

# News and Short Contributions

## *Special Studies*

### **Naturally Deposited Versus Intentionally Applied Gypsum on Archaeological Materials from Harappa, Pakistan**

DONNA K. STRAHAN

The Walters Art Gallery  
Baltimore, Maryland

*White deposits on archaeological vessels excavated at Harappa, Pakistan, were identified by x-ray diffraction analysis as pure gypsum. Because of the evenness and location of the layer it appeared to have been intentionally applied. But since we were aware that the site has an extreme salt problem there was a possibility that the layer was a post-depositional accretion. Through the comparison of x-ray diffraction (XRD) peak intensities and the crystal morphology using scanning electron microscopy (SEM) it was determined that natural and intentionally calcined/hydrated gypsum could be differentiated. This study should help archaeologists and conservators distinguish burial deposits from intentionally applied gypsum on archaeological material.*

#### *Introduction*

Archaeological ceramics often have a variety of insoluble salts on their surfaces, ranging from carbonates and sulfates to silicates. These white incrustations are hindrances to examination and are often removed to expose the surface of the vessel and any decoration present. Generally, removal is completed mechanically or with dilute acids such as hydrochloric or nitric. White incrustations on vessels are normally considered to have been deposited during burial as the result of soil and climatic conditions. Rarely are the incrustations thought to be calcined/rehydrated gypsum plaster intentionally applied during manufacture.

A study to evaluate whether the white layers are natural or intentionally calcined/rehydrated gypsum plaster (hereafter referred to as treated) was initiated when a number of excavated ceramic pots (grave offerings) from the site of Harappa, Pakistan, were unearthed with a thick (1 mm) white layer adhering to most of the exterior of the vessels that flaked off easily upon exposure to air. None of the incrustation was found on the interior of the vessels or on broken edges of examples found. The vessels were obtained from two of the burials excavated in the Harappan cemetery by the University of California–Berkeley during the 1987 and 1988 excavation seasons. One burial had three vessels with incrustation, while numerous such pots occurred in the other one. Eleven vessels of this kind were

sampled. Through x-ray diffraction (XRD) analysis using a powder diffractometer the incrustations were identified in every case as pure gypsum dihydrate ( $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$ ).

The analysis indicates that although the gypsum incrustation is pitted and eroded, it represents an artificial plaster of Paris application by the Harappans prior to burial of the pottery and not a natural accretion. The gypsum coating was applied as a slurry, without an organic binder, and it was not fired onto the surface of the vessel. It should be pointed out, however, that other vessels with white gypsum-like accretions may be the result of natural processes. One method of differentiating natural occurrence from artificial application is discussed below.

#### *Gypsum Properties*

Gypsum is the most common sulfate mineral and is widely distributed throughout the world. It is frequently found in sedimentary rocks or interstratified with limestones. Gypsum is a monoclinic crystal which is tabular or diamond-shaped on the {010} crystal plane. Heating gypsum to between 140 and 200°C will convert it to a hemihydrate (bassanite or plaster of Paris) (Wenk and Henkels 1978: 439; Deer, Howie, and Zussman 1966: 202–215). With the addition of water the hemihydrate readily reverts to the dihydrate and hardens. This property has made gypsum plaster an extremely useful material to humans for thousands of years.

#### *Method*

Joan Mishara of the Smithsonian Conservation Analytical Laboratory suggested that a difference in gypsum XRD peak intensities might distinguish natural gypsum from humanly heat-treated gypsum. In order to establish parameters with which to distinguish the two, a range of gypsum standards and samples, both natural and treated, were analyzed by XRD and scanning electron microscopy (SEM) before and after calcination and rehydration. The samples were as follows (TABLE 1): synthetically produced Fisher Scientific gypsum; commercial grade plaster of Paris; samples from Harappan pots; gypsum sediment or rock excavated from the site of Harappa; and naturally formed gypsum standards from many locations around the world obtained from the Mineral Sciences Department, Natural History Museum of the Smithsonian Institution.

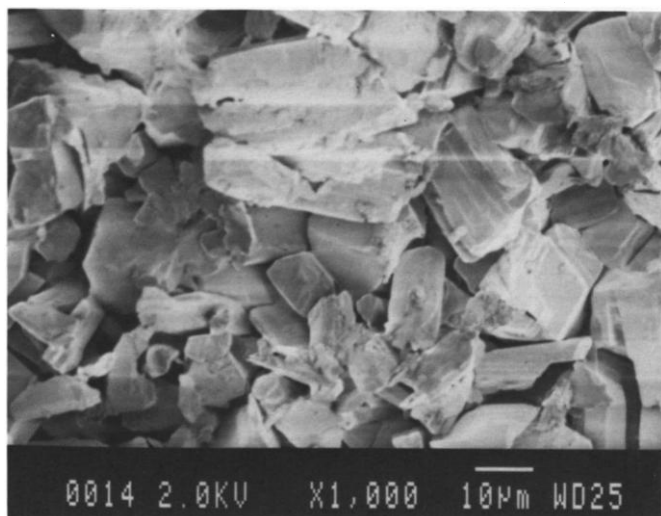


Figure 1. Gypsum as found on the exterior of Harappan pot H88/219.15. The needle-like shape of this chunk is not apparent, although the XRD peak intensities suggest a change in crystal morphology (taken at 1000x).

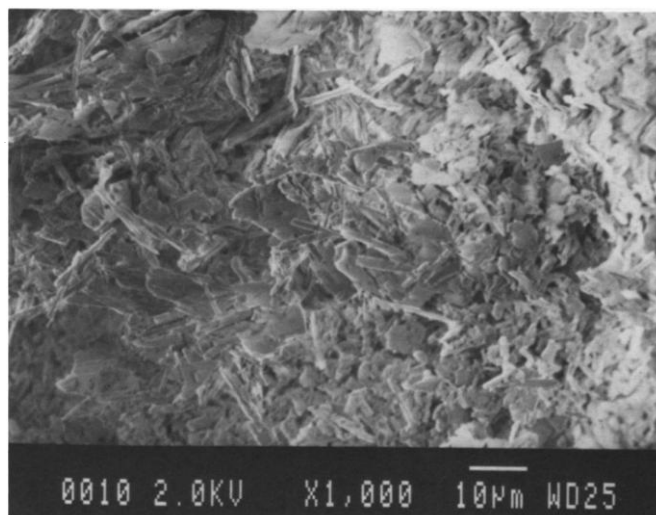


Figure 2. Gypsum from the same location on Harappan pot H88/219.15 after heating for two hours at 170°C and rehydrating. The crystal shapes have been altered to small regular needle-like morphologies (taken at 1000x).

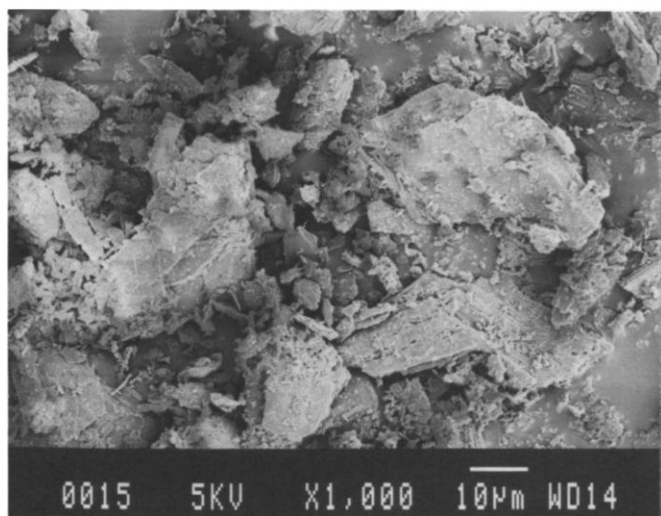


Figure 3. Natural gypsum from Austria (sample B12046) obtained from the Natural History Museum, Smithsonian Institution, has not been heated or rehydrated. The crystals are large, irregular, and tabular shaped (taken at 1000x).

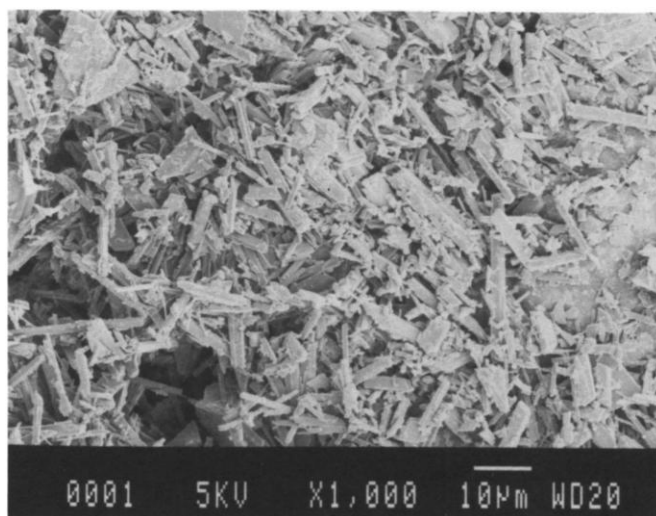


Figure 4. Austrian gypsum (sample B12046) after heating for two hours at 170°C and rehydrating. The crystal shapes have been altered to small regular needle-like morphologies (taken at 1000x).

Each sample was first ground in an agate mortar with acetone, then applied to a quartz plate XRD sample holder in an acetone slurry and allowed to air dry. By using an acetone slurry on a quartz plate the preferred orientation of the crystal formation was duplicated. Random orientation of the crystals would have occurred had the analyses been carried out using a highly viscous mounting medium. XRD examination of all samples was performed to identify them securely as gypsum. A Philips BW 1720 generator

and diffractometer with a copper tube, and a nickel filter at 50KV/40ma was used for all diffraction. (The intensity variations would not have been observed had the analyses been completed using a Gandolfi camera rather than the diffractometer.) Next the samples were each calcined at 170°C for two hours to dehydrate them. XRD analysis was again performed to ensure that complete dehydration to the hemihydrate ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ ) had occurred. Then a slight excess of deionized water was added to the sample,

Table 1. Normalized XRD peak intensities and SEM morphology of gypsum samples.

Samples	Morphologies: Raw to heated and rehydrated	Gypsum crystal faces:					
		Raw			Heated and rehydrated		
		020	121	041	020	121	041
Gypsum coatings from Harappan pottery, ca. 4500 b.p.							
H87/pot	tabular to needles	57	91	100	96	100	100
H88/219.10	tabular to needles	72	86	100	64	76	100
H88/219.11a	tabular to needles	76	62	100	56	81	100
H88/219.11b	tabular to needles	48	65	100	67	81	100
H88/219.15	tabular to needles	76	78	100	85	90	100
H88/219.20	tabular to needles	81	73	100	75	74	100
H88/219.22	tabular to amorphous	81	86	100	100	39	31
H88/219.23	tabular to needles	67	74	100	75	73	100
Commercially produced gypsum							
Fisher Sc.	needles to needles	45	92	100	79	79	100
Plas. Paris	needles to needles	—	—	—	37	87	100
Harappan rock and sediment gypsum							
H87/24	tabular to needles	100	16	38	70	89	100
H88/715	tabular to needles	100	24	57	63	76	100
H88/228.4	tabular to needles	100	17	53	95	80	100
Natural History Museum gypsums and other naturally occurring gypsums							
White Sands	tabular to needles	100	36	91	83	87	100
Carlsbad	tabular to needles	100	17	60	50	85	100
B12046	tabular to needles	100	46	49	75	81	100
B12046 rehy	tabular to needles	100	16	48	—	—	—
102224	tabular to needles	100	39	63	50	84	100
R15022	tabular to needles	100	60	41	74	77	100
114752 satin	tabular to needles	72	70	100	67	79	100

and it was allowed to rehydrate for 24 hours. Finally, the sample was ground again and analyzed by XRD. The relative peak intensities of the first XRD pattern of each sample were compared with those of the third XRD pattern. As an adjunct to the XRD analysis the crystal form of each sample before calcining and after rehydration was examined in the SEM.

### Results

Of the three major gypsum XRD peaks (7.56 angstrom peak [crystal face 020]; 4.28 angstrom peak [crystal face 121]; 3.06 angstrom peak [crystal face 041]), the intensity of the 7.56 angstrom peak varied relative to the other two in all samples. In the literature (JCPDS 1980: diffraction standard #33-311) the 7.56 angstrom peak is strong (100%) and reflects excellent cleavage on the {010} plane and its related planes. In this study the natural gypsum's peak 7.56 was 100%, while the treated or rehydrated gypsum's peak 7.56 was consistently lower than the other two peaks. This indicates that the crystal shape or size was altered (see TABLE 1). The diffraction results were detected by crystal orientation rather than by crystal shape and size. Again, had a viscous mounting medium been used the change might not have been obvious.

SEM examination showed natural gypsum and Harappan pot gypsum to have large, irregular, tabular crystals,

while the laboratory treated gypsum crystals were small, needle-like, and very regular in shape (FIGS. 1-4). Therefore, SEM examination of these samples is not a reliable method of distinguishing between the two.

In order to imitate the natural redeposition of gypsum one sample of natural gypsum (B12046) was redeposited by dehydration of the sample, soaking it for a week, and evaporating the water slowly in a closed, humid environment at room temperature. In this example the 7.56 angstrom peak became intense, supporting the idea that gypsum formed slowly in an excess of water, as in nature, had different XRD peak intensities from gypsum rehydrated with close to the smallest amount of water necessary for quick setting, as when applied by humans (Kingery, Vandiver, and Prickett 1988). This process also produced plate-like crystals.

It should be noted that inconsistent results were found in the case of the XRD analysis of satin spar (114752 in TABLE 1), a rare form of precipitate or evaporate of ground water and found in faults and seams (Hammond 1964: 16-17). Its needle-like morphology has the 4.28 and 3.06 angstrom intensities that were also found in calcined/hydrated gypsum on the Harappan vessels. It is unlikely, however, that satin spar would ever be found on archaeological material. Another exception was sample H88/219.22, which did not develop the needle-like growths

even after several calcinations and rehydrations. This analysis is consistent with other findings in that it shows that under certain conditions of heat and rehydration some plasters do not develop needle-like growth but produce fine plates such as were found in this sample under SEM (P.B. Vandiver, personal communication 1988). This crystal change was also reflected in the XRD peak intensities.

Since these deposits cannot be identified in the field it is necessary to collect samples for laboratory analysis. A 1–2 sq-cm sample in chunk form or powder is sufficient for analysis.

### Conclusions

The results of this study indicate that rapid deposition, in contrast to the slow growth of crystals, will give different crystal morphologies. When gypsum has been manipulated by calcination and rehydration, there is usually a change in the crystal shape in that crystals become smaller and more regular. This altered crystal morphology is apparent only in x-ray diffractographs evidenced by altered peak intensities, and is not visible in SEM photography. Barring unusual circumstances such as an extremely wet site or an acidic environment that would cause some resolution and reprecipitation of the gypsum, thus disturbing the regularity of the crystals, intentionally applied gypsum may be determinable through the use of XRD powder analysis and scanning electron microscopy. This study may help conservators and archaeologists identify intentionally heat-treated and applied gypsum deposits on excavated objects.

### Acknowledgments

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*Donna K. Strahan, Associate Objects Conservator at The Walters Art Gallery, received her M.A. in Museum Studies with a concentration in ethnographic and archaeological conservation from George Washington University. She was formerly an objects conservator at the Conservation Analytical Laboratory of the Smithsonian Institution and was the archaeological site conservator at Harappa, Pakistan, from 1986 to 1988. Current address: Department of Conservation and Technical Research, The Walters Art Gallery, 600 N. Charles St., Baltimore, MD 21201.*

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