PIXE Investigation of Ancient Linen Fabrics Dated from Old Kingdom to Ptolemaic Ages (2200-300 B.C.)

M. Rogante[1], I. Kovács[2], Z. Szőkefalvi-Nagy[2]
1. Rogante Engineering Office, Contrada San Michele, 61, 62012 Civitanova Marche, Italy
2. Wigner Research Centre for Physics of the Hungarian Academy of Sciences, Institute for Particle and Nuclear Physics, Konkoly Thege str., 29-33, 1121 Budapest, Hungary
E-mail: main@roganteengineering.it

Abstract: External milli-beam particle induced X-ray emission spectroscopy (PIXE) has been used as non-destructive technique to investigate ancient linen fabrics from pre-dynastic and Ptolemaic ages belonging to the archaeological collections of the Egyptian Museum of Turin and to the Civic Archaeological Museum of Bologna, Italy. 9 linen fabric samples dated from Old Kingdom to Ptolemaic ages (2200-300 B.C.) were investigated, as well as 5 modern linen fabric samples, added for comparison. The primary goal of this work has been to advance the correct material description of the fabrics providing scientific data for further and more comprehensive comparative analyses. PIXE has provided quantitative analyses for the major (Si, Cl, K, Ca and Fe) and minor or trace elements as P, Ti and Mn, supplying information on the near-surface elemental composition. The achieved results contribute to comprehend the structural basis for the chemical properties of the considered materials, as well as to set up a classification according to the chemical composition, allowing in general a better understanding of the studied linen cloths.
Keywords: Linen; PIXE; Spectrometry; Archaeometry.

1. Introduction

Linen is made from the fibres of the flax plant (Linum usitatissimum) and its textiles seem to be some of the oldest in the world: their past goes back several thousands of years. These fibres are composed of pure cellulose fibrils associated with complementary substances (hemicellulose, lignin, pectin) that form inter-fibre lamellae and cementing textiles, which go with the cellulose up to the finished product. Their number varies depending on the conditions of production and processing. Important properties of these fibres are the crystallites dimensions and crystallinity, the homogeneity and shape over the cross section, the orientation degree and the molecular flexibility inside the fibre at dissimilar situations. Linen fibres are an extremely stiff material in the longitudinal direction of the fibre; the macromolecules are generally oriented in the same direction. Since plant cell walls, they can be considered as composites made of cellulose nano-crystals (micro-fibrils) embedded in a disordered matrix [1].

Linen pleated tunics in the Egyptian Museum of Turin, Italy, come from archaeological excavations at Gebelein and Asyut. The basic manufacture of this kind of tunics is the same, although small variations are present, mainly in their sizes. A standard tunic is made of three elements cuts from the same textile: a large rectangular piece that is used for the skirt and two shaped pieces of the same size used for the bodice (yoke and sleeves). The skirt part is folded in four and pleated. Once opened, it shows 4 pleated sections running upwards and downwards alternately. The skirt is sewn along the selvedges sides. The two pieces of the bodice are juxtaposed then pleated twice: once horizontally (yoke) and once vertically (sleeve). The two sides of the bodice, then, are juxtaposed in the centre to form a V-shaped neckline at both the front and neck of the garment and they are sewn to the skirt with a overcast seam [2]. The linen fabric of the tunic has retained pleats for centuries. Over the years, several hypotheses have been made about the methods employed by the Ancient Egyptians to pleat linen and how they fixed it in position. In order to investigate the method to fix pleats, various studies have been focused on the possible presence of substances that might have been applied to the fabrics so that the pleats remained in place. At a preliminary macroscopic investigation, the textile appears heavily altered and contaminated, as the fibres are very fragile and dark brown in colour. The presence of contaminating materials, either from external or of internal origin, may make difficult to detect the substances possibly employed as a stiffener. A first attempt to investigate the nature of the stiffener (if any) was performed by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). Such investigations have shown that, generally, fibres are parallel one to another, attesting that the structure of the thread was maintained despite the macroscopic degradation of the textile. Some of the fibres, in particular, are glued one to another, thus suggesting the possible presence of something that stiffens the fabric. The interpretation of the infrared spectra

obtained on the external layer of the fibre pressed in a diamond cell as well as from extracts in acetone, did not yield conclusive results, mainly since it is not possible to distinguish the materials originally present in the fabrics from those deriving from subsequent contaminations; moreover, since the very complex matrix yielded signals could be only tentatively attributed. A mix of resins and waxes may be present; nevertheless the presence of a siccative oil such as linseed oil cannot be excluded. Inorganic contaminants, moreover, were also detected. At this point, further analyses are appropriate, to contribute to the investigation of the considered fabrics and the stiffener.

The present experiment concerns the characterization by PIXE of various specimens of linen cloths belonging to different ages, in order to supply the researchers, complementarily with the classical methodologies, additional knowledge to be inserted in the information mosaic already obtained.

PIXE can be useful to complement the often very restricted investigations by cross section analysis, since it is a non-destructive method and allows the study of a high number of spots within a comparatively short period, typically some hours [3]. This technique has been already adopted to analyse textiles, especially for pigment identification, e.g. with respect to a sequence of mixed pigment layers on a linen support [4]. PIXE implemented with an external microprobe has also shown great ability to infer the elemental composition of ink as well as paper, papyrus and parchment. In that case, the rarity of the involved ancient archaeological piece suggested the use of a model sample of currently manufactured linen for comparison purposes and optimization of the experimental conditions [5]. PIXE was also adopted to analyse (e.g., detecting the presence of aluminium) a group of modern wool and cotton samples prepared as mordanted standards: the mordents applied were potassium aluminium sulphate, cupric sulphate, ferrous sulphate, stannous chloride, and potassium dichromate. Results agreed with analyses of identical mordanted standards by energy dispersive x-ray spectrometry in a scanning electron microscope [6].

2. Materials and method

In this experiment, 14 samples have been investigated: 9 samples are dated from the Old Kingdom to Ptolemaic ages (2500-300 B.C.) and 5 samples are made of modern linen fabric. Currently manufactured samples have been chosen with similar weave styles with respect to the historic samples. These linen fabrics have been used for comparison purposes. Table 1 reports the description of the samples.

Figure 1 shows the sample n. 1 and the pleated tunic original fragment, while Figure 2 shows the original mummy bandage, of which a fragment (sample n. 9) has been investigated.

Tab. 1. Samples description.

Sample	Inventory	Findspot	Object	Period	Material and manufacture
1	S.16792A	Gebelein	fragment of a pleated tunic	2490-2180 B.C.	Linen, tabby weave, warp-faced 26-32/cm warp count 11/cm weft count Pleating cm 1
2	S.16792B	Gebelein	(?) not a tunic, textile find with S. 16792 A (same context)	2490-2180 B.C.	Linen, tabby weave, warp-faced not pleated
3	S.16807	Gebelein	fragment of a pleated tunic	2590 – 2290 B.C. (^{14}C date)	Linen, tabby weave, warp-faced 26-28/cm warp count 9/10/cm weft count Pleating cm 1,5 Preserved inside out.
4	S.16788A	Gebelein	fragment of a fringed shawl (?)	2490-2180 B.C.	Linen, tabby weave, warp-faced
5	S.16788B	Gebelein	fragments of a pleated tunic	2490-2180 B.C.	Linen, tabby weave, warp-faced
6	S.5306	Queen Valley	2fragments of textile	1500 B.C. (?)	Linen, tabby weave, warp-faced not pleated
7	P.1457	unknown	fragment of textile	1500-300 B.C. (?)	Linen, tabby weave, warp-faced not pleated
8	BO2054	Saqqarah (?)	fragment of animal (ibis bird) mummy bandage	600-300 B.C. (?)	Linen, tabby weave, warp-faced not pleated
9	BO 2055	Saqqarah (?)	fragment of animal (ibis bird) mummy bandage	600-300 B.C. (?)	Linen, tabby weave, warp-faced not pleated

10	PW15 WHITE	(#)	fabric fragment	modern	Linen, tabby weave, 15 picks per cm, whitened (*)
11	PW11 IVORY	(#)	fabric fragment	modern	Linen, tabby weave, 11 picks per cm, ivory colour (**)
12	PW6 IVORY	(#)	fabric fragment	modern	Linen, tabby weave, 6 picks per cm, ivory colour (***)
13	PW11 WHITE CREAM	(#)	fabric fragment	modern	Linen, tabby weave, 11 picks per cm, white cream colour (****)
14	PW15 IVORY	(#)	fabric fragment	modern	Linen, tabby weave, 11 picks per cm, ivory colour (*****)

Notes:
samples n. 1-7, from the Egyptian Museum of Turin, Italy
samples n. 8-9, from the Civic Archaeological Museum of Bologna, Italy
(#) samples n. 10-14 (modern production), raw material coming from Normandy, yarns selected and worked in Italy
(*) once weaved, the fabric is submitted to a flame that burns up the superfluous furs; successively, it is submitted to a washing in order to remove the residual dirt produced by the weaving machine; finally, it is bleached by using bleaching additives (sodium hypochlorite)
(**) once weaved, the fabric is bleached by using bleaching additives (sodium hypochlorite) - then, a fixative of the colour is added
(***) once weaved, the fabric is only submitted to a washing in order to remove the residual dirt produced by the weaving machine
(****) once weaved, the fabric is submitted to a flame that burns up the superfluous furs - successively, it is submitted to a washing in order to remove the residual dirt produced by the weaving machine
(*****) once weaved, the fabric is submitted to a flame that burns up the superfluous furs - successively, it is submitted to a washing in order to remove the residual dirt produced by the weaving machine - then, a fixative of the colour is added

Fig. 1. Sample n. 1: fragment of a pleated tunic(Old Kingdom) from Gebelein, Egypt.

Composition of an artefact is frequently linked to its functions, therefore to identify the component materials is a main step in planning a conservation action or preservation measures. Appropriate analyses methods to get accurate information on composition, thus, are essential to archaeological research, since they identify the constitutive elements giving a substantial help to classify the object. Chemical analysis of archaeological artefacts has become, lately, a key tool for source identification and provenance study based on the assessment of major- and trace elements. The most usual analytical approaches require partial or total destruction of the samples, which often is not allowed in case of valuable whole or fragmental artefacts.

Fig. 2. Original ibis bird mummy linen bandage (late Ptolemaic age) and the investigated fragment - sample n. 9.

PIXE spectroscopy is a powerful elemental analysis technique adopted to assess the elemental composition of a material or object. The method was proposed in 1970 by S. Johansson et al. [7]. For a detailed treatment of the theoretical bases, see [8-10]. Its version, when the particle beam is extracted trough a properly thin "window" foil, the so-called external-beam PIXE technique is especially suitable for non-destructive analysis of art and archaeological objects providing data to support answering questions as authenticity, dating, provenance, manufacturing technologies, etc. [11]. The identification of elements, in fact, not only provides dating information, recognition and distinction of the different elemental composition, but it can distinguish original and false artworks as well. In the present work this ion-beam technique has been used for identifying and quantifying main and trace elements, supplying data complementary to those from other investigations techniques.

The measurements have been carried out at the external millibeam PIXE facility of the Wigner Research Centre for Physics of the Hungarian Academy of Sciences, Budapest, Hungary. The collimated proton beam of 3 MeV energy was extracted to air through a 7.5 micrometre thick Kapton foil. The samples were mounted on a holder and were investigated directly without any surface coating. The objects to be analysed were positioned at a distance of 10 mm from the exit window by a computer controlled 3D positioning platform. A mechanical pointing device helped the proper adjustment of the target spot. The diameter of the extracted proton beam was about 1mm, the estimated beam current was 2-4 nA. The characteristic X-rays produced were collected by an Amptek X-123 spectrometer. The SDD type detector of 25 mm^2×500 μm active volume positioned at 135° with respect to the beam direction. The energy resolution of the spectrometer was 130 eV for the Mn-Ka line. A polycarbonate PC 60 μm thick was used to stop the backscattered protons and attenuate the low energy X-rays. Measuring times of a selected spot varied in the range of 600 -1800 s. The experimental set-up and a the obtained PIXE spectrum related to one of the investigated ancient samples are displayed in Figure 3.

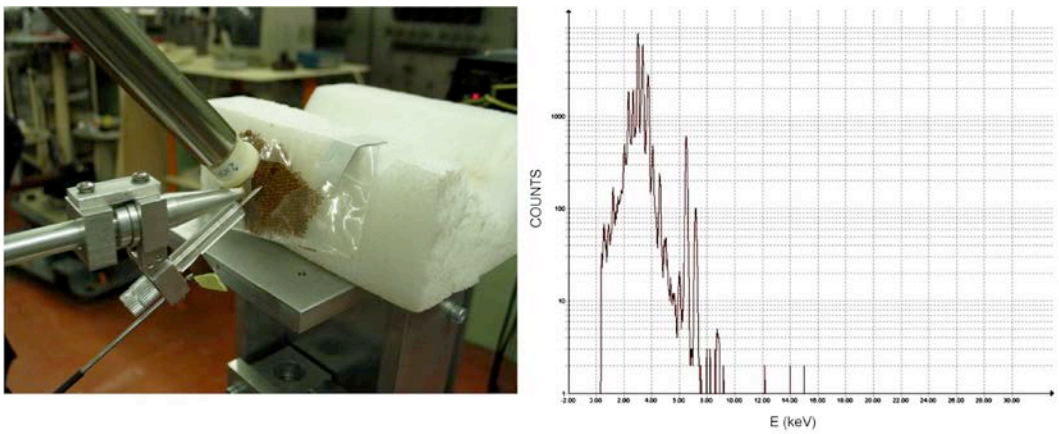

Fig. 3. The experimental set-up with a fragment of linen fabric during the investigation and a PIXE spectrum related to one of the investigated ancient samples.

3. Results and discussion

Table 2 reports the resulted elements' content related to each of the ancient samples investigated by PIXE, while Table 3 reports the resulted limit of detection for each element and sample with reference to Table 2.

Table 4 reports the resulted elements' content related to each of the modern samples, while Table 5 reports the resulted limit of detection for each element and sample with reference to Table 4.

Tab. 2. Elements' content (concentration in %m/m) for the investigated ancient samples.

sample	code	file	Si	P	S	Cl	K	Ca	Ti	Mn
1	P1457	9907	24.42	3.06	6.52	8.21	5.43	41.35	2.56	0.37
2	S16792A	9908	22.22	3.82	4.37	12.39	5.66	44.77	1.10	0.20
3	S16792B	9914	7.81	8.49	18.54	13.61	29.13	16.42	1.36	0.07
4	S16788B	9913	13.40	3.70	16.33	18.26	13.68	26.23	0.87	0.19
5	S5306	9909	15.40	10.73	15.54	15.22	21.27	16.55	0.90	0.06
6	BO2055	9910	30.06	0.85	7.30	1.72	3.49	48.38	2.44	0.16
7	BO2054	9906	2.63	0.72	9.01	6.93	23.20	56.38	0.17	0.08
8	S16788A	9912	9.46	0.96	12.94	29.28	8.19	33.51	0.71	0.18
9	S16807	9911	7.89	1.79	8.38	32.88	8.56	34.55	0.97	0.14
sample	code	file	Fe	Co	Ni	Cu	Zn	As	Sn	Pb
1	P1457	9907	7.89	0.15	0.01	0.05	#	#	#	#
2	S16792A	9908	5.37	0.07	#	0.03	0.03	#	#	#
3	S16792B	9914	4.51	0.04	#	#	0.05	#	#	#
4	S16788B	9913	4.61	0.06	0.01	#	0.02	#	2.68	#
5	S5306	9909	4.24	0.04	0.01	0.01	0.07	#	#	#
6	BO2055	9910	5.33	0.05	#	0.02	0.08	0.02	#	0.10
7	BO2054	9906	0.80	0.01	0.01	#	0.02	#	#	#
8	S16788A	9912	4.15	0.05	0.02	0.06	0.40	#	#	0.12
9	S16807	9911	3.43	0.04	0.04	0.02	0.08	#	1.17	0.05

Tab. 3. Limit of detection (in %m/m) for each element and sample with reference to Table 2.

sample	code	file	Si	P	S	Cl	K	Ca	Ti	Mn
1	P1457	9907	3.812	1.924	0.649	0.41803	0.219	0.168	0.056	0.024
2	S16792A	9908	7.087	3.454	1.300	0.80826	0.473	0.276	0.153	0.063
3	S16792B	9914	2.696	0.879	0.377	0.32635	0.195	0.305	0.068	0.033
4	S16788B	9913	2.885	1.075	0.400	0.32716	0.244	0.171	0.064	0.015
5	S5306	9909	1.528	0.595	0.239	0.18334	0.125	0.159	0.028	0.012
6	BO2055	9910	1.481	1.054	0.280	0.16273	0.081	0.067	0.026	0.011
7	BO2054	9906	2.097	0.646	0.164	0.11564	0.059	0.199	0.043	0.014
8	S16788A	9912	2.269	0.790	0.250	0.17697	0.182	0.114	0.038	0.045
9	S16807	9911	1.626	0.539	0.169	0.10156	0.122	0.095	0.028	0.011
sample	code	file	Fe	Co	Ni	Cu	Zn	As	Sn	Pb
1	P1457	9907	0.074	0.114	0.018	0.02171	0.028	0.058	5.162	0.141
2	S16792A	9908	0.081	0.122	0.053	0.02569	0.031	0.055	9.056	0.163
3	S16792B	9914	0.037	0.077	0.022	0.02718	0.022	0.031	4.162	0.071
4	S16788B	9913	0.038	0.069	0.010	0.0166	0.014	0.019	5.053	0.046
5	S5306	9909	0.034	0.049	0.006	0.00805	0.011	0.019	1.768	0.040
6	BO2055	9910	0.024	0.053	0.009	0.00634	0.012	0.026	1.508	0.069
7	BO2054	9906	0.021	0.024	0.011	0.00819	0.009	0.013	1.899	0.054
8	S16788A	9912	0.048	0.074	0.025	0.01029	0.026	0.070	2.959	0.086
9	S16807	9911	0.028	0.043	0.009	0.00945	0.007	0.032	2.222	0.038

Tab. 4. Elements' content (concentration in %m/m) for the modern samples.

sample	code	file	S	K	Ca	Ti	Mn	Fe	Cu	Zn
10	1 new	11402	14.64	47.78	34.66	1.81	0.07	0.73	0.11	0.21
11	2 new	11403	14.86	20.70	55.84	4.48	0.09	3.66	0.18	0.20
12	3 new	11404	10.35	19.63	62.48	4.65	0.79	1.34	0.46	0.37
13	4 new	11401	20.62	18.51	47.69	5.56	0.10	7.30	0.32	0.00
14	5 new	11405	9.42	15.58	69.95	2.24	0.13	2.13	0.36	0.20

Tab. 5. Limit of detection (in %m/m) for each element and sample with reference to Table 4.

sample	code	file	S	K	Ca	Ti	Mn	Fe	Cu	Zn
10	1 new	11402	1.41	0.75	1.01	0.43	0.16	0.12	0.06	0.09
11	2 new	11403	2.93	1.41	1.02	0.87	0.32	0.23	0.17	0.16
12	3 new	11404	10.81	5.04	2.93	2.88	1.04	0.86	0.36	0.60
13	4 new	11401	8.41	4.68	2.61	2.04	0.94	0.23	0.47	0.68
14	5 new	11405	1.30	0.54	0.47	0.39	0.15	0.13	0.06	0.08

Some of the analysed historic textile samples were in a strict dry condition, such that they could be easily being fragmented. They showed ageing damage, brittleness, soiling and dark brown spots, which could be the eventual effect of resins adopted to protect mummies from the moisture of the surrounding air.

PIXE allowed us getting information on the elemental composition of the textiles for each investigated area, in particular detecting the major components (Si, Cl, K, Ca and Fe) and minor or trace elements as P, Ti and Mn. The elements that are not expected to be constitutive of the considered fabrics may be a part of the history of these textiles. In particular, what we have detected in the ancient materials is probably also the dust and grime of centuries, particularly the Si, some of the Ca, Ti. In both the ancient and the modern samples, elements such as S and Ca are likely to be very minor components of what are carbon-based substances. Si as the dioxide (silica), Ca as a carbonate (calcite) and Ti as the mineral ilmenite are major components of the all-pervasive dust of the Middle East (and more generally). A suitable protocol to clean these fabrics could probably let the results better relate to stiffening or original fabric composition, which is supposed of various carbon-based compounds. Concerning the higher presence of Mn in the sample n. 2, moreover, it may be that originally the fabric was coloured, and such colour was containing the Mn element (e.g., the green colour). Supplementary analyses by gas chromatography-mass spectrometry would be useful to address these, but Fourier transform infrared spectroscopy might also be informative and so would scanning electron microscopy studies.

The information supplied by the PIXE investigation on the near-surface elemental composition can be considered also complementary to the nano-structural data obtained from neutron analyses. The obtained results can be interpreted also as possible indications to create replicas (as secondary standards) of the major element compositions and in accordance with the supposed manufacturing process, and also to analyse that as a standard to compare with the original fabrics.

4. Conclusion

PIXE, as multielemental non-destructive detection technique efficient of measuring elements' concentrations with a sensitivity down to the ppm scale, has been adopted to investigate ancient linen fabrics dated from Old Kingdom to Ptolemaic ages (2200-300 B.C.), providing data on major and trace constitutive elements, as well as information on the dusts accumulated on the surface of the considered ancient fabrics over the centuries.

The results supply a contribution to the study of linen textiles, either considering each single sample, or making comparisons between them, complementing the analytical and microstructural information, which are important to comprehend the structural basis for the chemical, physical, and biological properties of the considered materials.

The progress of research and the formation of a rich and reliable database on these ancient textiles will allow researchers gathering interesting features, also contributing in preserving and sustaining this cultural heritage for present and future generations.

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6. References

[1] M. Rogante, L. Rosta. Feasibility Study for Neutron Beam Investigation of the Turin Shroud. International Journal of New Technology and Research. 2016; 2(3): 86-95. https://doi.org/10.31871/IJNTR.2.3.23.

[2] M. Borla, C. Oliva. Pleated dresses from the Museo Egizio of Turin: study of the thechnical data of fabrics. Preliminary results. In: A. De Moor, C. Fluck, P. Linscheid (Eds.), Textiles, tools and techniques of the 1st millennium AD from Egypt and neighbouring countries. Proc. 8th Conference of the research group 'Textiles from the Nile Valley', Antwerp 2013 (Tielt, 2015).p.104-130.

[3] A. Denker, J. Opitz-Coutureau. Paintings – high-energy protons detect pigments and paint-layers. Nuclear

Instruments and Methods in Physics Research B. 2004; 213: 677-682. https://doi.org/10.1016/S0168-583X(03)01685-9.
[4] M. Griesser et al., Non-destructive investigation of works of art using portable XRF and high energy PIXE/PIGE. In: A. Adriaens, C. Degrigny, J. Cassar (Eds.), Benefits of non-destructive analytical techniques for conservation. Report EUR 21636 EN; 2005.p.51-58.
[5] H.E. Ahmeda, O.A. Nassef. From Ptolemaic to modern inked linen via Laser Induced Breakdown Spectroscopy (LIBS). Analytical Methods. 2013;5: 3114-3121. https://doi.org/10.1039/C3AY26358D.
[6] E.T. Williams, N. Indictor. Detection of Metallic Mordants on Textiles by Particle-Induced X-Ray Emission. Scanning Electron Microscopy. 1986;3: 847-850.
[7] T.B., Johansson, R., Akselsson, S.A.E. Johansson. X-ray analysis: elemental trace analysis at the 10^{-12} g level. Nuclear Instruments and Methods. 1970;84: 141-143. https://doi.org/10.1016/0029-554X(70)90751-2.
[8] W. Maenhaut, K.G. Malmqvist. Particle-Induced X-ray Emission Analysis. In: R.E. Van Grieken, A.A. Markowicz (Eds.), Handbook of X-Ray Spectrometry, Second Edition, M. Dekker, New York; 2002. p.719-810. http://hdl.handle.net/1854/LU-231821.
[9] P.A. Mandò, W.J. Przybyłowicz. Particle-Induced X-Ray Emission (PIXE). Encyclopedia of Analytical Chemistry, John Wiley & Sons, Ltd.;2016. https://doi.org/10.1002/9780470027318.a6210.pub3.
[10] M.D. Puc, M. Budnar, M. Kavčič, P. Pelicon. Detector response function for fitting PIXE spectra. Nuclear Instruments and Methods in Physics Research B. 2002;189:123-130. https://doi.org/10.1016/S0168-583X(01)01017-5.
[11] I. Gyódi, I. Demeter, K. Hollós-Nagy, I. Kovács, Z. Szőkefalvi-Nagy. External-beam PIXE analysis of small sculptures. Nuclear Instruments and Methods in Physics Research Section B.1999;150: 605-610. https://doi.org/10.1016/S0168-583X(98)00948-3.