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The role of post-mortem alteration in tooth enamel revisited: A combined strontium isotope and geochemical evaluation

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A R T I C L E I N F O

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A B S T R A C T

Assessing post-mortem alteration of tooth enamel in archaeological burial sites of interest is critical and required in order to accurately interpret the isotope composition of bioavailable Sr for use in determining migration patterns of populations in ancient civilizations. Several statistical approaches have been established to evaluate the degree of post-mortem alteration within tooth enamel, and these are based on the incorporation of trace elements (Mn, V, Fe, REEs, Th, U) typically present within the burial environment. In this study, both new and previously reported chemical data and radiogenic Sr isotope ratios for both modern-day and archaeological tooth enamel samples are presented, which range from pristine to altered in nature. Significant correlations between elevated abundances of mobile elements (V, Fe, Nd, U) and their corresponding Sr isotope signatures are limited and are most prevalent when the latter are compared to their Fe contents. Tooth enamel samples affected by diagenesis based on their outlier chemical composition do not necessarily record perturbed Sr isotope signatures, and therefore should not be precluded precipitously from provenance studies.

1. Introduction

Post-mortem diagenetic alteration of tooth enamel, if it has occurred, must be evaluated properly prior to radiogenic Sr isotopic analysis since combined post-burial physical, chemical, and biological processes may lead to alteration of original bioavailable Sr isotopic signatures (e.g., Wilson and Pollard, 2002). The formation of secondary minerals, such as brushite ($CaHPO_4{\cdot}2H_2O$) or carbonate ($CaCO_3$) in voids and lattice vacancies, and recrystallization of the hydroxyapatite lattice may result in the addition of diagenetic Sr and consequently alter the original (in vivo) radiogenic isotope signatures (Nelson et al., 1986; Kohn et al., 1999; Nielsen-Marsh and Hedges, 2000; Prohaska et al., 2002; Hoppe et al., 2003). For example, Sr (and Pb) within groundwater at the burial site may become incorporated within tooth enamel subsequent to burial and alter the original Sr and Pb isotopic signatures, respectively (e.g., Simonetti et al., 2021). Diagenetic processes typically involve interaction with groundwater, especially if the burial site is subjected to periodic flooding (e.g., Simonetti et al., 2021), and may be accompanied by strong dissolution/recrystallization effects and microbial bioerosion. In arid environments, the formation of secondary phases occurs more frequently compared to bacterial corrosion (Maurer et al., 2012; Dudás et al., 2016).

In radiogenic isotope systems, open system behavior for a suite of samples is typically identified by the existence of linear correlations between the elemental concentrations of the element in question and its corresponding isotope ratios (Faure and Mensing, 2005). For example, in a plot of 1/Sr abundances vs. $^{87}Sr/^{86}Sr$ ratios binary mixing between two endmember components will produce a linear correlation; a closed system is characterized by a horizontal line on the same plot. Previous studies in human enamel have also focused on the Sr mass fractions as a method for evaluating the degree of diagenesis (e.g., dentine vs. enamel; Retzmann et al., 2019), such that samples characterized by either elevated (>250 μg g-1) and depleted (<100 μg g-1) abundances should be considered suspect (Dudás et al., 2016). Additionally, fossilized biogenic (human and animal) samples with elevated Ca/P mass fraction ratios above the theoretical value of biogenic hydroxyapatite (2.16; Sillen, 1986), along with elevated contents of various types of elements (transition, ultra-trace), such as Al, Si, Ba, V, Fe, Mn, rare earth elements (REEs), Y, Hf, Th, and U are all indicators of post-mortem alteration (Kohn et al., 1999; Trueman et al., 2008; Koenig et al., 2009; Benson et al., 2013; Kohn and Moses, 2013; Willmes et al., 2016; Kamenov et al., 2018).

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Evaluating post-mortem diagenesis is a complicated issue that has involved various approaches, such as those cited above. The degree of diagenesis is also matrix-dependent and site-specific (Dudás et al., 2016), and it is generally accepted that tooth enamel is less affected by diagenesis due to its compact structure and minor organic content (~2 %). Consequently, most samples of tooth enamel will likely preserve their biogenic radiogenic isotope values, and therefore represent a reliable sample type for investigation of mobility and migration patterns of ancient populations (Kyle, 1986; Lee-Thorp and Sponheimer, 2003; Bentley, 2006; Montgomery, 2010; Slovak and Paytan, 2012; Szostek et al., 2015). In contrast, it is well established from numerous previous studies that human dentine is more likely affected by diagenesis and consequently, its use in terms of archaeological migration studies is somewhat controversial (Driessens and Verbeeck, 1990; Budd et al., 2000; Lee-Thorp and Sponheimer, 2003; Copeland et al., 2010).

In previous investigations of enamel samples (e.g., de Winter et al., 2019), the elemental distribution is evaluated by plotting the data as box and whisker (BW) plots to identify distinct populations and/or visually identify outliers (i.e., values outside the 1.5 interquartile range-IQR). Alternatively, post-mortem alteration may be assessed by adopting biplots among selected elements, such as REEs, Y, or U (e.g., Simonetti et al., 2021). However, the *in-vivo* elemental abundances of certain elements (e.g., Mg, Fe, Cu, Zn, Sr, and Ba) may be highly variable both in terms of single individuals due to diet (or via bioaccumulation for U; Kohn et al., 2013), but also in relation to the local geolithology. This implies that establishing elemental thresholds to detect diagenesis may be problematic.

In an alternative approach, Kamenov et al. (2018) established maximum threshold concentrations (C/MTC) values for archaeological tooth enamel, such that a C/MTC (sample elemental concentration-C/MTC) value ≤ 1 is representative of non-altered samples and equivalent to modern-day tooth enamel (i.e., in vivo). The MTC is determined by the addition of the maximum concentration of an element and its corresponding 2-sigma standard deviation based on samples of modern (pristine) tooth enamel. Kamenov et al. (2018) established the MTC values for in-vivo or modern-day tooth enamel based on 77 samples from various regions of the world.

This study reports the elemental distributions and radiogenic isotope ratios for several suites of tooth enamel that were either studied previously (Simonetti et al., 2008; 2021; 2023; Kamenov et al., 2018) or newly acquired data (Table 1); the latter consist of enamel samples originating from burial sites of Nuri and Old Dongola within the Nile River Valley System (NRVS), and exhibit varying degrees of alteration from pristine to significantly altered based on the abundances of highly mobile elements. This study focuses on highlighting the concentrations of Fe, Mn, Zn, Sr, Nd, and U within tooth enamel samples because of their well-established enhanced mobility associated with diagenetic, post-mortem alteration processes (e.g., Kamenov et al., 2018; Retzmann et al., 2019). The compiled trace element compositions for all samples reported here are then compared to their corresponding Sr isotope ratios in order to determine the presence, if any, of the correlation between the degree of alteration and the Sr isotope ratios recorded within the samples of tooth enamel.

Table 1
Trace element abundances (in ppm) for tooth enamel samples from Nuri and Old Dongola.

Sample	Mg	V	Mn	Fe	Zn	Sr	Nd	U	$^{87}Sr/^{86}Sr$	2σ uncertainty
NURI										
NUR-1	3712	0.56	11.2	228	247	264	0.04	0.006	0.70994	0.000006
NUR-2	4145	0.09	5.2	217	146	235	0.03	0.004	0.70895	0.000010
NUR-4	3147	0.99	54.3	263	185	323	0.15	0.009	0.70996	0.000011
NUR-5	2220	0.88	32.6	281	281	282	0.53	0.037	0.71095	0.000016
NUR-6	2990	1.34	6.80	234	266	206	0.20	0.014	0.70887	0.000007
NUR-7	3082	0.81	8.63	247	140	340	0.07	0.013	0.70838	0.000007
NUR-8	3327	5.15	17.0	217	175	617	0.08	0.120	0.71010	0.000009
NUR-9	3985	0.83	16.2	277	148	383	0.04	0.009	0.70813	0.000009
NUR-10	2882	0.68	23.2	300	220	305	0.35	0.018	0.71108	0.000007
NUR-11	4621	0.29	12.8	204	200	632	0.09	0.007	0.70858	0.000008
NUR-13	3620	0.26	5.14	234	234	167	0.08	0.014	0.70829	0.000008
NUR-14	4899	0.14	5.18	209	216	164	0.05	0.009	0.70834	0.000011
NUR-15	3200	1.57	24.2	223	198	738	0.20	0.033	0.70880	0.000015
NUR-16	2998	4.39	11.0	181	190	915	0.13	0.068	0.70852	0.000021
NUR-17	4164	0.56	68.4	223	172	664	0.11	0.011	0.70774	0.000011
NUR-18	2960	4.63	131	206	253	565	0.11	0.045	0.70850	0.000013
NUR-19	3346	1.12	49.2	195	179	1309	0.10	0.049	0.70809	0.000014
NUR-20	5601	0.28	14.9	168	206	653	0.04	0.017	0.70820	0.000014
NUR-21	2567	0.63	9.73	178	177	406	0.05	0.003	0.70683	0.000013
NUR-22	2444	0.58	10.7	162	180	412	0.07	0.012	0.70710	0.000015
NUR-23	2710	0.88	12.2	184	209	666	0.03	0.005	0.70721	0.000012
NUR-24	4580	0.18	13.0	226	189	404	0.03	0.001	0.70827	0.000017
NUR-25	2905	0.50	6.13	176	190	180	0.06	0.008	0.71010	0.000012
NUR-26	3050	0.72	13.2	206	213	194	0.15	0.012	0.71012	0.000010
NUR-27	2998	1.65	40.2	227	250	278	0.20	0.168	0.70799	0.000013
NUR-28	2525	2.61	40.2	213	212	380	0.09	0.019	0.70838	0.000009
NUR-29	2356	0.41	4.95	137	133	215	0.05	0.009	0.70788	0.000011
NUR-30	2705	0.47	8.71	191	153	164	0.04	0.022	0.70902	0.000012
NUR-31	2671	0.82	6.67	178	175	175	0.04	0.008	0.70920	0.000011
NUR-32	3134	2.52	13.2	203	215	248	0.10	0.018	0.70822	0.000010
Old Dongola										
OLD-1	5627	0.11	3.19	304	128	93.7	0.015	0.003	0.70716	0.000014
OLD-2	5257	0.06	6.97	362	155	87.0	0.022	0.001	0.70811	0.000068
OLD-3	7894	0.10	5.97	540	186	170	0.019	0.005	0.70933	0.000300
OLD-4	1668	0.04	2.71	191	60.7	68.2	0.006	0.001	0.70765	0.000034
OLD-6	6768	0.12	2.68	385	166	124	0.007	0.001	0.70824	0.000110

The 2σ level relative standard deviation (RSD% = standard deviation/average concentration x 2 x 100) is a function of absolute elemental concentration, and thus varies between ~2.5 and ~6.0 % for the more abundant elements (Mg, Mn, Fe, Sr, Ba) and between ~15 and ~46 % for Nd, Pb, and U (≪1 ppm).

2. Samples

Trace element and Sr isotope compositions for modern (n = 77) and archaeological (n = 45) tooth samples are both taken from Kamenov et al. (2018), which include individuals from several countries for the modern suite (Europe, North America, Central America, South America, Caribbean, and Africa). Archaeological samples are from pre-historic and early historic Florida sites, the Philippines, and from an early historic site in Peru (Lofaro, 2016). Sr isotope ratios and elemental abundances for tooth enamel samples from various burial sites within the NRVS (Tombos, Selib Bahri, Selib 1, Shendi, El-Kurru; n = 102 samples in total) are from Simonetti et al., (2008, 2021, 2023). Tooth enamel samples newly investigated here are from the burial sites of Nuri (n = 30) and Old Dongola (n = 5), NRVS.

Nuri is an ancient necropolis located near the Nile's Fourth Cataract. Pyramids mark the Kushite royal burials constructed during the Napatan period. Archaeological evidence and relative dating indicate the site was in continual use throughout later periods. The Nuri Archaeological Expedition team has identified three non-royal burial focal points. For this study, enamel samples date from the Meroitic period (c. 300 BCE – 400 CE) through the Medieval period (c. 550 CE − 1300 CE).

Old Dongola was the capital of the Nubian Christian kingdom of Makuria situated south of the Third Cataract of the Nile River. The site was an active religiopolitical center from the Medieval period through Funj-period (16th–17th century). Archaeological fieldwork at Old Dongola is conducted by members of The Polish Centre of Mediterranean Archaeology (PCMA) team. Human enamel samples, from Old Dongola used in this study date through the Medieval and Funj periods. Enamel samples from Nuri and Old Dongola were mechanically cleaned and abraded as well as chemically purified to reduce post-depositional contamination (Nielsen-Marsh and Hedges, 2000) prior to subsequent chemical and isotopic analyses.

3. Methods

Detailed information in relation to the analytical methods employed here are contained within Simonetti et al. (2023) and briefly summarized here. Enamel samples were digested and processed at the University of Notre Dame Midwest Isotope and Trace Element Research Analytical Center (MITERAC). Samples of tooth enamel (between ~ 70 and ~ 300 mg) were digested in Savillex® Teflon beakers using ~ 4 mL of concentrated 16 N, ultrapure HNO_3 and placed on a hotplate at 110° C for 24 h. The samples were then removed from the hotplate and cooled for one hour with subsequent dry down of the ultrapure HNO_3 acid. Five milliliters of ultrapure 16 N HNO_3 acid was then added into the beaker and the solution diluted with ultrapure water until a final total volume of ~ 25 mL was achieved.

3.1. Trace element geochemistry

The trace element abundances for enamel samples from Nuri and Old Dongola (Table 1) were determined using an Attom (Nu Instruments Ltd., Wales, UK) high resolution inductively coupled plasma mass spectrometer (HR-ICP-MS) operating in medium mass resolution mode ($M/\triangle M \approx 3000$). Samples were processed using a wet plasma, solution mode introduction system, and prior to each analytical session the Attom instrument was tuned and calibrated using a multi-elemental 1 ppb (ng g-1) standard solution. The abundances of the trace elements (Table 1) were determined by an external calibration method, which includes correction for matrix effects and instrumental drift.

3.2. Sr isotope compositions

Strontium aliquots were separated and purified for Sr isotope analysis subsequent ion exchange chromatography. Following the ion exchange chemistry, Sr-bearing aliquots were aspirated into the ICP torch using a desolvating nebulizing system (DSN-100 from Nu Instruments Ltd.) and Sr isotope measurements were conducted using a NuPlasma II MC-ICP-MS (multi-collector inductively coupled plasma mass spectrometer; Nu Instruments Ltd.) instrument. Strontium isotope data were acquired in static, multi-collection mode using 5 Faraday collectors for a total of 400 s, consisting of 40 scans of 10 s integrations. The analytical protocol's accuracy and reproducibility were verified by analyzing the NIST SRM 987 strontium isotope standard during three analytical sessions, which yielded an average value of 0.710230 ± 0.000022 (2σ STDEV; n = 10), in agreement with the certified value of 0.71025 (Faure and Mensing, 2005). The Sr isotope ratios for tooth enamel samples from Nuri and Old Dongola sites are listed in Table 1.

4. Results

Table 1 lists the newly reported abundances of key trace elements (Fe, Mn, Zn, Sr, Nd, and U) within tooth enamel samples from Nuri and Old Dongola burial sites (NRVS), whereas those for the remaining NRVS samples (Tombos, El-Kurru, Selib Bahri, Selib 1, Shendi) are reported in published studies (Simonetti et al., 2008; 2021; 2023). Fig. 1 is modified from Simonetti et al. (2023) and illustrates the plot of average C/MTC values as described earlier and established by Kamenov et al. (2018) for tooth enamel samples from burial sites within the NRVS. The average.

C/MTC values for most of the samples depicted in Fig. 1 plot below a value of 1 except for those for V, Fe, Nd, and U. Also depicted in Fig. 1 is the range of concentrations for the average, non-altered archaeological enamel sample and corresponding high value (=average + one standard deviation). Of note and in general terms, the C/MTC patterns for the enamel samples investigated by Simonetti et al. (2023) display similar patterns compared to that for the average archaeological sample (Kamenov et al., 2018; Fig. 1). The abundances of Sr for all samples investigated yield C/MTC values that are < 1 (Fig. 1; Table 2), and these are not correlated with their corresponding $^{87}Sr/^{86}Sr$ compositions (not shown).

Fig. 2 illustrates a series of box and whisker (BW) plots for six elements, Fe, Mn, Zn, Sr, Nd, and U for suites of tooth enamel from various burial sites worldwide, including those representing modern-day and deemed non-altered (pristine) archaeological samples (from Kamenov et al., 2018). Table 3 lists the 1st and 3rd quartile, quartile range (QR) and 1.5 and −1.5QR values for each suite of enamel samples depicted in Fig. 2. In general, the mean values and range of elemental abundances for the elements shown in Fig. 2 for tooth enamel exhibiting varying degrees of alteration are overlapping/similar (Mn, Nd, and U) with the exception of Fe (Fig. 2a); the latter are clearly higher and more scattered in the enamel samples from various burial sites within the NRVS (Simonetti et al., 2023), Nuri and Old Dongola (Table 1), and those from El-Kurru (high Sr isotope group; Simonetti et al., 2021) compared to modern-day enamel and pristine archaeological samples (Kamenov et al., 2018), and enamel samples from Tombos (Simonetti et al., 2008). Distinctively higher U concentrations are recorded in the high Sr isotope group samples from El-Kurru (as defined by Simonetti et al., 2021; Fig. 2f), which was attributed to post-mortem alteration of enamel by U-bearing groundwater during burial site flooding events (Simonetti et al., 2021).

In Figs. 3 and 4, the C/MTC values for Fe, Sr, V, Nd, and U are plotted against their corresponding Sr isotope ratios. Fig. 3a highlights enamel samples with high Fe contents (based on Fig. 2a) namely those from various NRVS burial sites (Tombos, Selib Bahri, Selib 1, Shendi), El-Kurru (high Sr isotope group), Nuri, and Old Dongola. Enamel samples from El-Kurru and Old Dongola show the most significant positive correlations between Fe contents and Sr isotope compositions (Fig. 3a), whereas those from Nuri show a weak but positive correlation as well. Despite having higher Fe contents compared to those for modern-day and pristine archaeological enamel samples (Fig. 2a), those from the various remaining burial sites within the NRVS (Tombos, Selib Bahri, Selib 1, Shendi) do not show any significant correlations between their

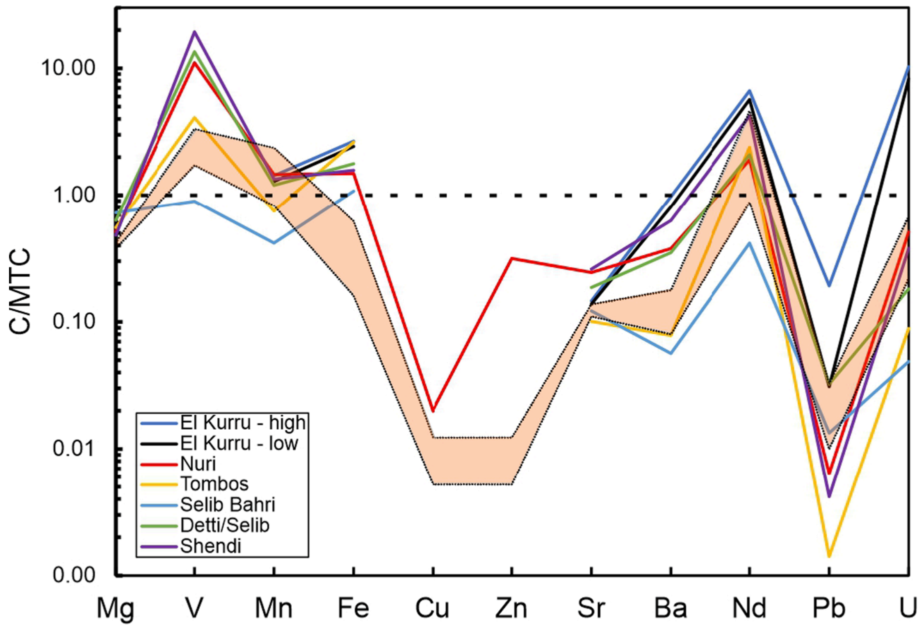

Fig. 1. Log plot displays average concentration (C) of trace elements for tooth enamel from various burial sites within the NRVS divided by the Mean Threshold Concentration (MTC) values for each element from Kamenov et al. (2018). Elements with C/MTC values > 1 (dashed line) are interpreted to have been impacted by post-mortem alteration. Field outlined in brown represents range of trace element abundances (average values plus 1σ standard deviation) for typical, non-altered fossilized tooth enamel (Kamenov et al., 2018). Diagram modified from Simonetti et al. (2023).

Table 2
C/MTC values for tooth enamel samples from Nuri and Old Dongola.

Sample	Mg	V	Mn	Fe	Zn	Sr	Nd	U
NURI								
NUR-1	0.57	5.05	0.73	1.60	0.39	0.16	0.64	0.13
NUR-2	0.64	0.82	0.34	1.52	0.23	0.14	0.60	0.08
NUR-4	0.49	9.02	3.53	1.84	0.29	0.19	2.63	0.18
NUR-5	0.34	7.98	2.12	1.96	0.45	0.17	9.18	0.73
NUR-6	0.46	12.2	0.44	1.64	0.42	0.12	3.50	0.28
NUR-7	0.48	7.33	0.56	1.73	0.22	0.20	1.27	0.26
NUR-8	0.51	46.8	1.10	1.52	0.28	0.36	1.46	2.39
NUR-9	0.62	7.57	1.05	1.94	0.23	0.23	0.66	0.18
NUR-10	0.45	6.14	1.50	2.10	0.35	0.18	6.02	0.35
NUR-11	0.71	2.63	0.83	1.43	0.32	0.37	1.55	0.13
NUR-13	0.56	2.36	0.33	1.64	0.37	0.10	1.29	0.28
NUR-14	0.76	1.24	0.34	1.46	0.34	0.10	0.90	0.17
NUR-15	0.49	14.3	1.57	1.56	0.32	0.43	3.40	0.67
NUR-16	0.46	39.9	0.71	1.26	0.30	0.54	2.28	1.37
NUR-17	0.64	5.09	4.44	1.56	0.27	0.39	1.82	0.23
NUR-18	0.46	42.1	8.48	1.44	0.40	0.33	1.86	0.90
NUR-19	0.52	10.2	3.19	1.36	0.29	0.77	1.70	0.98
NUR-20	0.87	2.58	0.97	1.18	0.33	0.38	0.66	0.35
NUR-21	0.40	5.69	0.63	1.24	0.28	0.24	0.91	0.06
NUR-22	0.38	5.29	0.69	1.13	0.29	0.24	1.27	0.23
NUR-23	0.42	7.96	0.79	1.28	0.33	0.39	0.50	0.10
NUR-24	0.71	1.65	0.85	1.58	0.30	0.24	0.56	0.03
NUR-25	0.45	4.50	0.40	1.23	0.30	0.11	1.06	0.16
NUR-26	0.47	6.56	0.86	1.44	0.34	0.11	2.56	0.24
NUR-27	0.46	15.0	2.61	1.59	0.40	0.16	3.39	3.35
NUR-28	0.39	23.7	2.61	1.49	0.34	0.22	1.57	0.37
NUR-29	0.36	3.75	0.32	0.96	0.21	0.13	0.82	0.19
NUR-30	0.42	4.24	0.57	1.33	0.24	0.10	0.74	0.43
NUR-31	0.41	7.41	0.43	1.25	0.28	0.10	0.64	0.15
NUR-32	0.48	22.9	0.86	1.42	0.34	0.15	1.70	0.36
Old Dongola								
OLD-1	0.87	1.04	0.21	2.13	0.20	0.06	0.26	0.05
OLD-2	0.81	0.54	0.45	2.53	0.25	0.05	0.38	0.02
OLD-3	1.22	0.87	0.39	3.78	0.30	0.10	0.33	0.10
OLD-4	0.26	0.34	0.18	1.34	0.10	0.04	0.11	0.02
OLD-6	1.05	1.08	0.17	2.69	0.26	0.07	0.13	0.02

Calculated Concentration/Mean Threshold Concentration (C/MTC) values for samples from Nuri and Old Dongola burial sites as outlined in Kamenov et al. (2008) and described in text.

Fe abundances and Sr isotope compositions (Fig. 3b); in fact, Fig. 3b indicates that these NRVS samples display either essentially horizontal arrays, or a tight cluster of data points. The same lack of correlations is displayed for this group of NRVS enamel samples in the remaining plots for C/MTC – Sr, V, Nd, and U vs. their corresponding Sr isotope ratios (Fig. 4), even though C/MTC values for certain elements (V, U) attain highly elevated values close to 100.

5. Discussion

It is well established that Fe is one of the most important dietary trace elements that is widespread in the environment, and it is poorly absorbed by the human body except for iron consumed within red meat (Williams and Siegele, 2014). Moreover, body iron homeostasis in healthy humans is regulated at the sites of absorption, utilization, and recycling (Wallace, 2016), and will therefore result in constant abundances of Fe in tooth enamel. It is believed that Fe is deposited in the enamel at the time of tooth formation with very little change subsequently (Brown et al., 2004). As shown in Fig. 2, Fe contents in whole modern tooth enamel are low and range from 10 to 104 ug g^{-1} (Anttila and Anttila, 1987; Arshed et al., 1994; Kamenov et al., 2018), and for modern surface enamel vary between 10 and 140 ug g^{-1} (Cutress, 1972; Preoteasa et al., 2008; Rautray et al., 2010). In their in-situ examination of archaeological teeth using both PIXE (proton induced X-ray emission) and electron microprobe methods, Williams and Siegele (2014) determined that iron levels in the surface enamel record abundances well above those found in modern teeth, which was attributed to post-mortem alteration; however, the enrichment in Fe was limited to the outer 100 μm of enamel. The study by Shipman et al. (1984) reported that enamel within cremated remains tends to develop pores and fissures due to exposure to increased temperatures, which may facilitate migration of Fe into the enamel but no other trace elements (e.g., Zn). Post-burial iron oxide precipitation in bioapatites has indeed been reported in other previous studies (Jacques et al., 2008; Kuczumow et al., 2010). However, de Winter et al. (2019) conclude that in general post-mortem diagenesis causes increases in the concentrations of Sr, Zn and Fe concentrations, which implies that tooth enamel absorbs these trace

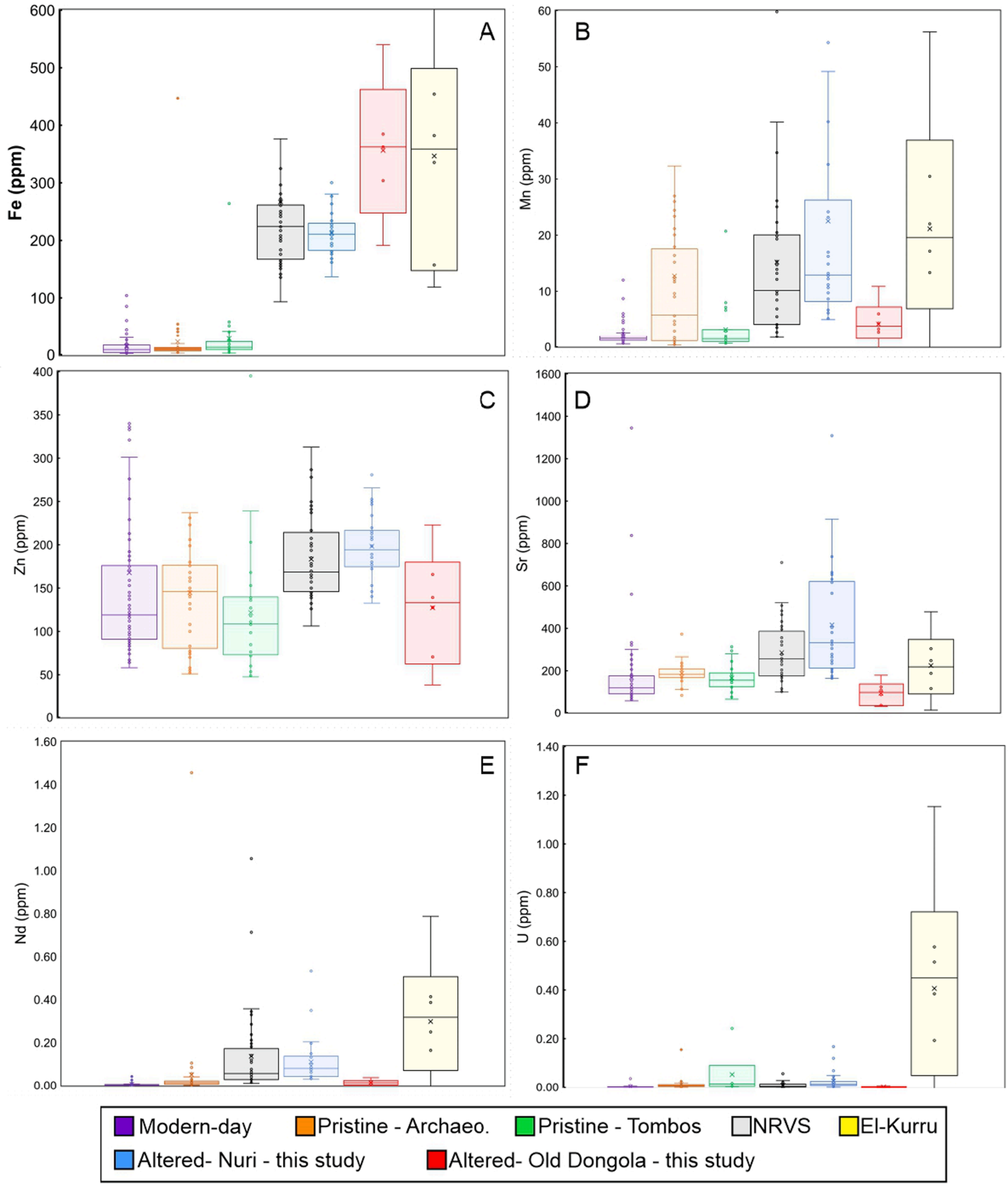

Fig. 2. Box and Whisker (BW) plots of concentrations (ppm) for various trace elements (a) Fe, (b) Mn, (c) Zn, (d) Sr, (e) Nd, and (f) U for samples of tooth enamel from various sources. Data for modern-day and pristine archaeological samples are from Kamenov et al. (2018); pristine samples from Tombos (Simonetti et al., 2008); NRVS are from Simonetti et al. (2023); altered samples from Nuri and Old Dongola – this study (Table 1); El-Kurru (high Sr isotope group) from Simonetti et al. (2021).

elements from its surroundings. It is argued that the trace element concentrations in the pore fluid is key to modeling their incorporation into tooth enamel at individual burial sites, which is consequently dependent on the soil composition and local geology (Millard and Hedges, 1996; Kohn and Moses, 2013; de Winter et al., 2019). Additionally, de Winter et al. (2019) show that diffusion and adsorption (DA) modeling associated with leaching experiments can explain most of the variability in Zn, Sr, and Fe concentrations in tooth enamel profiles investigated. Their DA modeling indicates that leaching of Fe into tooth enamel takes place during a shorter time period (<100 yr) than Zn, Sr

Table 3
Box and Whisker statistical values for tooth enamel samples reported here and from previous studies.

Location / Sample Population	Mg	V	Mn	Fe	Zn	Sr	Nd	U
Modern-day								
Mean	3075	0.03	1.94	15.0	215	168	0.006	0.003
1st Quart	2574	0.02	1.20	4.0	161	92	0.002	0.001
3rd-Quart	3456	0.04	1.90	16.9	262	175	0.005	0.003
Quartile Range	882	0.02	0.70	12.9	102	83	0.004	0.002
−1.5	1251	−0.01	0.15	−15.4	9	−33	−0.004	−0.002
1.5	4779	0.06	2.95	36.3	415	300	0.011	0.006
Archaeological								
Mean	2429	0.19	12.7	22.8	145	188	0.051	0.011
1st Quart	2194	0.06	1.1	7.2	83	169	0.006	0.003
3rd-Quart	2696	0.26	16.8	12.6	176	207	0.020	0.011
Quartile Range	502	0.20	15.6	5.4	93	38	0.014	0.008
−1.5	1441	−0.25	−22.3	−0.9	−57	112	−0.014	−0.009
1.5	3449	0.57	40.2	20.8	316	264	0.040	0.023
Tombos								
Mean	3478		3	28	122	166		0.053
1st Quart	2632		1	10	75	128		0.007
3rd-Quart	4029		3	22	139	185		0.033
Quartile Range	1397		2	12	64	57		0.027
−1.5	537		−2	−8	−21	43		−0.034
1.5	6125		6	39	235	271		0.073
NRVS								
Mean	3843	1.12	15.2	267	183	285	0.14	0.01
1st Quart	2826	0.10	4.13	173	149	177	0.03	0.00
3rd-Quart	4581	1.40	19.9	261	210	369	0.15	0.01
Quartile Range	1756	1.30	15.8	88	61	193	0.13	0.01
−1.5	192	−1.85	−19.6	41	57	−113	−0.16	−0.01
1.5	7215	3.34	43.6	393	301	659	0.34	0.03
Nuri								
Mean	3318	1.2	22.5	213	198	416	0.11	0.03
1st Quart	2753	0.5	8.7	185	175	220	0.04	0.01
3rd-Quart	3689	1.3	23.9	228	215	604	0.13	0.02
Quartile Range	936	0.8	15.3	43	40	384	0.08	0.01
−1.5	1349	−0.7	−14.2	121	115	−357	−0.08	−0.01
1.5	5093	2.5	46.8	292	275	1181	0.25	0.04
Old Dongola								
Mean	5443	0.09	4.3	356	139	109	0.01	0.002
1st Quart	5257	0.06	2.7	304	128	87	0.01	0.001
3rd-Quart	6768	0.11	6.0	385	166	124	0.02	0.003
Quartile Range	1511	0.05	3.3	81	38	37	0.01	0.002
−1.5	2991	−0.02	−2.2	183	71	32	−0.01	−0.002
1.5	9034	0.20	10.9	506	223	179	0.04	0.005
El-Kurru (High group)								
Mean	2296		22	382		248	0.39	0.51
1st Quart	2198		13	335		188	0.16	0.19
3rd-Quart	2640		30	454		304	0.41	0.58
Quartile Range	442		17	119		116	0.25	0.38
−1.5	1535		−12	157		14	−0.21	−0.38
1.5	3304		56	632		478	0.79	1.15

Box and Whisker (BW) statistical values and plots (Fig. 2) were determined and produced using Microsoft Excel 2019.

and Pb (±300 yr) and is independent of both the pore fluid concentrations and the type of burial site (de Winter et al., 2019). Thus, the interval during which leaching occurs is approximately an order of magnitude lower than the age of the samples (de Winter et al., 2019). This same study also reports that leaching fronts associated with fossilized teeth that are ± 3000 years in age penetrate to a depth of ~300–400 μm, and hence recommends that this outer portion be removed in order to determine the endogenous trace element and isotopic signatures of the tooth enamel. Hence, the results from both the Williams and Siegele (2014) and de Winter et al. (2019) investigations indicate that post-mortem alteration is most likely restricted to the outer ~100 to 300 μm of the tooth enamel and therefore, a substantial portion of the sample will still retain its endogenous chemical and isotopic signatures.

In relation to this study, enamel samples from El-Kurru, Nuri and Old Dongola are characterized both by highly variable Sr isotope compositions and contents in mobile elements (Fig. 3a, 4), and display positive correlations between their Fe contents and Sr isotope compositions (Fig. 3a). However, these do not show any correlations between their C/MTC – Sr, V, Nd, and U values and their corresponding Sr isotope compositions (Fig. 4) except for those from El-Kurru (High Sr isotope group) that indicate a positive correlation between C/MTC -Sr, -Nd vs. $^{87}Sr/^{86}Sr$ ratios (Fig. 4a, c); however, C/MTC -Sr values for El-Kurru enamel samples are nonetheless all well below 1 (Figs. 1, 4a). Hence, if the degree of post-mortem alteration had been based solely on the C/MTC values (most ≤ 1) for Nd, Sr, and U for the enamel samples from Nuri and Old Dongola (Fig. 4), then this would have led to an inaccurate interpretation that these samples were either pristine or minimally altered, and that their Sr isotope compositions correspond to their endogenous signatures. Thus, the key indicators for assessing the elevated degree of alteration for tooth enamel samples from both the Nuri and Old Dongola burial sites are their Fe (Figs. 1 to 3) and to a lesser degree Nd contents (Fig. 4c). Of importance and as stated earlier, both sample suites were thoroughly cleaned and visually inspected for diagenetic alteration prior to processing for both trace element and Sr isotope analyses, which suggests that exterior, micron-scale altered regions of tooth enamel may be difficult to identify and can evade even the most diligent macro-scale sample preparation techniques.

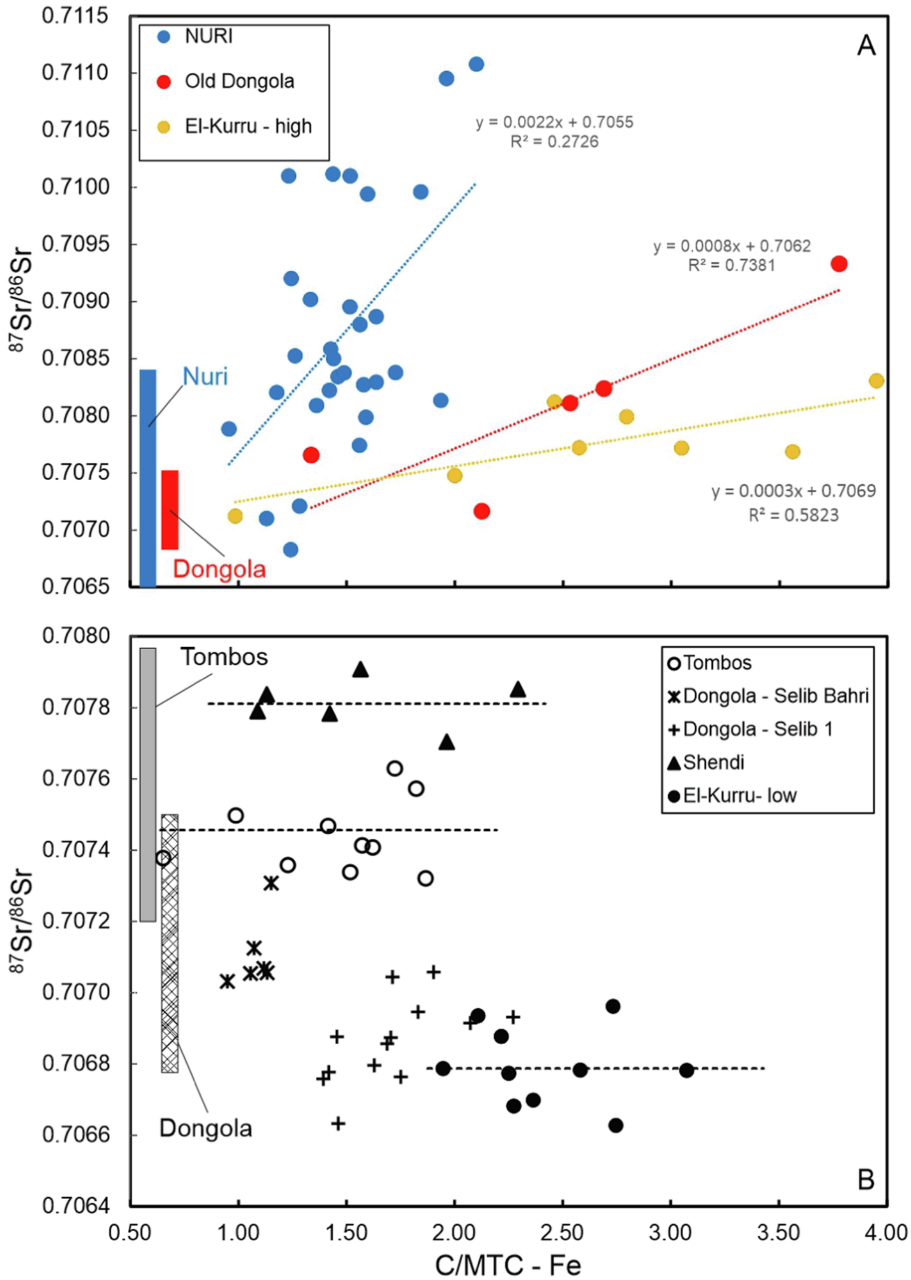

Fig. 3. Plots of C/MTC -Fe values vs. $^{87}Sr/^{86}Sr$ ratios for tooth enamel samples characterized by elevated Fe contents (BW Fig. 2a) from (a) Nuri and Old Dongola (Table 1) and El-Kurru burial sites (Simonetti et al., 2021), and (b) those from remaining NRVS sites at Tombos, Selib Bahri, Selib 1, and Shendi are from Simonetti et al. (2023). Rectangles represent range of Sr isotope compositions for faunal samples from the burial sites of Tombos and Nuri (from Buzon and Simonetti, 2013; Simonetti et al., 2023) and Dongola (Schrader et al., 2019).

Based on the data reported and compiled here, elevated abundances in trace elements (other than Fe) that are considered highly mobile during post-mortem alteration, as defined by the two statistical approaches adopted here (BW distributions and C/MTC values), need not be associated with perturbed Sr isotope compositions for fossilized tooth enamel samples (Fig. 3b, 4). This interpretation is corroborated in Fig. 3b since the relatively constant $^{87}Sr/^{86}Sr$ ratios for tooth enamel samples from both Tombos and Selib Bahri and Selib 1 (Dongola) overlap with those for their respective faunal (local) signatures despite having C/MTC-Fe values > 1.0; in contrast, the variable Sr isotope ratios for enamel samples from Nuri and Old Dongola solely overlap those from their respective faunal samples at low C/MTC-Fe values (~1; Fig. 3a). In summary, evaluation of post-mortem alteration is rendered somewhat complex based on chemical compositions of tooth enamel and should not be considered as a “one size fits all approach”. Post-mortem diagenetic alteration is certainly a reflection and interplay of the many factors that are present in the burial environment, such as temperature, pore fluid composition, hydrological conditions, soil type and local geology. However, as stated earlier and in previous studies (e.g., Retzmann et al., 2019), the impact of diagenetic processes on Sr isotope values for archaeological tooth enamel samples is a mass balance dependent outcome, and thus it is very difficult to perturb the original Sr isotope composition given the relatively high abundance of Sr within tooth enamel (e.g., Kamenov et al., 2018).

6. Conclusions

A detailed evaluation based on the distribution of elemental

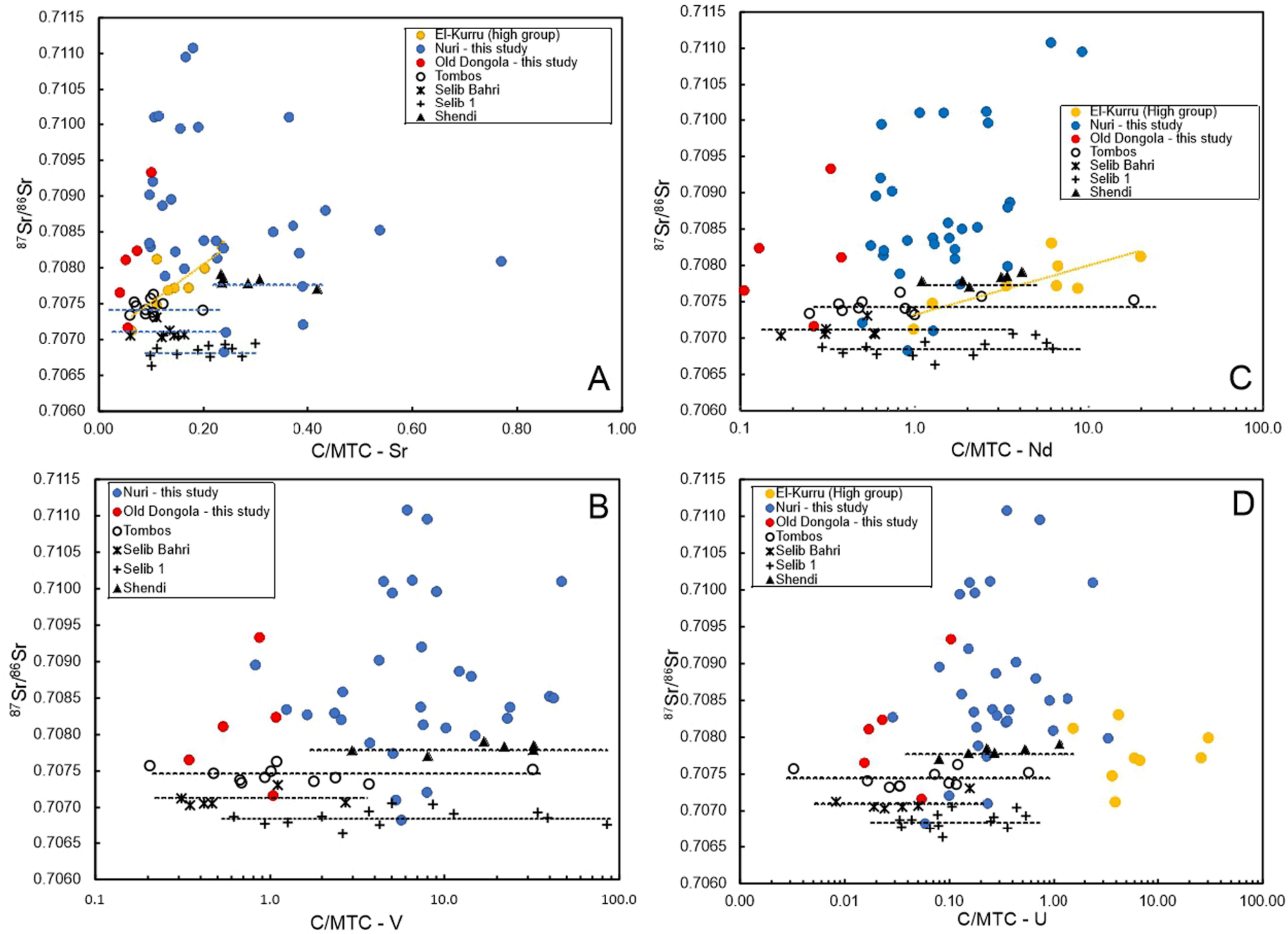

Fig. 4. Diagrams display C/MTC values for Sr (a), V (b), Nd (c), and U (d) vs. their corresponding Sr isotope compositions for tooth enamel samples from various burial sites as outlined in figure caption 3. Note C/MTC values for V, Nd, and U are plotted using log scales.

abundances of V, Mn, Fe, Zn, Sr, Nd, and U within the various suites of tooth enamel samples investigated here reveals that Fe is perhaps most sensitive in identifying post-mortem alteration that potentially impacts $^{87}Sr/^{86}Sr$ ratios. In instances where tooth enamel samples from a single burial site define a wide range of Sr isotope ratios, such as is the case with the samples from both Nuri and Old Dongola, trace element compositions may provide helpful insights into assessing their degree of post-mortem alteration. However, despite having Fe contents deemed much higher than those for pristine modern-day and archaeological enamel samples (as well as C/MTC values > 1 for V, Nd), previously investigated tooth enamel samples from several burial sites within the NRVS (Simonetti et al., 2023) are nonetheless characterized by relatively uniform Sr isotope compositions (Figs. 3 and 4). Therefore, the decision to either include or exclude enamel samples for provenance purposes should not be based solely on their anomalous trace element composition since physical and/or chemical agents responsible for any post-mortem alteration may be Sr-poor in nature.

CRediT authorship contribution statement

Antonio Simonetti: Conceptualization, Funding acquisition, Investigation, Visualization, Writing – original draft. **Michele R. Buzon:** Funding acquisition, Investigation, Resources, Writing – review & editing. **Kari A. Guilbault:** . **Stefanie S. Simonetti:** Investigation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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