Combined trace element and multiple isotopic ratio analysis of minute samples for the provenance of raw materials in an Art history and Archaeology context

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The unambiguous provenancing of lithic, paint & metal artefacts is hindered by; i) the non-unique nature of their composition & individual isotopic systems; ii) the need for non-destructive analysis. To overcome these problems we present a new methodology that incorporates a portable "non-destructive" laser ablation technique (Fig.1) that deposits samples on inert filters that are returned to the laboratory for ultra-low blank (<pg) geochemical procedure that allows trace element analysis by ICPMS & combined isotope analysis of sub nanogram amounts of Sr-Nd-Pb by thermal ionisation mass spectrometry (TIMS).

The key enabling development is the introduction of 10^{13} Ω resistors to Faraday collectors providing a factor of 10 improvement in signal to noise & the precise analysis of sub nanogram amounts of Sr-Nd. (Fig. 2, Koornneef et al., 2014). Moreover the use of ^{207}Pb - ^{204}Pb double spike allows the determination of Pb isotope data with a precision of ~100 ppm on sub nanogram samples (Fig. 3, Klaver et al., submitted).

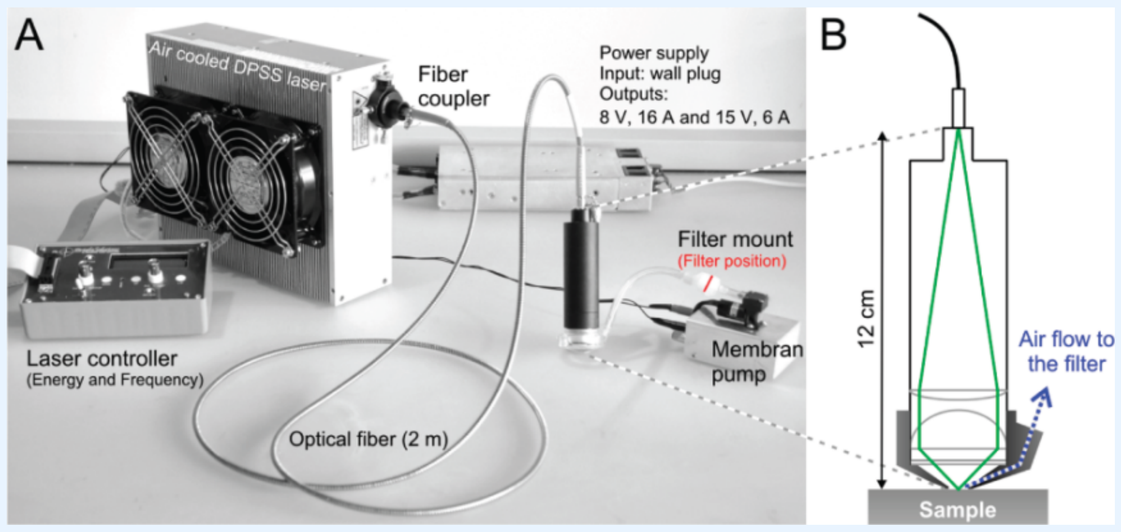

Fig.1: Assembled portable laser ablation sampling device (A) & details of the LA module (B) (system modified from Glaus et al., 2012).

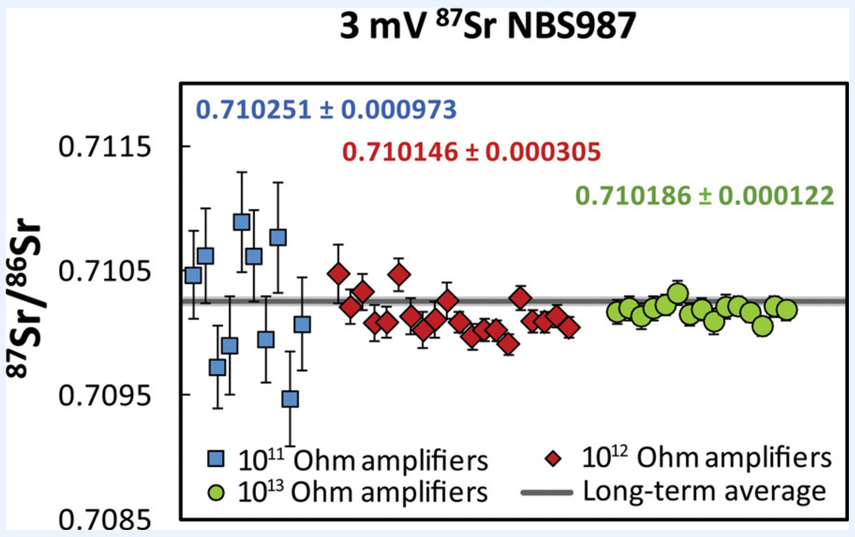

Fig.2: External reproducibility of multiple analyses of $^{87}Sr/^{86}Sr$ ratios at 3 mV ^{87}Sr beam intensity measured using 10^{11} Ohm, 10^{12} Ohm & 10^{13} Ohm amplifiers. Error bars are propagated internal precision (2 standard error) (Koornneef et al., 2014).

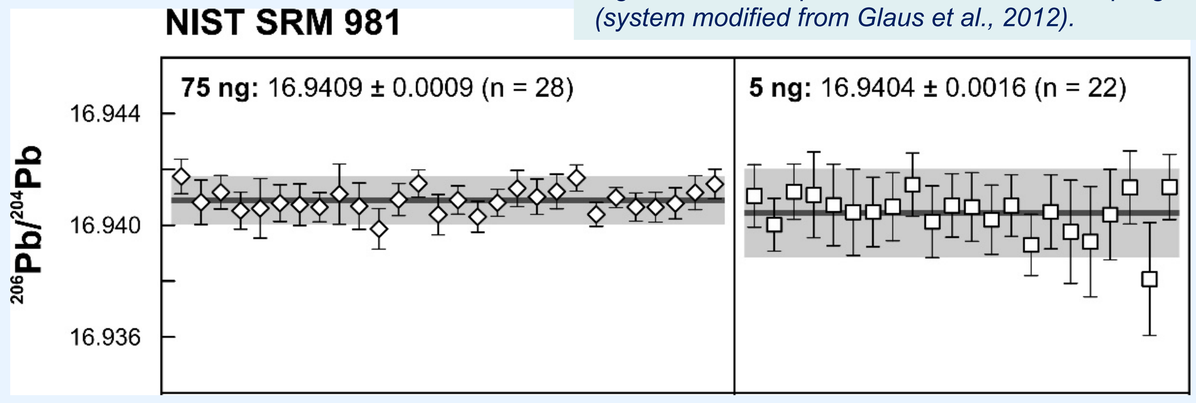

Fig.3: External reproducibility of multiple analyses of NIST standard reference material 981 for 75 ng & 5 ng aliquots. The 5 ng data were acquired using a 10^{13} Ω resistor in the Faraday cup amplifier feedback loop for the collection of ^{204}Pb. Error bars are propagated internal precision (2 standard error), shaded field indicates 2 standard deviation (2 SD) around the mean. (Klaver et al. in submission

Fig.7: Dutch jeton from 1584 showing the assassination of William of Orange.

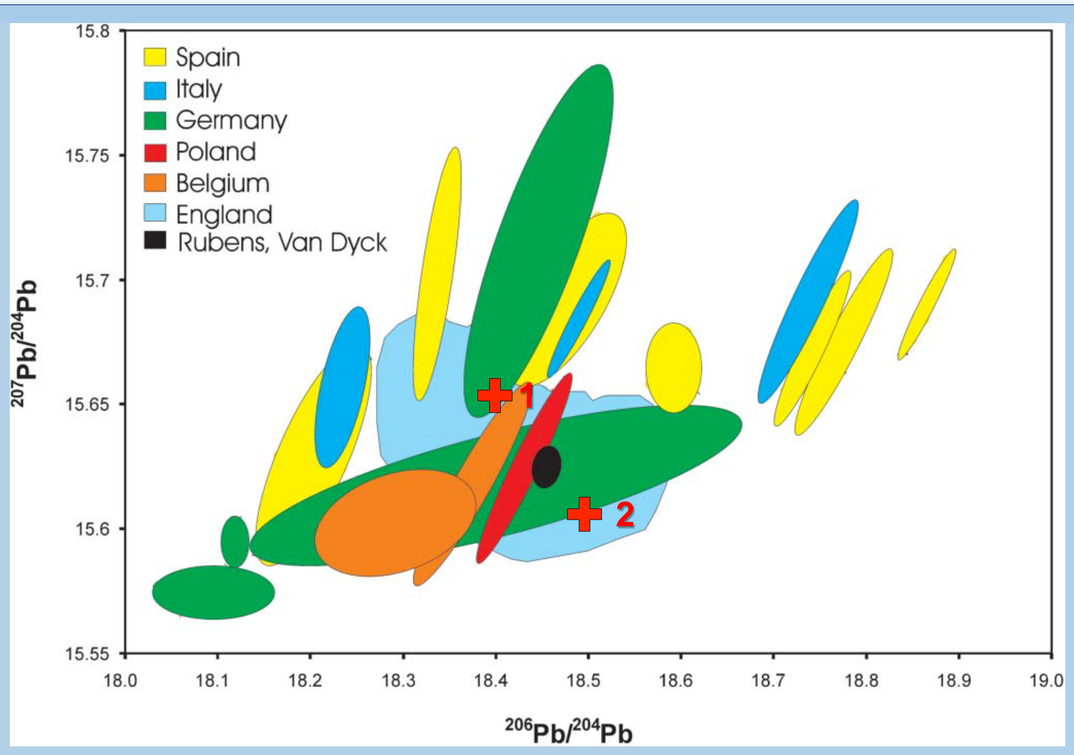

Fig.4: Lead isotope ratios for lead ores from Europe, including values from lead white pigments (Fortunato et al., 2005). Red crosses represent *Pb-white isotope data from the 2 generations of lead white from the Adoration of the Kings, Faranti ca 1592; Fig 6. 1 = older paint derived from Austro-Alps; 2 from Derbyshire UK, typical of Pb imported into the "lowlands" in the 17th to 19th century.*

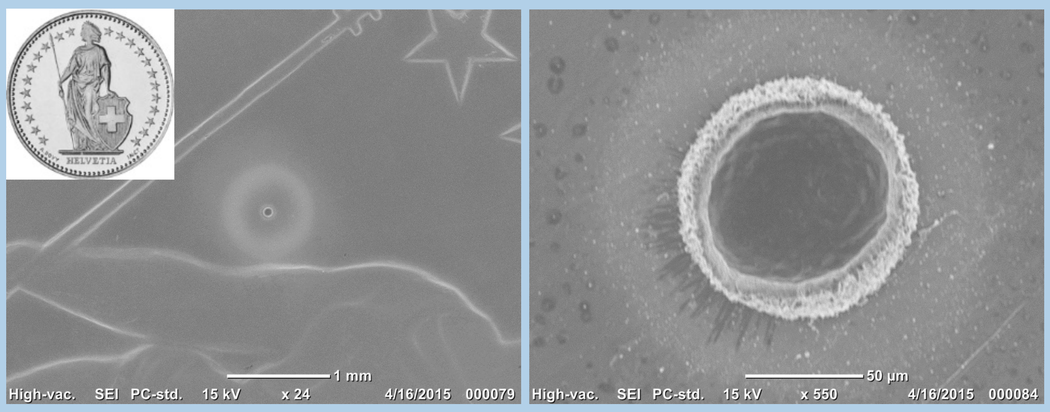

Fig.5: Microscopic images of an ablation crater on a steel surface produced using the portable laser ablation sampling device. The resulting crater diameter is 70 µm: note discolouration around the ablation pit will become invisible after gentle cleaning.

Pb isotope provenancing is used to help authenticate 15th to 19th century paintings but as shown by figure 4 from Fortunato et al. 2005, the three distinct isotopic systems of Pb are insufficiently diagnostic to distinguish the different ores produced in Europe, as most metal artefacts & paints are made of multiple raw materials. The techniques we have developed allow the analysis of multiple isotopes (Sr-Nd-Pb), greatly adding to the provenancing power of the different components; five isotope systems in total.

Fig.6: Adoration of the Kings; Faranti ~1592 (inv. SK-C-1352), bought by Willen I in 1821 from Victor de Rainer from Brussels. Oil on Canvas, 117 x 162.5 cm. White arrows indicate sampling positions.

To obtain essentially non-destructive sampling from artefacts & paintings in situ, a portable laser device has been modified from Glaus et al., 2012 (Fig.1). The laser beam results in an ablation crater of 50 - 100 µm (Fig. 5) in width & depth & a mass removal of approximately 0.5 µg for 1000 pulses. The ablated material is transported by an air flow onto a filter. Filters can be taken back to the laboratories for analyses. A miniaturised multi-isotopic technique has been set-up to measure sub-nanogram amounts of strontium (Sr), neodymium (Nd) and lead (Pb) (Fig. 2).

A key aspect of this project will be documentation of how the production & use of these different metal ores varied over time. This goal will be achieved by radically expanding the current data base of raw materials & artefacts-paints of known provenance & age of manufacture. For example the Rijksmuseum has ~1600 dated jetons (copper accounting coins), mostly from 1540-1680 (Fig 7).

Fortunato, G., Ritter, A., Fabian, D., (2005): Old Masters' lead white pigments: investigations of paintings from the 16th to the 17th century using high precision lead isotope abundance ratios. Analyst, 130, 898-906.Glaus, R., Koch., J., Günther, D., (2012): Portable Laser Ablation Sampling Device for Elemental Fingerprinting of Objects Outside the Laboratory with Laser Ablation Inductively Coupled Plasma Mass Spectrometry. Anal. Chem., 84, 5358−5364. Klaver, M., Smeets, R.J., J.M. Koorneef, Davies, G.R., Vroon, P.Z., (subm.): Pb isotope analysis of ng size samples by TIMS equipped with a 10^{13} Ω resistor using a ^{207}Pb-^{204}Pb double spike. Submitted to JAAS.Koornneef, J.M., Bouman, C., Schwieters, J.B., Davies, G.R., (2014): Measurement of small ion beams by thermal ionisation mass spectrometry using new1 0^{13} Ohm resistors. Analytica Chimica Acta, 819, 49-55.

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