CONSTRUCTION AND DESCRIPTION OF THE UNIBONN BLACK BOXES

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Abstract

*In the framework of the Ancient Charm Project (*Analysis by Neutron resonant Capture Imaging and other Emerging Neutron Techniques: new Cultural Heritage and Archaeological Research Methods, http://ancient-charm.neutron-eu.net/ach), *imaging potentials of non-destructive neutron analytical methods are evaluated for archaeological applications. Prior to working on real archaeological specimens, so-called 'black boxes' were constructed (and characterised) for tests of the various methods. This paper is about the construction of these test boxes as realised by the Bonn University team.*

Kivonat

*Az Ancient Charm Program keretében (*Analysis by Neutron resonant Capture Imaging and other Emerging Neutron Techniques: new Cultural Heritage and Archaeological Research Methods, http://ancient-charm.neutron-eu.net/ach), *különféle neutron analitikai vizsgálatok képalkotási lehetőségeit vizsgáljuk a kulturális örökség körébe tartozó tárgyakon. Mielőtt a régészeti műtárgyakat vizsgálnánk, a különféle vizsgálatok lehetőségeinek felmérésére kísérleti tárgyakat, úgynevezett "fekete dobozokat" készítettünk, amelyeken a módszereket kipróbálhattuk. Az alábbi cikk a Bonni Egyetemen készült próbatestek előállítását mutatja be.*

KEYWORDS: NEUTRON BASED IMAGING ANALYSIS, EXPERIMENTS

KULCSSZAVAK: NEUTRON ALAPÚ KÉPALKOTÁSI TECHNIKÁK, KÍSÉRLETEK

Introduction

According to the intense discussions in WP1, particularly with HNM, UNIBONN designed and manufactured 12 boxes, 11 of them filled with various items composed of materials of potentially archaeological relevance or else suited to assess the individual strengths of the different probe methods. The 11th box was empty in order to serve for calibration(s) and/or assessment of the wall materials contribution.

- all boxes were cubes of dimensions 50 x 50 x 50 mm^3 made of Al-sheets of 1 mm thickness.
- each box carries its own (engraved) coordinate system with axes directions x, y, z for unique and reproducible orientations with respect to local primary beams and experimental setups
- except for the open boxes I and III, all other boxes were sealed. Their contents were defined, analysed and documented by UNIBONN and only disclosed to HNM.

The envisaged hard X-ray tomography and neutron experiments to be carried out on selected (if not all) boxes were expected to reveal the strengths and potentials as well as the weaknesses or shortcomings of the different analytical methods and thus help to set up a sequence of analytical steps that is fit to yield maximum information with respect to the elemental and phase compositions as well as the geometrical arrangements of the sample materials within shortest possible time.

Box D-I

This box featured open (001) faces. It housed 3 rows of rods with different diameters (3, 6, 10 mm) made of 3 different materials : Cu, brass, Fe (steel). All rods were parallel x. The sequence of the materials was iron, brass, copper with respect to the y-direction (**Fig. 1**). The rods (as the sheets contained in the below following box D-III) were machined from the same pieces of bulk materials.

Fig. 1. - View of box D-I

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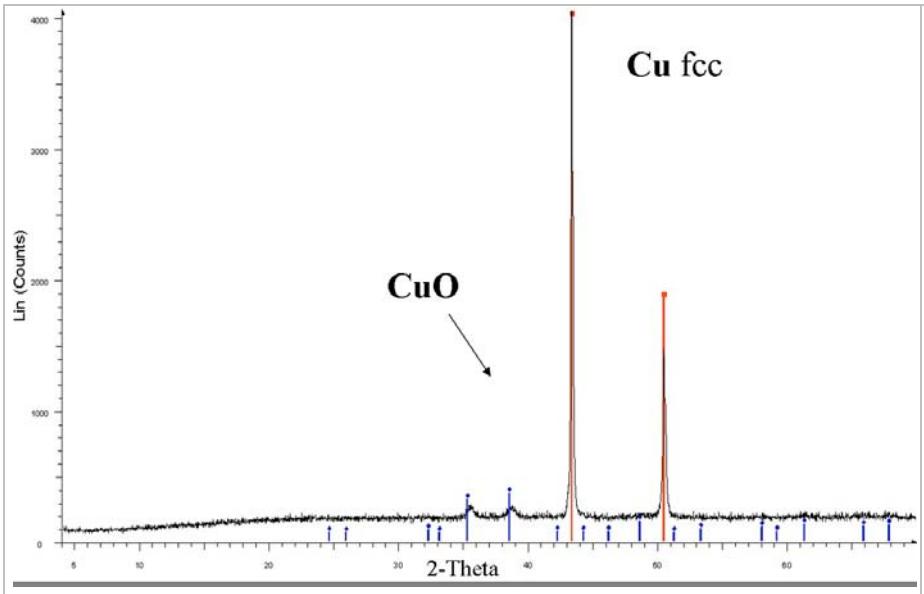

Fig. 2.

Diffraction pattern of Cu-rod

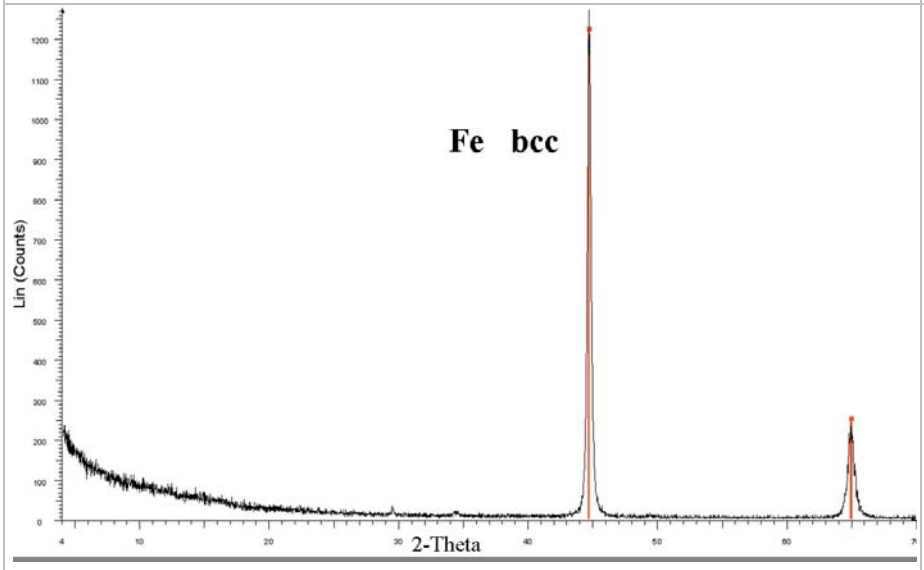

Fig. 3.

Diffraction pattern of steel rod

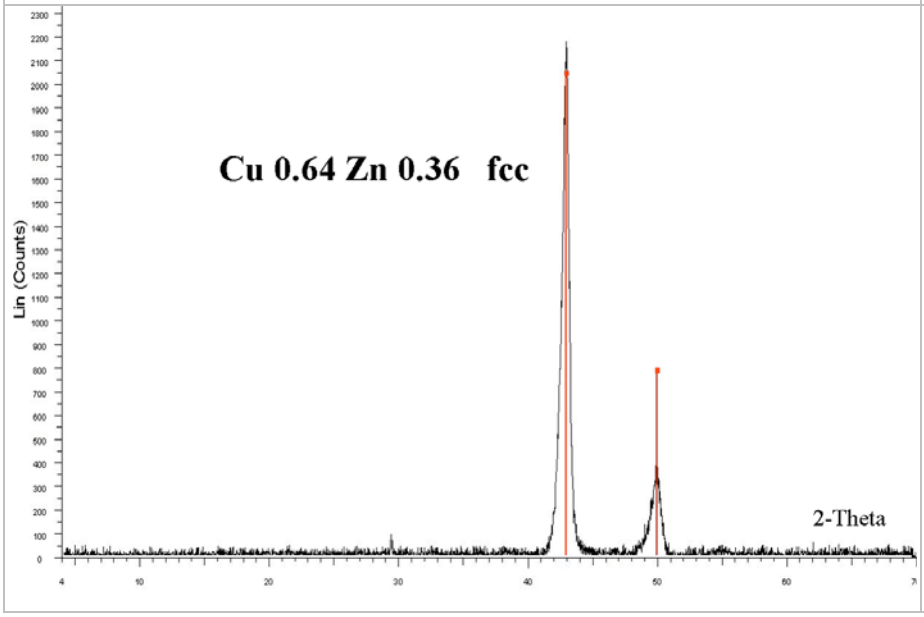

Fig. 4.

Diffraction pattern of brass rod

X-ray powder diffraction (Cu-Kα radiation) performed on these materials revealed:

1) pure Cu (fcc structure, a = 3.615 Å) along with an almost negligible amount of the oxidation product CuO (**Fig. 2**).

2) pure Fe with cubic bcc-structure (a = 2.866 Å, **Fig. 3**), and

3) brass (cubic fcc-structure) of composition Cu0.64Zn0.36 (a = 3.647 Å) along with a tiny contamination by hexagonal Pb (**Fig. 4**).

Comments :

This open box was designed mainly for calibration and exercising purposes so that X-ray or neutron tomography was neither needed nor (to my knowledge) done.

Box D-II

Contained two pairs of equally dimensioned and parallel oriented spirals made of 2 mm thick copper and brass wires, respectively. The helix axes of the spirals were along the x-direction. In z-direction, the sequence of the spiral pair materials was Cu, brass (**Fig. 5**). There was no filling material in the box.

According to X-ray powder diffraction experiments (Cu-Kα radiation) carried out on pieces of the two wire materials the copper wire turned out as pure Cu (**Fig. 6**) whereas the brass wire diffraction pattern indicated Cu0.64Zn0.36 crystallising in the cubic fcc-structure (a = 3.647 Å, **Fig. 7a**). Later, a part of the brass wire piece was ground in order to obtain a sample from the wire's interior. Its diffraction pattern (**Fig. 7b**) clearly showed a second phase of cubic symmetry, a = 2.85 Å in presence of Cu0.64Zn0.36.

This latter phase is most likely beta-brass (CuZn, Pn-3m, a = 2.95 Å) with Cu:Zn exceeding 1.

Comments:

It should be noted that in the laboratory diffraction analyses of the wire materials, due to absorption the Cu-radiation probed only the surfaces of the wire pieces. Differences between X-ray and neutron diffraction findings can therefore be caused by the much higher penetration of neutrons. Thus, the later reported neutron finding of a second brass phase in the brass spiral is not necessarily at variance with the X-ray result. It simply implies that the interior of the brass wire may differ from the surface region, as proved by the second diffraction analysis. This result presents a good example for the importance of bulk material analysis by neutrons because it non-destructively revealed the inhomogeneous nature of the brass wire.

For whatever reasons, the box coordinate system used in the tomographic X-ray experiment differs from that given on the box itself: $x_{tomo} = - z_{true}$; $y_{tomo} = - x_{true}$; $z_{tomo} = y_{true}$

Box D-III

As D-I box D-III featured open (001)- faces. **Fig. 8** shows the arrangement of parallel Cu- and iron-sheets of different thickness, all oriented perpendicular to x. The sheet sequence with respect to x was Cu 1 mm, Cu 3 mm, Fe 8 mm, Cu 4 mm, Fe 4 mm. All spacings between the sheets were 4.66 mm. This design was chosen in order to enable tests of the spatial resolution potentials of the different methods.

Comments:

The copper and iron material was the same as used for box D-I.

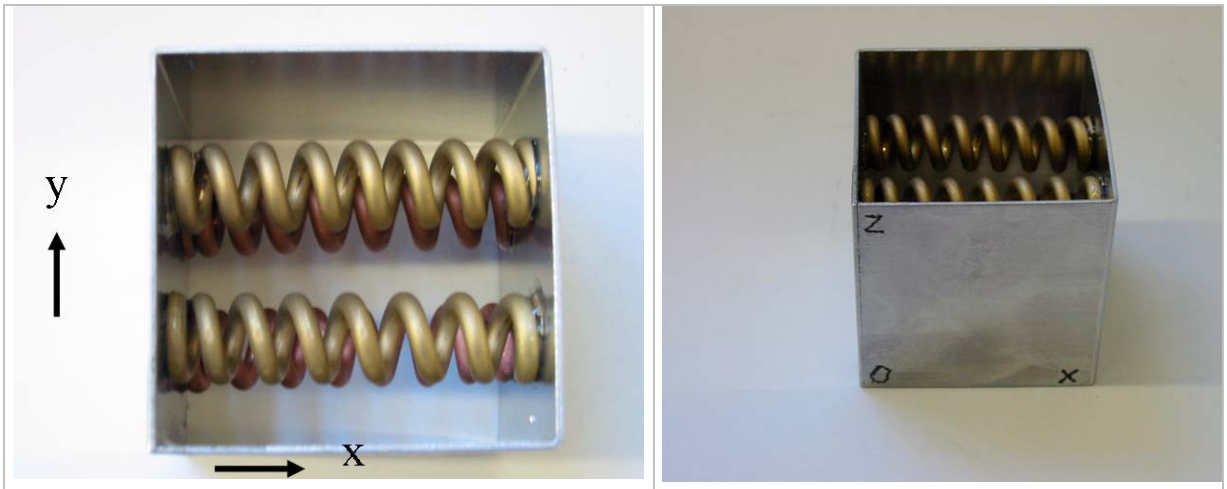

Fig. 5. - views of box D-II

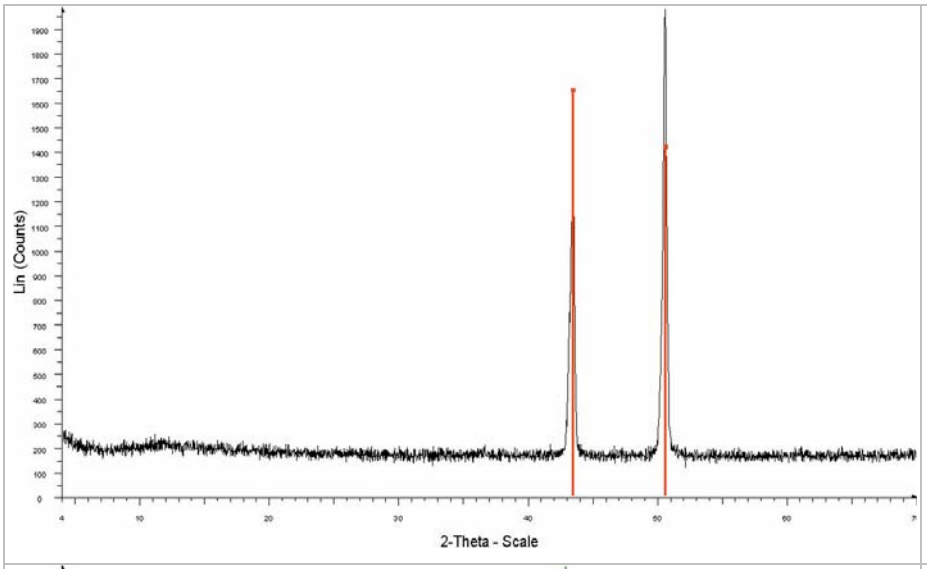

Fig. 6.

Diffraction pattern of Cu-wire

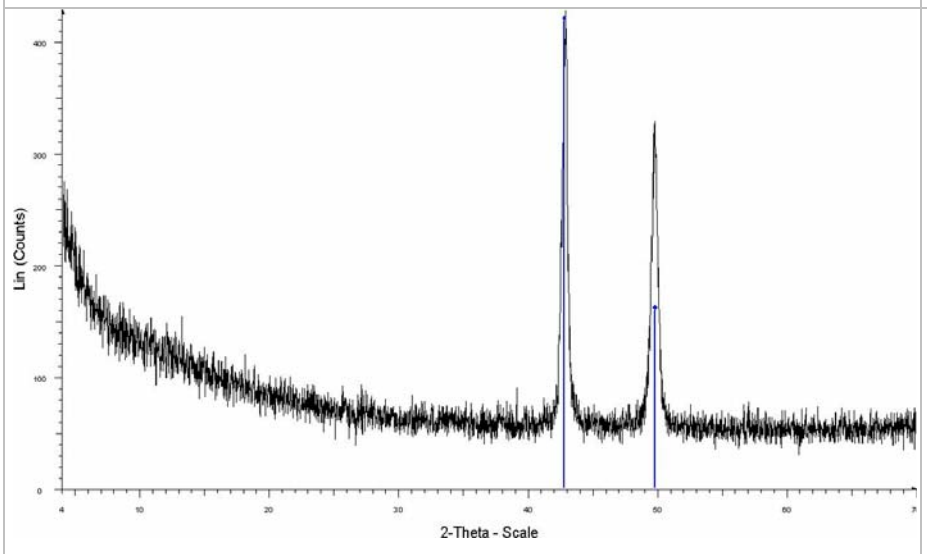

Fig. 7a.

Diffraction pattern of brass wire (surface region)

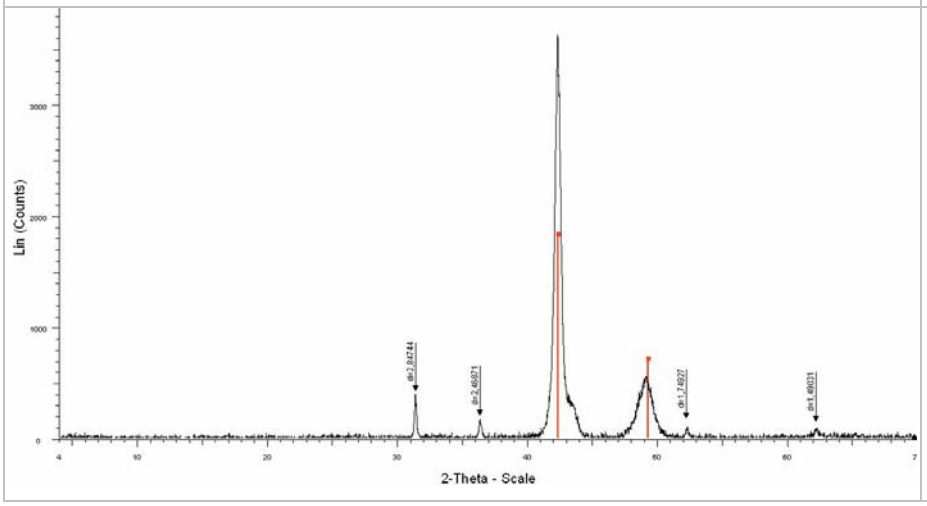

Fig. 7b.

Diffraction pattern of brass wire (bulk)

Box D-IV

Box D-IV (**Fig. 9**) contained a 1 mm thick Al-wall perpendicular to the x-direction creating two chambers of equal size. Each chamber housed two metal rods mounted parallel z and with diameters of 6 mm (low y) and 10 mm (high y), respectively. The rod material at low x was Cu, that at high x iron, both the same as used for D-I and D-III.

The Cu-rods were completely embedded in rocksalt (halite, NaCl), the steel rods in clay purchased in a hobby market. Both filling materials were analysed

by X-ray powder diffraction (Cu-Kα radiation): rocksalt was found as pure NaCl (**Fig. 10**). The clay pattern (**Fig. 11**) showed a mineral mixture which according to quantitative Rietveld analysis consisted of 51 % calcite, $CaCO_3$, 20 % quartz, SiO_2, 12 % muscovite 2M1, $KAl_2(AlSi_3O_{10})(OH)_2$ and 17 % kaolinite, $Al_4(OH)_8(Si_4O_{10})$.

Comments:

Due to the complicated mixture of low symmetry structures the clay material presents a challenge to ND considering phase identification and abundance determination. Also, the box presents a great variety of elements to PGAA: Cu, Fe, Na, Cl, Ca, Si, Al, Mg, O, C. Thus, it is particularly interesting to explore the degree to which elemental analysis can help with the characterisation of the clay material.

Box D-V

Box D-V contained no filling material. The hidden items (**Fig. 12**) were 3 concentric Cu-tubes of 48 mm length oriented along the z-direction. The first tube with circular cross section had a diameter of 40 mm and a wall thickness of 1.2 mm. This tube contained a second tube with a square cross section, edge lengths of 23 mm, a wall thickness of 1.4 mm and the faces parallel to x and y. The third tube inside the second possessed a regular triangular cross section with edge length of 15 mm and wall

Fig. 8. - Views of box D-III

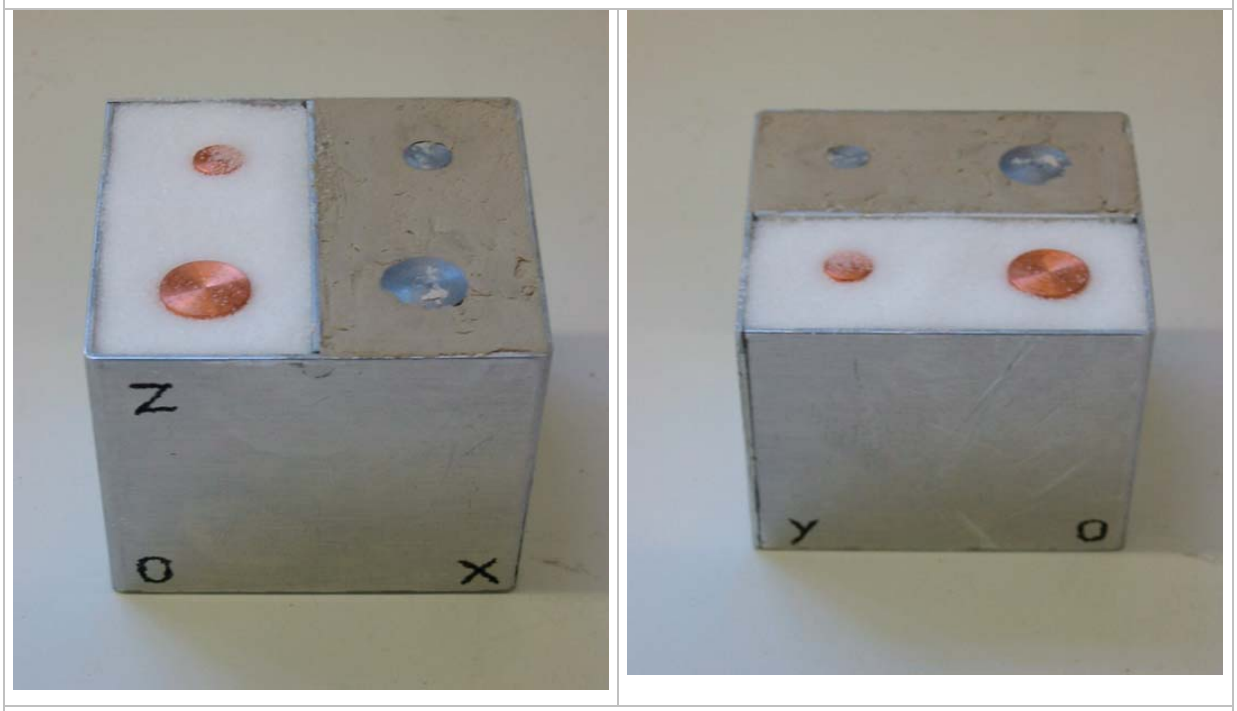

Fig. 9. - Views of box D-IV

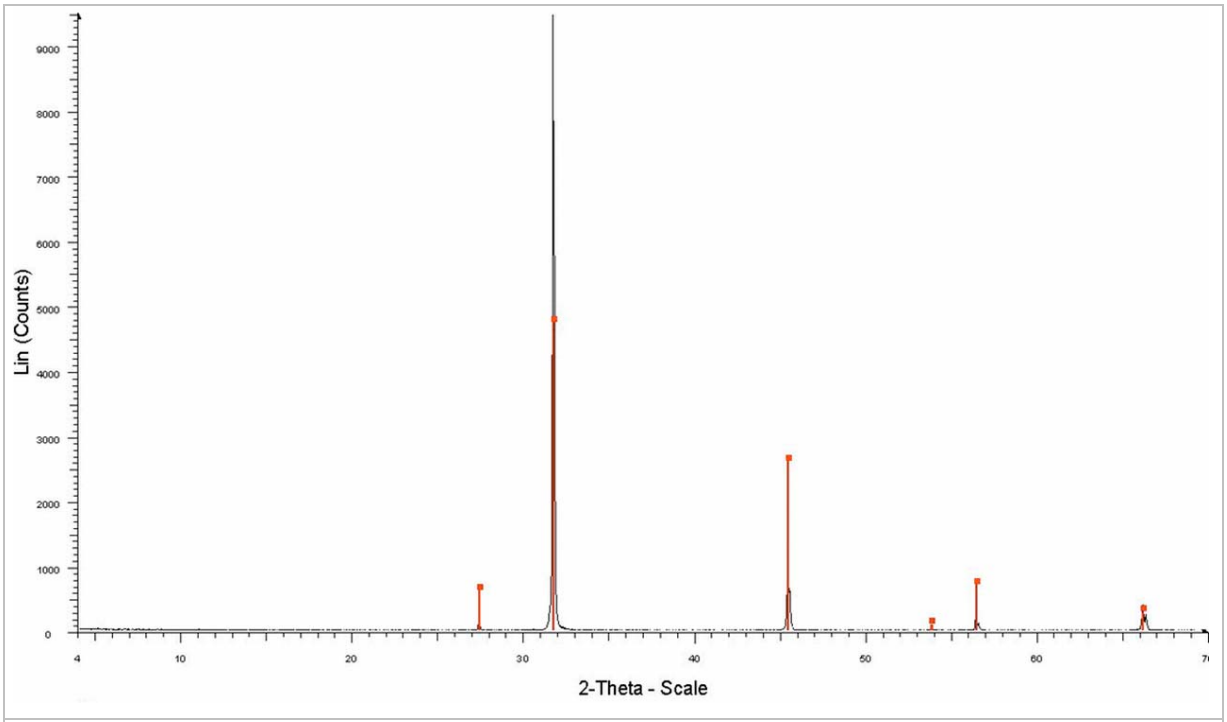

Fig. 10. - Diffraction pattern of cubic rocksalt

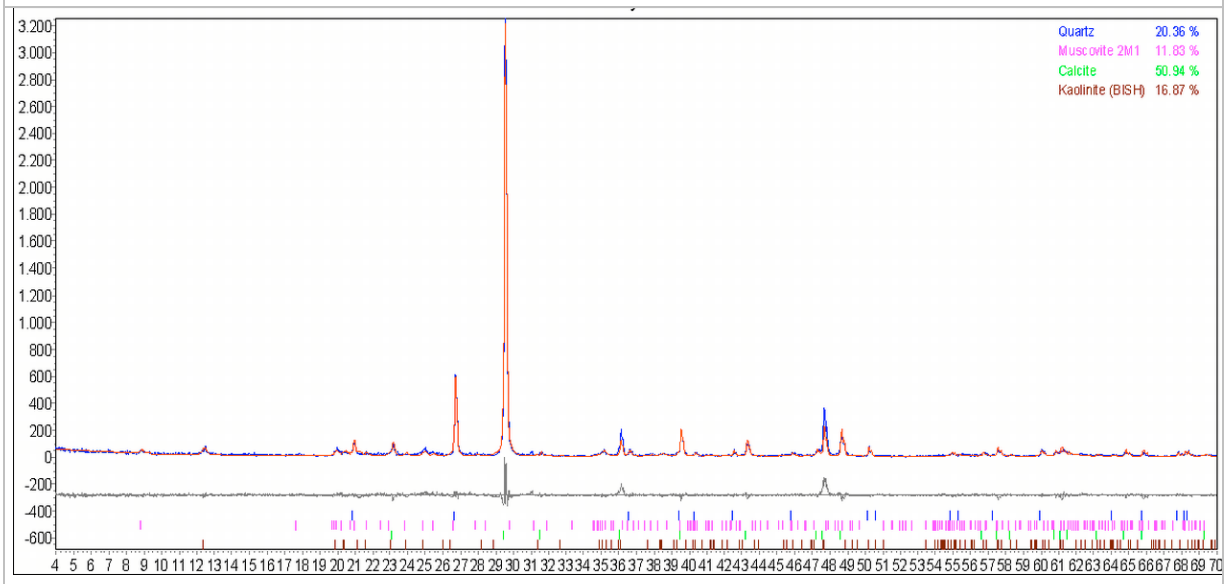

Fig. 11. - Diffraction pattern of clay

thickness of 1.4 mm, one tube face being perpendicular to the x-direction. With respect to ND the resulting concentric arrangement allowed for exploring the effects of transmission through and diffraction from up to 8 walls (Al included).

Comments:

Cu-material as before.

Box D-VI

The design of box D-VI is characterised by two iron plates of 6 mm thickness forming a 'Λ' in the x,y-plane, i.e. a wedge parallel z with mirror symmetry perpendicular to x (**Fig. 13**). The remaining space in the box was filled with synthetic hematite powder, Fe_2O_3, as possible oxidation product. The X-ray powder diagram is depicted in **Fig. 14**.

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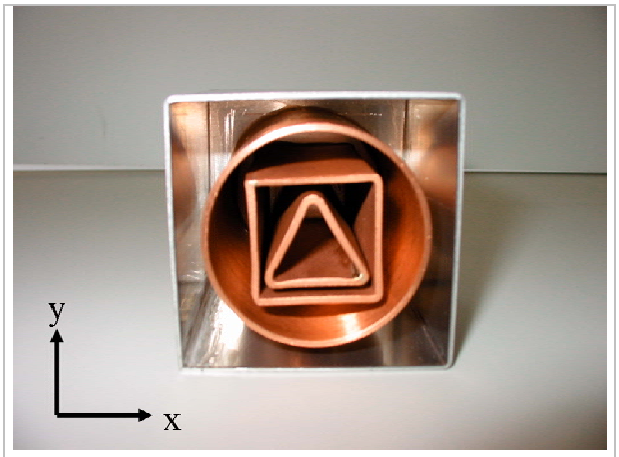

Fig. 12. - View of box D-V

This simple arrangement was expected to demonstrate that once exclusively Fe is identified by PGAA, ND is the method of choice to elucidate the nature of the Fe-bearing material(s).

Comments:

Fe-material as before. X-ray absorption tomography expected to exhibit only little phase contrast.

Box D-VII

Box D-VII was simply filled with three 16 mm thick layers of different materials oriented normal to z (**Fig. 15**). With respect to increasing z the layer sequence was: pre-sintered corundum), Al_2O_3, (with a central drill hole of 16 mm diameter), hot pressed graphite and commercial pyrophyllite, $Al_2Si_4O_{10}(OH)_2$.

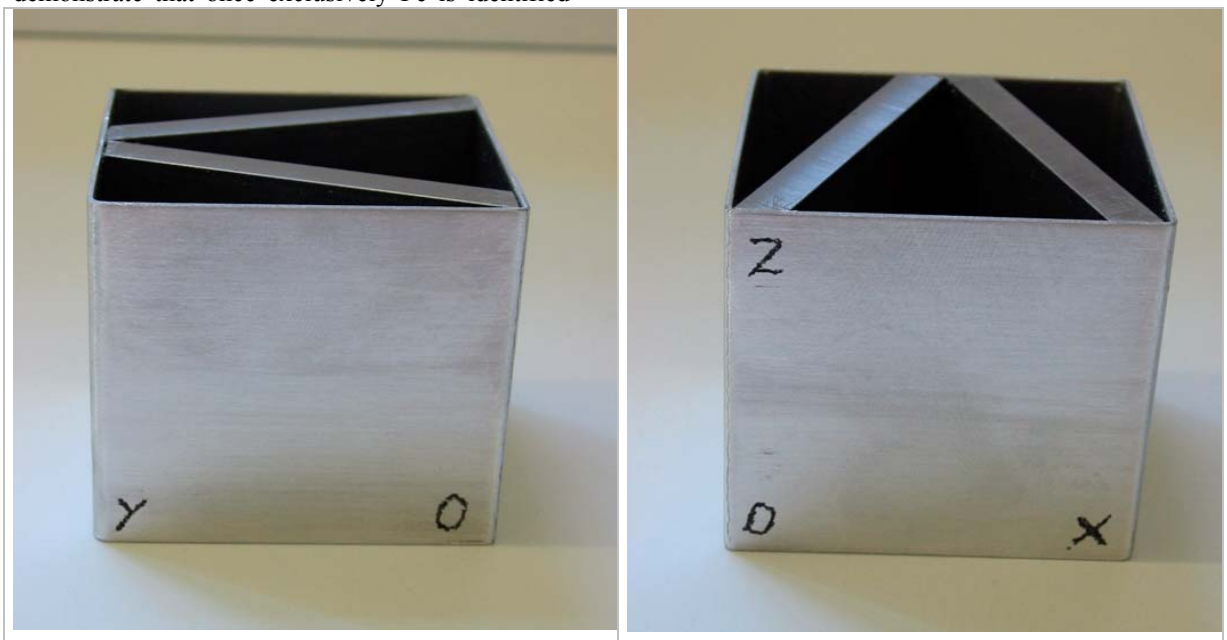

Fig. 13. - Views of box D-VI

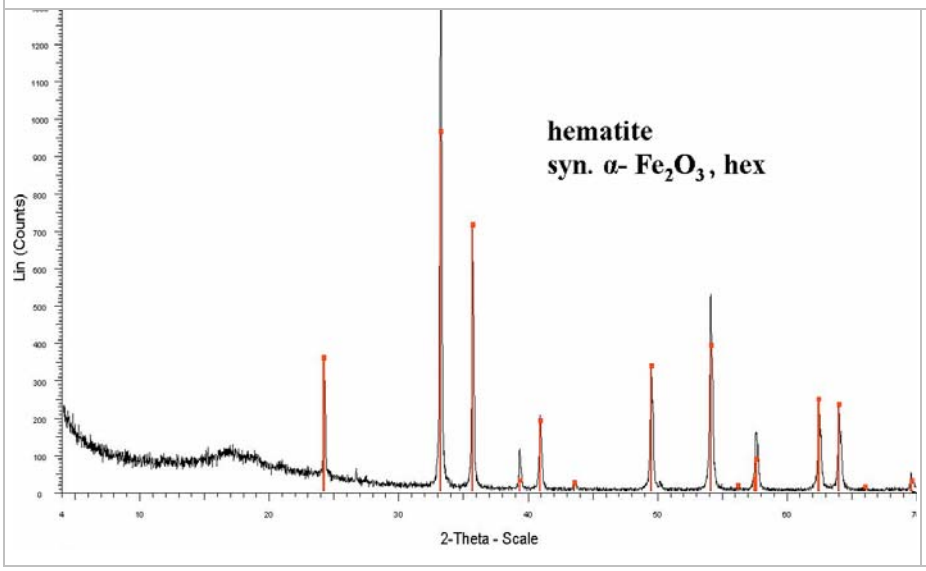

Fig. 14.

Diffraction pattern of trigonal hematite

Fig. 15 - Views of box D-VII

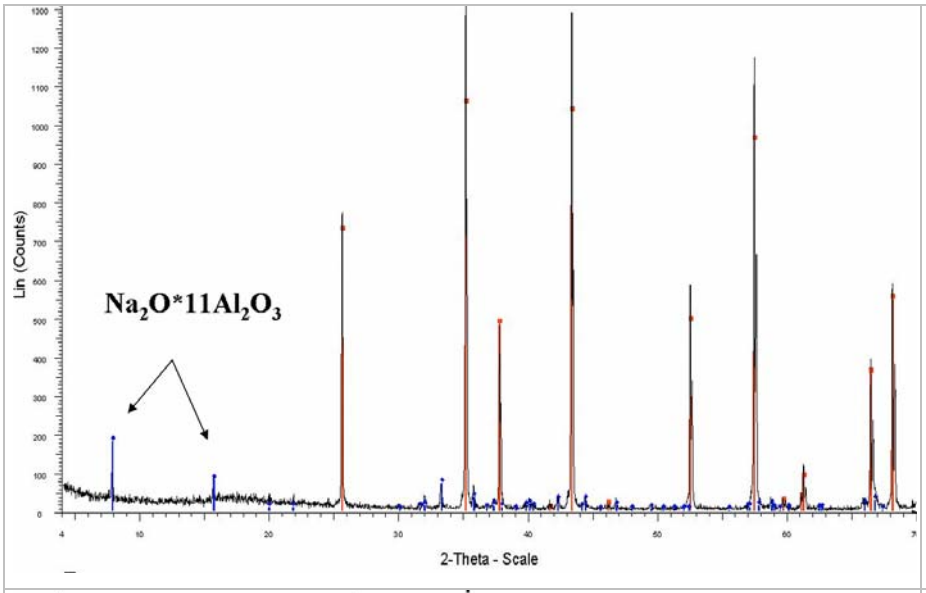

Fig. 16.

Diffraction pattern of trigonal corundum

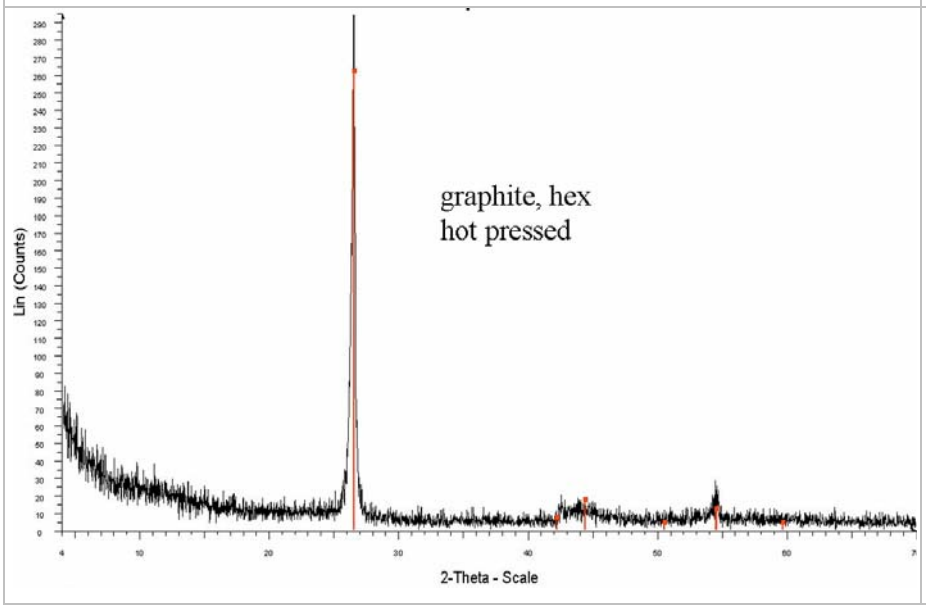

Fig. 17.

Diffraction pattern of commercial hot pressed graphite

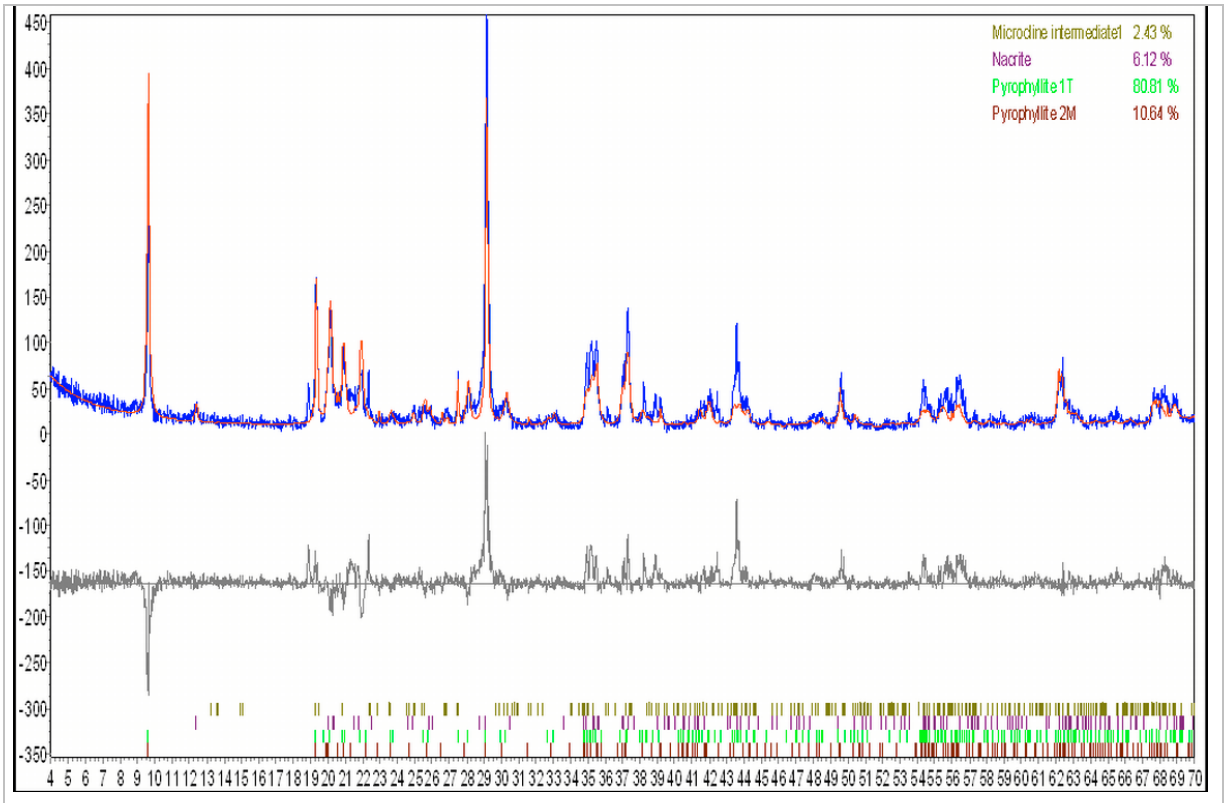

Fig. 18. - Rietveld refined diffraction pattern of commercial pyrophyllite

X-ray powder diffraction analyses (CuKα-radiation) revealed some contamination of corundum by diaoyudaoite, $Na_2O*11Al_2O_3$ (**Fig. 16**) , adding Na to the list of elements.

While the graphite plate showed the simple, typical pure carbon diagram (**Fig. 17**), the pyrophyllite diagram exhibited additional small amounts of the phyllosilicate mineral nacrite, $Al_2(Si_2O_5)(OH)_4$ and of the feldspar mineral microcline, $KAlSi_3O8$. Quantitative Rietveld analysis yielded 81 % pyrophyllite 1T, 11 % pyrophyllite 2M, 6 % nacrite, and 2 % microcline (**Fig. 18**). Due to the complex composition of the box content comprising K, Si, Al, Na, O, C and H, box D-VII challenged both PGAA and ND.

Fig. 19. - Views of box D-VIII

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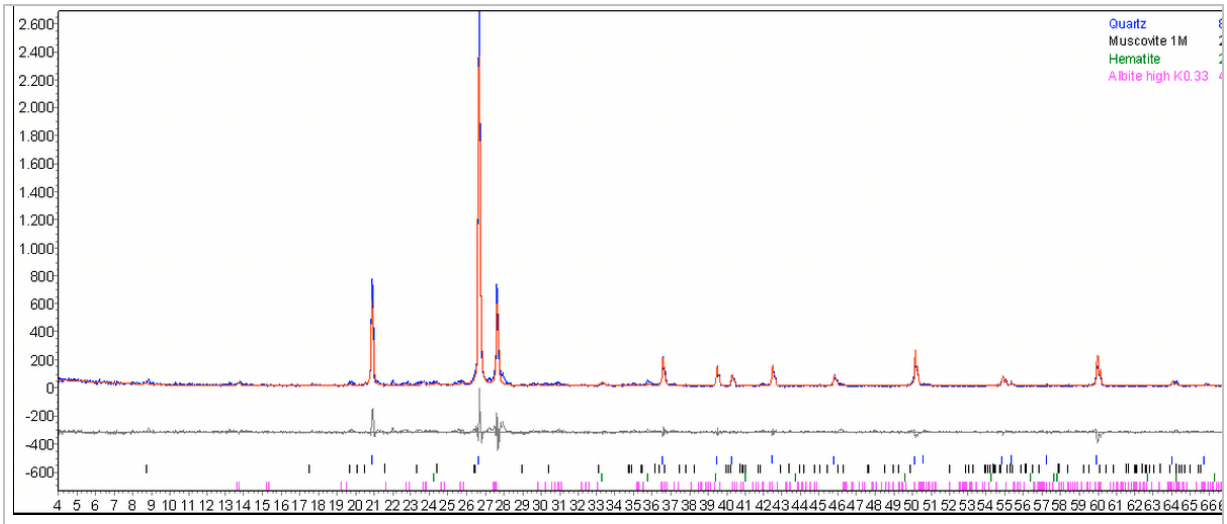

Fig. 20. - Rietveld refined diffraction pattern of fired clay (earthenware)

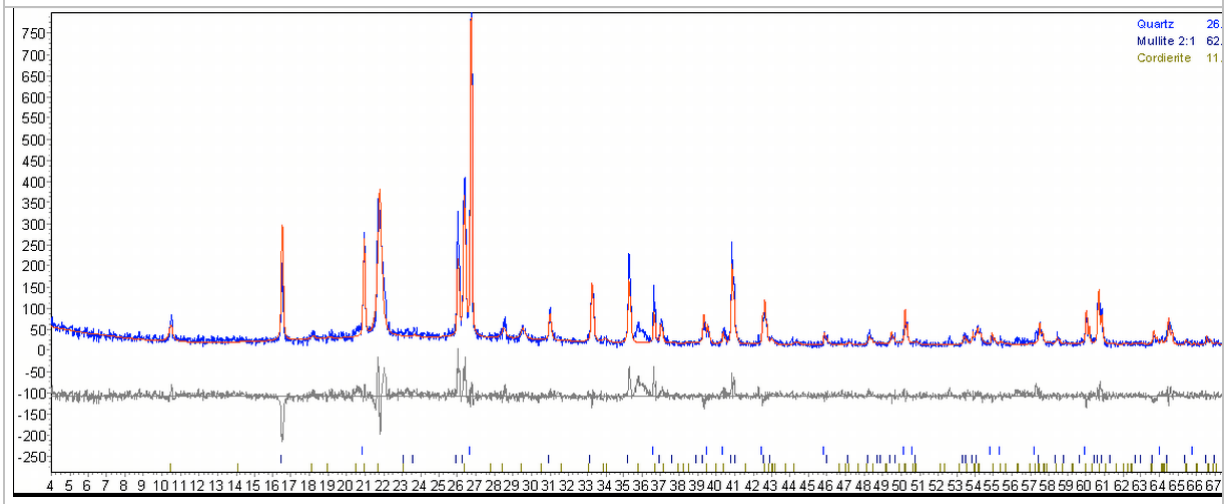

Fig. 21. - Rietveld refined diffraction pattern of fire brick (chamotte)

Comments:

Particularly for ND, it is of great interest to learn which information can be retrieved from an unknown diffraction diagram not only containing a large number of possibly overlapping reflection peaks but also peaks that can be offset from their true positions depending on the position of the scattering volume in the box. Can PGAA contribute to phase identification(s) ?

Box D-VIII

Apart from the drill hole in the bottom layer of D-VII, the design of box D-VIII repeated that of D-VII, however, with more difficult matter (**Fig. 19**). Again with respect to the z-direction, there was a sequence of three layers, here: clay, fired clay (earthenware) and fire brick (chamotte). Thus, different stages of pottery were simulated by earthenware as an intermediate firing product being sandwiched by a clay (educt) and a high firing product. Geometrically simple, D-VIII presented a very demanding case, because all three components consisted of mineral mixtures with low symmetry diffraction patterns. The X-ray diffraction patterns obtained on the earthenware and fire brick slabs are given in the **Figs. 20** and **21**, that of clay is shown in **Fig. 11.** According to Rietveld analyses the compositions of the materials were:

clay: 51 % calcite, , 20 % quartz, 12 % muscovite 2M1, 17 % kaolinite

earthenware: 90 % quartz, 5 % albite, 3 % muscovite 1M, 2% hematite

fire brick: 26 % quartz, 63 % mullite 2:1, 11 % cordierite

presenting the pottery typical list of elements: Fe, K, Ca, Si, Al, Mg, O, H

Fig. 22. - Views of box D-IX

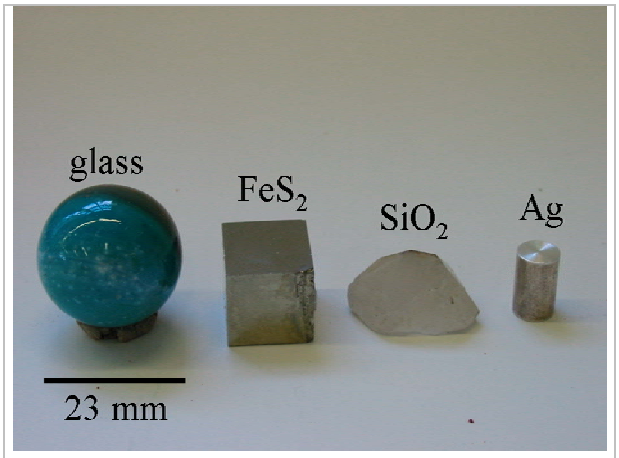

Fig. 23. - Items buried in gypsum

Comments:

The slabs were of different origins and not produced from the clay denoted as educt.

In view of the complexity of the whole sample one could expect that D-VIII presented more than a challenge, but as such a case that is well suited to shed light on the potential of combined absorption tomography, PGAA and ND.

Box D-IX

The question as to which degree relatively small single items (e.g. metal pieces, gem stones or glass) embedded in a difficult environment can be recognised, located and characterised in terms of element composition and eventually crystalline phase led to the design of box D-IX .

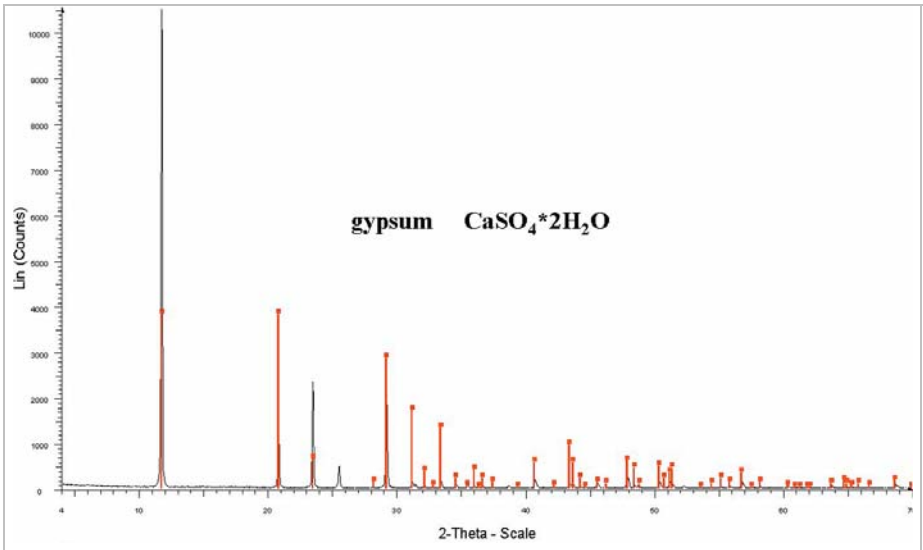

Fig. 24.

Diffraction pattern of gypsum

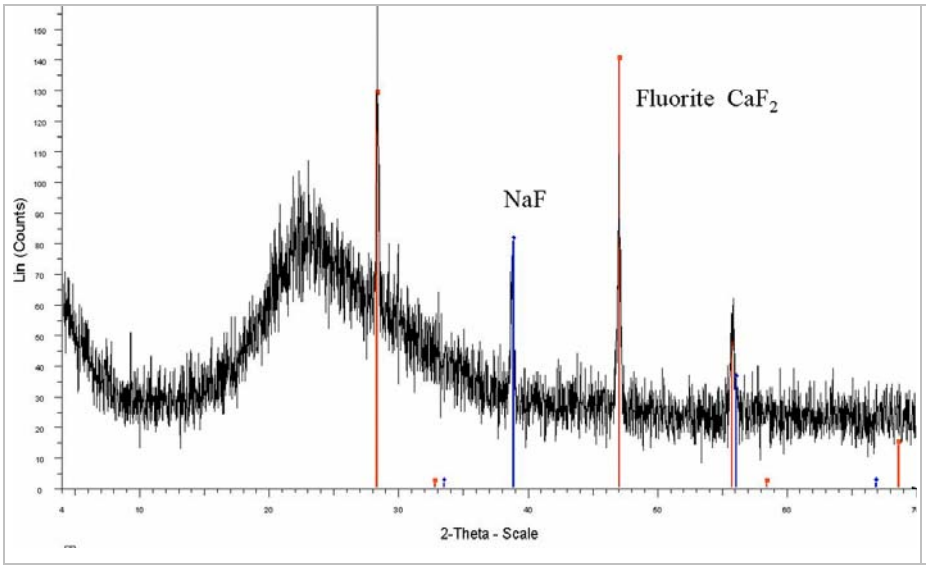

Fig. 25.

Diffraction pattern of blue coloured glass bead

As illustrated in **Fig. 22** and **23** the box contained separated from each other:

i) a quartz single crystal with pyramidal habitus, approximate dimensions 18 x 10 x 12 mm

ii) a coloured glass sphere of 23 mm diameter

iii) a pyrite (FeS_2) single crystal cube of edge lengths 14 x 14 x 16 mm^3

iv) an Ag rod of 7.5 mm diameter and 11 mm length

The remaining box volume was filled with gypsum, $CaSO_4$ *$2H_2O$, as difficult environment due to the presence of the large amount of hydrogen.

X-ray powder diffraction patterns showed pure synthetic gypsum (**Fig. 24**) and in particular (**Fig. 25**) for the glass sphere some inclusions of crystalline fluorite, CaF_2, and villaumite, NaF, causing the blue colour.

Comments:

Assumed absorption tomography could locate the 4 items, ND could be expected to identify the filling material and the Ag rod, and also to indicate the presence of the large single crystals by observation of single crystal reflections, which may even suffice to disclose the chemical composition by trial and error.

Box D-X

Contrary to the inorganic polycrystalline materials used so far the content of box D-X consisted to the greatest part of organic and thus 'amorphous' materials. The thigh bone of a badger was partly wrapped in leather and then deposited with orientation parallel to the z-direction in the centre of a closely fitting container made of beech wood. The assembly is shown in **Figs. 26** and **27**.

Fig. 26. - Views of box D-X

Fig. 27. - Items in box D-X

Clearly, apart from the 'bio-minerals' in the bone there was nothing in the box for which ND could produce structured diffraction patterns on top of a high background caused by hydrogen. On the other hand, due to the different absorption properties of the materials contrast rich tomography images could be expected.

Comments:

Most information would have to come from X-ray tomography and PGAA. However, a lack of results from ND would also present an important piece of information.

Box D-XI

Is an empty box for studying effects caused by the Al-walls.

Box D-XII

Box D-XII completes the series. It was built on special request by the PGAA group. This box housed a cubic tin box of 30 mm edge length and about 1 mm wall thickness positioned in the centre of the Al-cube. The tin box itself contained 2 discs made of copper and lead, respectively (both with 28 mm diameter and 9.3 mm height) and a third disc of Ag (10 mm diameter, 10.4 mm height). The material sequence along the z-direction was Cu, Pb, Ag. As shown in **Fig. 28** the remaining space in D-XII was filled with quartz sand.

Comments:

This box was directly dispatched to Gent and did not participate in the travelling program of the other boxes.

Fig. 26. - Views of box D-XII

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