

*Dedicated to Prof. Dr. H. J. Seifert on the occasion of his 60<sup>th</sup> birthday*

## **REHYDROXYLATION OF CLAY MINERALS AND HYDRATION IN ANCIENT POTTERY FROM THE 'LAND OF GESHUR'**

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Rehydroxylation of clay minerals and hydration in Bronze and Iron Age pottery from the 'Land of Geshur' (east of the Sea of Galilee), were investigated by IR thermospectrometry. A weak OH band, which resembles those in smectite or illite, exists in most samples, but it is masked by the water bands at lower temperature. Two types of transformation of clay minerals occur during firing of raw materials, reversible and nonreversible dehydroxylation, taking place at a relatively low and high firing temperatures, respectively.

Clay minerals rehydroxylate and reconstruct after relatively higher firing temperatures in noncalcareous raw materials than in calcareous ones. These processes take place after higher temperatures in cooking pots made from the former type of raw material as compared with storage and table-ware vessels made from the latter.

The absorbed water in the pottery is mainly connected with the dominant X-ray amorphous matter formed by the firing process.

During the firing of raw materials to pottery, processes of dehydration and dehydroxylation of clay minerals, as well as formation of X-ray amorphous matter, usually occur [1]. It is well known that after firing, some clay minerals in the fired matter may rehydroxylate and reconstruct [2, 3]. The most careful study of these processes by complementary methods was made for triphormic dioctahedral clay minerals [3]. In illite and smectite, rehydration and rehydroxylation occur at room temperature, after being dehydrated and dehydroxylated by heating to temperatures as high as 800<sup>o</sup>. Those processes include both picking up of adsorbed water and recovery of lattice hydroxyl groups. The rehydration of interlayer water in smectite is limited

due to penetration of small ions into empty octahedral sites and 'fixation' of these ions when heated above 450°. Removal of the recombined hydroxyl may take place at slightly lower temperature than that of the original hydroxyl [2].

The presence of expandable phyllosilicates in ancient sherds fired at low temperature has been noted [4–6] and explained as a rehydration with respect to the reconstitution process of primary montmorillonite, which was partially decomposed during firing. Another process, neoformation of smectite from the amorphous glass phase in the fired pottery, was observed in cooking pots and was related either to formation during use or in water-saturated soils [7].

Using results for pure clays [2, 3], it is interesting to follow the rehydroxylation and rehydration process after a long period of time, in ancient pottery that was heated to relatively high temperatures. This paper deals with pottery of the Intermediate Bronze (about 2200–2000 B.C.E.) and Iron Ages (about 1100–900 B.C.E.) from the 'Land of Geshur'. Geshur is the name of the Biblical kingdom that was located in southern Golan, east of the Sea of Galilee [8].

## Experimental

### *Samples*

Pottery from Bronze and Iron Age were collected from three sites: Tel-Hadar, Tel-Soreg and En-Te'enah in the 'Land of Geshur'. The pottery was excavated in the framework of 'Land of Geshur Archaeological Project' [8]. The samples included both bulk pottery powder and clay fractions which were separated from the tempers of the pottery (the sandy fraction) by crushing the sample (without grinding), followed by dissolution of the carbonate by HCl, ultrasonic treatment and repeated decantation and leaching until complete dispersion of the clay.

### *Methods*

The samples were investigated by IR thermospectrometry. The spectra were recorded using a Nicolet ZDX FT-IR spectrometer. Disks were prepared using 5 mg of the sample and 150 mg of KBr. These concentrated disks provided an opportunity to observe relatively weak OH bands in the

pottery after partial rehydroxylation. The mixtures were ground manually in an agate mortar and pressed into disks.

The spectra were recorded immediately after the preparation of the disks and also after heating to 110, 250, 300, 350, 400, 450, 500 and 550° for 24 h. Strong water absorption by the amorphous pottery matter during disk preparation prevents the study of dehydration and dehydroxylation by drying the pottery before preparing the KBr disks. Therefore, the pottery was investigated by heating the samples directly inside the KBr disks, despite the fact that at elevated temperature reaction of clay with KBr may occur [9]. Each heated disk was repressed before running in order to improve the resolution of the spectra.

## Results

Representative IR spectra of hydroxyl and water bands are shown for clay fractions of the pottery (Fig. 1) and bulk powder samples (Fig. 2) after heating the disks at different temperatures. The hydroxyl in the pottery has a relatively weak and narrow stretching band (Figs 1a, 2a), which at lower temperature is masked by the overlapping strong wide H<sub>2</sub>O stretching band. After drying the disks at an elevated temperature, the H<sub>2</sub>O band decreases and the OH band becomes visible. The OH band is stronger in the clay fraction of the pottery than in the bulk one which is characterized by a more complex composition. In some pottery only traces of OH were detected (Fig. 1b) and in a few there was no OH at all (Fig. 2b).

The relative amounts (in percentages) of hydroxyl and water under various temperatures are presented in Tables 1 and 2 for the Bronze and Iron Ages pottery from three sites: Tel-Hadar, Tel-Soreg and En-Te'enh. These relative amounts were calculated from the area of each band in the IR spectra as measured by integration, and normalized to the strongest band of hydroxyl or water, respectively. The strongest bands of water were taken after removing the moisture at 110° and those of hydroxyl were taken after diminishing the water at 300–400°.

As expected, the amounts of water and hydroxyl decrease with temperature. Various pottery show nearly the same changes in each temperature.

– At 110°: The H<sub>2</sub>O band is strong and wide. It is sometimes accompanied by a weak shoulder connected with an OH band;

– At 250°: The relatively strong OH bands are partly seen on the background of H<sub>2</sub>O band, while a weak hydroxyl band appears as a shoulder;

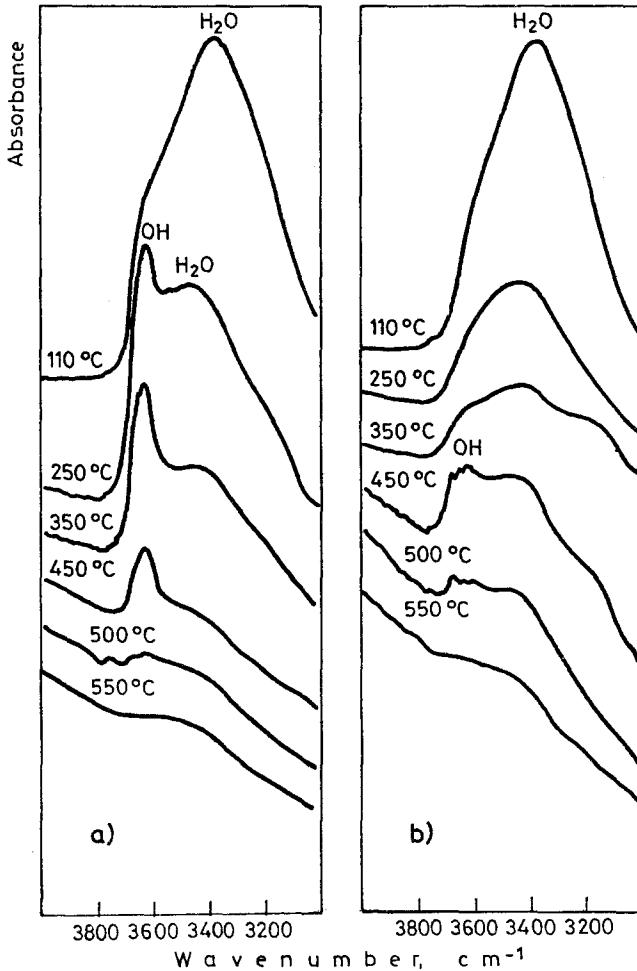


Fig. 1 Representative IR spectra of hydroxyl and water bands in the clay fraction of the pottery after heating to different temperatures: a) sample (Tel-Hadar 3) with a prominent OH band at high temperature and b) sample (En-Te'enhah 6) with a very weak OH band after the same treatment

– At 300–400°: The OH band appears most clearly in the IR spectra of the pottery. In some cases the OH bands are so weak that their traces are visible only at 450°.

– At 500°: The dehydroxylation is almost complete, but most samples contain traces of hydroxyl. Only a few samples contain traces of hydroxyl at 550°.

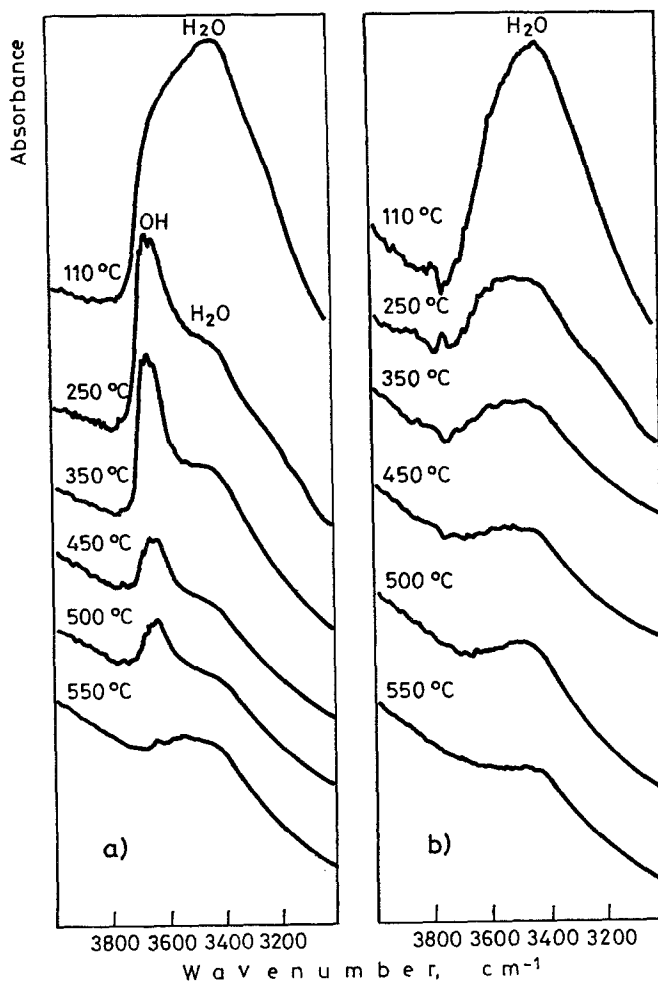


Fig. 2 Representative IR spectra of hydroxyl and water bands in the bulk pottery powder after heating at different temperatures: a) sample (Tel-Hadar 12) with a prominent OH band at high temperature and b) sample (Tel-Hadar 13) without OH band after the same treatment

In raw materials the OH band is clearly observed at room temperature and appears most predominant after treatment at 110–250°. Complete dehydroxylation occurs at slightly higher temperatures, as compared with the pottery, and only partial dehydroxylation takes place at 500°.

In most cases the OH band in the pottery is relatively broad and sometimes it splits at the maximum, while those bands in IR spectra of untreated clays are sharper and smooth.

**Table 1** Relative amounts (in percentages) of hydroxyl under various temperatures in Bronze and Iron Age pottery (bulk and clay fraction). The relative amounts of hydroxyl were calculated from the area of those bands

| Location and sample number             | Type | Temperature, °C |      |      |      |      |      |      |      |     |
|--|------|-----------------|------|------|------|------|------|------|------|-----|
|  |      | 110             | 250  | 300  | 350  | 400  | 450  | 500  | 550  |     |
| <b>INTERMEDIATE BRONZE AGE POTTERY</b> |      |                 |      |      |      |      |      |      |      |     |
| <b>-CLAY FRACTION</b>                  |      |                 |      |      |      |      |      |      |      |     |
| En-Te'enah                             | 1    | Cooking Pot     | N.O. | SH.  | P.O. | 100  | 88   | 69   | TR.  | 0   |
|  | 2    | Cooking Pot     | SH.  | P.O. | P.O. | 100  | 92   | 73   | 13   | TR. |
|  | 3    | Cooking Pot     | SH.  | P.O. | P.O. | P.O. | 100  | 74   | TR.  | 0   |
|  | 4    | Cooking Pot     | SH.  | P.O. | P.O. | 100  | 83   | 49   | TR.  | 0   |
|  | 5    | Cooking Pot     | N.O. | SH.  | P.O. | P.O. | 100  | 80   | TR.  | 0   |
|  | 6    | Storage Jar     | N.O. | N.O. | SH.  | SH.  | V.W. | V.W. | TR.  | 0   |
|  | 7    | Storage Jar     | N.O. | N.O. | SH.  | SH.  | V.W. | TR.  | 0    | 0   |
| Tel-Soreg                              | 1    | Storage Jar     | N.O. | N.O. | SH.  | SH.  | V.W. | V.W. | TR.  | 0   |
|  | 2    | Storage Jar     | N.O. | N.O. | N.O. | N.O. | N.O. | N.O. | N.O. | -   |
|  | 3    | Cup             | SH.  | P.O. | P.O. | 100  | 90   | 79   | TR.  | TR. |
|  | 4    | Holemouth Jar   | N.O. | SH.  | V.W. | V.W. | V.W. | TR.  | 0    | 0   |
| <b>-BULK POTTERY POWDER</b>            |      |                 |      |      |      |      |      |      |      |     |
| Tel-Soreg                              | 5    | Cooking Pot     | SH.  | P.O. | P.O. | 100  | 88   | 51   | TR.  | 0   |
|  | 6    | Cooking Pot     | N.O. | SH.  | P.O. | 100  | 83   | 36   | 0    | 0   |
|  | 7    | Storage Jar     | N.O. | N.O. | SH.  | V.W. | V.W. | V.W. | TR.  | 0   |
|  | 8    | Cup             | N.O. | N.O. | N.O. | SH.  | V.W. | TR.  | 0    | 0   |
|  | 9    | Holemouth Jar   | SH.  | P.O. | P.O. | P.O. | 100  | 74   | 36   | TR. |
| <b>IRON AGE POTTERY</b>                |      |                 |      |      |      |      |      |      |      |     |
| <b>-CLAY FRACTION</b>                  |      |                 |      |      |      |      |      |      |      |     |
| Tel-Hadar                              | 1    | Cooking Pot     | SH.  | P.O. | 100  | 100  | 83   | 55   | TR.  | 0   |
|  | 2    | Cooking Pot     | SH.  | P.O. | 100  | 100  | 90   | 41   | TR.  | 0   |
|  | 3    | Cooking Pot     | SH.  | P.O. | 100  | 100  | 75   | 44   | TR.  | 0   |
|  | 4    | Cooking Pot     | SH.  | P.O. | 100  | 100  | 78   | 49   | TR.  | 0   |
|  | 5    | Cooking Pot     | N.O. | SH.  | P.O. | 100  | 76   | 31   | 0    | 0   |
|  | 6    | Krater          | SH.  | P.O. | 100  | 100  | 85   | 55   | 14   | TR. |
|  | 7    | Krater          | SH.  | P.O. | 100  | 100  | 82   | 79   | TR.  | 0   |
|  | 8    | Krater          | SH.  | P.O. | P.O. | 100  | 79   | 49   | TR.  | 0   |
|  | 9    | Krater          | N.O. | SH.  | V.W. | V.W. | V.W. | V.W. | TR.  | 0   |
|  | 10   | Krater          | N.O. | SH.  | V.W. | V.W. | V.W. | TR.  | 0    | 0   |
| <b>-BULK POTTERY POWDER</b>            |      |                 |      |      |      |      |      |      |      |     |
| Tel-Hadar                              | 12   | Cooking Pot     | SH.  | P.O. | 100  | 100  | 85   | 50   | 15   | 0   |
|  | 13   | Cooking Pot     | N.O. | N.O. | N.O. | N.O. | N.O. | N.O. | N.O. | -   |
|  | 14   | Cooking Jug     | N.O. | N.O. | N.O. | N.O. | N.O. | N.O. | N.O. | -   |
|  | 15   | Jug             | N.O. | N.O. | SH.  | V.W. | V.W. | TR.  | 0    | 0   |
|  | 16   | Storage Jar     | N.O. | N.O. | N.O. | N.O. | N.O. | N.O. | N.O. | -   |

N.O. = Not Observed; P.O. = Partly Observed; V.W. = Very Weak; SH. = Shoulder;

**Table 2** Relative amounts (in percentages) of water under various temperatures in Bronze and Iron Age pottery (bulk and clay fraction). The relative amounts of water were calculated from the area of those bands

| Location and sample number             | Type | Temperature, °C |     |     |     |     |     |     |   |
|--|------|-----------------|-----|-----|-----|-----|-----|-----|---|
|  |      | 110             | 250 | 300 | 350 | 400 | 450 | 500 |   |
| <b>INTERMEDIATE BRONZE AGE POTTERY</b> |      |                 |     |     |     |     |     |     |   |
| <b>-CLAY FRACTION</b>                  |      |                 |     |     |     |     |     |     |   |
| En-Te'enah                             | 1    | Cooking Pot     | 100 | 42  | 30  | 24  | 12  | 11  | 9 |
|  | 2    | Cooking Pot     | 100 | 43  | 31  | 24  | 15  | 10  | 9 |
|  | 3    | Cooking Pot     | 100 | 40  | 36  | 22  | 11  | 10  | 9 |
|  | 4    | Cooking Pot     | 100 | 42  | 24  | 22  | 13  | 6   | 4 |
|  | 5    | Cooking Pot     | 100 | 34  | 28  | 26  | 16  | 14  | 9 |
|  | 6    | Storage Jar     | 100 | 35  | 29  | 25  | 12  | 11  | 5 |
|  | 7    | Storage Jar     | 100 | 31  | 14  | 12  | 6   | 5   | 3 |
| Tel-Soreg                              | 1    | Storage Jar     | 100 | 38  | 34  | 30  | 12  | 7   | 3 |
|  | 2    | Storage Jar     | 100 | 30  | 22  | 20  | 10  | 6   | 4 |
|  | 3    | Cup             | 100 | 45  | 34  | 31  | 16  | 14  | 9 |
|  | 4    | Holemouth Jar   | 100 | 28  | 20  | 15  | 9   | 7   | 3 |
| <b>-BULK POTTERY POWDER</b>            |      |                 |     |     |     |     |     |     |   |
| Tel-Soreg                              | 5    | Cooking Pot     | 100 | 43  | 32  | 14  | 8   | 8   | 5 |
|  | 6    | Cooking Pot     | 100 | 45  | 38  | 19  | 15  | 12  | 6 |
|  | 7    | Storage Jar     | 100 | 44  | 34  | 12  | 9   | 6   | 4 |
|  | 8    | Cup             | 100 | 35  | 25  | 12  | 9   | 6   | 5 |
|  | 9    | Holemouth Jar   | 100 | 36  | 25  | 19  | 10  | 7   | 5 |
| <b>IRON AGE POTTER</b>                 |      |                 |     |     |     |     |     |     |   |
| <b>-CLAY FRACTION</b>                  |      |                 |     |     |     |     |     |     |   |
| Tel-Hadar                              | 1    | Cooking Pot     | 100 | 49  | 33  | 24  | 9   | 6   | 5 |
|  | 2    | Cooking Pot     | 100 | 42  | 24  | 20  | 9   | 5   | 5 |
|  | 3    | Cooking Pot     | 100 | 30  | 17  | 12  | 8   | 4   | 3 |
|  | 4    | Cooking Pot     | 100 | 28  | 18  | 16  | 9   | 7   | 6 |
|  | 5    | Cooking Pot     | 100 | 47  | 20  | 14  | 7   | 6   | 3 |
|  | 6    | Krater          | 100 | 54  | 29  | 25  | 16  | 8   | 7 |
|  | 7    | Krater          | 100 | 25  | 23  | 20  | 15  | 12  | 7 |
|  | 8    | Krater          | 100 | 28  | 23  | 12  | 8   | 3   | 3 |
|  | 9    | Krater          | 100 | 49  | 22  | 15  | 9   | 4   | 4 |
|  | 10   | Krater          | 100 | 34  | 14  | 10  | 8   | 4   | 1 |
| <b>-BULK POTTERY POWDER</b>            |      |                 |     |     |     |     |     |     |   |
| Tel-Hadar                              | 12   | Cooking Pot     | 100 | 26  | 18  | 16  | 9   | 6   | 5 |
|  | 13   | Cooking Pot     | 100 | 35  | 25  | 20  | 14  | 10  | 6 |
|  | 14   | Cooking Jug     | 100 | 33  | 23  | 16  | 9   | 8   | 5 |
|  | 15   | Jug             | 100 | 30  | 20  | 11  | 8   | 6   | 5 |
|  | 16   | Storage Jar     | 100 | 36  | 24  | 17  | 9   | 5   | 5 |

In none of the spectra were OH bands of kaolinite detected. Similar results were obtained by X-ray diffraction, where diffractions of smectite and/or illite (or collapsed smectite) were detected in clay fractions of some pottery [10]. The clay fraction of this pottery contains mainly X-ray amorphous matter and in some cases high temperature silicates.

## Discussion

### *Hydroxyl in the pottery*

The presence of weak hydroxyl bands in the IR spectra of pottery indicates that clay minerals are present only in small amounts. The shape and location of the OH stretching band in the spectra resemble the OH bands in smectite or illite [11]. The relative broadness of the bands in our samples and the splitting at the maximum, indicate a low degree of crystallinity [10].

Some possible sources of the clay minerals in the pottery are:

- Original clay minerals that were fired at low temperature, but remained stable in the fired matter and did not dehydroxylate;
- Reconstructed clay minerals which were dehydroxylated at the firing temperature and later rehydroxylated;
- Neofomed clay minerals from the amorphous glass phase of the fired pottery (devitrification);
- Decomposing of high temperature Ca-plagioclase and forming Ca-montmorillonite and calcite, by weathering reactions when pottery was buried.

There are several indications that most of the clay minerals in the examined pottery were reconstructed:

- The low intensity of OH bands in most of the pottery and predominance of X-ray amorphous matter indicate that the firing temperatures were high enough for complete dehydroxylation of the original clay minerals.
- The absence of clay minerals in some pottery containing amorphous matter, the small and different quantities of them in pottery excavated in the same place and period, as well as their low crystallinity, indicate that neofomation of clay minerals from the amorphous glass phase in the fired matter did not occur.
- The appearance of clay minerals in pottery that do not contain high temperature plagioclase, and the absence of those minerals in pottery rich



with this type of plagioclase, indicate that transformation of plagioclase to montmorillonite during burial are not predominant.

The slightly lower dehydroxylation temperature of the pottery samples compared with possible original raw materials, is typical for reconstructed clay minerals [2]. Since the dehydroxylation of the samples was studied by heating in KBr disks, at the temperatures at which the OH bands disappeared (about 550°), reaction between the salt and structural hydroxyls is probable ( $-\text{OH} + \text{KBr} \rightarrow -\text{OK} + \text{HBr}$ ), which also could influence the dehydroxylation process [9]. Similarly, since the pottery and raw materials were treated in the same conditions, we assume that the earlier dehydroxylation is evidence of reconstruction.

The rehydroxylation of clay minerals in the pottery depends on the firing temperature. Experimental data demonstrate that two types of transformation of clay minerals take place depending on the conditions of firing the raw materials to pottery:

- Reversible dehydroxylation takes place at relatively low firing temperatures. This process allows the reconstruction of clay minerals by rehydroxylation after firing.

- Nonreversible dehydroxylation takes place at relatively higher firing temperatures. This process does not allow rehydroxylation and reconstruction of clay minerals after firing.

As the temperature of firing increases, the extent of the reversible dehydroxylation decreases and the extent of the nonreversible dehydroxylation increases. The pottery examined contains small amounts of clay minerals and large amounts of X-ray amorphous matter, indicating that the main process on firing was nonreversible dehydroxylation. However, in some decomposed clay minerals reversible dehydroxylation occurs and results in reconstructed clay minerals in the pottery.

The reversible or nonreversible nature of the process may depend on the following factors:

- The group of precursor clay mineral in the fired matter. Kaolinite dehydroxylates at a lower temperature than smectite, and illite [12].

- The cations presence in the octahedral sheet (bonded to the  $\text{OH}^-$  ions) in smectite group. Generally, the temperature of dehydroxylation varies, depending on the cation in the following way:  $\text{Mg}^{2+} > \text{Al}^{3+} > \text{Fe}^{2+} > \text{Fe}^{3+}$ . However, most smectites contain primarily  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$ , and their structure is preserved up to 550° [12].

– The degree of crystallinity in each group of clay minerals in the raw materials. Clay minerals with a higher degree of crystallinity dehydroxylate at a higher temperature [10].

It is expected that reversible dehydroxylation will be more frequent in clay minerals which are stable up to higher temperatures. Raw materials usually contain different groups of clay minerals and each group may present various degrees of crystallinity. Therefore, it is possible that even at relatively high firing temperatures some stable and well crystallized clay minerals undergo reversible dehydroxylation, and later reconstruct, while most of the clay minerals in the fired matter undergo nonreversible dehydroxylation and remain amorphous, or partly react to form high temperature silicates.

The nature of the process probably depends on the intensity of the destruction of the clay minerals during the firing. It seems that in the case of a reversible dehydroxylation, the fundamental structure of the clay minerals is preserved in the fired matter, although it becomes amorphous to X-ray diffraction. This preservation of fundamental structure facilitates the rehydroxylation and reconstruction, although the reconstructed clay minerals have a lower degree of crystallinity than the original material [10]. This may be the reason for the slightly lower dehydroxylation temperatures of the reconstructed clay minerals, compared with those in the raw material. On the other hand, it seems that in the case of nonreversible dehydroxylation, the progressive amorphisation prevents the reconstruction of clay minerals. As will be shown, formation of high temperature minerals in the pottery is also an obstacle to reconstruction.

As a results, it may be concluded that the amounts of hydroxyl in the pottery (Table 1) and the reconstructed clay minerals depend on the reversible dehydroxylation, due to the degree of destruction of clay minerals in the fired matter. The extent of clay minerals destruction increases with temperature and decreases with degree of crystallinity. The changes in the rate of dehydroxylation of the reconstructed clay minerals in the pottery probably depends on their degree of crystallization. Badly crystallized reconstructed clay minerals undergo dehydroxylation at lower temperatures. It is expected that with the increasing temperature the destruction of clay minerals increases and the crystallinity of reconstructed clay minerals decreases.

#### *Water in the pottery*

The pottery contains a relatively large amount of water that is preserved at relatively high temperatures (Table 2). There are two possible sources for

the water in the pottery, the adsorbed water on amorphous matter and the interlayer water in expandable reconstructed clay minerals.

Since most pottery examined contains mainly X-ray amorphous matter and only some amount of reconstructed smectite and/or illite, the hydration of pottery is mainly connected with the former rather than with the latter. Amorphous matter has a very large active surface that adsorbs water very strongly and retains it to relatively high temperatures. The amount of amorphous matter depends on the firing temperature and, consequently, on the destruction of clay minerals in the fired matter.

The changes in the rate of dehydration of the pottery may depend on the type of amorphous matter present. Each amorphous variety may hold different amounts of adsorbed water and retains it with different strength. On the other hand, crystallization of high temperature silicates may decrease the amount of adsorbed water and retain it to lower temperatures. Formation of those minerals in the fired matter increases with temperature and consequently reduces the amount of amorphous matter in the pottery and the amount of adsorbed water.

It may be concluded that as firing temperature increases, the amount of adsorbed water firstly increases due to the formation of amorphous matter, and later decreases due to crystallization.

#### *Rehydroxylation and rehydration in calcareous and noncalcareous pottery*

Two main types of raw materials were used for the investigated pottery: calcareous and noncalcareous clays [10]. The lime content in the raw materials may influence the rehydroxylation and rehydration processes:

– In calcareous raw materials at high firing temperature lime reacts with the clay, and forms high temperature Ca-silicates [13–15].

– In noncalcareous raw materials the decomposed clay minerals do not undergo noticeable changes up to very high temperatures, where they crystallize, forming mullite or other high temperature silicates.

The formation of high temperature minerals reduces the amount of X-ray amorphous matter in the pottery. This process prevents reversible dehydroxylation and reconstruction of clay minerals in the pottery. Therefore, the rehydroxylation process and reconstruction of clay minerals take place in noncalcareous pottery after higher temperatures than in calcareous one. Consequently, the amount of adsorbed water decreases by the formation of high temperature minerals. Therefore, the amount of adsorbed water reduces in calcareous pottery at lower temperatures than in noncalcareous ones. As expected among the pottery examined, clay minerals were not

detected in samples rich with high temperature Ca-silicates and that pottery contains relatively small amounts of water.

The pottery examined demonstrated that certain raw materials were selected for the certain types of vessels. Noncalcareous matter was used for cooking pots, while calcareous matter was preferable for the storage and table-ware vessels. Therefore, it seems that in cooking pots rehydroxylation and reconstruction may occur after firing at relatively higher temperatures. In accordance with expectations, these vessels do have more intense hydroxyl bands than the other types (Table 1).

### Conclusions

The presence of weak hydroxyl bands in the IR spectra of the pottery indicates the presence of clay minerals, smectite and/or illite, in small amounts.

Two types of dehydroxylation processes may occur according to the firing temperature of the pottery:

– Reversible dehydroxylation takes place at a relatively low firing temperature. It seems that in this process the fundamental structure of clay minerals is preserved in the fired matter, although those minerals become amorphous to X-ray diffraction. This process allows reconstruction of clay minerals by rehydroxylation after the firing.

– Nonreversible dehydroxylation takes place at relatively higher temperatures. It seems that in this process the destruction of clay mineral structure to amorphous matter progressed so much that reconstruction of clay minerals is impossible. Formation of high temperature minerals in the pottery also prevents reconstruction.

Firing at relatively high temperatures leads to a higher destruction of the clay minerals, and consequently decreases the amount of reconstructed clay minerals and their degree of crystallinity and increases the dehydroxylation rate of the reconstructed clays.

As the temperature of the firing increases, the extent of reversible dehydroxylation decreases and that of the nonreversible increases. Most pottery examined contains low amounts of clay minerals and mainly X-ray amorphous matter. Therefore, it may be concluded that the main process on firing of this pottery was nonreversible dehydroxylation. But some original stable and well crystallized clay minerals were reversibly dehydroxylated and are represented by reconstructed clay minerals in the pottery investigated.

The rehydroxylation process and reconstruction of clay minerals take place in noncalcareous pottery after firing at higher temperature than in calcareous ones. In the latter, lime reacts under firing conditions with clay and forms high temperature Ca-silicates. As a result, the clay fundamental structure is not preserved. Compared with storage and table-ware vessels made from calcareous materials, noncalcareous cooking pots may rehydroxylate and reconstruct at a relatively high firing temperature.

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**Zusammenfassung** — Mittels IR-Thermospektrometrie wurde die Rehydroxylierung von Tonerdemineralien und die Hydratierung in Geschirr aus dem Bronze- und Eisenzeitalter, aus dem "Land der Geshur" (Osten des Galiläischen Meeres) untersucht. Eine schwache OH-Bande, die denen in Smektit oder Illit ähnelt, existiert in den meisten Proben, es wird aber bei niedrigeren Temperaturen durch Wasserbanden verdeckt. Während des Brennens

von Rohmaterial finden zweierlei Umwandlungen der Tonerdemineralien statt, bei relativ niedrigen Temperaturen reversible und bei relativ hohen Temperaturen nichtreversible Dehydroxylierung.

Tonerdemineralien werden in kalkfreiem Rohmaterial nach relativ höheren Brenntemperaturen rehydroxyliert und wiederaufgebaut als in kalkhaltigen. Diese Prozesse verlaufen nach höheren Temperaturen in Kochtöpfen aus ersterem Rohmaterial im Vergleich zu Vorrats- und Eßgeschirr aus letzterem Material.

Das in der Töpferware adsorbierte Wasser ist in erster Linie an dem beim Brennprozeß gebildeten, röntgenmäßig amorphen Material gebunden.