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Thermal analyses of selected soil samples from the tombs at the Tianma-Qucun site, Shanxi, China

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Abstract

This paper describes a study of selected soil samples from three of the tombs at the Tianma-Qucun site, Shanxi province, China, using thermogravimetry and differential scanning calorimetry. The results of the analyses indicate that these soil samples are calcite-rich and contain a few percent of organic matter. The soil from the location of one of the tombs was found to have less calcite than the soil from the other two tombs. There was, however, only a small difference in organic matter in the soils from the different tombs. Results for soil samples taken from regions in the proximity of archaeological objects, however, demonstrated that the microenvironment as characterised by the soils for objects in various locations of the one tomb varied. Some evidence for the presence of charcoal and collagen based material was found. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Burial soil; Thermogravimetric analysis (TGA); Differential scanning calorimetry (DSC); Soil samples; Tianma-Qucun China

1. Introduction

The Tianma-Qucun site, excavated between 1980 and 1995, is located in the southwest, Shanxi, province in China. The cemetery of Jin state, including 17 tombs of Jin lords was discovered at this site. The Jin state was one of vassal states of the Zhou period (1027–221 B.C.); it made fundamental contributions to the economy, commerce and industry to the Zhou, as well as to Chinese culture.

A large number of objects including bronze, jade and pottery were unearthed from the tombs. The majority of the finds were bronze artefacts. The preservation conditions of these bronze artefacts vary greatly from tomb to tomb, and even from object to object in one tomb. Soil conditions can greatly affect corrosion of buried bronzes [1,2]. In an attempt to relate corrosion to soil conditions, six soil samples were collected for the study. These samples, labelled in this paper as M91, M92, and M93, include one from the bottom of each tomb in the location where the bronze fragments were collected. The other three samples were taken from the surface of the three vessels in the tomb from where the soil sample M93 was taken, and are labelled accordingly as M93:31, M93:43, and M93:62. These samples were taken from soils surrounding the outer surface of ritual vessels. The ritual vessels were from the Chinese Bronze Age. Soil samples M93:31, M93:43 and M93:62 were taken from the soil surrounding the ritual vessel *zhong*, a wine drinking vessel, from a

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ritual vessel *hu*, a wine or water containing vessel, and from a ritual vessel *gui*, a cooking vessel.

The soil samples have been examined and data concerning their composition, pH, and redox potential have been presented elsewhere [3]. The aim of this paper is to provide further characterisation of the soils and then quantification of calcite and quartz content using thermal techniques TGA and DSC. It also aims to provide some evidence for variation in soil microenvironment in the proximity of the object and conditions which further contribute to the corrosion of bronzes in the burial environment. Thermal techniques have been previously used for the analysis of the environment at burial sites [4]. However, burial soils from archaeological sites in China have never been previously analysed.

2. Experimental

Archaeologists' methods for determination of organic matter and carbonate content of soils is usually performed by weighing samples after a prescribed thermal treatment. Organic matter of soil sample is estimated by the following procedure: 2 g of dry soil is heated at 500°C for 1 h, cooled down in a desiccator, and re-weighed, the loss in weight represents the organic matter [1]. The quantity of organic matter of the soil samples was measured using this conventional method. Total carbonate content determination is performed by measuring the total loss of carbon dioxide from the soil on heating. The sample used for measuring the organic matter is reheated at 1000°C for 1 h, cooled down in a desiccator and then re-weighed, the loss in weight then represents the loss in total amount of CO_2 evolved from the decomposition of all the carbonates present in the soil.

These methods, however, only provide information on the amount of total organic matter and total carbonates, they do not assist with the characterisation of the type of organic matter or type of carbonates which may be present. In the present study TGA was applied to characterise both the carbonate present in the soil and to quantify that carbonate in the soil. DSC was used both under oxidising and inert conditions to determine whether differences in soil type could be determined on the basis of the observed thermal processes. It is known that the quartz content of soils can be determined in this way. Characterisation of the nature of the organic matter in the soil can be made on the basis of the shape of obtained DSC curves and comparison with standard materials.

Thermogravimetry measurements were carried out using the Shimadzu TGA-50 analyser. The sample was heated in an alumina crucible up to 900°C at 10°C/min in flowing nitrogen with a rate flow of 60 cm^3/min. Differential scanning calorimetry measurements were performed using a Perkin-Elmer DSC-7 analyser. The samples were heated in alumina crucibles at 40°C/min.

3. Results and discussion

The TGA curves for the soils from the different tombs, and then the soils from the surface of different vessels in one of the tombs (M93), are shown in Figs. 1 and 2, respectively. The curves show three stages of weight loss over the temperature range ambient to 900°C. The most clearly defined weight loss is the one occurring in the final stage and which represents the expected temperature range for the decomposition of calcium carbonate. The actual temperatures at which calcite decomposes vary to some extent and depend on experimental factors such as the flow rate of the gas, and the partial pressure of the evolved gas surrounding the sample. The first two processes, which are not clearly defined, correspond to the loss of physically adsorbed moisture, which occurs up to the region of 200°C, and this is followed by the oxidation of any organic components present in soils (from about 200 to 500°C). Table 1 summarises the weight losses for each of the three stages and gives the overall weight loss as calculated from the TGA curves. Table 2 gives the calculated calcite content obtained from the weight loss in the following manner. The calcite content calculation is obtained as a percentage based on expected weight loss for calcite only (i.e. 44%) (Eq. (1)). Values are given in Table 2 and show that sample M91 contains the lowest calcite content. In general values indicate that the soils from the three tombs at Tianma-Qucun are calcite-rich.

$$\%CaCO_3 = \frac{\text{weight loss}\ (\%)}{44\%} \tag{1}$$

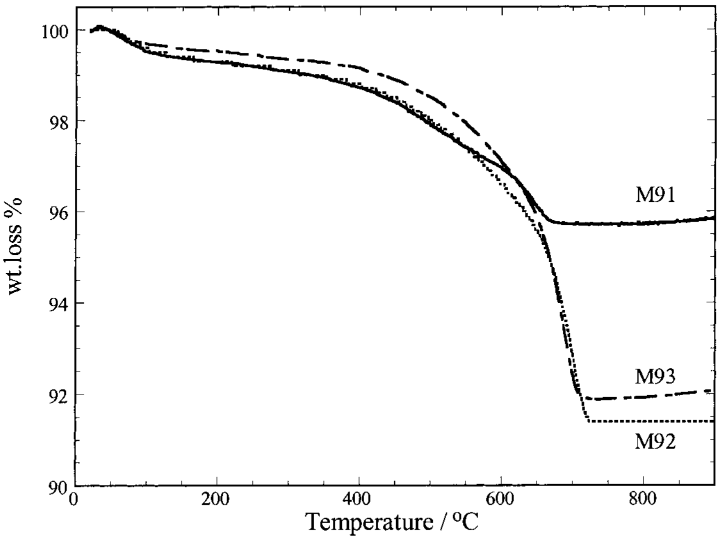

Fig. 1. TGA curves (in N_2) of the soils from different tombs, showing that the M91 soil is more complex than the other two samples.

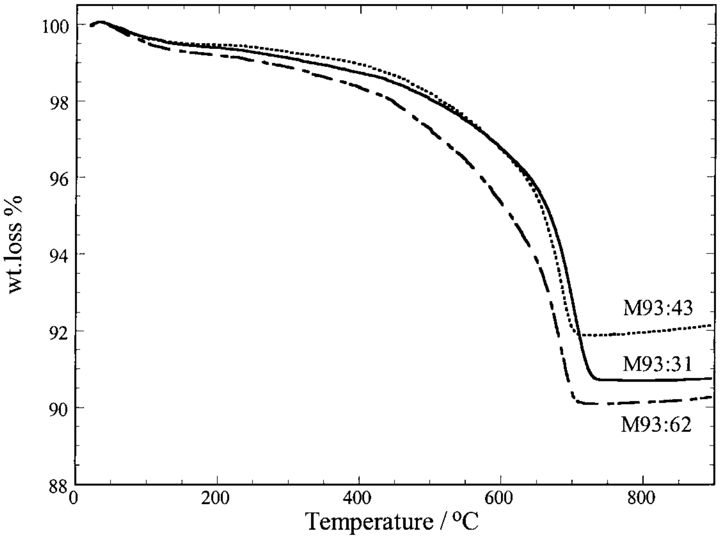

Fig. 2. TGA curves (in N_2) of the soils from the surfaces of different vessels in tomb M93, showing little difference in carbonate content.

Table 1
TGA results of the soil samples (percentage of weight loss at different stages, measured in N_2)

Sample	M91	M92	M93	M93:31	M93:43	M93:62
Moisture loss (%)	0.97	1.03	0.85	0.96	0.71	1.48
Pyrolysis (organic)	1.85	2.53	2.35	2.12	1.85	2.72
Carbonate decomposition	1.45	5.00	4.58	6.09	5.41	5.55
Total weight loss	4.27	8.56	7.78	9.17	7.97	9.75

Table 2
Analytical results of the soil samples

Sample	M91	M92	M93	M93:31	M93:43	M93:62
Quartz content (%)	14.9	12.1	13.7			
Organic matter (%)	2.2	2.7	1.9	2.0	2.5	4.7
Calcite content (%)	9.4	19.5	18.0	21.0	17.9	22.1
Number of exothermic peaks	2	2	1	1	3	3
Peak temperature (°C)	360	350	332	266	317	396
	412	390			374	481
Overall range of exothermic peaks (T_{start}–T_{end}) (°C)	254–511	310–511	280–525	202–512	248–512	258–550

Fig. 1 shows that soil sample from M91 differs to some extent from M92 and M93, in that the 2nd and 3rd stages of weight loss are more clearly separated. This indicates some difference in chemical composition which is evident in the smaller amount of calcite present (9.4% compared to 19.5% and 18.0% for M92 and M93, respectively). This can also be seen in the DSC curves of the oxidative degradation of soil samples (Fig. 4) where the shape of the DSC curve for M91 differs in shape from M93, although it has some similarity with M92.

The TGA curves (Fig. 2) for the samples from the same tomb (M93) are on the whole similar to that obtained for M93 but show small differences, in particular sample M93:62, which may be due to differences in the microenvironment of the soil samples.

Fig. 3 provides the DSC curves for sample M93:62 measured under both inert and oxidising conditions. In the curve obtained in N_2 the upward endothermic drift is caused by the carbonate decomposition process and this is followed by a small endothermic peak for the quartz transition ($\alpha \rightarrow \beta$) (575°C); in the curve obtained in O_2 for the same sample two exothermic peaks are present for the oxidation of the organic matter. These are then followed by the endothermic drift which represents onset of carbonate decomposition and then the small endothermic quartz peak. Fig. 4 as already

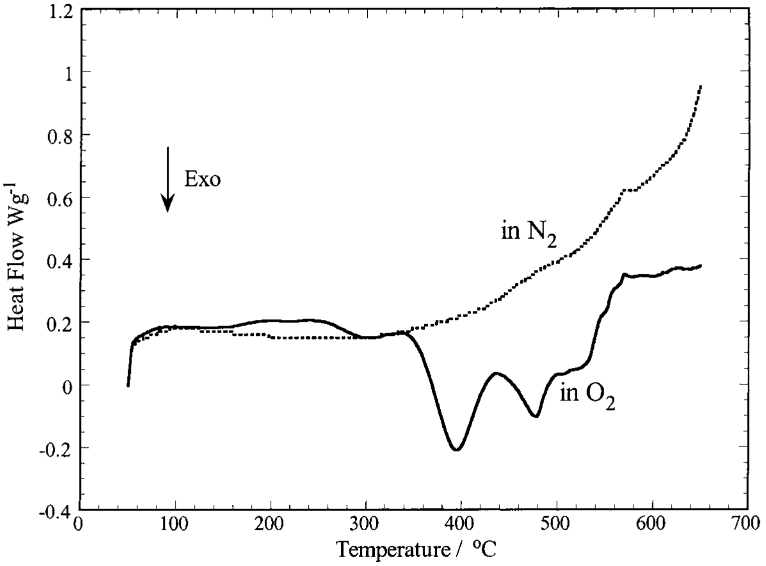

Fig. 3. DSC curves of the soil from the surface of vessel M93:62, run in N_2 and O_2 respectively. The curve run in O_2 shows the presence of quartz as well as organic materials.

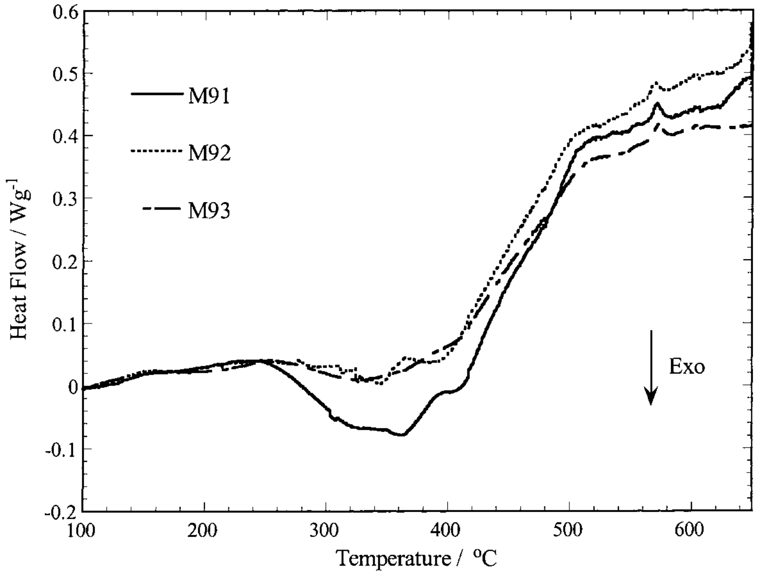

Fig. 4. DSC curves (in O_2) of the soils from the three different tombs.

mentioned shows that the soils from different tombs have small differences in organic matter. It seems that soil from M91 differs only to a small extent from that of M92 and then more so from M93.

The DSC curves for soils from the surfaces of different objects in one tomb (M93) (Fig. 5) showed greater differences, which suggests that the chemical composition of the soil microenvironment differs for each object. Characterisation on basis of the shape of the DSC curve was used to provide some information on likely chemical composition given the comprehensive database of DSC oxidative degradation curves for

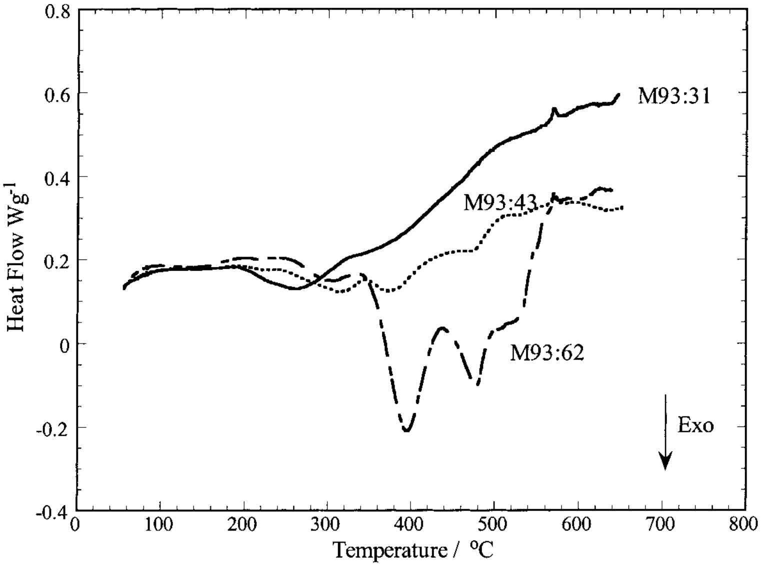

Fig. 5. DSC curves (in O_2) of the soils from the surface of different vessels in tomb M93, showing significant differences in microenvironment.

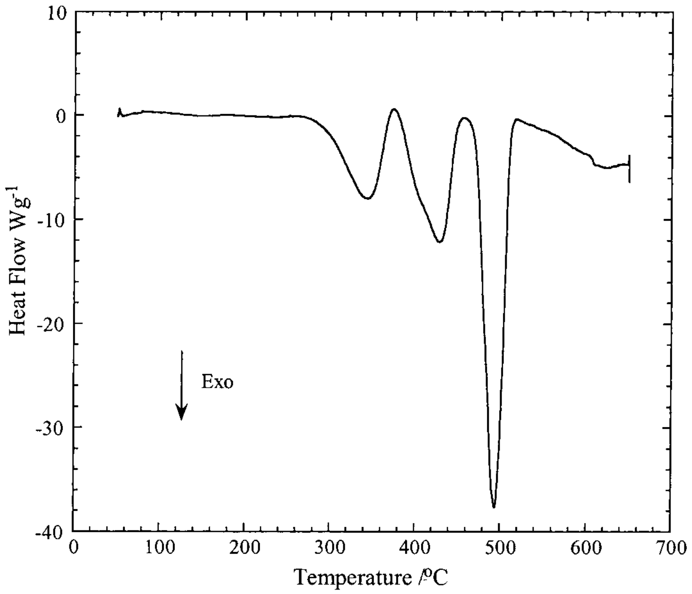

Fig. 6. DSC curve (in O_2) of a sample of charcoal.

known materials collected by one of the authors and reported elsewhere [5]. Comparison of the DSC curves with those for charcoal, archaeological bone, and animal skin, indicates that some charcoal and archaeological bones are likely to be present in the soils, especially in the samples from the surface of vessels M93:43 and M93:62. Exothermic degradation of samples of archaeological bone generally show a broad exothermic peak with a peak maximum in the region of 320°C. This can be observed in samples of M93:43 and M93:62 and can be considered as evidence for the presence of archaeological bone (i.e. historic collagen based material). In the DSC curve for sample M93:31 this is not observed. There is instead a more broad exotherm at slightly lower temperatures which coincides more with region for oxidation of lipid-based materials. The DSC curve of the sample from the vessel M93:62 shows the largest exothermic peaks, this is in accord with the previously obtained result that this sample contains more organic matter (both from heating and weighing the sample, and from TGA).

The suggestion for charcoal is interesting as it was reported to have been found beneath and surrounding the chambers in the tomb. It was used to retard the deleterious effect of moisture on the body and the accompanying burial goods, and so protect them from decay. Animal skeletons such as sacrificial horses were also reported in these tombs [6]. DSC results appear to confirm the archaeological investigation. In Fig. 6, the DSC curve for the oxidative degradation for a sample of charcoal indicates that three exothermic processes are involved. The temperatures at which these occur correspond to the exothermic peaks recorded for sample M93:62 (Fig. 3). The third process is modified probably through the overlapping endothermic calcium carbonate decomposition.

Most of the Jin tombs at Tianma-Qucun contained large amounts of charcoal. The earliest use of charcoal in burial so far found in China was tomb M7 at Tianma-Qucun, which dates to the middle western Zhou period [7]. Charcoal was widely in use in burials of the Warring state (475–221 B.C.) and following periods in China. It was recorded in the ancient literature “Lu Shi Chun Qiu: Jie Zang Pian” that charcoal was used to keep the tomb dry [8].

The burial construction for all tombs of the cemetery of Jin lord at Tianma-Qucun has the following features: wood (or stone) sticks were placed at the bottom to support the wooden chamber (outer coffin); charcoal was put around the chamber on all six sides. Next to the charcoal was pounded soil. Charcoal was found mixed with soil in the tombs probably due to the collapse of the tombs.

In addition to the calcium carbonate content, the quartz content of the soils could also be calculated. The endothermic peak at 575°C was seen to be present in all the samples. This peak is due to the phase transition in quartz ($\alpha\rightarrow\beta$). The content of quartz can be determined by Eq. (2). In which, ΔH is enthalpy change (J/g) of quartz measured from the DSC curve of the sample, and ΔH_0 is the standard enthalpy change of pure quartz mineral, which is 7.5 J/g [9].

$$C_{\text{quartz}} = \frac{\Delta H}{\Delta H_0} \tag{2}$$

Geologically, northern China is mainly covered with loess soil. The territory of Shanxi province is one of the areas with loess [10]. Loess in northern China has the following common features: yellow colour, uniform size, and uniform composition, which is calcite-rich. The DSC results of the soil samples are identical with these general features. Nevertheless, the burial environment was not purely local loess. It had artificial additions such as charcoal and archaeological bone.

4. Conclusions

The results obtained from TGA and DSC have demonstrated that the techniques are extremely useful for characterisation of archaeological materials where sample size is limited. In addition to small sample size the thermal techniques are also highly sensitive and specific for thermal processes such as calcium carbonate decomposition and quartz content. The results of these analyses indicate that the soils from the tombs at Tianma-Qucun are calcite-rich, which is typical loess of northern China. However, the burial environments contain added materials such as charcoal and other organic materials, both collagen and lipid based, as characterised by DSC. The presence of additional materials, possibly of human origin, could assist in the interpretation of social activities of ancient people. Therefore, thermal methods can play an important role in the field of archaeometry.

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References

[1] R.F. Tylecote, J. Archaeol. Sci. (London) 6 (4) (1979) 345.
[2] E. Mattsson, A.G. Nord, K. Tronner, M. Ejaested, A. Lagerlöf, I. Ullén, G.C. Bord, Deterioration of Archaeological Materials in Soil: Results on Bronze Artefacts, General Board of National Antiquities, National Historical Museum, Stockholm, 1996, p. 25.
[3] Q. Wang 2000. Metalworking technology and deterioration of Jin bronzes from the Tianma-Qucun site, Shanxi, China. Unpublished Ph.D. Thesis, University of London.
[4] J.E. Smeaton, G. Burn, in: P.B. Vandiver, J.R. Druzik, G.S. Wheeler, I.C. Freestone (Eds.), Materials Issues in Art and Archaeology I, 299–304, Materials Research Society, Pittsburgh, 1988, p. 299.
[5] M. Odlyha, Thermochim. Acta 269/270 (1995) 705–727.
[6] Wen Wu, Department of Archaeology, Peking University and Shanxi Provincial Institute of Archaeology, Wen Wu (Beijing) 7, 1995, p. 4.
[7] Wen Wu, Department of Archaeology, Peking University and Shanxi Provincial Institute of Archaeology, Wen Wu (Beijing) 1, 1994, p. 7.
[8] Yu Jie, Kao Gu Tong Xun, Beijing Vol. 4, 1957, p. 94.
[9] G. Widmann, R. Riesen, Thermal Analysis: Terms, Methods, Application, Dr. Alfred Hüthig Verlag Heidelber, Germany, 1987, p. 90.
[10] Wang Jingming, Huang Tu Gou Zao Ji Li de Li Lun ji qi Ying Yong (The Theory on Tectonic Joints in Loess and Its Application), Waterpower and Hydroelectricity Publishing House, Beijing, 1996, p. 3.