

THE DEHYDRATION OF GISMONDITE

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ABSTRACT

Continuous-heating X-ray photography, D.T.A., and T.G.A. revealed that reversible thermal dehydration of gismondite involves the occurrence of five different meta-stable crystallographic phases before the irreversible high temperature feldspar phase is reached.

INTRODUCTION

Due to the remarkable property of zeolites to dehydrate in part reversibly upon heating, the thermal behaviour of this group of minerals has been studied extensively (Milligan and Weiser, 1937; Koizumi, 1953, 1958; Peng, 1955; Barrer and Langley, 1958; Moss and Roy, 1960; Pecs-Donath, 1962, 1968; Aumento, 1966). However, due to the employment of inadequate equipment and techniques, detailed and accurate information as to phase transformations, phase characterization, ascertainment of corresponding temperatures as well as energies involved is still scanty and often controversial or unreliable. Systematic investigation of a wide variety of natural zeolites in our laboratory with the use of a Guinier-Lenné continuous heating and recording X-ray diffraction camera combined with D.T.A., T.G.A., and D.S.C. (differential scanning calorimetry) has produced much of the information that was hitherto lacking. The preliminary results of the study of dehydration of gismondite are reported here.

MATERIAL AND METHODS

Hand-picked gismondite crystals from Capo di Bove, Rome, Italy were ground in an agate mortar. A slight contamination with chabazite and harmotome, with which the gismondite was inter- and overgrown, could not be avoided. The powder was stored at ~51 percent relative humidity in a desiccator over a saturated $\text{Ca}(\text{NO}_3)_2$ solution in a constant temperature room (25°C) where the relative humidity was equally kept at 51 percent. D.T.A., T.G., and D.S.C. were performed in this room on Dupont 900 assemblies, each with a heating rate of 3.5°C/minute. T.G. was carried out with an air stream at a flow rate of 0.2 l/minute. Air from the room was used to prevent any loss of weight before the run was started. A continuous-heating X-ray photograph was taken with an average heating rate of ca. 7.5°C/hr. and a film speed of 2 mm/hr. $\text{Cu K}\alpha$ radiation at 40 kV and 50 mA was used.

RESULTS AND DISCUSSION

Heating X-ray photograph. Figure 1 shows the five different phases of gismondite during heating. Transformations occur at ca. 70°C, 87°C, 108°C, 196°C, 280°C, and 350°C respectively. Although the last two transformations are of a gradual kind in that reflections of the two phases

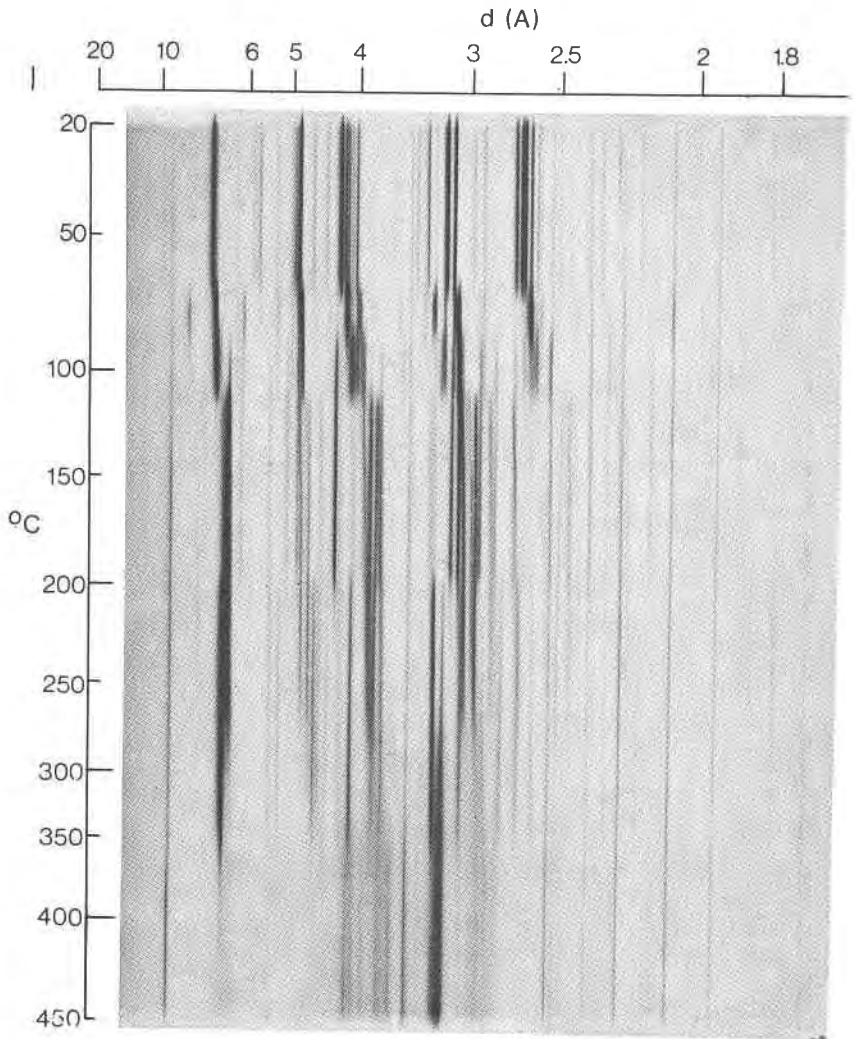


FIG. 1. Continuous heating X-ray photograph of gismondite.

co-exist transiently,¹ it appears that both in these as well as in most of the other transformations certain reflections are unaffected and continue in the next phase or even persist during more than two phases. Until *ca.* 330°C, where formation of high temperature Ca-feldspar starts,

¹ The apparent co-existence of phases with abrupt transition is due to the diaphragm width of the camera. The continuous reflections from top to bottom of the photo are due to the *Pt* sample grid and added α - Al_2O_3 ; The reflection at 9.5 Å is due to chabazite.

the lattice transformations are completely reversible, *i.e.*, on cooling in air each phase reappears in reverse sequence. Repeated dehydration (4X) caused no noticeable break-down of the lattice. The formation of feldspar at such a low temperature without an intermediate X-ray amorphous phase was observed in a number of other members of the phillipsite group and deviates from what is exhibited by most other zeolites.

Apparently the structure of the preceding phase is sufficiently favorable for such a direct transformation. Attempts to characterize the meta-gismondite phases are presently being undertaken.

Thermal analysis. D.T.A. and T.G. traces are presented in Figure 2. All endothermic peaks correspond with loss-in-weight steps and dehydration is involved in the crystallographic transformations of the meta-phases.

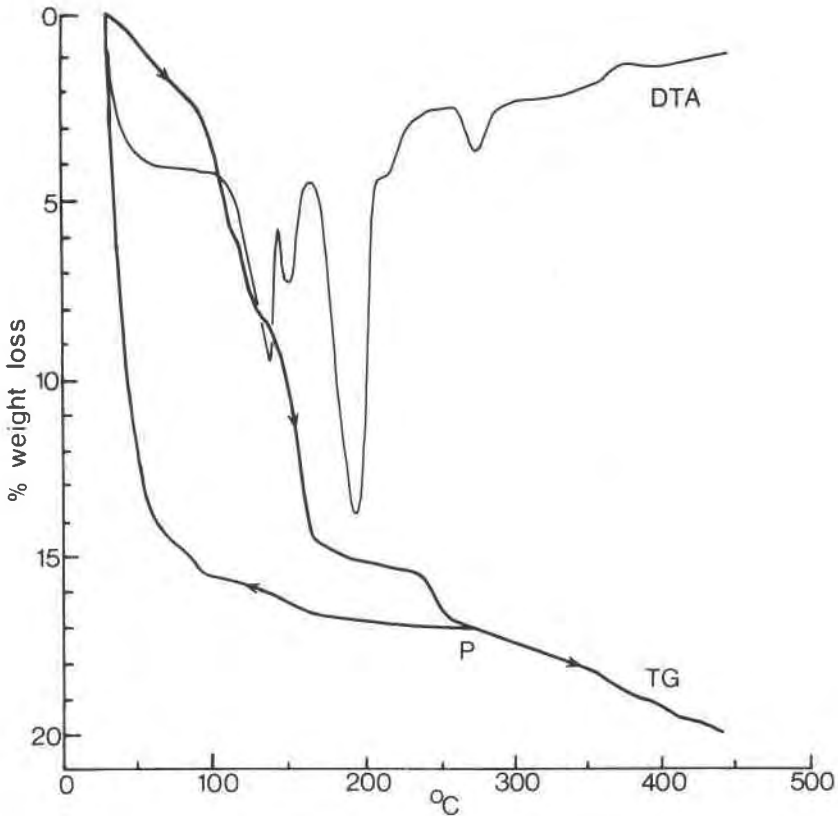


FIG. 2. DTA and TG curves of gismondite. For complete rehydration no heating beyond P.

The exothermic peak at about 375°C indicates the irreversible formation of high temperature Ca-feldspar.

The first step in the dehydration curve (from *ca.* 50°–80°C) is not accompanied by a real endothermic peak in the D.T.A., but merely a general lowering of the base line. The water lost in this range, being 2.3 percent of the total weight or more than 13 percent of the reversibly removable water (~17.5 percent of total weight) can also be removed by flushing the reaction chamber with "dry" N₂ gas² or evacuating it to a pressure of 5 cm Hg. Similar experiments with the aforementioned X-ray camera showed that this water loss is not accompanied by a lattice transformation indicating that for this heat is a prerequisite.

Rehydration in air (relative humidity 51 percent at 25°C) showed a strong hysteresis and was practically complete within a few hours.

Experiments showed that on cooling to 70°C the original gismondite phase had reappeared although the sample was rehydrated to only 20 percent of its capacity. In an N₂ stream (flow rate 0.2 l/min.; relative humidity ~0.015 percent at 25°C) the original phase reappeared at a rehydration of 10 percent of its capacity. This gas appeared to be too dry for further rehydration and humid air was required to accomplish this. These observations would suggest that for the reversal of transformations to occur a complete population of each phase is not necessary. When any rehydration was prevented by heating the sample in a glass capillary and

² N₂ gas containing 5 v.p.m. H₂O.

Table 1. Number of molecules H₂O lost per unit cell per dehydration step and associated heats (ΔH).¹

Temperature range	Number of molecules H ₂ O	ΔH (kcal/mole H ₂ O)
r.t. - 73°C	3.7	-
73° - 88°C	6	10.0
88° - 115°C	4	6.4
115° - 208°C	11	13.8
208° - 290°C	3	5.9

¹ Calibrated with heats of fusion of pure metals.

sealing it off before cooling, X-ray diffraction at room temperature revealed that the meta-phases were preserved.

The number of H₂O molecules lost per dehydration step per unit cell together with the heats of reaction (ΔH) involved are given in Table 1. The calculations are based on a chemical formula of Ca_{8.4}Na_{1.0}K_{1.7}Al_{14.9}Si_{16.9}O₆₄·34.8H₂O as analysed by T.G., X-ray fluorescence, and wet chemical analysis.

Interpretation of such heats of reaction is hampered by the fact that they are composed of at least two contributions *viz.* heat of volatilization of water and heat of lattice transformation.

The ascertainment of the temperatures of phase transformation is more accurately achieved with the continuous heating X-ray camera than by the D.T.A. by virtue of its much lower heating rate.

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