# Reducing firing of an early pottery making kiln at Batán Grande, Peru: A Mössbauer study

U. Wagner [a], R. Gebhard [b], W. Häusler [a], T. Hutzelmann [a], J. Riederer [c], I. Shimada [d], J. Sosa [e] and F.E. Wagner [a]

[a] *Physik-Department E15, Technische Universität München, D-85747 Garching, Germany*
[b] *Prähistorische Staatssammlung, D-80535 München, Germany*
[c] *Rathgen-Forschungslabor, D-14103 Berlin, Germany*
[d] *Southern Illinois University, Carbondale, IL 62907, USA*
[e] *Piura, Peru*

Material from field firing experiments using a 2,700-year old Formative kiln at Batán Grande, Peru, was studied by X-ray diffraction and Mössbauer spectroscopy. The experiments explore the technology involved in producing the gray and black reduced ware for which Cupisnique and other Formative ceramics are justly known. During firing, the iron-bearing compounds in clays undergo characteristic changes which depend on kiln temperature and atmosphere. These changes can be observed in the Mössbauer spectra. By comparing spectra of an appropriate clay fired in field experiments and in the laboratory with the spectra of ancient ceramics, a description of Formative firing techniques in a reducing environment is attempted.

**Keywords:** archaeometry, Mössbauer spectroscopy, X-ray diffraction, clays, early ceramics, authentic kiln, reducing firing

## 1. Introduction

In 1990 a field firing experiment was performed in a 2,700 year old Formative kiln in the Poma Archaeological Reserve at Batán Grande in Northern Peru [1–3]. Replica pottery, small bricks and the lumps of clay covering the thermocouples used to monitor the temperature were made from clay found at the kiln site. In these experiments air was admitted abundantly during the firing. A second set of experiments, which will be described in this paper, was conducted in 1997. In these experiments a reducing atmosphere was sustained during most of the firing cycle, since firing in a reducing atmosphere was a common technique in the production of prehistoric ceramics and resulted in the black ware for which the Formative period is famous.

## 2. Description of the material

While locally found yellow clay was chosen to make the replica vessels in our 1990 experiments, a darker coloured local clay was used in the experiments of 1997.

The latter clay will be called clay Batán Grande in the following. Both clays were taken from different strata in the walls of the Poma Canal directly at the kiln site. Both the yellow and the darker coloured clay were analysed by neutron activation analysis and found to exhibit equal concentrations of trace and major elements [2,3]. About 40 replica vessels were made for test firing. The temperature at different positions in the kiln (figure 3) was monitored by thermocouples whose tips were embedded in balls of about 4 cm diameter, made of the same clay as the vessels. In this way temperature spikes were averaged out and the temperature experienced in a vessel was described more adequately. Laboratory experiments have shown that temperature transfer from the surface of such a ball to the center takes less than 10 min [2].

## 3. Study of clay Batán Grande

### *3.1. X-ray diffraction*

According to the X-ray diffraction data, the mineral content in the clay from the Poma Canal (clay Batán Grande) before and after treatment for pottery making is nearly identical (figure 1). The samples contain mica, kaolinite and minerals of the 14.4 Å mineral group, like chlorite and expandable layer silicates. Amphiboles as well as feldspars can also be identified. Quartz is predominant and makes the clay self-

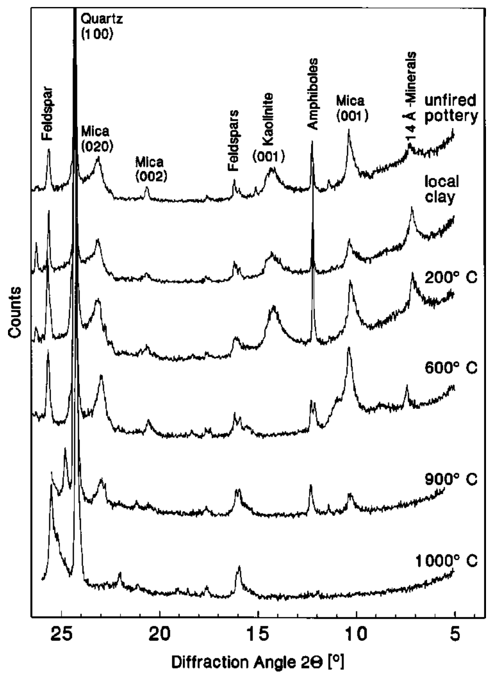



Figure 1. X-ray diffraction diagrams measured with Co-$K_\alpha$ radiation for unfired replica pottery, for local Batán Grande clay, and for samples heated to 200, 600, 900 and 1000°C in air for 48 h.

tempered. The presence or absence of certain minerals can serve as a thermometer for firing temperatures [4] as will be described in the following section. The mineral content depends but very little on the oxidizing or reducing nature of the kiln atmosphere.

### *3.2. Mössbauer measurements*

Mössbauer spectra were measured in transmission geometry at room temperature (RT) and 4.2 K. The spectra were fitted with the minimum number of doublets and sextets necessary. Systematic isochronal annealing series were performed in the laboratory in air for 48 h, in air also for 48 h after a preceding 3 h reduction at 800°C with charcoal in a closed quartz vessel, and during 3 h in a reducing environment also produced by charcoal. In this manner, the transformations and decompositions of the various silicates and oxides at different temperatures and in different atmospheres can be established. The Mössbauer spectra for all three procedures are shown in figure 2 as 3-dimensional plots. They will be used for comparison with the Mössbauer spectra of samples from the field firing and of ancient ceramics from the region.

During heating in air (figure 2(a)) a strong increase of the quadrupole splitting of $Fe^{3+}$ species from 0.66 mm/s in the fresh clay to 1.05 mm/s on firing at 400°C takes place. The splitting reaches a maximum of 1.35 mm/s on firing at 700°C. The transformations of the clay minerals can also be seen in the X-ray diagrams (figure 1). Between 200 and 600°C the expandable layer silicates collapse, resulting in an increasing peak at $10°2\theta$. After heating to 600°C a small peak of primary chlorite can still be observed in the region of $7°2\theta$. Kaolinite disappears at 400–450°C. Only traces of mica are left after heating to 900°C. Amphiboles also decompose near this temperature. The Mössbauer spectra show that between 700 and 900°C haematite forms from iron set free from the clay matrix. This haematite formation escapes detection by X-ray diffraction, presumably because of the small particle size of the haematite. Above 900°C vitrification starts and spinels are formed, which can be seen by X-ray diffraction.

For firing in air after a preceding reduction (figure 2(b)), oxidation of $Fe^{2+}$ species is dominant between 450 and 600°C [5]. The $Fe^{3+}$ species formed by reoxidation of $Fe^{2+}$ have a quadrupole splitting of about 0.9 mm/s, which is much smaller than the quadrupole splitting of the $Fe^{3+}$ species formed in the same temperature region during direct oxidizing treatment of fresh clay. One can thus distinguish between a reduction followed by reoxidation and a firing in oxidizing conditions only.

Reduction with charcoal in a closed vessel (figure 2(c)) starts at 450°C. At around 800°C all $Fe^{3+}$ is reduced. Metallic iron starts to form above 900°C and can be easily recognized by its typical magnetic hyperfine field of 33 T. It is worth noting that the Mössbauer patterns observed for samples fired near 600°C under reducing conditions are similar to those observed after a reduction at 800°C and a subsequent partial reoxidation between 450 and 500°C. If reducing treatment is involved, different firing cycles can thus cause similar Mössbauer patterns.

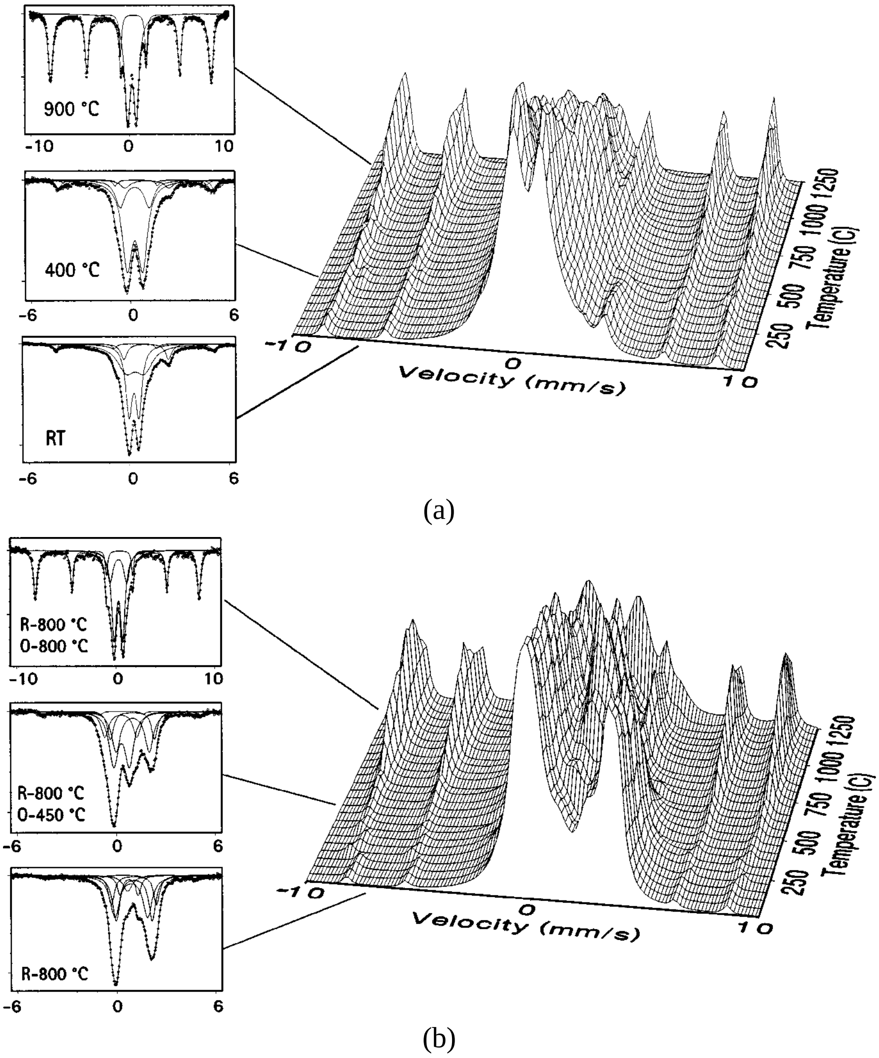
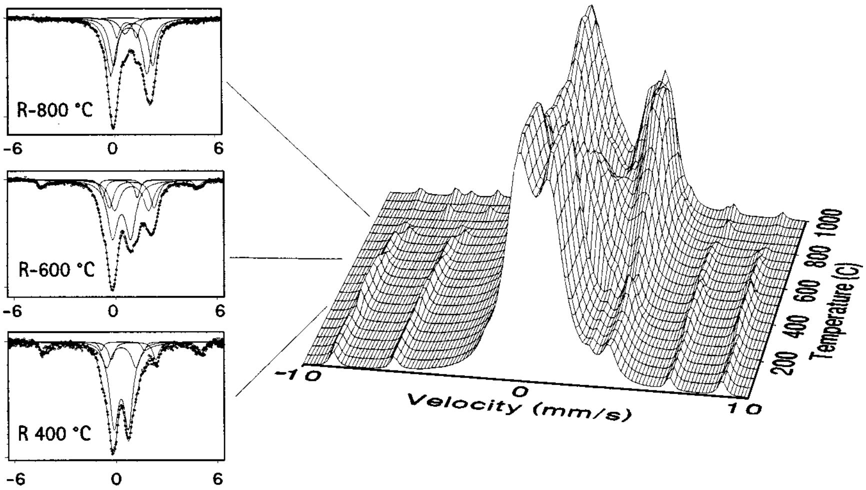



Figure 2. RT Mössbauer spectra of clay Batán Grande: (a) fired in air for 48 h at increasing temperatures, (b) fired in air for 48 h after a preceding 3 h reduction with charcoal at 800°C in a closed vessel, and (c) fired for 3 h under reducing conditions only. Selected spectra are shown on the left of the 3-dimensional plots. (Adapted from [1].)

## 4. Field firing

Kiln 38 at the Poma Archaeological Reserve [6] was used for field firing. A reducing kiln atmosphere was established by using dried cow dung together with algarrobe wood as fuel. By stacking a mixture of wood and dung in the entrance to the main chamber of the kiln it was possible to sustain a draft through the kiln and still maintain a reducing environment. A temperature close to 800°C prevailed at some localities in the kiln for more than one hour (figure 3).




(c)

Figure 2. (Continued.)

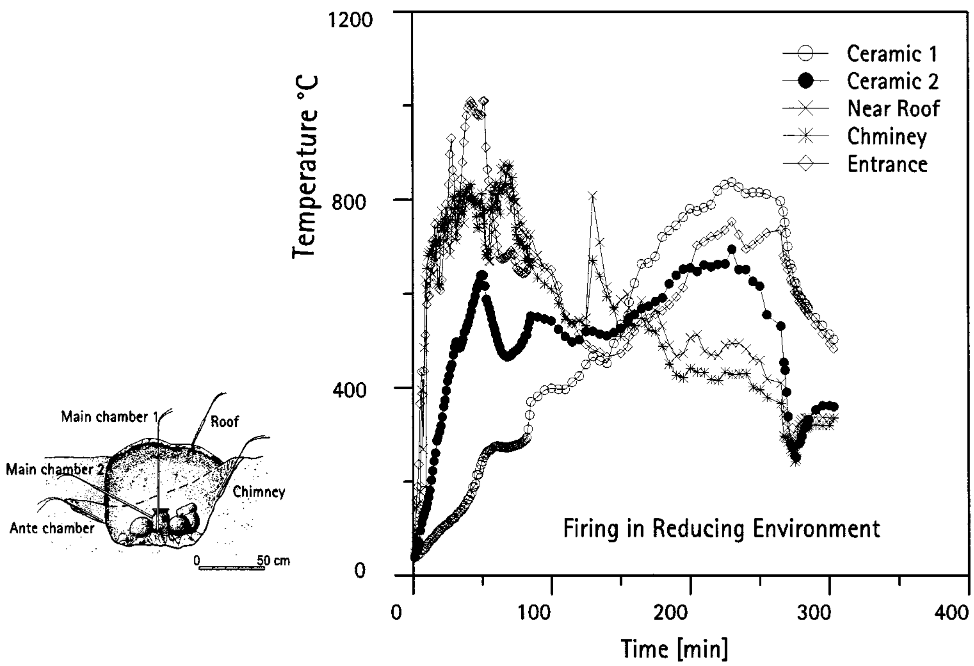
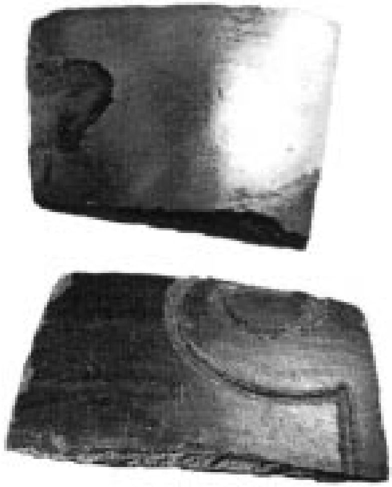



Figure 3. Temperature history of a firing of kiln 38 under reducing conditions. The rapid temperature changes recorded by the thermocouples near the roof and the chimney are due to the fact that the clay balls covering the respective thermocouples broke during the experiment and thus lost their capability of averaging the temperature over a timescale of several minutes.



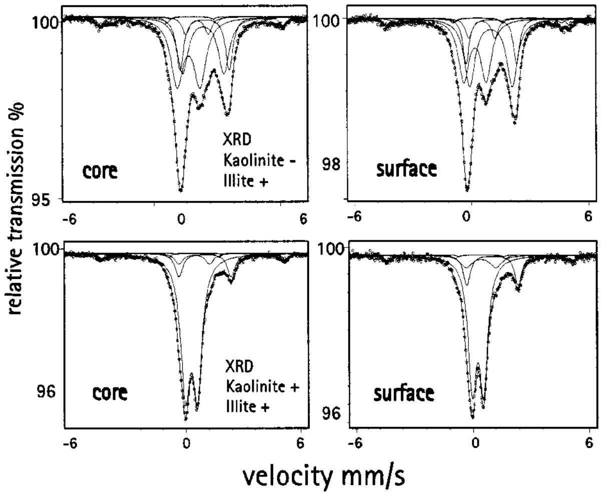



Figure 4. Room-temperature Mössbauer spectra of sherds (left) of two different replica vessels fired in a reducing environment. The firing temperatures were estimated from the mineral content observed to have been around 700°C for the upper sherd and well below 600°C for the lower sherd by X-ray diffraction and by comparing the Mössbauer spectra of the sherds with those observed in the clay balls covering the thermocouples.

## 5. Study of replica vessels

40 replica vessels were fired in 4 different field experiments, during which the kiln temperature was monitored with thermocouples whose tips were embedded in clay balls. The temperatures the pots have experienced are assumed to be the same as those measured by the nearby thermocouples. Some of the balls covering the tips of the thermocouples and several of the replica vessels were selected for studies by X-ray diffraction and Mössbauer spectroscopy. These studies are still in progress. It is, however, already clear that the agreement between filed and laboratory fired material is sufficiently good to warrant the use of laboratory experiments for assessing ancient firing procedures (figure 4). Even the black surface colouring so often observed in the ancient vessels could be reproduced in the field firing experiments. It arises when soot developing during the reducing firing is deposited on the surface of the vessels and penetrates into the sherd, creating a black surface without causing a reduction of the iron-bearing compounds if the temperature is not sufficiently high. On polished surfaces and at sufficiently high temperature graphite is formed and gives rise to a metallic sheen.

## 6. Study of formative sherds

The results described above were used to interpret the production techniques of Formative ceramics. About 60 Formative sherds have been studied in this context, 20 sherds from the kiln site and 40 found at the neighbouring site of Huaca

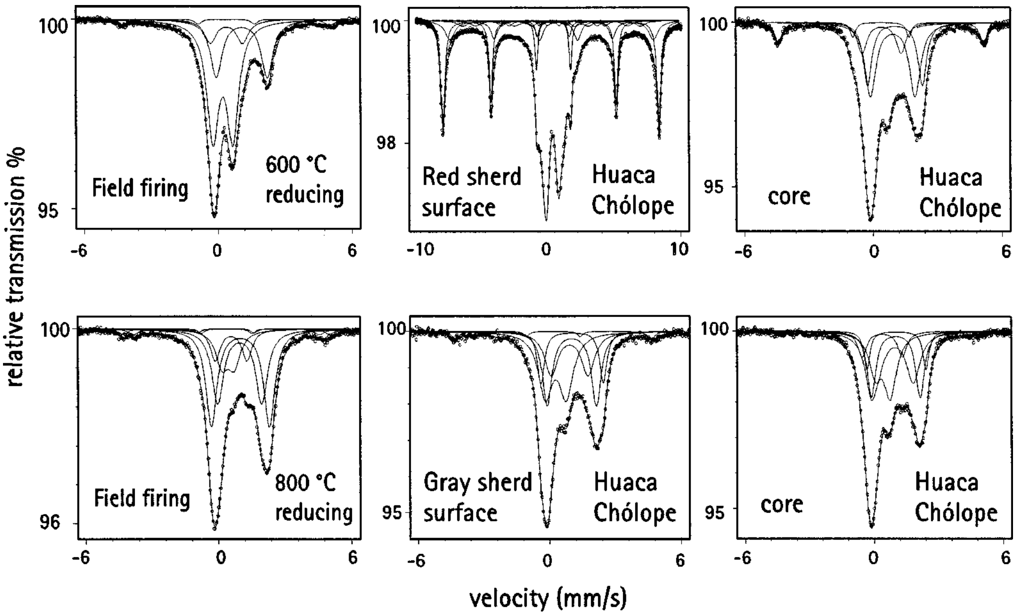



Figure 5. Comparison of room-temperature Mössbauer spectra of different layers of two sherds from the site of Huaca Chólope with two samples from the field firing.

Chólope. The Mössbauer spectra of the core and the surface of two sherds from Huaca Chólope are shown in figure 5. Both sherds could be shown to have been fired at temperatures of about 800°C in reducing conditions by comparing the spectra of their cores with spectra observed for the clay balls covering the thermocouples during the field firing. The red surface colour of one of the sherds is due to a short period of oxidation at the end of the firing cycle, while the second sherd is gray throughout and its core and surface exhibit the same Mössbauer patterns (figure 5).

## 7. Conclusions

Field firings in an authentic kiln presented a unique opportunity to reconstruct the firing techniques of the Formative period. Three main firing cycles can be proposed: firing in air, without and with a preceding reduction, and firing in a purely reducing environment. In reality one has to assume a more complicated sequence of firing conditions, changing on purpose or incidentally. It could be shown that with the necessary skill and expertise all the materials and the surface structures observed in Formative ceramics can be achieved in simple kilns like the one studied at Batán Grande.

## Acknowledgements

We would like to thank the Deutsche Forschungsgemeinschaft for financial support. One of us (I. S.) is thankful to the National Geographic Society for sponsoring the 1989 excavation of the kilns in the Poma Archaeological Reserve.

## References

[1] U. Wagner, R. Gebhard, E. Murad, G. Grosse, J. Riederer, I. Shimada and F.E. Wagner, Hyp. Interact. 110 (1997) 165.
[2] U. Wagner, R. Gebhard, E. Murad, J. Riederer, I. Shimada, C. Ulbert and F.E. Wagner, in: *Andean Ceramics: Technology, Organisation, and Approaches*, ed. I. Shimada, MASCA Research Paper in Science and Archaeology, Supplement to Vol. 15 (1998) p. 173.
[3] U. Wagner, R. Gebhard, E. Murad, J. Riederer, I. Shimada, C. Ulbert, F.E. Wagner and A.M. Wippern, in: *Tecnología y Organización de la Producción Cerámica Prehispánica en los Andes*, ed. I. Shimada (Pontífica Universidad Católica del Perú, Lima, 1994) p. 121.
[4] M. Maggetti, in: *Archaeological Ceramics*, eds. J.S. Olin and A.D. Franklin (Smithsonian Institution Press, Washington, DC, 1982) p. 121.
[5] U. Wagner, R. Gebhard, G. Grosse, T. Hutzelmann, E. Murad, J. Riederer, I. Shimada and F.E. Wagner, Hyp. Interact. 117 (1998) 323.
[6] I. Shimada, G. Elera and V. Chang, Gaceta Arqueológica Andina 5 (1990) 19.