this study, including some alkali hydroxides, microcosmic salt, some fluorides, lead oxide, lithium tungstate, vanadium pentoxide, etc. Some like NaOH and KOH are hygroscopic and too volatile at elevated temperatures; microcosmic salt showed too many reactions and also was rather volatile; PbO and the fluorides were not tried because of their poisonous nature and the relatively high melting point of PbO. Li_2WO_4 and V_2O_5 were found to be the best choices of the compounds originally considered, mainly due to their relatively low melting points, non-hygroscopic nature, ability to react with silicates, and availability. In this study, Li_2WO_4 was investigated as a reactant. (Since this preliminary study was completed some other potential reactants such as lithium tetraborate have come to our attention).

Procedure

A 50–50 mixture by weight of the sample and Li_2WO_4 was prepared using the 100–200 mesh size fraction for both. It was realized that for any given compound a different ratio of weight of mineral and reactant might give better results; however, in the interest of uniformity of results and ease of preparation a 1 : 1 ratio was selected. The total amount used in each run was 3 g. The mixture was homogenized with a Wig-L-Bug mixer for five minutes. The mixture was then transferred to the platinum sample cup which was lightly tapped to settle the powder. During the first melting the molten Li_2WO_4 and sample sank to the bottom of the cup where further reactions proceeded, so that the initial packing had a negligible effect on what followed. Typically the mixture was heated and cooled more than once. The maximum
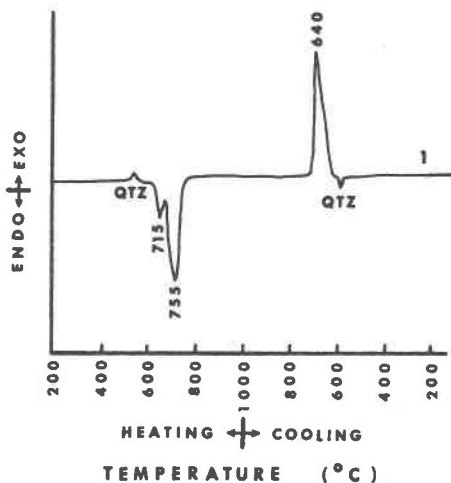

FIG. 2. DTA curve for Li_2WO_4

temperature reached during each run was 1000°C. Both the heating and cooling curves were recorded in order to see if there were any major differences between the subsequent DRA curves. If a reaction took place between Li_2WO_4 and the sample during the first heating, the nature of the sample would be changed and it would be expected to behave differently during subsequent heatings (and coolings) producing different DRA patterns. If no detectable reactions took place during the first heating, the later DRA curves would be expected to be similar to the first one. It should be noted that DRA curves (although they may change in appearance with subsequent heatings) are reproducible provided the experimental parameters are standardized.

Heating and cooling curves

The rate of heating used in this study averaged about 14°/minute and was essentially linear throughout the range up to 1000°C. The present apparatus contains no provision for controlled cooling, so cooling curves were obtained by turning off the power to the furnace. The cooling rates were non-linear but averaged about 20°/minute from 1000°C to 850°C, 10°/minute from 850°C to 600°C and 5°/minute from 600°C to 300°C. To reduce errors brought about by the placement of the sample and standard cups, thermocouples, etc., quartz was used as an internal standard so that a correction could be made for any thermal lags in the system. The quartz inversion takes place at approximately 575°C (actually at 573°C, but the small recording chart used can only be read to the nearest 5°C). If, on cooling, the quartz

TABLE 1. Summary of DRA data

	First		Second		Third	
	Heating	Cooling	Heating	Cooling	Heating	Cooling
Lithium Tungstate	715 ↓S 755 ↓V	640 ↑V				
Wollastonite	740 ↓L 980 ↓V	930 ↑V	980 ↓L	925 ↑V		
Grossular	765 ↓L 955 ↓V	845 ↑?	775 ↑L 935 ↓L	810 ↑M	775 ↑L 915 ↓L	810 ↑M
Albite	710 ↓L	450 ↑L*	535 ↓L*	475 ↑L		
Microcline	745 ↓L	(520,505) ↑L 465 ↑S	640 ↓L	(530,520) ↑L 470 ↑S		
Enstatite	750 ↓L	635 ↑V	750 ↓L	635 ↑V	750 ↓L	630 ↑V

*Actual temperature not corrected for thermal lag because quartz inversion missing or masked.

↑Exothermic;   ↓Endothermic

V – very large; L – large; M – medium; S – small; ? – Questionable

inversion peak appeared at 560°C, a correction of +15° was added to all the peak temperatures on the DRA curve. The peak temperatures reported here include this correction. The peak temperatures reported were not corrected by any other means, hence the temperatures cannot be considered very accurate.

FIG. 3. DRA curves for wollastonite–Li_2WO_4

Differential thermal curve for Li_2WO_4

Lithium tungstate has a rather simple DTA curve, with one small endothermic peak at about 715°C, and a larger endothermic peak on initial heating at about 755°C representing its melting point. One exothermic peak at about 640°C represents its solidification temperature (Fig. 2). [In the absence of a second solid phase (the "inert" substance being studied), most of the Li_2WO_4 volatilizes when heated to 1000°C; however, during the course of a typical run, the amount of Li_2WO_4 lost by volatilization is typically less than 5%.]

Results and discussion

DRA curves for selected silicate minerals

The specimens used in this study were obtained from the mineralogical collections of this department. They were examined by optical and X-ray diffraction methods for the presence of impurities. The microcline used was perthitic, and the grossular contained detectable diopside; the other specimens appeared to contain less than 2 or 3 percent total mineral impurities. The total iron contents (reported here as FeO) for enstatite (7.8%), olivine (7.7%), and grossular (2.9%) were determined by X-ray spectroscopy.

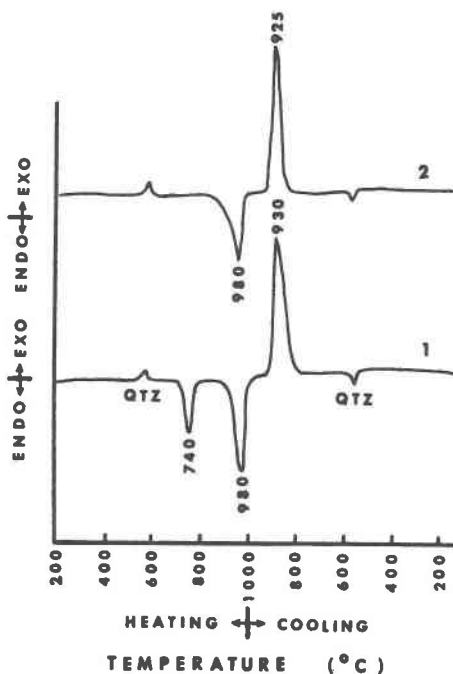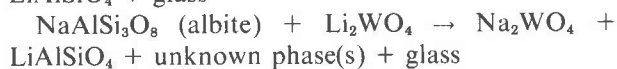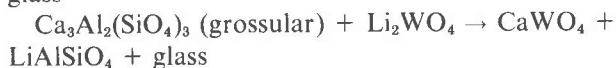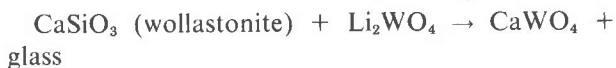The DRA data is summarized in Table 1, and sample DRA curves for wollastonite, grossular, albite

and (perthitic) microcline are shown in Figures 3 through 6. No reactions were detected for enstatite, olivine, or zircon. The absence of detectable reactions for these minerals does not mean that no usable DRA data can be determined for them. The temperature limit of the furnaces (1000°C) may be below the temperatures at which these minerals will react with molten Li_2WO_4.

Reaction products

The reaction products of each run were examined using optical and X-ray diffraction methods. Depending on the composition of the original mineral phase, one or more of the following new phases were detected in the reaction products: $CaWO_4$ (scheelite), Na_2WO_4, $LiAlSiO_4$, and glass. Some X-ray peaks could not be identified positively. In general, some unreacted mineral remained at the completion of the DRA analysis. Of the minerals studied, wollastonite reacted most thoroughly, while minerals like enstatite, olivine, and zircon appeared to be unreacted.

No attempt was made to determine the specific reactions that occurred or to attempt to construct any type of "phase diagram" to illustrate the nature of the reactions that took place. However, on the basis of X-ray data and optical examinations of the final products, the following reactions are suggested:

$CaSiO_3$ (wollastonite) + Li_2WO_4 → $CaWO_4$ + glass

$Ca_3Al_2(SiO_4)_3$ (grossular) + Li_2WO_4 → $CaWO_4$ + $LiAlSiO_4$ + glass

$NaAlSi_3O_8$ (albite) + Li_2WO_4 → Na_2WO_4 + $LiAlSiO_4$ + unknown phase(s) + glass

(It was not possible to identify any of the new phases formed by the reaction between perthitic microcline and Li_2WO_4 even though many known compounds of K, Al, Na, Si, Li, W and O were considered).

Possible applications of DRA

Initially, the basic application of DRA will probably be to obtain differential thermal data for "inert" minerals, although it should be noted that the technique need not be restricted to the study of "inert" substances since detectable reactions should occur with clays, carbonates, etc., as well as for wollastonite, feldspars, etc.

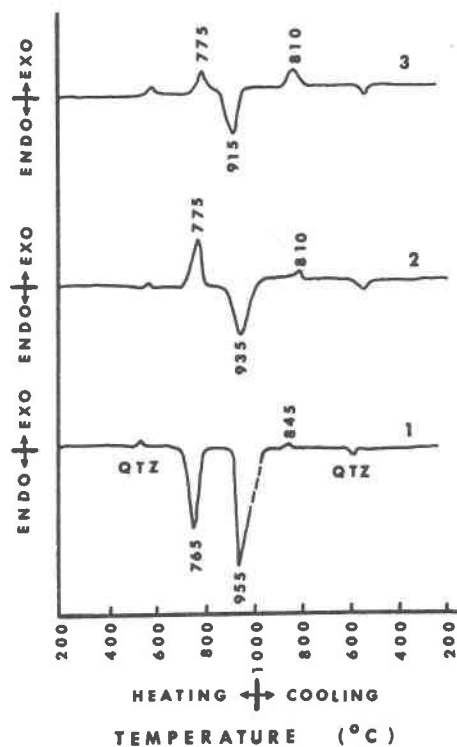The results of the analyses performed thus far suggest that DRA curves are strongly influenced by the

FIG. 4. DRA curves for grossular–Li_2WO_4

chemistry of the mineral-reactant melt. On this basis, it may be possible to rapidly distinguish different species of feldspars, pyroxenes, amphiboles, etc. In a similar manner, it may be possible to distinguish intermediate members of solid solution series.
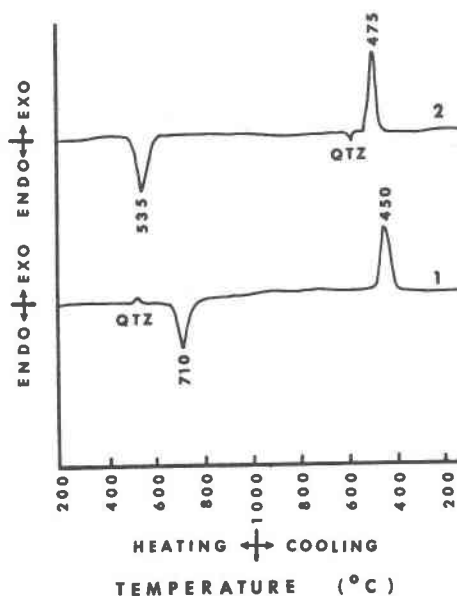
FIG. 5. DRA curves for albite–Li_2WO_4

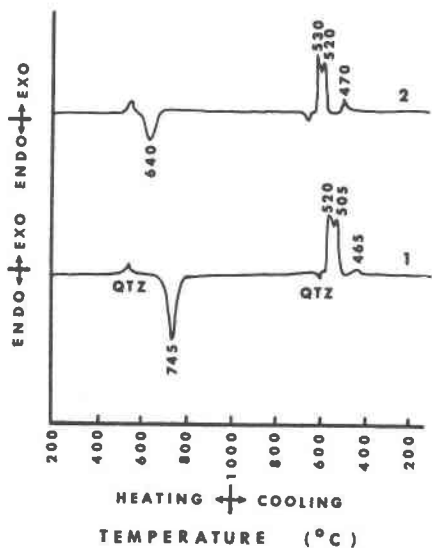FIG. 6. DRA curves for perthitic microcline–Li_2WO_4

Whether differences in crystalline structure will exert enough influence on the shape and/or temperatures of DRA curves to permit the distinction of polymorphs or polytypes must await future study.

Conclusions

This study was not intended to set any standards for qualitative or quantitative DRA for these or other minerals, but rather to demonstrate that it is possible to develop techniques for studying thermally "inert" substances using modified differential thermal methods. In fact, we strongly recommend that *no* attempt be made at this time to fix experimental parameters or to compile data for interlab comparisons. We hope to undertake a study of the effects of each of the important parameters of differential reaction analysis so that the most suitable experimental procedures can be established. This study will include investigation of a number of alternative reactants, the effect of sample: reactant ratio and blending, accurate determination of characteristic temperatures instead of peak temperatures, etc., as well as the effects of standard parameters such as heating rate, grain size, sample holder geometry, etc. We welcome the input and parallel effort of other workers in the field of differential thermal analysis.

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