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Mineralogical and Thermal Analyses of a Bangle Shard from Harrappa, an Indus Valley Settlement in Pakistan

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Abstract

The present research paper presents the results of a recent study during which mineralogical and thermal analyses were carried out on a terracotta bangle shard from Harrappa, an Indus valley settlement in Pakistan. Bentonite clay was identified as the major constituent of the bangle shard. The knowledge acquired with respect to the mineralogical structure, determined through X-ray diffraction, along with the results derived from the thermal analysis, were used to predict the value of the firing temperature of the bangle shard.

Keywords: X-ray diffraction, thermal analysis, Indus valley, bentonite clay.

Introduction

In Pakistan, Harrappa is recognized as one of the most important and magnificent sites of the Indus Valley Culture, which flourished around 2600 BC. Research carried out on this settlement has provided a wealth of information about its inhabitants and their life style. One fascinating aspect regarding Harrappa is the abundance and variety of the pottery that has been unearthed at this site. This includes everyday utensils, storage tanks for grain, toys for children, trading seals, figurines, and terracotta jewellery, including bangles, beads, and necklaces.

The ancient potters and artisans displayed great ingenuity in creating forms and styles of jewellery that were appealing to the eye and, at the same time, light-weight and tough, thus easy to wear and long-lasting. Given the use of these ornaments, it is likely that the potters employed different or especially-processed raw materials in fabricating them. In order to determine the type of materials used in making bangles in Harrappa, a specimen shard (Fig. 1) was tested using

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the technology available in the Geoscience Advance Research Laboratories (a facility of the Geological Survey of Pakistan) in Islamabad.

Fig. 1 Bangle shard photographed with Pakistani one rupee coin as reference. Diameter: 0.95-1cm, length: 5.65cm or about 2/5th of the complete bangle.

The mineralogical make-up of the clay used in the bangle shard was determined through XRD analysis, while simultaneous TG/DT analyses were carried out in order to establish the thermal properties and the nature of the phase changes that took place while the bangle was being processed. The XRD analysis was carried out using a Philips X'Pert PRO X-ray diffractometer, while the thermal analysis (TG/DTA) was carried out on a Shimadzu DTG-60H differential thermal and thermogravimetric analyzer.

Results and Discussion

The XRD analysis indicates that the mineralogical make-up of the clay used in the bangle shard includes montmorillonite ($(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$), gypsum ($CaSO_4 \cdot 2H_2O$), and quartz ($SiO_2$). The X-ray diffractogram (Fig. 2) was developed using a PW3050/60 goniometer. The generator settings were 30mA/40kV with a CuKα radiation of $\lambda = 1.5406$Å. Continuous scanning was carried out from 10.01 as 2θ start position, to 79.99 as 2θ end position, with a step size of 0.02 and a step time of 1s.

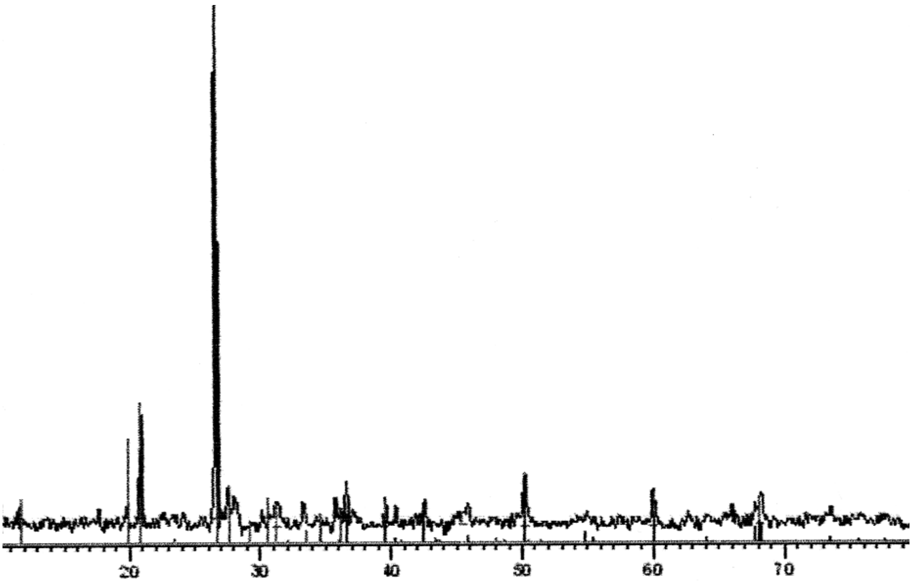

Fig. 2 X-ray diffractogram of tested specimen.

The results of the thermal analysis have been included in Figure 3. The temperature varied in steps of 20°C/min, from room temperature to 1200°C. For a sample mass of 20.32mg, a loss of 1.471mg or 7.239% was observed. There is a regular trend in mass loss over the entire heating range, which shows that the clay or clays used in the bangle shard are nearly uniform in composition and properties. Mass loss in clays during thermogravimetric analysis can be divided into three stages: dehydration from room temperature to about 200°C, decomposition of hydroxyls from 400°C to 650°C, and decomposition of carbonates in the 700-800°C range (Drebushchak et al., 2005). The TGA curve for the specimen shows mass loss occurring in three distinct steps. The initial mass loss (0.15mg) attributed to dehydration is very small, but it coincides with an endothermic peak at 139.16°C on the DTA curve. (An endothermic effect attributed to the presence of gypsum is also observed in the 100-120°C range (Moropoulou et al., 1995)). From this temperature onwards, there is a gradual mass loss of 0.75mg up to 850°C. Finally, a mass loss of 0.5mg is recorded from 850°C to 1200°C on the last portion of the TGA curve.

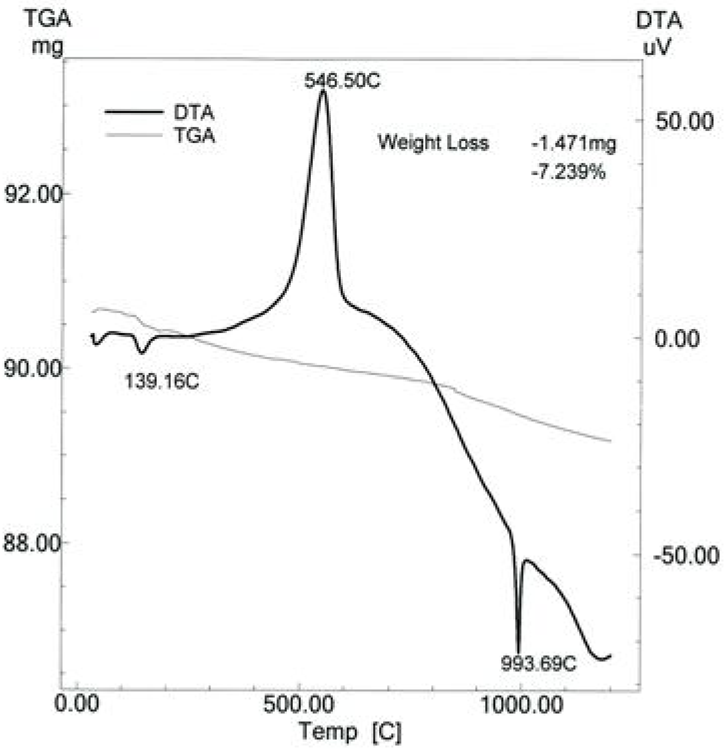

Fig. 3 Results of simultaneous TG/DT analyses.

The mass loss around 400-650°C, which coincides with a sharp exothermic peak at 546.5°C on the DTA curve, can be attributed to the combustion of organic material in the tested specimen (Moropoulou et al., 1995). This organic material may have been added by ancient potters as a binder. (From the XRD analysis, the abundance of montmorillonite and the two characteristic endothermic peaks on the DTA curve prove that the major constituent of the tested specimen is bentonite. The thermal analysis curves for the tested specimen can be compared with modern industrial bentonite (from India) and the trends are almost similar (Venkatathri, 2006). A difference (in peaks and ranges) may exist due to the addition of other components in the raw ceramic material of the bangle shard specimen.) Studies have shown that montmorillonite is destroyed when fired at a temperature of 860°C (Drebushchak et al., 2005). If montmorillonite survived the firing stage during the processing of the bangle, it appears that the temperature in the firing kiln was not above 860°C. As progress in pottery making is related to the firing temperature (the higher the firing temperature, the more advanced the technique), it is evident that the skills of ancient Harrappan potters were well-developed and fairly advanced for their time (Schomburg, 1991).

Quartz has also been detected during the XRD analysis. It is a non-plastic material, whereas bentonite is known to be very flexible and suitable for complex shapes. Quartz may have been added to the raw ceramic material as a temper, to allow water to evaporate smoothly (thus avoiding cracking) and to improve the handling of the raw clay. However, what the ancient potters of Harrappa did not know was that this addition may cause the bangles made out of this raw material to become less resistant to mechanical stress while in use.

An endothermic effect is observed starting with 600-950°C. There is a sharp endothermic peak at 993.69°C, followed by an exothermic effect at about 1020°C. The endothermic effect, especially around 800-950°C, can be attributed to the decomposition of any carbonates in the raw ceramic material used in the making of this particular bangle. Given the inability of the XRD apparatus to detect minerals less than 10wt% of the sample, no amount of calcite or dolomite, the most frequent carbonates in ancient ceramic materials, has been identified during the XRD analysis (Moropoulou et al., 1995). The endothermic peak at 993.69°C can be interpreted as an indication of the appearance of a crystalline phase (i.e. due to the vitrification of quartz) in the sample (above 800°C), which might have undergone a solid-phase polymorphic transformation at this high temperature (Krapukaityte et al., 2008; Moropoulou et al., 1995).

Conclusions

The bangle shard specimen studied in the present paper was collected from the northern side of mound AB at Harrappa. This mound is surrounded by a massive mud brick wall and excavation on this side of the mound started in 1996. It displays about 17m of vertical deposits: from the first settlement of a pre-urban village at Harrappa, to post-Harrappan abandonment. Based on the mineralogical and thermal analyses discussed above, there is sufficient evidence for the identification of bentonite clay as the main constituent of the bangle shard specimen. While preparing the ceramic mix, the potters may have combined quartz with bentonite, as a temper for easy handling and processing, and in order to improve the drying process, as well. Finally, we can identify that the bangle to which this shard belongs was fired at a temperature no lower than 860°C.

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