Appendix 1

Smithsonian Museum Conservation Institute Slag Report for Finds from the 2008 Deer Stone Project Field Season

---

MCI request number: *6249*

Object: *objects from an archaeological context near deerstones in Mongolia, mostly copper slag*

Material: *various (metal slag, geological)*

Cultural Area: *Khyadag East deerstone site, Khovsgol Aimag, Burentogtokh sum, Mongolia (49° 48,900' N, 99° 53,042' E, elevation 1589 m)*

Date: *2500 BP*

Accession Number/Identification: *n/a*

Requested by: Dr. William Fitzhugh
Department: Arctic Studies Center, Department of Anthropology
Unit: *NMNH*

Report Author: *Judy Watson, Physical Scientist, MCI*

Further Contributions to the report by: Martha Goodway, Jeffrey Speakman
Date of request: *February 20th, 2009*

Report dates: *September 4th, 2009*

Requested analysis

Photography; analysis and imaging using SEM-EDS; analysis using XRF, DTA, metallography as appropriate.

Purpose of analysis

To gain an understanding of the fragments in order to determine if local iron smelting was taking place around 500 BC. The site is being investigated as part of the American-Mongolian Deer Stone Project, directed by Dr. William Fitzhugh and co-directed by Jamsranjav Bayarsaikhan (head of Research Department/Archaeologist, National Museum of Mongolia, Ulaanbaatar, Mongolia).

Executive Summary
33 samples from an archaeological context at the Khyadag East deerstone site in Mongolia were analyzed using SEM-EDS and XRF in order to determine whether they presented evidence of local iron smelting around 500 BC. Results indicate no evidence of iron smelting, but most of the objects are consistent with copper smelting slag.

SEM background

Scanning electron microscopy with energy dispersive spectrometry (SEM-EDS) works by sending a focused beam of electrons at a sample and measuring the energy of the x-rays emitted by the excited area of the sample. The emitted x-rays provide information about the elements present, and in some cases about elemental abundance. Previously this type of analysis has required destructive sampling, embedding, polishing, carbon coating, and analysis under high vacuum. The development of low vacuum (environmental (ESEM) or variable pressure (VP-SEM)) SEM, specially adapted detectors, and larger sample chambers has allowed the introduction of whole objects (up to 30 cm. in diameter and 8 cm high) into the chamber of the SEM for imaging and analysis without being altered.

For imaging, SEM provides two options. The first makes use of secondary electrons, which are generated near the surface of a sample when it is excited by the electron beam. Secondary electron imaging therefore provides good topographic information. The other type of imaging uses backscattered electrons, which come from deeper within a sample and provide information about the elemental composition of a sample, as heavier elements appear brighter than lighter ones. Backscatter imaging therefore offers not only morphological information about a sample, but also information about compositional differences within a sample.

Instrumental parameters for SEM analysis

The samples were imaged and analyzed using a Hitachi S3700-N scanning electron microscope and a Bruker XFlash energy dispersive spectrometer with Quantax 400 software. Samples were placed onto an aluminum sample holder and analyzed at either full vacuum (< 1 Pa) or at 40 Pa, between 8 and 16 mm working distance, and 15–20 kV accelerating voltage.

Instrumental parameters for XRF analysis

The samples were analyzed using a handheld x-ray fluorescence spectrometer (Bruker Tracer III-V ED-XRF) at 12 kV and 15 µA for 60 seconds.

Results and discussion

Thirty-three samples were analyzed, the majority of which did seem to be metal slag. The presence of copper in these samples is inconsistent with an identification of iron slag, but is consistent with copper slag. The variation between the slag samples indicates that they are the product of more than one smelting event.

The remaining samples include one that is likely to be rock (sample 3), and a possible fragment of furnace lining or crucible (sample 2) (see Tables 1 and 2).

Attached as an appendix to this report are some results and images for each of the samples. Each sample summary contains photographs of the sample, sample mass, an XRF spectrum, and a table with rough SEM-EDS results. Some sample summaries also contain one or more SEM images and one or more elemental maps.

The SEM results are qualitative only and should be taken as approximations. This is due to the fact that sample topography has an effect on the analysis (and analytical totals were low). The results were normalized, but in the tables presented in the sample summaries, only the most commonly abundant elements were presented for comparative purposes (as well as S, Cl, and P).

The raw data from the analyses conducted on these samples will be deposited and archived in the project folder in the R drive at MCI.

Group	Samples in Group	Supporting Factors
non-slag	2, 3, 4, 27	chemistry, morphology, density
copper slag	1, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 28, 29, 30, 31, 32, 33	chemistry, morphology

Table 1. *Possible groups found and the samples that fall into them.*

Sample no.	Group
1	Cu slag
2	non-slag
3	non-slag
4	non-slag
5	Cu slag
6	Cu slag
7	Cu slag
8	Cu slag
9	Cu slag
10	Cu slag
11	Cu slag
12	Cu slag
13	Cu slag
14	Cu slag
15	Cu slag
16	Cu slag
17	Cu slag
18	Cu slag
19	Cu slag
20	Cu slag
21	Cu slag
22	Cu slag
23	Cu slag
24	Cu slag
25	Cu slag
26	Cu slag
27	non-slag
28	Cu slag
29	Cu slag
30	Cu slag
31	Cu slag
32	Cu slag
33	Cu slag

Table 2. *Samples assigned to groups.*

Addendum to Investigation of Mongolian Slag by Jeffrey Speakman

Copper rarely occurs in native form but instead is primarily found in nature in other forms, such as chalcopyrite ($CuFeS_2$) which accounts for about 50% of modern copper production. Copper in these ores typically averages 0.6 %. In Mongolia most copper is derived from Porphyry copper deposits. These are copper ore bodies that are associated with porphyritic intrusive rocks and the fluids that accompany them during the transition and cooling from magma to rock. Porphyry orebodies typically contain between 0.4 and 1 % copper. In order to concentrate the copper in chalcopyrite and porphyritic ores, it is necessary to employ an extractive process such as smelting. At this end of this process one is left with copper that can then be used for making tools, etc. and a slag that contains the unwanted materials. Copper slag is typically enriched in iron, silica, and aluminum, and other elements. Depending on the efficiency of the smelting technology, copper will be present in weight percent quantities.

Below is a comparison of data published by Maldonado and Rehren (2009) and data generated by Watson for the Khyadag slags. As can be seen from the table and accompanying figures, the Khyadag slag quite similar to that from Mexico. Based on the presence of copper in the Khyadag ores there is little doubt that these samples are slag resulting from copper production.

Sample	SiO_2 (%)	Al_2O_3 (%)	FeO (%)	CaO (%)	MgO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	SO_3 (%)	CuO (%)
1-1c	34.1	7.20	49.7	0.63	1.88	0.36	0.92	0.05	0.13	2.41
1-2b	32.4	10.86	46.9	1.46	2.06	0.56	0.82	0.11	0.27	1.29
1-4a	35.0	9.65	43.7	1.72	2.30	0.61	1.11	0.07	0.26	1.48
1-4c	35.2	6.40	50.3	2.44	1.62	0.58	0.82	0.09	0.59	0.73
2-1b	40.0	3.44	46.2	4.29	0.61	0.56	0.50	0.01	0.24	1.44
Sample	**SiO_2 (%)**	**Al_2O_3 (%)**	**Fe2O3 (%)**	**CaO (%)**	**MgO (%)**	**Na_2O (%)**	**K_2O (%)**	**P_2O_5 (%)**	**SO_3 (%)**	**CuO (%)**
Khyadag1_1_1	22.7	10.3	51.7	4.3	2.1		1.2	0.7	0.6	6.0
Khyadag1_2_1	27.9	13.5	40.8	4.5	2.6	1.4	1.8	0.9	1.1	4.6
Khyadag1_3	20.5	10.6	49.7	4.4	2.3	1.6	1.6	0.7	1.0	6.3
Khyadag1_4_1	18.2	9.6	54.1	3.9	2.3	1.3	1.2	1.0	1.4	6.2
Khyadag1_5	20.8	9.9	56.5	3.5	1.9	0.9	1.1	0.7	0.7	3.6

Table 3. *Bulk element composition of "Platy" Copper slag from Mexico (XRF data reported in Maldonado and Rehren 2009) compared to 5 SEM-EDS analyses of Khyadag sample 1. Note that Maldonado and Rehren report iron as FeO, whereas Watson reported values for the Khydag slag as Fe2O3. To convert FeO to Fe2O3 multiply the FeO values by 1.1114.*

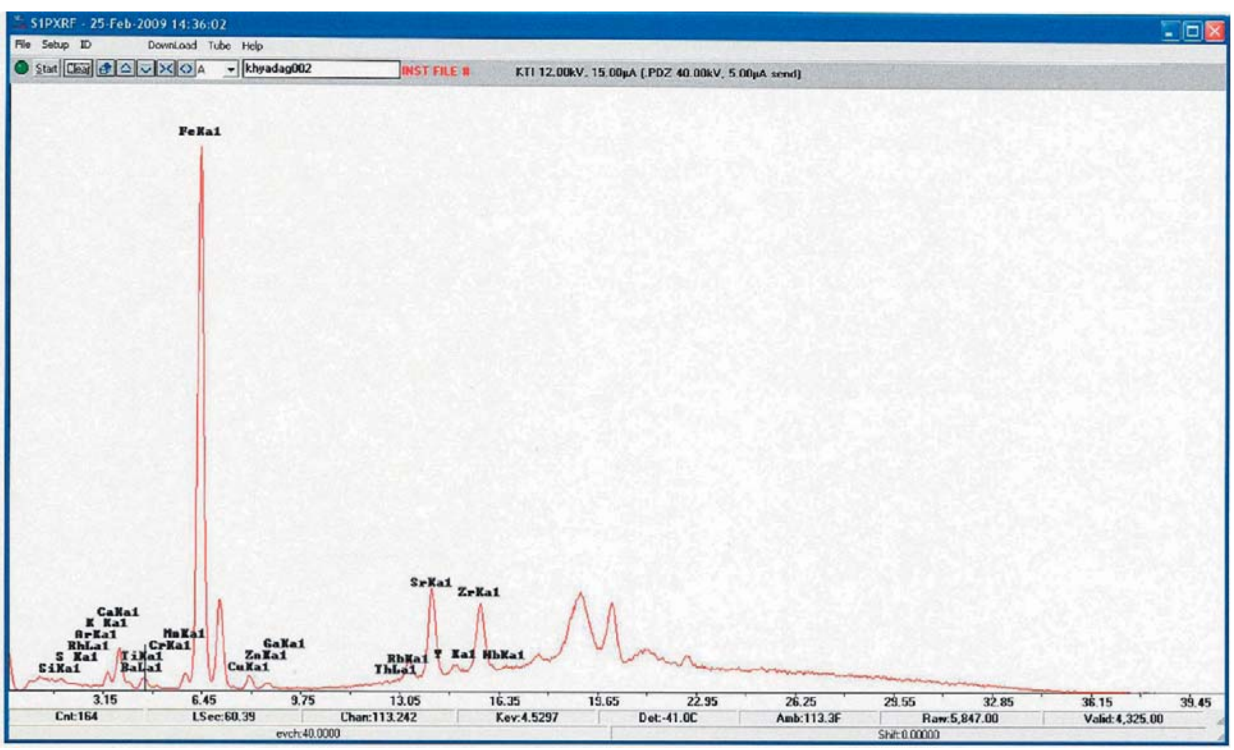
Figure 1. *Left*: Example of a platy slag fragment from Mexico (Maldonado and Rehren 2009). *Right*: Khyadag sample 1

Maldonado, B., Rehren, Th., 2009, Early Copper Smelting at Itziparátzico, Mexico, *Journal of Archaeological Science* 36, 1998-2006

MCI6249 Khyadag slag Sample 2

Mass 4.0 g

Spectrum	Na2O	MgO	Al2O3	SiO2	P2O5	SO3	ClO	K2O	CaO	Fe2O3	CuO
khyadag2n_1_1	2.7	2.5	20.8	53.4	0.6	0.6	0.2	2.1	6.4	9.8	0.0
khyadag2n_2_1	2.4	2.8	22.6	50.5	0.5	0.6	0.2	2.2	6.6	10.7	0.0
khyadag2n_3_1	2.8	2.9	23.2	50.6	0.6	0.6	0.3	2.2	6.2	9.6	0.1
khyadag2n_4_1	2.5	2.9	22.3	52.0	0.7	0.6	0.2	2.4	5.8	9.6	0.0
khyadag2n_5_1	1.3	3.6	23.6	47.2	0.8	0.6	0.0	1.9	8.0	11.6	0.3



MCI6249 Khyadag slag Sample 3

Mass 7.8 g

Spectrum	Na2O	MgO	Al2O3	SiO2	P2O5	SO3	ClO	K2O	CaO	Fe2O3	CuO
khyadag3_1_1	0.6	1.1	6.0	83.4	0.6	0.5	0.2	1.0	2.0	4.2	0.2
khyadag3_2_1	0.9	1.5	8.3	78.7	0.7	0.4	0.2	1.3	2.4	4.4	0.7
khyadag3_3_1	1.2	1.4	7.3	73.9	2.6	0.5	0.4	1.4	5.1	5.8	0.2
khyadag3_4_1	0.8	1.6	8.8	75.0	1.0	0.4	0.3	1.4	3.2	7.0	0.1
khyadag3_5_1	0.7	1.7	8.2	73.6	2.3	0.4	0.2	1.3	4.8	6.0	0.4