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POSSIBILITY OF THERMAL ANALYSIS OF DIFFERENT TYPES OF BONDING OF WATER IN MINERALS

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Various types of water bonding were studied, e.g. water bound by occlusion, by adsorption, by capillary condensation, by chemisorption and as a solid solution, zeolitic water, interlayer water, crystal water and structural water bound in form of hydroxil groups. The differentiation of these various types of bonding is rather difficult, for on heating water is evolved at various temperatures and in rather wide temperature domains which overlap to different extents. Efforts were made to improve the detection by applying the quasi-isothermal quasi-isobaric measuring technique.

Water can be bound in different manners in minerals. Table 1 lists the most frequent types of occurrence of water in minerals, and summarizes the most important features. The Table clearly reveals that the different water types form a continuous sequence.

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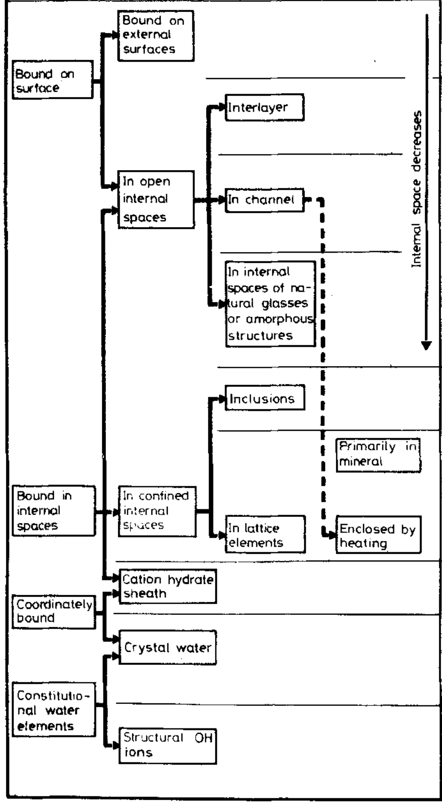
Table 1



Type and location of water				Bonding types	Form of water elements	Factors governing quantity of water	Reaction of water removal		Temperature of water removal	Character of water removal	Influence of water on structure
Bound on surface	Bound on external surfaces		Internal space decreases	van der Waals forces	H_2O	External condition and surface features	Dehydration	Desorption	40-100 °C	Non-equilibrium process; non-isothermal under quasi-equilibrium conditions	No structure-determining functio
Bound on surface Bound in internal spaces	In open internal spaces	Interlayer		Free water, physically adsorbed water (van der Waals forces or H-bonding), capillary condensation	Mainly H_2O OH traces	Size and features of surface of internal space			Wide temperature range, depending on physical and energetic conditions		
		In channel			Mainly H_2O, some OH (primarily on AlO_4 tetrahedra)						
		In internal spaces of natural glasses or amorphous structures			Mainly OH, further H_2O layers						
Bound in internal spaces	In confined internal spaces	Inclusions			Liquid or gaseous H_2O molecules	Size of internal space		Decrepitation	Temperature of emergence of inclusion	Explosion-like for unpulverized sample	
		In lattice elements	Primarily in mineral Enclosed by heating		"Solid solution" as compound crystal				Temperature of rearrangement of lattice elements	Nonisothermal	
Bound in internal spaces Coordinately bound	Cation hydrate sheath			Coordinate H-bonding around cations	H_2O molecules	Cation hydration energy			Depends on cation hydration energy		
Coordinately bound Constitutional water elements	Crystal water					Stoichiometric			Depends on phase equilibrium	Equilibrium process; isothermal under quasi-equilibrium conditions	Except for last molecule essentially no structure-determining function
Constitutional water elements	Structural OH ions			Ionic-covalent bonding	OH ions		Dissociation (dehydroxylation)		Depends on bonding forces and lattice structure	Essentially isothermal; for complex structures nonisothermal due to diffusion processes	Structure-determining

Adsorption water: Minerals are capable of binding .different amounts water, both on their external and on their internal surfaces, for the crystals contain interstitial channels and cavities of various shapes and sizes. The adsorption of water can be attributed to the dipole behaviour of water molecules. The polar ions or atomic groups on the surface of a solid bind polar water molecules by van der Waals forces. The resulting monomolecular layer creates a new polar surface, which permits the oriented adsorption of further molecule sequences. As the water layers become thicker, they become less ordered, while their tension increases. At a given layer thickness and temperature, there is a fixed partial pressure of water vapour in the gas phase. Under ·conditions of thermoanalytical investigations, the adsorbed water can be removed at 40–100°. The internal channels may be capillaries, where capillary condensation plays a prominent role in the water binding. For 20 Å capillaries a water vapour pressure of 100 kPa is achieved only at 120°. Capillaries less than 20 Å in radius may hinder the removal of residual water even at temperatures of several hundred degrees.

The types of water binding by internal surfaces are shown in Fig. 1, where TG curves of alumina are given. All three samples were obtained from the same gibbsite by heating and subsequent storage in a wet atmosphere.

Large internal spaces can generally be bound with less ordered structures in materials of amorphous type.

A typical example of water adsorbed on external and internal surfaces of minerals is provided by silicates, which contain polar AlO_4 and SiO_4 tetrahedra.

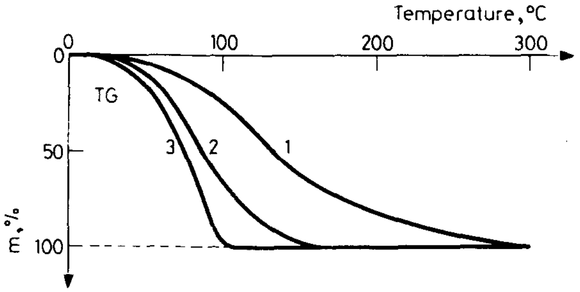


Fig. 1 Dehydration of alumina. Sample 1 was heated at 350 °C (the resulting large internal space rendered it suitable for use as a catalyst support and for the filling of chromatographic columns). Sample 2 was heated up to 1000 °C (a major part of the internal surfaces was lost by sintering). Sample 3 was sintered corundum (water adsorption only on the external surface).

Interlayer water is found in phyllosilicates, for example. The interlayer space may contain free water molecules, and water adsorbed to the active sites directly or in the second or third layer. Due to the large spaces and hence the comparatively weak binding, this water can escape at a relatively low temperature. The remaining water is coordinated around the interlayer cations. This binding energy is larger, its value depending on the size of the cation.

The amount of interlayer water provides important genetic information. The diagenetic transformation of clay minerals, established via the interlayer water content, is especially important from the point of view of hydrocarbon prospecting. Similar measurements allow determination of the temperatures of transformation of metasomatic rocks [1].

Zeolitic water, sometimes found in non-zeolitic minerals too, is accompanied by other water types and primarily by crystal water. The zeolitic water is found in the channels of the SiO_4 and AlO_4 tetrahedra, where it moves more or less freely. Relatively free movement is possible in the wide channels, whereas, narrower channels or capillaries impede the movement, or the water is adsorbed on the surface, mainly bound to the AlO_4 tetrahedra, partly in the form of OH groups. Some of the water may form a hydrate sheath around the exchangeable cations in the channels.

The water is bound with different energies, and the thermal curve usually reveal its steady loss in a wide temperature range, with large irregular peaks. The OH groups are lost at higher temperature than the molecular water.

The water content of a zeolite may be an indicator of the temperature of its formation.

Natural glassy rocks and amorphous formations often contain water bound similarly to zeolitic water. In glassy rocks, most of this water is bound in OH form. The network forming the glassy rock comprises primarily SiO_4 and to a much lesser extent AlO_4 tetrahedra to which the OH groups are bound free or by hydrogen-bonds. Further water molecules can be hydrogen-bonded to the OH layers of the surface if the internal space is large enough to permit this. Such binding is much weaker. The water loss from rock glasses is shown by the thermal curves within the range 25–350°.

Inclusion water involves the most primitive form of appearance of water in minerals, with no special chemical or physical reason for its occurrence. In the case of unpulverized samples, removal of the water can be revealed by TG investigation (Fig. 2).

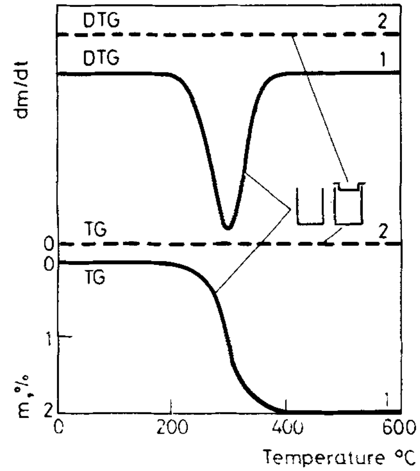


Fig. 2 Decomposition of unpulverized barite. Curve 1, plotted with uncovered crucible. Weight loss caused when exploding grains jumped from the crucible. Curve 2, with covered crucible.

Water bound in solid solution. Here, the ions do not occupy the entire space, thereby permitting the presence of 2–3 water molecules, as observed with $BaSO_4$ [2]. The escape of water molecules from their fixed positions is possible only if the process of self-diffusion within the crystal achieves a considerable rate. This process usually takes place at about the Tamman temperature.

The rapid departure of such water can also be caused by a change in a modification of the mineral; during the rearrangement of the lattice elements, the water bound by occlusion is liberated. Figure 3 illustrates such an example. Aragonite is transformed into calcite at 450°. The 450° peak in the DTA curve is due to this tranformation, the weight loss of 1.5% relating to the loss of water bound by occlusion.

In the case of zeolites and perlites, water escapes at higher than 900°. This can be considered as confined water from the silicate melts.

Crystal water is an integral and stoichiometric part of the structure. Cations within an aqueous solution coordinate water molecules, and are built into the lattice as aquo complexes in the course of precipitation of the mineral. On heating, this water generally escapes at low temperatures in several, more or less overlapping stages. Due to the overlapping, discrepancies are to be found among the reported data on such reactions.

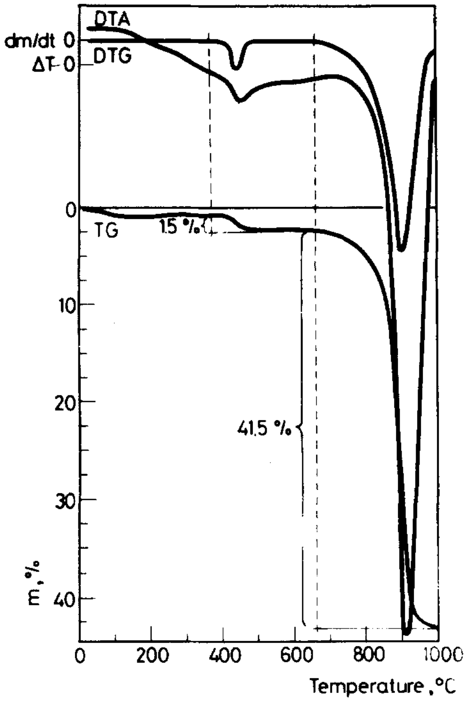


Fig. 3 TG, DTG and DTA curves of aragonite.

For example, the TG curve of chalcanthite in Fig. 4 indicates that the dehydration is a two-stage process. In contrast, the simultaneously recorded DTG and DTA curves clearly demonstrate that it is a three-stage process, where the first two steps of the dehydration can strongly overlap, depending on the circumstances. New infomation can be obtained by means of the derivatograph under quasi-isobaric and quasi-isothermal conditons [3, 4]. The Q-TG curve recorded by using a labyrinth crucible [3, 4] reveals that, under optimal conditions, the first two dehydration processes can be completely separated; they take place isothermally, leading to equilibrium, whereas the third process does not.

If the Q-DTG and Q-DTA curves are also plotted [5, 6], we obtain further information (Fig. 5.). With regard to the phase diagram in Fig. 6, the transformation process can be explained as follows. Between room temperature and 95°, there is no change (section A–B). According to the phase diagram, at 95° $CuSO_4 \cdot 5H_2O$ melts incongruently (indicated by the DTA peak with 95° onset temperature), and solid $CuSO_4 \cdot 3H_2O$ and a

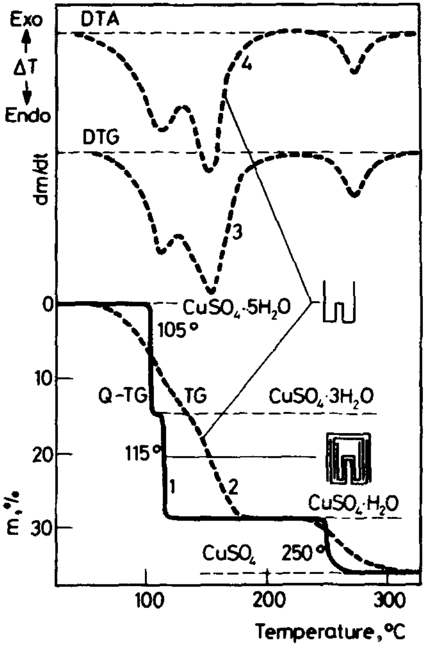


Fig. 4 Dynamic TG, DTG, DTA and Q-TG curves of chalcanthite.

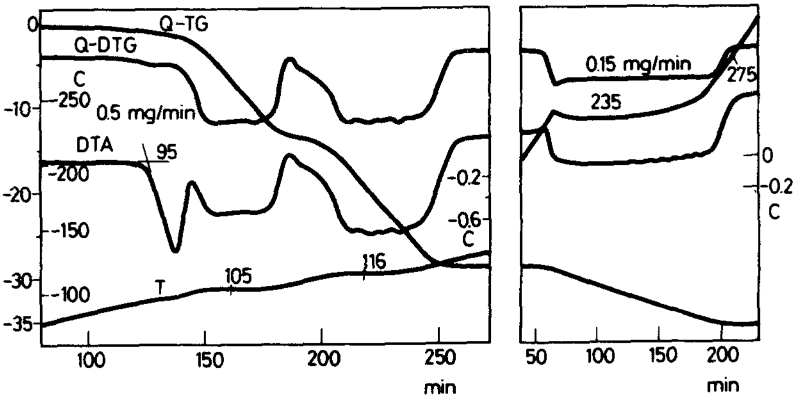


Fig. 5 Q-TG, Q-DTG and Q-DTA curves of chalcanthite.

satured solution are formed (point B). Weight loss starts only at 105°, when the saturated solution begins to boil (point C). Below this temperature, water cannot escape from the labyrinth crucible. The temperature then remains unchanged, and the solution is gradually concentrated until solid $CuSO_4 \cdot 3H_2O$

separates out (section C–D). The temperature is raised to 116° isothermally, when solid $CuSO_4 \cdot 3H_2O$ also decomposes (section E–F). During this process, solid $CuSO_4 \cdot 3H_2O$ is in equilibrium with water vapour at 100 kPa. $CuSO_4 \cdot H_2O$ decomposes at 250° (section G–H).

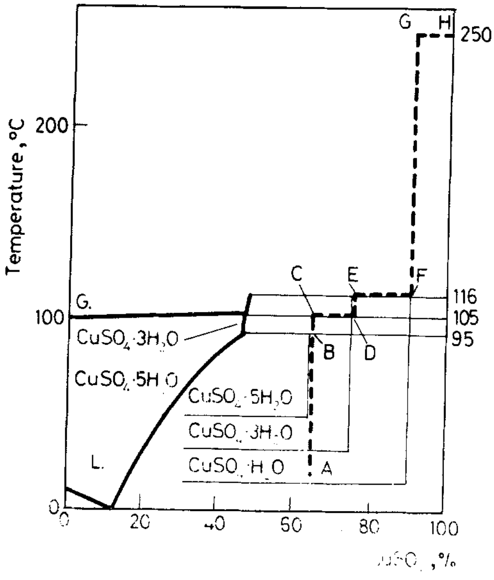


Fig. 6 Phase diagram of $CuSO_4 \cdot 5H_2O$.

Dehydroxylation. The dissociation of OH-containing compounds, providing water in the course of thermal decomposition, differs from several aspects. This is a two-step process: (i) formation of the H_2O molecule: $OH^- + OH^- = H_2O + O^{2-}$, and (ii) it is generally escape of the H_2O molecule from the crystal lattice.

It is generally impossible to separate the two steps in the thermal curves. However, simultaneous TG, DTG, DTA and IR investigations on colemanite ($CaB_3O_4(OH)_3 \cdot H_2O$) showed its dehydroxylation to be in general a two-step process.

Dehydroxylation generally takes place at a much higher temperature than dehydration, because the OH ions are strongly bound to the lattice structure through ionic or covalent bonds. There are correlations between the dissociation temperature and (i) the electronegativity of the cation to which the OH (or other anion) is attached, (ii) the number and distance of OH groups

Table 2 Dehydroxylation temperature of the different minerals

	B	Fe^{3+}	Al	Mn^{3+}	Mg	Ca
Electronegativity/After Pauling	2.0	1.8	1.5	1.5	1.2	1.0
Simple Hydroxides (H_2O = 18–43%)	Sassolite 120–210 °C		Gibbsite 270–380 °C		Brucite 410–540 °C	Portlandite 480–610 °C
Oxyhydroxides (H_2O = 10–15%)		Goethite 300–410 °C	Boehmite 450–580 °C	Manganite 310–410 °C		
Sulphates with OH-group (H_2O = 11–13%)		Jarosite 250–460 °C	Alunite 450–580 °C			
Silicates						
Phyllosilicates				Al–Mg		
1:1 layer type (H_2O = 11–13%)			Kaolinite group 490–630 °C Kaolinite 610–760 °C Dickite		Mg-Serpentines 550–690 °C Crysotile 620–770 °C Antigorite	
2:1 layer type (H_2O = 4–5%) With interlayer cation and water						
1. Smectites		Nontronite 400–510 °C	Beidellite 490–610 °C	Montmorillonite 620–780 °C	Saponite 730–900 °C	
2. Hydromicas		Glauconite 500–630 °C	Illite 520–650 °C		Ledikite 770–930 °C	
Free of interlayer cation and water			Pyrophyllite 640–800 °C		Talc 820–1000 °C	
Free of interlayer water (Micas)			Muscovite 780–950 °C		Flogopite 1100–1300 °C	

yielding water during thermal dissociation, and their position within the lattice structure (diffusion processes), and (iii) the energetic conditions of the process, influenced by the rearrangement of the residual structures.

Table 2 lists temperatures of dehydroxylation of minerals, classified according to the above criteria. The data refer to results of standard measurements, and within the 1–1000 mg range indicate the temperature shifts due primarily to the partial pressure of the escaping gas [8].

The Table clearly shows that a decrease in electronegativity of the cation results in an increase in strength of the bond, and accordingly in an increase in the dissociation temperature [9]. Let us consider row 2 in the Table. In the oxide-hydroxides, the OH groups are more distant from each other than in the simple hydroxides, and require a higher temperature for transformation into water. The dehydroxylation process of phyllosilicates well reflect their structural differences. For the different structural types, however, the electronegativity of the cation directly bonded to the OH group is of primary importance. The different sequences of layers of polytypes generally determine the thermoanalytical domain, thereby leading to differences in intracrystalline pressure, which influence the dehydroxylation [10].

The quasi-isothermal heating techniques are suitable for obtaining information on the features of water loss. The loss of adsorbed water from the internal spaces is not an equilibrium reaction, and the dehydration curves from quasi-isothermal heating techniques are always essentially nonisothermal (Fig. 7).

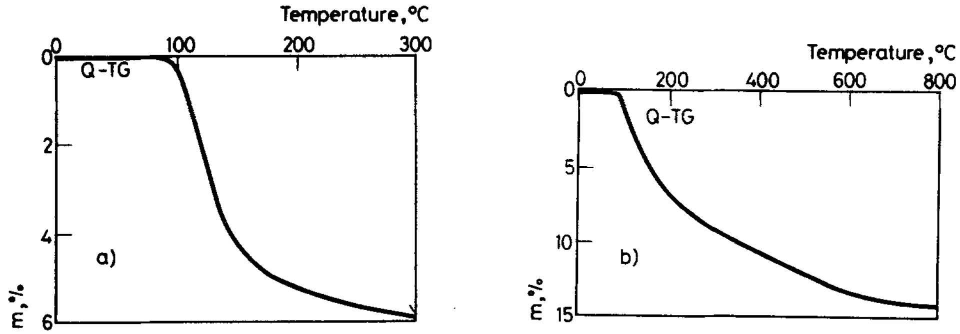


Fig. 7 Q-TG curves of water bound on surfaces of internal spaces. a: interlayer water of montmorillonite, b: zeolitic water in mordenite.

Similarly to the loss of crystal water, dehydroxylation essentially is an isothermal process, striving for equilibrium (see Fig. 8, portlandite). In more complicated structures, when the formation of water from the OH groups is hindered by the conditions, and where the diffusion processes play a greater role in the formation and loss of water molecules, the order of the reaction is increasingly further from zero. This phenomenon can be well followed in the Q-TG curves of boehmite, kaolinite and pyrophillite in Fig. 8.

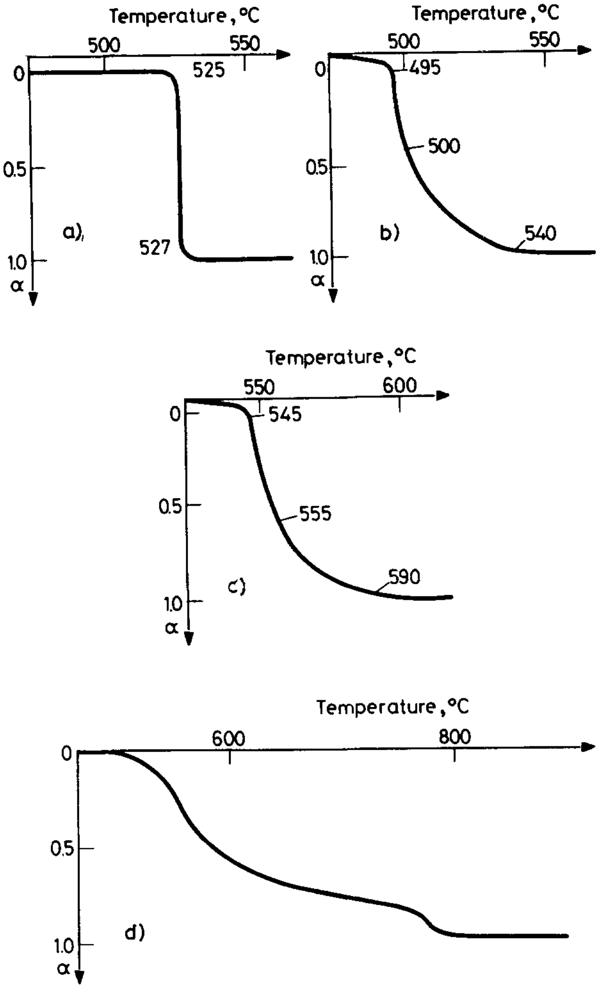


Fig. 8 Q-TG curves of different dehydroxylation processes, a: portlandite, b: boehmite, c: kaolinite, d: pyrophillite.

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Zusammenfassung – Es wurden verschiedene Bindungstypen von Wasser untersucht. Wasser kann unter anderem durch Einschlüsse, Adsorption, Kapillarkondensation, Chemisorption und in Form von Mischkristallen, zeolitisch, schichteingebettetem und Kristallwasser sowie als OH-Form gebunden sein. Die Untersuchung dieser zahlreichen Bindungstypen ist äußerst schwierig, da die Wasserabgabe bei verschiedenen Temperaturen geschieht und die ziemlich breiten Temperaturintervalle mehr oder weniger überlappen. Mittels quasiisothermen und quasiisobaren Meßtechniken wurde versucht, die Möglichkeit der Bestimmung zu verbessern.

РЕЗЮМЕ — Изучены различные типы связанной воды. Среди различных типов молекул воды, связанной окклюзией, адсорбцией, капиллярной конденсацией, хемисорбцией, найдена структурная вода в виде твердого раствора, цеолитной межслоевой, кристаллической и в виде OH-формы. Дифференциация всех типов связанной воды довольно трудная задача, поскольку выделение воды происходит в широкой области температур, интервал которых в большей или меньшей мере перекрывается. Путем использования квазиизотермических квазиизобарических методов измерения, были предприняты попытки улучшить обнаружение различных типов связанной воды.