CHAPTER 7

THERMAL ANALYSIS

This chapter deals with the differential thermal analysis (DTA) of the pottery specimens recovered from stratified layers of excavations at Vagad and Nageswar. Besides pottery, a sample of clay from Nageswar was also analysed. The chapter contains the survey of literature on the effects of heat on clays and a discussion of the results of thermal analysis of these samples.

The differential thermal analysis involves recording the difference in temperature between a substance which is thermally active and a reference material like aluminium oxide which is thermally inert as the two specimens are subjected to identical temperature regimes in an environment heated or cooled at a controlled rate (MacKenzie 1970:4).

7.1 Effect of heat on clays

Chemical, mineralogical and structural changes that take place in the clay during the process of its firing have been extensively studied by various scholars (Grim et al. 1948, Comeforo et al. 1948, Brindley et al. 1960).
Hill 1960, Hedges 1961, Cole et al. 1962 and 1963, Freeman et al. 1968, Segnit et al. 1971 and 1972, Tite et al. 1975, Peters et al. 1978, Maggetti 1981, Heimann et al. 1981). Searle and Grimshaw (1960) have classified the reactions which take place when clays are fired. These reactions can be summarized as follows. When clay is heated, first the hygroscopic water and the physically attached water molecules are lost. The loss of hygroscopic water (moisture on the surface) is usually complete at a temperature of 110°C. The physically attached water molecules (water trapped between the tiny platy crystals of clay) are lost at a higher temperature, that is about 150°C. Many of the minerals associated with clay contain water as an inherent part of its structure. When the clay is further heated it decomposes and the water that the clay contains as a constituent part of its crystal structure is lost. This decomposition of the clay accompanied with the loss of water of crystallisation occur in different clays at different temperatures. This temperature ranges from 300°C to 800°C (Smykatz-Klozz 1974: 64-86, Searle et al. 1960: 668). Further heating of the clay leads to the crystallisation of new phases. The dehydration and structural decomposition reactions of clays are endothermic while crystallisation of new phases is exothermic. Thus DTA is used in identifying the clay minerals by studying the diagnostic changes in the clay minerals while heating.
According to Grim and Bradley (1948) some of the clays fired at a temperature at less than 800°C gradually become rehydrated and regain a measure of their original structure over a period of time. An experiment conducted by them on montmorillonite heated to 600°C, regained one quarter of its original crystal lattice water within 268 days (Grim et al 1948).

Only a few attempts have been made to analyse archaeological ceramic samples using DTA. Anna Shepard (1965) has expressed doubts about the applications of DTA on fired wares because the temperature at which the most useful and diagnostic changes take place are usually passed in the original firing and hence these characteristic heating curves are lost. But Kingery (1974) has observed some important exceptions in this and has studied the pottery from Tepe Sialk using DTA. He quotes the observations of Grim and Bradley that the clays fired at a temperature less than 800°C gradually become rehydrated and regain a measure of their original structure over a period of time and hence for those archaeological pottery specimens that are originally fired at a temperature less than 700°C - 800°C., DTA is useful. There is another study that has been carried out on some Amazonian pottery using DTA (Enriquez et al 1978), aiming at establishing the possible correlations between the hydration phenomena and observed changes in the iron oxide in the pottery.
Fig. E-1 DIFFERENTIAL THERMAL ANALYSIS CURVES OF HARAPPAN POTTERY AND CLAY SAMPLE FROM NAGESWAR
Fig. E-2 DIFFERENTIAL THERMAL ANALYSIS CURVES OF HARAPPAN POTTERY FROM VAGAD
7.2 Analysis and Results

The pottery specimens analysed included Red Ware, Buff Ware, Chocolate Slipped Ware and a vitrified sherd. Besides these, a sample of raw material, clay collected from the edge of the lake close to the excavated site at Nageswar was also analysed. The thin-section studies and x-ray diffraction analysis of these samples have been given in Chapter 4.

The differential thermal analysis was carried out by heating the samples at a rate of 20°C/min. up to 1000°C. with calcined alumina as the reference standard in nitrogen atmosphere.

The DTA curves are shown in figures E.1 and E.2. Table 6.1 gives the details of the samples and the exothermic and endothermic peaks formed at different temperatures in the DTA.

Table 6.1: Nomenclature of the Samples and the Temperatures at which Peaks are obtained.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Material</th>
<th>Site</th>
<th>Endothermic</th>
<th>Exothermic</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Sturdy Red Ware</td>
<td>Nageswar</td>
<td>150°C</td>
<td>810°C</td>
</tr>
<tr>
<td>2.</td>
<td>Chocolate Slipped</td>
<td>Nageswar</td>
<td>118°C</td>
<td>758°C</td>
</tr>
<tr>
<td></td>
<td>Ware</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Buff Ware</td>
<td>Vagad</td>
<td>110°C</td>
<td>770°C</td>
</tr>
<tr>
<td>4.</td>
<td>Buff Ware (Sample No.</td>
<td>Vagad</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3, heated</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>at 580°C for 2½ hours)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Vitrified pottery</td>
<td>Nageswar</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Clay sample</td>
<td>Nageswar</td>
<td>126°C</td>
<td>782°C</td>
</tr>
</tbody>
</table>
The first endothermic peak seen in samples number 1, 2 and 3 at 150°C, 118°C and 110°C are due to the moisture absorbed by the sherds during its burial. The clay sample (sample No. 6) shows an endothermic peak at 126°C. This is due to the loss of moisture and the physically attached water molecules in the clay sample. No endothermic peaks at these temperatures was observed in the case of samples 4 and 5. Sample number 4 was heated at 580°C for 2½ hours before doing DTA. The second endothermic peak that was observed in samples number 1, 2, 3, 4 and 6 at temperatures 810°C, 758°C, 770°C, 780°C and 782°C respectively (Table 6.1) are due to the decomposition of calcite. In the case of vitrified pottery an endothermic peak was noticed at 1020°C. The clay sample (sample No. 6) shows an exothermic peak at 390°C. Mac Kenzie (1970:520) describes that most of the micas give an exothermic effect at 350°C. This exothermic effect observed in the clay samples seems to be identical with that of the exothermic effect given by the micas. Besides these, a discernible hump was observed in the case of samples number 2 at 577°C and 4 and 5 at 585°C (Figure E.1 and E.2). This appears to be of quartz, that is the $\alpha \rightarrow \beta$ inversion of quartz.

7.3 Discussion

Experiments conducted by Grim and Bradley (1948) have proved that clays fired at a temperature less than
800°C, gradually become rehydrated and regain a measure of their original form over a period of time. Hence many of the archaeological ceramics originally fired in the temperature ranges below 700°C - 800°C; re-acquire many of the characteristics of an unfired clay over a period of time. Thus Kingery (1974) points out that it is possible to identify the clay mineral constituents of ancient pottery samples using DTA.

From the present analysis it appears that in none of the pottery samples clay had undergone recrystallisation during the time of its burial. Because the expected dehydration peak and decomposition peak at a temperature range of 300°C to 800°C, is missing. This is because when clay was fired at a high temperature (above 800°C) while baking the pots, the clay minerals in these samples got altered irreversibly and hence development of original nature of clay was not achieved. The x-ray diffraction analysis also revealed that the clay minerals were permanently altered (Figure B.9 to B.13). Since these changes in the clay minerals take place at above 800°C, it is possible to conclude that the baking of Harappan and Red Ware, Buff Ware, Chocolate Slipped Ware were carried out at a temperature that was higher than 800°C.
References


