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THERMAL ANALYSIS IN EARTH SCIENCES

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ABSTRACT

A survey of the application of thermal analytical methods in the earth sciences with respect to various materials and temperature ranges is presented. Five papers presented at the ICTA 1985 in Bratislava serve as excellent examples of the diversity of TA investigations in earth sciences. In these papers fields such as organic and inorganic components of soils and coal, properties of uranium minerals and silica transitions are discussed. Typically, the TA studies are combined with other methods such as IR spectroscopy and X-ray diffraction.

Geoscientists were among the first to make use of the possibilities of thermal analysis (TA) and today TA methods are an important tool in many investigations made by mineralogists and geologists. The applications cover a wide range of materials, including natural minerals, ores, rocks and soils and related industrial products such as ceramics and refractories. Traditionally, DTA and TGA are mostly used but DSC, TMA and other modern techniques are also applied. The temperature range of interest starts slightly above room temperature (e.g., dehydration of hydrate minerals, zeolites, organic soil components, peat, coal), covers medium temperatures up to 1200 °C (dehydration and dehydroxylation of clays, decarbonization of carbonates, phase transitions) and reaches high temperatures above 1200 °C (oxide minerals, oxide ceramics and refractories). In addition, DTA and electrical conductivity measurements are used at very high pressures (up to several hundred kbars) for the simulation of conditions in deeper parts of the Earth's crust.

Publications up to 1965 were compiled by Smothers and Chiang [1]. Some of the numerous recent textbooks and publications containing geoscientific data, results and references are those by Mackenzie [2], Smykatz-Kloss [3], Pope and Judd [4] and Earnest [5]. Many articles and reference collections are accessible via Thermal Analysis Abstracts (edited by the International Confederation for Thermal Analysis, ICTA) and the journals Thermochimica Acta (Elsevier, Amsterdam) and Journal of Thermal Analysis

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(Heyden, London). Good surveys of recent developments are provided by the Proceedings of the ICTA conferences that are held every 2–4 years, and usually contain sections on "Earth Sciences" and "Ceramics" (e.g., Hemminger [6] and Miller [7]).

As examples of the variety of TA applications in earth science, some papers presented at the ICTA conference in Bratislava (1985) will be summarized. The materials investigated are coal, sapropelic acids, uranium minerals and silicon dioxide.

In the first two papers the determination of volatile inorganic and organic constituents of coal, oil shale and sapropels is described. As in particular the organic constituents change with time and temperature, their thermal properties can be used to characterize and identify such materials.

Warne et al. [8] discussed the difficulties of the thermoanalysis of pyrite (FeS_2) owing to interference from siderite ($FeCO_3$) and ankerite [Ca(Mg, Fe) $(CO_3)_2$]. To overcome these difficulties a combination of thermomagnetometry and SO_2 evolved gas analysis was proposed. For the latter, non-dispersive IR detectors (Stach et al. [9]) were tested using low-grade oil shale from the UK and bituminous coals from Australia. Evolution profiles of SO_2, CO_2 and CO volatiles from the oil shale are shown in Fig. 1. The SO_2 profile shows the oxidation of organic S at 300°C and the complex oxidation of pyrite above 350°C. Probably the SO_2 is "flushed" out of the sample by the much stronger CO_2–CO stream (see scale in Fig. 1). In addition, the markedly exothermic nature of the carbon combustion may cause a rapid increase in sample temperature, resulting in premature oxidation of pyrite and consequent merging of the SO_2 peaks due to organic and inorganic S.

Taal et al. [10] investigated sapropelic acids from Estonian sapropels of different ages (0–300000 years) by TG and DTA to elucidate diagenetic changes and changes in depositional conditions. Typical results in Fig. 2 show the thermo-oxidative degradation with two major steps. The first is attributed to the burning of hydrogen-rich compounds and the liberation of oxygen-containing functional groups of the sapropelic acids and always

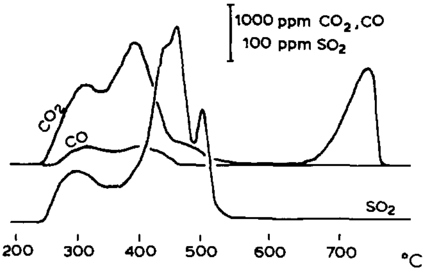

Fig. 1. Evolution profiles of volatiles from oil shale.

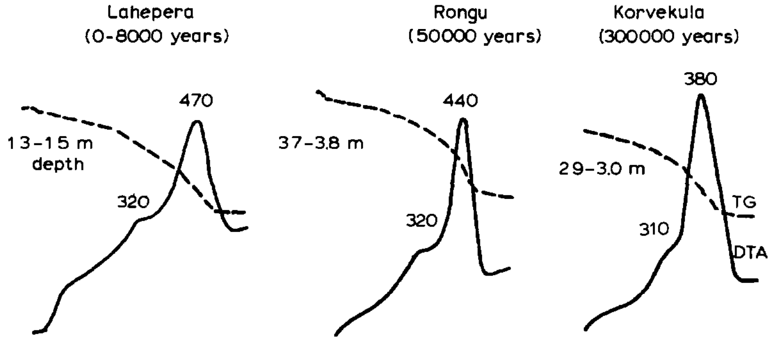

Fig. 2. Typical DTA and TG curves for sapropelic acids.

appears at 310–320 °C. The second peak decreases in temperature with the age of the sapropel and is believed to be the burning of the non-volatile constituents predominantly formed during the first thermo-oxidation event, but also being part of the original organic matter.

In two studies, uranium minerals from the National Museum in Prague were investigated by TG and DTA, XRD and IR spectroscopy. Identifications were based on the JCPDS Powder Data File. Six minerals were studied, nearly all having layer structures: (a) curite, $3PbO \cdot 8UO_3 \cdot 5H_2O$ (approximate formula); (b) uranophane and β-uranophane, $CaO \cdot 2UO_3 \cdot 2SiO_2 \cdot nH_2O$; (c) sklodowskite, $MgO \cdot 2UO_3 \cdot 2SiO_2 \cdot nH_2O$; (d) cuprosklodowskite, $CuO \cdot 2UO_3 \cdot 2SiO_2 \cdot 7H_2O$; (e) kasolite, $PbO \cdot UO_3 \cdot SiO_2 \cdot H_2O$; and (f) soddyite, $2UO_3 \cdot SiO_2 \cdot 2H_2O$.

Curite was studied by Čejka et al. [11]. It has a layer structure (Mereiter [12]) and also contains water molecules and OH groups in varying amounts. On heating (Fig. 3), these H_2O and OH groups are released continuously below 700 °C, even though possibly in two steps. A slight weight loss between 700 and 900 °C was attributed to vaporization of PbO. The end product of the decomposition was not U_3O_8 but a lead uranate, possibly PbU_3O_{10}. Further investigations of this product and of the Pb–U–O system are in progress.

Also in most of the uranyl silicates (b)–(f) (Urbanec et al. [13]), the roles and amounts of the H_2O, OH^- and H_3O^+ contents still remain open,

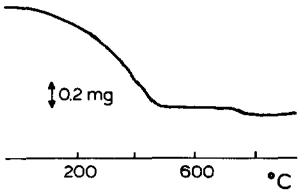

Fig. 3. TG curve of curite.

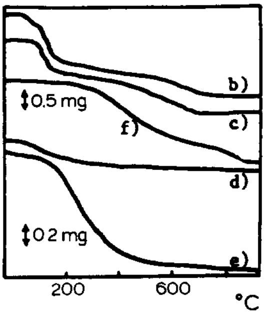

Fig. 4. TG curves of uranyl silicates.

resulting in variable formulae. Information on the crystal structures and IR spectra (Stohl and Smith [14]) was used to interpret the TG and DTA curves (Figs. 4 and 5).

All the results indicate stepwise dehydrations and thus the presence of different types of water. However, the more detailed assignment on the basis of IR spectra requires a study of deutero analogues, which is in progress.

Stoch et al. [15] applied DTA to SiO_2 in a study related to the industrial production of silica glass. The melting behaviour of SiO_2 and the properties of the glass depend on the SiO_2 phases formed during the heating of the quartz raw material. In particular, the quartz-cristobalite transformation is of interest, which proceeds via an amorphous transition phase and is influenced by impurities.

Fifteen quartzes of different origins were analysed by AAS, heated at 1500°C for 0.5–12 h, cooled and analysed for their quartz and cristobalite contents. The quantitative phase analysis was carried out by X-ray diffraction (using $d = 3.35$ Å of quartz and $d = 4.04$ Å of cristobalite) and by DTA (using the heights of the $\beta \rightarrow \alpha$ transition signals of quartz at 573°C and $\beta \rightarrow \alpha$ of cristobalite at 230–240°C). In addition, the activation energies of

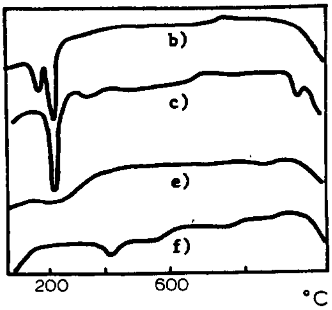

Fig. 5. DTA curves of uranyl silicates.

both transitions (Piłojan and Nowikowa [16]) and the crystallinity index (Murata and Norman [17]) were determined. The X-ray and DTA results differed considerably and the sum of both phases was always below 100%, possibly owing to different amounts of the amorphous transition phase and disorder in the crystalline phases. Nevertheless, the results indicate two types of quartz: all rock quartzes and two of the vein quartzes showed only a weak tendency to transform into cristobalite whereas the remaining vein quartzes had a strong tendency to transform into cristobalite. The chemical analyses indicated that alkaline and alkaline earth metal ions promote the formation of the amorphous transition phase and the subsequent cristobalite phase, whereas Al^{3+} stabilizes the transition phase, thus preventing the formation of cristobalite.

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