

Tracking radioactive contaminants in the environment at the micro/nano scale through isotope geochemistry

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Abstract: This work investigates the relevant role of isotope geochemistry in tracking sources of radioactive contaminants in the environment. Isotopic and elemental “fingerprints” are essential for identifying contamination sources and tracking their evolution over time and space. We emphasize the complementary capabilities of advanced analytical techniques, such as SIMS and NanoSIMS, for micro- and nanoscale analysis, compared to traditional bulk sample analysis for isotope and elemental characterization; bulk analysis has significant limitations, primarily the loss of critical information about contamination sources due to concentration dilution and/or isotopic mixing with other sources with different isotope signatures. Furthermore, bulk analyses often fail to reveal specific details about the nature and stability of radionuclide-bearing phases. To highlight the relevance of microscale analysis, we present an application that enabled the discrimination of U contamination sources in a wetland, which was nearly undetectable using bulk analysis.

1 INTRODUCTION

In recent decades, the nuclear industry, along with industrial processes such as coal and phosphate mining and shale gas extraction, has released significant quantities of radionuclides into the environment. The persistence of these radionuclides continually exposes populations and ecosystems to ionizing radiation. It is crucial to thoroughly characterize historic contaminations—legacy radioactivity from past nuclear cycle activities, including incidents, accidents, global fallout from nuclear weapons testing, and radioactive discharges from non-nuclear industries (NORM industries) which could in turn increase our capacity to anticipate consequences of new contamination sources in the frame of the nuclear industry’s resurgence. Indeed, accurately identifying contamination sources, ideally at an early stage, and refining our understanding of contaminant spatiotemporal evolution constitutes an important radiological protection issue for public authorities and nuclear institutions contributing to the development of effective strategies for managing contaminated sites and associated waste.

Isotope geochemistry provides relevant tools for identifying contamination sources and tracking their evolution across time and space through isotopic and elemental “fingerprints”. This approach hinges on the precise isotopic and elemental characterization of environmental samples. However, traditional bulk analyses of samples, such as sediments or soils, can obscure important information about contamination origins. This is due to isotopic mixing between different contamination sources, which alters the original signatures, and/or dilution of contaminant concentrations caused by mixing with the sample matrix, making them more difficult to detect. Moreover, bulk analyses often fail to reveal important details, such as the nature and stability of radionuclide-bearing phases. The primary goal of this study is to demonstrate how isotope geochemistry can be applied at the micro and nano-scale to resolve ambiguities in contamination source identification that are not detectable through bulk analysis.

Isotope and elemental analysis at the micro to nanometric scale can offer valuable insights. Secondary Ion Mass Spectrometry (SIMS) and Nano-scale Secondary Ion Mass Spectrometry (NanoSIMS) are particularly well-suited techniques for this purpose, providing isotope and elemental ratios, including stable Pb and activity ratios of the ^{238}U decay products.

In the context of tracking contamination sources from U mining and milling activities, stable Pb isotopes are relevant. The high ^{238}U and ^{235}U content in U-ores produces significant amounts of radiogenic ^{206}Pb and ^{207}Pb , with ^{206}Pb being the most abundant. In contrast, the low ^{232}Th content results in minimal ^{208}Pb production, creating a distinct isotopic contrast with natural Pb, where ^{208}Pb is dominant. The natural $^{206}\text{Pb}/^{208}\text{Pb}$ ratio is about 0.48 [1], while soils affected by mining discharges can show ratios as high as ~ 10 , highlighting U contamination from mining activities [2]. Additionally, analyzing U-series disequilibrium at the mineral and individual grain scale helps to trace interactions between minerals and their environments. This approach reveals the mechanisms of radionuclide incorporation and release and identifies processes controlling their environmental dispersion. By treating ^{230}Th as geochemically immobile, the activity ratios of ($^{230}\text{Th}/^{238}\text{U}$) and ($^{226}\text{Ra}/^{230}\text{Th}$) provide insights into U and Ra mobility. Ratios of 1 indicate no mobility (secular equilibrium), while ratios greater than 1 suggest U loss and Ra gain, and ratios less than 1 indicate U gain and Ra loss. These variations are relevant for understanding the mobility of these elements at the grain scale and, by extension, in the environment.

The project's main objective is to explore cutting edge analytical methods that provide high-precision isotopic and elemental information at micro- to nanometric scales for tracking sources of radioactive contaminants in the environment. We have developed a method for stable Pb isotope analysis using SIMS, and ongoing work aims to develop simultaneous analysis of stable Pb isotope ratios and ^{238}U decay products by NanoSIMS. Despite its potential, especially in terms of spatial resolution which is critical for small particles, NanoSIMS is rarely used to study radionuclide distribution in the environment due to significant analytical challenges, including low counting rates due to low isotopic abundances and issues with spectral interferences [3].

In this work, we demonstrate how to track contamination sources using Pb isotope signatures at the particle scale in a wetland affected by discharges from a former U-mine. Bulk analysis of stable Pb isotopes in soil samples revealed that local U mineralization, consisting exclusively of parsonsite ($\text{Pb}_2(\text{UO}_2)(\text{PO}_4)_2$), exhibited Pb isotope signatures similar to natural Pb, due to the high natural Pb content in parsonsite ($^{206}\text{Pb}/^{208}\text{Pb} \sim 0.48$) [4]. However, some soil core levels in the wetland showed slight variations in the $^{206}\text{Pb}/^{208}\text{Pb}$ ratio (up to 0.6), suggesting the presence of a secondary source of U contamination. This slight isotope variation may be attributed to the substantial amounts of natural Pb from parsonsite and local Pb-bearing veins, making the second potential U-source (ex. with a $^{206}\text{Pb}/^{208}\text{Pb} > 10$ for uraninites, [5]) nearly undetectable. The aim of this work is to utilize micro-scale analysis to identify potential inherited U-bearing phases from mining activities that may be overlooked by bulk sample analysis.

2 MATERIAL AND METHODS

2.1 Samples

Samples were collected from a wetland near the former Rophin U mine (Massif Central, France), where over 30,000 tons of mining materials and U mill tailings are stored. This site, is designated as registered environmental facility (ICPE), operated from 1949 to 1952 [6]. The wetland, located at the confluence of the ICPE drainage and the Gourgeat stream, is seasonally flooded and records dose rates up to $2,000 \text{ nSv}\cdot\text{h}^{-1}$. The main uranium mineralization is dominated by parsonsite ($\text{Pb}_2(\text{UO}_2)(\text{PO}_4)_2$) [4]. It should also be noted that significant Pb veins were observed at the Rophin site, along with abundant Pb-bearing phases in the wetland [7]. Different soil cores

were collected from the wetland, and this work focused on the C5 core, specifically on the soil layers exhibiting a slight deviation of $^{206}\text{Pb}/^{208}\text{Pb}$ from natural values [4].

2.2 SEM analysis

Pb- and U-bearing phases in selected soil samples were identified using a Hitachi S3500N Scanning Electron Microscope (SEM) with two Brücker 5030 Flash SDD detectors at the LUTECE platform (IRSN). The samples were embedded in epoxy resin, polished, and coated with a thin carbon layer to prevent charging. SEM observations were performed using SE and BSE detectors at 15–25 keV. Elemental composition was determined by Energy Dispersive X-ray Spectroscopy (EDS), providing detailed element distribution and semi-quantification information.

2.3 SIMS and NanoSIMS imaging

SIMS was used to localize radiogenic Pb within U-bearing particles at the grain scale using a CAMECA IMS 7F-E7 at IRSN's PATERSON mass spectrometry platform. A carbon-coated sample (C5, 8.5–9.5 cm) was introduced at 1.9×10^{-9} mbar, with a 5 nA, 15 kV O_2^+ primary ion beam scanning a $250 \mu\text{m} \times 250 \mu\text{m}$ area. After a 2 min of pre-sputtering to remove the carbon layer, 500 integration cycles measured isotopes including stable Pb isotopes and ^{238}U . Calibration was done using a Pb-rich metal plate.

NanoSIMS imaging on the same samples enhanced spatial resolution for small particles, measuring Pb isotopes as well as U-238 decay products, including ^{226}Ra and ^{230}Th . Analyses were performed at IMPMC, Museum National d'Histoire Naturelle, Paris, France with a $\sim 1 \mu\text{m}$, 50 pA O_2^- primary ion beam, achieving $\sim 1 \mu\text{m}$ spatial resolution. Up to 10 isotopes can be measured simultaneously, with typical precision of 10-20% on U-238 series ratios at $1 \mu\text{m}$ scale.

3 RESULTS AND DISCUSSION

3.1 Discriminating Rophin U sources

Thanks to SEM analyses, various U-bearing phases were identified in soil core C5, specifically at a depth of 8.5–9.5 cm [4]. These phases were then analyzed using SIMS to obtain stable Pb isotope characterization and gather information about their origin. Three distinct types of particles were observed (areas 1, 2, and 3), as shown in Figure 1. In the same figure, ^{28}Si was analyzed in the first row for all three areas to visualize the particle shapes, while U analysis in the second row confirmed the presence of U-bearing phases.

As shown in Figure 1, U-bearing phases with a Pb isotope signature ($^{206}\text{Pb}/^{208}\text{Pb}$) close to that of natural Pb were observed in Area 1. Stoichiometric observations from SEM indicated a chemical composition similar to that of parsonsite. Chemical and isotopic data confirmed the presence of parsonsite-like phases that have been inherited from the local mineralization, resulting from particle dissemination due to U-mining and milling activities. A significant finding of this study is the identification of phases with a uraninite-like stoichiometry exhibiting a high $^{206}\text{Pb}/^{208}\text{Pb}$ isotope ratio (~ 9), typical of natural Pb-free U-bearing phases in Area 2. This suggests the presence of a uranium-bearing phase that is distinct from the local mineralization. These phases would have remained undetectable through bulk analysis due to the high presence of Pb (e.g., soils rich in Pb minerals: plumbogummite, [7]). This mixture explains the lower Pb isotope signature in the bulk sample analysis compared to reported values for U-ore and tailings [5]. This distinction, provides critical insights into the dispersion patterns of uranium contaminants. Historic documents revealed that uraninite from the Bois Noirs Limouzat site (Massif Central, France) was processed at the Rophin site, and SIMS analysis demonstrated that significant particle dissemination has taken place in the environment.

A different type of U-bearing phase is present in Area 3. These particles are characterized by a complete absence of Pb, suggesting the neof ormation of U-rich particles, likely due to the alteration of primary U-bearing particles and the mobility of uranium within the C5 soil core. Previous studies have reported significant uranium resupply from residual U-mine particles in the soil into the pore water, supporting this observation [8, 9].

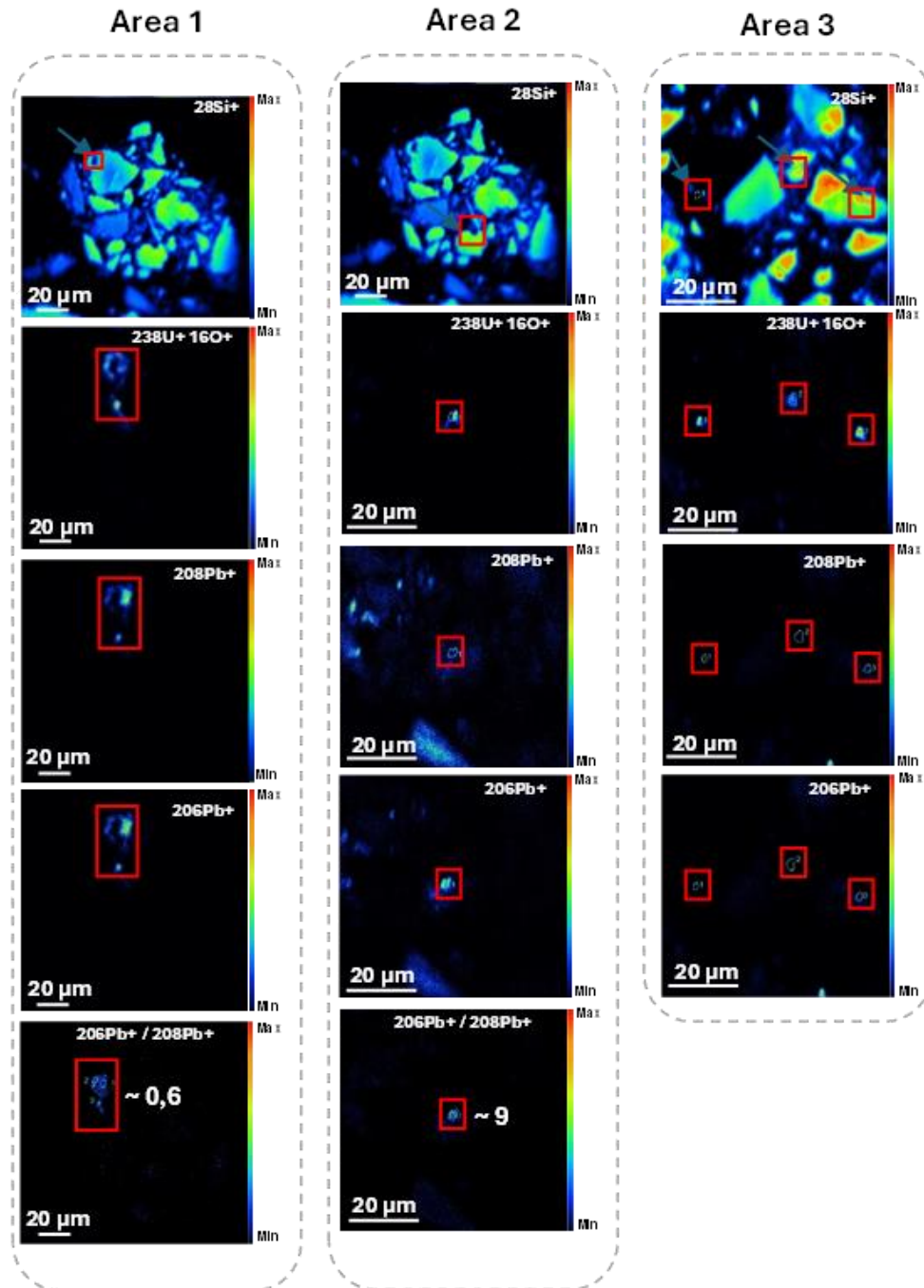


Figure 1. SIMS isotope and isotope ratio imaging of three different areas from the 8.5–9.5 cm depth level of core C5 from the Rophin wetland. Modified from Geng et al. JHM 2024 [4].

To confirm the mobility of U (and Ra), U-series disequilibrium plays a pivotal role. Analyzing ($^{230}\text{Th}/^{238}\text{U}$) and ($^{226}\text{Ra}/^{230}\text{Th}$) ratios at the grain scale can provide relevant insights into particle

alteration and phase neoformation. In some cases, it may even be possible to estimate the timing of uranium mobility (system opening). For this reason, ongoing work focuses on simultaneously analyzing stable Pb isotopes and U-series decay products by NanoSIMS.

3.2 Ongoing NanoSIMS developments

The higher spatial resolution provided by NanoSIMS, combined with Pb isotope and U-series disequilibrium analysis at the mineral and individual grain scale, will significantly enhance our understanding of the dissolution/adsorption processes of U-bearing minerals.

A first attempt at analyzing mineral phases in core C5, preliminarily identified by SEM, was performed using NanoSIMS to create isotope maps of the ^{238}U decay products. Figure 2, highlights NanoSIMS imaging of ^{138}Ba , ^{238}U , ^{206}Pb , ^{208}Pb , ^{226}Ra , and ^{230}Th , focusing on U-rich particles from the 0-2 cm section of the C5 soil core. Besides its slight $^{206}\text{Pb}/^{208}\text{Pb}$ isotope deviation from the natural value, this sample was specifically selected due to its notably high concentrations of U and Pb, providing a key opportunity to investigate the complex interactions between U-decay products of the particles and their surrounding environment. Although activity ratios can be calculated in individual grains from the spatial distribution of trace isotopes, their low abundance makes it difficult to obtain quantitative maps of the ($^{230}\text{Th}/^{238}\text{U}$) and ($^{226}\text{Ra}/^{230}\text{Th}$) activity ratios and requires the development of image processing tools.

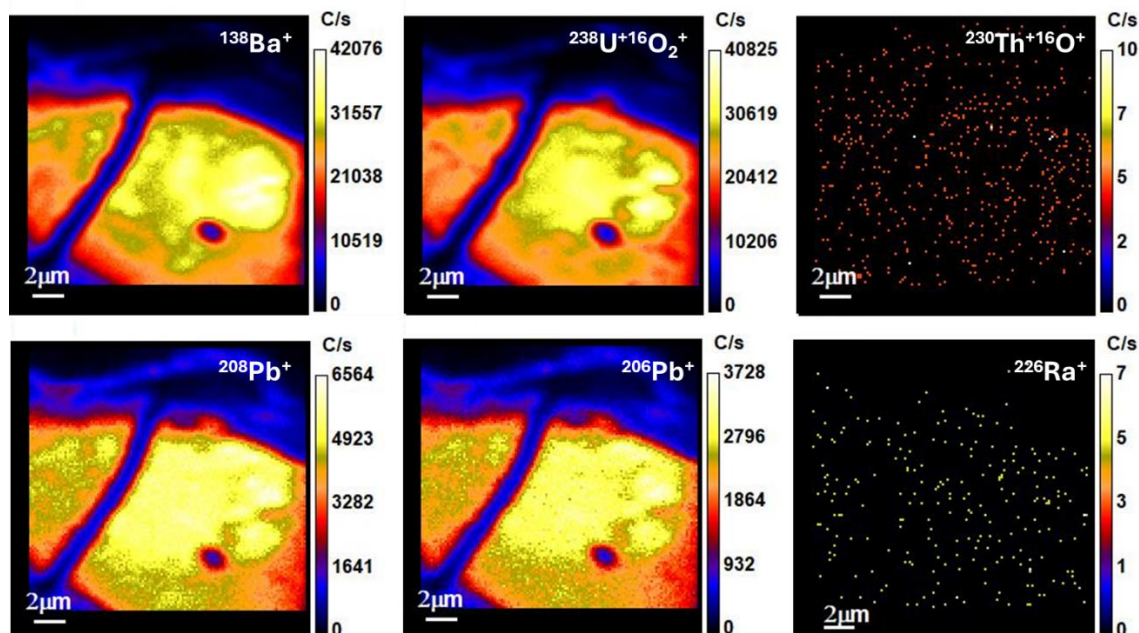


Figure 2. NanoSIMS isotope imaging from the 0-2 cm depth section of C5 soil core from the Rophin wetland.

Ongoing work within the MINIRAP project (Multi-Isotope Nano-scale Imaging RATios on radioactive Particles), supported by CNRS and IRSN, aims to achieve quantitative imaging of radionuclide isotope ratios at a submicrometric scale while accounting for measurement uncertainty. The project focuses on three main areas: (1) calibrating NanoSIMS for isotopes with very low counting rates, (2) processing NanoSIMS outputs with spatial analysis tools from geostatistics, and (3) integrating NanoSIMS imaging with qualitative to semi-quantitative imaging from other techniques.

4 CONCLUSIONS

In this work, we demonstrated how SIMS and NanoSIMS (ongoing work) complement traditional bulk analysis by providing precise isotope and elemental information at the micro- and nanoscale. This approach improves our ability to track contamination sources and understand radionuclide mobility. Specifically, we presented a case study of a wetland located downstream from a former uranium mine. Contrary to our initial assumption of a single contamination source from local mining activity, Pb stable isotope analysis of U-bearing phases revealed the presence of U-bearing phases inherited from the Bois Noirs mine. These phases are almost undetectable through bulk analysis due to the predominance of Pb present in the wetland's geochemical background. Ongoing NanoSIMS analyses aim to explore the crucial role of U-series disequilibrium alongside stable Pb isotopes to investigate U and Ra mobility at the grain scale. This data will enhance our understanding of wetland dynamics and refine models of U and ^{226}Ra migration by considering the different physicochemical properties of the U-bearing phases. Ultimately, the project's goal is to broaden the application of this methodology and its findings to significantly improve the management of ecosystems contaminated by radionuclides.

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