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# Application of Lead and Strontium Isotope Ratio Measurements for the Origin Assessment of Uranium Ore Concentrates

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Lead and strontium isotope ratios were used for the origin assessment of uranium ore concentrates (yellow cakes) for nuclear forensic purposes. A simple and low-background sample preparation method was developed for the simultaneous separation of the analytes followed by the measurement of the isotope ratios by multicollector inductively coupled plasma mass spectrometry (MC-ICPMS). The lead isotopic composition of the ore concentrates suggests applicability for the verification of the source of the nuclear material and by the use of the radiogenic  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio the age of the raw ore material can be calculated. However, during data interpretation, the relatively high variation of the lead isotopic composition within the mine site and the generally high contribution of natural lead as technological contamination have to be carefully taken into account. The  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratio is less prone to the variation within one mine site and less affected by the production process, thus it was found to be a more purposeful indicator for the origin assessment and source verification than the lead. The lead and strontium isotope ratios measured and the methodology developed provide information on the initial raw uranium ore used, and thus they can be used for source attribution of the uranium ore concentrates.

Illicit trafficking of radioactive material and especially nuclear material (thorium, uranium, and plutonium) poses a serious threat to the international community. The inappropriate handling, transport, or storage of these materials can lead to considerable hazard, not only due to their radiotoxicity but also as a result of possible diversion and proliferation. Since the beginning of the 1990s, when the first seizures of nuclear material were reported, the International Atomic Energy Agency (IAEA) has recorded over 200 incidents of illicit trafficking of nuclear materials, mostly involving low-enriched, natural, and depleted uranium.<sup>1</sup> As it is of high importance to obtain information on the origin and intended use of these materials for prosecution and for the

reinforcement of preventive measures, a new scientific discipline, nuclear forensics, has evolved.<sup>2–4</sup>

Uranium ore concentrate (UOC), commonly known as yellow cake, is a generic term which refers to the intermediate product of the front-end of the uranium nuclear fuel cycle. This intermediate product is produced by various metallurgical methods from uranium ores or recovered as a byproduct of other products, such as copper (e.g., at Olympic Dam mine, Australia) or phosphoric acid (e.g., Earth Sciences Extraction Company, Calgary, Canada). The physical and chemical composition of uranium ore concentrates (typically uranium oxide, ammonium diuranate, or uranyl peroxide), as well as the impurity content, are highly variable depending on the raw materials used for production, the milling process, and the production stage.<sup>5</sup> Thus, by means of such parameters, the source and production route of a declared material can be verified or the origin of an unknown nuclear sample can be identified. Several characteristics have been evaluated for their applicability for source attribution of uranium ore concentrates, such as elemental impurities and uranium and lead isotopic composition.<sup>6–8</sup> The general impurity vector of the sample bears valuable information on the chemical composition of the initial raw material, the production and purification method (e.g., leaching of uranium from the ore, ion exchange, or solvent extraction used for concentration and purification), as well as on reagents used throughout the process, which can be either added deliberately (e.g., oxidants used for leaching) or through contamination. This complex data set of elemental impurities, which correlates with the history of the material, can then be applied to compare samples by statistical tools in order to trace back to their origin. However, because of the high variability of the ore chemical composition within the mines, the various possible production schemes (where details are sometimes not described in the open literature) and the high risk of technological contamination during the milling process, the correct interpretation of the data is very

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difficult. The high variability of the trace element impurity pattern can lead to ambiguity on the origin assessment, which becomes more serious if the number of the ore sources and production schemes increase.<sup>6,9</sup> Using the elemental data to compare samples was found to be more applicable, i.e., verification that the sample derives from the same facility and production step by comparison with known samples and as a supplement to other measured parameters to support the source attribution.<sup>6,7</sup>

During the production of uranium ore concentrates, isotopic fractionation for the heavy elements is expected to be negligible so the use of isotope ratios for source attribution is an obvious possibility, provided one can identify isotope ratios that are characteristic of the starting raw material. For instance, Svedkauskaitė et al. found a large variation of lead isotopic compositions in uranium ore and yellow cake samples of different origin.<sup>7,9</sup> As the isotopes of radiogenic lead (<sup>206</sup>Pb, <sup>207</sup>Pb, and <sup>208</sup>Pb) derive from the decay of the parent uranium and thorium radionuclides, their relative amount depends on age and the history of the ore deposit (e.g., fractionation of U and Pb within the ore deposit due to weathering). Another advantage of using Pb isotope ratios is that since uranium is present at elevated levels in uranium ores compared to the average values of the Earth's crust, the lead isotopic composition is significantly different from the natural lead variation (representative natural isotopic composition:  $1.4 \pm 0.1\%$  <sup>204</sup>Pb,  $24.1 \pm 0.1\%$  <sup>206</sup>Pb,  $22.1 \pm 0.1\%$  <sup>207</sup>Pb, and  $52.4 \pm 0.1\%$  <sup>208</sup>Pb).<sup>10</sup> However, high variations in the lead isotopic composition (up to 50% relative standard deviation in the case of the <sup>207</sup>Pb/<sup>206</sup>Pb ratio and up to a factor of 4 in the case of <sup>208</sup>Pb/<sup>206</sup>Pb) were also observed in ore and yellow cake samples originating from the same mine.<sup>7,9</sup> This is probably a result of the fact that natural U–Pb systems within the ore bodies rarely behave as closed systems after formation (i.e., they have either gained or lost Pb or U) due to weathering and chemical fractionation. This effect is highly disadvantageous for nuclear forensics, as it can lead to higher variability of the investigated indicator and causes possible overlaps between the samples. Another drawback of using lead isotope ratios as nuclear fingerprints is that radiogenic lead content of the ore is continually separated from the uranium during the chemical purification steps and gradually substituted and diluted with natural lead introduced into the material as the contaminant of the reagents. Therefore, the lead isotopic composition of the uranium ore concentrate can differ significantly from that of the initial uranium ore depending on the degree of processing, which prevents matching the measured values of the ore concentrate to the initial ore. Correction for the natural lead content can overcome this problem, although if the material is highly purified and the natural lead content is high, the high correction increases the uncertainty in the final, calculated value and can even give rise to erroneous results (e.g., too high or low ratios or even negative isotope ratios) if natural lead is present in excess amounts compared to the radiogenic lead component.<sup>7,9</sup>

Besides lead isotope ratios, other isotopics such as uranium,<sup>8,11</sup> oxygen, nitrogen, and carbon<sup>2,12</sup> have already been investigated

as a possible fingerprint for source attribution of uranium ore concentrates. Natural variation in the <sup>234</sup>U/<sup>238</sup>U isotope ratio, which is the consequence of preferential leaching of <sup>234</sup>U from the mineral crystal following  $\alpha$  decay, can be effectively used to discriminate some ore concentrates.<sup>8,11,12</sup> However, the range of natural variation in the <sup>234</sup>U/<sup>238</sup>U isotope ratio is small (for instance, in the case of Australian ore concentrates, less than 1% relative standard deviation<sup>11</sup>), which requires highly precise measurement and leads to overlaps when comparing high numbers of samples. Stable isotope analysis of nitrogen and carbon provide essential information about the production method (e.g., organic acid and ammonia used for uranium concentration and separation), but they are less capable of providing clues on the origin of the initial raw material.<sup>12</sup>

The aim of this study is to develop a reliable method to determine the lead isotopic composition and <sup>87</sup>Sr/<sup>86</sup>Sr ratios in uranium ore concentrates and apply it for nuclear forensic purposes. These elements were chosen, as their isotopic compositions are presumed to reflect that of the ore and give information on the type and age of the ore body, thereby on the source material. The variation of the <sup>87</sup>Sr/<sup>86</sup>Sr is due to the decay of long-lived <sup>87</sup>Rb (half-life,  $4.8 \times 10^{10}$  year) to <sup>87</sup>Sr and the highly variable Rb/Sr ratio in nature. The <sup>87</sup>Sr/<sup>86</sup>Sr isotope ratio, which is widely used in geology for age determinations and during the past decade more extensively used for origin assessment (e.g., ivory, human bone, or food products),<sup>13–15</sup> was chosen as a possible indicator of provenance because it is characteristic of the geological background. Also, within mine site variation is expected to be less pronounced compared to the lead isotope ratios. The applicability and limitations of lead isotope ratios for source attribution by the measurement of a larger set of samples are critically discussed. The measurements were also used to give an estimate of the raw ore type and ore formation date by the conventional Pb–Pb dating method. In this work 25 uranium ore concentrate samples originating from 19 different regions were used to investigate the possibility of origin assessment by lead and strontium isotope ratio measurement. By the comparison of samples deriving from the same mine, but with different sampling time, variation of these parameters (within-mine variation) is also assessed, which is of vital importance for the data interpretation.

## EXPERIMENTAL SECTION

**Instrumentation.** A NuPlasma (NU Instruments, Oxford, United Kingdom) double-focusing multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS), equipped with 11 Faraday collectors and 3 discrete dynode electrode multipliers, was used for both Pb and Sr isotope measurements. The instrument was operated in low mass resolution mode. The

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**Table 1. Optimized Instrumental Settings and Data Acquisition Parameters**

MC-ICPMS instrument settings	
forward power (W)	1225
cooling gas flow rate (L min <sup>-1</sup> )	14.0
auxiliary gas flow rate (L min <sup>-1</sup> )	0.94
nebulizer gas flow rate (L min <sup>-1</sup> )	0.85–0.9
sample introduction conditions	
solution uptake rate (μL min <sup>-1</sup> )	50
spray chamber temperature (°C)	110
membrane temperature (°C)	160
sweep gas flow rate (L min <sup>-1</sup> )	4.20
data acquisition	
resolution	~300
number of spectra acquired	3 × 10
magnet delay between blocks (s)	2
scan type	static multicollection
cup configuration: Pb measurements <sup>a</sup>	L2, <sup>204</sup> Pb; Axial, <sup>206</sup> Pb; H1, <sup>207</sup> Pb; H2, <sup>208</sup> Pb
cup configuration: Sr measurements <sup>a</sup>	IC2, <sup>83</sup> Kr; L3, <sup>84</sup> Sr; L2, <sup>85</sup> Rb; Axial, <sup>86</sup> Sr; H2, <sup>87</sup> Sr; H4, <sup>88</sup> Sr

<sup>a</sup> L3, L2, Axial, H1, H2, and H4 denote Faraday detectors; IC2 denotes a discrete dynode electron multiplier operated in pulse counting mode.

samples were introduced into the plasma using a low-flow Teflon microconcentric nebulizer operated in a self-aspirating mode in combination with a desolvation unit (Aridus, CETAC Technologies Inc., Omaha, NE). The instrument settings and the data acquisition parameters are summarized in Table 1.

Prior to the analysis of samples, the instrument was tuned using a 50 ng g<sup>-1</sup> Pb monoelemental solution (Alfa Aesar, Karlsruhe, Germany) for the lead measurements and 10 ng g<sup>-1</sup> Sr monoelemental solution (Alfa Aesar, Karlsruhe, Germany) for the Sr isotope analyses. The optimization was carried out with respect to maximum sensitivity. Sensitivities were approximately 500 and 210 mV for 100 ng g<sup>-1</sup> <sup>208</sup>Pb and 10 ng g<sup>-1</sup> <sup>88</sup>Sr, respectively.

**Reagents and Materials.** As blanks are of critical importance for Sr and Pb analyses, all laboratory materials were thoroughly cleaned before use. Monoelemental Pb and Sr standard solutions used for the optimization of the MC-ICPMS instrument were prepared by the dilution of a 1000 μg g<sup>-1</sup> standard solution (Alfa Aesar, Karlsruhe, Germany). For the lead isotope ratio measurements, SRM-982 isotope standard (equal-atom lead isotopic standard, National Bureau of Standards, Washington, DC) was used to correct for instrumental mass discrimination. The Sr Resin extraction chromatographic columns (100–150 μm particle size) were supplied by Eichrom Technologies Inc. (Darien, IL). The Sr Resin was cleaned before use with 25 bed volumes of 8 M HCl in order to remove residual lead from the resin. For the preparation of the small-volume columns, 200 μL of the resin was placed in plastic Bio-Rad holders (diameter, 0.8 mm; length, 5 mm) and plugged with a porous Teflon frit (Reichert Chemietechnik Heidelberg, Germany) on the top of the resin to avoid mixing. Hydrochloric acid (Suprapur grade, Merck, Darmstadt, Germany) was used for the sample preparation. Suprapur grade HNO<sub>3</sub> was further purified by subboiling in quartz distillation equipment. High-purity water (UHQ System, USF Elga, Germany) was used for dilutions. The certified reference materials used for measurement validation were SRM-981 (common lead isotopic standard, National

Institute of Standards and Technology, Gaithersburg, MD), SRM-987 (SrCO<sub>3</sub> isotope standard, National Institute of Standards and Technology, Gaithersburg, MD), BCR-2 (Columbia River basalt, U.S. Geological Survey, Denver, CO), and JB-2 (Volcano basalt, Geological Survey of Japan, Ibaraki, Japan).

**Investigated Samples.** A total of 25 uranium ore concentrates originating from 19 different mines were included in this study (Table 2). The chemical compositions of the investigated ore concentrates vary with the milling process used in the different facilities. The uranium deposit type, from which the ore concentrates were milled, is also included in Table 2. In some instances the raw uranium ore was processed at a milling facility some distance from where it was mined (e.g., CAN ESI sample was processed in Calgary, Alberta, Canada, from phosphate rock from Idaho),<sup>5,16</sup> but the lead and strontium isotopic composition is expected to be characteristic of the ore type rather than the milling plant. The four replicate Beverley samples were taken at the beginning of the 2000s and derive from two different production batches produced within a short time interval (Beverley-1 and Beverley-3 are from one batch, and Beverley-2 and Beverley-4 were both from another batch).<sup>17</sup> The replicate samples from Rabbit Lake, Ranger, and Rössing mines were taken a few years apart. Rabbit Lake-1, Ranger-1, and Rössing-1 are more recent samples, taken at the beginning of the 2000s, while Rabbit Lake-2, Ranger-2, and Rössing-2 derive from an older sampling campaign conducted during the 1980s. These replicate samples can be used to assess the robustness of the parameters investigated, i.e., how these parameters change over the course of time.

**Sample Preparation.** Approximately 300–500 mg of uranium ore concentrate was weighed into a Teflon vial and dissolved in 9 mL of 10 M ultrapure nitric acid while heating to 90 °C on a hot-plate for 3 h. After cooling to room temperature, 1 mL of this stock solution corresponding to about 44 mg of sample (approximately 35 mg of uranium) was used for the separation of lead and strontium isotopes.

For the separation of lead and strontium from the uranium ore concentrates, a sequential extraction chromatographic separation method was adapted, which enables the simultaneous separation of the elements of interest from one aliquot. Lead and strontium were separated from the sample and preconcentrated by extraction chromatography using Sr Resin columns. The method applied was based on the work of Deniel and Pin<sup>18</sup> and used slightly different volumes of the eluents in order to completely remove the overwhelming uranium matrix and to avoid the loss of analytes due to matrix effect. Use of a small-volume column and less chemicals highly reduced the background signal on the MC-ICPMS and the generated waste.

For the separation, 2 mL of ultrapure water was added to 1 mL of the dissolved stock solution of the ore concentrate, which was necessary to adjust the nitric acid concentration (to approximately 2–3 M). After cleaning the column with 8 M HCl (2 × 0.5 mL), the sample was loaded onto the column. The flow-rate of the eluents was about 200 μL min<sup>-1</sup>. After loading, the matrix

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**Table 2. Investigated Uranium Ore Concentrate Samples and Deposit Type of the Uranium Ores Used for Production**

sample name	mine	country of ore origin	uranium deposit type
Beverley-1	Beverley	Australia	sandstone-basal channel
Beverley-2	Beverley	Australia	sandstone-basal channel
Beverley-3	Beverley	Australia	sandstone-basal channel
Beverley-4	Beverley	Australia	sandstone-basal channel
Blind River	Elliot Lake	Canada	quartz-pebble conglomerate
Lagoa Real	Lagoa Real	Brazil	metasomatite
CAN ESI	Idaho phosphate deposit	United States	phosphorite
Cluff Lake	Cluff Lake	Canada	unconformity-proterozoic fracture-bound
El Mesquite	El Mesquite	United States	sandstone-roll front
Key Lake	Key Lake	Canada	unconformity-proterozoic fracture-bound
Mary Kathleen	Mary Kathleen	Australia	metamorphic
Olympic Dam	Olympic Dam	Australia	hematite breccia complex
Queensland	Nabarlek	Australia	unconformity-proterozoic fracture-bound
Rabbit Lake-1	Rabbit Lake	Canada	unconformity-proterozoic fracture-bound
Rabbit Lake-2	Rabbit Lake	Canada	unconformity-proterozoic fracture-bound
Ranger-1	Ranger	Australia	unconformity-proterozoic fracture-bound
Ranger-2	Ranger	Australia	unconformity-proterozoic fracture-bound
Ranstad	Ranstad	Sweden	black shale
Rossing-1	Rössing	Namibia	intrusive
Rossing-2	Rössing	Namibia	intrusive
Rum Jungle	Rum Jungle	Australia	unconformity-proterozoic fracture-bound
Stanleigh	Stanleigh	Canada	quartz-pebble conglomerate
Stanrock	Stanrock	Canada	quartz-pebble conglomerate
Straz	Straz	Czech Republic	sandstone-tabular
USA ESI	Florida	United States	phosphorite

components were stripped from the resin using 600  $\mu\text{L}$  of 2 M  $\text{HNO}_3$ , 1 mL of 7 M  $\text{HNO}_3$ , and 240  $\mu\text{L}$  of 2 M  $\text{HNO}_3$ . Thereafter, strontium was eluted from the column using 1.25 mL of 0.05 M  $\text{HNO}_3$ . Prior to the elution of Pb, residual strontium was completely stripped from the column using 1 mL of 3 M  $\text{HCl}$ . This step also converted the resin to the chloride form. Finally, lead was stripped from the column with 1.8 mL of 8 M  $\text{HCl}$ .

Following separation of the Pb and Sr, 200  $\mu\text{L}$  of ultrapure  $\text{HNO}_3$  was added to each of the lead and strontium fractions which were then evaporated to almost complete dryness on a hot-plate in order to destroy any residual organic resin. The evaporated fractions were dissolved in 1 mL of 2 mass/mass % ultrapure nitric acid while heating slightly. The final samples were analyzed by MC-ICPMS.

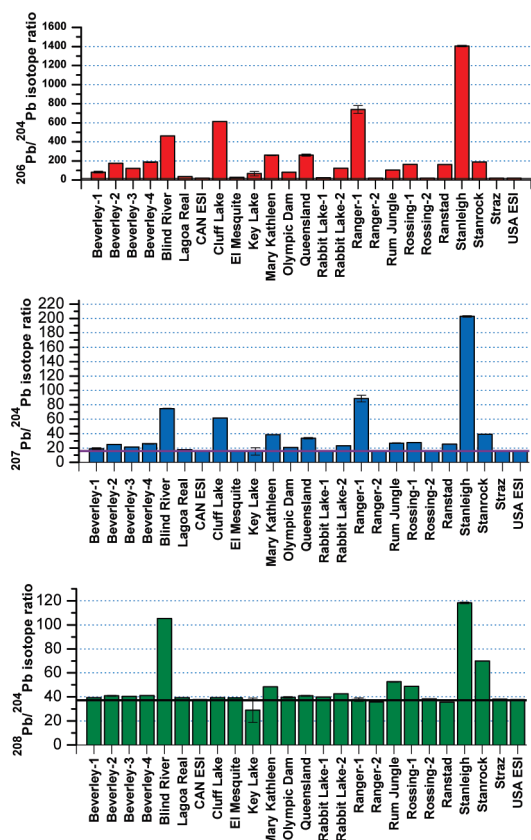
The chemical reagents used were carefully checked for their background contribution. A procedural blank sample was run through the entire dissolution and separation procedure with each batch of samples. This blank was also used for the background correction of the MC-ICPMS analysis. The Pb and Sr concentrations in the final 1 mL blank solutions were 1.2 and 0.63  $\text{ng g}^{-1}$ , respectively. The uranium concentrations in the Pb and Sr fractions were 47 and 1.8  $\mu\text{g g}^{-1}$ , respectively, thus sufficiently low to protect the instrument from contamination and to avoid serious matrix effects.

**Data Evaluation.** The raw data obtained were first corrected for the procedural blank using on-peak zeroing. In the case of the lead isotope ratio measurements, the mass bias correction was performed externally using a mass bias correction factor obtained by the measurement of  $^{208}\text{Pb}/^{206}\text{Pb}$  ratio in the SRM-982 equal-atom lead isotopic standard, while for the strontium isotope ratio measurements the mass discrimination was corrected internally using the  $^{88}\text{Sr}/^{86}\text{Sr}$  isotope ratio, which is constant in nature ( $^{88}\text{Sr}/^{86}\text{Sr} = 8.3786 \pm 0.0030$ <sup>19</sup>). The use of internal normalization for mass discrimination correction is a

common practice in MC-ICPMS and greatly improves the precision. For both Pb and Sr, the Russell mass bias correction model was used.<sup>19</sup> Although strontium was chemically separated from the matrix components and from Rb, the signal for  $^{85}\text{Rb}^+$  was measured simultaneously with the  $\text{Sr}^+$  signals and the contribution of  $^{87}\text{Rb}^+$  to the  $^{87}\text{Sr}^+$  signal was mathematically corrected for using the  $^{87}\text{Rb}/^{85}\text{Rb}$  isotope ratio of 0.385 71.<sup>10</sup> The correction was typically less than 0.001%. Similarly, the interference of  $^{86}\text{Kr}^+$ , present as a contaminant in argon gas, was also corrected for by the measurement of  $^{83}\text{Kr}^+$  ( $^{86}\text{Kr}/^{83}\text{Kr}$  isotope ratio of 1.5048 was used<sup>10</sup>). The correction was typically 0.005%. The final results were calculated taking into account the uncertainty of the certified isotope ratio used for the mass bias correction, the measured isotope ratios, and the atomic weights and abundances of the isotopes of interest.

**Validation of the Method.** Unfortunately no standard reference materials are available which have a uranium matrix and are certified for lead and strontium isotopic composition. Therefore, for validation of the lead measurement by MC-ICPMS, SRM-981 was used. The measured  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios were  $16.945 \pm 0.007$ ,  $15.501 \pm 0.005$ , and  $36.730 \pm 0.007$  at 95% confidence level, respectively, which was in good agreement with the certified values ( $16.937 \pm 0.015$ ,  $15.492 \pm 0.013$ , and  $36.722 \pm 0.031$ , respectively). For strontium isotope analysis, SRM-987 was measured with each batch of samples to validate the measurement procedure. The  $\text{SrCO}_3$  reference material was analyzed after dissolution in ultrapure nitric acid and subsequent dilutions. The measured  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratio of  $0.710\,28 \pm 0.000\,13$  (at 95% confidence level) was in good agreement with the certified value ( $0.710\,34 \pm 0.000\,26$ ). However, in order to validate the total procedure including the sample preparation, two basaltic rock geological reference materials were also measured using the dissolution and

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**Figure 1.** The measured lead isotope ratios in the investigated uranium ore concentrates. The present-day natural  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios of  $17.2 \pm 1.2$ ,  $15.8 \pm 1.1$ , and  $37.4 \pm 2.6$ , respectively, are also marked (solid line).

separation procedure described above but with a modified digestion necessary for the more resistant geological matrix. Approximately 0.5 g of the powdered rocks was dissolved in 6 mL of concentrated ultrapure  $\text{HNO}_3$  and 1 mL of concentrated HF in a Teflon beaker. The sample solutions were covered with a Teflon lid and heated on a hot plate for 15 h. Thereafter the samples were evaporated to dryness, and the residue was taken up in 10 mL of 3 M  $\text{HNO}_3$  and filtered through a 0.45  $\mu\text{m}$  cellulose acetate membrane filter. Subsequently, Sr was isolated from the matrix components (including Rb) using the separation procedure described above and was measured by MC-ICPMS. The measured  $^{87}\text{Sr}/^{86}\text{Sr}$  values of the BCR-2 and JB-2 samples were  $0.70510 \pm 0.00026$  and  $0.7038 \pm 0.0012$  at 95% confidence level, respectively, which are in good agreement with the certified values ( $0.70499 \pm 0.00003$  and  $0.703669 \pm 0.000011$ , respectively<sup>20</sup>).

## RESULTS AND DISCUSSION

**Lead Isotope Ratio Measurement.** *Lead Isotopic Composition.* The lead isotope ratios measured in the investigated uranium ore concentrates are shown in Figure 1. All ratios are presented relative to  $^{204}\text{Pb}$ , which is the only primordial lead isotope. The present-day natural  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios of  $17.2 \pm 1.2$ ,  $15.8 \pm 1.1$ , and  $37.4 \pm 2.6$ , respectively, are

also indicated in Figure 1. The higher the deviation of the radiogenic lead from the natural lead composition, the higher the age of the deposit and/or the higher the uranium and thorium content (the amount of the parent radionuclide) in the source rock.

In most cases the lead isotopic composition of ore concentrates are vastly different from that of the representative natural lead and the ratios vary over a wide range. The variability of the  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios between the samples from different origin (between-mine variability) is several orders of magnitude. This wide range of variation is highly advantageous and can possibly be applied to distinguish ore concentrates and to verify the origin of a declared yellow cake by the comparison with a standard sample of known origin. However, assignment by only the lead isotopic composition has to be done carefully, as can be seen from the replicate samples from Beverley, Rabbit Lake, Ranger and Rössing, the variation of the lead isotopic composition in samples deriving from the same mine (within-mine variability) can be very high and can lead to false conclusions. The variation of the lead isotopics in the replicate samples is the consequence of two effects: the inhomogeneity of lead isotopic composition within the ore body and the gradual removal of the radiogenic lead by the chemical separation and its continuous isotope dilution with natural lead due to the contaminant of reagents during the milling process. As the  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios increase with the radiogenic lead contribution, their value during the production process continually decrease, while they are diluted with the natural lead having lower  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and  $^{208}\text{Pb}/^{204}\text{Pb}$  ratios. The isotopic composition of the four Beverley samples reflects the two distinct batches from which they were sampled: the isotopic compositions of the parallel samples of Beverley-1 and Beverley-3 and Beverley-2 and Beverley-4 are indistinguishable, but the two pairs have different lead isotopic composition. This difference between the two batches was also observed in the impurity pattern and the anion profile.<sup>9,17</sup>

In extreme cases, this isotope dilution can result in natural lead isotopic composition in the UOC by the complete substitution of radiogenic lead, such as for Rabbit Lake-1, Ranger-2, and Rossing-2 samples. In several cases, the measured lead isotopic composition in the yellow cake samples is indistinguishable from that of the natural lead (e.g., CAN ESI, Rabbit Lake-1, Ranger-2, Straz, and USA ESI samples). There can be three reasons for such results: if the UOC sample is very well purified (i.e., the radiogenic and/or natural lead present in the ore is extracted from the material and substituted with natural lead); if the ore concentrate is produced from a young uranium ore (e.g., Cambrian or more recent deposits), where the radiogenic lead isotopes have not yet grown-in due to the long-lived U and Th parent radionuclides; if the U content and therefore also the radiogenic lead content of the ore is low. In such cases no further information on the feed ore type can be deduced only on the basis of the lead isotopic composition. It is noteworthy that although natural lead is introduced into the yellow cake during purification and therefore would be expected that for the replicate samples the total lead concentration should be higher in the more radiogenic lead containing samples (i.e., less purified) is not true. All Rabbit Lake, Rössing, and Ranger samples contain similar amounts of lead (between 0.68 and 8.12  $\mu\text{g g}^{-1}$ , while the lead concentration in

(20) Geological and Environmental Reference Materials (GeoReM); <http://georem.mpch-mainz.gwdg.de/>, Max-Planck Institute: Mainz, Germany, 2009.

**Table 3. Measured and Natural-Lead Corrected  $^{207}\text{Pb}/^{206}\text{Pb}$  Ratios of the Investigated Ore Concentrates and the Calculated and Literature Values of the Age of the Deposit<sup>a</sup>**

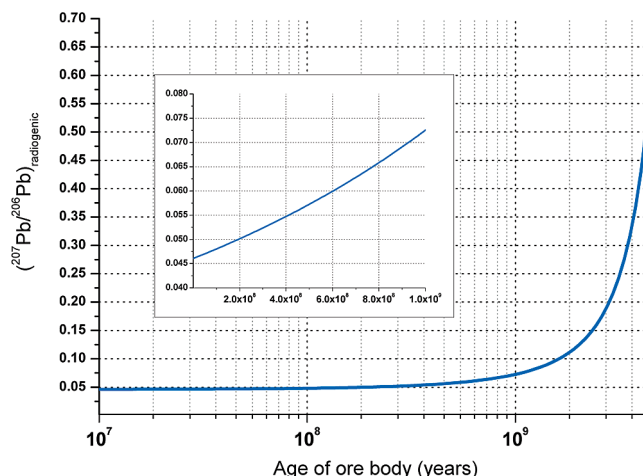
sample	natural $^{206}\text{Pb}$ contribution (%)	natural $^{207}\text{Pb}$ contribution (%)	measured $^{207}\text{Pb}/$ $^{206}\text{Pb}$ ratio	$^{207}\text{Pb}/^{206}\text{Pb}$ corrected for natural lead	calculated age of the deposit (Ma)	literature value of deposit age (Ma)
Beverley-1	20.8	81.6	$0.2332 \pm 0.0252$	$0.050 \pm 0.076$	<2050	$2.5\text{--}23^{22}$
Beverley-2	9.6	61.9	$0.142\,98 \pm 0.000\,72$	$0.059 \pm 0.030$	<1430	
Beverley-3	14.0	72.6	$0.1765 \pm 0.0011$	$0.054 \pm 0.046$	<1620	
Beverley-4	9.0	60.1	$0.1379 \pm 0.0029$	$0.059 \pm 0.028$	<1430	
Blind River	3.7	20.7	$0.162\,36 \pm 0.000\,37$	$0.133 \pm 0.011$	$2140^{+140}_{-150}$	$2139 \pm 100^{23}$
Lagoa Real	46.9	87.4	$0.492\,28 \pm 0.000\,72$	$0.103 \pm 0.248$	NA <sup>b</sup>	$1710^{24}$ $500\text{--}700^{c,25}$
CAN ESI	92.6	99.5	$0.853\,10 \pm 0.000\,11$	$-0.14 \pm 3.5$	NA <sup>b</sup>	$299\text{--}251^{26}$
Cluff Lake	2.8	25.2	$0.100\,49 \pm 0.000\,63$	$0.0768 \pm 0.0080$	$1130^{+210}_{-740}$	$1300\text{--}1380^{27}$
El Mesquite	64.8	94.1	$0.632 \pm 0.018$	$0.08 \pm 0.052$	<640	$5\text{--}30^{28}$
Key Lake	25.7	102.6	$0.2294 \pm 0.0051$	$-0.014 \pm 0.16$	NA <sup>b</sup>	$1350 \pm 4^{29}$
Mary Kathleen	6.5	40.4	$0.1479 \pm 0.0023$	$0.093 \pm 0.020$	$1480^{+390}_{-430}$	$1737 \pm 15$ $1500\text{--}1550^{c,22}$
Olympic Dam	21.2	75.7	$0.2575 \pm 0.0027$	$0.075 \pm 0.076$	$1090^{+1270}$	$1590^{22}$
Queensland	6.5	46.3	$0.1291 \pm 0.0053$	$0.073 \pm 0.020$	$1070^{+400}_{-730}$	$1616 \pm 50$ $900^{c,22}$
Rabbit Lake-1	68.8	96.8	$0.6521 \pm 0.0033$	$0.032 \pm 0.62$	NA <sup>b</sup>	$1075^{21}$
Rabbit Lake-2	13.7	67.0	$0.1868 \pm 0.0011$	$0.069 \pm 0.044$	$890^{+930}$	
Ranger-1	2.3	17.5	$0.1201 \pm 0.0046$	$0.1011 \pm 0.0079$	$1650^{+130}_{-140}$	$1720\text{--}1822^{22}$
Ranger-2	92.0	99.2	$0.851\,02 \pm 0.000\,16$	$-0.098 \pm 3.3$	NA <sup>b</sup>	
Rum Jungle	16.1	58.0	$0.2544 \pm 0.0016$	$0.124 \pm 0.054$	$2020^{+610}_{-1100}$	$1627 \pm 45$ $1015^{b,22}$
Rossing-1	10.4	56.5	$0.168\,20 \pm 0.000\,87$	$0.0798 \pm 0.032$	$1160^{+680}_{-1010}$	$600\text{--}1200^{30}$
Rossing-2	88.2	98.2	$0.823\,90 \pm 0.000\,14$	$0.005 \pm 2.1$	NA <sup>b</sup>	$510 \pm 40^{b,21}$
Ranstad	10.5	61.7	$0.155\,28 \pm 0.000\,75$	$0.064 \pm 0.033$	$745^{+800}$	$509.8 \pm 5.1^{31}$
Stanleigh	1.2	7.6	$0.144\,51 \pm 0.000\,38$	$0.1349 \pm 0.0035$	$2160^{+30}_{-40}$	$2250\text{--}2500^{28}$
Stanrock	8.9	39.6	$0.207\,38 \pm 0.000\,22$	$0.136 \pm 0.028$	$2190^{+320}_{-450}$	$2250\text{--}2500^{28}$
Straz	88.6	100.1	$0.8119 \pm 0.006\,1$	$-0.13 \pm 2.2$	NA <sup>b</sup>	$86\text{--}99.6^{32}$
USA ESI	90.3	99.4	$0.833\,36 \pm 0.000\,12$	$-0.099 \pm 2.6$	NA <sup>b</sup>	$1.8\text{--}23^{33}$

<sup>a</sup> All data presented at the 95% confidence level (with a coverage factor of 2). <sup>b</sup> NA: not applicable. <sup>c</sup> Metamorphism or alteration date of the ore deposit.

the other ore concentrates varied between 0.05 and  $5\,\mu\text{g g}^{-1}$ , which suggests that the lead impurity level is relatively invariable after the first purification stages.

The contribution of the natural lead in the samples can be estimated using a two-component mixing model: as the primordial  $^{204}\text{Pb}$  isotope in the sample derives from the natural lead, with the use of the natural  $^{206}\text{Pb}/^{204}\text{Pb}$  and  $^{207}\text{Pb}/^{204}\text{Pb}$  ratios, the natural  $^{206}\text{Pb}$  and  $^{207}\text{Pb}$  can be obtained (Table 3). As the ingrowth of  $^{207}\text{Pb}$  is slower than that of  $^{206}\text{Pb}$  due to the lower abundance of the parent  $^{235}\text{U}$  radionuclide,  $^{207}\text{Pb}$  content is more affected by the natural lead (Figure 2 and Table 3).

Correction for the natural lead can be useful in some instances as it allows the comparison of just the radiogenic lead isotopes. However, if the natural lead contribution is high, this correction can be very high (especially for the  $^{207}\text{Pb}$  and  $^{208}\text{Pb}$  isotopes, for which the radiogenic lead content is lower (Figure 1)) and can result in high uncertainty in the final corrected isotope ratio. Previous studies by Svedkauskaitė et al.<sup>9</sup> have shown that the within-mine variability can be decreased by the use of natural lead correction. However, variability was still high and reached up to 40–50% relative standard deviation, which caused serious overlaps between samples and encumbers the origin assessment. In this study, as the natural lead contribution in the yellow cake sample was quite high, the correction did not improve the possibility for origin assessment because of the higher uncertainty. For instance, Table 3 shows the influence of the natural lead correction on the  $^{207}\text{Pb}/^{206}\text{Pb}$  isotope ratios. The main uncertainty derives from the high variability of the natural Pb isotopic composition (the present-day representative natural  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$ , and



**Figure 2.** The variation of the radiogenic  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio as a function of time (for a closed system).

$^{208}\text{Pb}/^{204}\text{Pb}$  ratios of  $17.2 \pm 1.2$ ,  $15.8 \pm 1.1$ , and  $37.4 \pm 2.6$ , respectively<sup>10</sup>).

$^{208}\text{Pb}$  content plays a special role in the origin assessment as this isotope derives from the decay of natural thorium-232 present in the uranium ore. Thus, for certain deposit types, such as the quartz-pebble conglomerate, which have a high thorium content and the mineralization date is comparable to the half-life of  $^{232}\text{Th}$  ( $4.101 \times 10^{10}$  year),<sup>16,21</sup> elevated  $^{208}\text{Pb}$  content is observable. Blind River, Stanrock, and Stanleigh yellow cake samples from the Blind River–Elliot Lake district (Ontario, Canada), which are quartz-pebble conglomerate



deposits, can be easily identified by the  $^{208}\text{Pb}/^{204}\text{Pb}$  ratio (Figure 1). A similar isotopic pattern is expected in samples from other old quartz-pebble conglomerate deposits, such as in Witwatersrand (South Africa), which is a geological analogue of the Blind River–Elliot Lake province.<sup>21</sup>

Therefore, in general, lead isotopic composition can be used for origin assessment only in limited cases, when the sample possesses a unique isotopic composition (e.g., elevated  $^{208}\text{Pb}$  content) and the contribution of natural lead is low. Lead isotopes are more applicable for the comparison with known samples or for verifying that the material derives from the declared facility and a certain production batch. In addition, with the use of the deposit age as an additional parameter identification of the source of the ore concentrates, and the confinement of the possible provenance of the initial raw material can be also performed.

**Estimation of the Age of the Deposit.** As the major uranium isotopes, the long-lived  $^{235}\text{U}$  and  $^{238}\text{U}$  decay to two isotopes of Pb,  $^{207}\text{Pb}$  and  $^{206}\text{Pb}$ , respectively, the ratio of these radiogenic isotopes depends on the age of the rock (Pb–Pb age). For a closed system, where no U or Pb loss or gain has occurred, the radiogenic  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio varies as a function of elapsed time ( $t$ ) since the formation of the ore body according to the general decay equation as follows:

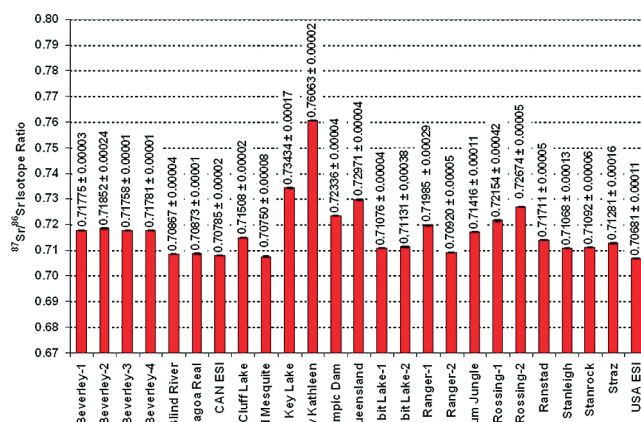
$$\left(\frac{^{207}\text{Pb}}{^{206}\text{Pb}}\right)_{\text{rad}} = \frac{^{235}\text{U}e^{\lambda_{235}t} - 1}{^{238}\text{U}e^{\lambda_{238}t} - 1} \quad (1)$$

where  $(^{207}\text{Pb}/^{206}\text{Pb})_{\text{rad}}$  is the ratio of the radiogenic Pb isotopes,  $^{235}\text{U}/^{238}\text{U}$  is the present-day  $^{235}\text{U}/^{238}\text{U}$  ratio, which is constant in the Earth at 1/137.88 and  $\lambda_{238}$  and  $\lambda_{235}$  are the decay constants of  $^{238}\text{U}$  and  $^{235}\text{U}$ , respectively. The variation of the  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio as a function of time is shown in Figure 2.

For the age assessment, only the ratio of the radiogenic lead isotopes is required so the measured values of the ore concentrates were corrected for the natural lead contribution. It is also assumed that primordial lead is negligible compared to the radiogenic and natural lead. In contrast to the conventional Pb–Pb dating, the isochron equation cannot be used, as for each sample only one data point is available. As eq 1 cannot be solved algebraically for  $t$ , the age and its uncertainty of the deposit can be obtained graphically from Figure 2. As the  $^{207}\text{Pb}/^{206}\text{Pb}$ – $t$  graph is asymmetrical, the upper and lower uncertainties are different, and thus both uncertainties are given in Table 3. The ages reported in the literature of the various ore deposits are also included in Table 3.

For those samples, in which the natural lead contribution is relatively low (typically below 60%), a good estimate on the age can be obtained (Table 3). In some instances, if the natural lead correction is relatively high (between 60 and 95%), an estimated upper age value can be given, which can be used to distinguish ore concentrates produced from young or old uranium ore (e.g., Beverley and El Mesquite). Similar to the origin assessment on the basis of lead isotopic composition, if the radiogenic lead content of the UOC is low, no age estimation can be performed due to the high uncertainty in the calculated  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio.

**Strontium Isotope Ratio Measurement.** The measured  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratios of the investigated uranium ore concentrates



**Figure 3.** The measured  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratios of the investigated uranium ore concentrates. All data are presented at the 95% confidence level.

are shown in Figure 3. The strontium isotope ratios vary over a wide range (between 0.7068 and 0.7606) and can be used to distinguish samples of different origin as well as to apply for the verification of the source by the comparison with known samples. For the comparison, use of significance tests (e.g.,  $t$ -test) can be a method of choice. As the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio correlates with the age of the deposit and/or its Rb/Sr ratio, it may be expected that samples from deposits of similar age would have similar value in ore concentrates in distinct geological settings. However, the  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratio is influenced by other factors such as the presence of minerals with high alkali metal content. In general it is not in connection with the deposit type, as other associated minerals having higher alkali metal content can change the isotope ratios, and the same types of deposit can have different  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios. In this study, however, the  $^{87}\text{Sr}/^{86}\text{Sr}$  value bears a relation to the deposit: for instance, the young phosphorite-type deposits, which have high alkali-earth (and also strontium) content but is incompatible with parent rubidium nuclide, have low  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratios (Figure 3). Nevertheless, in most cases the  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratio has to be supplemented with other characteristics for origin assessment in the case of the identification of an unknown sample.

The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is less variable for the replicate samples from Beverley and Rabbit Lake compared to the lead isotope ratios, which suggests that strontium isotopic composition is less affected by the milling process and less varied within one mine site. In contrast to the lead isotopic composition, all four Beverley samples have the same strontium isotope ratio, thus

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this parameter was found to be more robust to the sampling time. The difference between the replicate samples from Rössing mine is higher than in the Beverley and Rabbit Lake samples: this is probably the consequence of the high heterogeneity of the Rössing mine, where the granitic rocks vary widely in texture, thickness, and uranium grade.<sup>16</sup> For instance, between 2003 and 2007 the annual ratios of ore processed to waste rock removed in Rössing were between 0.59–1.61,<sup>34</sup> which suggests that for such deposits higher spread of the parameters could be expected. In the case of the Ranger samples, the difference in the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios can be explained by the ore processed at the Ranger mill, which derived from two different ore bodies. Between 1981 and 1994, the uranium ore was mined from Ranger No. 1. ore body, while open cut mining commenced at Ranger No. 3 ore body in October 1996.<sup>22</sup> These ore bodies are approximately 1200 m apart. Thus, the sample Ranger-1 ore concentrate (sampling date, October 2001) was produced from the No. 3. ore body, while sample Ranger-2 (sampling was done during the 1980s) was milled from the previous ore body. Although the ore bodies are similar in many ways (e.g., their host rock and uranium mineralogy are identical), their uranium grade, several associated gangue minerals, and trace element content are different,<sup>22</sup> which can explain the difference in the strontium isotopic composition in the two independent ore bodies.

## CONCLUSIONS

Lead and strontium isotope ratios were shown to be applicable tools for the origin assessment of uranium ore concentrates (yellow cakes) in nuclear forensics. A simple and low-background sample preparation method was developed, and it was demonstrated to be suitable for the simultaneous separation of the two

analytes under investigation. Chemical separation was followed by the accurate measurement of the isotope ratios using MC-ICPMS. The lead isotopic composition is a useful signature of the ore concentrates, as it bears information on the starting ore material; hence it enables one to trace the material back to its origin. The lead isotopic composition varies significantly between the mining locations depending on the geological settings, thus it can be used to distinguish the samples and, in some instances, to identify the initial raw material (e.g., in the case of the samples originating from quartz-pebble conglomerate type deposits). However, in the course of the data evaluation and assignment, the relatively high variation in the lead isotopic composition within the mine sites has to be advisedly taken into account. Additionally, the isotope dilution of the informative radiogenic lead with natural lead throughout the milling process can result in a higher variability of the data. If the natural lead contribution in the investigated sample is low, another important parameter, the age of the ore deposit can be obtained by the means of  $^{207}\text{Pb}/^{206}\text{Pb}$  ratio, thus further complementing the signatures used for attribution. Strontium isotopic composition of the uranium ore concentrates appears to be less prone to the variability within the mining site and to the milling process. However, the within mine variability of the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is much smaller than that of the lead isotope ratios, thus the strontium isotope ratio offers a higher degree of confidence for origin attribution. The combination of the two parameters offers a significantly increased degree of confidence in the source attribution of uranium ore concentrates.

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