Journal of Thermal Analysis, Vol. 33 (1988) 1253—1257

PROGRESS OF THERMAL ANALYSIS IN EARTH SCIENCES

W. Smykatz-Kloss and *K. Heide**

MINERALOGISCHES INSTITUT, UNIVERSITÄT KARLSRUHE,
7500 KARLSRUHE, G.F.R.,
*SEKTION CHEMIE, "OTTO-SCHOTT-INSTITUT", FRIEDRICH-SCHILLER-UNIVERSITÄT- JENA,
6900 JENA, G.D.R.

The historical origins of the present state of thermal analysis investigations in geosciences are outlined. The majority of about 80 contributions to ESTAC 4 concerning geosciences dealt with applied and technical mineralogy and crystallography. Others are discussed with respect to new of improved techniques, minerals and rocks, thermodynamics and kinetics of minerals, and archeometry. Finally, subjects are suggested that could be treated at future meetings.

In the history of the development in geosciences, the thermal methods have had a remarkable influence only in a relatively small field of research. Especially clay and soil mineralogy was stimulated to use and to develop these methods for the determination of mineral phases, which are difficult to characterize by means of conventional methods such as X-ray diffraction or microscopy.

Let us think back to the beginning, when there were only three techniques: DTA, TG and dilatometry; step by step, these techniques improved, as did the equipment. From the simple identification of minerals, and the determination of the amount of water or CO_2 by means of the improved methods and equipment, we came to the determination of mineral properties, crystallinity, order/disorder, sintering behaviour, the chemical compositions of solid solutions, phase transitions and phase stabilities.

These investigations are topics in the modern geoscience, as are the thermodynamics of minerals and melts, the kinetics and equilibria in mineral reactions, metamorphic reactions, and the chemistry and physics of the planets. Many relations exist in the traditional topics of TA methods, but these need not be emphasized in particular here.

At present we are able to use many combined and new methods (DTG, DDTA, thermosonimetry, heating X-ray diffraction, thermomicroscopy, mass spectrometry and dynamic calorimetry, such as DSC), which make possible the quantitative

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

determination not only of rock compositions and of mineral properties, but also of the thermal stabilities of minerals, crystalline or glassy rocks.

This means that on the basis of much pioneering work, through the improvement of the methods, and partly by means of very special techniques, we came to a better understanding and measurement of (a) the thermodynamics, (b) the kinetics, and (c) the mineral properties of both natural and technological processes. In this way, the broad field of geoscientific research, from the fundamental to the economic aspects in high-temperature technology, came into contact with the objects of thermoanalytical research.

Review and discussion

As we can see from the contents of both the plenary lectures and the posters at ESTAC 4 in Jena, the emphasis of this conference was focused on Applied and Technical Mineralogy and Crystallography. Numerous special and well-developed TA techniques and instruments have become available for application for the characterization and even the prospecting of raw materials, for the characterization and production of technologically interesting materials, for the prevention of water pollution, and in other environmental sciences.

More than 80 contributions on TA can be discussed here under the context of research in the earth sciences. A mention of all these papers is impossible, but we shall summarize them under 6 different headings:

1. New or improved techniques

The Institute of Solid-State Chemistry, Novosibirsk, USSR, presented some interesting lectures dealing with investigations of crystal structural changes by synchroton radiathon diffraction or scattering, not only at high heating rate (A24, A25, A28), but also at high pressure (A36). Such investigations provide a successful means of investigating various processes of structural change in progress, and comprise an important topic in modern crystallography.

The use of emanation thermal analysis to study solid-state reactions is cultivated in the Nuclear Research Institute, Řež, Czechoslovakia. In paper F18, a further example was given of the investigation of the hydration reaction of cement minerals. This method promises many more possibilities for the characterization of solid-state reactions than are used at present.

The possibility of the determination of organic pollutants in the air by thermal vacuum desorption (p. 371) is an interesting example of applied thermal analysis in environmental science.

2. Minerals, rocks and their properties

The heart of geoscientific investigations by means of thermal methods still relates to the clays and clay minerals. The thermal dehydration and decomposition of clay minerals include intercrystalline and intrastructural processes, which are also significant for different steps of diagenetic and metamorphic processes. In general, the different types of bonding of water provide information about metamorphic transformations of minerals and rocks. An interesting compilation on the bonding types of water in minerals was given in PL17 (p. 121).

The modern techniques also permit the determination of complicated intercalation compounds of kaolinite (p. 401), and the different dehydration steps of swelling clay minerals (F14). The knowledge of such intercalation compounds seems to be really important in environmental science: more and more wastes for disposal are sealed into different types of clays, but not very much is known yet on the interactions between sewage waters and clay minerals (e.g. on the formation of organo-clay complexes, caused by the contact of sewage waters with clays).

The classification of meteorites on the basis of TG measurements (F20) is an interesting proposal, even though the investigations in air are less suitable in general.

Further reports dealt with special mineral properties and give examples of the development of the equipment, e.g. the re-formation of $Al(OH)_3$ in a wet atmosphere (p. 765), or the thermal behaviour of TiO_2 minerals (p. 803) or colemanite (F11).

3. Thermodynamics of minerals

The paper (p. 113) on the formation and decomposition of double salts is of great economic interest, and an excellent example of the very correct name of this conference (ESTAC), because the methods involved in this study were DTA/TG, optics and calorimetry as well.

One interesting aspect was the determination of the heats of crystallization of borate glasses and the influence of the ordering of the boron–oxygen network during the crystallization process (p. 923).

4. Kinetics of mineral formation and decomposition

The mechanisms of phase transitions and the thermodynamic, crystal structural and mechanistic approaches to their description were reviewed in a very enthusiastic and outstanding way in a plenary lecture (p. 107). The situation of measurements and interpretation reminds us of what was expressed in the final discussion on the thermal analysis and kinetic concepts of solid-state reactions.

Orientations for a new concept were found in the description of the formation of whewellite and wedellite (p. 707), and the investigation of calcite decomposition (C61). In geoscientific research, such papers have only a small influence on the discussion of the origins of minerals and rocks. An exchange of opinions and results should be useful in both directions.

5. Applied and technical mineralogy

Several papers were concerned with the thermal characterization of minerals as regards technical use, e.g. investigations on cement minerals, and especially the influence of sulphate on the hydration process (p. 677), or the analysis of concrete additives in a cement slurry (p. 1147). Further main discussion points were the characterization of coals (e.g. F16, F17) and the thermal reactions of absorption of sulphur dioxide (p. 407).

The investigation of slags (p 425, 431) and waste products are tasks of interest for applied mineralogical investigations into the recycling of waste materials and environmental science too. The synthesis of silicates (p. 909), dilatometric investigations of fibre-reinforced Ca-hydrosilicate (F19) or ceramic-metal interface bonding (p. 633) and the study of the thermomagnetic behaviour of ferrites (G32) may be mentioned under this heading.

6. Archeometry

In the exciting evening lecture, a very interesting paper was given on artifacts from ancient China (PL18). Special investigations dealing with clays and their significance as archeological thermometers (F3) show that thermal analysis can cover a broad field in historical research.

Though not falling into the geosciences, the attempts (p. 1041) to characterize and to date the age of paintings by means of DTA results may be mentioned here.

Conclusions

To summarize, we can say that ESTAC 4, with its lectures and papers, presented the main topics of thermal analysis in geosciences, but, as we can see, an interdisciplinary discussion can also stimulate the research in special fields in earth science, including the broad field of technological and environmental research. For further meetings and discussions we propose:

— a consequent decision for the standardization of measurements and procedures for "routine" investigations and their adequate publication;

— the creation of calibration standard materials, especially for high-

temperature thermometry and enthalpy calibration, but also for special types of phase transitions (glass transition, order-disorder transition);

— the problem of mineral equilibria and high-temperature calorimetry should be treated more extensively;

— the discussion, in small groups on national or international minimeetings, of special problems, such as the kinetics of phase transitions, the determination of thermodynamic data on minerals, the interpretation of thermoanalytical results through the investigation of rocks and raw materials, and the use of raw materials in industry.

Zusammenfassung — Der historische Ursprung des gegenwärtigen Standes thermoanalytischer Untersuchungen auf dem Gebiet der Geowissenschaften wird diskutiert. Von den auf dem ESTAC-4 vorgestellten ca. 80 Beiträgen zu Geowissenschaften mit Schwerpunkt Angewandte und Technische Mineralogie und Kristallographie werden einige unter den Aspekten: Neue oder verbesserte Methoden, Mineralien und Gesteine, Thermodynamik und Kinetik von Mineralen, Archäometrie diskutiert. Abschliessend werden Vorgeschläge für Themen künftiger Treffen gemacht.

Резюме — В общих чертах обсуждены исторические причины настоящего состояния термических методов исследования в геонауках. Большинство из 80 статей представленных на конференцию ESTAC 4 и касающихся геонаук, относились к прикладной и технической минералогии и кристаллографии. Обсуждены другие аспекты, касающиеся новых и улучшенных методов, минералов и горных пород, термодинамики и кинетики исследования минералов, а также археометрии. Обсуждены темы, которые должны быть рассмотрены на будущих вотречах.