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# Radiochronometry in the CMX-4 Exercise

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## The Application of Radiochronometry During the 4th Collaborative Materials Exercise of the Nuclear Forensics International Technical Working Group (ITWG)

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## Abstract

In a recent international exercise, 10 international nuclear forensics laboratories successfully performed radiochronometry on three low enriched uranium oxide samples, providing 12 analytical results using three different parent-daughter pairs serving as independent chronometers. The vast majority of the results were consistent with one another and consistent with the known processing history of the materials. In general, for these particular samples, mass spectrometry gave more accurate and more precise analytical results than decay counting measurements. In addition, the concordance of the $^{235}$U-$^{231}$Pa and $^{234}$U-$^{230}$Th chronometers confirmed the validity of the age dating assumptions, increasing confidence in the resulting conclusions.

## Keywords

nuclear forensics, radiochronometry, uranium oxide, inductively coupled plasma mass spectrometry, thermal ionization mass spectrometry, gamma spectrometry, alpha spectrometry

# Introduction

## Nuclear Forensics

Over the past decade, nuclear forensics has developed into an integral part of a robust nuclear security program. It has been specifically identified in the Communiqués, Plans, and Joint Statements of the Nuclear Security Summits in 2010, 2012, 2014, and 2016 as an important focus area for research. The fundamental tenet underlying nuclear forensics is that identifying the origin of nuclear materials found outside of regulatory control can help identify gaps and weaknesses in the physical security and/or safeguards of a particular country or facility, which can then be strengthened in response. In addition, any country or organization that considers thwarting international law or practice by trafficking in such nuclear materials might be deterred by the knowledge that their complicity in such trafficking is likely to be identified [1]. The currently accepted definition of nuclear forensics is "the examination of nuclear or other radioactive materials or of evidence contaminated with radionuclides in the context of international or national law or nuclear security. The analysis of nuclear or other radioactive material seeks to identify what the materials are, how, when, and where the materials were made, and what were their intended uses [2]. "

## Radiochronometry

At the same time that the policy implications of nuclear forensics have become increasingly mature, laboratories around the world have continued to develop the underlying science, as well as the applications of that science to actual cases. The development of radiochronometry, or "age dating," and its application to nuclear materials is one area of intense research [3-9]. Radiometric model ages are determined from measurements of parent and progeny isotopes (typically daughter, but also granddaughter) that accumulate in a material due to decay of the radioactive parent isotope. U- and Pu-series disequilibrium dating are most often used for nuclear forensic investigations. Calculated model ages are based on two fundamental assumptions: 1) the material was completely purified from decay products at the time it was produced, and 2) since the time that it was produced, the material has remained a closed system with neither gain nor loss of parent or progeny except through radioactive decay. The age of nuclear material is an important forensic signature because it can be used to constrain the time of purification or production (a predictive signature) and establish or eliminate potential genetic links among different samples of nuclear materials (a comparative signature). Ideally, the age inferred from the laboratory analysis of a sample (referred to as a “model age”) represents the actual production, processing, or purification age of the nuclear material of interest (referred to as a “sample age”). Model ages may, of course, differ from sample ages due to familiar sources of bias in the measurement process. However, model ages may also differ from sample ages because the sample production history is inconsistent with the model assumptions on which the chronometry determinations are based. Understanding the physical and chemical causes of these inconsistencies and developing experimental and theoretical approaches to address them is an active focus area of nuclear forensics research. Increasing emphasis is being placed on using multiple chronometers to better understand the chemical or physical processes that might “reset” certain chronometers.

## The 4th Collaborative Materials Exercise (CMX-4)

The 4th Collaborative Material Exercise (CMX-4), conducted by the Exercise Task Group of the Nuclear Forensics International Technical Working Group (ITWG) [10-11], was designed to test the resolving power of isotope measurement techniques using low-enriched uranium (LEU) samples of very similar isotopic abundances [12]. However, based upon the outcomes of previous ITWG exercises, information provided by material characteristics other than isotopic abundances, including radiochronometic age, were identified to be of growing interest to the nuclear forensics community. In keeping with ITWG practice, the identity of individual laboratories is obscured through the use of designators or code names. For this exercise, the laboratories were given the name of a famous artist.

## Experimental

## Sample Materials

Three exercise samples (designated as ES-1, ES-2, and ES-3) were generated from two sources of materials and distributed to each laboratory participating in CMX-4. Details regarding the history and preparation of these samples are provided in the introduction to this special section of the Journal [12].

## Radiochronometers

### *$^{234}U$-$^{230}Th$ Chronometer*

Because the half-life of $^{234}$U is relatively short ($2.45\times10^{5}$ years) compared to the other naturally occurring uranium isotopes, $^{235}$U and $^{238}$U, the $^{234}$U-$^{230}$Th chronometer is one of the most straightforward chronometers to measure, and certainly the most widely applied [3, 5, 6, 8, 13]. The chronometer becomes increasingly easy to measure as the $^{234}$U abundance, and hence the amount of its progeny, $^{230}$Th, increases. Because the $^{234}$U abundance tends to increase with $^{235}$U enrichment for most enrichment technologies, its ease of application increases with increasing enrichment of the sample. Since the samples for CMX-4 were LEU, measuring the $^{234}$U-$^{230}$Th chronometer should have been relatively straightforward,—certainly easier than in natural uranium samples—although not as easy as with highly enriched uranium (HEU) samples.

The two most commonly applied techniques for quantifying the level of $^{234}$U and $^{230}$Th in uranium samples are mass spectrometry and alpha spectrometry. Due to the relatively long half-lives of $^{234}$U and $^{230}$Th, mass spectrometry, as an atom counting technique, normally provides lower detection limits and greater precision than alpha spectrometry, which is a decay counting technique. However, an alpha spectrometer is a relatively inexpensive instrument that can be found in many laboratories that do not have the necessary mass spectrometer. Note that both thermal ionization mass spectrometers (TIMS) and inductively coupled plasma mass spectrometers (ICP-MS), which may be equipped with either a single or multiple collector(s), can be used for age dating. The utilization of these techniques and instruments for age dating in CMX-4 are given in Table 1.

**Table 1** List of Instruments Used for Age Dating in CMX-4

| Technique/Instrument | Th Analysis | U Analysis |
|---|---|---|
| Alpha spectrometry | 3 | 2 |
| Multicollector ICP-MS | 2 | 2 |
| Sector field ICP-MS | 3 | 2 |
| Quadrupole ICP-MS | 1 | 1 |
| Multicollector TIMS | 2 | 4 |

Regardless of technique, isotope dilution is typically used for quantification. With this method, quantification is achieved by measuring the isotope of interest (e.g., $^{234}$U) relative to a spike or tracer isotope (e.g., $^{233}$U). However, in CMX-4, two laboratories used unspiked isotopic analysis in combination with other assay techniques, delayed neutron counting (Cezanne) and external calibration using NIST SRM 4321C (Manet), to calculate the $^{234}$U concentration necessary for age dating. For those laboratories that used isotope dilution for U quantification, seven laboratories used $^{233}$U spikes, one laboratory used a $^{232}$U spike, and another used the NBL U930 standard as $^{235}$U spike. For Th quantification, eight laboratories used $^{229}$Th, while the remaining three laboratories used $^{232}$Th, as isotopic spikes for Th quantification.

All three laboratories that performed alpha spectrometry used chemical separation of the Th from the U, followed by fluoride microprecipitation to create plates for alpha counting. Both TIMS and ICP-MS also typically require chemical separation of Th from the U matrix prior to analysis. This is necessary to improve ionization efficiency (TIMS) and reduce matrix effects, low-mass tailing effects, and memory effects that may result from loading the instrument with high concentrations of U (ICP-MS). However, one of the laboratories used a procedure published by Varga et al. [13], which offers an offline correction for the peak tailing effect and provides accurate Th results using ICP-MS. Purification of a bulk U sample prior to U analysis by TIMS or ICP-MS may not be necessary, depending on the purity of the sample. If the bulk sample is sufficiently pure, then molecular isobaric interferences in the U mass range, for example, $^{232}$ThH$^{+}$, will be insignificant. In addition, tailing to nearby masses and hydride formation usually occur in the range of $10^{-5}$ – $10^{-6}$ [14], there will not be a need for correction due to tailing or hydride formation from $^{232}$Th on m/z=233.

For this exercise, all laboratories separated and purified the Th fraction prior to analysis by alpha spectrometry or mass spectrometry. However, only three laboratories purified the U fraction (two from the bulk solution; one from the U fraction after separation from Th prior to analysis by alpha spectrometry). Seven laboratories used a TEVA column to separate the U and Th; three laboratories performed a subsequent purification using another TEVA column.  three laboratories used a multi-step purification starting with an anion exchange column. Cezanne used an anion exchange column followed by a TRU-Spec column, and finished with a cation exchange column. Gauguin used an anion exchange column, followed by a TEVA column, and finished with another anion exchange column. Bondone used back-to-back anion-exchange columns, the first of 120-µm particle size and the second of 25-µm particle size. Monet used a separation procedure based upon a macroporous Lewatit MP5080 ion-exchange resin. All procedures used by the different participants for the $^{234}$U-$^{230}$Th chronometer can be found in Table 2.

**Table 2** Analytical Procedures Used by Each Participant

| Participant | Analyte | Instrument | Purification prior to measurement | Separation | Spikes added | Reference if applicable |
|---|---|---|---|---|---|---|
| Rembrandt | $^{230}$Th | α spectrometry | Yes | TEVA® resin cartridge | $^{229}$Th | |
| | $^{234}$U | α spectrometry | Yes | Fe(OH)$_2$ precipitation; stacked TEVA®/TRU resin cartridges | $^{232}$U | |
| Cezanne | $^{230}$Th | α spectrometry | Yes | anion exchange resin column; TRU resin column | $^{229}$Th | |
| | $^{234}$U | α spectrometry | Yes | TRU resin column; cation exchange resin column | N/A | |
| Pollock | $^{230}$Th | α spectrometry | Yes | TEVA® resin cartridge | $^{229}$Th | |
| | $^{234}$U | MC-TIMS | No | | NBS930 ($^{235}$U) | |
| Picasso | $^{230}$Th | SF-ICP-MS | Yes | TEVA® resin column | $^{229}$Th | 13 |
| | $^{234}$U | SF-ICP-MS | No | | $^{233}$U | 13 |
| Vermeer | $^{230}$Th | SF-ICP-MS | Yes | TEVA® resin column (two times) | $^{229}$Th | 13 |
| | $^{234}$U | SF-ICP-MS | No | | $^{233}$U | 13 |
| Bounarotti | $^{230}$Th | SF-ICP-MS | Yes | TEVA® resin column | $^{232}$Th | 13 |
| | $^{234}$U | MC-TIMS | No | | $^{233}$U | 13 |
| Monet | $^{230}$Th | MC-TIMS | Yes | anion exchange resin column | $^{229}$Th | |
| | $^{234}$U | MC-TIMS | Yes | anion exchange resin column | $^{233}$U | |
| Gauguin | $^{230}$Th | MC-ICP-MS | Yes | anion exchange resin column; TEVA® resin column; anion exchange resin column | $^{229}$Th | 6 |
| | $^{234}$U | MC-ICP-MS | No | | $^{233}$U | 6 |
| Caravaggio | $^{230}$Th | MC-ICPMS | Yes | TEVA® resin column | $^{232}$Th | |
| | $^{234}$U | MC-ICPMS | No | | $^{233}$U | |
| Bondone | $^{230}$Th | MC-TIMS | Yes | anion exchange resin column (two times) | $^{229}$Th | |
| | $^{234}$U | MC-TIMS | No | | $^{233}$U | |
| Manet | $^{230}$Th | Q-ICP-MS | Yes | TEVA® resin column | $^{232}$Th | |
| | $^{234}$U | Q-ICP-MS | No | | N/A | |

TEVA® and TRU resins are products of Eichrom® Technologies

### *$^{235}$U-$^{231}$Pa Chronometer*

Even though $^{235}$U is much more abundant than $^{234}$U in almost all uranium materials, the much longer half-life of $^{235}$U (7.04×10$^{8}$ years) and the absence of a long-lived spike isotope for Pa has limited routine application of this chronometer until relatively recently. Although radiometric techniques (gamma spectrometry, alpha spectrometry) have been used to quantify $^{231}$Pa for age dating in the past [15], the only participant in CMX-4 to apply the $^{235}$U-$^{231}$Pa chronometer (Gauguin) used mass spectrometry, according to the procedure developed by Eppich et al. [4]. The key feature of the method is the use of a $^{233}$Pa spike for quantifying $^{231}$Pa. Due to the short half-life of $^{233}$Pa (26.97 days), no certified $^{233}$Pa reference material exists; neither does a certified $^{231}$Pa reference material that may be used for a newly prepared $^{233}$Pa spike. Rather, the spike must be prepared immediately prior to use and calibrated for $^{233}$Pa concentration (atoms of $^{233}$Pa g$^{-1}$), typically using a geologic material as a secular equilibrium standard, for its working-lifetime of approximately 3 – 4 months.

### *$^{234}$U-$^{214}$Bi Chronometer*

Age dating U samples using high-resolution gamma spectrometry (HRGS) [16-20] has the advantage of being nondestructive, hence no sample preparation is required. Analogous to the $^{234}$U-$^{230}$Th chronometer the progenies of $^{234}$U are used, however nuclides detectable by gamma-spectrometry must be chosen. For practical reasons $^{214}$Bi-$^{234}$U ratio is used based on the secular equilibrium between $^{214}$Bi ↔ $^{226}$Ra. The method does not require the use of reference materials of known ages. It is most suitable for measuring U samples of higher enrichments and older ages (higher $^{214}$Bi levels).

## Results and discussion

The age dating results for CMX-4 are presented in Table 3 and Fig. 1 (Sample ES-1), Table 4 and Fig. 2 (Sample ES-2), and Table 5 and Fig. 3 (Sample ES-3). All uncertainties are expanded combined standard uncertainties with k=2. For ES-1 and ES-3, the material processing date is encompassed by a one-year range (2004), delineated by dashed red lines on the figures, during which the samples were reported to have been manufactured. For ES-2, the material processing date is encompassed by a range extending from the known enrichment date (February 12, 2002) to the known manufacturing date (September 24, 2002), which is the pelletization process. We expect the actual sample material processing date to be the date of conversion from enriched $UF_6$ to $UO_2$, since neither Th nor Pa form volatile fluorides and would, therefore, be expected to deposit out and remain in the cylinder during $UF_6$ release. The conversion date for these samples is unknown, but must have occurred sometime between enrichment and manufacturing of the fuel pellets. For the $^{234}\text{U}$-$^{214}\text{Bi}$ chronometer, an upper limit of $\approx 11$ years was estimated uniformly for the three samples from the $^{214}\text{Bi}$ activity corresponding to the detection limit, because of the low enrichment and age of the samples.

**Table 3** Age dating results for ES-1

| **Designator** | **Chronometer** | **Technique** | **Instrument** | **Ref Date** | **Model Age (years)** | **EU (years)** | **Model Date** | **EU (days)** |
|---|---|---|---|---|---|---|---|---|
| Picasso | $^{234}\text{U}\rightarrow{}^{214}\text{Bi}$ | Gamma Spec | well-type HPGe Model Canberra GCW6023<br>planar HPGe Model Canberra GL2020R | | <11 | N/A | NLT 1/1/2004 | N/A |
| Rembrandt | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | Alpha Spec | Canberra Alpha Analyst | 16-Dec-14 | 12.0 | 2.7 | 28-Dec-02 | 1000 |
| Cezanne | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | Alpha Spec | Canberra Alpha Apex | Mar-15 | 7.3 | 2.1 | Jan-08 | 780 |
| Pollock | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | Alpha Spec (Th)<br>MC-TIMS (U) | Ortec SOLOIST & spectrometer (AMETEK)<br>MAT 262 TIMS (Finnigan) | 15-Oct-14 | 7.62 | 0.50 | 6-Mar-07 | 180 |
| Picasso | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | SF-ICP-MS | Element 2(Thermo) | 25-Mar-15 | 10.90 | 0.86 | 24-Mar-04 | 310 |
| Vermeer | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | SF-ICP-MS | Element XR<br>(Thermo Fisher Scientific) | 6-Oct-14 | 10.19 | 0.37 | 30-Jul-04 | 140 |
| Buonarotti | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | SF-ICP-MS (Th)<br>MC-TIMS (U) | Element 2<br>(Thermo Finnigan) | 3-Nov-14 | 10.20 | 0.20 | Aug-04 | 73 |
| Monet | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | MC-TIMS | VG Sector 54 TIMS<br>GV instruments Isoprobe T TIMS | 1-Nov-14 | 10.23 | 0.46 | 10-Aug-04 | 170 |
| Gauguin | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | MC-ICP-MS | Nu Instruments NuPlasma HR | 23-Oct-14 | 10.356 | 0.075 | 14-Jun-04 | 27 |
| Gauguin | $^{235}\text{U}\rightarrow{}^{231}\text{Pa}$ | MC-ICP-MS | Nu Instruments NuPlasma HR | 23-Oct-14 | 10.14 | 0.25 | 30-Aug-04 | 92 |
| Caravaggio | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | MC-ICP-MS | Neptune Plus<br>(Thermo Fisher Scientific) | 13-Nov-14 | 9.80 | 0.40 | 4-Feb-05 | 150 |
| Bondone | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | MC-TIMS | Triton Plus<br>(Thermo Fisher Scientific) | 2-Dec-14 | 9.90 | 0.21 | 9-Jan-05 | 78 |
| Manet | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | Q-ICP-MS | Perkin-Elmer Elan DRC II | 25-Nov-14 | 11.00 | 0.90 | 25-Nov-03 | 330 |

EU = expanded uncertainty (k=2); NLT = not later than

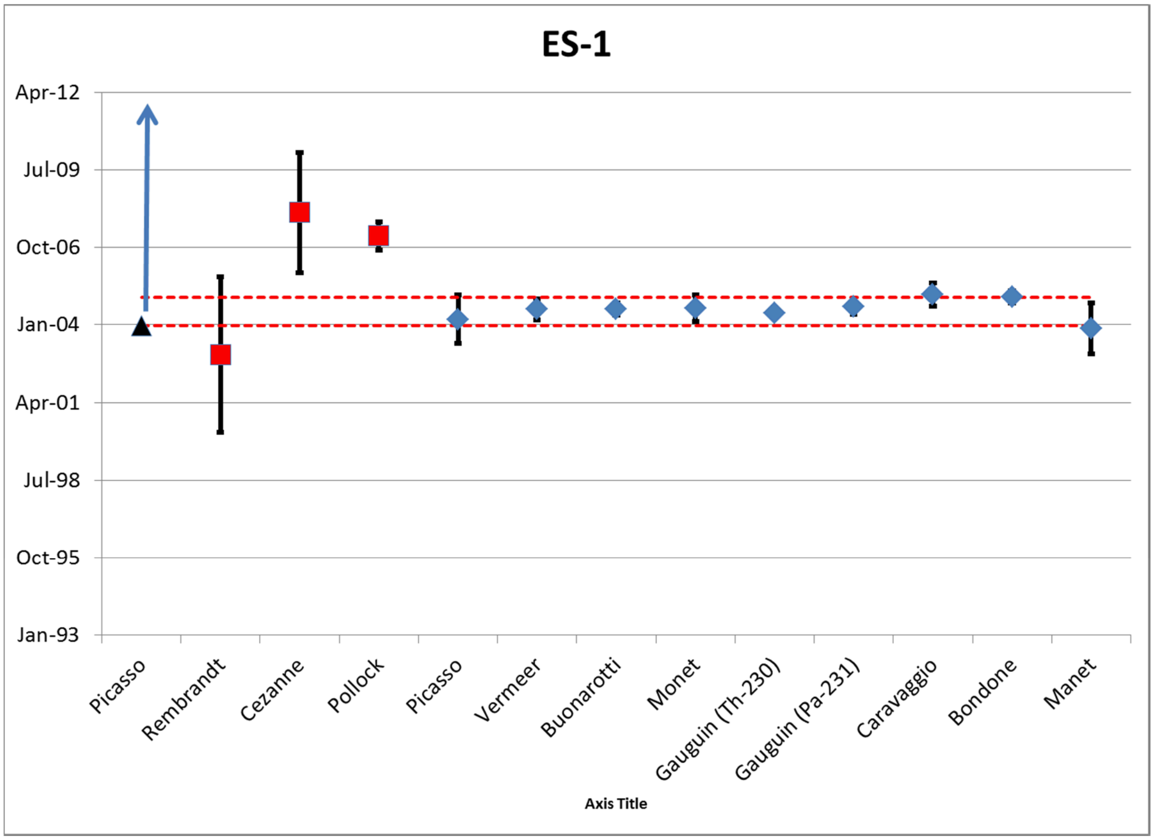

**Fig 1** Age dating results for ES-1 compared against known sample processing history. The dashed red lines (----) indicate the range of probable processing dates according to the known history of the samples (see text). Results using gamma spectrometry are indicated by black triangles (▲); a blue arrow indicates a method detection limit and extends from the age determined from the detection limit to younger ages. Alpha spectrometry results are indicated by red squares (■). Mass spectrometry results are indicated by blue diamonds (♦).

**Table 4** Age Dating Results for ES-2

| Designator | Chronometer | Technique | Instrument | Ref Date | Model Age (years) | EU (years) | Model Date | EU (days) |
|---|---|---|---|---|---|---|---|---|
| Picasso | $^{234}\text{U}\rightarrow{}^{214}\text{Bi}$ | Gamma Spec | well-type HPGe Model Canberra GCW6023<br>planar HPGe Model Canberra GL2020R |  | <11 | N/A | NLT 1/1/2004 | N/A |
| Rembrandt | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | Alpha Spec | Canberra Alpha Analyst | 16-Dec-14 | 14.5 | 0.52 | 10-Jun-00 | 190 |
| Cezanne | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | Alpha Spec | Canberra Alpha Apex | Mar-15 | 5.5 | 2.2 | Sep-09 | 820 |
| Pollock | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | Alpha Spec (Th)<br>MC-TIMS (U) | Ortec SOLOIST & spectrometer (AMETEK)<br>MAT 262 TIMS (Finnigan) | 15-Oct-14 | 10.65 | 0.50 | 24-Feb-04 | 180 |
| Picasso | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | SF-ICP-MS | Element 2(Thermo) | 25-Mar-15 | 11.00 | 0.71 | 23-Sep-01 | 260 |
| Vermeer | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | SF-ICP-MS | Element XR (Thermo Fisher Scientific) | 7-Oct-14 | 11.22 | 0.79 | 21-Jul-03 | 290 |
| Buonarotti | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | SF-ICP-MS (Th)<br>MC-TIMS (U) | Element 2 (Thermo Finnigan) | 3-Nov-14 | 12.51 | 0.30 | Apr-02 | 110 |
| Monet | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | MC-TIMS | VG Sector 54 TIMS<br>GV instruments Isoprobe T TIMS | 1-Nov-14 | 12.53 | 0.53 | 23-Apr-02 | 190 |
| Gauguin | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | MC-ICP-MS | Nu Instruments NuPlasma HR | 23-Oct-14 | 12.677 | 0.092 | 17-Feb-02 | 34 |
| Gauguin | $^{235}\text{U}\rightarrow{}^{231}\text{Pa}$ | MC-ICP-MS | Nu Instruments NuPlasma HR | 23-Oct-14 | 12.50 | 0.31 | 22-Apr-02 | 110 |
| Caravaggio | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | MC-ICP-MS | Neptune Plus (Thermo Fisher Scientific) | 13-Nov-14 | 11.90 | 0.20 | 5-Jan-03 | 73 |
| Bondone | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | MC-TIMS | Triton Plus (Thermo Fisher Scientific) | 2-Dec-14 | 12.10 | 0.19 | 29-Oct-02 | 69 |
| Manet | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | Q-ICP-MS | Perkin-Elmer Elan DRC II | 24-Nov-14 | 12.10 | 0.60 | 18-Oct-02 | 220 |

EU = expanded uncertainty (k=2); NLT = not later than

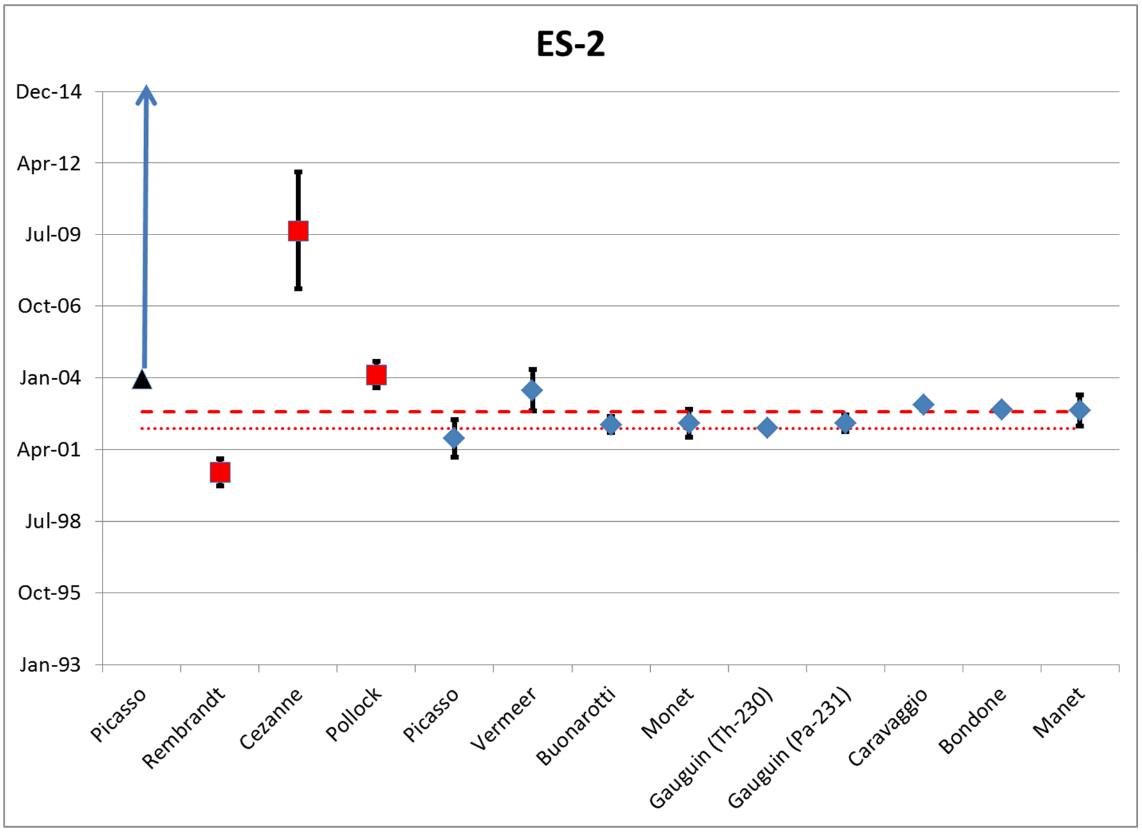

**Fig 2** Age dating results for ES-2 compared against known sample processing history. The dashed red line (----) indicates the pellet production date; the dotted red line (•••) indicates the uranium enrichment date. Results using gamma spectrometry are indicated by black triangles (▲); a blue arrow indicates a method detection limit and extends from the age determined from the detection limit to younger ages. Alpha spectrometry results are indicated by red squares (■). Mass spectrometry results are indicated by blue diamonds (♦).

**Table 5** Age dating results for ES-3

| Designator | Chronometer | Technique | Instrument | Ref Date | Model Age (years) | EU (years) | Model Date | EU (days) |
|---|---|---|---|---|---|---|---|---|
| Picasso | $^{234}\text{U}\rightarrow{}^{214}\text{Bi}$ | Gamma Spec | well-type HPGe Model Canberra GCW6023<br>planar HPGe Model Canberra GL2020R | | <11 | N/A | NLT 1/1/2004 | N/A |
| Rembrandt | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | Alpha Spec | Canberra Alpha Analyst | 16-Dec-14 | 12.20 | 0.64 | 19-Sep-02 | 230 |
| Cezanne | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | Alpha Spec | Canberra Alpha Apex | Mar-15 | 11.5 | 3.6 | Sep-03 | 1300 |
| Pollock | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | Alpha Spec (Th)<br>MC-TIMS (U) | Ortec SOLOIST & spectrometer (AMETEK)<br>MAT 262 TIMS (Finnigan) | 15-Oct-14 | 7.25 | 0.50 | 16-Jul-07 | 180 |
| Picasso | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | SF-ICP-MS | Element 2(Thermo) | 25-Mar-15 | 13.5 | 0.61 | 29-Apr-04 | 220 |
| Vermeer | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | SF-ICP-MS | Element XR<br>(Thermo Fisher Scientific) | 15-Oct-14 | 9.94 | 0.65 | 7-Nov-04 | 240 |
| Buonarotti | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | SF-ICP-MS (Th)<br>MC-TIMS (U) | Element 2<br>(Thermo Finnigan) | 3-Nov-14 | 10.22 | 0.18 | Aug-04 | 66 |
| Monet | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | MC-TIMS | VG Sector 54 TIMS<br>GV instruments Isoprobe T TIMS | 1-Nov-14 | 10.19 | 0.46 | 23-Aug-04 | 170 |
| Gauguin | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | MC-ICP-MS | Nu Instruments NuPlasma HR | 23-Oct-14 | 10.380 | 0.076 | 5-Jun-04 | 28 |
| Gauguin | $^{235}\text{U}\rightarrow{}^{231}\text{Pa}$ | MC-ICP-MS | Nu Instruments NuPlasma HR | 23-Oct-14 | 10.22 | 0.25 | 5-Aug-04 | 93 |
| Caravaggio | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | MC-ICP-MS | Neptune Plus<br>(Thermo Fisher Scientific) | 13-Nov-14 | 9.80 | 0.20 | 8-Feb-05 | 73 |
| Bondone | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | MC-TIMS | Triton Plus<br>(Thermo Fisher Scientific) | 2-Dec-14 | 9.72 | 0.51 | 16-Mar-05 | 190 |
| Manet | $^{234}\text{U}\rightarrow{}^{230}\text{Th}$ | Q-ICP-MS | Perkin-Elmer Elan DRC II | 25-Nov-14 | 10.80 | 0.60 | 6-Feb-04 | 220 |

EU = expanded uncertainty (k=2) ; NLT = not later than

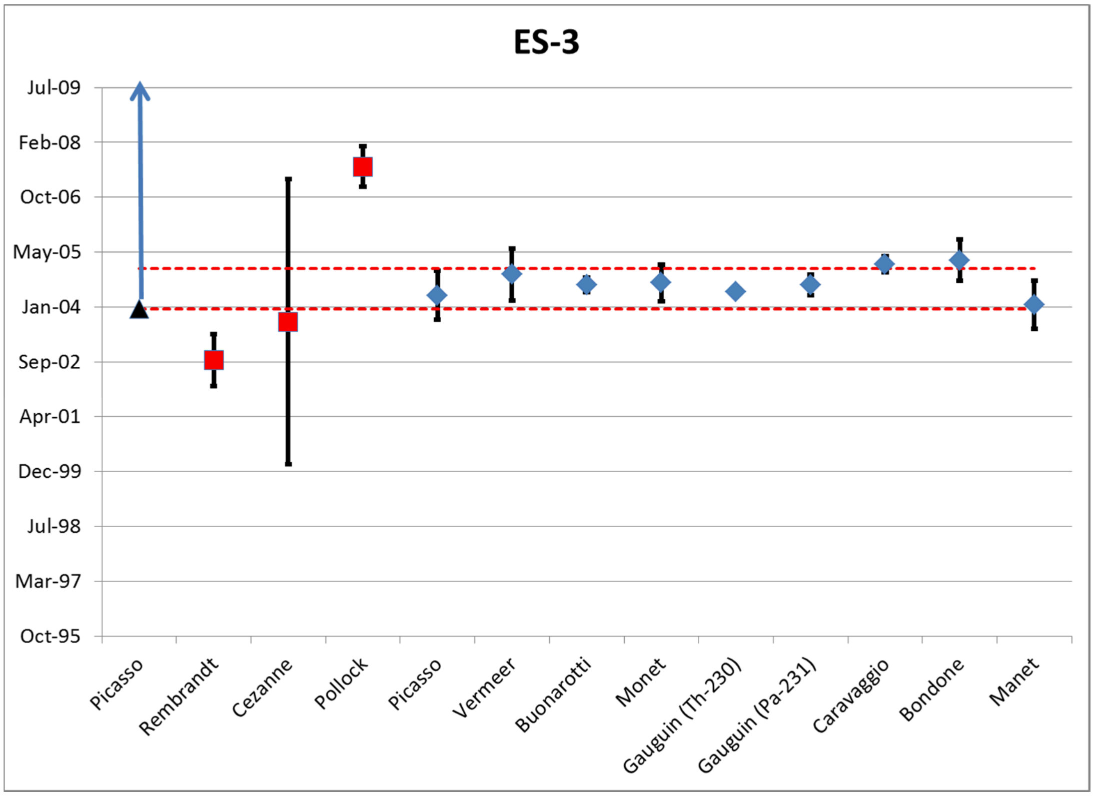

**Fig 3** Age dating results for ES-3 compared against known sample processing history. The dashed red lines (----) indicate the range of probable processing dates according to the known history of the samples (see text). Results using gamma spectrometry are indicated by black triangles (▲); a blue arrow indicates a method detection limit and extends from the age determined from the detection limit to younger ages. Alpha spectrometry results are indicated by red squares (■). Mass spectrometry results are indicated by blue diamonds (♦).

## Interpretation of Results

Upon reviewing the results, the first conclusion is that most of the laboratories measured ages consistent with one another and consistent with the known history of the material. For ES-1 and ES-3, only two of 12 results did not overlap the known history of the material within their stated analytical uncertainty. For ES-2, only three of 12 results did not overlap the known history of the material within their stated analytical uncertainty.

The second conclusion is that these age-dating results were useful in comparing the three samples (ES-1, ES-2, and ES-3) with one another, one of the key points of the exercise. When combined with other signatures, including the similarity of the U isotopic composition between ES-1 and ES-3, these age-dating results supported the conclusion that ES-1 and ES-3 might have had a similar processing history. Again, when combined with other signatures, these age-dating results also supported the conclusion that ES-2 was a different material from ES-1 and ES-3, sharing neither isotopic similarity nor processing history.

The third conclusion is that mass spectrometric methods of measuring these chronometers provided more accurate and precise results than counting methods offered for these samples. Picasso reported that the level of enrichment in these samples was too low to measure more than an upper limit on the age using gamma spectrometry and the $^{214}$Bi-$^{234}$U chronometer. In addition, those laboratories that used alpha spectrometry to perform chronometry provided results that tended to be either less accurate or less precise than results provided by laboratories that used mass spectrometry. In particular, for ES-2, none of the alpha spectrometry results agree with the stated sample history or with one another. Following the conclusion of the exercise, Rembrandt (who conducted only a single U/Th column separation to generate their Th alpha sources) further purified their Th alpha sources. The repurified sources yielded comparable ages to mass spectrometry. This finding clearly demonstrates the need for multiple U/Th separation steps to adequately remove $^{234}$U from the $^{230}$Th spectral region.

The final conclusion, drawn from Gauguin's results, is that the consistency of the $^{234}$U-$^{230}$Th and $^{235}$U-$^{231}$Pa results validated the age-dating assumption, namely that there was a real purification event that removed Th and Pa from the U quantitatively. It is highly unlikely that there would be a process that would partially purify both Th and Pa, but in a proportion that retained the concordancy of the two chronometers. This is a different conclusion than that of ITWG round robin #3, in which, due to the complex production history of the HEU metal samples, these two chronometers differed remarkably from one another (7, 21, 22). Knowing the true material processing date (assumed to be the conversion date) would be helpful in a real investigation in identifying potential material sources and excluding others.

## Conclusions

In the CMX-4 exercise, 10 international nuclear forensics laboratories successfully performed radiochronometry on the three CMX-4 samples (ES-1, ES-2, and ES-3), providing 12 analytical results using three different parent-daughter pairs serving as independent chronometers ($^{234}$U-$^{230}$Th, $^{235}$U-$^{231}$Pa, $^{234}$U-$^{214}$Bi). The vast majority of the results were consistent with one another and consistent with the known processing history of the materials. In general, for these particular samples, mass spectrometry gave more accurate and more precise analytical results than decay counting measurements. In addition, the concordancy of the $^{235}$U-$^{231}$Pa chronometer with the $^{234}$U-$^{230}$Th confirmed the validity of the age dating assumption, increasing confidence in the nuclear forensic conclusions, and in the model age in particular. When combined with other analytical results, age dating helped confirm a relationship between ES-1 and ES-3 and a lack of relationship between ES-2 and ES-1 and ES-3

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