EARTH SCIENCES, RAW MATERIALS

THERMAL AND INFRARED SPECTRUM ANALYSES OF NATURAL AND SYNTHETIC ANDERSONITES

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The thermal decompositions of natural and synthetic andersonites were studied. Two partly overlapping dehydration steps and three partly overlapping decarbonation steps were observed. The second dehydration and the first decarbonation steps also partly overlap. During decarbonation, the gradual formation of sodium diuranate and monoclinic and hexagonal phases in the $Na_2U_2O_7–CaUO_{4-x}$ system was proved. The results were correlated with measured infrared spectra using site and factor group analysis and X-ray structure analysis. The chemical formula inferred for natural andersonite, $Na_2Ca[UO_2(CO_3)_3] \simeq 5.6H_2O$, agrees with that proposed for its synthetic analogue.

Andersonite has been found in several deposits and also synthetized by several authors. Infrared spectra of both natural and synthetic specimens and luminescence spectra of the mineral have been published.

A thermal analysis of synthetic andersonite has been described. According to the crystal structure of synthetic andersonite [1], only five water molecules in the formula were found in the final Fourier map. The possible statistical distribution of the remainder in a structure channel is presumed. On the basis of our preliminary conclusions [2, 3], the formula $Na_2Ca[UO_2(CO_3)_3] \cdot \simeq 5.6H_2O$ was proposed for synthetic andersonite [1].

In this paper, attention is especially paid to the content of molecular water in natural andersonite and for comparison in synthetic andersonite, using combined TG and DTA and IR spectroscopy. A complex contribution to the crystal chemistry of andersonite will be published elsewhere [4]. The paper forms part of the scientific reassessment of secondary uranium minerals from the collections of the National Museum in Prague.

Experimental

Synthetic andersonite was prepared by the method described by Čejka [5]. The specimen of natural andersonite (Jáchymov deposit, Czechoslovakia) was obtained from Dr. Zdeněk Mrázek. Identifications were based on the JCPDS Powder Data File. Chemical analysis of synthetic andersonite was carried out. The DTA curve of synthetic andersonite was recorded with a DTA instrument constructed at the Department of Silicates, Prague Institute of Chemical Technology: sample weight 739.2 mg, heating rate 10 deg·min^{-1}, static air atmosphere, reference material Al_2O_3, vessels made of a Pt–Rh alloy, and Pt–Rh wires as thermocouples. Simultaneously recorded TG–DTG–DTA curves of synthetic andersonite, obtained with a MOM derivatograph (sample weight 253.8 mg, heating rate 10 deg·min^{-1}, and gaseous CO_2 quantitatively determined [6]) were taken into account. TG curves of both natural and synthetic specimens were studied by using a Stanton Redcroft TG 750 Thermobalance (dynamic air atmosphere, 10 ml·min^{-1}, heating rate 10 deg·min^{-1}, sample weight 1.923 and 1.87 mg, respectively). The IR spectra were measured with Perkin–Elmer spectrophotometers (Model 225: Nujol; and Model 325: KBr disk).

Results and discussion

Thermal analysis

Dehydration

Andersonite undergoes dehydration in two steps (Figs 1–3). The dehydration process is manifested by an endotherm at 190–200°. Four water molecules are liberated within the interval 50–155° (natural) or 50–~200° (synthetic). The
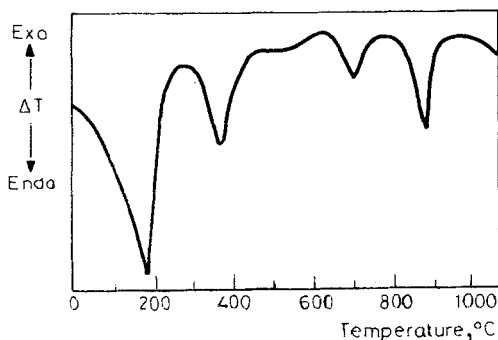

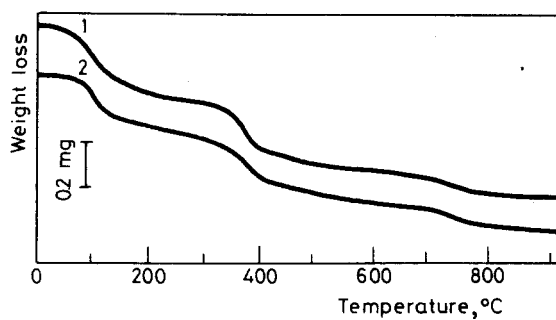Fig. 1 DTA curve of synthetic andersonite (sample mass 739.2 mg)

Fig. 2 TG curves of (1) natural (sample mass: 1.923 mg) and (2) synthetic (sample mass: 1.87 mg) andersonites
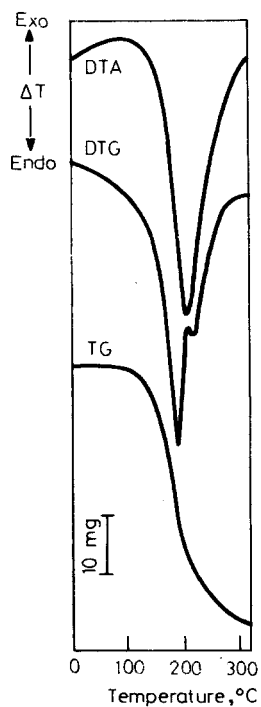

Fig. 3 Simultaneous TG–DTG–DTA curves of the dehydration region of synthetic andersonite (sample mass: 253.8 mg), recorded by F. Paulik [6]

remainder (approximately 1.6 H_2O) is released up to $\sim 315°$. The maximum rate of dehydration was observed at 190° [6]. It is evident that water molecules are bound by different coordination forces , as indicated by the two-step dehydration. Paulik [6] pointed out that the small inflexion point at 210° on the 190° DTG maximum (Fig. 3) shows that these two dehydration processes strongly overlap: the H_2O curve was derived by calculation from the difference between values represented by the CO_2 thermo-gas-analytical measurement and TG curves. The reason for this was the fact that the losses of water and carbon dioxide (the start of decomposition of the anhydrous phase) are also overlapping processes. In the final Fourier map, there is no trace of one of the six water molecules in the formula of andersonite proposed earlier [1]. Five water molecules are coordinated to two sodium atoms and one calcium atom: the remaining approximately 0.6 H_2O distributed in the structure channel is probably important for the stability of the entire crystal structure. Preferred release of the statistically distributed molecular water was not detected. On the basis of all the available experimental data, it was inferred that the molecular water content is approximately 5.6 H_2O in both natural and synthetic andersonites.

Decarbonation and solid-state reactions

At 300–315°, the weight loss corresponds to the formation of an anhydrous phase. Any increase in temperature leads to its decomposition connected with its amorphization, marked by the endotherm at 360–365°. The thermal decomposition of the anhydrous phase also occurs in several overlapping steps (three or four, the resolution depending on the experimental conditions). The endotherms observed (710 and 870°) correspond to the decarbonation, which is connected with the gradual formation of $Na_2U_2O_7$ and amorphous calcium and sodium carbonates. $Na_2U_2O_7$ is isotypic with $CaUO_4$ [7] and is stable up to 1200° [8]. $CaUO_4$ loses oxygen above 750° and is generally oxygen-deficient [9, 10]. The reaction between $Na_2U_2O_7$, $CaCO_3$ and Na_2CO_3 are manifested by the formation of $Na_2U_2O_7$–$CaUO_{4-x}$ solid solutions, whose symmetry (monoclinic or hexagonal) is temperature-dependent. Crystalline phase formed over 700° can be generally formulated as $(Na, Ca)(UO_{4-n})$, the composition of which may vary to some extent [5, 11].

IR spectroscopy

The site symmetry of the uranyl group in andersonite is C_s: the double degenerate bending vibration $v_2UO_2^2$ is split (300?, 320 and 347 cm^{-1}—mineral; 317 and 344 cm^{-1}—synthetic), and the symmetric stretching vibration $v_1UO_2^{2+}$ becomes IR-active (795 cm^{-1}—mineral; 780–790 cm^{-1}—synthetic) (Fig. 4). An absorption band at 903 cm^{-1} with a shoulder at 915 cm^{-1} is assigned to the antisymmetric stretching vibration $v_3UO_2^{2+}$. The absorption band at 215 cm^{-1} can be connected
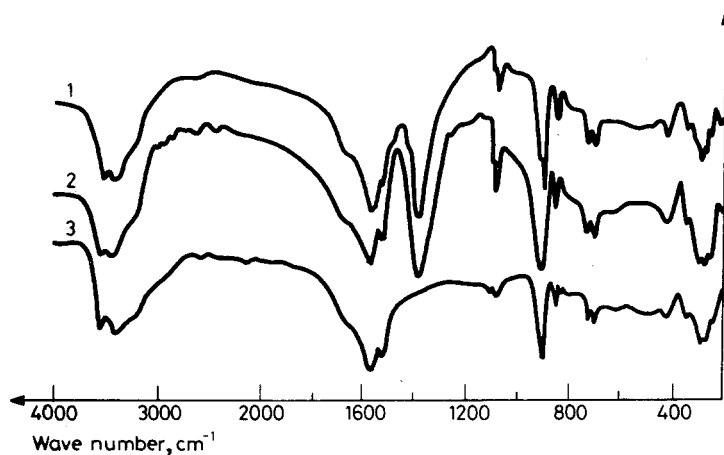
Fig. 4 Infrared spectra of natural (1 — KBr disk) and synthetic (2 — KBr disk, 3 — Nujol) andersonites

with the vibration mode of the carbonate group, and those at 254, 268–272 and 284–286 cm^{-1} with the $U-O_{ligand}$ vibrations. Both these vibrations overlap with those of $v_2UO_2^{2+}$. The number of observed absorption bands assigned to the carbonate vibrations indicates a symmetry decrease of the carbonate ions from D_{3h} to C_{2v} or lower. The $v_1CO_3^{2-}$ vibration becomes IR-active and $v_4CO_3^{2-}$ are split. The absorption bands assigned to water molecules occur in three regions: vibration modes (425, and probably also 475 and 545 cm^{-1}), the bending vibration δH_2O (1662 cm^{-1}), partly coinciding with the absorption band at 1578 cm^{-1} of the bidentate carbonate group, $v_3CO_3^{2-}$, and the stretching vibrations vOH (3430 and 3220 cm^{-1}). An absorption band at 3563 cm^{-1} is characteristic for hydroxyl groups or adsorbed surface water molecules. The remainder of the water (~ 0.6 H_2O) is probably statistically distributed in a structure channel and does not participate in the coordination of Na^+, Ca^{2+} and UO_2^{2+} cations. The absorption band at 3563 cm^{-1} could therefore be assigned to the vibration of this remaining molecular water.

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Zusammenfassung — Die thermische Zersetzung von natürlichem und synthetischem Andersonit wurde untersucht. Sie umfasst zwei teilweise überlappende Entwässerungs- und drei teilweise überlappende Decarboxylierungsstufen. Der zweite Entwässerungs- und der erste Decarboxylierungsschritt überlagern einander ebenfalls teilweise. Während der Decarboxylierung wird die allmähliche Bildung von Natriumdiuranat und monoklinen und hexagonalen Phasen des Systems $Na_2U_2O_7$–$CaUO_{4-x}$ nachgewiesen. Die Ergebnisse wurden mit den gemessenen IR-Spektren unter Benutzung der site- und Faktor-Gruppenanalyse sowie Röntgenbeugungsuntersuchungen korreliert. Die für natürlichen Andersonit abgeleitete Formel $Na_2Ca[UO_2(CO_3)_3] \approx 5,6H_2O$ stimmt mit der für synthetischen Andersonit vorgeschlagenen überein.

Резюме — Изучено термическое разложение природного и синтетического андерсонита. Установлены два частично перекрывающихся процесса дегидратации и три частично перекрывающихся процесса декарбонизации. Вторая стадия дегидратации частично также перекрывается с первой стадией декарбонизации. Показано, что в процессе декарбонизации происходит постепенное образование диураната натрия и моноклинной и гексагональной фаз в системе $Na_2U_2O_7$–$CaUO_{4-x}$. Результаты коррелировались с измеренными ИК спектрами и данными рентгенофазового анализа. Химическая формула $Na_2Ca[UO_2(CO_3)_3] \approx 5,6H_2O$, предложенная для природного андерсонита, согласуется с предложенной для его синтетического аналога.