

# TRACE ELEMENT GEOCHEMISTRY OF ANCIENT SLAGS

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## **Abstract**

About one hundred samples from bloomery sites in Viby parish in Närke (Sweden), dated between 900 BC to 1000 AD, have been investigated using petrographic methods, microprobe analyses as well as chemical analyses for major, minor and trace elements. Samples from a 16<sup>th</sup> century smithy were included. The results are used to discriminate between bloomery and smithing slags according to the physico-chemical conditions reached. They also provide clues to whether or not a certain ore was used, and can be applied for estimating the amount of iron produced at the site.

The archaeological excavations for the new motorway (E20) through Viby parish in the county of Närke in Sweden, carried out by the Department of Archaeological Excavations have brought forward a number of bloomery sites dated from late Bronze Age to late Viking period (900 BC – AD 1000). Twenty-five furnaces were found at four sites (Skävi A-C, Vreten, Sågebol, Västra Backa). Details on the furnace constructions have been given elsewhere (Hjärthner-Holdar & Kresten 1996). In addition, a 16<sup>th</sup> century smithy was excavated. About one hundred samples have been investigated using polished thin sections for petrographic studies and electron microprobe analyses, as well as chemical analyses for major, minor and trace elements using ICP-AES and ICP-MS.

## **Geothermometry of slag samples**

The principal components of ancient iron slags are fayalitic olivine, wüstite, and glass. Spinel such as hercynite or magnetite are present in many samples, as are iron droplets. The distribution of, e.g. iron, manganese and magnesium between olivine crystals and the melt are determined by the temperature of olivine crystallisation, provided that the phases are in chemical equilibrium. The latter is usually attained only after prolonged heating, in practice, a minimum of several hours. On rapid cooling, the original compositions are preserved, while slow cooling promotes continued exchange of matter between olivine and melt.

Therefore, electron microprobe analyses of olivine and residual melt (now: glass) can provide essential information on the thermal history of the sample. We have applied the calibration of Leeman & Scheidegger (1977) for rocks of basaltic composition to ancient iron slags (Kresten, Larsson & Hjärthner-Holdar 1996). Calculated crystallisation temperatures are reliable, with a median value of about 1100°C for 806 olivine-glass pairs from bloomery slags. Equilibrium conditions have been attained for most of these samples. For smithing slags, this is not the case, most likely due to

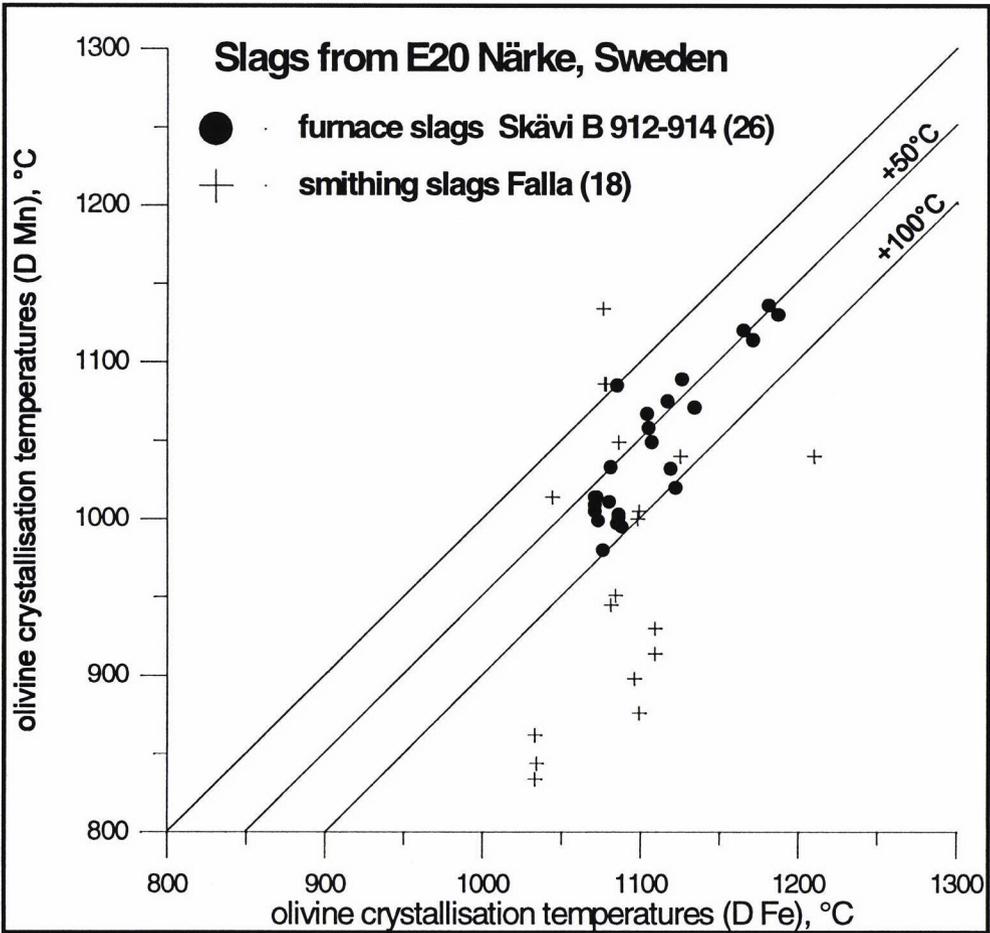


Fig. 1. Calculated olivine crystallisation temperatures for furnace slags (apparently in equilibrium) and smithing slags (scatter = disequilibrium).

1) the relatively short duration of the process, and 2) the highly variable physico-chemical conditions during smithing. Full details on the method and its applications are given by Kresten, Larsson & Hjärthner-Holdar (1996).

An example is shown in Fig. 1. For furnace slags, olivine crystallisation temperatures calculated for iron are about 50°C higher than those calculated for manganese, but all values plot within a 100°C wide band, confirming equilibrium conditions during crystallisation. Smithing slags show no apparent correlation between the two sets of calculated temperatures. Therefore, disequilibrium, which is one of the characteristic features of the smithing process, can be confirmed.

Consequently, the cation distribution between olivine and glass in ancient slags is an important tool for deciding whether or not a “slag cake” is derived from smelting or from smithing. Preferentially that tool is used in combination with other sources of information, such as petrography.

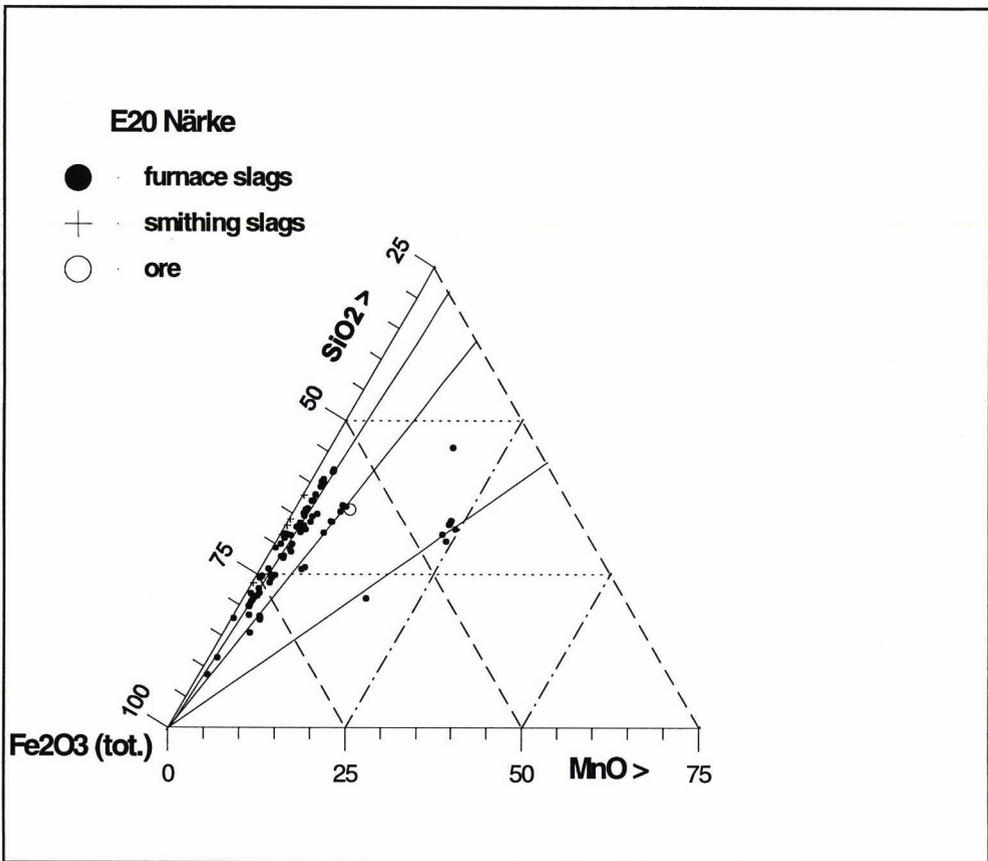


Fig. 2. Plot illustrating that three principal ore types were used: one with low MnO contents, one with moderate MnO contents, and a manganese-rich ore.

### Major and minor element geochemistry

The ternary plot SiO<sub>2</sub> – total iron – MnO is particularly useful for examining the possible relationships between furnace slags and ore (Kresten 1987). The plot for furnace slags from E20 Närke indicates three possible types of ore: the majority of slags are derived from ores with very low MnO contents, other slags are derived from ores with low to moderate MnO contents similar to the analysed one from Lillvreten, while some slags indicate a manganese-rich ore source (Fig. 2). Six of the latter samples are from two furnaces at Skävi C dated to Migration Period and Viking Age, respectively, and one sample from Sångebol A31, dated to late Bronze Age. Thus it seems that manganese-rich ore was used occasionally during the whole time span of the furnace sites.

Some of the furnace slags are markedly enriched in phosphorous, an enrichment which seems to follow the “bone line”, i.e. the calcium to phosphorous ratio in analysed bone material, particularly the samples from Skävi B, A914-6 (Fig. 3). These are three adjacent shaft furnaces dated from Vendel to Viking periods. A plausible explanation would be that crushed bone was added to the charge during smelting, e.g. in order to reduce the viscosity of the slag. This assumption appears to be strengthened by the occurrence of crushed and/or charred animal bones at most of the sites excavated. Still, trace elements show that this explanation is unlikely.

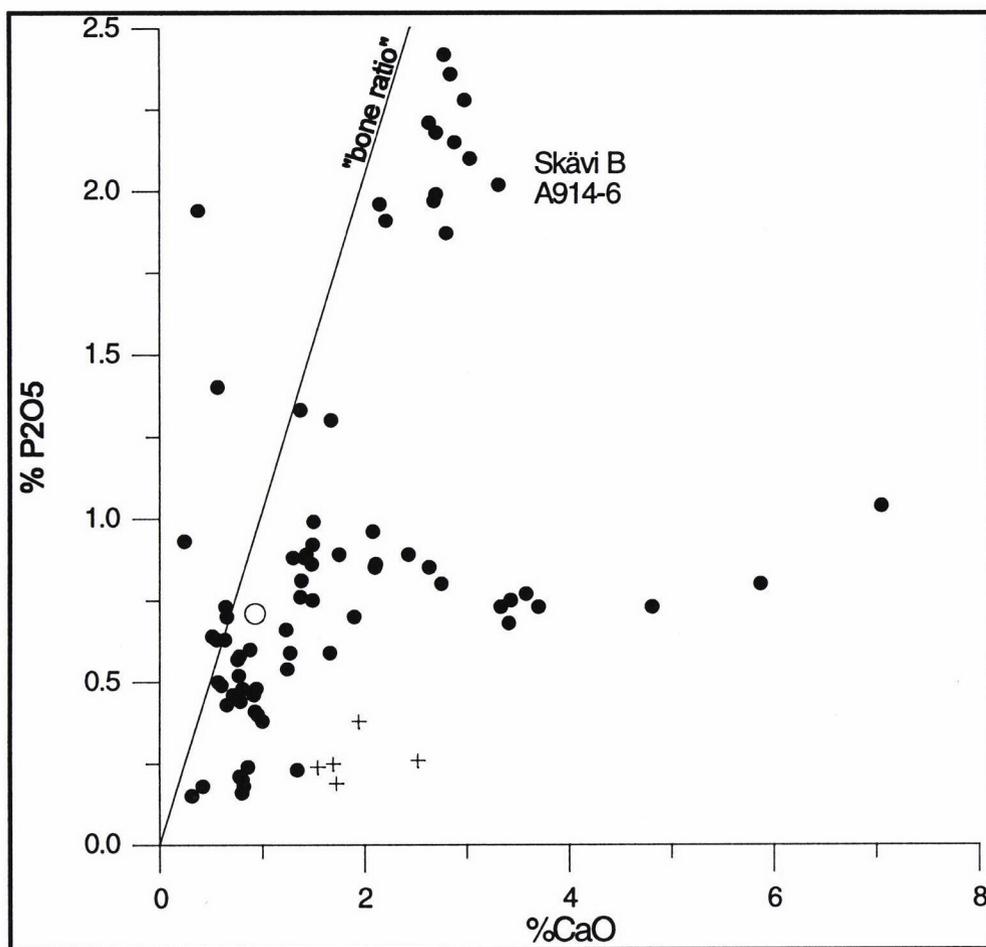


Fig. 3. Phosphorous-rich slags from Skävi B plot near the ratio of calcium and phosphorous in bones and could therefore be interpreted as having formed as a result of fluxing the charge with bones. Symbols as in Fig. 2.

### Trace element geochemistry

Trace elements are powerful tools in deciphering materials used, and processes employed. With reference to ancient slags, we are as yet only at the beginning of quantitative trace element geochemistry. Fig. 4 shows the uranium contents of slags and ore, versus phosphorous. The samples from Skävi B, A914-6, are distinctly different from all other samples. If one assumes that phosphorous comes from crushed bone (about one part bone per twenty parts of ore), these bones would have had uranium contents in the level of about 0.6% U. This is not only implausible but quite impossible. A tentative explanation would be that bog ore had been used which was mixed up with bone material that had adsorbed uranium from percolating water.

Rare earth elements (REE), or lanthanides, are a group closely related elements, from lanthanum (atomic number 57) to lutetium (71). REE distribution patterns are commonly shown in chondrite-normalised form; we have used "chondrite CI" (Evensen, Hamilton & O'Nions 1978). Experimental iron smelting, carried out by the Lab-

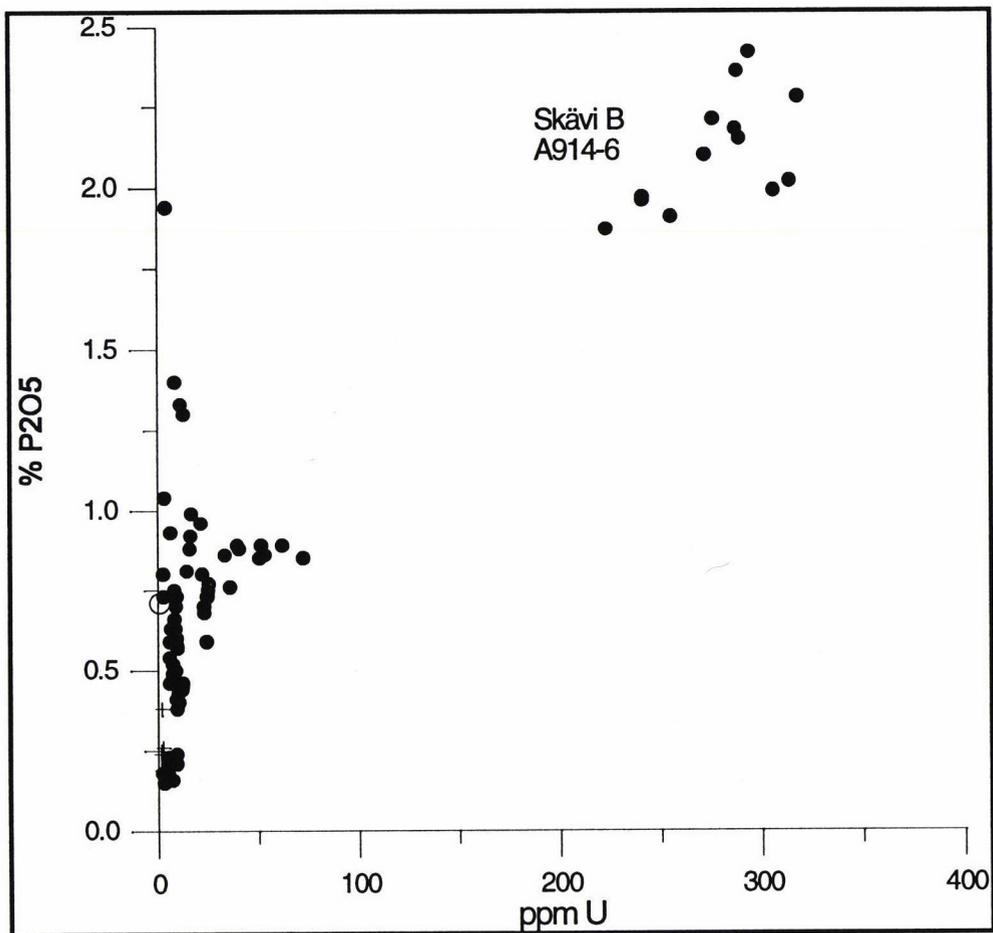


Fig. 4. Anomalously high uranium contents disqualify bones as causing the high phosphorous contents, unless they had adsorbed uranium from percolating groundwater. Symbols as above.

oratory in cooperation with Peter Crew, Plas Tan Y Bwlch, Wales, has shown that the REE pattern of the ore is conserved in the furnace slags, but REE contents increase as a result of the extraction of iron. Contributions of REE by furnace lining or charcoal ash seem to be negligible. The REE patterns of furnace slags from E20 Närke (Fig. 5) seem to confirm these observations, with REE patterns mirroring the one for the ore at commonly higher levels. Slightly positive cerium anomalies (No 58, Fig. 5) for many slag samples can be related to the reduction process. The two samples with lowest REE contents and the most deviating patterns are the most iron-rich samples and may possibly represent, partly or wholly, primary smithing slags.

Proper smithing slags (Fig. 6) have REE contents at much lower levels than the ore (and the furnace slags) and quite deviating patterns. The experimental evidence seems to confirm that behaviour. From the plot, it does not seem likely that fluxing with sand was used, as REE contents decrease dramatically during that process. This is confirmed by a "spidergram" for a number of elements, normalised against the standard reference slag from Gryssen, Dalecarlia (Kresten & Hjärthner-Holdar 1995). If

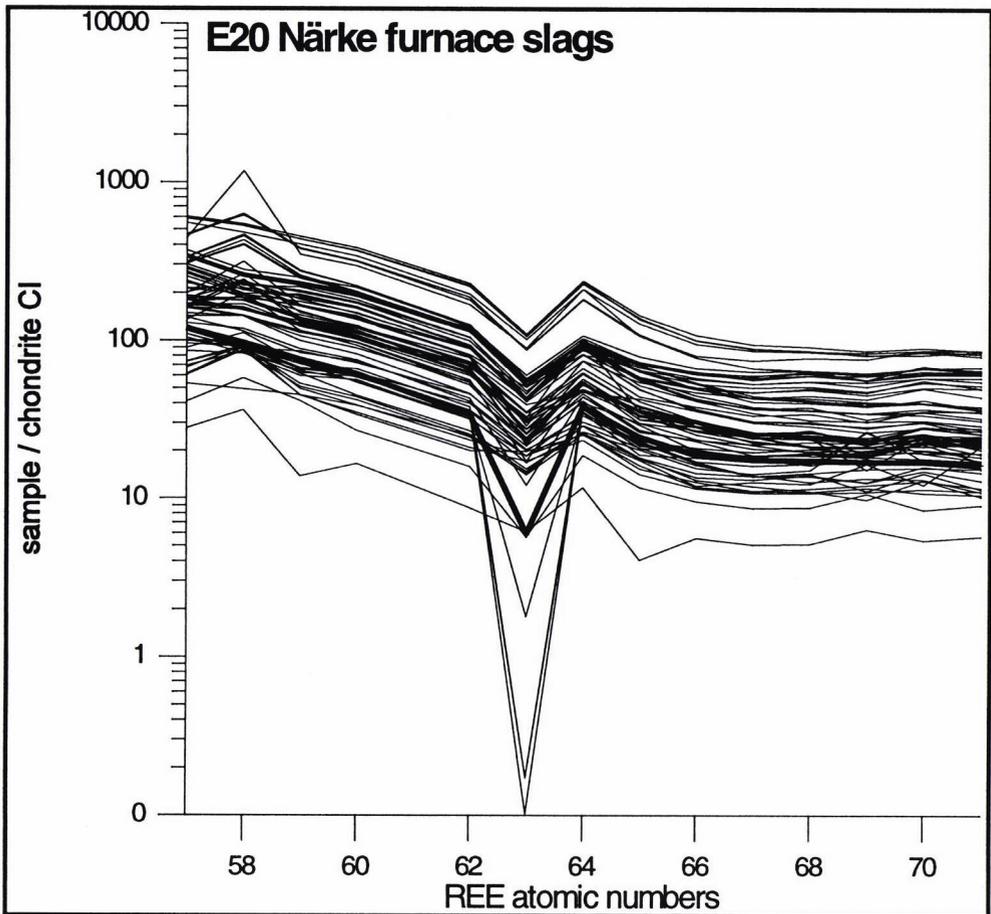


Fig. 5. Rare earth element (REE) distribution patterns, normalised to chondritic abundances. Thin lines denote furnace slags while the ore is shown by a heavy line. The similarities of the curves, with higher levels for most of the slags, confirm them as furnace slags, derived from an ore similar in REE composition than the analysed one.

sand fluxing was used, the contents of titanium, zirconium, and hafnium would increase, as ordinary sand almost invariably contains rutile (Ti) and zircon (Zr, Hf). This is not the case; instead, the contents of these elements mirror those for the ore, at lower levels (Fig. 7).

### Iron recovery

Elements which quantitatively partition into the slag phase and which are not to any essential extent contributed by charcoal or furnace lining are suitable for estimating the iron recovery. The experimental evidence has shown that the REEs, in particularly the heavy REEs, are almost ideal in that respect. For the experiment, where everything was weighed and recorded, the iron recovery calculated from the lutetium contents was virtually identical to the observed recovery. The result of the iron recovery calculation is the *metallic iron that was extracted*, i.e. not the bloom weight which

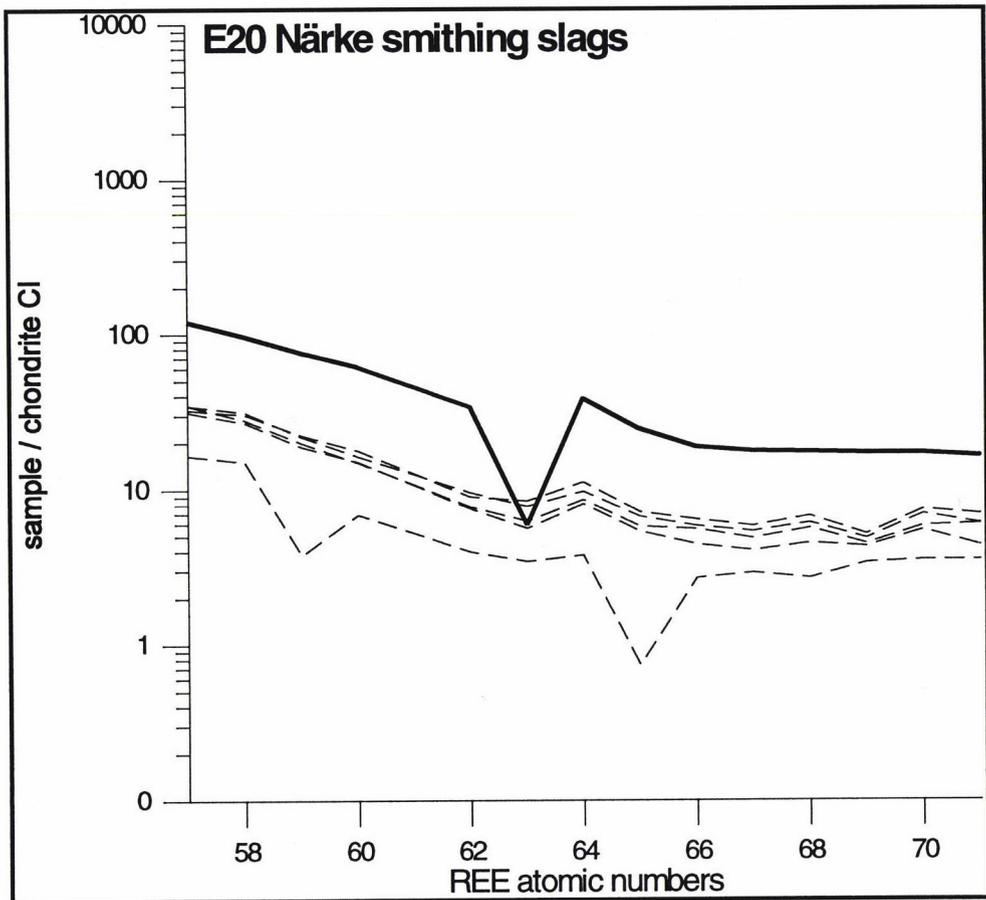


Fig. 6. As above, for smithing slags, which have REE patterns deviating from that of the ore, and much lower REE levels. If sand fluxing had been used, deviating patterns and low levels would be even more enhanced.

would be higher due to slag inclusions. The calculated average iron recovery for the furnace slags from E20 Närke is that 52% of the iron present in the ore was converted into metal.

### Concluding remarks

The data and interpretations presented in this paper bear witness on the importance of materials and processes rather than of time. In other words, a bloomery furnace will yield comparable slags and metals, whether it has been operated at Närke during the Vendel period, or by an experimenting archaeologist today, provided that the furnace type, the ore used, and the modes of operation are comparable. This is illustrated by the fact that the results of modern experiments seem to be strictly applicable to ancient iron slags.

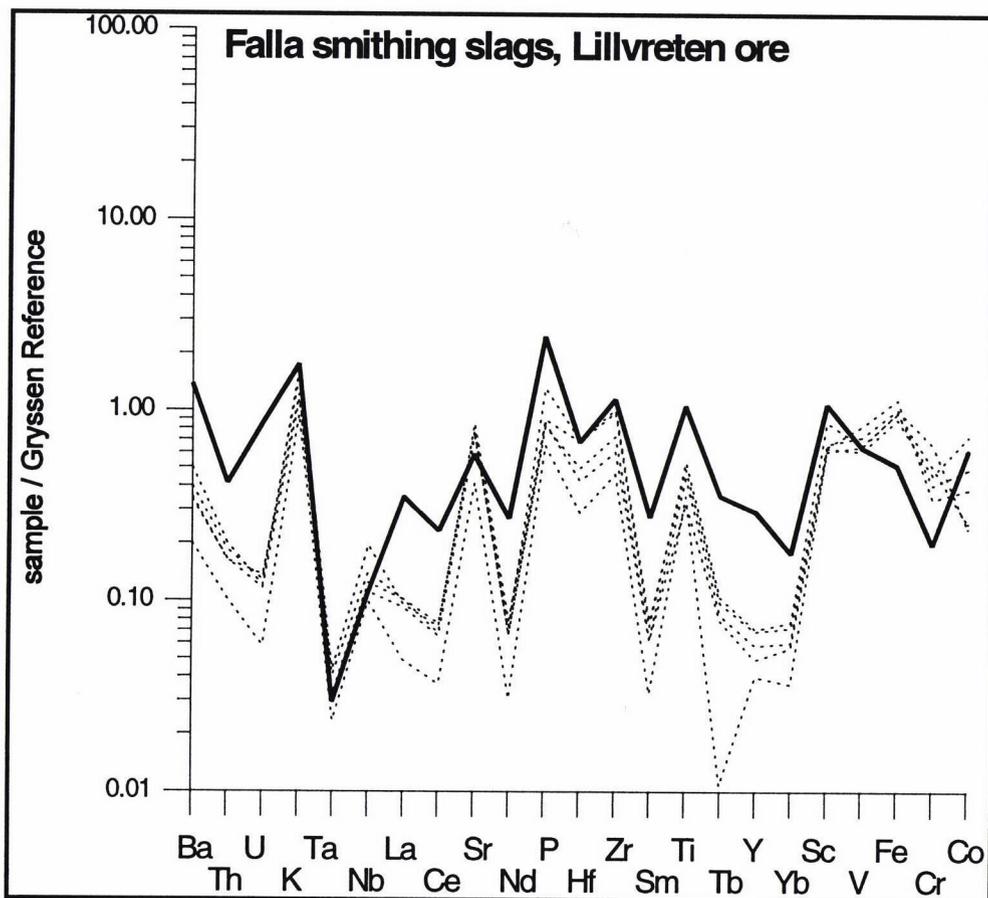


Fig. 7. "Spidergram" of selected elements, normalised to Gryssen abundances, for smithing slags. Low levels of titanium, zirconium, and hafnium confirm that sand fluxing had not been used.

## References

- Evensen, N.M., Hamilton, P.J. & O'Nions, R.K. 1978. Rare-earth element abundances in chondritic meteorites. *Geochimica et Cosmochimica Acta* 42, 1199–1212.
- Hjärthner-Holdar, E. & Kresten, P. 1996. Continuity and change during 2000 years of ironmaking. pp. 29–46 in G. Magnusson (ed.) *The importance of ironmaking. Technical innovation and social change, Volume II. Jernkontorets Bergshistoriska Utskott H62*. Stockholm.
- Kresten, P. 1987. The ore-slag-technology link: Examples from bloomery and blast furnace sites in Dalarna, Sweden. pp. 29–33 in B.G. Scott & H. Cleere (eds.) *The crafts of the blacksmith, UISPP Comité pour la Sidérurgie Ancienne*. Belfast.
- Kresten, P. & Hjärthner-Holdar, E. 1995. *Kemiska analyser av malm och slagg. En jämförelse mellan olika laboratorier – Analysvärden för referensslaggen W-25:R*. Geoarkeologiskt Laboratorium, UV Uppsala, Forskningsrapport R02-1995.
- Kresten, P., Larsson, L. & Hjärthner-Holdar, E. 1996. Thermometry of ancient iron slags from Sweden, and of vitrified material from various hill-forts in western Europe. *Geoarchaeological Laboratory, UV Uppsala, Research Report R01-1996*.
- Leeman, W.P. & Scheidegger, K.F. 1977. Olivine/liquid distribution coefficients and a test for crystal-liquid equilibrium. *Earth and Planetary Science Letters* 35, 247–257.