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**Mobility of lead (Pb) isotopes during weathering of black shales in
central Hunan (China): Implications on Pb isotopes used as an
environmental tracer**

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Abstract: This study analyzed Pb isotopic and elemental compositions in rocks from
the Muzi weathering profile and acid rock drainage from a black shale outcrop in
Hunan (China). Results showed that fresh black shales had major elemental
composition comparable to that of North American Shale. However, elemental
composition in profile rocks varied with depth suggested varying degrees of chemical
weathering supported by visual observation for fresh black shales, weathered black
shales, and black shale soils. Lead, U, Mn, Cu, and Mo were enriched in profile rocks,
while Pb, Cd, Co, Ni, Cu, Mo, Ba, and Sr were released during weathering. Fresh

black shales had variable Pb isotopic compositions, while profile rocks had Pb isotope ratios with minor variations. Mass balance calculation suggested that isotopes ^{206}Pb , ^{207}Pb , and ^{208}Pb were released during black shale weathering. Linear correlation ($R^2 = 0.98$) of $^{206}\text{Pb}/^{207}\text{Pb}$ to $^{208}\text{Pb}/^{206}\text{Pb}$ ratios of profile rock, fresh black shale, pyrite grain, and acid rock drainage samples suggested that Pb isotope composition of profile rocks was of two-endmember sources: unradiogenic Pb isotopes in pyrite grains, and more radiogenic Pb isotopes in accessory minerals and organic matter. Lead isotopes of profile rocks resulted from preferential release of unradiogenic Pb isotopes from pyrite grains and more radiogenic Pb isotopes from accessory minerals and organic matter during weathering. The study highlighted that Pb isotopes are a powerful tool that can be used to discriminate environmental Pb of natural sources from those of anthropogenic inputs at small spatial scale, and to identify Pb contamination in soils and sediments in the weathering catchments.

Key words: Mobility of Pb isotopes; Unradiogenic Pb isotope; Radiogenic Pb isotope; Preferential release; Black shale weathering.

1. Introduction

Lead isotopes have been widely utilized as a geochemical tracer to identify and apportion the source of Pb in a variety of environmental media such as atmospheric aerosols (e.g., Brid, 2011; Kousehlar and Widom, 2019; Lee et al., 2022), riverine and lake sediment (e.g., Peng et al., 2022a, b; Wu et al., 2022; Guillevic et al., 2024; Mao

et al., 2024), loess and soil (e.g., Sun and Zhu, 2010; Reimann et al., 2016; Shetaya et al., 2019; Pacín et al., 2025; Richardson et al., 2026), and water systems (e.g., Åhlgren et al., 2021; Kamenov and Scott, 2026). Lead in the environment has resulted from the mixing of naturally sourced and anthropogenic contributed Pb (Walraven et al., 2013; Pacín et al., 2025), and thus discriminating these sources is important for apportioning Pb contributions (Sangster et al., 2000; Cheema et al., 2020; Peng et al., 2022a, b). As Pb pollution in the environment results from the dispersion from anthropogenic activities including ore mining and smelting, coal combustion, waste incineration, agricultural fertilization and traffic emission (Kousehlar and Widom, 2019; Jeong et al., 2022; Guillevic et al., 2024; Rosca et al., 2024), Pb isotope signatures of these anthropogenic sources have been documented by numerous studies, as detailed in several review papers (Sangster et al., 2000; Komárek et al., 2008; Cheng and Hu, 2010; Brid, 2011; Cheema et al., 2020; Geng et al., 2024). Pb isotopic ratios vary widely in both lithogenic and anthropogenic samples and often overlap (Sangster et al., 2000; Komárek et al., 2008). However, successful application of Pb isotopes to geochemical source apportionment requires quantitative characterization of potential sources and for there to be sufficient differentiation between isotopic signatures of anthropogenically and geogenically-derived Pb (Rosca et al., 2024). Changes in Pb concentrations in environment media may originate from natural rock weathering (Komárek et al., 2008) with weathering playing a significant role in changes in environmental Pb isotopic composition (Cheema et al., 2020). As such, understanding the mobility and changes in Pb isotopes during rock weathering is

important for quantitative source characterization (Brid, 2011; Cheema et al., 2020; Rosca et al., 2024).

Pb isotopes have been used to elucidate mineral alterations during weathering of granite (e.g., Erel et al., 2004; Harlavan et al., 2009; Millot and Négrel, 2013; Söfke et al., 2019; Dausmann et al., 2019). Pb isotope studies of black shale weathering have assessed the distribution of Pb isotopes in soils derived from black shales (Kong et al., 2018; Wen et al., 2020), and the application of Pb isotopes to discriminate Pb and other relative metals of natural sources from those of anthropogenic inputs in different black shale weathering profiles (Peng et al., 2014; Johnson and Graney, 2015; Wei et al., 2021). However, fewer studies have assessed the mobility of Pb isotopes during rock weathering (Komárek et al., 2008; Brid, 2011; Rosca et al., 2024). Black shales around the world are recognized to be enriched in Pb and other trace metals such as Cd, Co, Ni, V, U, and Mo (e.g., Peng et al., 2004; Rimstidt et al., 2017; Vind et al., 2023). Trace metals in black shales are hosted mainly in sulfide minerals (e.g., pyrite), organic matters, and accessory minerals (e.g., apatite, zircon) (Derkowski and Marynowski, 2018; Charbonnier et al., 2022; Wang et al., 2023; Wu et al., 2024a), which have distinct Pb isotope composition due to differences in processes controlling mineral formation. Generally, sulfide minerals (e.g., pyrite) in black shales are characterized by unradiogenic Pb isotopes (Peng et al., 2014; Armstrong et al., 2019; Noireaux et al., 2021), while other mineral phases such as accessory minerals (e.g., apatite, zircon) and organic matter contain more radiogenic Pb isotopes (e.g., Jiang et al., 2006; Johnson and Graney, 2015; Wang et al., 2023). The former results from the

exclusion of radiogenic U and Th from the mineral crystal lattice during mineralization, while the later occurs due to daughter decay products of ^{238}U , ^{235}U and ^{232}Th in these minerals (Cheng and Hu, 2010; Peng et al., 2022a, b; Rosca et al., 2024). Thus, black shales have variable Pb isotope compositions (e.g., Jiang et al., 2006; Johnson and Graney, 2015; Wang et al., 2023), which present an opportunity to study the mobility of Pb isotopes during rock weathering. Therefore, the present study addresses this knowledge gap by investigating samples collected from a black shale outcrop in central Hunan Province, China, with the aims of: (1) characterising the distribution of Pb isotopes within the black shale weathering system; (2) assessing the mobility of Pb isotopes during black shale weathering; and (3) evaluating the potential of Pb isotopes as environmental tracers.

2. Materials and methods

2.1 Field site description and sampling

This study was performed on a black shale outcrop at the Dongping town in Anhua county of Hunan province, China (Fig. 1a). Black shales in the area (Fig. 1b) are enriched in organic matter (content up to 11%) and sulfide minerals (e.g., pyrite, content up to 8%) (Peng et al., 2004; Wu et al., 2024b). Excavation activities have led to black shale exposure to atmospheric oxygen, accelerating oxidative weathering thereby producing typical weathering profiles and acid rock drainage in the outcrop for this study.

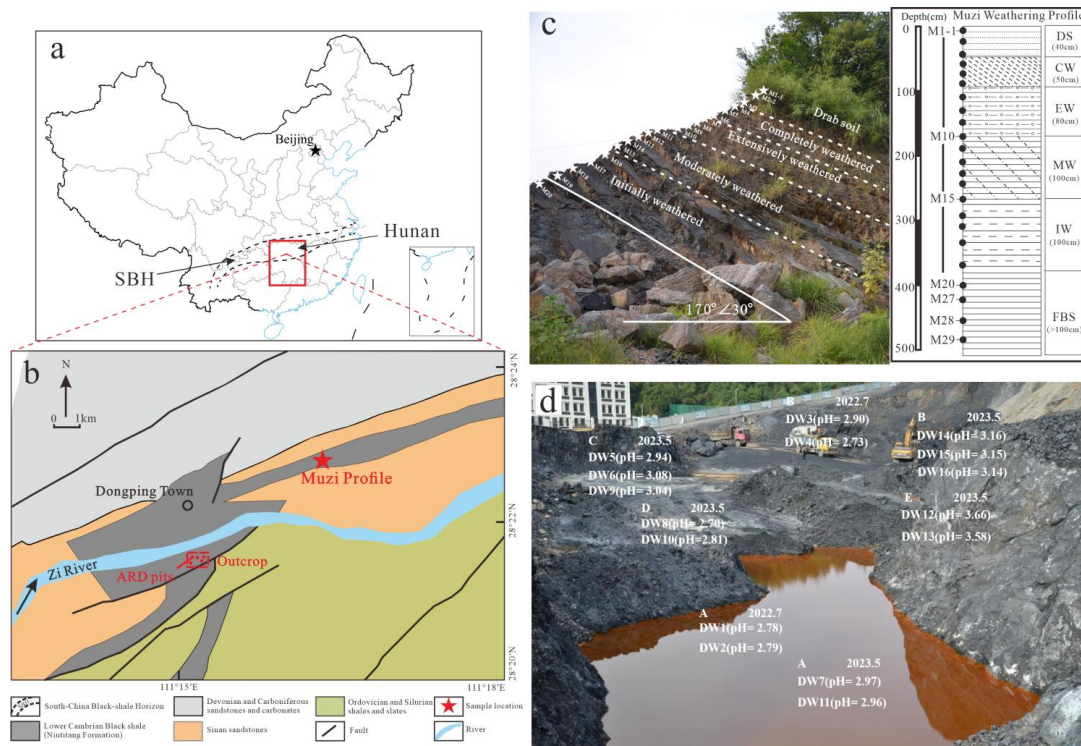


Fig. 1 Location of the black shale outcrop (a), a map showing general geology of the

Dongping outcrop, and locations of the Muzi profile and acid rock drainage (ARD) pits (b), a sketch showing weathering horizons and sampling locations along the Muzi profile (c), and a photo showing an ARD pit and surrounding sampling locations (d)

The profile selected for sampling was a 5-year-old road cutting at the Muzi village (Fig. 1a). It comprises a vertical sequence showing well developed weathering horizons from top to bottom (Fig. 1c): a drab soil horizon (DS), a completely weathered (light-yellowish) horizon (CW), an extensively weathered (yellowish-red) horizon (EW), a moderately (grey white fragment) weathered horizon (MW), an initially weathered (browish grey) shale horizon (IW), and a fresh black shale. Macroscopic features of samples are summarized in supplementary STable 1.

Acid rock drainage (ARD) was collected from five pits in the outcrop in May 2024, representing solutions from black shale weathering (Balci and Gunes, 2024; Wu

et al., 2024b). Rocks including fresh black shales (FBS) and weathered black shales (WBS), and soils derived from black shales (BSS) around ARD pits were also sampled (Fig. 1d). Details of sampling were summarized in STable 1.

2.2 Geochemical analyses

2.2.1 Analyses of rock and soil samples

Rock and soil samples were dried (40 °C), ground and then sieved using a nylon sieve to < 75 µm. The resulting powder was baked at 105 °C to remove adsorbed water prior to analysis. Major elements were measured using X-ray fluorescence (XRF; Rigaku ZSX100e) by fusing 0.5 g of powder and 4.0 g of Li₂B₄O₇ at 1200 °C into a glass disc. Pb and other trace metals were measured using a Perkin–Elmer Elan 6000 ICP-MS instrument with detection limits of approximately 100 µg kg⁻¹ in solid samples. Details of sample chemical treatment, standard materials, and analysis precision can be found in Peng et al. (2024a).

For Pb isotopic analyses, 100 mg of sample (< 75 µm) was solubilized in 1 mL of 8N HBr (overnight), dried, and then dissolved using sub-boiling distilled HF (1 mL) and 14N HNO₃ (0.5 mL) (two days, then dried). The residue was dissolved with 1:1 MilliQ water : concentrated HNO₃. Pb was extracted using a microexchange column of DOWEX-I anion resin (200–400 mesh) in HBr solution. Procedural blanks were lower than 100 mg L⁻¹ for Pb. Pb isotopic ratios (²⁰⁶Pb/²⁰⁴Pb, ²⁰⁷Pb/²⁰⁴Pb, ²⁰⁸Pb/²⁰⁴Pb, ²⁰⁸Pb/²⁰⁶Pb and ²⁰⁷Pb/²⁰⁶Pb) were determined using a VG354 mass spectrometer at the State Key Laboratory of Isotope Geochemistry at Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. Pb isotopic standard NIST-981 was

measured every five samples to determine and update the ratio correction factor. Each sample was measured in 10 replicates with Pb isotopic ratio RSD being < 0.5%. The average Pb isotopic composition values of the standard NIST-981 were $^{206}\text{Pb}/^{204}\text{Pb} = 16.934 \pm 0.007$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.486 \pm 0.012$, and $^{208}\text{Pb}/^{204}\text{Pb} = 36.673 \pm 0.033$ (n = 20). These values are in good agreement with the recalibrated values from a double-spike determination: 16.9322, 15.4855, and 36.6856, respectively (Todt et al., 1993). The precision (2δ) for isotope determination was 0.08%.

2.2.2 Analyses of ARD waters

For analyses of ARD samples, 2 mL of ARD was diluted using 2% ultrapure HNO_3 . Then, Pb isotopic ratios, and concentrations of Pb and other metals were measured also using a VG354 mass spectrometer at the State Key Laboratory of Isotope Geochemistry at Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. Anions (SO_4^{2-} , Cl^- , F^- , and NO_3^-) were also determined using ion chromatography using a Dionex model 2010i as per (Wu et al., 2024b).

2.3 1M HCl extraction

To obtain labile Pb that may include Pb in exchangeable carbonate-, organic-, and oxide-bound fractions, and in acid volatile sulfides (e.g., pyrite) and accessory minerals (e.g., zircon), 0.2 g of selected samples were extracted with 1M HCl (2 mL) for 24h (Philippe et al., 2008). Leachate and residual samples were numbered by adding a suffix S and R on the original sample number, respectively. Residual samples were dissolved as the bulk sample, while leachate samples were dried and MilliQ water washed and then dried again, reconstituted in 1:1 MilliQ water : concentrated

HNO₃. Pb isotopic ratios, and concentrations of Pb and other metals in extractants (leachates and residues) were determined using a Perkin Elmer Optima 5300 ICP-MS at the Future Industries Institute, Adelaide University of Australia.

2.4 Data treatments

2.4.1 Degree of black shale weathering

The degree of rock chemical weathering was estimated using major element compositions of weathered rocks, for which the CIA (chemical index of alteration) (Nesbitt and Young, 1982) has been widely used. The present study also employed this index to rate the black shale weathering, and it was calculated using the Eq.(1) below.

$$CIA = 100 \times Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O) \quad (1)$$

where all variables represent the molar ratios of elements; and CaO* represents CaO in silicate minerals, which is normalized after Roddaz et al. (2006).

2.4.2 Enrichment of Pb and other metals in profile rocks

The enrichment degree of Pb and other trace metals in profile rocks was assessed by calculating enrichment factor (EF) (Peng et al., 2014) using Eq. (2),

$$EF = (C/M)_{\text{sample}} / (C/M)_{\text{NASC}} \quad (2)$$

where (C/M)_{sample} is the ratio of concentration of metal of interest (C) and a reference element (M) in the sample, and (C/M)_{NASC} is that in the NASC (North American

Shale Composition, Gromet et al., 1984). Here, Ti was selected as the reference element as it is less mobile and relatively homogeneously distributed in profile rocks (Peng et al., 2014).

2.4.3 Quantifying mobility of Pb and other metals during weathering

The mobility of Pb, other metals, and Pb isotopes during weathering was estimated using a mass balance calculation. The concentrations of metals of interest and a reference element in both weathered samples ($C_{j,w}$, $C_{i,w}$) and parent rock ($C_{j,p}$, $C_{i,p}$) were compared, and the relative proportion ($\tau_{i,j}$ value) of metal loss was calculated using Eq. (3) (Chadwick et al., 1990) below.

$$\tau_{i,j} = [(C_{j,w} / C_{j,p}) \times (C_{i,p} / C_{i,w})] - 1 \quad (3)$$

where $\tau_{i,j}$ represents the mass transfer coefficient that can inform the loss ($\tau_{i,j} < 0$), re-enrichment ($\tau_{i,j} > 0$), and immobile ($\tau_{i,j} = 0$) of the calculated metals. Here, the FBS samples represented reference parent rock, and Ti was selected as the reference element i for calculation (Peng et al., 2014).

Concentrations of ^{206}Pb , ^{207}Pb , and ^{208}Pb were calculated using isotope ratios based to the primordial stable ^{204}Pb in constant proportion of 1.4% (Sangster et al., 2000; Komárek et al., 2008).

3. Results and discussions

Results from this study focused on the mobility of Pb isotopes during black shale weathering. Data for major elements, Pb and other elemental concentrations, and Pb

isotopic ratios in profile rock and ARD samples from the outcrop are presented in supplementary STable 2. Data from the UCC (upper continental crust, Gao et al., 1999), NASC (North American Shale composition, Gromet et al., 1984), and HBS (Hunan black shales, Peng et al., 2014) were included for comparison.

3.1 Distribution of major elements and chemical weathering

Fresh black shale samples from the outcrop had major element compositions (STable 2) comparable to that of HBS (Peng et al., 2014), but had distinctly lower concentrations of Al_2O_3 and K_2O compared to NASC (Gromet et al., 1984). For the Muzi profile, concentrations of Al_2O_3 , Fe_2O_3 , and K_2O increased slightly from the bottom FBS (M28~M20) to WBS (M18~M4), and to the top BSS. For example, averaged concentrations of Al_2O_3 increased from 9.59% in FBS, to 11.39% in WBS, and to 11.0% in BSS samples. In contrast, MnO, MgO, CaO, Na_2O , P_2O_5 , and LOI (loss on ignition) varied oppositely in rocks along the profile (STabl 2). CIA values ranged from 67 to 74 (mean = 71) in FBS, 75 to 83 (mean = 80) in WBS, and 85 to 87 (mean = 86) in BSS samples (STable 2), increasing significantly in rocks upward the profile. The vertical increase in CIA values corresponds to vertical concentration decreases of mobile elements (MgO, CaO, Na_2O , and LOI) in the rock upward profile (STable 2), matching weathering degree changes identified by rock macroscopic features (e.g., color, texture, Fig. 1b).

3.2 Mobility of Pb and other trace metals

Profile rocks had distinctly higher concentrations of trace metals (Pb, U, Mn, Cu, Mo), but lower concentrations of Th, Zn, V, Cr, Co, Ni, Cd, Ba, Sr, Zr, Hf, Nb, and Ta

(STable 2) compared to NASC (Gromet et al., 1984). Vertical variations of trace metal concentrations were not observed in rocks along the profile, except metals V, Co, Ni, Ba and Sr, which had concentrations decreasing from the FBS to the WBS, and to the BSS samples (STable 2). The EF values relative to NASC (Gromet et al., 1984) showed that Pb, U, Mn, Cu, and Mo were enriched ($EF > 1.5$) while Th, Zn, Cd, V, Cr, Ba, Sr, Zr, Hf, Nb, and Ta were not enriched or deficient in profile rocks ($EF < 1.5$) (Fig. 2a-d).

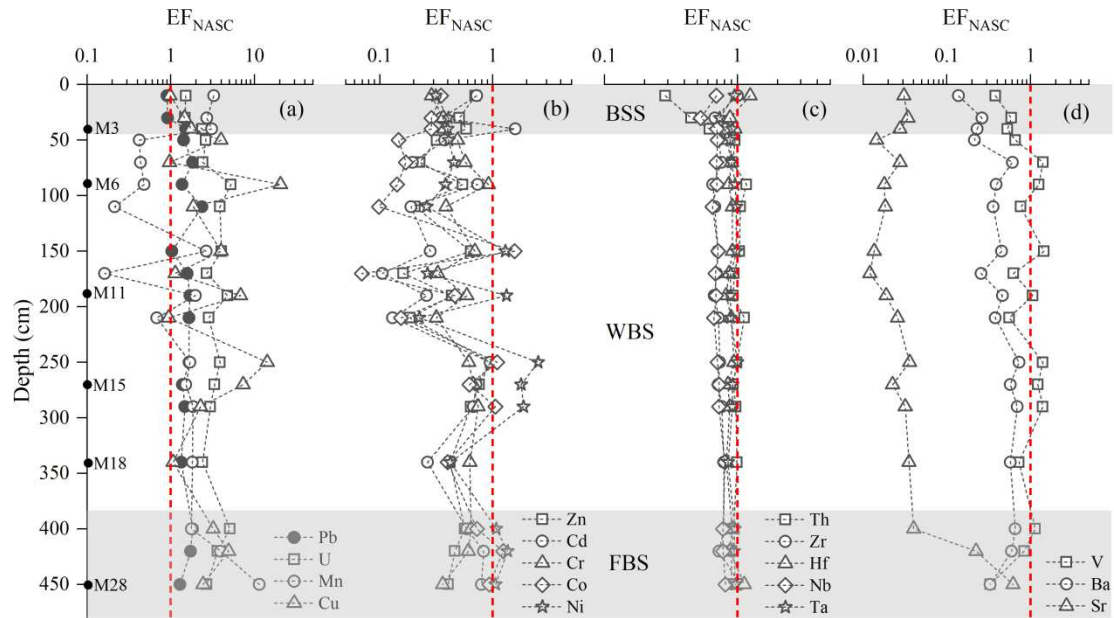


Fig. 2 Vertical variations of EF values of Pb and other trace metals in rocks along MZ profile at the Dongping outcrop in central Hunan province of China

Moreover, the enrichment (EF values) of Pb, U, Th, Mn, V, Co, Ni, Ba, and Sr decreased significantly from the FBS, to WBS, and to the BSS samples (Fig. 2a-d). This may result from either chemical weathering that leads to mass loss of trace metals (e.g., Peng et al., 2004, 2014; Perkins and Mason, 2015; Armstrong et al., 2019;

Wu et al., 2024a), or the heterogeneous distribution of trace metals in parent black shales (e.g., Yu et al., 2012; Wang et al., 2016; Vind et al., 2023), or from both. In contrast, EF values for Zn, Cd, Cr, Cu, Zr, Hf, Nb, and Ta showed negligible vertical variations (Fig. 2a-c).

Mass balance calculations (Eq. 3) showed that Pb, Cd, Co, Ni, Cu, Mo, Ba, and Sr had $\tau_{i,j}$ values mostly < 0 (Fig. 3a, b), with means of -18.8 , -52.0 , -67.0 , -58.0 , -57.5 , -36.4 , -23.7 , and -88.8 (%), respectively, suggesting these metals were released from black shales. As these trace metals are generally hosted in black shale sulfide minerals (e.g., pyrite) and/or carbonates (e.g., calcite), their release is attributed to oxidation of sulfide minerals and carbonate dissolution during weathering (e.g., Yu et al., 2012; Peng et al., 2014; Perkins and Mason, 2015; Wu et al., 2024a; Richardson et al., 2026). Trace metals U, Zn, V, and Cr, had both positive and negative $\tau_{i,j}$ values in profile rocks (Fig. 3c), suggesting these metal were either released or secondary enriched in profile rocks during weathering. While, Th, Zr, Hf, Nb and Ta had $\tau_{i,j}$ values mostly around 0 (Fig. 3d). This suggested that these metals neither released nor secondary enriched in profile rocks, and they were less mobile during black shale weathering (e.g., Wallrich et al., 2020; Santofimia et al., 2022; Qu et al., 2025). Thus, Pb may behave similarly to Cd, Co, Ni, Cu, Mo, Ba and Sr, but differently to U, Zn, V, Cr Th, Zr, Hf, Nb and Ta during black shale weathering.

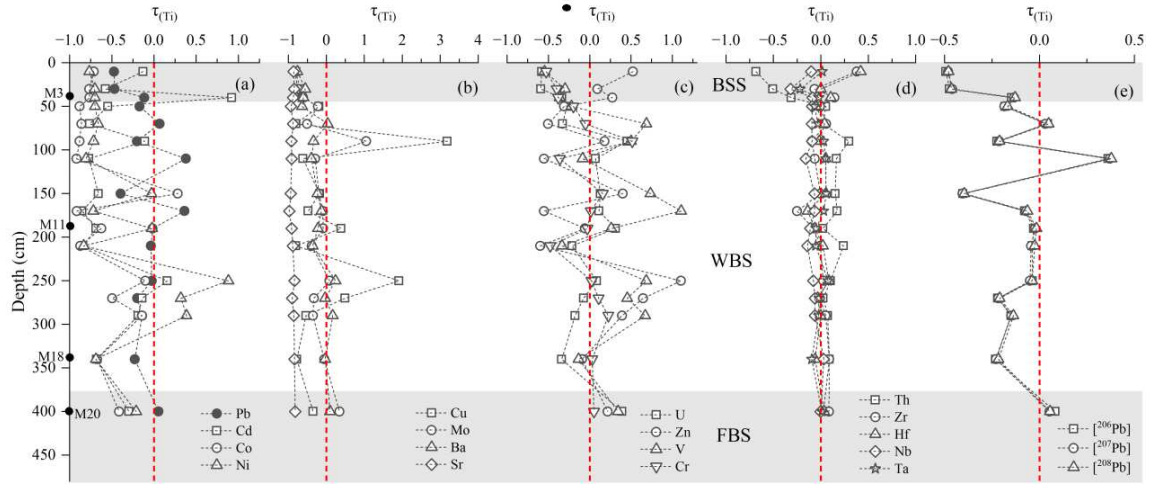


Fig. 3. Vertical variations in mass Change (τ_{ij} values) of Pb and other trace metals in rocks along the Muzi profile at the Dongping outcrop in central Hunan province of China

3.3 Mobility of Pb isotopes during weathering

3.3.1 Distribution of Pb isotopes in profile rocks and ARD

WBS and BSS samples from the profile had Pb isotope ratios (Table 1) ranging from 19.0993 to 19.8902 ($^{206}\text{Pb}/^{204}\text{Pb}$, mean = 19.5344), 15.3946 to 16.0048 ($^{207}\text{Pb}/^{204}\text{Pb}$, mean = 15.6789) and 38.5245 to 39.7648 ($^{208}\text{Pb}/^{204}\text{Pb}$, mean = 39.0056), which exhibited low variability ($C_v < 0.011$) and low vertical variations along the profile. In contrast, the FBS samples had distinctly variable Pb isotope compositions, with $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios ranging from 18.3180 to 33.5710 (mean = 25.4963), 15.5920 to 16.5780 (16.0772), and 38.0637 to 39.2560 (38.7299), respectively. Such variable Pb isotope composition of black shales has been attributed to Pb hosted in different mineral phases such as sulfide minerals (e.g., pyrite), accessory minerals (e.g., apatite, zircon), organic matter, and carbonates (e.g., calcite), which have distinct Pb isotope compositions due to geological process (Jiang et al.,

2006; Derkowski and Marynowski, 2018; Wang et al., 2023; Vind et al., 2023). Compared to profile rock and FBS samples, the black-shale hosted pyrite grains exhibited lower Pb isotope ratios, which ranged from 17.871 to 18.012 ($^{206}\text{Pb}/^{204}\text{Pb}$), 15.501 to 15.693 ($^{207}\text{Pb}/^{204}\text{Pb}$), and 37.571 to 38.342 ($^{208}\text{Pb}/^{204}\text{Pb}$), with $^{208}\text{Pb}/^{206}\text{Pb} \sim 2.1159$ and $^{206}\text{Pb}/^{207}\text{Pb} \sim 1.1506$ (Table 1, STable 2). These values displayed unradiogenic Pb isotopic compositions as those observed in ore deposits in South China (Sangster et al., 2000; Zhu et al., 2001; Cheng and Hu, 2010). Plots of $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{208}\text{Pb}/^{204}\text{Pb}$ ratios showed that the FBS samples were characterized by both less and more radiogenic Pb isotope compositions with Pb isotope ratios significantly linearly correlated ($R^2 > 0.40$). In contrast, profile rock samples were plotted in a field between those of FBS samples and pyrite grains (Fig. 4a, b).

304 **Table 1 Statistical results of Pb isotope ratios in FBS, WBS, BSS, ARD water, and pyrite grin samples from Dongping black shale outcrop in central**
305 **Hunan province of China.**

Ratio		$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$
FBS (n = 16)	Range	18.3180 ~ 33.5710	15.5920 ~ 16.5780	38.0637 ~ 39.2560	1.1660 ~ 2.0887	1.1673 ~ 2.0250
	Mean	25.4963	16.0772	38.7299	1.5922	1.5797
ARD (n = 11)	Range	22.0567 ~ 37.4257	15.8873 ~ 16.8191	38.2704 ~ 38.8887	1.0359 ~ 1.7496	1.3883 ~ 2.2252
	Mean	29.5495	16.3434	38.7234	1.3345	1.8048
WBS (n = 15)	Range	19.0993 ~ 19.8902	15.3946 ~ 16.0048	38.5245 ~ 39.7648	1.9666 ~ 2.0194	1.2208 ~ 1.2675
	Mean	19.5344	15.6789	39.0056	1.9969	1.2460
BSS (n = 5)	Range	18.6839 ~ 19.5048	15.6026 ~ 15.9789	38.5688 ~ 39.1076	2.0049 ~ 2.0697	1.1911 ~ 1.2242
	Mean	18.9675	15.8555	38.7865	2.0449	1.1963
Pyrite (n = 12)	Range	18.8710 ~ 18.0120	15.5010 ~ 15.6930	37.5710 ~ 38.3420	2.1022 ~ 2.1354	1.1409 ~ 1.1552
	Mean	17.9524	15.6034	37.9864	2.1159	1.1506

306 FBS, ARD, WBS, and BSS represent fresh black shales, acid rock drainage waters, weathered black shales, and soils derived from black shales,
307 respectively; for details, see supplementary STable 2

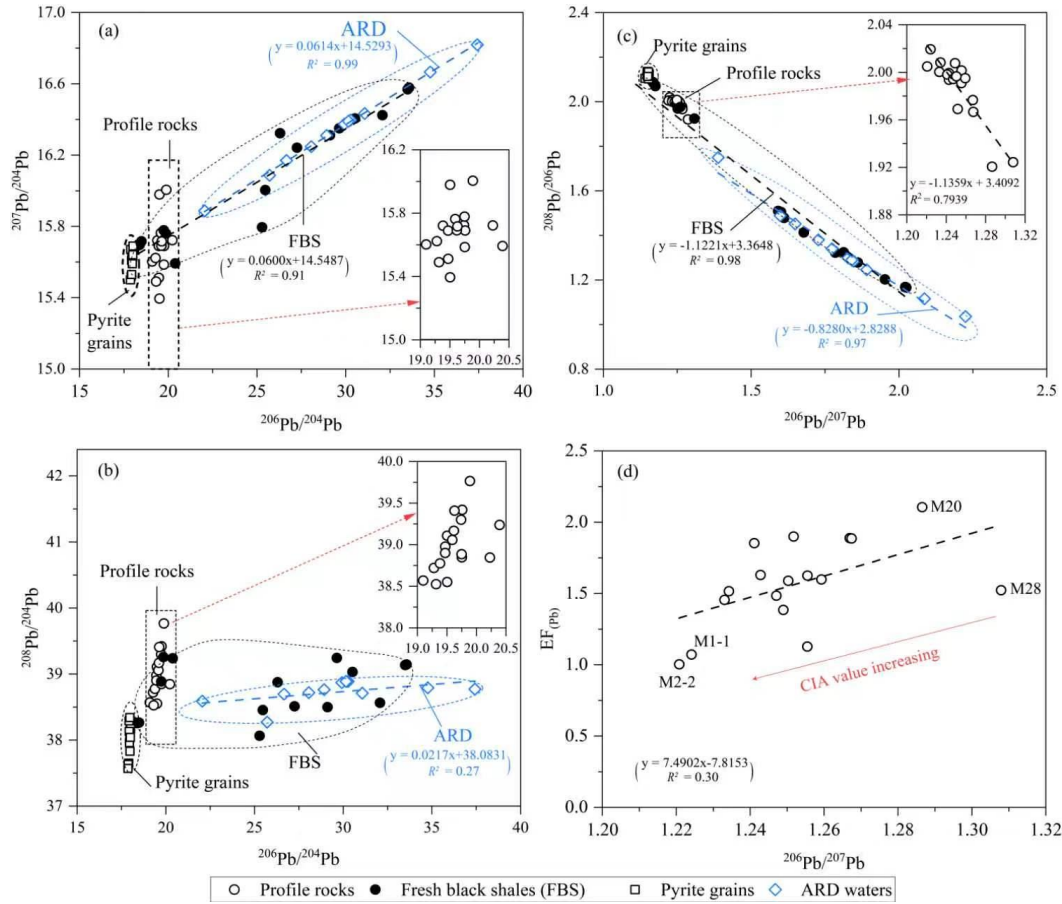


Fig. 4. Plots of $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ (a), $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{208}\text{Pb}/^{204}\text{Pb}$ (b), and $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$ (c) ratios of profile rock, FBS (this study, and Jiang et al., 2006), pyrite grain, and ARD samples. Plots of $^{206}\text{Pb}/^{207}\text{Pb}$ ratios vs. enrichment factor (EF) values of Pb (d) in profile rocks from the Dongping outcrop in central Hunan province of China are also shown

ARD that were dominated by Fe^{3+} and SO_4^{2-} (Wu et al., 2024b) also had distinctly variable Pb isotopic composition with ratios ranging from 22.0567 to 37.4257 ($^{206}\text{Pb}/^{204}\text{Pb}$, mean = 29.5495), 15.8873 to 16.8191 ($^{207}\text{Pb}/^{204}\text{Pb}$, mean = 16.3434) and 38.2704 to 38.8887 ($^{208}\text{Pb}/^{204}\text{Pb}$, mean = 38.7234) (Table 1). Plots of $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{208}\text{Pb}/^{204}\text{Pb}$ ratios for ARD samples were similar to FBS samples (Fig. 4a, b), with distinct $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{207}\text{Pb}$

ratios (Table 1). This indicates that the Pb isotopes of ARD were resulted from black shale weathering (Komárek et al., 2008; Bird, 2011).

3.3.2 Mobility of Pb isotopes during black shale weathering

Mass balance calculations for Pb isotope concentrations based on ^{204}Pb (Sangster et al., 2000; Komárek et al., 2008) showed that ^{206}Pb , ^{207}Pb , and ^{208}Pb had $\tau_{i,j}$ values mostly $< -10.0\%$ (except sample M7), suggesting release of Pb isotopes during weathering (Fig. 3e). Mass loss of total Pb isotopes ($^{206}\text{Pb} + ^{207}\text{Pb} + ^{208}\text{Pb}$) was equal to that determined by quantifying Pb concentration in bulk samples. For example, the calculated mass loss of total Pb isotopes in sample M1-1 was 12.75 mg/kg compared to a measured concentration loss of 12.26 mg/kg (Table 2). The release of ^{206}Pb , ^{207}Pb , and ^{208}Pb (Fig. 3e) can be illustrated by positive correlation of Pb EF values to $^{206}\text{Pb}/^{207}\text{Pb}$ ratios (Fig. 4d) and by negative correlations of CIA values to $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$, and $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of profile rocks (Fig. 5a-d).

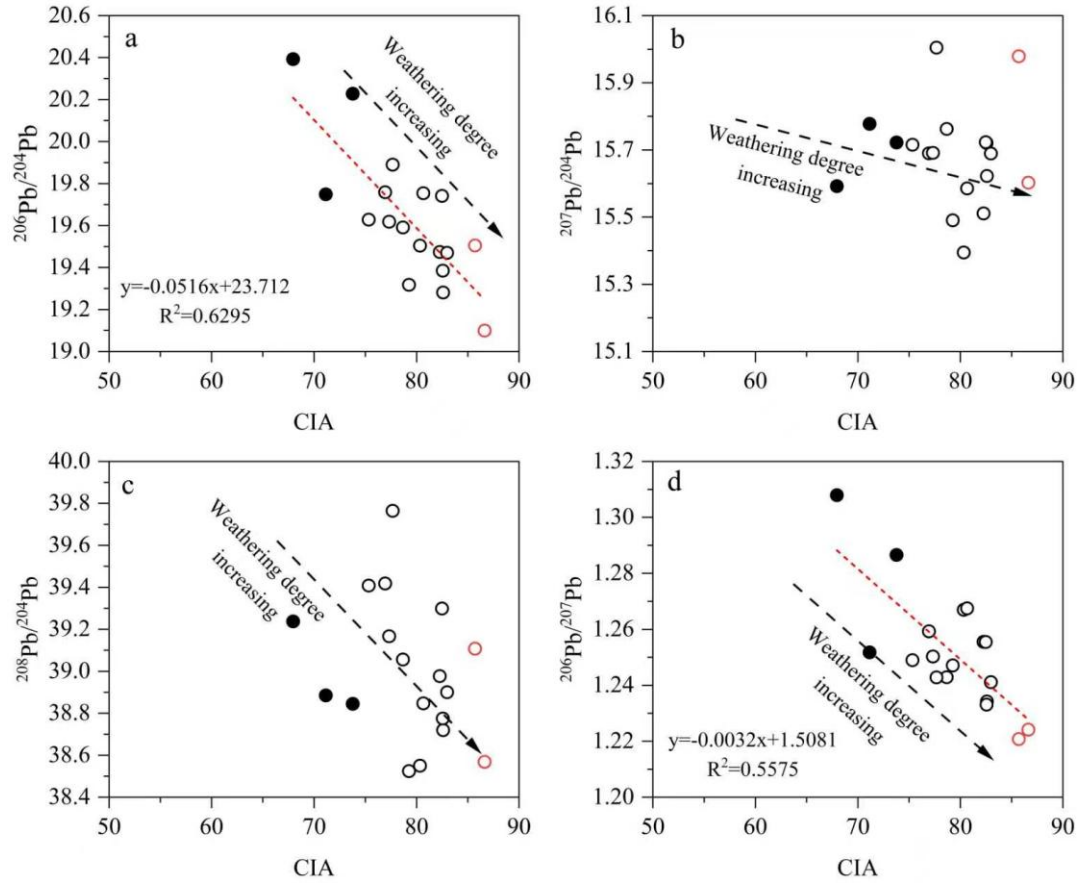


Fig. 5 Plots of CIA values against $^{206}\text{Pb}/^{204}\text{Pb}$ (a), $^{207}\text{Pb}/^{204}\text{Pb}$ (b), $^{208}\text{Pb}/^{204}\text{Pb}$ (c), and $^{206}\text{Pb}/^{207}\text{Pb}$ (d) ratios of profile rocks, showing release of Pb isotopes due to weathering along the Muzi profile at the Dongping outcrop in central Hunan province of China. FBS: black dot, WBS: black circle, and BSS: red circle

The plot of $^{206}\text{Pb}/^{207}\text{Pb}$ vs. $^{208}\text{Pb}/^{206}\text{Pb}$ ratios (Fig. 4c) shows that Pb isotope ratios of the profile rock, FBS, pyrite grain, and ARD samples, align along a characteristic mixing line ($R^2 = 0.98$), in which profile rock ratios also align along this mixing line ($R^2 = 0.79$). In addition, isotopic ratios of profile rocks fell in a field between pyrite grains and FBS samples (Fig. 4c) indicating that profile rocks may have originally consist of two-endmember sources: the unradiogenic Pb isotopes in pyrite grains, and the more radiogenic Pb isotopes in FBS. Pb isotopic ratios of profile

rocks may thus result from the release of unradiogenic Pb isotopes in pyrite grains and of the more radiogenic Pb isotopes in accessory minerals and organic matter where the more radiogenic Pb isotopes can be produced by the decay of ^{235}U , ^{238}U and ^{232}Th (Perkins and Mason, 2015; Rimstidt et al., 2017; Wang et al., 2023). Therefore, Pb isotope mobility during black shale weathering is characterized by preferential release of both unradiogenic and more radiogenic Pb isotopes (^{206}Pb , ^{207}Pb , and ^{208}Pb) (e.g., Perkins and Mason, 2015; Dausmann et al., 2019; Wang et al., 2023), as also indicated by plots of $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{208}\text{Pb}/^{204}\text{Pb}$ ratios (Fig. 4a, b).

Moreover, the similar Pb isotope compositions of ARD and FBS samples (Fig. 4a-c) can provide direct evidence of release of both unradiogenic and more radiogenic Pb isotopes from black shales, as ARD represent weathering solutions leached from weathering systems (Cheema et al., 2020; Guillevic et al., 2024; Rosca et al., 2024; Kamenov and Scott, 2026), collecting Pb isotopes released from alterations of different mineral phases (Millot and Négrel, 2013; Dausmann et al., 2019). In addition, 1M HCl extraction of FBS samples illustrated that leachates (S) and residues (R) had distinctly variable Pb isotope compositions, for which leachates had Pb isotope ratios lower than that of residues and bulk FBS samples (except samples MR1 and M33) (Fig. 6a, b; and STable 2) highlighting that there were mobile Pb isotopes (both the unradiogenic and radiogenic) in FBS samples. In contrast, leachates (S) and residues (R) from 1M HCl extracted profile rocks had Pb isotope compositions similar to each other and to that of bulk profile rocks (Fig. 6a, b, and STable 2), suggesting that

profile rocks had limited mobile Pb isotopes, which were poorly extracted by 1M HCl (Philippe et al., 2008; Peng et al., 2022a) due to their prior release during weathering.

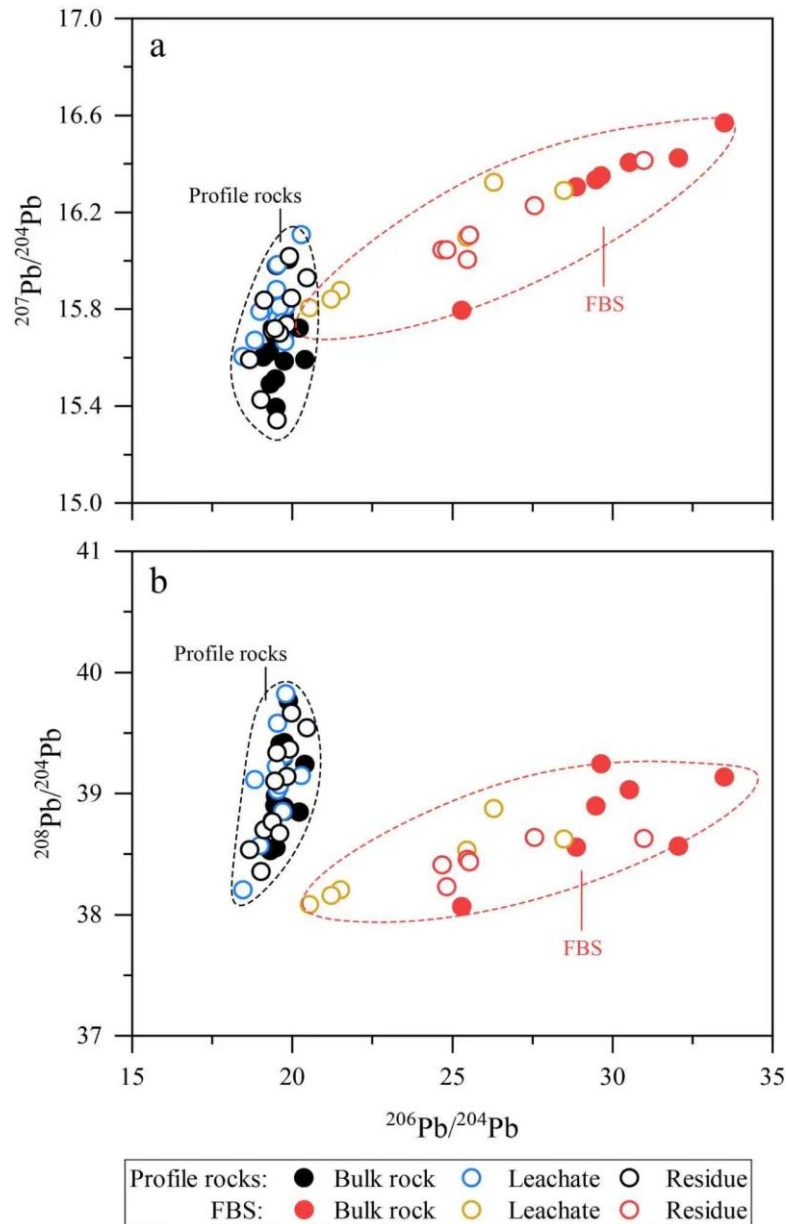


Fig. 6 Plots of $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{207}\text{Pb}/^{204}\text{Pb}$ (a) and $^{206}\text{Pb}/^{204}\text{Pb}$ vs. $^{208}\text{Pb}/^{204}\text{Pb}$ (b) ratios of bulk rocks, leachates (S) and residues (R) from 1M HCl extractions of profile rock and FBS samples, illustrating leachates from FBS extractions having Pb isotope ratios lower than bulk FBS, while extracts from profile rocks having similar Pb isotope ratios to bulk rock samples

3.4 Implications on Pb isotopes used as an environmental tracer

Although non-traditional isotopes such as Mn, Zn, Cu, and Cr have been widely used in tracing and apportionment of metal contaminant sources in the environment (e.g., Ostrander et al., 2022; Scheiderich et al., 2023), Pb isotopes will still be utilized in the environmental source study because analysis of Pb isotopes is less costly and labor-intensive (Cheng and Hu, 2010), and Pb isotopes are immeasurably differentiated during surface processes such as rock weathering, soil erosion, metal transportation, and precipitation (Cheyne et al., 2018; Cheema et al., 2020; Geng et al., 2024).

Natural archives are important for evaluating and discriminating natural and anthropogenic sources of metallic contaminants in the environment (Komárek et al., 2008). Distribution of Pb isotopes in the FBS, pyrite grain, profile rock, and ARD samples (Table 1) from the Dongping outcrop identified that Pb isotopes represent a powerful fingerprinting tool that can identify Pb in different geological materials. Pyrite grains have Pb isotope ratios similar to that dispersed from metallic ore mines (Sangster et al., 2000; Zhu et al., 2001), and unradiogenic Pb isotopes can represent signatures of Pb isotopes contributed from anthropogenic inputs in the environment. Therefore, discriminating environmental Pb from natural sources to those of anthropogenic inputs is achievable at small spatial scale (Cheng and Hu, 2010; Bird, 2011).

Profile rocks from the outcrop had Pb isotopic ratios with minor variation, ranging between those of FBS samples and pyrite grains (Table 1, Fig. 4a-c). Such a

homogeneous distribution pattern of Pb isotopes in profile rocks (Fig. 4a-c) may result from averaging the Pb isotopic compositions of black shales by chemical weathering (Peng et al., 2022a). Profile rocks provide an important source of material for the formation of local sediments and soils and, consequently, impart their Pb isotopic signatures to these natural environmental matrices. Relatively homogeneous Pb isotopic ratios have been reported in riverine sediments (Shetaya et al., 2019; Söfke et al., 2019; Peng et al., 2022a), soils (Walraven et al., 2013; Wei et al., 2021), and Chinese eolian deposits (Sun and Zhu, 2010), reflecting that the Pb isotopic composition of the underlying geological units was modified by weathering. This relatively consistent isotopic signature provides a basis for using Pb isotopes to distinguish natural geological sources from subsequent anthropogenic inputs of Pb and other metal contaminants (Sangster et al., 2000; Komárek et al., 2008; Cheng and Hu, 2010). Anthropogenic Pb inputs can alter the natural isotopic composition of sediments and soils (Peng et al., 2022a, b), with deviations from the prevailing geological signature providing evidence of contamination and insights into its potential sources. Therefore, the present study suggests that if the homogeneous Pb isotope ratios of local sediments and soils have shifted to distinctly heterogeneous Pb isotope ratios, local sediments and soils in the environment may have been contaminated by additional anthropogenic inputs.

4. Conclusions

Results of this study describe Pb isotopic ratios and elemental composition of rocks from the Muzi weathering profile and acid rock drainages from the Dongping

black shale outcrop in central Hunan (China). The following conclusions were supported by this study.

(1) Black shales in the area had major elemental compositions comparable to that of North American Shale. Major elements in profile rocks showed that weathering degree increased from the bottom of fresh black shales, upward to weathered black shales, and to top soils. This was complemented with vertical decreases in the concentration of mobile elements including MnO, MgO, CaO, Na₂O, P₂O₅ and LOI, and by increases in CIA values along the rock profile.

(2) Profile rocks were significantly enriched in trace metals Pb, Cu, Ni, Zn, Cd, and Mo (EF > 1.5), and mass balance calculation for metal τ_{ij} values showed that metals Pb, Cd, Co, Ni, Cu, Mo, Ba and Sr were released (τ_{ij} < 0) from black shales during weathering.

(3) Black shales from the outcrop had distinctly variable Pb isotope compositions, while profile rocks were characterized by Pb isotope ratios in minor variation, with Pb isotopic ratios ($^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and, $^{208}\text{Pb}/^{204}\text{Pb}$) ranging between those of black shales and pyrite grains that were hosted in black shales. Pb isotopes (^{206}Pb , ^{207}Pb , and ^{208}Pb) were mobile during weathering, while mobility of Pb isotopes was characterized by preferential release of unradiogenic Pb isotopes in pyrite grains and more radiogenics from the decay of U and Th in accessory minerals and organic matter during black shale weathering.

(4) Pb isotopes represent a powerful fingerprinting tool that can be used to discriminate environmental Pb of natural sources from those of anthropogenic inputs at small spatial scale. The relatively homogeneous distribution of Pb isotopes in profile rocks set a geological background for using Pb isotopes to trace and identify metallic contamination in the environment.

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References

- Åhlgren, K., Sjöberg, V., Allard, B., Bäckström, M. (2021). Groundwater chemistry affected by trace elements (As, Mo, Ni, U and V) from a burning alum shale waste deposit, Kvarntorp, Sweden. *Environ. Sci. Pollut. Res.*, 28, 30219-30241.
- Armstrong, J. G. T., Parnell, J., Bullock, L. A., Boyce, A. J., Perez, M., Feldmann, J. (2019). Mobilisation of arsenic, selenium and uranium from Carboniferous black shales in west Ireland. *Appl. Geochem.*, 109, 104401.
- Balci, N., Gunes, Y. (2024). Generation and geochemical characteristics of acid rock drainage (ARD) in Barton Peninsula, King George Island (KGI), maritime, Antarctica. *Sci. Total Environ.*, 954, 176727.
- Bird, G. (2011). Provenancing anthropogenic Pb within the fluvial environment: Developments

and challenges in the use of Pb isotopes. *Environ. Intern.*, 37, 802-819.

Chadwick, O. A., Brimhall, G. H., Hendricks, D. M. (1990). From a black to a gray box: a mass balance interpretation of pedogenesis. *Geomorphology*, 3, 369-390.

Charbonnier, Q., Bouchez, J., Gaillardet, J., Calmels, D., Dellinger, M. (2022). The influence of black shale weathering on riverine barium isotopes. *Chem. Geol.*, 594, 120741.

Cheema, A. I., Liu, G., Yousaf, B., Abbas, Q., Zhou, H. (2020). A comprehensive review of biogeochemical distribution and fractionation of lead isotopes for source tracing in distinct interactive environmental compartments. *Sci. Total Environ.*, 719, 135658.

Cheng, H., Hu, Y. (2010). Lead (Pb) isotopic fingerprinting and its applications in lead pollution studies in China: A review. *Environ. Pollut.*, 158, 1134-1146.

Cheyne, C.A.L., Thibodeau, A.M., Slater, G.F., Bergquist, B.A. (2018). Lead isotopes as particulate contaminant tracers and chronostratigraphic markers in lake sediments in northeastern North America. *Chem. Geol.*, 477, 47-57.

Dausmann, V., Gutjahr, M., Frank, M., Kouzmanov, K., Schaltegger, U. (2019). Experimental evidence for mineral-controlled release of radiogenic Nd, Hf and Pb isotopes from granitic rocks during progressive chemical weathering. *Chem. Geol.*, 507, 64-84.

Derkowski, A., Marynowski, L. (2018). Binding of heavy metals by oxidised kerogen in (palaeo)weathered black shales. *Chem. Geol.*, 493, 441-452.

Erel, Y., Blum, J. D., Roueff, E. (2004). Lead and strontium isotopes as monitors of experimental granitoid mineral dissolution. *Geochim. Cosmochim. Acta*, 68(22), 4649-4663.

Gao, S., Lu, T. C., Zhang, B. R., Zhang, H. F., Han, W. L., Zhao, Z. D. (1999). Structure and chemical compositions of East China upper continental crust. *Sci. China (series-D)*, 42(2), 129-140 (in Chinese).

Geng, T., Péron, O., Mangeret, A., Montavon, G., Gourgiotis, A. (2024). Tracing the impact of former uranium mine sites using stable Pb isotopes: A review. *J. Environ. Radioactivity*, 280, 107547.

Gromet, L. P., Dymek, R. F., Haskin, L. A., Korotev, R. L. (1984). The "North American shale composite": its compilation, major and trace element characteristics. *Geochim. Cosmochim. Acta*, 48, 2469-2482.

500 Guillevic, F., Rossi, M., Resongles, E., Freydier, R., Ferrari, C., Quantin, C., Monvoisin, G.,
 501 Poulenard, J., Arnaud, F. (2024). Multi-isotope (Pb, Sb) approach to trace metallic contaminant
 502 sources at a historical mining and metallurgical site. *Chem. Geol.*, 649, 121958.
 503 Harlavan, Y., Erel, Y., Blum, J. D. (2009). The coupled release of REE and Pb to the soil labile
 504 pool with time by weathering of accessory phases, Wind River Mountains, WY. *Geochim.*
 505 *Cosmochim. Acta*, 73, 320-336.
 506 Jeong, H., Ryu, S., Ra, K., 2022. Characteristics of potentially toxic elements and multi-isotope
 507 signatures (Cu, Zn, Pb) in non-exhaust traffic emission sources. *Environ. Pollut.* 292, 118339.
 508 Jiang, S.Y., Chen, Y.J., Ling, Y.F., Yang, Z.H., Feng, H.Z., Ni, P. (2006). Trace- and rareearth
 509 element geochemistry and Pb–Pb dating of black shales and intercalated Ni–Mo–PGE–Au
 510 sulfide ores in Lower Cambrian strata, Yangtze Platform, South China. *Miner. Deposita*, 41,
 511 453-467.
 512 Johnson, J. D., Graney, J. R. (2015). Fingerprinting Marcellus shale waste products from Pb
 513 isotope and trace metal perspectives. *Appl. Geochem.*, 60, 104-115.
 514 Kamenov, G. D., Scott, S. (2026). New insights on the Pb isotopic compositions of drinking water
 515 lead pipes in the United States. *Appl. Geochem.*, 196, 106639.
 516 Kong, J., Guo, Q., Wei, R., Strauss, H., Zhu, G., Li, S., Song, Z., Chen, T., Song, B., Zhou, T.,
 517 Zheng, G. (2018). Contamination of heavy metals and isotopic tracing of Pb in surface and
 518 profile soils in a polluted farmland from a typical karst area in southern China. *Sci. Total*
 519 *Environ.*, 637/638, 1035-1045.
 520 Komárek, M., Ettler, V., Chrastný, V., Mihaljevič, M. (2008). Lead isotopes in environmental
 521 sciences: A review. *Environ. Intern.* 34, 562-577.
 522 Kousehlar, M., Widom, E. (2019). Sources of metals in atmospheric particulate matter in Tehran,
 523 Iran: Tree bark biomonitoring. *Appl. Geochem.*, 104, 71-82.
 524 Lee, S., Han, C., Ahn, J., Han, Y., Lee, A., Ro, S., Hong, S. (2022). Characterization of trace
 525 elements and Pb isotopes in PM_{2.5} and isotopic source identification during haze episodes in
 526 Seoul, Korea. *Atm. Pollut. Res.*, 13, 101442.
 527 Mao, C., Rao, W., Li, T., Jin, K., Wang, S. (2024). Lead isotope compositions and modern
 528 sediments sources in the radial sand ridges from the Jiangsu coast, East China. *Appl. Geochem.*,

160, 105858.

Millot, R., Négrel, P. (2013). Chemical weathering of granitic rocks: an experimental approach and Pb-Li isotope tracing. *Procedia Earth and Planetary Science*, 7, 590–593.

Nesbitt, H. W., Young, G. M. (1982). Early Proterozoic climates and plate motions inferred from major element chemistry of lutites. *Nature*, 299, 715-717.

Noireaux, J., Sullivan, P. L., Gaillardet, J., Louvat, P., Steinhofel, G., Brantley, S. L. (2021). Developing boron isotopes to elucidate shale weathering in the critical zone. *Chem. Geol.*, 559, 119900.

Ostrander, C. M., Severmann, S., Gordon, G. W., Kendall, B., Lyons, T. W., Zheng, W., Roy, M., Anbar, A. D. (2022). Significance of ^{56}Fe depletions in late-Archean shales and pyrite. *Geochim. Cosmochim. Acta*, 316, 87-104.

Pacín, C., Aboal, J. R., Fernández, J. A., Vázquez-Arias, A., Šípková, A., Komárek, M., Chrástný, V. (2025). The return of natural lead to the Northeast Atlantic Ocean captured by brown algae. *J. Hazard. Mater.*, 496, 139289.

Peng, B., Song, Z. L., Tu, X. L., Lv, H. Z., Wu, F. C. (2004). Release of heavy metals during weathering of the Lower Cambrian black shales in western Hunan, China. *Environ. Geol.*, 45(8), 1137-1147.

Peng, B., Rate, A., Song, Z., Yu, C., Tang, X., Xie, S., Tu, X., Tan, C. (2014). Geochemistry of major and trace elements and Pb-Sr isotopes of a weathering profile developed on the Lower Cambrian black shales in central Hunan, China. *Appl. Geochem.*, 51, 191-203.

Peng, B., Juhasz, A., Fang, X. H., Jiang, C. X., Wu, S. C., Li, X. M., Xie, S. R., Dai, Y. N. (2022a). Lead isotopic fingerprinting as a tracer to identify the sources of heavy metals in sediments from the Four River inlets to Dongting Lake, China. *Catena*, 219, 106594.

Peng, B., Chen, H. S., Fang, X. H., Xie, S. R., Wu, S. C., Jiang, C. X., Dai, Y. N. (2022b). Distribution of Pb isotopes in different chemical fractions in bed sediments from lower reaches of the Xiangjiang River, Hunan province of China. *Sci. Total Environ.*, 829, 154394.

Perkins, R. B., Mason, C. E. (2015). The relative mobility of trace elements from short-term weathering of a black shale. *Appl. Geochem.*, 56, 67-79.

Philippe, S., Leterme, C., Lesourd, S., Courcot, L., Haack, U. (2008). Bioavailability of

558 sediment-borne lead for ragworms (*Hediste diversicolor*) investigated by lead isotopes. *Appl.*
559 *Geochem.*, 23, 2932-2944.

560 Qu, Y., Peng, B., Wu, S., Du, X., Wu, N., 2025. Mobility of high strength elements during
561 weathering of black shales in central Hunan province, China. *Quaternary Sci.*, 45(6), 1511-1526.

562 Reimann, C., Fabian, K., Flem, B., Schilling, J., Roberts, D., Englmaier, P. (2016). Pb
563 concentrations and isotope ratios of soil O and C horizons in Nord-Trøndelag, central Norway:
564 Anthropogenic or natural sources? *Appl. Geochem.*, 74, 56-66.

565 Richardson, J. B., Porterfeld, O. C., Schroth, A. S., Friedland, A. J., Kaste, J. M. (2026).
566 Pollutant lead mobility in forest soils of the northeastern United States evaluated with a 40-Year
567 resampling study. *Water Air Soil Pollut.*, 237, 564.

568 Rimstidt, J. D., Chermak, J. A., Schreiber, M. E. (2017). Processes that control mineral and
569 element abundances in shales. *Earth-Sci Reviews*, 171, 383-399.

570 Rosca, C., Junginger, A., Kübler, S., Babechuk, M. G., Olaka, L. A., Schoenberg, R. (2024).
571 Isotopic and trace element record of changing metal source contributions to tropical freshwater
572 Lake Naivasha (Kenya). *Sci. Total Environ.*, 951, 175082.

573 Sangster, D. F., Outridge, P. M., Davis, W. J. (2000). Stable lead isotope characteristics of lead ore
574 deposits of environmental significance. *Environ. Rev.*, 8, 115-147.

575 Santofimia, E., González, F. J., Rincón-Tomás, B., López-Pamo, E., Marino, E., Reyes, J., Bellido,
576 E. (2022). The mobility of thorium, uranium and rare earth elements from Mid Ordovician
577 black shales to acid waters and its removal by goethite and schwertmannite. *Chemosphere*, 307,
578 135907.

579 Scheiderich, K., Zerkle, A. L., Damby, D. (2023). Chromium isotopes in an acidic fluvial system:
580 Implications for modern and ancient Cr isotope records. *Geochim. Cosmochim. Acta*, 354,
581 123-145.

582 Shetaya, W. H., Marzouk, E. R., Mohamed, E. F., Baileyc , E. H., Young, S. D., 2019. Chemical
583 and isotopic fractionation of lead in the surface soils of Egypt. *Chem. Geol.* 608,121046.

584 Sun, J., Zhu, X. (2010). Temporal variations in Pb isotopes and trace element concentrations
585 within Chinese eolian deposits during the past 8 Ma: Implications for provenance change. *Earth*
586 *Planet. Sci. Lett.*, 290, 438-447.

587 Sűfke, F., Gutjahr, M., Gilli, A., Anselmetti, F. S., Glur, L., Eisenhauer, A. (2019). Early stage
588 weathering systematics of Pb and Nd isotopes derived from a high-Alpine Holocene lake
589 sediment record. *Chem. Geol.*, 507, 42-53.

590 Todt, W., Cliff, R. A., Hanser, A., Hofmann, A. W. (1993). Re-calibration of NBS lead standards
591 using a $^{202}\text{Pb}+^{205}\text{Pb}$ double spike. *Terra Abstracts*, 5 (Suppl 1), 396.

592 Vind, J., Offli, S., Mänd, K., Soesoo, A., Kirsimäe, K. (2023). Redox-sensitive trace metal
593 hyper-enrichment in Tremadocian alum Shale (graptolite argillite) in northwestern Estonia,
594 Baltic Palaeobasin. *Chem. Geol.*, 640, 121646.

595 Wallrich, I. L. R., Stewart, B. W., Capo, R. C., Hedin, B. C., Phan, T. T., 2020. Neodymium
596 isotopes track sources of rare earth elements in acidic mine waters. *Geochim. Cosmochim. Acta*.
597 269, 465-483.

598 Walraven, N., van Gaans, P.F.M., van der Veer, G., van Os, B.J.H., Klaver, G.T., Vriend, S. P.,
599 Middelburg, J.J., Davies, G.R., 2013. Lithologically inherited variation in Pb isotope ratios in
600 sedimentary soils in The Netherlands. *Appl. Geochem.* 37, 228-241.

601 Wang, Z., Hill, R., Williams, G., Dwyer, G. S., Hu, J., Schnug, E., Bol, R., Sun, Y., Coleman, D. S.,
602 Liu, X. M., Sandstrom, M. R., Vengosh, A., 2023. Lead isotopes and rare earth elements
603 geochemistry of global phosphate rocks: Insights into depositional conditions and
604 environmental tracing. *Chem. Geol.* 639, 121715.

605 Wen, Y., Li, W., Yang, Z., Zhang, Q., Ji, J., 2020. Enrichment and source identification of Cd and
606 other heavy metals in soils with high geochemical background in the karst region, Southwestern
607 China. *Chemosphere* 245, 125620.

608 Wei, W., Li, X., Ling, S., Wu, X., Liao, X., 2021. Heavy metal(loid) and Pb isotope compositions
609 of black shale weathering profiles on the northern Yangtze Platform: insights into geochemical
610 behavior, contamination assessment, and source apportionment. *Environ. Sci. and Pollut. Res.* 28,
611 50230-50244.

612 Wu, B., Wu, X., Qiao, S., Shi, X., Hu, L., Song, J., Li, X., Liu, S., Liu, J., Bai, Y., Zhang, J., Zhu,
613 A. Kornkanitnan, N., Khokiattiwong, S., 2022. Sedimentary lead isotopic signatures in relation
614 to anthropogenic emissions in Asia: A comparative study in the Yellow Sea and Gulf of
615 Thailand. *Chem. Geol.* 608, 121046.

616 Wu, B., Peng, B., Zhang, K., Kuang, X., 2016. A new chemical index for identifying the
617 weathering degree of black shales. *Acta Geologica Sinica* 90(4), 818-832.

618 Wu, S. C., Peng, B., Wu, N. Q., Xie, S. R., Yang, X., Fang X. H., Song, Z. L., 2024a. Mobility and
619 environmental impact of cadmium (Cd) during weathering of carbonaceous black shales in
620 western Hunan, China. *J. Hazard. Mater.* 470, 134267.

621 Wu, N., Peng, B., Juhasz, A., Hu, H., Wu, S., Yang, X., Dai, Y., Wang, X., 2024b. Mobility and
622 fractionation of rare earth elements during black shale weathering: Implications from acid rock
623 drainage and sequential extraction study. *Sci. Total Environ.* 954,176282.

624 Yu, C., Peng, B., Peltola, P., Tang, X., Xie, S. (2012). Effect of weathering on abundance and
625 release of potentially toxic elements in soils derived from Lower-Cambrian black shales, P. R.
626 China. *Environ. Geochem. Health.*, 34, 375-390.

627 Zhu, B. Q., Chen, Y. W., Peng, J. H. (2001). Lead isotope geochemistry of the urban environment
628 in the Pearl River Delta. *Appl. Geochem.*, 16, 409-417.

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