Elemental and Isotopic Tracers as Tools for Understanding Mine Water Geochemistry – Insights from an Iron Ore Mine Site in Northern Sweden

Vimbainashe Lorraine Dzimbanhete[1], Torbjörn Karlsson[2], Oscar Paulsson[1], Lena Alakangas[1]

[1]Luleå University of Technology; [2]Luossavaara-Kiirunavaara AB Gällivare

Abstract

Understanding the geochemical controls on uranium (U) release and mobility in mining environments is essential for predicting water quality and supporting proactive management. This study integrates minewall and laboratory leaching experiments with ^{234}U/^{238}U activity ratios (AR) to identify U sources and mobilization regimes at an iron ore mine in Northern Sweden. Uraninite was the most reactive U-bearing mineral. Carbonate complexation enhanced U mobility under circumneutral conditions. Groundwater AR values distinguished low U recoil-dominated flow paths from high U, dissolution, and complexation-enhanced flow paths. The high U end member contributes the highest U loads and should be prioritized for monitoring and mitigation.

Keywords: Uranium, ^{234}U/^{238}U activity ratios, elemental tracers, carbonate complexation, weathering regimes, mine water

Introduction

Uranium (U) mobility in mining environments is controlled by mineralogical composition and reactivity, water-rock interaction processes, redox conditions, and aqueous complexation reactions. Although U commonly occurs at low concentrations in many host rocks, mining activities expose fresh mineral surfaces and fracture networks, increasing contact with oxygenated groundwater and enhancing U-mineral dissolution. Oxidation of U(IV) bearing minerals such as uraninite (UO_{2+X}) converts relatively insoluble U(IV) to the more soluble U(VI) oxidation state, which readily forms aqueous complexes with ligands including CO_3^{2-}, SO_4^{2-}, and PO_4^{3-} over a wide pH range (Smedley and Kinniburgh 2023). Groundwater U concentrations and associated elemental signatures may therefore reflect the geochemical characteristics of the underlying bedrock or dominant groundwater flow paths. Identifying such geochemical fingerprints is particularly important in mining environments where multiple lithologies and flow systems may contribute differently to dissolved U loads.

U isotopes provide an additional tracer for evaluating U mobilization in groundwater systems. The ^{234}U/^{238}U activity ratio (AR) can be used to distinguish between different U mobilization mechanisms in the subsurface (Basu *et al.* 2015). In undisturbed systems, secular equilibrium results in ^{234}U/^{238}U AR = 1. Deviations arise from the combined effects of alpha recoil and mineral dissolution. During the radioactive decay of ^{238}U, emission of an alpha particle may displace the ^{234}Th daughter nuclide (precursor to ^{234}U), within the crystal lattice or into adjacent pore water if decay occurs near a grain boundary (Brown *et al.* 2016). Recoil-damaged lattice sites enriched in ^{234}U are more susceptible to leaching during oxidative dissolution, therefore groundwater may become enriched in ^{234}U (^{234}U/^{238}U AR > 1), while the solid phase comes depleted in ^{234}U (^{234}U/^{238}U AR < 1).

Leväniemi open pit in Northern Sweden is comprised of several rock types with variable U content and differing U-bearing mineral assemblages. U concentrations of up to 100 µg/L have been detected in groundwater entering the open pit through drainage pipes installed at different elevations for pit slope stability. This groundwater mixes with surface water runoff and is pumped to the processing plant, influencing U concentrations in process water and U loads discharged to a downstream recipient river. This study combines field observations with controlled laboratory leaching experiments and $^{234}U/^{238}U$ AR systematics to improve the understanding of mineral phase reactivity and groundwater mobilization regimes controlling U mobility. The objectives of the study were to (1) evaluate the reactivity of U-bearing mineral phases, (2) define lithology-specific elemental fingerprints, and (3) distinguish groundwater weathering regimes using $^{234}U/^{238}U$ AR.

Methods

Minewall weathering stations and field sampling

Different rock types, including pegmatite and trachyandesite, were collected from Leveäniemi open pit to assess their potential for U release (Fig.1). To estimate U leaching rates per unit surface area in µg/m2/week, minewall weathering stations were installed on selected rock faces following the established field protocols (Morin and Hutt 2004; Dzimbanhete *et al.* 2025). The rock surfaces were cleaned with Milli-Q water before installation. A sealed frame was constructed using inert silicone, and a transparent cover was installed to allow for sunlight exposure and atmospheric exchange while preventing direct rainfall, wind disturbance, and dust contamination (Fig.1C). During sampling campaigns, each station was flushed with Milli-Q water proportional to its surface area to collect leachates for analysis. Leachates were filtered through 0.22 µm nitrocellulose membrane filters into lab-controlled HDPE bottles and submitted to ALS Scandinavia in Luleå for elemental and isotope analysis.

Groundwater and drainage ditch sampling

Groundwater was sampled from drainage pipes drilled approximately 150 m into the open-pit walls for slope stability (Fig.1C). Discharged groundwater mixes with seepage and precipitation runoff in drainage ditches that run alongside open-pit benches (Fig.1C). All collected water flows towards a central sump at the base of the open pit and is subsequently pumped to the processing plant. Sampling campaigns were conducted between 2021 and 2023 at selected drainage pipe and drainage ditch locations (Fig.1B). Field parameters, including pH, temperature, and electrical conductivity (EC), were measured on site with a calibrated VWR multimeter. Water samples were filtered on-site using a 0.22 µm nitrocellulose membrane filter before storage and subsequent elemental and isotope analysis at ALS.

Batch leaching experiments

Batch leaching experiments were conducted on crushed pegmatite and trachyandesite samples to evaluate the reactivity of U-bearing minerals under controlled geochemical conditions. Acid leaching tests were performed over 24 hours using H_2SO_4, and HNO_3 (pH 0.7 to 3.3), whereas alkaline conditions were simulated using Na2CO3 and $NaHCO_3$ (pH 9.8 to 10). Additional experiments at circumneutral pH (7 to 8) were performed using solutions replicating mine water chemistry containing SO_4^{2-}, NO^{3-}, Cl^-, and HCO^{3-} at representative average and maximum concentrations. A constant solid-to-liquid ratio was maintained for all the experiments. Leachate and residual solids samples were sent to ALS for element and isotopic analysis.

Elemental and uranium isotope analysis

Element concentrations in groundwater, drainage ditch water, minewall leachates, batch leachates, and residual solids were determined using sector field inductively coupled plasma mass spectrometry (ICP-SFMS) at ALS. Solid samples were analysed following lithium metaborate fusion and acid digestion. Quality control included blank correction and analysis of certified reference materials. U isotope ratios were measured using multi-collector inductively coupled plasma mass spectrometry (ICP-MS) after chemical separation of U. The $^{234}U/^{238}U$ AR was calculated from measured isotope ratios ($^{238}U/^{235}U$ and $^{235}U/^{234}U$) using decay constants. The $^{234}U/^{238}U$ AR were used to distinguish between recoil-dominated U release and dissolution-driven U mobilization processes. To identify lithology-specific elemental fingerprints, Spearman rank correlation analysis (ioGAS) and hierarchical cluster analysis (IBM SPSS) were applied to the batch leaching data.

Results and Discussion

U release from minewall weathering stations

Pegmatite minewall stations exhibited the highest U leaching rates overall, although substantial variation was observed between them. At minewall station 2, where uraninite was the dominant U-bearing mineral, U leaching reached approximately 1800 µg/m²/week. In contrast, the other pegmatite station, dominated by pyrochlore, showed lower leaching rates of up to 400 µg/m²/week (Fig.2). Trachyandesite (stations 3 and 4) displayed lower but consistent U release rates with uraninite identified as the main U-bearing phase. The elevated leaching rate in pegmatite (station 2) reflects both its higher bulk U content and the accessibility of uraninite within the rock matrix. Trachyandesite, although lower in U, covers an extensive surface area in the open pit as it is the main rock type in the hanging and footwall and therefore represents an important cumulative source of U. Based on their release rates and surface area coverage, pegmatite and trachyandesite were selected for subsequent batch leaching tests.

U mineral dissolution and pH influence

Batch leaching experiments at acidic and alkaline pH demonstrate that uraninite is the reactive U-bearing mineral in both pegmatite and trachyandesite, whereas other U-bearing minerals, including fergusonite, thorite, and xenotime, were largely refractory. Under circumneutral conditions representative of open pit mine water (pH 7 to 8), bulk mineral dissolution was limited (Fig.3). However, dissolved U concentrations increased in carbonate-bearing solutions relative to sulfate, nitrate, and chloride-dominated systems. This enhanced mobilization likely reflects the formation of stable aqueous uranyl–carbonate complexes, which increase U(VI) solubility and inhibit reprecipitation at circumneutral pH. Consequently, groundwater chemistry, particularly carbonate availability, exerts strong control on U mobility.

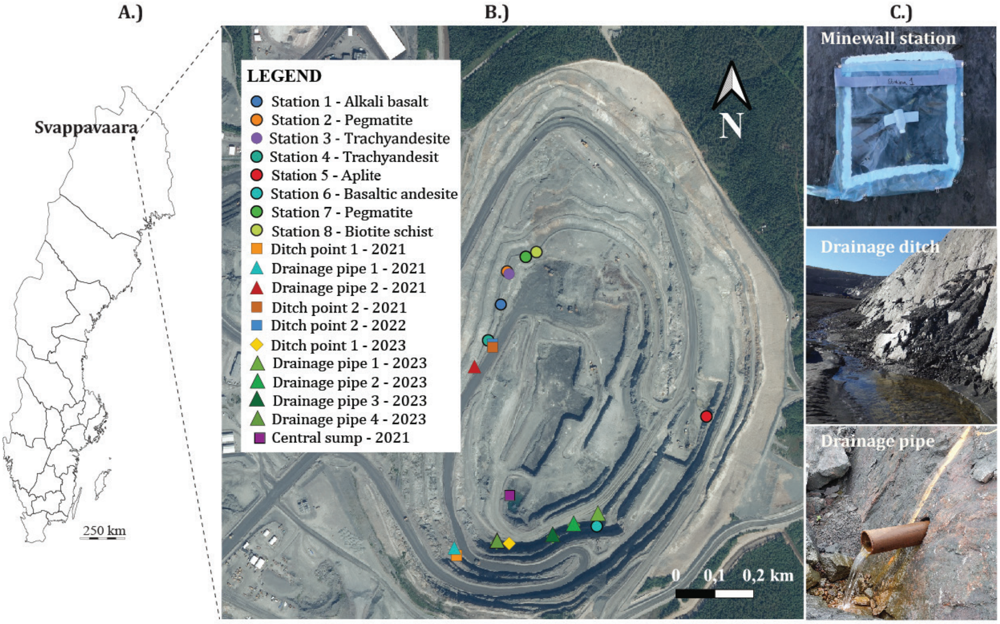

Figure 1 *Orthophoto of Leveäniemi open pit showing minewall station, drainage pipe, and drainage ditch locations, and photographs showing minewall weathering station, drainage ditch, and drainage pipe in the open pit.*

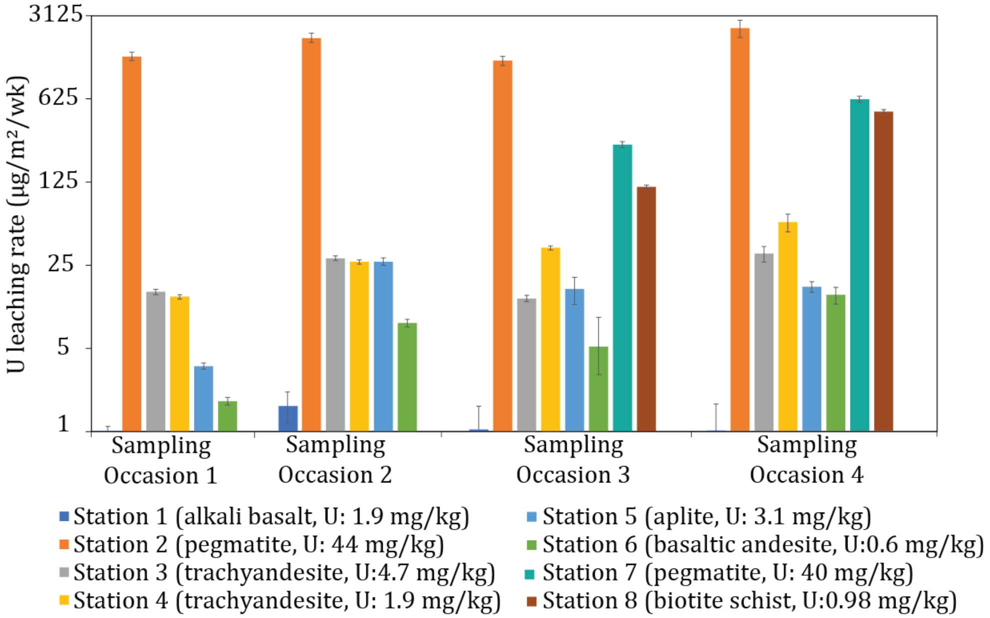

Figure 2 *Uranium leaching rates at minewall stations 1 – 8. Stations 7 and 8 could not be sampled on occasions 1 and 2 due to open-pit bench safety concerns.*

Batch leaching at circumneutral pH and element associations

At circumneutral pH, HCO_3^- was the most effective ligand for U mobilization in pegmatite (Fig.4A), whereas the groundwater solution containing multiple complexing ligands produced the highest release in trachyandesite (Fig.4B). Speciation modelling indicated that uranyl-carbonate and Ca-U-CO_3 complexes dominated under groundwater conditions, confirming carbonate complexation as the primary control on U mobility at around pH 8. In the groundwater solution, pegmatite exhibited a clear U-Pb-Th association reflecting release from uraninite and associated trace elements hosted within this mineral. Electron microprobe analyses showed that uraninite in pegmatite contains 63–68 wt.% UO_2, together with significant PbO (18–20 wt.%), ThO2 (4–7 wt.%) and Y_2O_3 (3–8 wt.%) (Dzimbanhete *et al.* 2025). In contrast, uraninite in trachyandesite contained 70–73 wt.% UO2, 19–22 wt.% PbO but lower ThO_2 (<1.5 wt.%) and Y2O3 (<2.5 wt.%). In the groundwater solution, trachyandesite showed U mobilization primarily associated with Ca rather than Pb and Th, indicating that Ca-U-

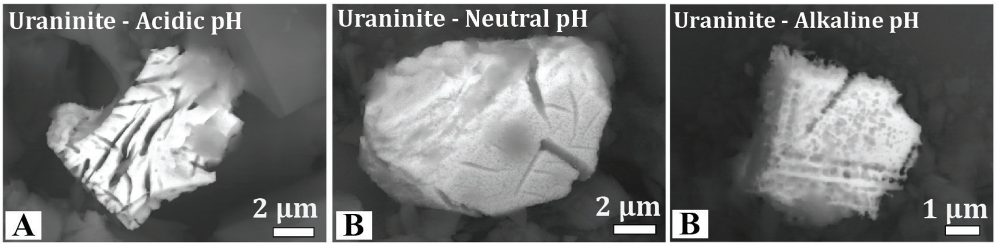

Figure 3 *SEM images of uraninite in residual solids after leaching at acidic pH (0.5 M H_2SO_4), neutral pH (203 mg/L $NaHCO_3$), and alkaline pH (0.5 M $NaHCO_3$/Na_2CO_3).*

CO$_3$ complex formation can exert a stronger influence on dissolved U concentrations than dissolution of U-bearing minerals. These results demonstrate that elemental associations derived under groundwater solution conditions can reflect mineral-host signatures in pegmatite, whereas in trachyandesite, aqueous complexation processes may partially overprint mineralogical signals.

Uranium isotopes and groundwater mobilization regimes

Groundwater discharged from the drainage pipes exhibited $^{234}U/^{238}U$ activity ratios (AR) consistently greater than one, indicating isotopic disequilibrium and active water-rock interaction processes. Two groundwater mobilization regimes were identified based on combined U concentrations and $^{234}U/^{238}U$ AR values (Tab.1): a low U recoil-dominated regime and a high U dissolution and complexation enhanced regime. Samples with intermediate U concentrations are interpreted as mixed or transitional waters.

The low U end member is characterized by U concentrations (< 20 µg/L) and high AR values of 2.7 to 3.8, consistent with preferential release of 234U from alpha-recoil damaged lattice sites or mineral surfaces under limited bulk dissolution(Kronfeld 1974; Cowart and Osmond 1977). The high U end member is characterized by U concentrations >30 µg/L, reaching up to 100 µg/L) and a moderately elevated AR value of 2.6. This pattern is interpreted as dissolution or complexation-enhanced U mobilization, where oxidative dissolution of uraninite and other U-bearing minerals increases dissolved U, while carbonate/Ca complexation promotes U(VI) transport and preferential ^{234}U release maintains isotope disequilibrium (Andersen *et al.* 2009; Coyte *et al.* 2018). Pegmatite and biotite schist produced high U minewall leachates with lower AR values of 1.1 to 1.5, and the corresponding rocks

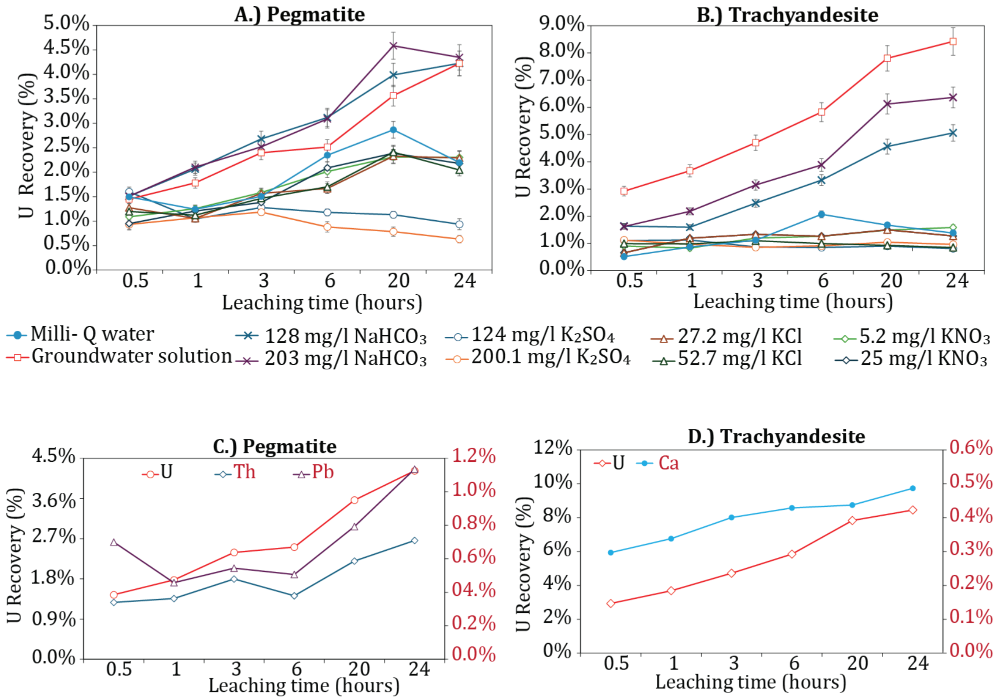

Figure 4 *A and B: U recovery vs leaching time for pegmatite and trachyandesite for batch leaching with NaHCO$_3$, KCl, K$_2$SO$_4$, MQ water, and groundwater solution at neutral pH, C and D: U recovery vs leaching time for elements showing similar leaching behavior to U in pegmatite and trachyandesite.*

Table 1 *Groundwater mobilization regimes identified using U concentrations and $^{234}U/^{238}U$ AR.*

Parameter	Recoil-dominated, low-U regime	Dissolution and complexation enhanced, high U regime
U concentration (µg/L)	<20 µg/L	>30 µg/L, up to 100 µg/L
$^{234}U/^{238}U$ (AR)	High, 2.7 – 3.8	Moderately elevated, 2.6 in the high-end member
U mobilization process	Preferential ^{234}U release by alpha recoil; limited bulk dissolution	Oxidative dissolution of U-bearing minerals, U(VI)-carbonate/Ca complexation
Relative U load contribution/ management priority	Low	High

were ^{234}U-depleted, supporting bulk mineral dissolution as the dominant process in high U-source materials. Drainage ditch waters had intermediate U concentrations and AR values consistent with mixing between drainage pipe groundwater and surface runoff. Since the high U end member contributes most to dissolved U loads, it represents the main target for monitoring and management.

Implications for environmental management

The combined minewall, batch leaching, and isotope results indicate that management should focus on the high U dissolution or complexation enhanced end member. Flow paths with elevated U concentrations and moderately enriched AR values contribute most to dissolved U loads and should therefore be prioritized for monitoring and mitigation. In contrast, recoil-dominated groundwater is isotopically distinct but has lower U concentrations and represents a lower immediate management priority.

Minewall weathering data identify pegmatite and biotite schist as important U source rocks, particularly where uraninite is the main U-bearing mineral. These rocks produced high U leaching rates and relatively low leachate AR values, supporting bulk dissolution of U-bearing minerals as the main process of U release. The corresponding rocks are also ^{234}U-depleted, supporting the interpretation that preferential ^{234}U loss and active U release have occurred in these rocks. Uraninite-bearing rocks should therefore be prioritized during waste rock characterization and, where possible, managed to limit exposure to limit water exposure, excessive particle-size reduction, and co-storage with acid-generating rocks.

Batch-leaching results further show that carbonate-rich, circumneutral waters enhance U mobility through uranyl-carbonate and Ca-U-carbonate complexation. Mine water management should therefore consider both mineralogical source control and groundwater chemistry, particularly alkalinity, Ca, and bicarbonate concentrations. Although direct control of carbonate and calcium may be difficult at the field scale, monitoring alkalinity, Ca, bicarbonate, and U along key drainage-pipe flow paths can help identify conditions that favour U transport. Overall, the results show that combining mineralogical observations, elemental tracers, and $^{234}U/^{238}U$ AR values provides a practical framework for identifying high-risk U sources and reactive flow paths in the mine water system.

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