Journal of Thermal Analysis, Vol. 12 (1977) 117—124

DTA OF NATURAL AND SYNTHETIC URANIUM COMPOUNDS

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(Received December 10, 1976)

A brief outline of structural considerations is given, concerning compounds one can meet as secondary uranium minerals. The authors report the thermal analysis of minerals deposited at the National Museum Collection in Prague. Three different types of instruments were used: a MOM derivatograph, a Netzsch DTA equipment, and an instrument constructed according to Rosický for microspecimens. The thermal analysis results were correlated with X-ray structure analysis and infrared spectra analysis data. The examples applied were: synthetic rutherfordine and related compounds, synthetic andersonite and the minerals liebigite and schoeckingerite, and synthetic schoepite.

Secondary uranium minerals represent one of the most important and outstanding groups of minerals. Most of them are characterized by a layer structure, the formation of which is inferred from the crystallochemical properties of hexavalent uranium [1]. The uranium(VI) forms layers of coordination polyhedra. Two apex oxygen atoms belong to the uranyl group and another 4, 5 or 6 oxygen atoms are located in the equatorial plane of the uranyl; consequently, the coordination polyhedra are tetragonal, pentagonal or hexagonal bipyramids [2]. The equatorial oxygen atoms have their origin in anions containing oxygen, e.g. OH^-, CO_3^{2-}, SiO_4^{4-}, PO_4^{3-}, AsO_4^{3-}, etc., which are bound with uranyl groups within layers. The interlayer space is filled up by cations (e.g. alkali and alkaline earth metals), water molecules or oxonium ions. These components link layers by electrostatic forces or hydrogen bonds. The differences in mineral structures containing an identical anion are determined by the interaction between layers and by the location of cations and water molecules in the interlayer space [3, 4]. Water in minerals plays a significant role. It occurs in a molecular form or as hydroxyl and oxonium ions. (Some authors have discussed polymerized forms of oxonium ion[5]). There are minerals where water has a zeolitic nature. The majority of water-containing minerals, however, do not have a zeolitic character, but exactly defined hydration stages, as was proved by thermal analysis in complex dioxophosphato- or arsenatouranates(VI), uranium micas [6]. The water content depends upon the valency and the diameter of the interlayer cations to a significant extent [6]. Evidence regarding oxonium ions within the interlayer space is a much-discussed problem, that could be solved with difficulty, even with the use of infrared spectroscopy and nuclear magnetic resonance [7]. Direct confirmation of oxonium ion existence has been given for uranium micas [7, 8]. On the other hand, doubts concerning several uranyl silicates (e.g. ref. 9) were proved to be justified [4]. The layer structures for secondary uranium minerals are extensively characterized by isomorphism, where anions can interchange each other in layers, e.g. PO_4^{3-} and AsO_4^{3-}, and also cations between layers can be substituted.

The complex nature of the majority of secondary uranium minerals made investigators use a combination of various methods in order to solve the outstanding problems. The shortage of natural material, which is almost a rule, leads at the same time to an intense study of the preparation of synthetic analogues of these minerals and their properties. Nevertheless, the synthesis of some minerals remains open. The interpretation of their properties and structure, and the conditions for their formation simultaneously also contribute to knowledge about the genesis and paragenesis of minerals and their subsequent transitions under natural conditions. Even if analogues of minerals prepared by synthesis are available, it is still useful to study microamounts of natural compounds to the maximum extent too, naturally if we can obtain them in pure and non-contaminated form. It is obvious that working techniques and methods put into practice in these cases require only microamounts of materials studied. How to use micropellets of KBr to obtain infrared spectra of uranium minerals was reported elsewhere [10]. In the present paper, we wish to describe possibilities for the thermal analyses, and especially DTA, of secondary uranium minerals and their synthetic analogues, with comparison of extensive experimental data obtained from a scientific revision of the mineral collection at the National Museum in Prague. The results were correlated with X-ray structure analysis and infrared spectroscopy data.

Ambartsumyan et al. [11] dealt with in detail the thermal decomposition of uranium minerals. They analysed samples of 50 to 100 mg with a heating rate of 75 to 100 K/min. The apparatus used was in most cases similar to that constructed and recommended for the DTA study of minerals by Ivanova et al. [12]. The main necessity for us was the use of micro DTA, especially for the study of very rare uranium minerals. We tried to exploit a DTA apparatus with exchangeable heads, constructed by Rosický [13].

Experimental

We used a MOM derivatograph, a Netzsch DTA instrument and a micro DTA instrument according to Rosický for the study of thermal decomposition. The described apparatus consists of a measuring head, control and recording parts. The measuring head involves a holder of two micropots formed in platinum wire of 1 mm radius by boring 1.5 mm deep pots. The pots are welded to chromel-alumel thermocouples. The measured sample weighed less than 1 mg and the maximum heating rate was 11 K/min. The instrument was calibrated according to the ICTA instructions. It was established that results up to 700° are reliable, while, at higher temperatures than 800°, they reach the resolution limit. The disadvantage of the measurement was a baseline shift.

Infrared spectra were measured with a Perkin-Elmer 225 instrument, using KBr micropellets and a microilluminator. The X-ray structure analyses were accomplished with a *Micrometa* apparatus, with a 114.6 mm camera and CuK_α radiation filtered by Ni foil, applying the Debye–Scherrer powder method. In all cases, the heating rate was deliberately constant, at 10 K/min.

The MOM derivatograph and similar instruments offer an ideal source of information about investigated materials because of simultaneous TG, DTG and DTA recordings. A disadvantage, with regard to rare minerals, is the relatively high sample amount necessary, tens or hundreds of milligrams. We investigated, for example, synthetic analogues of rutherfordine, a phase with a high carbonate content in the $UO_3-CO_2-H_2O$ system. These phases possess the rutherfordine structure from the aspect of X-ray structure analysis. On the other hand, thermal analysis proved differences between the individual hydrothermal phases, due to different compositions. The phase with molar ratios 1 UO_3 : 1.05 CO_2 : 0.59 H_2O (Fig. 1) shows only one peak in the DTA and DTG curves, corresponding to the endothermic decomposition of uranyl carbonate, while there is a continouus mass decrease in the TG curve in the range from 20 to 550° (adsorbed and interlayer water molecules and OH^-), followed by a marked decrease attributed to uranyl carbonate decomposition. An additional endothermic peak at 440° was observed in the DTA curve for the phase with molar ratios 1 UO_3 : 0.83 CO_2 : : 0.49 H_2O (Fig. 2), probably connected with loosening of the majority of the

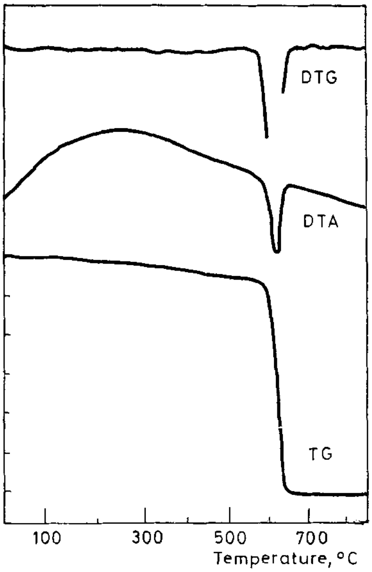

Fig. 1. TG, DTG and DTA curves of uranyl carbonate phase (molar ratios 1 UO_3 : 1.05 CO_2 : 0.59 H_2O) measured simultaneously in air. MOM derivatograph, 200 mg, 10 K/min.

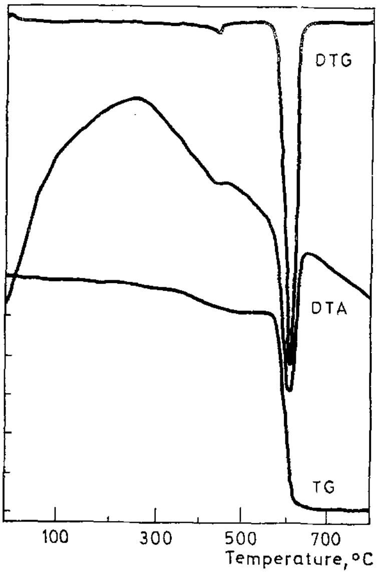

Fig. 2. TG, DTG and DTA curves of uranyl carbonate phase (molar ratios 1 UO_3 : 0.83 CO_2 : 0.49 H_2O) measured simultaneously in air. MOM derivatograph, 200 mg, 10 K/min.

Fig. 3. DTA curves of synthetic schoepite, $UO_3 \cdot 2\,H_2O$, measured in air. Netzsch, DTA instrument, 10 K/min. 1) 0.75 g; 0.25 mV; 2) 0.15 g; 0.25 mV; 3) 0.030 g; 0.05 mV; 4) 0.006 g; 0.05 mV.

OH^-. Corresponding changes in the TG and DTG curves and measured infrared spectra are in agreement with this. Thus, the thermal analysis gives evidence of structural differences between these phases, in spite of identical debyegrams.

The value of the use of simultaneous recording of DTA, TG and DTG curves in the uranium mineral investigations was confirmed by observations on the thermal decomposition of a synthetic andersonite, $Na_2Ca(UO_2(CO_3)_3) \cdot 6\,H_2O$. The dehydration step is shown in the DTA curve by an endothermic peak at about 200°, which is associated with a continuous decrease of mass in the range from 100 to 300°, comperable to the loss of 6 water molecules. The DTG curve, however, shows two distinct peaks: a large one at 180°, and a small one at about 220°. The dehydration actually consists of two overlapping processes, with different kinetics. Isothermal decomposition confirms that the dehydration of andersonite is a two-step process, where 4 water molecules are lost in the first step and 2 water molecules in the second. This means that the water molecules in the aqua complex are coordinated by different forces. Decomposition of the molecule starts during the second dehydration step. Similar thermal decomposition courses were recorded for liebigite, schroeckingerite and zellerite.

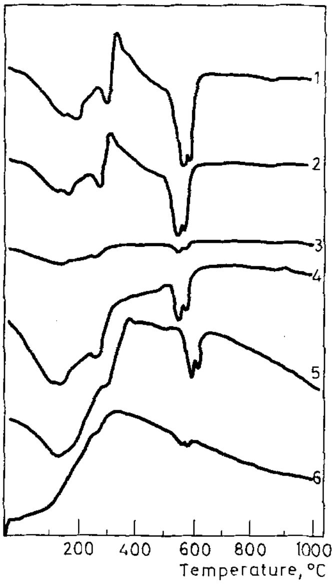

Fig. 4. DTA curves of uranyl carbonate phase (molar ratios 1 UO_3 : 0.80 CO_2 : 1.0 $6H_2O$) measured in air. Netzsch DTA instrument, 10 K/min. 1) 0.58 g; 0.25 mV; 2) 0.35 g; 0.25 mV; 3) 0.030 g; 0.25 mV; 4) 0.030 g; 0.05 mV; 5) 0.030 g; 0.05 mV; 6) 0.006 g; 0.05 mV.

The Netzsch DTA instrument was used to study the thermal decomposition of a synthetic schoepite, $UO_3 \cdot 2\,H_2O$ (Fig. 3), a synthetic phase (prepared at laboratory temperature and pressure) characterized by molar ratios 1 UO_3 : 0.80 CO_2 :

: 1.06 H_2O (Fig. 4), and a product resulting from hydrolysis of the latter compound, the structure of which was determined by X-ray as being close to $UO_3 \cdot 2\,H_2O$, (Fig. 5). Variable parameters were the weight of sample and the resolution of the instrument, at a constant heating rate of 10 K/min. A Pt/PtRh thermocouple was located directly within the sample. The sandwich packing method was applied if small amounts were available. Calcined alumina was used as reference material. The weight of samples was varied from 0.006 to 0.030 g at a sensitivity 0.05 mV, and from 0.030 to 0.75 g at a sensitivity 0.25 mV. It was proved that the decrease in weight at a constant sensitivity has no effect on the baseline. Areas of thermal effects, however, are lower. DTA of 0.030 g samples at a sensitivity 0.05 mV produces curves of the same features as for amounts higher than 100 mg at a sensitivity 0.25 mV. Only the baseline is shifted. On the other hand, analysing a sample of 0.006 g at a sensitivity 0.05 mV, we can observe thermal effects in the DTA curve, but the interpretation of these is difficult. A compensation of the differences between the individual endothermic effects occurs in the range of dehydration. The whole feature of the curve and even of the single effect, if it does not disappear altogether, is affected by the baseline shift. Even if we consider that a conveniently-chosen heating rate should improve the DTA curves of investigated minerals, it appears that exceptional, very rare minerals, the abundance of which in nature is very fortuitous, are not conveniently studied with the Netzsch instrument by the treatment discussed above, because we do not always reach correct conclusions about the thermal decomposition of the material studied.

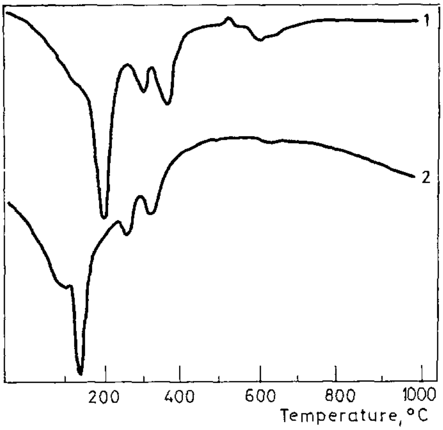

Fig. 5. DTA curves of hydrolysis product of uranyl carbonate phase (see Fig. 4), with an X-ray structure close that to $UO_3 \cdot 2\,H_2O$, measured in air. Netzsch DTA instrument 10 K/min. 1) 0.40 g; 0.25 mV; 2) 0.030 g; 0.05 mV.

The given facts led us to test the possibilities of the micro DTA instrument made according to Rosický [13]. Our experience with this instrument and its application were published in detail elsewhere [14, 15].

References

1. A. S. Povarennykh and M. Bednár, Geol. Zh., 34 (1974) 42.
2. H. T. Evans, Jr., Science, 141 (1963) 154.
3. I. Kh. Moroz and G. A. Sidorenko, Rentgenografiya mineral'nogo syr'ya (Roentgenography of Mineral Raw Materials), Vol. 10, p. 37. Izd. Nedra Moscow 1974.
4. G. A. Sidorenko, I. Kh. Moroz and I. G. Zhil'tsova, Zap. vses. miner. obshch., 104 (1975) 559.
5. Ye. V. Rozhkova et al., K voprosu o klassifikatsii molekulyarnoy vody v mineralakh (On the Classification of Water Molecules in Minerals), Izd. Nedra Moscow, 1971, 80 pp.
6. Walenta, Chem. Erde, 24 (1965) 254.
7. R. W. T. Wilkins, A. Mateen and G. W. West, Am. Mineral., 59 (1974) 811.
8. I. Kh. Moroz, A. A. Valuyeva, G. A. Sidorenko, I. G. Zhil'tsova and L. N. Karpova, Geokhimiya (1973) 20.
9. V. S. Mel'nikov and Yu. M. Mel'nik, Mineral. Sb., No. 23 (1969) 235.
10. Z. Urbanec and J. Čejka, Infrared Spectroscopy of the Secondary Uranium Minerals, Interan '76, Prague 1976, Report No. P 86.
11. Ts. L. Ambartsumyan, G. I. Basalova, S. A. Gorzhevskaya, N. G. Nazarenko, and R. P. Khodzhayeva, Termicheskie issledovaniya uranovykh i uransoderzhashchikh mineralov (Thermal Investigation of Uranium and Uranium-bearing Minerals), Gosatomizdat Moscow, 1961, 148 p.
12. V. P. Ivanova et al., Termicheskiy analiz mineralov i gornykh porod (Thermal Analysis of Minerals and Rocks), Izd. Nedra Leningrad, 1974, 400 p.
13. J. Rosický, Silikaty, 12 (1968) 295.
14. K. Tobola, J. Čejka and Z. Urbanec, Micro-DTA of Minerals. Thermal Analysis of Secondary Uranium Minerals, Interan '76, Prague 1976, Report No. p. 81.
15. J. Čejka, K. Tobola and Z. Urbanec, Thermal Analysis of Some Uranium Minerals and Related Synthetic Compounds, Proc. 1st Europ. Symp. Thermal Analysis (D. Dollimore, Ed), Heyden, London 1976, p. 353.

Résumé — Un bref rappel sur les considérations structurales concernant les composés que l'on peut rencontrer comme minéraux secondaires d'uranium est donné. Les auteurs ont eu l'intention de faire partager leur expérience acquise lors de la révision des minéraux déposés dans la Collection du Musée National de Prague, à l'aide de l'analyse thermique. Trois types d'instruments ont été utilisés le Derivatograph MOM, l'appareil ATD Netsch et un instrument construit d'après Rosický, pour l'étude de microéchantillons. On a établi une corrélation entre les résultats de l'analyse thermique et ceux obtenus lors des analyses de structures par rayons X et par spectroscopie infrarouge. Les exemples cités concernent la rutherfordine synthétique et les composés analogues, l'andersonite synthétique, ainsi que les minéraux liebigite et schoeckingérite et la schopite synthétique.

Zusammenfassung — Ein kurzer Bericht über strukturelle Erwägungen bezüglich sekundärer Uraniumerz-Verbindungen wird gegeben. Es werden an die durch thermoanalytische Überprüfung der in der Sammlung des Nationalmuseums zu Prag befindlichen Erze gewonnenen Erfahrungen mitgeteilt. Drei verschiedene Typen von Geräten wurden eingesetzt: der Derivatograph MOM, die DTA-Vorrichtung Netzsch und ein nach Rosický gebautes Gerät für Mikroproben. Die Ergebnisse der Thermoanalyse wurden mit den Daten der Röntgen-Strukturanalyse und denen der Analyse des Infrarotspektrums in Zusammenhang gebracht. Als Beispiele wurden synthetisches Rutherfordin und verwandte Verbindungen, synthetisches Andersonit, sowie die Erze Liebigit und Schoekingerit und synthetisches Schopit verwendet.

Резюме — Приведены основные принципы структурных соображений относительно соединений, которые встречаются как вторичные урановые минералы. Авторы хотели бы тоделиться своим опитом при исследовании минералов, находящихся в коллекции Пражкого Национального музея, используя термический анализ. Были использованы три различных инструмента: дериватограф МОМ, прибор ДТА Netzch и прибор, сконструированный согласно Росицки, для микрообразцов. Результаты термического анализа были скоррелированы с данными рентгено-структурного анализа и инфракрасных спектров. В качестве образцов были использованы синтетический разерфодин и родственные ему соединения, синтетический андерсонит, минералы либигит и шокингерит, а также синтетический скупит.