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THERMAL ANALYSIS OF MINERALS

SHMUEL YARIV
Department of Inorganic and Analytical Chemistry
The Hebrew University of Jerusalem
Jerusalem 91 904, Israel

ABSTRACT

Presentations at the 9th ICTA Congress on thermal analysis of minerals other than clays, are reviewed. The paper stresses the contribution of new advanced technologies in traditional thermal analysis methods to the study of earth materials.

INTRODUCTION

From its beginnings thermal analysis has been applied to the study of geological materials [1, 2]. The pioneering DTA measurements of Le-Chatelier, who is considered to be the "father" of thermal analysis, were done on clay minerals. Since that time DTA and TGA have been widely applied as major tools for the identification and determination of various minerals. In the first half of this century earth scientists participated in the development of instruments and techniques for thermal analysis. Among the founders of ICTA there were also several prominent mineralogists and the number of earth and soil scientists who participated and contributed papers in the first ICTA Congress in 1965 was relatively high. With the development of X-ray and other spectroscopic techniques, the use of thermal analysis in earth sciences diminished and the number of presentations in this field in ICTA Congresses decreased from congress to congress. The ninth ICTA Congress seems to be a partial reverse of this trend. In this congress the section on geology, mineralogy and geochemistry (including organic geochemistry and fuels) was the largest of all the sections. In addition, there were some presentations in other sections which, in part, dealt with minerals. In this connection the paper of Stoch [3] on the relation between the structure and thermal reactions of inorganic solids should be mentioned. The paper describes topochemical and intraframework processes, thermal

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dissociations and framework rebuilding of various inorganic solids. It includes the description of a thermal transformation of quartz into cristobalite through an amorphous phase. As well as oral presentations, there were many poster presentations of earth materials and I must confess that the ninety minutes that were dedicated each day to the poster session were insufficient for dealing with the many posters on earth materials.

It appears that the revival of thermal analysis for earth materials is first of all due to the development of more advanced instruments and techniques. By reviewing contributions to ICTA 9, the present review shows how the application of new advanced technologies in traditional thermal analysis methods contributes to the study of earth materials. A more comprehensive review is needed to cover all recent developments. This will be done in a later stage. However, most modern trends which have been discussed in the literature since the 8th ICTA Congress, were presented at the 9th ICTA Congress. It should be noted that only those contributions which were published in the Conference Proceedings are covered here. Some passing remarks are made on the Congress Abstracts Book. Clay mineralogy is not covered here, as papers on clay minerals have been reviewed by Langier-Kuzniarowa in another paper included in the present issue [4].

EVOLVED GAS ANALYSIS (EGA)

The section on Earth Sciences started with an invited lecture by David Morgan reviewing earth science applications of EGA [5]. Determination of evolved volatiles is carried out alone or coupled with DTA or TGA. The most common volatiles evolved on heating geological materials are water, carbon dioxide and sulfur dioxide. Less common are oxygen, hydrogen or carbon monoxide. Evolved gases can be detected by non-dispersive infrared (NDIR) detectors [6] or by mass spectrometers (MS) [7, 8]. EGA was used for quantitative analysis of mineral mixtures. It has the potential for determining certain minerals well below XRD detection limits. This has implications for studies of oil-reservoir sandstones and argillaceous strata for low level radioactive waste disposal. It is possible to identify and determine amounts of calcite, magnesite and strontianite down to 50 ppm. An amount of 2% chrysotile was detected in a mixture containing brucite and calcite. Volatile evolution profiles were used for the study of organic rich clays. EGA was used for the study of decomposition processes of minerals containing many anion groups. This includes leadhillite, caledonite and Fe-bearing carbonate minerals. Further applications are characterization of volcanic ashes from different environments and the study of the kinetics of pyrolysis of oil shales.

EGA coupled with TGA, DTA and X-ray powder photography was employed by Morgan et. al. [9] for the study of thermal decomposition of manganite in different atmospheres. Three distinct weight loss regions were identified in the TGA curves below 900°C. The ratio between weight loss regions depends on the atmosphere and heating rate in which the reaction was carried out. The following reaction series took place in the presence of oxygen:

$4MnO.OH + O_2 \dashrightarrow 4MnO_2 + 2H_2O$

$4MnO_2 \dashrightarrow 2Mn_2O_3 + O_2$

$2Mn_2O_3 \dashrightarrow 4/3Mn_3O_4 + 2/3O_2$

With decreasing partial pressure of oxygen the thermal reaction was as follows:

$20MnO.OH + O_2 \dashrightarrow 4Mn_5O_8 + 10H_2O$

$4Mn_5O_8 \dashrightarrow 10Mn_2O_3 + O_2$

$10Mn_2O_3 \dashrightarrow 20/3Mn_3O_4 + 5/3O_2$

In the presence of inert gases, such as argon, nitrogen or carbon dioxide, the following reaction series took place:

$8MnO.OH + O_2 \dashrightarrow Mn_5O_8 + Mn_3O_4 + 4H_2O$

$Mn_5O_8 \dashrightarrow 5/2Mn_2O_3 + 1/4O_2$

$5/2Mn_2O_3 \dashrightarrow 5/3Mn_3O_4 + 5/12O_2$

Mn_3O_4 undergoes $\beta \rightarrow \tau$ transition at 1169°C and decomposes to MnO at 1450°C.

The combined DTA-EGA seems to have great potential for the study of adsorption mineralogy. At the 9th ICTA congress this method was applied in two papers. Shuali et al. [10] applied this technique for the study of the adsorption of D_2O by sepiolite and palygorskite. They proved that in the case of sepiolite, deuterium is trapped in the meta-sepiolite structure during the first stage of dehydroxylation. This deuterium is released as HDO during the recrystallization of the amorphous meta-sepiolite which accompanies the second dehydroxylation stage.

DTA was occasionally used for the study of adsorption of organic molecules by clay minerals. Although the DTA peaks were successfully used for defining the presence of different associations on the clay surface, in a previous review on this subject [11] the author wrote that sophisticated thermal methods and analysis of the combustion products are necessary in order to obtain a better understanding of the different peaks. In the 9th ICTA Congress Yariv et al. [12] showed from combined DTA-TGA-EGA that the oxidation of an organic dye adsorbed by montmorillonite or laponite is characterized by two or three exothermic peaks. The first peak is due to the oxidation of H atoms. The second and third peaks are mainly due to the oxidation of C and to some extent also N atoms. Montmorillonite retains the organic matter to higher temperatures than laponite.

THERMOLUMINESCENCE (TL)

Although TL was applied to the study of mineral crystals for many years, it is only recently that intensive research has been carried out. This research, apart from its importance in clarifying the dynamics of point defects, is used for archeological and geological dating. A comprehensive review on thermoluminescence research in the study of geological materials was published in 1983 [13]. A monograph on techniques and applications of thermoluminescence (including minerals) was published recently [14].

A paper by Calderon, Aguilar and Coy-Ill [15] describes the thermoluminescence (TL), photoluminescence (PHL) and radioluminescence (RL) of X-irradiated natural carbonates (calcite, aragonite, dolomite and smithsonite from several localities) related to their optical absorption and electron paramagnetic resonance (EPR) spectra. The UV spectrum of these minerals was affected by the X-irradiation. All carbonates showed complex TL peaks above RT, which could be related to changes in the UV spectrum. Intrinsic emission as well as Mn^{2+} impurities emission were identified among the TL peaks. Mn^{2+} impurities were identified by EPR. Their signal decreased after irradiation. EPR identified some paramagnetic centers such as CO_2^-, CO_3^- and CO_3^{3-} formed by self-trapped holes or electrons. The experimental results support a new model for the radiation damage and for the TL process in carbonates. It was suggested that the intrinsic emission is due to electron-hole recombination in the anionic sub-lattice. The origin of the TL peaks is the thermal liberation of quasi-self-trapped electrons from different traps that migrate to a luminescent impurity which has a trapped hole. The electrostatic attraction forces the CO_3^{3-} + M^{3+} recombination that can produce the intrinsic and impurity luminescence.

A paper dealing with the TL of albite and zircon was presented by Kirsh [16]. Kinetic analysis of TL is usually aimed at expressing the experimental curve as a superposition of several peaks. Each peak results from a single recombination process in which the depletion of a specific trap is involved. Using TL curves of albite and zircon, the author demonstrated that in TL kinetic analysis monochromatic curves are more useful and give more reliable information than the polychromatic glow curves.

DIFFERENTIAL SCANNING CALORIMETRY (DSC) AND DIFFERENTIAL THERMAL ANALYSIS (DTA)

These techniques are employed for the identification and determination of minerals and for the study of their thermal properties [17, 18]. DTA was employed as a tool in oil exploration and in environmental science [19, 20]. The progress made during the last years was mainly in the resolution of the various peaks and in relating the peaks to definite reactions. DTA was also applied in combination with other methods (mainly spectroscopic methods) to the study of thermal reactions occurring between mixtures of minerals, simulating natural environments or to the study of industrial systems. For example, DTA and high temperature X-ray diffraction methods were used for the study of the reactions between silicon dioxide and dolomite and between kaolinite and organic and inorganic alkali metal salts [21, 22].

Dubrawski and Warne [23] reported on the DSC of the dolomite-ankerite group recorded under flowing N_2, O_2 and CO_2. This group consists of a solid solution between the theoretical limits of $CaMg(CO_3)_2$ - $CaFe(CO_3)_2$ and contains increasing replacement of Mg by Fe. A DSC curve of dolomite in N_2 or CO_2 shows two endotherms. The low and high temperature peaks are associated with the $MgCO_3$ and $CaCO_3$ decomposition, respectively. Substitution by Fe causes further peaks to appear. A complex series of reactions occurs in N_2 in which $MgO.Fe_2O_3$ and $2CaO.Fe_2O_3$ are formed. Under nitrogen the resolution is not sufficient to enable calculation of the change in enthalpy which is associated with each single peak. Only the total change in enthalpy can be calculated from the total area of all the peaks. The total enthalpy change drops down with increasing Fe content. Best resolution of the DSC peaks is obtained under carbon dioxide. The low temperature peak results from the formation of FeO, MgO and $MgO.Fe_2O_3$. The second peak is due to a reaction of $CaCO_3$ with $MgO.Fe_2O_3$ to form $2CaO.Fe_2O_3$. In this case it is possible to measure the peak area and to calculate the change in enthalpy which is associated with each of the three peaks. In flowing oxygen the DSC curves of this series show less peaks than seen in nitrogen or carbon dioxide. The observed peaks shift to higher temperatures. FeO does not accumulate but is oxidized to Fe_2O_3.

Dunn, De and Fernandez [24] studied the effects of particle size, heating rate, oxygen concentration and total sample mass on the characteristics of the DTA and DSC curves of pyrite. A characteristic feature observed in a DTA or DSC curve of pyrite recorded in air is the appearance of several sharp peaks which precede the major exotherm. They have been attributed to oxygen starvation, preferential oxidation of some particles or periodic cracking of protective oxide coatings which expose fresh sulphide for reaction. The authors concluded that these small sharp peaks are due to the oxidation of the fine fraction. The number of these peaks increased with a decrease in the heating rate and in the sample mass or an increase in the partial pressure of oxygen.

Nathan, Panczer and Gross [25] describe thermal analysis of four rare phosphate minerals which had recently been found in Israel. These are strengite - $FePO_4.2H_2O$,
lipscombite - $Fe''Fe'''_2(PO_4)_2(OH)_2$,
cyrilovite - $NaFe'''_3(PO_4)_2(OH)_4.2H_2O$ and
goyazite - $(Ca,Sr)Al_3(PO_4)_2(OH)_5.H_2O$. They concluded that the thermal behaviour of hydrous aluminum phosphates is very similar to that of hydrous iron phosphates. Endothermic peaks at low and medium temperatures indicate loss of water of crystallization and hydroxyls, respectively. This results in a breakdown of the structure. An exothermic peak at 650-800°C is due to structural reordering which leads to the crystallization of α-$FePO_4$.

Shoval [26] applied thermal analysis together with X-ray and IR spectroscopoy to the study of mineralogical changes which occur upon heating natural marl rocks containing kaolinite, montmorillonite, illite and mixed layers, together with calcite or dolomite. This investigation was undertaken as part of an archeological study, in order to obtain a better understanding on the thermal reactions which occur during calcination and pottery formation. This study is expected to help in relating ancient potteries with their source material. The decomposition of the precursors (dehydration, dehydroxylation and evolution of CO_2) gives rise to endothermic peaks. The formation of new silicates gives rise to exothermic peaks.

Dobiejewska [27] showed that DTA can be applied to predict certain technological properties of quartz-clay moulding sands. These sands consist of quartz, clay minerals (kaolinite and montmorillonite) and water. The strength of moulding sands depends on the type of clay and on the water adsorption capacity. The information which can be obtained from the DTA study is water adsorption capacity, bonding properties and their thermal stability and the effect of certain additives (e.g. carbon) on the thermal behavior of the moulding sand.

THERMAL WEIGHT LOSS, THERMOGRAVIMETRY (TGA) AND DIFFERENTIAL THERMOGRAVIMETRY (DTG)

Measurements of dynamic or isothermal weight changes were carried out mainly as an auxilary tool in different studies. The appearance of commercial instruments which combine TGA with DTA, has in several cases suppressed the use of DTA.

Grinding of materials can induce dramatic changes in their texture, structure and chemical reactivity. Criado, Gonzales and Macias [28] studied the influence of grinding on the stability and thermal decomposition mechanism of siderite $(Fe_{0.7}Mg_{0.3})CO_3$. From X-ray diffraction and analytical results of the products as a function of grinding time it was concluded that a mechanochemical decomposition of the siderite takes place during the grinding yielding an amorphous product. The mechanochemical decomposition was described by the following equation:

$$(Fe_{0.7}Mg_{0.3})CO_3 \longrightarrow x/2\ Fe_3O_4 + 2x/3\ CO + (Fe_{0.7-x}Mg_{0.3})CO_{3-x}$$

The value of x increases with the grinding time. Thermal decomposition was studied by TG under vacuum. The original siderite decomposes under vacuum in a single step giving FeO and MgO as final products whereas two steps are observed in the thermal decomposition of the ground sample, the first one producing MgO and the second one MgO, FeO and Fe_2O_3. The peak temperature in the DTG curve shifts to lower temperatures with increase in the time of grinding. The authors concluded that the mechanical treatment of siderite leads to a redistribution of Mg and Fe ions yielding patches of magnesite dispersed in the lattice of substituted siderite. The effect of mechanochemical treatment on thermal properties of apatite was also studied [29].

Kaushansky and Yariv [30] using TG and DTG studied the effect of equilibrating calcite with different salt solutions on the thermal behaviour of this mineral. Topochemical substitution of Ca by the various cations may occur during equilibration, shifting the DTG decarboxylation peak of the calcite to lower temperatures. From the relation between the DTG peak temperature and the concentration of the "foreign" cation in the calcite, they concluded that topochemical substitution of Ca by smaller cations such as Mg or Zn occurs during the equilibration. Sr and Ba have larger radii than Ca and their carbonate salts crystallize with the aragonite structure. The DTG showed that equilibrating calcite with $BaCl_2$ results in the precipitation of witherite. In the case of Sr it seems that this cation is specifically adsorbed by calcite.

Wieczorek-Ciurowa, Kokkonen and Lajunen [31] studied the reaction between limestone or calcined limestone and sulfur dioxide. This interaction results in the sulfation of the limestone. Weight measurements were carried out under dynamic heating conditions and then isothermally at 827°C. The TG curves showed a complex adsorption reaction with different regions characteristic for complex reactions. Reaction rates are governed by chemical and physical factors.

Ullibari, Barriga and Cornejo [32] reported on the kinetics of thermal dehydration of a synthetic anionic clay-like mineral, hydrotalcite, $Mg_6Al_2(OH)_{16}CO_3.4H_2O$. The basis for this mineral is a brucite layer. If Mg^{2+} is substituted by Al^{3+} or another tri-valent cation, the layer gains a positive charge which is balanced by anions such as CO_3^{2-}, located between the layers together with interstitial water. Previous thermal analysis of this mineral showed that below 300°C only interstitial water was lost reversibly and the structure did not change. Between this temperature and 550°C dehydroxylation and evolution of carbon dioxide resulted in the destruction of the layered structure and formation of a mixture of metallic oxides. Four samples were used in the present study, with Fe or Al substituting Mg in the brucite layer. From the kinetics data it was concluded that the water loss occurs through a diffusion mechanism. These results are characteristic for layer structures.

DILATOMETRY

Dilatometry is used in mineral product industries. An atlas with dilatometric curves of clay minerals and related raw materials was recently published by Schomburg and Storr [33]. In addition to 106 dilatometric curves of various samples, the atlas contains a comprehensive review on the use of dilatometric techniques in mineralogy and in the ceramic industry.

Dilatometric curves are used as a rapid method for the semi-quantitative determination of quartz in ceramic bodies, by the evaluation of the volume increase during the transition of low quartz to high quartz. Schuller, Sladek and Huse [34] studied certain parameters which affect the dilatometric determination of quartz. For this study they used mixtures containing potassium feldspar, quartz and china clay in different proportions, fired at 1100 or 1200°C. The determination is impaired by two effects (a) the increase in volume of quartz can be partly compensated for by a decrease in the pore volume; (b) when very fine quartz is present an anomaly in the dilatometry curve is spread over. The start and end of the anomaly depends on the firing temperature. The phase transformation of quartz occurs at a certain temperature range around 573°C and the corresponding peak area in the derivative dilatometric curve (dl/dt) is applied for the quantitative determination of quartz. With fine or disordered quartz the transition range is extended. Consequently, separate calibration curves are needed for different types of ceramic materials. The high-low inversion of quartz was also used for DTA analysis of this mineral [17].

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