APPENDIX. ANALYSIS RESULTS

I. Gold. X-ray Fluorescence Analysis (XRF)

	Au %,	Ag %,	Cu %,	Pb
137	88.4	11.5	0.1	nd
182	90.2	8.1	1.6	nd
277	97.0	n	3.0	
278	96.0	n	4.0	
279	97.0	2.0	1.0	
280	92.0	n	8.0	
281	93.0	n	7.0	
336	97.0	n	2.5	
364	66.0	30.0	4.0	

1938.1110 'Ring of Minos', two replicas

The larger, better replica, stamped '850': Au 27.33%, Ag 69.96%, Cu 2.71%, Pb 0.30%

The smaller, yellower, less detailed replica, stamped '585': Au 99.01%, Ag 0.35%, Cu 0.64%, Pb 0.96%.

'Thisbe' Treasure

Four beads and four pieces of gold foil, ancient. One bead was 86.2% Au, 8.6% Ag, 5.1% Cu. The other seven items were in a range 66.2–74% Au, 23.2–29.1% Ag, 3.7–4.6% Cu.

Five forged seals virtually 100% Au. Selected from among 1938.1113–1938.1125.

II. Bronze. X-ray Fluorescence Analysis (XRF). Cf. VI.

	Fe%	Co%	Ni%	Cu%	Zn%	As%	Au%	Pb%	Bi%	Ag%	Sn%	Sb%
463	0.5	n.n.	0.5	83.0	n.n.	0.5	n.n.	n.n.	0.0	?1.0	14.0	n.n.
513	0.5	n.n.	n.n.	86.0	n.n.	1.0	n.n.	0.5	n.n.	n.n.	12.0	n.n.

III. 'White pieces'. Scanning Electron Microscopy and Electron-Probe Microanalysis. Magnification up to 400×. Surface penetration up to 5 μm. Cf. VI.

8 similar to **11.**

11 Both front and back showed major quantities of Si and Mg. The back also showed relatively high levels of Al. Minor quantities of K, Ca, Fe and S were found. The S could result from finger grease and is not thought to be significant. Where an apparently 'vitreous' layer was observed, the analysis revealed the presence of an organic material in the form of a characteristic background on the spectrum. Further visual examination suggested that this was probably varnish which was flaking off in some areas.

The presence of Mg at relatively high levels suggests that both seals are made of soapstone. They are both certainly magnesium silicates and could be talc or sepiolite. A full analysis would have to be destructive, using a technique such as X-ray Diffraction. (Adapted from J. Henderson apud H. Hughes-Brock in CMS Beih. 3, 87f.)

9, 10. A very soft stone, probably steatite, containing significant Ca, therefore perhaps talc and calcite mixed.

IV. Glass. Scanning Electron Microscopy. Cf. VI.
447 Many impurities. Cobalt revealed by filter.

V. Pyrite. X-ray Fluorescence Analysis and Scanning Electron Microscopy. Cf. VI.
1989. 75 (CMS X No. 53) Pyrite with miscellaneous iron oxides and hydroxides on the surface and a very small amount of Ca.

Acknowledgements

8, 11: J. Henderson, 1986
9, 10: C. Fogg, 1986 (Department of Earth Sciences)
137, 182; ancient 'Thisbe' beads and foil: Z. Stós, 1978
277–281, 336, 364; forged 'Thisbe' 'bead-seals' and rings: R. M. Hedges, 1975
447: A.J. Shortland
463, 513: Z. Stós-Gale
1989.75 (CMS X No. 53): Z. Stós-Gale 1990 (XRF), M.T. Price, 1993 (SEM)
1938.1110 (replicas): B. Gilmour, 2001

The work was carried out at the Research Laboratory for Archaeology and the History of Art, Oxford University, except where specified otherwise.

VI. 'White pieces', bronze, ?vitreous material, pyrite. Proton Induced X-ray Emission (PIXE). Cf. II-V.

Objects analysed: **8**, **9**, **10**, **11**, **12**, **463**, **513**, also 1989.75 (= CMS X No. 53) and AE 1237 (see Introduction, pp. 19, 21, 27).

The technique used for analysis was Proton Induced X-ray Emission (PIXE) using a focused microbeam in air. In this technique a beam of high energy protons issued to stimulate the atoms of the sample to emit photons of X-ray radiation which are detectable in a suitable detector. The energy of the X-rays identifies the atoms and the quantity of X-rays at each energy can be used to determine the amount of each element present. PIXE is sensitive (parts per million under favourable conditions) and rapid (all elements are detected simultaneously). By extracting the proton

beam into air, PIXE analysis can be carried out on samples which cannot be placed in a vacuum because of their size, value or physical condition. Although the protons have a high energy, the beam current used is very low and this technique is non-destructive to virtually all samples and is essentially non-marking.

Analysis was carried out using protons of energy 2.5 MeV (mega electron volts) and a beam current of approximately 1 nanoampere. The beam was extracted into air and focused so that the beam diameter on the sample was approximately 100 micrometres. The air path between the air exit window and the sample was 4 mm.

X-rays were detected using a lithium-drifted silicon detector (Gresham Scientific Ltd., Marlow, Bucks., England) with a resolution of 150 eV at 5.9 keV and an active area of 80 mm^2. The air path between the sample and the detector was 25 mm. An X-ray absorber of 75 μm of Kapton foil was fitted to attenuate the intense low energy silicon X-rays. Because of this, and because of absorption in the air path from the sample to the detector, the analysis is not sensitive to elements lighter than silicon ($Z < 14$).

The X-ray spectra were processed using the industry standard software package GUPIX.

The seals were supported on an adjustable mounting stage. Using a video microscope and a low power alignment laser, selected points on the surface of the sample were moved into the analysis position. The exposure time of the beam on the sample was 2–6 minutes for each analysis point. The photographs show some of the samples in the analysis position.

The samples were not cleaned before analysis.

At least one analysis was carried out on each object and more than one analysis in cases where there were obvious differences in the surface appearance.

A certified glass standard reference material (BCR 126A lead glass, EC Institute for Reference Materials) was analysed to provide correction factors for the measured data.

Object	Time (seconds)	Run no.
BCR 126 glass	95	335078P0
BCR 126 glass	144	335079P0
1989.75 (broken surface)	114	335080P0
11	96	335081P0
11 (new point)	224	335082P0
11 (seal surface)	151	335083P0
12	354	335084P0
8	68	335085P0
10	215	335087P0
463 (polished seal surface)	104	335088P0
AE 1237	157	335089P0
AE 1237 (fresh surface)	214	335090P0
9	173	335092P0
513	216	335093P0
1989.75 (seal surface)	212	335095P0
1989.75 (cleaved surface)	192	335096P0
1989.75 (brown spot on cleaved surface)	106	335097P0

For quality control standard, the composition of the BCR 126A lead glass standard was measured (assuming that the only invisible element is oxygen bound to each metal in a stoichiometric ratio) and the values were used to fix the various parameters in the description of the detector. The composition of the glass measured following adjustment is as follows (values in percentage by weight of the oxide).

Oxide	Certified	Measured
SiO_2	57.8	58.4
K_2O	10.0	9.11
CaO	1.03	0.95
ZnO	1.02	0.95
BaO	1.04	0.83
PbO	24.0	27.5

i. 'White pieces' **8**, **9**, **10**, **11** with **12**; also AE 1237 (Table 1)
The major constituent in all analyses was SiO_2 with varying minor amounts of S, FeO and other trace elements. An earlier mineralogical assessment of **8–11** had suggested that the material is steatite or soapstone ($Mg_3Si_4O_{10}(OH)_2$: MgO 32% w/w, SiO_2 64% w/w). Unfortunately this was not known during the analysis and the PIXE setup used was not sensitive to Mg, so the identification could not be confirmed. The concentrations of silicon, however, are consistent with what we would expect from steatite. The presence of highly variable amounts of Fe, S and other elements is very likely to be from the surface layers, which are impossible to avoid if the surface is not cleaned. Some of these elements might also be present in the steatite mineral as natural impurities not homogeneously distributed.

ii. Loop signet 1989.75 = CMS X No. 53 (Table 2)
The major components are iron and sulphur in amounts consistent with the earlier identification as pyrite (FeS_2, Fe 46% w/w, S 54% w/w). The apparently high value of Fe in run 335095 c could indicate that we are measuring a surface layer of iron oxidation. The analysis is not sensitive to oxygen, so the normalisation procedure results in an artificially high value for iron. Minor variations between the different runs are likely to be due to the inhomogeneity of surface contamination and chemical modification due to wear and cleaning.

iii. Bronze lentoid seals **463**, **513** (Table 3)
One analysis was performed on each object. These revealed a copper-tin alloy with a very high proportion of tin. The metal is certainly tin bronze, but without analysis of the uncorroded interior it is not at all certain what the original composition was. Copper is more chemically active than tin; the surface is therefore almost certainly enriched in tin owing to the leaching of copper corrosion products or through surface treatment. Small amounts of lead and arsenic together with other trace elements are quite consistent with typical Minoan bronze. The 4% of iron indicates iron oxides rather than metallic iron, again typical for Bronze Age copper and bronze metals from the Mediterranean.

This was a short preliminary analysis to investigate the potential of the technique. The potential is certainly increased if results of previous analyses are taken into account, so that the technique can be optimised for light element determination and for the non-destructive measurement of the thickness and composition of the surface layers. The length of time devoted to the procedures also improves the quality of the results for archaeological purposes. Used to its full potential, Ion Beam Analysis is an excellent tool for analysis of ancient materials.

G. W. Grime, 2007 (Advanced Technology Institute, Ion Beam Centre, University of Surrey, Guildford, England)

Table 1. 'White' and ?vitreous seals. Values are presented as percentage by weight of the element oxide (except C_1).

Object	SiO_2	SO_3	C_1	K_2O	CaO	TiO_2	Cr_2O_3	MnO	FeO	NiO	Cu_2O	ZnO	PbO	Run no.
11	38.70	10.91	2.46	2.64	4.09	0.18	0.02	0.14	15.65	0.40	5.18	0.28		335081P0
11	58.18	2.47	0.50	1.18	2.00	0.12		0.05	5.44	0.08	0.72	0.08	0.11	335082P0
11	60.63	1.93	0.50	0.55	1.21	0.04		0.05	3.72	0.02	0.91	0.07	0.06	335083P0
12	55.62	5.18	0.27	0.52	2.13	0.04		0.02	8.21	0.04	0.07	0.07		335084P0
8	46.44	6.79	1.05	1.12	5.07	0.07		0.07	2.40		13.53	0.14	0.12	335085P0
10	46.18	16.00	0.38	0.73	5.58	0.04		0.10	5.72	0.01	1.93	0.16	0.06	335087P0
AE1237	42.44	4.91	0.92	0.30	11.36	0.05	0.09	0.08	18.35	0.21	0.04	0.03		335089P0
AE1237	53.53	0.52	0.45		1.08		0.08	0.09	17.04	0.37	0.04	0.03		335090P0
9	54.58	2.90	1.44	0.73	2.70	0.13		0.08	5.85	0.02	4.18	0.11		335092P0

Table 2. Pyrite loop signet. Values are presented as percentage by weight of the element (normalised to 100%).

Object	Si	S	C_1	K	Ca	Ti	V	Mn	Fe	Ni	Cu	Zn	Run no.
1989.75 (broken surface)		61.11	0.44	0.11	0.19	0.02		0.03	37.99	0.02		0.09	335080P0
1989.75 (seal surface)	1.49	1.65	0.47	0.27	0.85	0.06	0.02	0.07	95.08			0.03	335095P0
1989.75 (cleaved surface)		64.95	0.34	0.06	0.11				34.53		0.02		335096P0
1989.75 (brown spot on cleaved surface)		46.68	0.87	0.42	0.51	0.05			51.40		0.02	0.06	335097P0

Table 3. Bronze lentoid seals. Values are presented as percentage by weight of the element (normalised to 100%).

Object	Mn	Fe	Cu	Zn	As	Sn	Pb	Run no.
463 (polished seal surface)	0.02	0.43	61.8		0.21	37.3	0.20	335088P0
513	0.11	4.10	37.67	0.26	0.52	58.42	0.88	335093P0