Iron from continental weathering dictated soft-part preservation during the Early Ordovician

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Farid Saleh[1,2*], Victoire Lucas[3], Bernard Pittet[3], Bertrand Lefebvre[3], Stefan V. Lalonde[4], Pierre Sansjofre[5]

[1] Yunnan Key Laboratory for Palaeobiology, Institute of Palaeontology, Yunnan University, Kunming, China
[2] MEC International Joint Laboratory for Palaeobiology and Palaeoenvironment, Institute of Palaeontology, Yunnan University, Kunming, China
[3] Université de Lyon, Université Claude Bernard Lyon 1, École Normale Supérieure de Lyon, CNRS, UMR5276, LGL-TPE, Villeurbanne, France
[4] University of Brest, CNRS, IUEM Institut Universitaire Européen de la Mer, UMR 6538 Laboratoire Géosciences Océan, Place Nicolas Copernic, 29280 Plouzané, France
[5] MNHN, Sorbonne Université, CNRS UMR 7590, IRD, Institut de Minéralogie, Physique des Matériaux et de Cosmochimie, Paris, France
Corresponding authors:
F. Saleh (farid.nassim.saleh@gmail.com)

SHORT RUNNING TITLE: Continental Fe in the Fezouata Shale

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article.

ETHICAL AND CONFLICT OF INTEREST STATEMENTS

We hereby confirm that all the data and interpretations are new and have not been published elsewhere. All authors have been involved in this work, and approved the manuscript and agreed to this submission. Authors declare having no conflict of interest, and that they developed this study ethically, and according to the guidelines of Terra Nova.

STATEMENT OF SIGNIFICANCE

The Fezouata Shale (Morocco) is one of the rare sites preserving a diverse fossil assemblage with soft parts in the Ordovician. Fe played a role in the preservation of these labile anatomies. Here, it is shown that this Fe had a continental origin highlighting the importance of continental Fe fluxes in the preservation of soft parts during the initial stages of the Ordovician Radiation.

ABSTRACT

The Fezouata Shale in Morocco is the most diverse Lower Ordovician unit yielding soft-tissue preservation. Iron played a crucial role in the preservation of soft parts in this formation through the damage of bacterial membranes under oxic conditions and the pyritization of soft parts under the activity of bacterial sulfate reduction. However, the origin of Fe in this formation remains largely speculative. Herein, trace and rare earth elements were investigated in drilled-core sediments from the Fezouata Shale. It is shown that a correlation exists between Fe and Al suggesting that most Fe has a detrital source. Elemental concentrations in the Fezouata Shale are most comparable to rivers and are the least similar to loess and sediments deposited near active island arcs. In this sense, continental weathering and its related Fe in river fluxes dictated occurrences of exceptional fossil preservation in the Fezouata Shale.

INTRODUCTION

Exceptional fossil preservation, consisting of the preservation of soft anatomies in the rock record, is crucial to reconstruct accurate pictures of ancient ecosystems (Butterfield, 1995; Hou et al., 2004; Van Roy et al., 2010; Fu et al., 2020; Nanglu et al., 2020; Saleh et al., 2020a, 2021a). The Fezouata Shale discovered in Morocco is an Early Ordovician deposit bearing a large number of taxa that were previously unknown from this time interval (Van Roy et al., 2010, 2015; Martin et al. 2016). Exceptionally preserved fossils in the Fezouata Shale are discovered in levels that are relatively rich in iron (Saleh et al., 2019). It has been experimentally shown that Fe among other cations and Fe-rich clay minerals slow down the activity of decaying bacteria under oxic conditions through the destruction of bacterial membranes (Imlay et al., 1988; Butterfield, 1990; Guida et al., 1991; Kapoor and Arora, 1998; Petrovich, 2001; Amonette et al., 2003; Wilson and Butterfield, 2014; McMahon et al., 2016). In this sense, Fe availability in specific levels within the Fezouata Shale prevented the complete loss of labile anatomies (Saleh et al., 2020b, c). Moreover, Fe plays a major role in the fossilization of soft parts when bacterial-sulfate reduction (BSR) conditions are established (Raiswell et al., 1993; Gabbott et al., 2004; Saleh et al., 2020b, c). Under BSR conditions, Fe reacts with H_2S produced through the decay of organic material to form pyrite crystals replicating in fine detail the anatomy of soft parts that can be otherwise lost (Raiswell et al., 1993; Gabbott et al., 2004; Saleh et al., 2020b). Biogenic iron, from the decaying tissue, is one possible source, initiating the mineralization process by forming pyrite nuclei (Saleh et al., 2020c). However, abiotic Fe from sediments remains the main source for pyrite growth (Saleh et al., 2020c). Although abiotic Fe was pivotal for soft-tissue preservation under oxic and BSR conditions in the Fezouata Shale, the origin of this element remains speculative (Gaines et al., 2012; Saleh et al., 2019). This study investigates the concentrations of trace and rare earth elements in the Fezouata Shale aiming to answer the following questions: are elemental sources (including Fe) authigenic or detrital? What are these sources (e.g., eolian, volcanic, continental weathering)? Answering these questions will help to decipher the natural processes that dictated soft-part preservation in the Fezouata Shale.

MATERIAL AND METHODS

Geochemical protocol

Two ~6.5m cores from the Fezouata Shale (check Appendix 1 information for stratigraphic positions) were cut and scanned for their elemental composition using an Avaatech X-Ray Fluorescence (XRF) Scanner at IFREMER laboratory, Plouzané, France. XRF data was acquired with the precision of 1 analysis every 0.5cm and at 10kV. Considering that XRF data is only semi-quantitative, the concentrations of Fe, Al, trace, and rare earth elements were further explored using an HR-ICP-MS Element XR (Thermo Fisher Scientific) at the Pôle-Spectrométrie-Océan (PSO, IUEM/Ifremer, Brest, France). 154 samples were taken from the cores, one every 5 to 10cm. Then, powders were analyzed following a similar protocol to Wilmeth et al. (2020). An expanded version of this protocol is presented in Appendix 1.

Data visualization and analyses

In order to determine if a correlation exists between Fe and Al their XRF data were plotted. The degree of correlation between Fe and Al was confirmed by plotting ICP-MS data for these elements and the Fe/Al ratio was calculated. In order to see if this value is impacted by modern weathering, Fe and Al results were separated into two sets according to the degree of modern weathering the samples encountered (see Appendix 1 for information on how modern weathering was constrained). The newly obtained data were box-plotted and new Fe/Al ratios were obtained. Fe and Al concentrations were also represented as box plots for levels with and without exceptional fossil preservation. To further constrain modern weathering, the concentrations of all measured elements from the two separate sample sets were plotted and compared. Co/Th and La/Sc values were calculated and compared to data from McLennan et al. (1983) (original diagram in Appendix 1) in order to test if there is a detrital, volcanic source for Fe. A volcanic source was further investigated by comparing the concentration of Sc, V, Cr, Co, Ni, Rb, Zr, Nb, Cs, La, Hf, Ta, Pb, and Th between the Fezouata Shale and sediments deposited near active island arcs (McLennan, 2001). Furthermore, other potential sources for Fe, including modern rivers, and loess were investigated following the same comparative approach (McLennan, 2001). To quantify the dissimilarity between the Fezouata

Shale and these sources, a total dissimilarity index $TDiss_{index}$ was developed. This index can be obtained by calculating the average of each elemental dissimilarity $EDiss_{index}$ between the Fezouata Shale and the investigated sources according to the following equation (C is for concentration, E is for element, and Ni is used as an example).

$$(E)\mathrm{diss}_{\mathrm{index}} = \left|1 - \frac{C(E)_{\text{investigated source}}}{C(E)_{\text{Fezouata Shale}}}\right| \; ; \quad (Ni)\mathrm{diss}_{\mathrm{index}} = \left|1 - \frac{C(Ni)_{\text{investigated source}}}{C(Ni)_{\text{Fezouata Shale}}}\right|$$

Note that this is a semi-quantitative index that is different from classical significance tests. High index values mark a large heterogeneity between one source and the Fezouata Shale without necessarily investigating if this difference is significant or not. The raw data are provided in the Appendix 2.

RESULTS

XRF analyses show a relatively good correlation between Fe and Al (R^2=0.6, N=2100; Fig. 1A). This correlation is improved when using ICP-MS data (R^2=0.68, N=154; Fig. 1B). The mean ratio of Fe/Al is equal to 0.32 ± 0.01 (Fig. 1B). This ratio did not change significantly (t-test; p= 0.7064 > 0.05) when separating non-modernly weathered (Fe/Al= 0.34 ± 0.02, N=80) from modernly-weathered sediments (Fe/Al= 0.32 ± 0.004, N=74) (Fig. 2A). Both Fe and Al are more enriched in levels with soft-part preservation (Fe= 6.6 ± 0.27%, N=29; Al= 21.45 ± 1%; N= 29) than in levels without exceptional preservation (Fe= 5.89 ± 0.12%, N=125; Al= 18.35 ± 0.41%; N= 125) (Fig. 2B). The difference between intervals with and without exceptional fossil preservation (as indicated in Appendix 2) is significant for both Fe (t-test; p= 0.0162 < 0.05) and Al (t-test; p= 0.0023 < 0.05).

In a similar way to iron, the concentrations of other elements (e.g., Cs, Sr, V) did not change between weathered (N=74) and non-weathered sediments (N=80) except for some very minor drifts in Zn and Pb concentrations (Fig. 3). The Co/Th ratio is generally less than 3, with a mean of 1.07 ± 0.03 (N=154; Fig. 4), and the La/Sc ratio is generally between 1.2 and 3.6, with a mean of 2.54 ± 0.03 (N=154; Fig. 4). Furthermore, the geochemical signature of the Fezouata Shale is the most similar to modern rivers (TDiss= 0.31 ± 0.06) and less comparable to the continental crust (TDiss= 0.49 ± 0.06), sediments deposited near active island arcs (TDiss= 0.55 ± 0.07), and loess (TDiss= 0.71 ± 0.04) respectively (Fig. 5).

DISCUSSION

Al and Fe are well correlated in the Fezouata Shale (Fig. 1A, B). A similar correlation can reflect (1) a detrital signal (Tribovillard et al., 2006), (2) an authigenic signal if the latter is derived from a detrital source in what is effectively an isochemical system, or (3) an authigenic signal in euxinic waters similar to the Black Sea (Dekov et al., 2020). In the Fezouata Shale, the water column was dominantly oxic (Saleh et al., 2021b), favoring a primary detrital source (either scenario 1 or 2). The non-intercepted correlation between Al and Fe [in red; Fig. 1B (y = 2.8709x + 1.621)] is close to the intercepted trendline that passes through the origin {in black, Fig. 1B (y = 3.1255x)], indicating that in the absence of Al, only 20% of Fe can be found. Moreover, Fe/Al is low (i.e., ~ 0.32), only 2/3 of the average shale value of this ratio at ~ 0.5 (Lyons and Severmann, 2006). It is worth noting here that the low ratio in the Fezouata Shale likely represents a local signal and does not necessarily reflect a global value of Early Ordovician rocks. This ratio may reflect the original chemistry of the basin, result from diagenesis, metamorphism, or even modern weathering, although the Fezouata Shale was not affected by deep diagenesis and metamorphism (Saleh et al., 2020b, c, 2021b). Moreover, both Fe and Al show no major difference between modernly weathered and non-recently weathered sediments in the Fezouata Shale (Fig. 2A) with non-significantly different Fe/Al values. The minimal impact of modern weathering on Al and Fe concentrations is also evidenced for other elements (Fig. 3). These findings align with the results of previous studies showing that the main difference between non-modernly weathered and modernly weathered sediments in the Fezouata Shale is limited to the leaching of Ca, S, and C from altered sediments (Appendix 1; Saleh et al., 2020b, 2021b). In the absence of metamorphism, pronounced diagenesis, and modern weathering, it is most likely that the low

Fe/Al reflects the original signal in the basin. The significant enrichment of Fe in levels with exceptional preservation when compared to levels with no exceptional preservation (Fig. 2B), and the correlation of this enrichment with significantly higher Al values (Fig. 2B) indicate that detrital Fe was fluctuating in the Fezouata shale. This validates the findings of previous studies showing that the probability of exceptional fossil preservation to occur in the Fezouata Shale was augmented in specific levels in which Fe was present in the matrix (e.g., Saleh et al., 2019).

Co/Th and La/Sc plots indicate that the previously suggested volcanic origin for detrital Fe in the Fezouata Shale (Gaines, et al., 2012) is a minor source of chemical elements possibly accounting for 20% of Fe in the formation (Fig. 4). For instance, detrital Co/Th is considerably higher in sediments near volcanoes (i.e., Co/Th ~ 30; McLennan et al., 1983) than it is in the Fezouata Shale (i.e., Co/Th <3 except one point; Fig. 4). Furthermore, an aeolian source for Fe can be rejected because numerous elements show that the Fezouata Shale is most comparable to rivers, followed by the average surface continental crust (Fig. 5). The Fezouata Shale is almost twice more similar to rivers (smallest Tdiss index) than to siliciclastic sediments deposited near active island arcs ($Tdiss_{arcs}$ is slightly less than double $Tdiss_{rivers}$), and is least similar to aeolian sediments ($Tdiss_{loess}$ is higher than double $Tdiss_{rivers}$). All previous findings highlight that the source for Fe in the Fezouata Shale, is detrital, limited and fluctuating, and resulting from surface continental weathering through precipitations, and river inputs to the sea.

The positive impact of continental weathering on soft-tissue preservation may not have been limited to the Ordovician. It has been recently documented that kaolinite correlates with Cambrian and Precambrian soft-tissue preservation (Anderson et al., 2020, 2021). Kaolinite damages bacterial membranes and slows down oxic decay (in a similar way to Fe, and Fe-rich clay minerals; McMahon et al., 2016), and can even replicate labile anatomies in minute details (Anderson et al., 2021). Moreover, it has been argued that the importance of kaolinite in preserving soft-anatomies in the Cambrian can be further highlighted by the correlation of this type of preservation with tropical settings, where kaolinite is typically formed (Anderson et al., 2018; 2021). Kaolinite transport from the continents, where it is formed, to the sea must have occurred through continental weathering. Kaolinite is not evidenced in the Fezouata Shale and the primary clay precursor that aided the formation of Fe-rich clay minerals in this formation is yet to be identified (Saleh et al., 2019). The lack of kaolinite can be attributed to the deposition of the Fezouata Shale in polar settings. Regardless of the absence of kaolinite in the Fezouata Shale, and its presence in many other sites with soft-tissue preservation (e.g., Anderson et al., 2020, 2021) it appears that continental weathering is a unifying process that aided soft-part preservation through either Fe or kaolinite fluxes to the sea. In this sense, the Cambrian–Ordovician world with elevated atmospheric CO_2 (Trotter et al., 2008) and intense continental weathering might have favored soft-tissue preservation, which explains the dominance of exceptional preservation during that time frame. A corollary of this finding is that it is now possible to develop predictive approaches for the discovery of exceptionally preserved fossils in Early Paleozoic rocks based on geochemical proxies quantifying the magnitude of continental weathering.

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FIGURE CAPTIONS

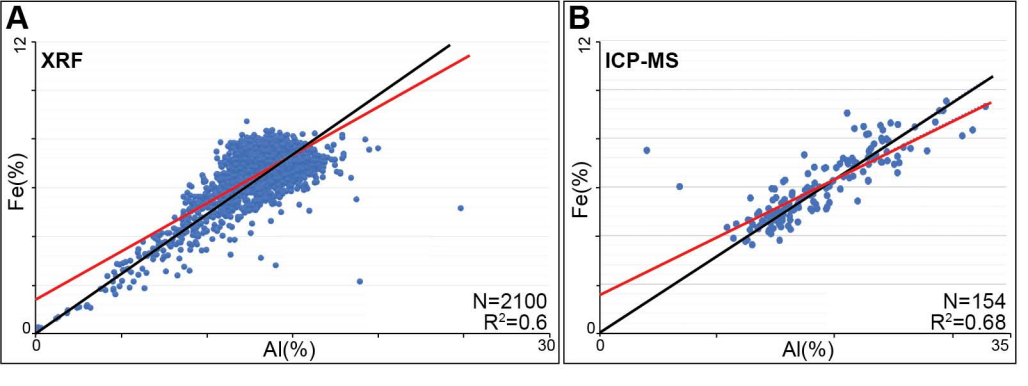
Figure 1. (A) XRF Al-Fe correlation in the Fezouata Shale (blue dots, and red trendline). (B) ICP-MS Al-Fe correlation (blue dots, and red trendline). The black lines in (A) and (B) represent intercepted trends for this correlation passing through the origin (0 value).

Figure 2. (A) Fe and Al differences between modernly weathered and non-modernly weathered sediments. (B) Fe and Al differences between levels with and without exceptionally preserved fossils.

Figure 3. Trace and rare earth elements differences between modernly weathered and non-modernly weathered facies.

Figure 4. Co/Th and La/Sc ratios in the Fezouata Shale plotted on the McLennan et al. (1983) diagram.

338 **Figure 5.** Chemical signature for the Fezouata Shale plotted against elemental data from
339 modern rivers, average surface continental crust, loess, and siliciclastic sediments near active
340 island arcs.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Al(%)
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Al(%)
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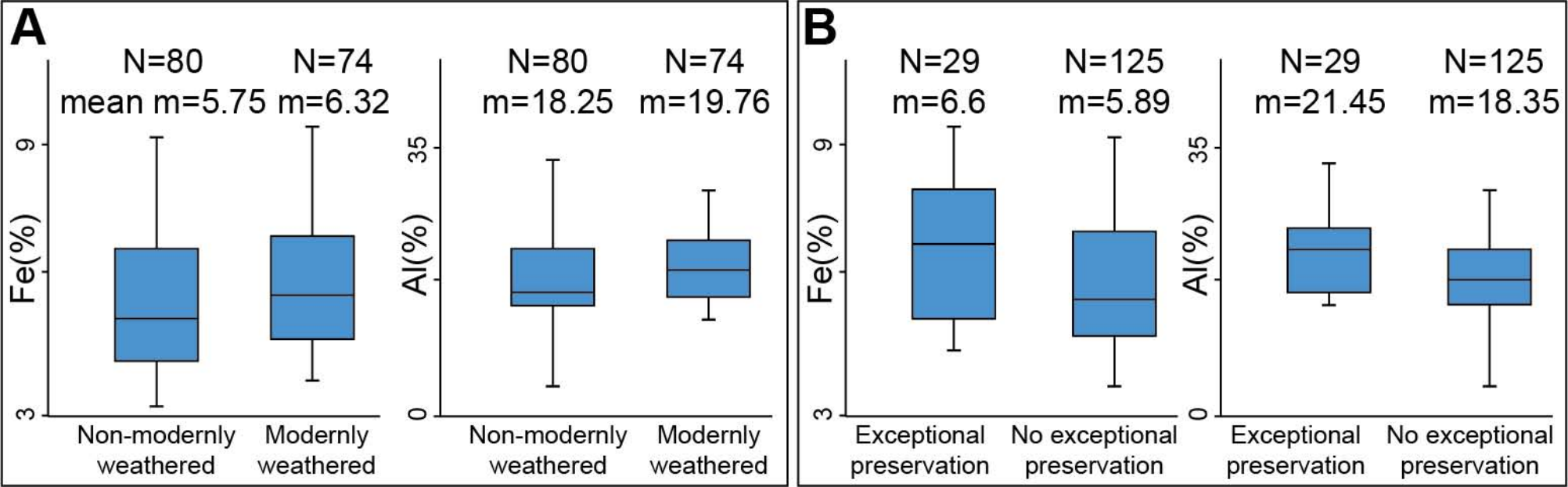
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Modernly weathered
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N=74
m=19.76
Al(%)
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0
Non-modernly weathered
Modernly weathered
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m=5.89
Fe(%)
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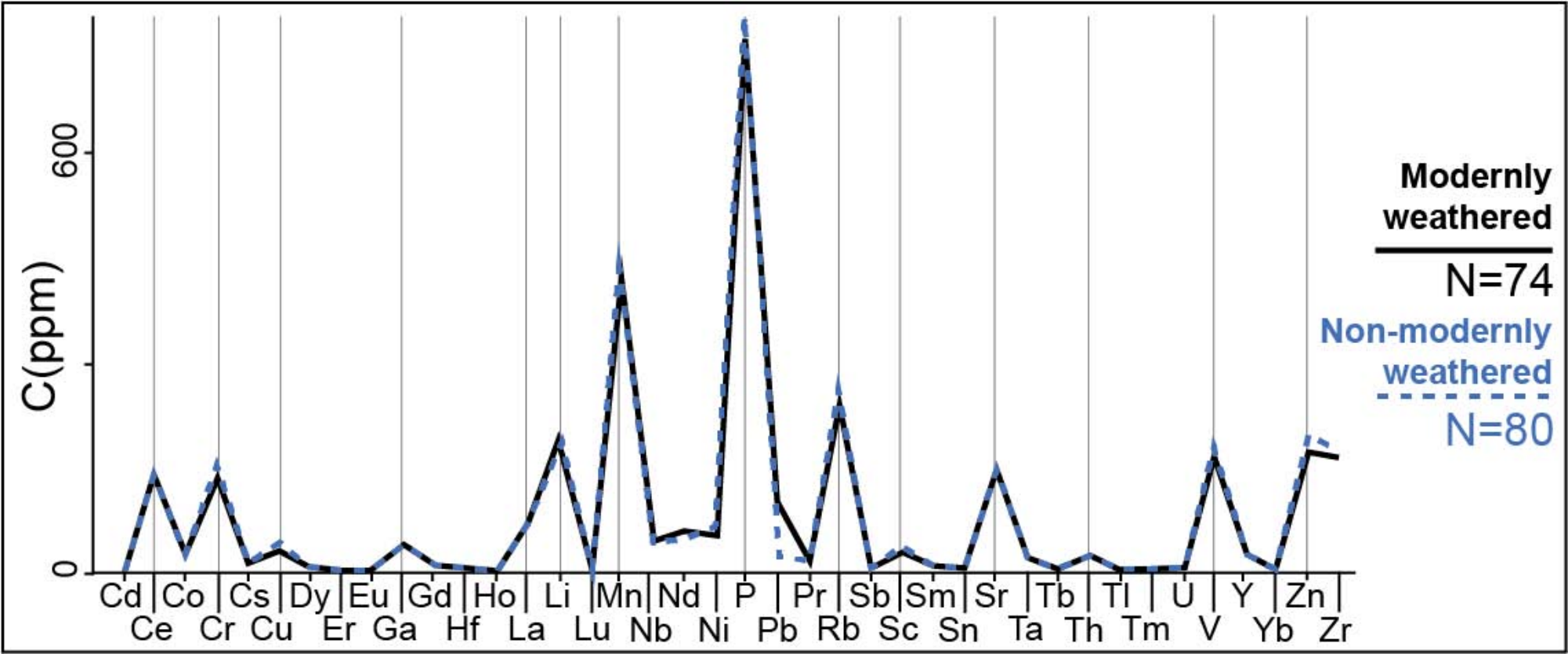
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Sn
Sr
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Non-modernly weathered
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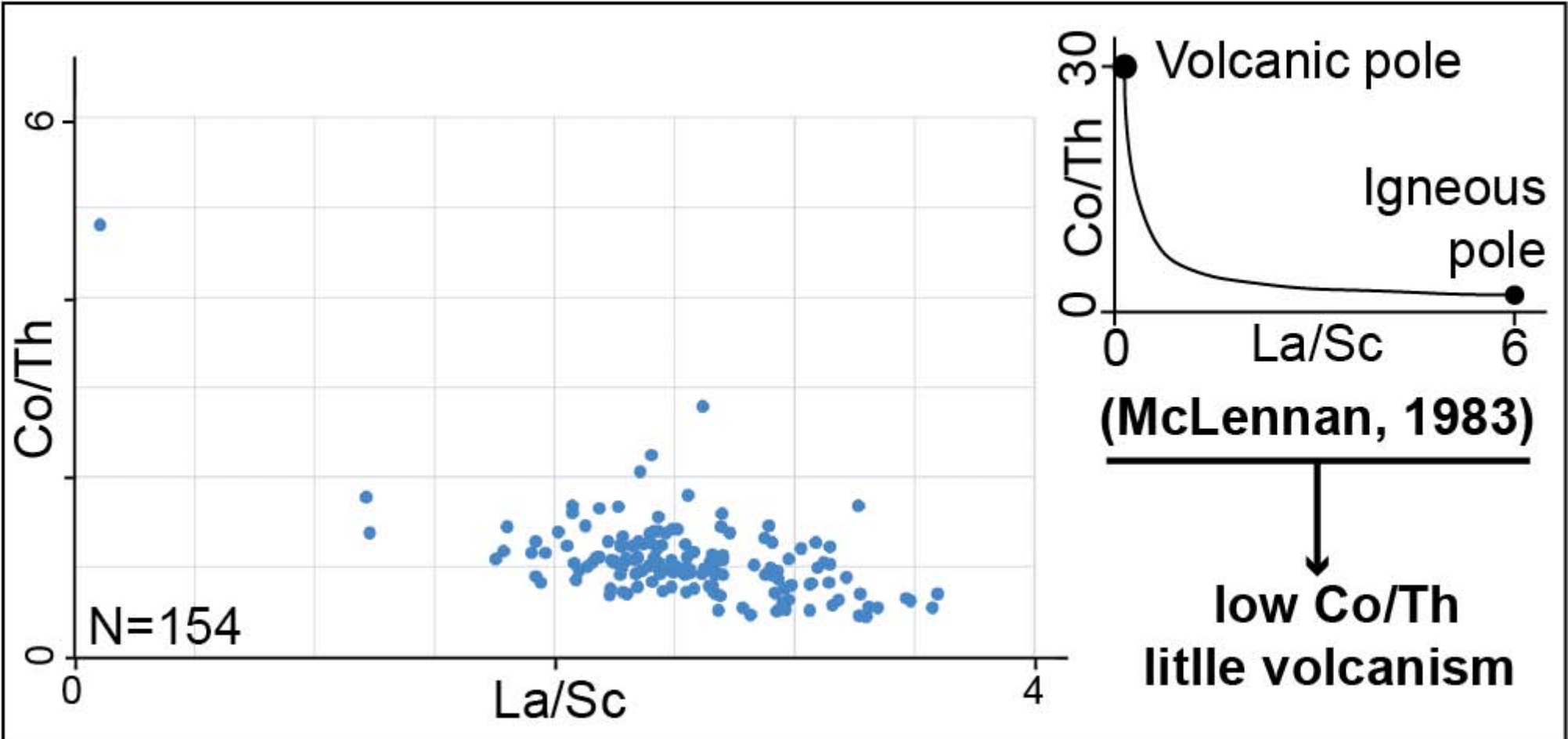
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La/Sc
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Volcanic pole
Igneous pole
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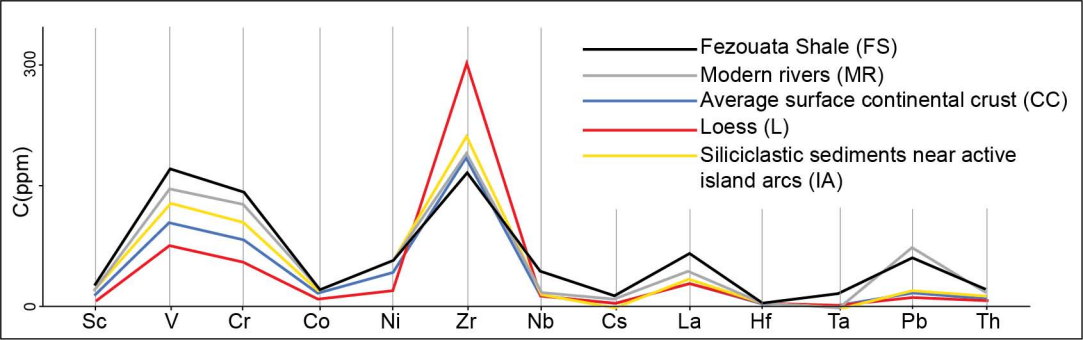
Co/Th
0
0
La/Sc
6
(McLennan, 1983)
low Co/Th
litlle volcanism


C(ppm)
300
0
Sc
V
Cr
Co
Ni
Zr
Nb
Cs
La
Hf
Ta
Pb
Th
Fezouata Shale (FS)
Modern rivers (MR)
Average surface continental crust (CC)
Loess (L)
Siliciclastic sediments near active island arcs (IA)