

PROMPT GAMMA ACTIVATION IMAGING ON 'BLACK BOXES' IN THE 'ANCIENT CHARM' PROJECT

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Abstract

The aim of the 'Ancient Charm' project is to combine Neutron Tomography (NT), Prompt Gamma Activation Analysis (PGAA), Time-of-flight Neutron Diffraction (TOF-ND), Neutron Resonance Capture Analysis (NRCA) and Neutron Resonance Transmission (NRT) in order to generate 3D images of the elemental and phase compositions of complex museum objects. For the development and benchmark of the combined methods, complex test samples, so called 'black boxes', were constructed and then analysed by the different techniques. These test objects are sealed iron or aluminium-walled cubes of 40 and 50 mm edge lengths, respectively, containing 2D or 3D arrangements of materials relevant to the compositions of archaeological samples. The Prompt Gamma Activation Imaging (PGAI) is a new terminology – introduced in the AC project – for determining the compositions of small volumes within the sample by scanning. The experimental results obtained from PGAI on boxes investigated at Budapest Neutron Centre (BNC, Hungary) are reported.

Kivonat

Az EU FP6 Ancient Charm projekt fő célkitűzése összetett, értékes műtárgyak elemeloszlásának, fázisszerkezetének háromdimenziós, roncsolásmentes feltérképezése neutronos analitikai módszerek kombinálásával: neutrontomográfia (NT), prompt-gamma aktivációs analízis (PGAA), repülési idő neutrontdiffrakció, neutron-rezonanciabefogás analízis (NRCA) és neutron-rezonanciáttranszmisszió (NRT). A kombinált módszerek fejlesztéséhez és teszteléséhez ún. fekete dobozok készültek, amelyek vas ill. alumínium falú próbatestek, belsejükben régészeti szempontból fontosnak tartott anyagok komplex elrendezésével. A prompt-gamma aktivációs leképezés (PGAI) egy új terminológia; olyan 3D-s elemösszetétel vizsgálatot jelent, amelynek során keskeny neutronnyalábbal a minta kis térfogategységeit lépésenként elemezzük. Jelen cikk a Budapesti Neutron Centrumban a fekete dobozokon végzett PGAI vizsgálatok eredményeit mutatja be.

KEYWORDS: PROMPT GAMMA ACTIVATION IMAGING, NEUTRON, 3D ELEMENT MAPPING, ANCIENT CHARM

KULCSSZAVAK: PROMPT-GAMMA AKTIVÁCIÓS LEKÉPEZÉS, NEUTRON, 3D ELEMTERKÉP, ANCIENT CHARM

Introduction

The ultimate goal of the Ancient Charm (AC) project is to obtain 3D imaging of elemental and phase compositions of considerably complex museum objects by combining different neutron analytical methods (<http://ancient-charm.neutron-eu.net/ach>, Gorini 2007). In this paper the emphasis is on the extension of Prompt Gamma Activation Analysis (PGAA) towards the position-sensitive Prompt Gamma Activation Imaging (PGAI), and its comparison to Neutron Tomography (NT) and Time-of-flight Neutron Diffraction (TOF-ND).

PGAI is a new terminology - introduced by the project - for determining the compositions of small volumes within the sample by scanning (Kasztovszky & Belgia 2006). This volume is determined by the intersection of the collimated neutron beam and the viewing angle of a gamma detector. In medical imaging this kind of intersection is called isocenter, which is a fix-point in a space and which is the source of the information. In our case, it is a small volume rather than a point;

therefore it is better called isovolume. If a sample is moved, with the isovolume fixed in space, we can collect spatially well-resolved analytical information by acquiring a gamma-spectrum at each sample position. This double-collimated arrangement substantially reduces the gamma counting rate thus increasing the time needed for the experiment. Usually such a measurement is not practical and economic. The solution comes at the price of reduced spatial resolution: the removal of the gamma collimation results in a wide viewing angle of the detector covering the whole object, thus photons emerging from a chord-shaped volume throughout the sample are detected. The schematic drawings of the two basic measurement setups are shown in **Figure 1**.

A complete 3D scan of the object - in either configuration - requires a lot of beam time. It is more efficient to identify first the regions of interest using the three-dimensional pattern obtained within few hours by X-ray and/or neutron tomography, and then to limit the (rather long lasting) PGAI experiment to the determination of the elemental compositions of these regions only.

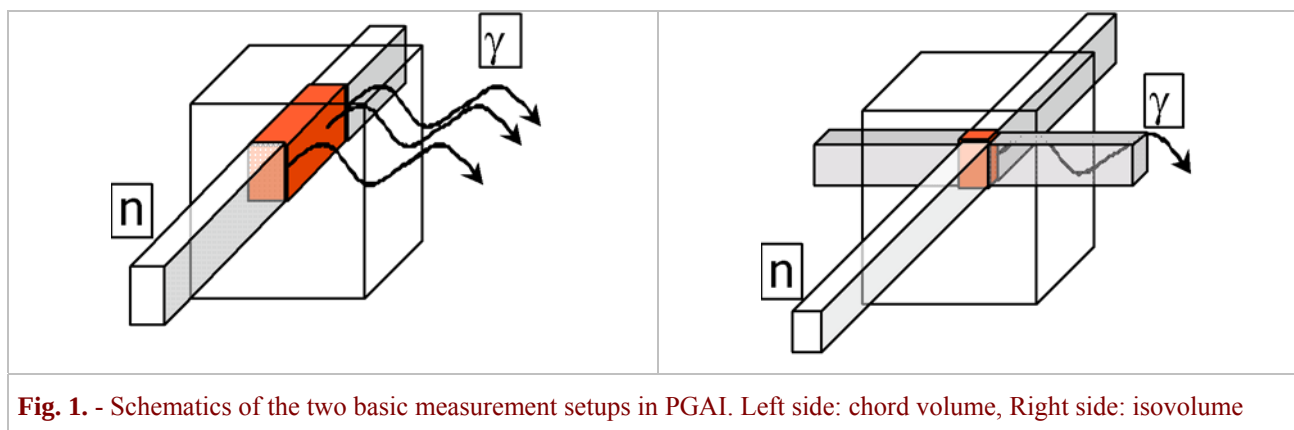


Fig. 1. - Schematics of the two basic measurement setups in PGAI. Left side: chord volume, Right side: isovolume

This approach considerably speeds up the investigation. As our first step towards the PGAI imaging method, the definition of such regions was based on 2D neutron radiography (NR) and X-ray radiography (XR) images provided by other members of the Ancient Charm consortium.

In order to establish a procedure to combine tomography, PGAI and diffraction data collected on the same archaeological object, test samples with varying degrees of complexity were analysed by the different methods. Two sets of sealed 'black boxes' were manufactured by the Hungarian National Museum (Dúzs 2008) and by the University of Bonn, Germany (Kirfel 2008). The contents of the boxes were constructed according to the design made by the archaeologists and conservators of the HNM, using typical materials occurring in archaeological contexts. The first set consists of ten iron cubes of 40 mm edge length (labelled as H-I through H-X, wall thickness 1 mm). The second set (labelled as D-I through D-X) comprises aluminium boxes with wall thickness of 1 mm and dimensions of 50 mm. The compositions of the internal parts, the filling materials, as well as the layout, were undisclosed to the experimentalists, however the constructors documented the production carefully.

The purpose of the experiments carried out at Institute of Isotopes (IKI), Budapest, was to reveal as much information as possible about the materials inside of the nine 'black boxes' selected for experiments applying PGAI-NR/NT. In several cases, complementary information from the other techniques was needed to find out the composition of the black boxes. There were cases, however, when PGAI-NR/NT yielded the same information about the boxes as was given by other method. It should be emphasised that all the boxes studied at IKI, Budapest, were investigated by TOF-ND at the ISIS Facility, Rutherford Appleton Laboratory (Chilton, UK) in the

framework of the Ancient Charm project as well. In this paper, we focus on the implementation of the PGAI-NR/NT but highlighting the cases where the combination of PGAI with TOF-ND was very useful.

Experimental

The PGAI experiments were carried out on the standard PGAA station and/or on the newly installed PGAI-NR/NT setup on NIPS (Neutron Induced Prompt Gamma Spectroscopy) station of the Budapest Neutron Centre (Budapest, Hungary) that is operated by the Institute of Isotopes (IKI). The TOF-ND measurements were accomplished on diffractometers ROTAX and GEM at the ISIS Facility, Rutherford Appleton Laboratory (Chilton, UK).

The standard setup at the PGAA station of IKI

The PGAA experimental station (Révay et al. 2004), being in operation since 1996, is installed at the end of a horizontal cold neutron beam guide at the Budapest Research Reactor. The neutrons leaving the reactor core are cooled and are guided to the experimental stations with a neutron guide. The PGAA/NIPS system is situated 35 m away from the reactor wall. With a split beam, the PGAA station operates on the upper half of the beam, while the NIPS station uses the lower one.

At the PGAA station, the maximum available beam size is $20 \times 20 \text{ mm}^2$, and the beam flux is $1.2 \times 10^8 \text{ neutrons cm}^{-2}\text{s}^{-1}$. The neutron beam can be collimated to different cross sections down to 5 mm^2 . Regularly, relatively small samples are positioned inside the sample chamber, while for larger objects the chamber can be removed. Prompt- and delayed gamma photons are detected with a 27% efficiency n-type HPGe detector, surrounded by a BGO annulus, operated in a background reduction mode called Compton-suppression.

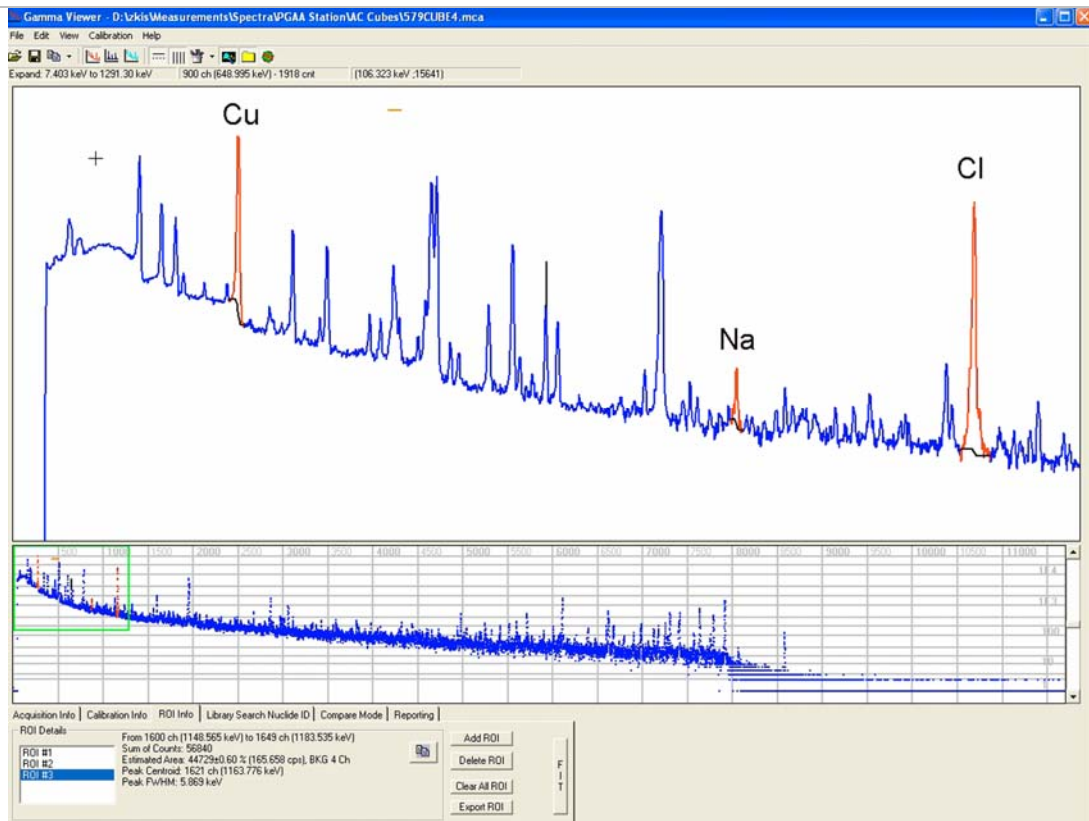


Fig. 2. - PGAA spectrum from the irradiation of black box D-IV (Al). The box was aligned so that the neutron beam could impinge on the top of one of the copper rods embedded in rock salt.

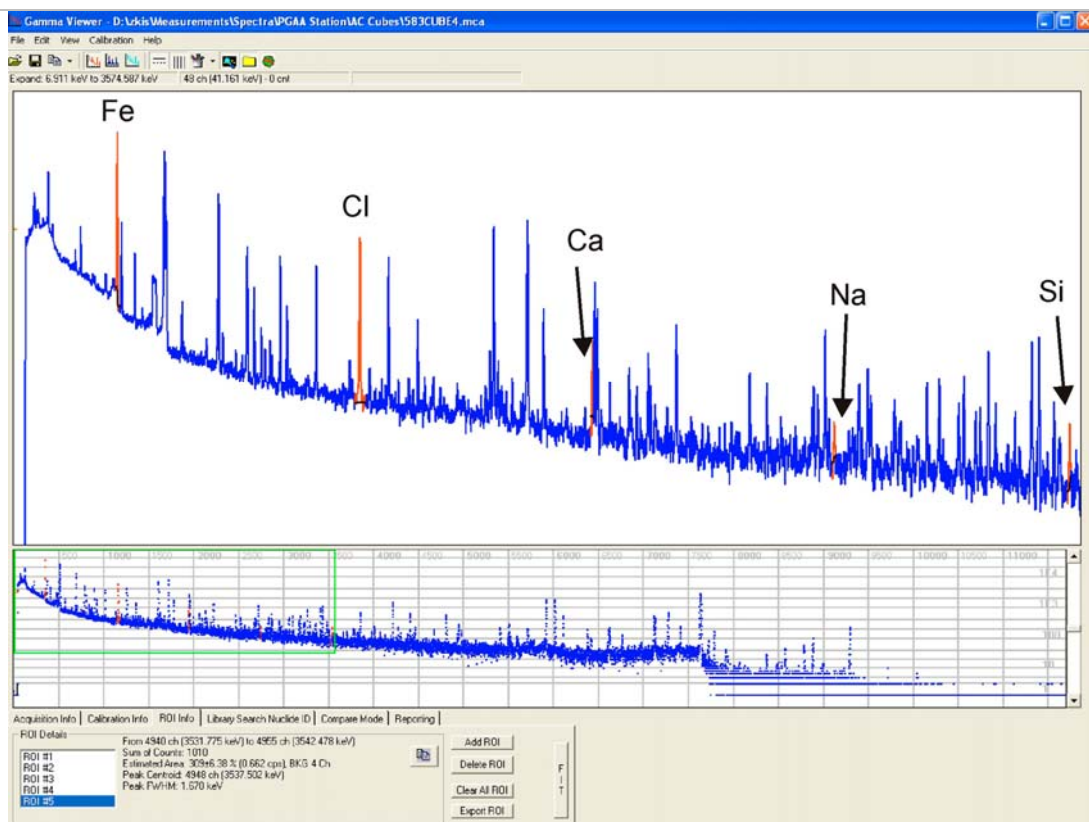


Fig. 3. - PGAA spectrum from the irradiation of black box D-IV (Al). The box was aligned so that the neutron beam could impinge on the top of one of the iron rods embedded in clay.

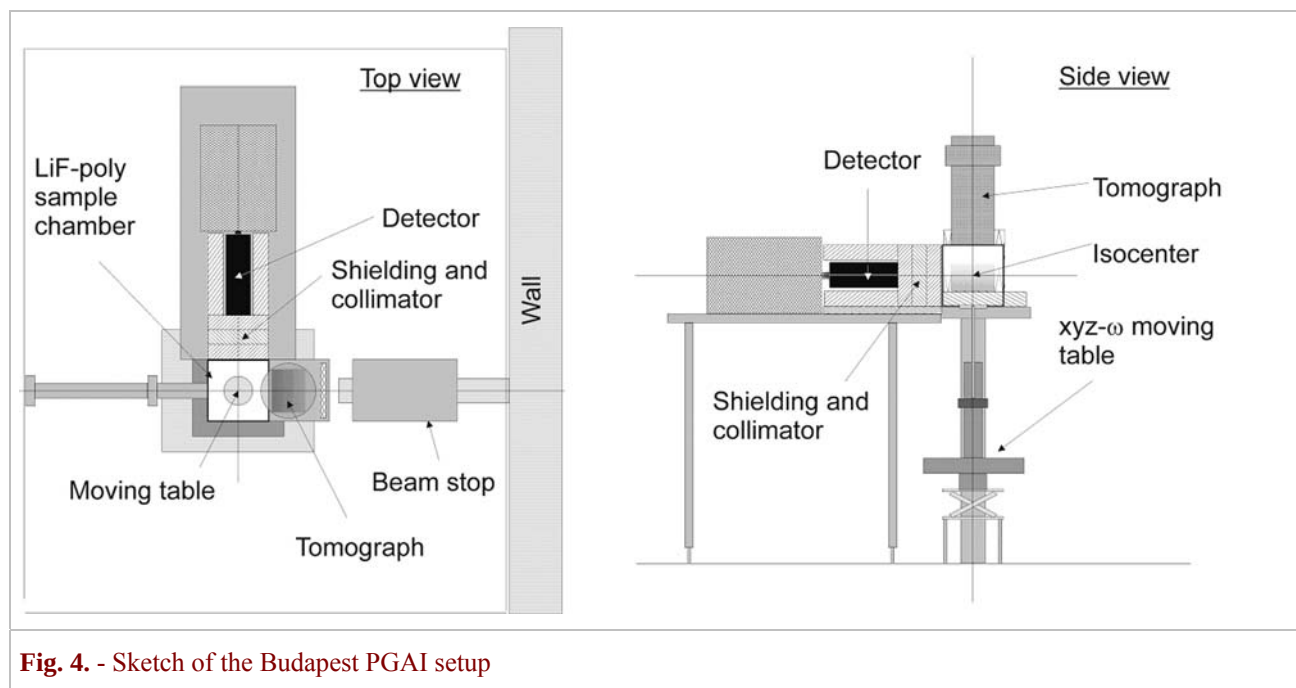


Fig. 4. - Sketch of the Budapest PGAI setup

The spectra are collected with a Canberra AIM 556 multichannel analyser and evaluated with Hypermet PC (Révay et al. 2005).

As examples, two PGAA spectra measured at the PGAA station are presented in **Fig. 2** and **Fig. 3**. The black box D-IV (Al) contains two iron and two copper rods parallel to z-axis, embedded in clay and rocksalt, respectively. During the irradiation it was aligned so that the neutron beam could impinge on the rods. One can find the several strong peaks of the composition materials. Some of the main peaks are labelled in the figures.

The new PGAI-NR/NT setup at the NIPS station of IKI

The setup is a result of the AC project and many consortium members contributed (design, hardware and/or software) to its realisation (Belgya et al. 2007). The schematic drawing of the PGAI-NR/NT setup is shown in **Figure 4**. This facility was designed to accommodate an object of maximum lateral size 10 cm by 10 cm, but the height of the object can be up to 20 cm. The available beam intensity is 7×10^7 neutrons $\text{cm}^{-2}\text{s}^{-1}$ and the L/D ratio is 150. The incident neutron beam has a maximum cross-section of ~ 23 mm by ~ 23 mm, when applied for neutron tomography. For PGAI, an adjustable neutron collimator was fabricated from a ^6Li -loaded polymer, with an aperture that shapes a 2-mm wide 'pencil beam' with a variable height of 2 to 20 mm. The sample is surrounded by a $20 \text{ cm} \times 20 \text{ cm} \times 20 \text{ cm}$ sample chamber, made also of a ^6Li -enriched polymer, which has no bottom. The neutron tomograph is placed downstream from the sample position. The

xyz- ω -moving table equipped with sample support is beneath the sample chamber. It holds the sample and reaches almost any point within the available space. A photograph of the setup is presented in **Figure 5**.

The gamma collimator is built up from lead bricks sitting on the top of an adjustable table. The collimator aperture can be adjusted from $2 \text{ mm} \times 2 \text{ mm}$ to any meaningful rectangular size. A 13%-efficiency HPGe detector is placed behind the collimator to view the isovolume of the system. The detector signals are processed with an XIA PIXIE-4 digital signal processor (<http://www.xia.com>). An integrated data acquisition system can control the moving table and can take either gamma spectra, NT images, or both of them in a batch run. The measurements result in a large number of prompt spectra, which are analysed with the batch evaluation feature of the spectroscopy software HyperLab 2005b (Simonits et al. 2003; <http://www.hlabsoft.com>).

The neutron tomograph (NT) was provided by the University of Cologne, Germany. The neutron converter scintillator is made of $^6\text{Li}/\text{ZnS}$, and the scintillation light is reflected to the optics by a silver-free mirror. The optics is attached to a high-resolution CCD camera (<http://www.pco.de>). The neutron beam stop placed after the tomograph is assembled from a ^6Li -enriched polymer, boron and lead. It is intended that for complex objects, to be investigated later in the project, the coordinates of regions of interest for PGAI will be taken from the NT reconstructions.



Fig. 5. - PGAI-NT setup

Prompt Gamma Activation Imaging

In total, nine black boxes were selected for the experiments at Institute of Isotopes, Budapest. They represented a wide range of material and structural variability and their measurements could be completed during the available beam time. Three aluminium and two iron boxes were investigated at the standard PGAA station, while three aluminium and four iron boxes were analysed at the newly installed PGAI-NT station of the Budapest Neutron Centre.

On the PGAA station of IKI, measurements were made in the sample chamber using standard neutron collimators available for normal PGAA. The appropriate sections of the objects were located using the radiography data collected earlier at the research reactor FRM-II in Garching, Germany, in cooperation with the ANTARES group (neutron radiography, hereafter referred as [NR-Gar]) and at the Center for X-ray tomography at the University of Ghent, Belgium (X-ray radiography [XR-Ghe]) (Kudejova et al. 2007).

Collimated neutron beams with 5 mm², 24 mm² and 44 mm² area cross-sections were available. The boxes were placed inside the chamber by hand, and positioned by eye as well as possible in the path of the neutron beam. All measurements were performed at ambient conditions, the acquisition times varied between 300 sec - 2700 sec depending on the analytical sensitivities of the elements present in the irradiated volumes. These measurements were made in PGAI chord type geometry for all five boxes investigated.

On the NIPS station of IKI, the positioning of the samples was carried out using the moving table and based on the radiography images taken with the neutron tomograph [NR-Bud]. The beam size was either 2mm × 20mm or 2mm × 10mm.

Table 1. - Comparison of the Budapest neutron facilities

PGAA station	NIPS station
☺ higher neutron flux	☺ more flexible geometry, larger sample chamber
☺ standardised geometry	☺ accurate positioning
☺ well-known efficiency	☺ radiography-driven PGAI
☺ background reduction with Compton-suppression	☺ better spatial resolution
	☺ use of multiple γ -detectors possible
☹ limited space in the sample chamber	☹ higher spectral background
☹ lower precision of sample positioning	☹ longer acquisition times in isovolume configuration
☹ no tomography/radiography possible	

Table 2. - Black boxes analysed by PGAI or PGAI-NR/NT at IKI, Budapest

Black box	Measurement setup	PGAI meas. type	Other measurement
D-IV (Al)	- PGAI on PGAA station - PGAI-NR on NIPS	- chord - isovolume	TOF-ND on ROTAX
D-V (Al)	PGAI-NR on NIPS	chord	TOF-ND on ROTAX
D-VI (Al)	PGAI on PGAA station	chord	TOF-ND on ROTAX
D-VII (Al)	- PGAI on PGAA station - PGAI-NR on NIPS	- chord - isovolume	TOF-ND on ROTAX
H-I (Fe)	PGAI-NR on NIPS	chord, isovolume	TOF-ND on GEM
H-III (Fe)	PGAI-NR on NIPS	chord	TOF-ND on GEM
H-IV (Fe)	PGAI-NR on NIPS	chord	TOF-ND on GEM
H-VI (Fe)	- PGAI on PGAA station - PGAI-NR on NIPS	- chord - chord, isovolume	TOF-ND on GEM
H-VIII (Fe)	PGAI on PGAA station	chord	TOF-ND on GEM

The height of the collimator aperture was chosen to fit the geometry of the selected section and to optimise the measurement time. The typical acquisition time varied between 200 sec and 3600 sec, depending on the investigated materials. All boxes measured on this station were studied in chord geometry, while four of them were also examined with the isovolume setup.

A comparison of the general features of the two experimental stations is shown in **Table 1**.

Time of Flight Neutron Diffraction

The complementary information content of time-of-flight neutron diffraction (TOF-ND) method was exploited in several cases in order to reveal the phase compositions of the sections investigated when the elemental compositions from PGAA did not provide the full information on the metal or mineral phases. Neutron diffraction experiments were performed on two different diffractometers at ISIS, on ROTAX (Kockelmann et al. 2000) and GEM (Day et al. 2004). The TOF-ND method (Kockelmann & Kirfel 2006) makes use of the polychromatic beam of neutrons possessing wavelengths over a broad wavelength range. For both diffractometers, the scattered neutrons are registered by detector banks at low and high scattering angles, i.e. each measurement on one of the instruments yields several diffraction patterns covering different crystallographic d-spacing ranges. For the data collections on the black boxes, the size of the incident beam was set to typically 10×10 mm². The boxes were measured at several analysis points where the neutron and X-ray tomographies [NR-Gar, XR-Ghe] indicated particular features. A more detailed description of the TOF-ND analysis on the black boxes is given by Festa et al. (2008).

List of experiments at IKI

The details of the experiments carried out on both stations of IKI can be found in **Table 2**. The particular details of the experimental conditions will be presented in the results section separately for each box. No gamma- and neutron self-absorption corrections were taken into account at this stage of the work, thus the results are only qualitative.

Results and discussion

After the experiments and following the data analysis, the layouts and the compositions of the boxes were revealed (Kirfel 2008, Dúzs 2008) and, hence can be compared to the measurement results. For the sake of clarity, we will compare the measured data and derived elemental compositions with the actual contents of the boxes.

Aluminium box D-IV.

For the layout, the description and the nominal composition of the box refer to Kirfel (2008).

Radiography images (Fig. 6a, b)

- the filling material greatly absorbs the cold neutrons, only the aluminium plates ‘shine’, as they are mostly transparent for neutrons [NR-Bud]
- for low-energy neutrons the depth of analytical information by PGAI is limited
- X-ray radiography [XR-Ghe] (left figure below) had to be used to move the parts of the box to the measuring position

Measurement points with PGAI (Fig. 6c)

- a chord type setup on the PGAA, beam size: 44 mm²
- an isovolume setup on the NIPS, 2 mm × 10 mm pencil beam
- irradiations n1 - n6 carried out perpendicular to the rods: information about the filling material
- irradiations n7 - n10: neutrons hit the top of the rods touching the wall of the box, avoiding the attenuation in the filling materials.

PGAI conclusions

- for low-energy neutrons, this box is indeed a 'black' box

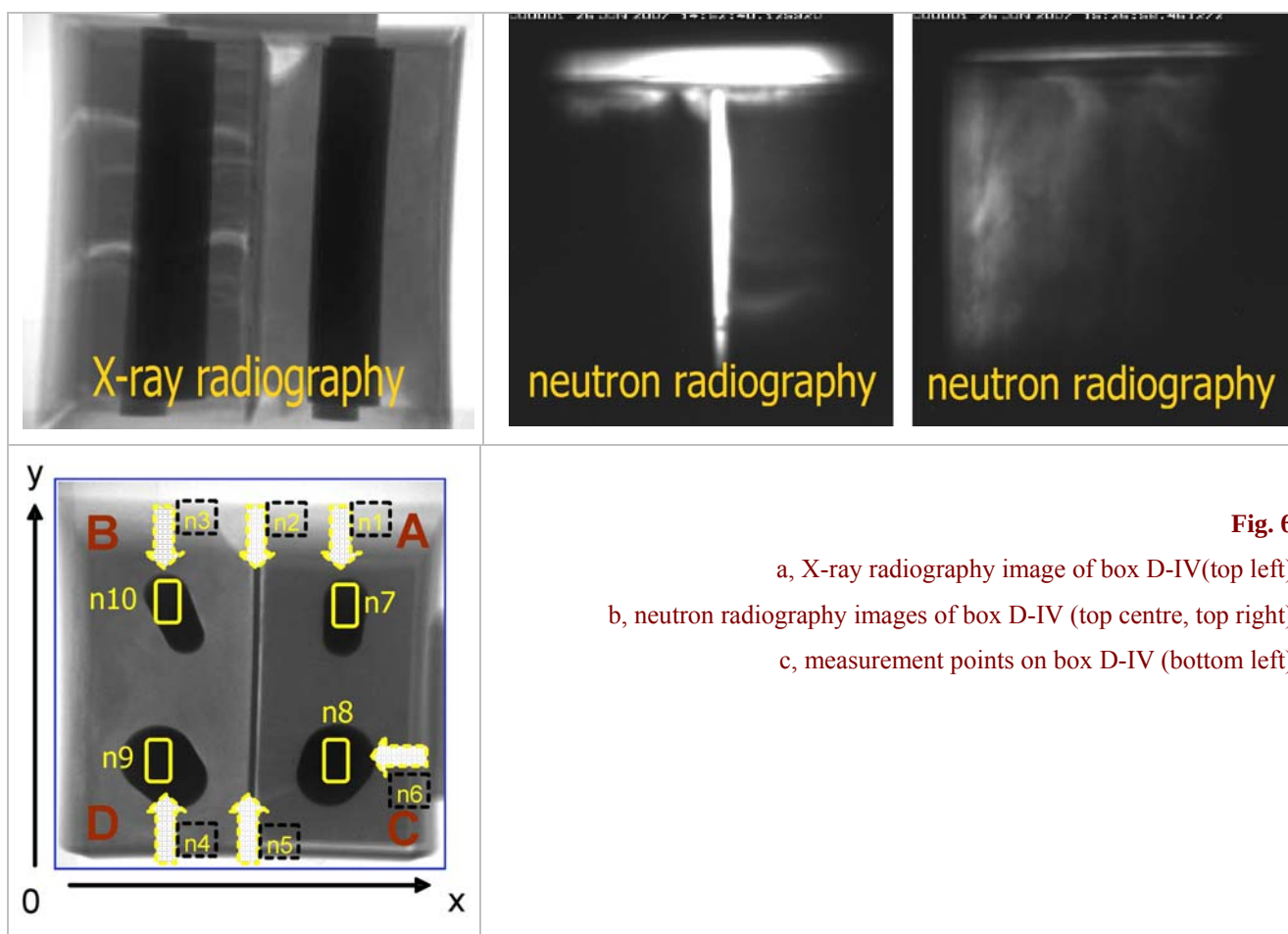
- 'A' and 'C' rods are made of iron, 'B' and 'D' are made of copper

- Na, Cl correctly identified; Si, Ca, Fe detected in the other section

- isovolume setup: hard to draw conclusions yet because of low count rate and too short acquisition time

TOF-ND conclusions (Festa et al. 2008)

- around 'A' and 'C' 75 wt% calcite (CaCO₃) and 25 wt% quartz (SiO₂)
- around 'B' and 'D' sodium chloride
- iron phase is ferrite (bcc iron), rather than steel

**Fig. 6**

a, X-ray radiography image of box D-IV (top left)

b, neutron radiography images of box D-IV (top centre, top right)

c, measurement points on box D-IV (bottom left)

Table 3. - Details of the composition of the box D-IV.

Nr.	Nominal composition	Meas. type and Nr. of PGAI beam	PGAI results	TOF-ND results (Festa et al. 2008)
1, 6, 7, 8	Fe in clay	chord: n1, n6, n7, n8	Na, Si, Cl, Ca, Fe	Fe-type = bcc: ferrite + cementite in calcite (75 wt%) + quartz (25 wt%)
2, 5	Al between clay and salt	chord: n2, n5	Na, Al , Si, Cl, Ca	No clear indications
3, 4, 9, 10	Cu in salt	chord: n3, n4, n9, n10	Na, Cl, Cu	Cu-type = fcc: steel (Fe) or copper (Cu), decision based on PGAA: Cu NaCl

Discussion

Based on PGAI measurements on the PGAA station, the 'A' and 'C' rods are made of iron, while the 'B' and 'D' are copper. PGAI can not distinguish between the phases of iron therefore a combination with neutron diffraction is fruitful. TOF-ND proves that the iron phase is ferrite (bcc iron), rather than steel. It is also important to note that TOF-ND has difficulties to distinguish between copper and steel (fcc-iron) which have the same structure and similar lattice parameters. In this case PGAI can help in the decision: rods 'B' and 'D' are made of copper.

According to PGAI, the filling material around rods 'A' and 'C' contains mainly Si and Ca apart from the Fe, while around 'B' and 'D' Na and Cl in equal atomic ratios were detected. TOF-ND confirms that the filling material surrounding 'B' and 'D' is sodium chloride, while that around 'A' and 'C' consists of 75 wt% calcite (CaCO_3) and 25 wt% quartz (SiO_2). There are no clear indications in the TOF-ND data about the compositions of the dividing sheet. The higher aluminium contribution observed in the n2 and n5 PGAI measurements may be originated from the irradiation of the dividing sheet. Detailed results are listed in **Table 3**.

Aluminium box D-V.

For the layout, the description and the nominal composition of the box refer to Kirfel (2008).

Radiography images (Fig. 7a, b)

- X-ray [XR-Ghe] and neutron radiography [NR-Bud] images: the embedded tubes aligned on an axis
- there is no sign of filling materials

Measurement points with PGAI (Fig. 7 c,d)

- chord type setup on the NIPS station, beam size: 2 mm $\times$ 20 mm.
- irradiations n1 - n3: parallel the common axis of the tubes.

PGAI conclusions

- all tubes are made of copper
- no filling material detected

TOF-ND conclusions (Festa et al. 2008)

- same results as in PGAI

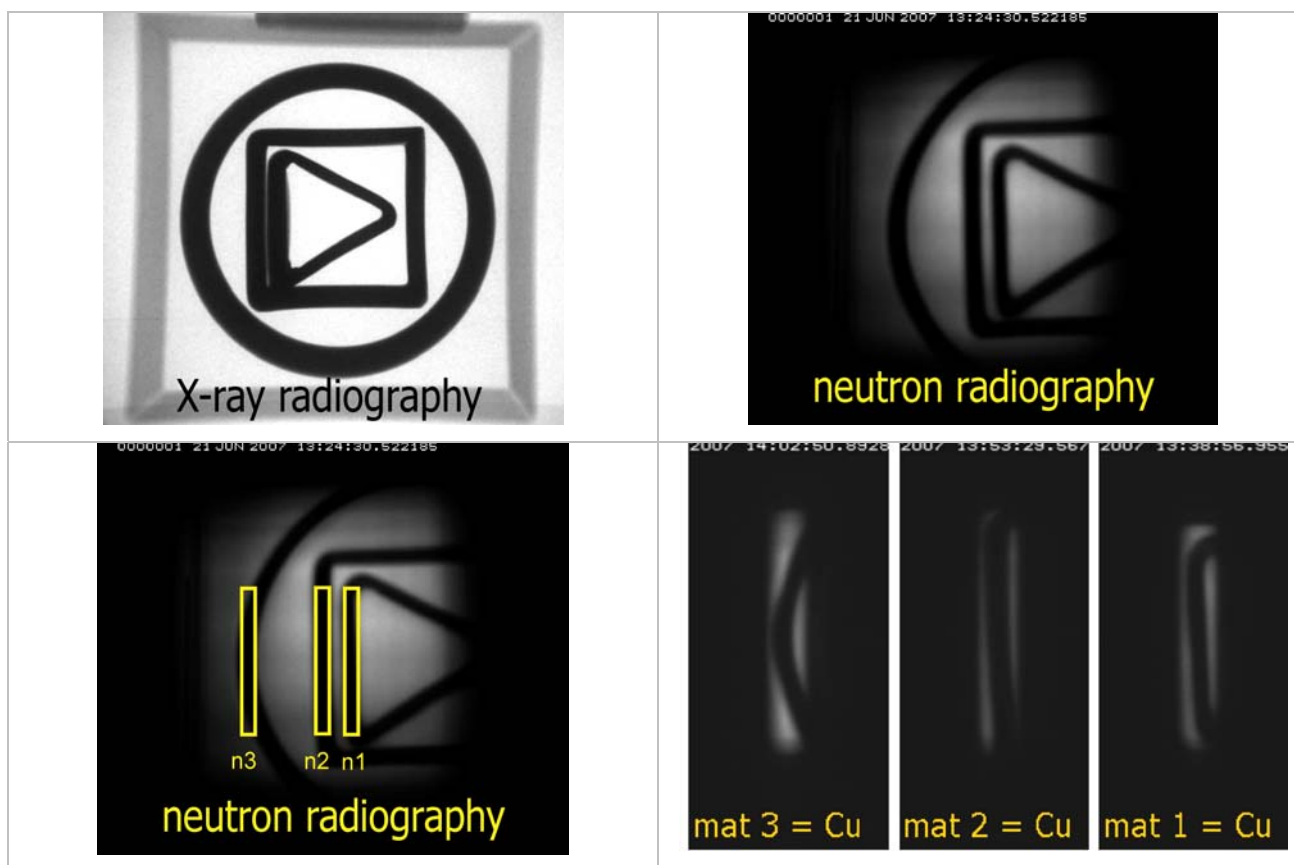


Fig. 7

a, X-ray radiography image of box D-V (top left); b, neutron radiography image of box D-V (top right)
c, measurement points on box D-V (bottom left); d, views through the collimator on box D-V (bottom right)

Table 4. - Details of the composition of the box D-V.

Nr.	Nominal composition	Meas. type and Nr. of PGAI beam	PGAI results	TOF-ND results (Festa et al. 2008)
1	Cu	chord: n1	Cu, Al	same result
2	Cu	chord: n2	Cu, Al	
3	Cu	chord: n3	Cu, Al	

Discussion

This box can be considered as an easy case for PGAI. Based on the results from the chord setup on NIPS it was concluded that all tubes are made of pure copper (see **Table 4**). In this case, TOF-ND and PGAI gave the same results.

Aluminium box D-VI.

For the layout, the description and the nominal composition of the box refer to Kirfel (2008).

Radiography image (Fig. 8a)

- the materials greatly attenuate the cold neutrons, neutron radiography images were not taken
- for low-energy neutrons, this box is again ‘black’; the depth of analytical information by PGAI is limited.

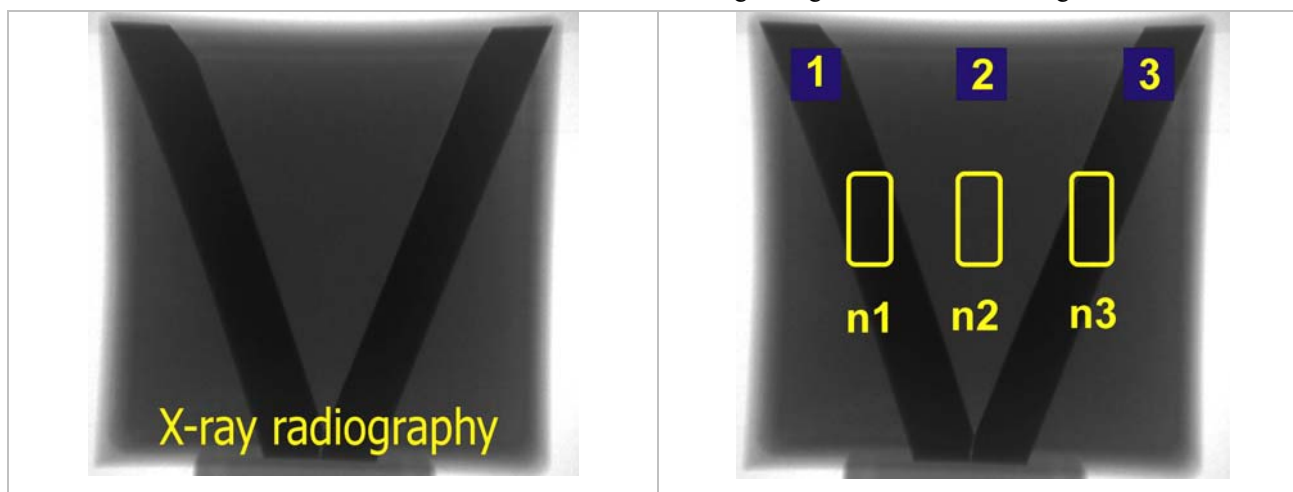
• X-ray radiography [XR-Ghe] (figure below) was used to move the interesting parts of the box to the measuring positions.

Measurement points with PGAI (Fig. 8b)

- chord type setup on the PGAA station, beam size: 24 mm².
- irradiations n1 - n3: perpendicular to the V-arrangement.
- irradiations n1 and n3: information about the material of the sheets
- irradiation n2: characterises the filling material.

PGAI conclusions

- only Fe was identified both for sheet and filling materials
- significant difference between the count rates originating from sheets and filling material

**Fig. 8**

a, X-ray radiography image of box D-VI (left), b, measurement points on box D-VI (right)

Table 5. - Details of the composition of the box D-VI.

Nr.	Nominal composition	Meas. type and Nr. of PGAI beam	PGAI results	TOF-ND results (Festa et al. 2008)
1	iron	chord: n1	Fe, Al	ferrite
2	hematite	chord: n2	Fe, Al	hematite (Fe ₂ O ₃)
3	iron	chord: n3	Fe, Al	ferrite

TOF-ND conclusions (Festa et al. 2008)

- sheets (1 and 2) are ferrite (Fe)
- filling material (3) is hematite (Fe_2O_3)

Discussion

The results from the chord setup on the PGAA station seemed to indicate that the components and fillings inside the box were only made of iron. However, there was a significant difference between the count rates due to the different density of the sheets and filling material. PGAI can not distinguish between the phases or different chemical forms of iron therefore a combination with neutron diffraction is useful. TOF-ND shows that the iron phase in the sheets is ferrite (bcc iron), and the filling material is hematite (see **Table 5**).

Aluminium box D-VII.

For the layout, the description and the nominal composition of the box refer to Kirfel (2008).

Radiography images (Fig. 9)

- X-ray radiography images [XR-Ghe]: three parallel layers with different absorption coefficients
- layers composed of smaller blocks and geometrical shapes: in the middle of the lowest layer, there seems to be a hole or a different material.

Measurement points with PGAI (Fig.10)

- chord type setup on the PGAA, beam size: 24 mm^2 : neutron beams are labelled as n1 and n2
- neutron radiography driven isovolume type measurements on the NIPS station, $2 \text{ mm} \times 10 \text{ mm}$ beam: neutron beams labelled as n3, n4 and n5; gammas from isovolume labelled as g3, g4 and g5

PGAI conclusions

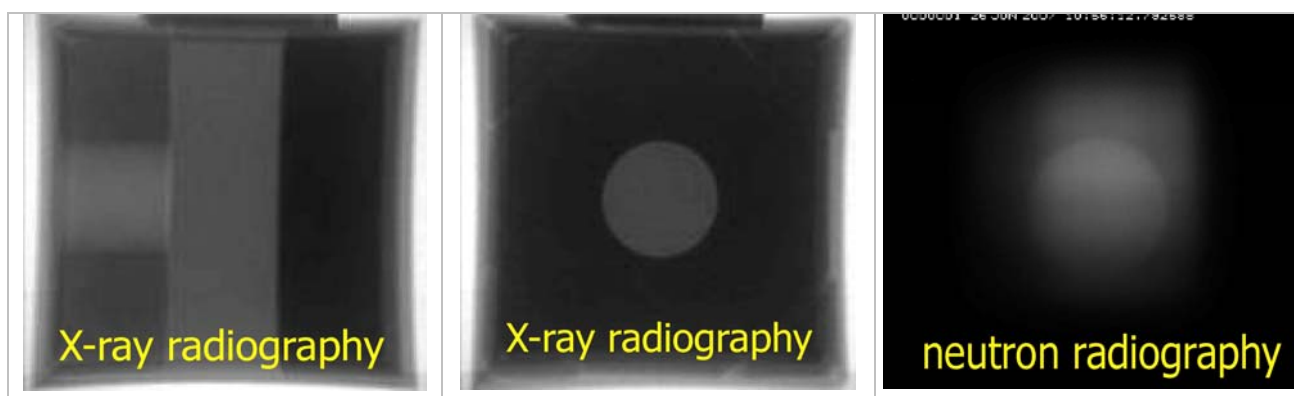
- very low count rate, hard to draw conclusions
- with PGAI on NIPS, mainly C and Al have been identified in the layers.
- PGAI identifies Na, which comes from diaoyudaoite.
- PGAI identifies Si and H, which comes from pyrophyllite

TOF-ND conclusions (Festa et al. 2008)

- TOF-ND indicates the presence of corundum (Al_2O_3), graphite (C) and other non-identified phases in layers z1, z2 and z3, respectively.

Discussion

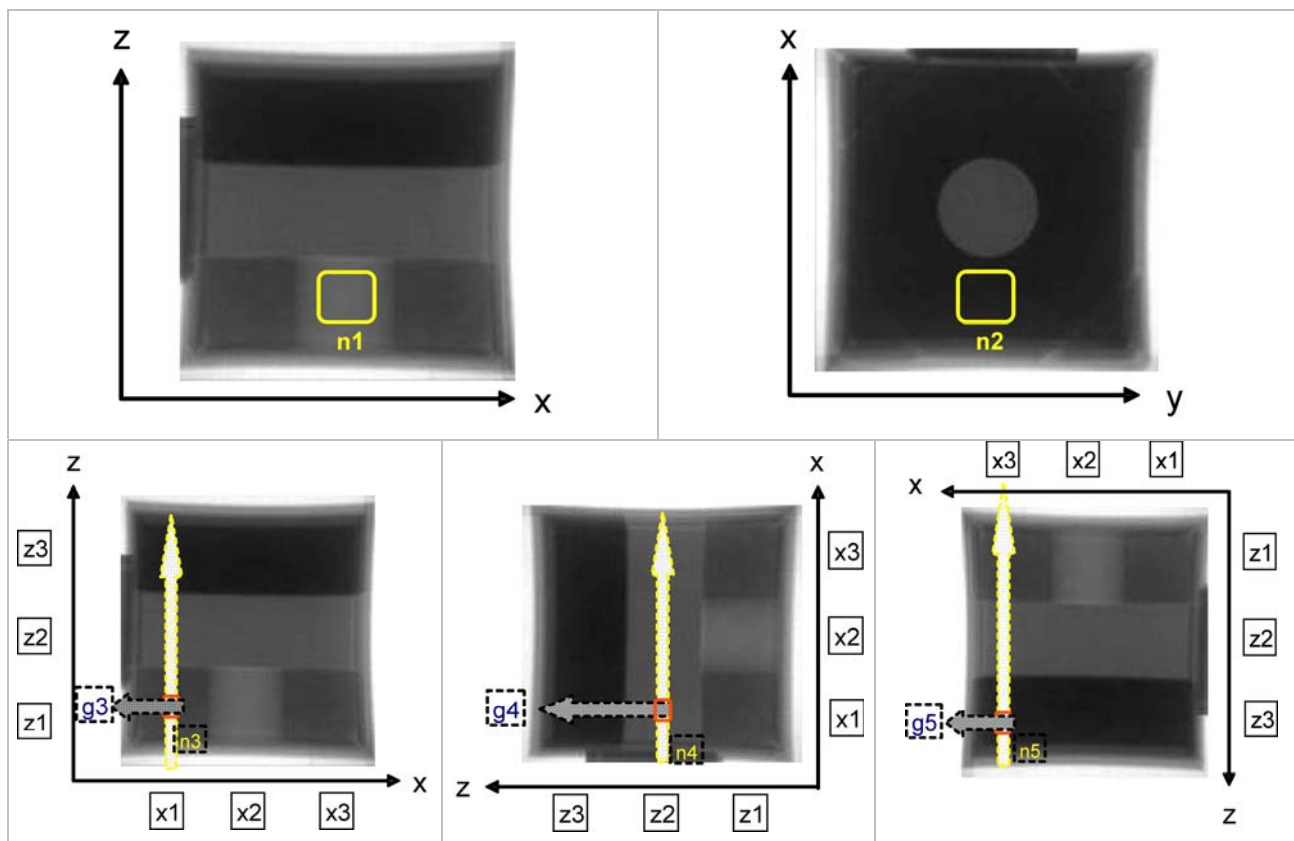
Two of the irradiations (n1 - n2) were carried out in chord setup, three (n3 - n5) in isovolume setup. In the case of n1 the gamma radiation gives information about the material in layer z1. Unfortunately, the results from n2 characterise all the three layers together because the neutron beam goes through all of them; therefore it is difficult to separate the contributions of the different layers.

**Fig. 9**

a-b, X-ray radiography images of box D-VII (left, centre);
c, neutron radiography image of box D-VII (right)

Table 6 - Details of the composition of the box D-VII.

Nr.	Nominal composition	Meas. type and Nr. of PGAI beam	PGAI results	TOF-ND results (Festa et al. 2008)
z1	corundum	chord: n1, n2 isovolume: n3	H, Na, Al	corundum (Al_2O_3), graphite (C)
z2	graphite	chord: n2 isovolume: n4	H, C, Na, Al, Si	corundum (Al_2O_3), graphite (C)
z3	pyrophyllite	chord: n2 isovolume: n5	H, Al, Si	phase not-identified

**Fig. 10**

a-e, measurement points on box D-VII from different orientation (a-b: chord, c-e isovolume)

In the isovolume arrangement one can better position the source of the analytical information (the isovolume) into the layer of interest, but in this case the count rate is very low. During the limited beam time, the counting statistics was not good enough to provide information about all components. A higher neutron flux could help to increase the low count rate.

With PGAI, mainly C and Al could be identified in the layers; however, other elements such as H, Na, and Si are also recognisable. TOF-ND indicates the presence of corundum (Al_2O_3), graphite (C) and some other non-identified phases in layers z1, z2 and z3 (see **Table 6**).

Iron box H-I.

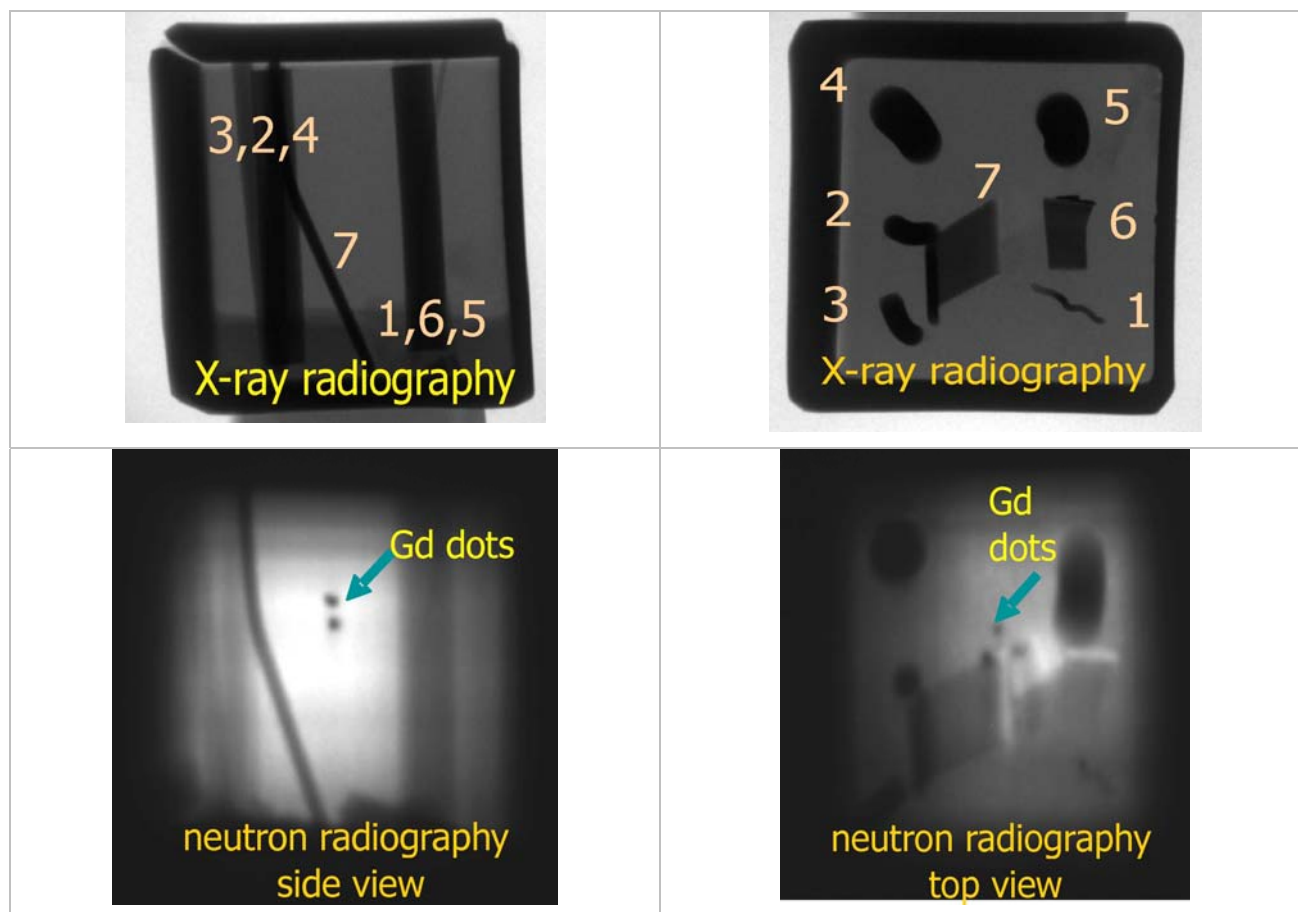
For the layout, the description and the nominal composition of the box refer to Dúzs (2008).

Radiography images (Fig. 11)

- X-ray [XR-Ghe] and neutron radiography [NR-Bud]: the parallel rods have different absorption coefficients. The darker the colour the higher is the absorption.
- removable Gd dots were painted on the surface of the box to help with the positioning

Measurement points with PGAI (Fig. 12)

- studied in chord type, as well as in isovolume setup on the NIPS station
- beam size: 2 mm × 20 mm (chord setup), 2 mm × 10 mm (isovolume setup)
- neutron radiography driven chord type measurements, the beams (n1 - n3) hit more rods behind each other:
- Neutron radiography driven isovolume type measurements: Gd dots (see on the images)

**Fig. 11**

a-b, X-ray radiography images of box H-I (top); c-d, neutron radiography images of box H-I (bottom)

Table 7. - Details of the composition of the box H-I.

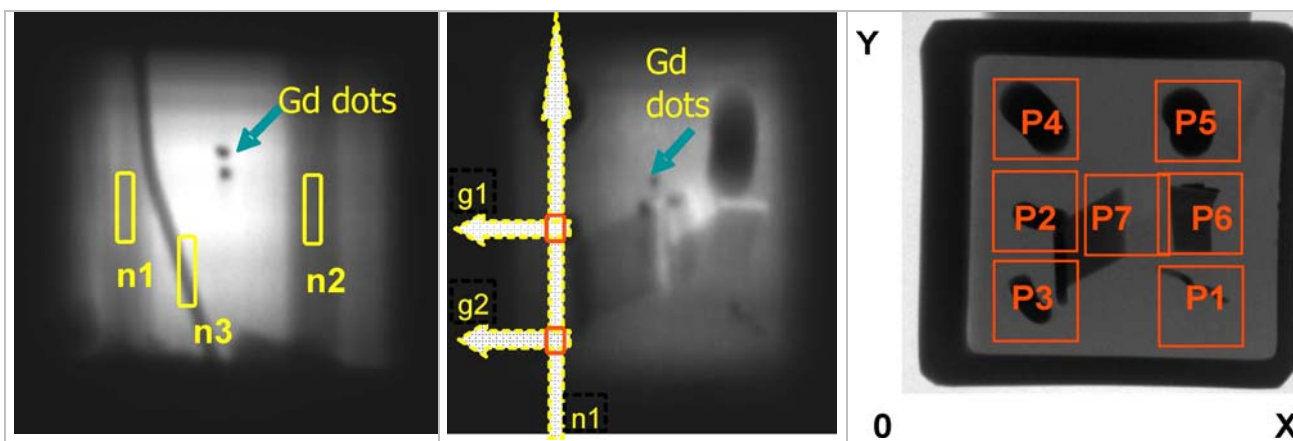
Nr.	Nominal composition	Meas. type and Nr. of PGAI beam	PGAI results	TOF-ND results (Festa et al. 2008)
1	copper wire	chord: n2	Cu, Zn	copper or steel
2	brass wire	chord: n1 isovolume: n1	Cu, Zn	copper
3	copper wire	chord: n1 isovolume: n1	Cu, Zn	brass or bronze
4	brass rod	chord: n1	Cu, Zn	brass or bronze
5	copper rod	chord: n2	Cu, Zn	copper, indications of Zn
6	zinc plate	chord: n2	Cu, Zn	copper or steel, strong Al/Ag peaks
7	iron plate	chord: n3	Fe	indications of copper/steel

PGAI conclusions

- chord setup: rods in a line are measured together
- isovolume: low count rate
- need for removable Gd dots to orientate the box

TOF-ND conclusions (Festa et al. 2008)

- gypsum at each measurement point
- P1, P4, P5 were assigned correctly
- P2, P3 analyses are wrong: misalignment error
- P6: Zn is not identified
- P7: fcc-phase, in agreement with steel

**Fig. 12**

a, measurement points on box H-I (chord); b, measurement points on box H-I (isovolume); c, TOF-ND measurement points on box H-I

Discussion

The X-ray radiography [XR-Ghe] and neutron radiography [NR-Bud] images present seven rods or wires arranged approximately parallel to each other. There are no clear differences in contrast visible in the radiographies. In the chord type experiments the gammas come from all the rods aligned with the neutron beam (n1 and n2). Therefore the rods in a line are indistinguishable. Based on the PGAI results the metal rods and wires contain copper and zinc; therefore some of them are brass or other zinc containing material. To find out the exact composition of two rods, the isovolume type arrangement was applied. The

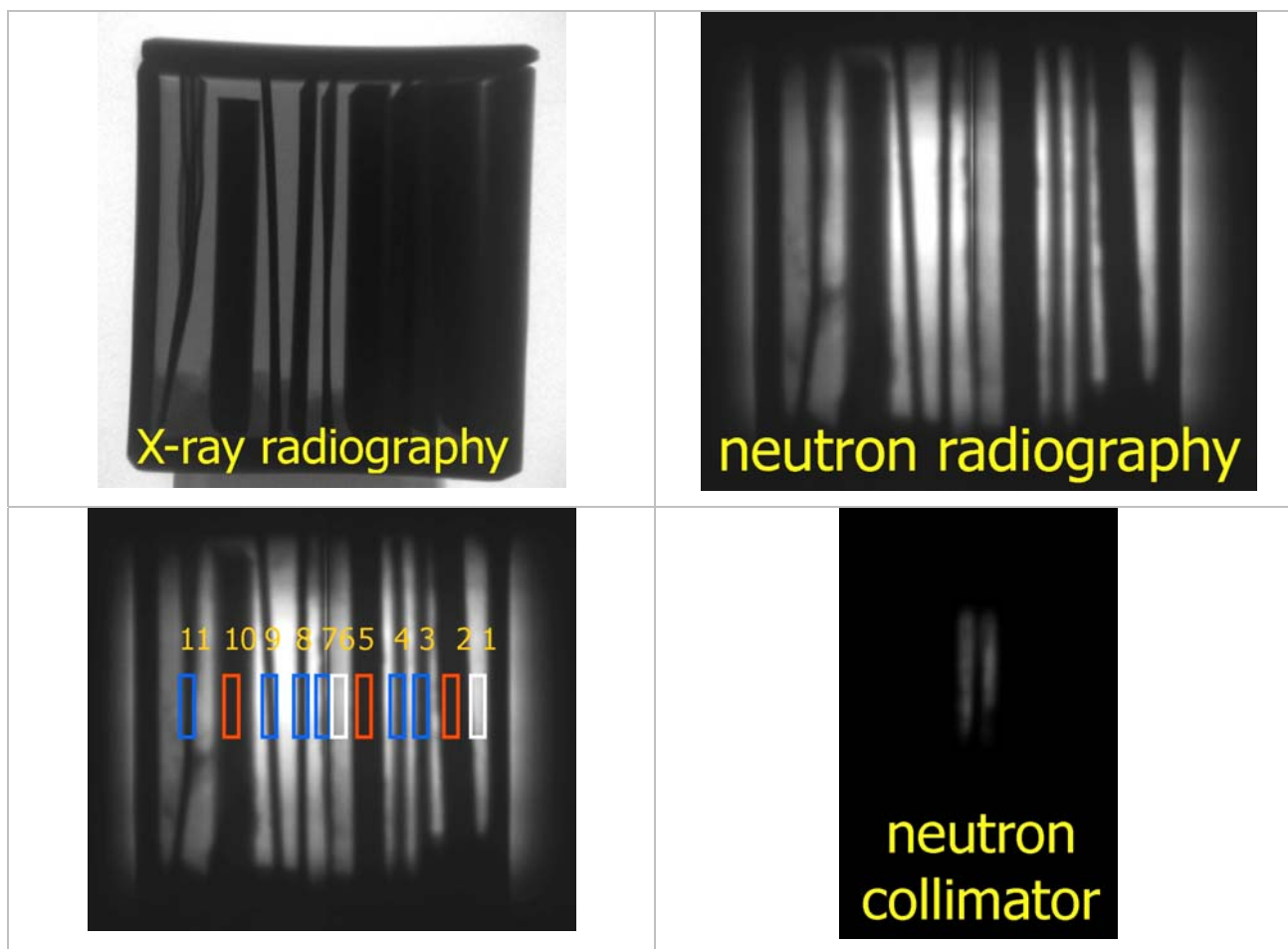
box was positioned using removable Gd dots painted on its surface. The neutron beam n3 impinged on a plate alone (it was bent for unknown reasons). PGAI yielded mainly iron and a negligible copper content. This latter may originate from the rods next to the path of the neutron beam. The detailed results can be seen in **Table 7**. The results from TOF-ND experiments which suffered from misalignment problems partially confirm the PGAI findings.

Iron box H-III.

For the layout, the description and the nominal composition of the box refer to Dúzs (2008).

Table 8. - Details of the composition of the box H-III.

Nr.	Nominal composition	Meas. type and Nr. of PGAI beam	PGAI results	TOF-ND results (Festa et al. 2008)
1	copper sheet	chord: n3	Cu	not used
2	iron sheet	chord: n2	Fe, Mn, Cu	
3	brass sheet	chord: n7	Cu, Zn	
4	copper sheet	chord: n8	Cu	
5	iron sheet	chord: n5	Fe, Mn, Cu	
6	brass sheet	chord: n4	Cu, Zn	
7	iron sheet	chord: n10	Fe, Mn, Cu	
8	brass sheet	chord: n9	Cu, Zn	
9	steel sheet	chord: n11	Fe, Mn, Cu	
-	void between Fe wall and 2	chord: n1	Fe, Mn	
-	void between 3 and 5	chord: n6	Fe, Mn, Cu	

**Fig. 13**

a, X-ray radiography image of box H-III (top left); b, neutron radiography images of box H-III (top right); c, measurement points for box H-III (bottom left); d, view through the collimator on box H-III (bottom right)

Radiography images (Fig. 13a, b)

- X-ray [XR-Ghe] and neutron radiography [NR-Bud] images: parallel sheets with different mass absorption
- neutron radiography image: prepared by merging two separate shots because the neutron beam size was smaller than the dimension of the box

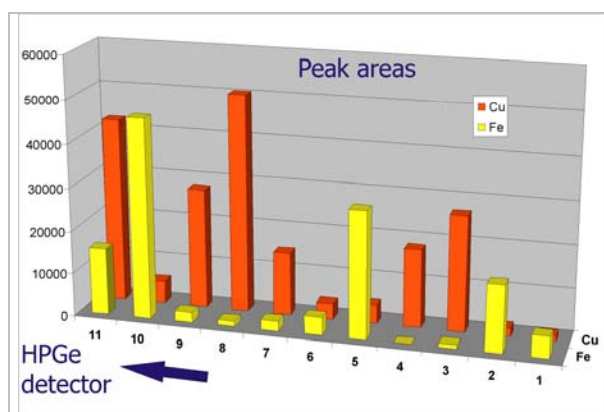
Measurement points with PGAI (Fig. 13c)

- neutron radiography driven chord type setup on the NIPS station: all nine sheets and two void volumes between them were analysed by PGAI
- beam size: 2 mm × 10 mm
- the collimated neutron beam is shown on **Fig. 13d**
- neutron beams are labelled as n1 - n11 (**Figs. 13c, 14**)
- distances on the neutron radiography image: determination of successive offsets of the moving table

PGAI conclusions

- 3 Fe sheets: n2, n5 and n10 (red rectangles) in accordance with the nominal ones, intensity indicates the self-absorption

- 2 Cu sheets: n3, n8 (blue rectangles) in accordance with the nominal ones
- 3 brass sheet: n4, n7, n9 (blue rectangles) in accordance with the nominal ones
- 1 Cu sheet: n11 (blue rectangle) in contradiction to the nominal one (Fe)

**Fig. 14 – Peak areas of measurements for box H-III**

TOF-ND conclusions (Festa et al. 2008)

- not used because of possible misalignment

Discussion

As seen in the X-ray radiography [XR-Ghe] and neutron radiography [NR-Bud] images, this box contains nine thicker and thinner metal sheets arranged parallel to each other. There is no visible filling material between the sheets. Based on the radiographs, eleven sections were measured by PGAI in a chord type setup. The successive offsets of the moving table are determined so that the sections to be measured are positioned in front of the neutron slit. In nine sections the neutron beam irradiated the metal plates and in two sections the void space between them.

The PGAI results indicated three iron, two copper and three brass sheets. The brass sheets were identified based on their copper and zinc contents (see **Table 8**). Sheet No. 9 showed different composition (copper) than to the nominal (steel). This issue will be verified by opening the box after all neutron measurements have been completed. The iron signal when measuring the voids is attributed to the box wall.

Significant gamma absorption can be observed by comparing the gamma intensities for spots n2, n5 and n10. The corresponding sheets are made of iron of similar thickness therefore the emission rate of their gammas should be equal. One can, however, note that the detected intensities from the sheets closer to the gamma detector are increasing. This is due to the decreasing amount of absorbing materials between the sheet of interest and the HPGe detector. The results from TOF-ND experiments were not involved into the assessment of the PGAI results, because all TOF-data show the same pattern. It has to be assumed that the scan was not, as planned, across the different plates. Maybe the incoming beam was impinging on the flat side of the sheets.

Iron box H-IV.

For the layout, the description and the nominal composition of the box refer to Dúzs (2008).

Radiography images (Fig. 15a-c)

- X-ray [XR-Ghe] and neutron radiography [NR-Bud] images: filling materials with different absorption coefficients.

Measurement points with PGAI (Fig. 15d)

- neutron radiography driven chord setup on the NIPS station, beam size: 2 mm × 10 mm.
- neutron beams: labelled as n1 - n5
- distances on the neutron radiography image: determination of successive offsets of the moving table
- beams n1 and n4 were let through the rods behind each other

PGAI conclusions

- very similar spectra from n1, n3, n4 and n5, except for the counting rates
- iron found
- some unexpected Cu and Al found
- spectrum from n2 is characteristic for sand

TOF-ND conclusions (Festa et al. 2008)

- at all points (P1-P9, Fig. 15d): quartz, gypsum and small amounts of copper alloys
- P1, P2, P4, P7 show iron oxides (FeO, Fe₃O₄)
- P1-3, P5, P6 indicate Al or Ag

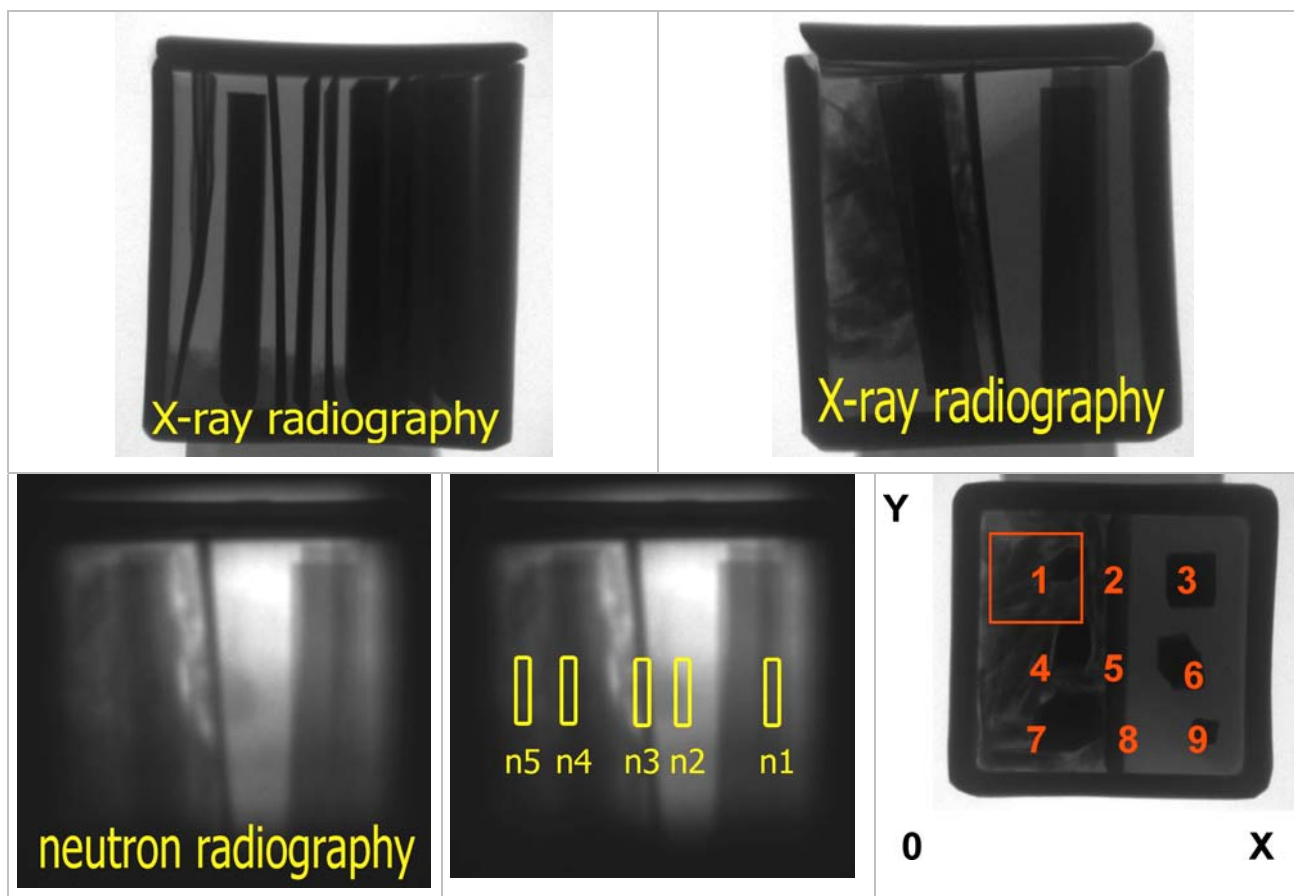
Discussion

Based on the PGAI results the metal rods can be identified as iron with manganese content. The count rates of the spectra differ, which may be due to the different elemental (iron) contents in the path of the beam. Some copper and aluminium components were identified, which is in disagreement with the expected nominal composition of the box. This will be checked by opening the box after all neutron measurements are completed. The signals of silicon and aluminium in both of the compartments may indicate a leakage of the sand from one side into the other. The results of TOF-ND experiments show copper and aluminium as well, which is in disagreement to nominal composition.

The details of the results are shown in **Table 9** (please note that Nr. refer to the numbering of the neutron beam used in PGAI measurements only).

Table 9. - Details of the composition of the box H-IV.

Nr.	Nominal composition	Meas. type and Nr. of PGAI beam	PGAI results	TOF-ND results (Festa et al. 2008)
1, 2, 3 (right)	iron rod	chord: n1	Fe, Mn , C, Al, Si?, Cu	measurement points are different
1, 2, 3 (left)	iron rod	chord: n4	Fe, Mn , C, Cu, Al?	
4	thin steel sheet	chord: n3	Fe, Mn , C, Cu, B?, Al?	
5	fill grit	chord: n5	Fe, Mn , C, Cu, B?, Al?	
6	fill sand	chord: n2	B, Al, Si , K?, Ti?, Fe, Mn, C	

**Fig. 15**

a-b, X-ray radiography images of box H-IV (top); c, neutron radiography image of box H-IV (bottom left); d, PGAI measurement points on box H-IV (bottom centre); e, TOF-ND measurement points on box H-IV (bottom right)

Iron box H-VI.

For the layout, the description and the nominal composition of the box refer to Dúzs (2008).

Radiography images (Fig. 16a-b)

- X-ray radiography images [XR-Ghe]: four sections of equal sizes with different absorption coefficients. Darker colours indicate higher absorption.
- section (1+2): filled with some chipping material.
- sections 3 and 5: visible homogeneous filling material
- section 4: filled with granulated pieces
- The neutron radiography images [NR-Bud] are presented in the section 'Measurement points with PGAI' because they show the positions of the neutron irradiations as well.

Measurement points with PGAI (Fig. 16c-d)

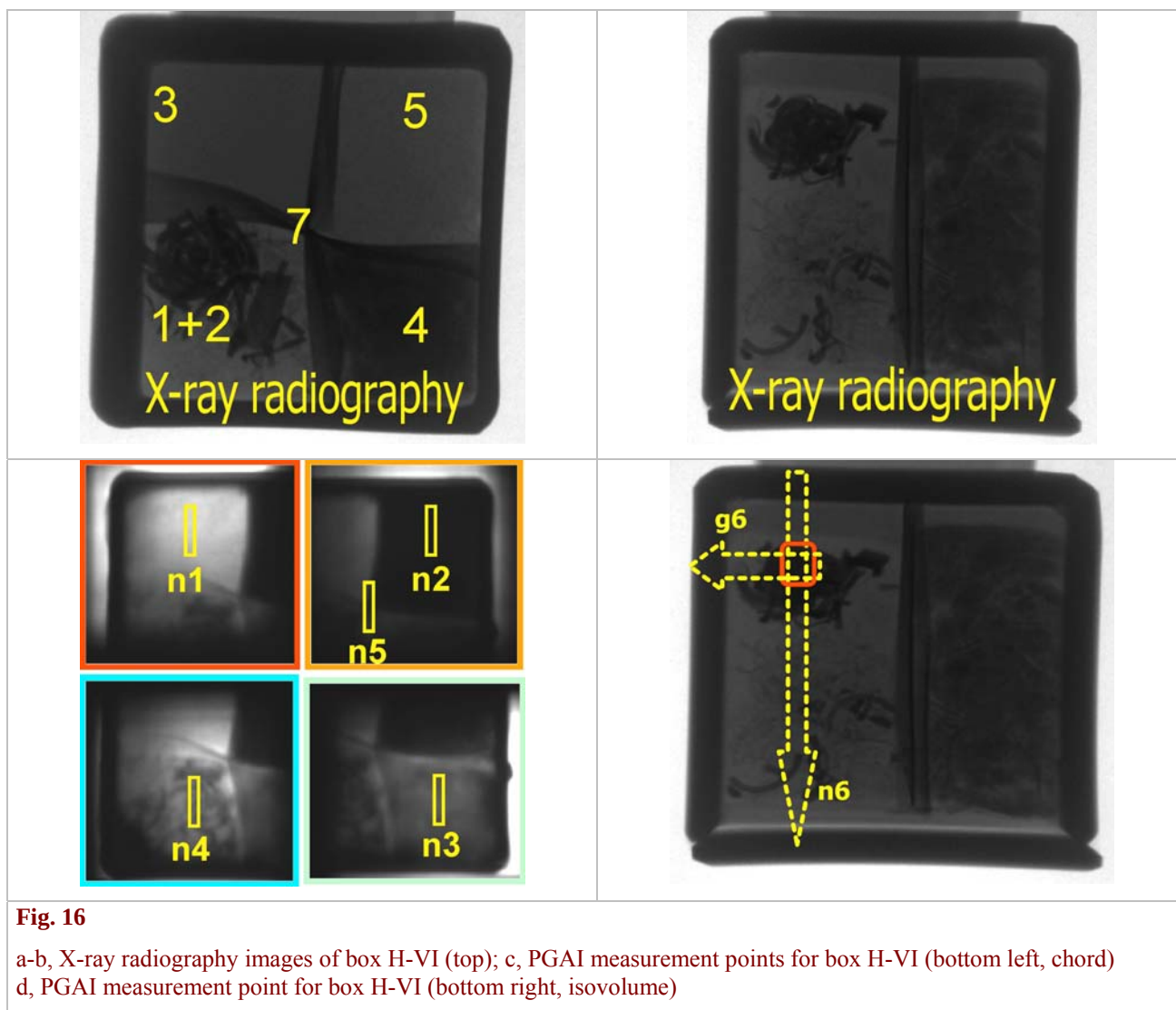
- materials of all four sections were analysed by PGAI separately

- box was studied in a chord type setup both on the PGAA and on the NIPS stations; in isovolume setup only on the NIPS station.

- PGAI on PGAA station, chord-type measurements (beam size: 44 mm²): the positions of the neutron beam in chord type setup are the same as on NIPS, only the irradiated areas are larger;
- PGAI-NT on NIPS, neutron radiography driven chord type and isovolume measurements (beam size 2 mm × 10 mm):
 - neutron beams: labelled as n1 - n5
 - beam used for isovolume experiment is labelled as n6, its gamma ray is g6.

PGAI conclusions

- section (1+2): fibre-like material (Ag chippings)
- section 3: predominantly Si
- section 4: predominantly Fe
- section 5: Na and Cl in a molar ratio 1:1
- Al in the sections (1+2) and 5
- Cu from the crossing point (7) of the sheets

**Table 10.** - Details of the composition of the box H-VI.

Nr.	Nominal composition	Meas. type and Nr. of PGAI beam	PGAI results	TOF-ND results (Festa et al. 2008)
1+2	Ag in talcum	chord: n4 isovolume: n6	H, Si, Cl, Mn, Fe, Cu, Ag	quartz (SiO ₂), gypsum (CaSO ₄ (H ₂ O) ₂), talc (Mg ₃ (OH) ₂ (Si ₄ O ₁₀)), Al or Ag, based on PGAI: Ag
3	sand	chord: n1	H, B, Na, Al, Si, Cl, K, Ti, Mn, Fe, Cu	quartz, gypsum, talc, Al or Ag, Cu-type fcc (bronze, brass)
4	iron grit	chord: n3	H, B, Al, Cl, Mn, Fe	gypsum, talcum, Cu-type fcc (bronze, brass), wuestite (FeO), magnetite (Fe ₃ O ₄)
5	salt	chord: n2	Na , Al, Cl , Cu	quartz, halite (NaCl), gypsum, talc, Cu-type fcc (bronze, brass)
6	Al plate	-	-	
7	Cu sheets	chord: n5	H, Na, Al, Si, Cl, Mn, Fe, Cu , Zn, Ag	halite (NaCl), gypsum, talc, Al or Ag, Cu-type fcc (bronze, brass), wuestite (FeO)

TOF-ND conclusions (Festa et al. 2008)

- gypsum and talc in all sections
- mainly Al or Ag in section (1+2) (cannot be distinguished)
- mainly quartz and sodium chloride in section 2
- mainly quartz in section 3
- mainly iron oxides in section 4

Discussion

According to the X-ray radiography [XR-Ghe] and neutron radiography [NR-Bud] images taken from different views, this box is divided into four sections of equal sizes with a crossing pair of separating sheets. Based on the different transmissions observed by radiography, the four sections apparently contain different materials. Moreover, a strong neutron absorber fibre-like material is placed in section (1+2). All four section materials were analysed by PGAI and TOF-ND. Details of the identified elemental and crystalline components are summarised in **Table 10**. With PGAI the fibre-like material in section (1+2) was identified as Ag. Predominantly Si was found in section 3 and Fe in section 4, whereas Na and Cl in section 5. Since the molar ratio of Na and Cl in section 5 is 1 to 1, it was asserted that this section contains simply sodium chloride. There were signals of Al in two measurements carried out in sections (1+2) and 5. It is due to the Al plate covering the sections. The measurement at the crossing points of the sheets confirmed the presence of Cu.

These results reasonably agree with the TOF-ND results. TOF-ND has identified gypsum and talc in all sections, probably as filling material. This result may indicate a misalignment or it may indicate that talc powder leaked from (1+2) into other compartments. TOF-ND identifies quartz in section (1+2) and 3, quartz and sodium chloride in section 5, iron oxides (wuestite, magnetite) in section 4, and Al or Ag in section (1+2) (see **Table 10**). TOF-ND cannot distinguish between Al and Ag, which have the same structure and almost the same lattice parameters. Based on PGAI results, the material proved to be Ag. The wuestite could probably be part of the iron box walls. TOF-ND shows an fcc-phase in some points with clearly larger lattice parameters than pure copper, indicating the presence of a copper alloy such as bronze or brass. The identification of Zn by PGAI decides for brass rather than bronze.

Iron box H-VIII.

For the layout, the description and the nominal composition of the box refer to Dúzs (2008).

Radiography image (Fig. 17a)

- investigated only on PGAA station, no neutron radiography images taken
- X-ray image [XR-Ghe]: the content of the box is almost homogeneous; some shadows of parts with higher absorption

Measurement points with PGAI (Fig. 17b-c)

- chord type setup on the PGAA station, beam size: 44 mm².
- spots are labelled as n1 - n8 in the figures below.

PGAI conclusions

- all spectra were very similar
- chord type measurements: not able to distinguish between different parts

TOF-ND conclusions (Festa et al. 2008)

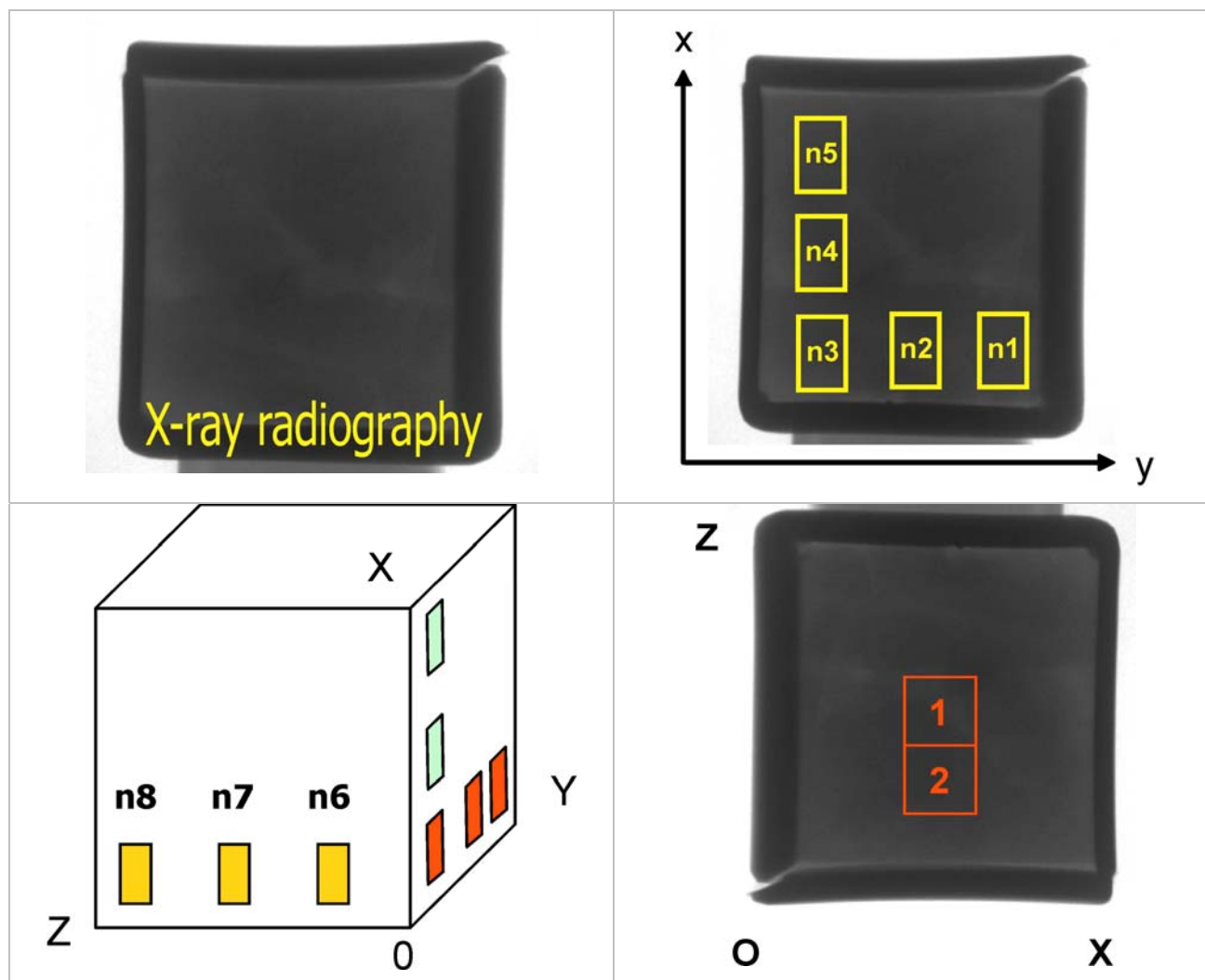
- beam does not pass through the box
- moderate amorphous background at spot 1 and 2 but no distinct crystalline material (Fig. 17d)

Discussion

The pottery fragments and the gypsum filling material seem to have very similar elemental composition and neutron mass absorption coefficients, thus PGAI and NT were not capable of making a good distinction. The gamma spectra taken at different parts of the box were too similar to each other (**Table 11**) and the contrast in neutron images was hardly visible. Unfortunately, the TOF-ND results can not reveal the composition of the box, only Bragg peaks of ferrite (front wall) are observed and no crystalline material could be identified.

Conclusions

PGAA and TOF-ND are standard non-destructive techniques for bulk elemental or phase analysis. They both provide information averaged over the irradiated volume, which is primarily determined by the neutron beam dimension. PGAA with a wide beam spot is fast, but the spatial resolution is not sufficient to reveal fine details inside the objects. Narrowing the neutron beam makes the use of a chord or an isovolume setup feasible; this is the advent of PGAI. The actual composition and structural issues of the sample being under investigation will determine the usefulness and effectiveness of PGAI, either alone or in combination with TOF-ND. In some cases, applying radiography driven PGAI alone yields the information needed. However, in many cases it turned clearly out that the combination of results from TOF-ND and PGAI-NR/NT can sufficiently reveal the properties of the materials. An unlucky situation may happen when even the combination of the methods is unable to identify the exact compositions and structures of details inside the object.

**Fig. 17**

a, X-ray radiography image of box H-VIII (top); b-c, PGAI measurement points for box H-VIII (top right, bottom left) d, TOF-ND measurement points for box H-VIII (bottom right)

Table 11. - Details of the composition of the box H-VIII.

Nr.	Nominal composition	Meas. type and Nr. of PGAI beam	PGAI results	TOF-ND results (Festa et al. 2008)
1	-	chord: n1	H, Si, S, K, Ca	moderate amorphous background; no distinct crystalline material identifiable
2	-	chord: n2	H, Al, Si, S, K, Ca, Ti	
3	-	chord: n3	H, Al, Si, S, K, Ca, Ti	
4	-	chord: n4	H, Al, Si, S, K, Ca, Ti	
5	-	chord: n5	H, Si, S, K, Ca	
6	-	chord: n6	H, Si, S, K, Ca	
7	-	chord: n7	H, Si, S, K, Ca	
8	-	chord: n8	H, Si, S, K, Ca	

According to the experiments on the black boxes, the methods (PGAI, TOF-ND and NR/NT) provide complementary information; usually none of them is being sufficient alone. NR/NT produces high-resolution 2D/3D images that are required to survey the object for geometrical structure and attenuation features. The contrast features observed in the NR/NT images is extended with a chemical and structural interpretation when information from PGAI and TOF-ND is added. PGAI can 'see' the elements in the chord and/or isovolume, which is an important analysis requirement in archaeological sciences. TOF-ND is phase sensitive and can identify structure and phases, for example distinguish between the different oxides of iron.

Furthermore, for a quantitative composition analysis, neutron self-shielding and gamma self-absorption correction should be introduced, using Monte Carlo calculations.

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