Bioavailable Sr and Pb isotope ratios of archaeological cattle bone from coastal India

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Abstract

We present the first measurement of bioavailable strontium ($^{87}Sr/^{86}Sr$) and lead ($^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$) isotope ratios from five cattle bones and one soil sample from Erenda, a chalcolithic archaeological site in coastal eastern India. Our findings demonstrate that bioavailable $^{87}Sr/^{86}Sr$ of bones differ from that of the soil, whereas Pb isotope ratios of bones are similar to soil. Our result suggests a potential influence of marine Sr in modifying the bioavailable $^{87}Sr/^{86}Sr$ ratio, although the current coastline is approximately 30 km from the site. The finding has implications in archaeological, geological, environmental and ecological research.

Keywords: Bioavailable Sr and Pb isotopes; Cattle bone; soil; Coastal India; Geoarchaeology; Mass Spectrometry

Introduction

Strontium (Sr) belongs to the alkaline earth element group and is one of the most abundant trace elements in the Earth's crust. In its natural state, Sr consists of four stable isotopes: ^{84}Sr (0.56%), ^{86}Sr (9.86%), ^{87}Sr (7.00%) and ^{88}Sr (82.58%). Among the isotopes, ^{84}Sr, ^{86}Sr, and ^{88}Sr are non-radiogenic, and ^{87}Sr, generated from Rubidium (^{87}Rb) through β-decay with a half-life ($t_{1/2}$) of 4.97×10^{10} years, is radiogenic [1]. The ^{87}Sr/^{86}Sr ratio depends on the Rb/Sr ratio and age of the host rock. Rubidium substitutes Potassium (K) in mineral lattice due to its geochemical similarity to K [1] leading to an increase in the ^{87}Sr/^{86}Sr ratio in K-bearing minerals such as K-feldspar and biotite, due to radioactive decay over geologic time. However, the ^{87}Sr/^{86}Sr ratio is not significantly fractionated by weathering or biological processes, and act as fingerprints of Sr sources in an open system. The ^{87}Sr/^{86}Sr in natural water reflects the minerals it dissolves making Sr a useful proxy for studying weathering processes [2]. The ^{87}Sr/^{86}Sr has been used in determining mineral weathering rates [3, 4], atmospheric versus mineral weathering source of nutrients [5] and role of changing climate on weathering rate [6].

Lead (Pb) is less abundant in nature and mobile in surface processes. Natural Pb consists of four stable isotopes: ^{204}Pb (1.4%), ^{206}Pb (24.1%), ^{207}Pb (22.1%) and ^{208}Pb (52.4%) where ^{206}Pb, ^{207}Pb and ^{208}Pb are radiogenic. ^{206}Pb and ^{207}Pb are radiogenic daughters of ^{238}U ($t_{1/2} = 4.47 \times 10^{9}$ y) and ^{235}U ($t_{1/2} = 7.04 \times 10^{8}$ y) respectively, while ^{208}Pb is the radiogenic daughter of ^{232}Th ($t_{1/2} = 1.40 \times 10^{10}$ y) [1]. Lead isotope ratios are useful in investigating natural variations in bioavailable isotopes [7, 8] where three independent isotope ratios, ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb, can be used as tracers for bioavailable Pb sources from a single measurement. Lead in soil can come from geological sources such as underlying bedrock and sediments deposited by rivers, and anthropogenic sources such as mining, metalwork and leaded petroleum [9-11]. Anthropogenic Pb is usually derived from Pb-Zn-Cu ores which have a high Pb/U ratio. This causes the ^{206}Pb/^{204}Pb, ^{207}Pb/^{204}Pb and ^{208}Pb/^{204}Pb to be much lower than other geological sources like crustal rocks and sediments (Fig. 1). Most Indian lead ores are Paleoproterozoic in age, making the ore isotopic ratios even lower compared to younger lead ores.

The Sr and Pb isotope ratios in soil and water depend on the underlying rock type from which Sr and Pb are leached during chemical weathering and erosion, and the geological evolution of the area [7, 12]. Present-day seawater exhibits a uniform ^{87}Sr/^{86}Sr ratio of 0.709179 ± 0.000008 (2σ) due to constant mixing and equilibrium induced by ocean currents [13]. Lead isotope ratios in modern-day seawater can be influenced by fossil fuel burning. In fact, a lower ^{206}Pb/^{204}Pb ratio in shallow waters of southern Bay of Bengal compared to higher ratios in deeper water is linked to the deposition of anthropogenic lead from fossil fuel burning [14].

Strontium, despite not being an essential nutrient [15], enters the body of living animals through food and water intake, and deposits as hydroxyapatite in bones by substituting calcium (Ca) in mineral lattices [7]. Strontium substitutes Ca because Sr is chemically similar to Ca [1, 16]. Lead, being a heavy metal, is toxic to the body. However, trace amounts of Pb enter body through food intake and deposit in bones as phosphates [7]. Studies suggest that environmental or anthropogenic sources with different Pb isotope ratios have insignificant influence on the bone isotope ratios [17].

The application of Pb and Sr isotope ratios in archaeology assumes that an animal consumes only locally grown foods and that there is sufficient geologic homogeneity to reconstruct the $^{87}Sr/^{86}Sr$, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ range of a locale. The $^{87}Sr/^{86}Sr$ ratio in archaeological faunal remains has been utilised as a useful tool to determine pastoral migration and mobility [18, 19]. Strontium isotope values of the domesticated animals of Indian Harappan sites (Figure S1) at Kotada Bhadli and Bagasra in Gujarat have been reported [20–24]. Using the average Sr isotope values of tooth enamel (0.7093 to 0.7096) and comparing it to modern-day biogenic $^{87}Sr/^{86}Sr$ of the region [21], it is interpreted that cattle and buffalo have been raised locally and consumed at Kotada Bhadli [20]. On the contrary, cattle/buffalo were acquired from a region outside Bagasra [24]. Sr and Pb isotopes in faunal and human teeth enamel from Harappa and Farmana have been used to decipher human migration patterns in the Indus Valley Civilization [25]. Valentine et al. (2015) established the effectiveness of combined Pb and Sr isotope analyses over Pb or Sr isotope alone in decoding complex migration history. Interestingly, the $^{87}Sr/^{86}Sr$ ratio of Indian coastal archaeological sites is rare, and data on biogenic and/or bioavailable Sr and Pb isotope data for archaeological studies are essentially non-existent outside of the Harappan sites. Although the application of Pb isotope in archaeological faunal remains is rare in India, it has been used to determine ancient migration patterns worldwide [7, 26–28]. The objective of this research is to analyse $^{87}Sr/^{86}Sr$, $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$, and $^{208}Pb/^{204}Pb$ ratios in cattle bones and soil excavated from a protohistoric-historic coastal site, Erenda, in eastern India, in order to define the local bioavailable Pb and Sr isotope ratios in the chalcolithic site and compare the variability with published regional and local soil Pb and Sr isotope ratios. Archaeological bones are considered susceptible to diagenetic alteration due to its high organic matter content, high porosity, and poor preservation of crystalline structure especially in the humid tropical coast of eastern India [29]. Nonetheless, it has been observed that even for bones contaminated with environmental Sr or Pb tend to preserve the biogenic isotopic signature due to the incorporation of the elements in the hydroxyapatite crystals of the bone that slows down the exchange of Sr and Pb ions with surrounding environment [7, 30].

Archaeological background

Table 1 Location and age of digs and taxonomic classification of bone fragments collected from Erenda

Trench	Dig	Sample type	Taxonomic Classification	Cultural association
ZA1	1	Bone fragment	Class-Mammalia Order-Artiodactyla Family- Bovidae Genus-*Bos.*	Medieval- modern.
ZA1	4	Bone fragment	Class-Mammalia Order-Artiodactyla Family- Bovidae Genus-*Bos.*	Early medieval/ medieval
ZA1	5	Bone fragment	Class-Mammalia Order-Artiodactyla Family- Bovidae Genus-*Bos.*	Early medieval/ medieval
ZA1	5	Soil		
ZA1	11	Bone fragment	Class-Mammalia Order-Artiodactyla Family- Bovidae Genus-*Bos.*	Early medieval
ZA1	18	Bone fragment	Class-Mammalia Order-Artiodactyla Family- Bovidae Genus-*Bos.*	Chalcolithic

Erenda (N 21°55′4.8″; E 87°34′ 42.4″) is located in the East Medinipur District of West Bengal in India. The earliest date of charcoals, measured using AMS ^{14}C methods, goes back to 950 BCE making Erenda the first known Chalcolithic site from Coastal West Bengal [31]. The scientific study of the excavated area and artefacts found from the site has revealed the subsistence practice of the settlers and site evolution in an environmental context [32, 33]. Evidence of faunal usage came from bones collected from the site.

The cultural periods of the site are divided into 2 phases, namely periods I and II. While it is safe to assume that the period I belongs to the early farming culture represented by Black and Red ware, period II was disturbed. A basic stratigraphic recording revealed that most of the preserved contexts relate to period I. The Black and Red ware is the characteristic pottery of the Chalcolithic and iron bearing early farming cultures of West Bengal (c1400-600 BCE). Period II is marked by pottery which belonged to post-Chalcolithic (earliest time period 300 BCE). A careful study of the pottery revealed material artefacts from the early medieval phase (*c.* 7th/8th centuries BCE to 12/13th centuries CE) [33]. The AMS ^{14}C dates confirm the cultural periods [31].

Experimental

Sampling

The archaeological site measures approximately 30 m by 30 m. The presence of human artefacts is recorded in a meter-thick brown silty clay deposit lying above an olive-yellow sticky to very sticky clay with calcium carbonate nodules, known as the 'Sijua’ formation. The depth of the trenches varied between 135 and 169 cm. A controlled excavation method was followed in which the earth was dug at an interval of 5-10 cm and recorded as digs. Human habitation is found in layers composed of dark brown silty clay. The floors were made with simple clay collected from the exposed ‘Sijua' surface as it has the compactness needed for building construction. It has been confirmed that reeds were added to the floor [32]. The floors are of a thickness of about 10 cm, and the top of the floors was composed of softer silty clay with pottery, bones, and artefacts during the chalcolithic or early village phase. The site was later converted into a waste disposal site and was covered by C4 plants [32]. Therefore, the diggings revealed a small village settlement that continued for thousands of years.

A large number of faunal bone fragments have been recovered from Erenda. Although the fragments are found throughout, their concentration is highest in the upper and middle levels. These bone fragments allow a comprehensive analysis of the faunal remains. The bones consist of both domesticated as well as wild species. Interestingly, young animal bones are also present, which could be due to local rearing. Cut marks and charred marks indicate meat processing and cooking at the site. Five representative cattle bones and one soil sample were collected from dig 1, 4, 5, 11 and 18 in trench ZA1 based on their preservation (Table 1). Details of the trench positions and digs are described by Gangopadhyay et al. (2017) [33] and Das et al. (2021) [32].

Sample preparation

Bone fragments were transported to the Presidency University in Kolkata, where they were cleaned using a nylon brush. A low-speed stainless steel dental drill was used to remove the soils from uneven bone surface that could not be cleaned using a brush. The soil sample was oven dried and stored in plastic bags. Samples were ground using an agate mortar and pestle.

Digestion and elemental separation for isotope analysis were conducted in a class 1000 clean room on a class 10 clean bench at the Laboratory of Igneous Rock Geochemistry (LIRG), Hiroshima University, Japan. Electronic grade HCl and HNO_3 and ultrapure grade $HClO_4$ and H_2O_2 were used throughout the procedure. All reagents were diluted using ultrapure Milli-Q water (>18.2 MΩ cm; Millipore system, USA). Sample digestion and collection were done in 7 ml beakers made of PFA (Savillex). 20-40 mg of bone powder were digested with HCl, H_2O_2 and $HClO_4$ before dilution in 0.6 ml 3M HNO_3. About 20 mg soil sample was baked at 700 degrees for one day to break down organic material before digesting with HF, $HClO_4$ and HCl [34], and finally diluted in 3M HNO_3. Complete dilution was confirmed by centrifuging the diluted samples at 3000 rpm for 5 minutes and visually checking for precipitation. Sr was separated using Sr-spec resin from Eichrom following a similar procedure as Dey et al. (2023) [35]. The sample solutions in 3M HNO_3 were loaded onto a 0.1 ml Sr-spec resin bed in an in-house column with ~3 mm inner diameter. Major elements were rinsed with 1 ml 3M HNO_3, and Sr was collected in a 7 ml PFA beaker (Savillex) using 1 ml 0.05 M HNO_3. Pb was collected subsequently using 3 ml 6M HCl. The column chemistry was repeated twice to ensure the effective removal of interfering elements. The collected Sr fraction was dried and loaded onto a single flat type Re filament using Ta solution and dilute HNO_3 for isotopic analysis. Pb was loaded on a single U-shaped Re filament using colloidal silica and H_3PO_4. Sr and Pb yields were >80%.

Isotope analysis

Isotope ratio measurements were conducted using a thermal ionisation mass spectrometer (TIMS) of the model MAT-262 from Thermo Fisher Scientific installed at the LIRG, Hiroshima University. Measurement was done in positive ionisation mode at >1200 °C with filament current ~2.8 A. Source vacuum was kept at $<5 \times 10^{-7}$ mbar during measurement. Data were collected in 5 to 10 blocks, with 10 scans per block for each sample. Amplifier gains were calibrated once a day, and the baseline was measured between blocks during measurement. The run time for each sample was ~30 minutes. Acquired data were corrected for instrumental mass fractionation using the internal normalisation method of $^{88}\mathrm{Sr}/^{86}\mathrm{Sr} = 0.1194$ [36] and double spike method for Pb [37]. Isotope standards measured alongside samples, NIST SRM 987 for Sr and NIST SRM 981 for Pb, yielded $^{87}\mathrm{Sr}/^{86}\mathrm{Sr} = 0.710255 \pm 0.000017$ (2SE) for Sr; and $^{206}\mathrm{Pb}/^{204}\mathrm{Pb} = 16.9425 \pm 0.0006$ (2SE), $^{207}\mathrm{Pb}/^{204}\mathrm{Pb} = 15.4994 \pm 0.0006$, and $^{208}\mathrm{Pb}/^{204}\mathrm{Pb} = 36.7279 \pm 0.0014$ for Pb. External reproducibility for isotope ratios in this lab were determined [34] and yielded $^{87}\mathrm{Sr}/^{86}\mathrm{Sr} = 0.710264 \pm 0.000014$ (2σ, $n = 10$) for NIST SRM 987 and $^{87}\mathrm{Sr}/^{86}\mathrm{Sr} = 0.703699 \pm 0.000018$ (2σ, $n = 7$) for reference rock JB-2. Pb isotope ratios yielded $^{206}\mathrm{Pb}/^{204}\mathrm{Pb} = 16.9397 \pm 0.0013$, $^{207}\mathrm{Pb}/^{204}\mathrm{Pb} = 15.4972 \pm 0.0014$, and $^{208}\mathrm{Pb}/^{204}\mathrm{Pb} = 36.7187 \pm 0.0024$ (2σ, $n = 5$) for NIST SRM 981 and $^{206}\mathrm{Pb}/^{204}\mathrm{Pb} = 18.3223 \pm 0.0097$, $^{207}\mathrm{Pb}/^{204}\mathrm{Pb} = 15.5575 \pm 0.0064$, and $^{208}\mathrm{Pb}/^{204}\mathrm{Pb} = 38.2442 \pm 0.0162$ (2σ, $n = 7$) for reference rock JB-2.

Results and discussion

Pb isotope ratios

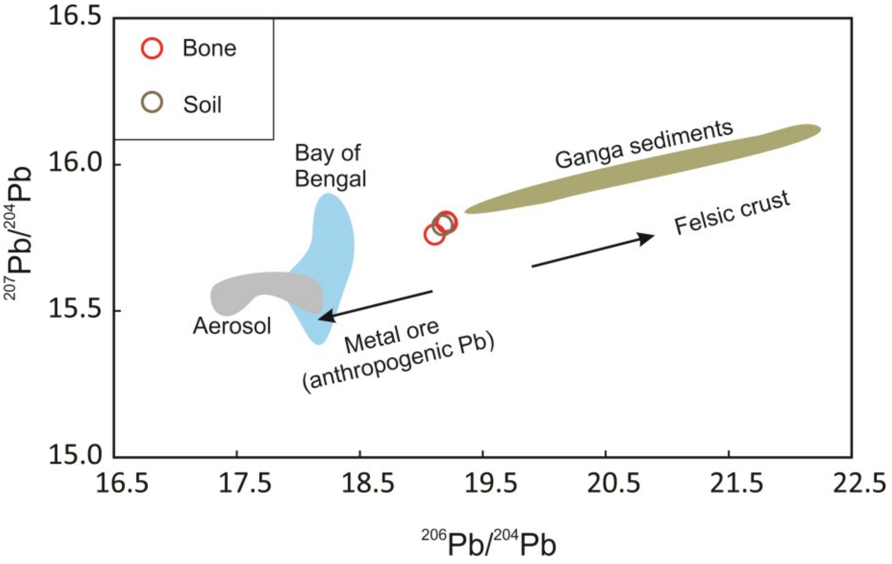

Fig. 1 ^{206}Pb/^{204}Pb vs ^{207}Pb/^{204}Pb data from measured samples compared to Ganga river sediments (Garçon et al. 2013), seawater from Bay of Bengal (Lee et al. 2015) and aerosol from south Bengal (Kolkata, Bandel and Sagar island) (Das et al., 2018).

Table 2 Sr and Pb isotope ratios measured from archaeological cattle bone and local soil.

	Cattle bone					**Soil**
	ZA 1	ZA 1	ZA 1	ZA-1	ZA-1	ZA-1
	Dig 1	Dig 4	Dig 5	Dig 11	Dig 18	Dig 5
^{87}Sr/^{86}Sr	0.715603	0.715681	0.715681	0.715561	0.715785	0.722706
$2\sigma_m$	0.000010	0.000011	0.000011	0.000010	0.000011	0.000012
^{206}Pb/^{204}Pb	19.1034	19.1959	19.2013	-	-	19.1675
$2\sigma_m$	0.0196	0.0141	0.0014	-	-	0.0006
^{207}Pb/^{204}Pb	15.7578	15.8016	15.7978	-	-	15.7899
$2\sigma_m$	0.0154	0.0119	0.0011	-	-	0.0006
^{208}Pb/^{204}Pb	39.3564	39.4693	39.4944	-	-	39.6423
$2\sigma_m$	0.0411	0.0297	0.0027	-	-	0.0015

The Pb isotope ratios of soil (Table 2) are less radiogenic compared to River Ganga sediments, which show $^{206}Pb/^{204}Pb$ ratios ranging from 19.77 to 22.16 [38], but more radiogenic than the Bay of Bengal water [14] and aerosols from Kolkata, Bandel and Sagar Island [39](Fig. 1). The Pb isotope ratios of bones are relatively uniform and similar to the Pb isotope ratio of soil collected from Trench ZA 1 (Table 1 and 2). Possible influence of diagenesis in the distribution of bioavailable Pb isotopes are unlikely because Pb is incorporated in the bone hydroxyapatite crystals which are not soluble under natural soil pH conditions [30]. Hence, similar Pb isotope ratios in cattle bones and soil indicate that the cattle have either been locally raised or brought from a region with similar soil Pb isotope ratios.

Sr isotope ratios

$^{87}Sr/^{86}Sr$ of the local soil is 0.722706 ± 0.000012 ($2\sigma_m$) which is higher than present-day seawater. The excavation site is situated in a middle Holocene fluvio-tidal sediment deposit (Panskura formation) covered with mid to late Holocene tidal sediments. The soil of this area is expected to show $^{87}Sr/^{86}Sr$ isotope ratios similar to the sediment load for nearby rivers like Subarnarekha, Ganga and its tributaries. $^{87}Sr/^{86}Sr$ isotope ratios reported from Ganga sediments show $^{87}Sr/^{86}Sr$ isotope ratios ranging from 0.75 to 0.84 [40, 41] which are higher than the measured soil sample. Water from the Ganga and its tributaries also show higher $^{87}Sr/^{86}Sr$ (0.73 to 0.79) [42]. $^{87}Sr/^{86}Sr$ isotope ratios from Subarnarekha sediments are not available, however, river water shows 0.805 to 0.718 [43] suggesting Subarnarekha sediments are likely to be the source of the local soil.

The $^{87}Sr/^{86}Sr$ in five cattle bones from Erenda ranges from 0.715561 to 0.715785, all of which are significantly lower than the local soil. The $^{87}Sr/^{86}Sr$ ratio within cattle bones (Table 2) show a little variation. (Fig. 2). The highest ratio is measured from the deepest (i.e., oldest) layer (dig 18) and the lowest ratio from an intermediate layer (dig 11). Samples from two consecutive layers, digs 4 and 5, show the same $^{87}Sr/^{86}Sr$ ratio, while other samples from dig 1, 11 and 18 show minor variations. The overall variation (0.000224) is greater than the external reproducibility of measurement for natural samples (0.000018) which suggests that the bioavailable $^{87}Sr/^{86}Sr$ for locally raised cattle may have changed over time.

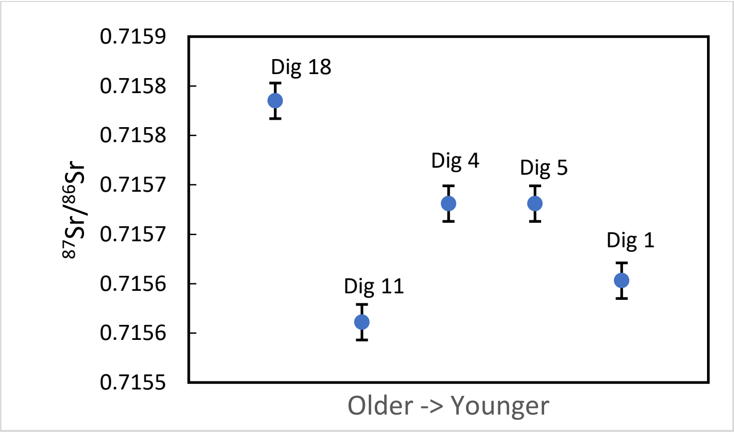

Fig. 2 $^{87}Sr/^{86}Sr$ ratios of five cattle bones from archaeological dig site Erenda. Error bars represent external reproducibility (2σ) for natural samples. samples show a variation in $^{87}Sr/^{86}Sr$ ratio with time which is larger than the external reproducibility denoted by the error bars.

Average $^{87}Sr/^{86}Sr$ ratio of bones (0.71566 ± 0.00015) is significantly lower than the local soil ($^{87}Sr/^{86}Sr = 0.722706 \pm 0.000012$, Table 2). This may have several explanations. Assuming that the initial $^{87}Sr/^{86}Sr$ was similar to that of the local soil, contamination from a source (e.g., groundwater) bearing lower $^{87}Sr/^{86}Sr$ ratio may have caused the bone $^{87}Sr/^{86}Sr$ to reduce. However, this is unlikely as the reported groundwater $^{87}Sr/^{86}Sr$ ratios

(Table S1) are generally higher than the measured bone isotope ratio. Nearby river sediments and surface water are also higher than measured ratios [40, 41, 42], and are unlikely to be the source for contamination.

Sr isotope ratio in cattle bones may differ from dietary sources such as grass, as well as that from that of the local soil [17]. Scott et al. (2020) [17] showed that cattle bone $^{87}Sr/^{86}Sr$ ratio was lower than the local soil and grass, and similar to local rainwater. They suggested that the variation of $^{87}Sr/^{86}Sr$ may be due to isotopic fractionation due to biological processes after ingestion of food as one possibility. However, mass dependent $^{87}Sr/^{86}Sr$ isotopic fractionation in the animal body can be ruled out because internal normalization [36] is used to correct mass dependent fractionation during analysis. This correction would initialize any mass dependent isotopic fractionation in the animal body after ingestion of food and water, considering both instrumental and biological processes produce mass dependent fractionation according to Rayleigh law.

Considering these factors, we can safely conclude that the difference in average bone $^{87}Sr/^{86}Sr$ ratio from that of the local soil is due to the local bioavailable $^{87}Sr/^{86}Sr$ being different from that of the local soil. Previous research such as Maurer et al. (2012) [44] also suggests that water and vegetation are better proxies for bioavailable Sr than soil or soil leachates. However, Pb and Sr isotope signatures of present-day surface water and vegetation may be affected by anthropogenic activities [45, 46] and cannot be used for comparison with archaeological samples. The relatively uniform Sr isotope ratios from five bone samples ranging over two thousand years [31] suggests that the bioavailable Sr isotope ratio has not changed significantly over this time.

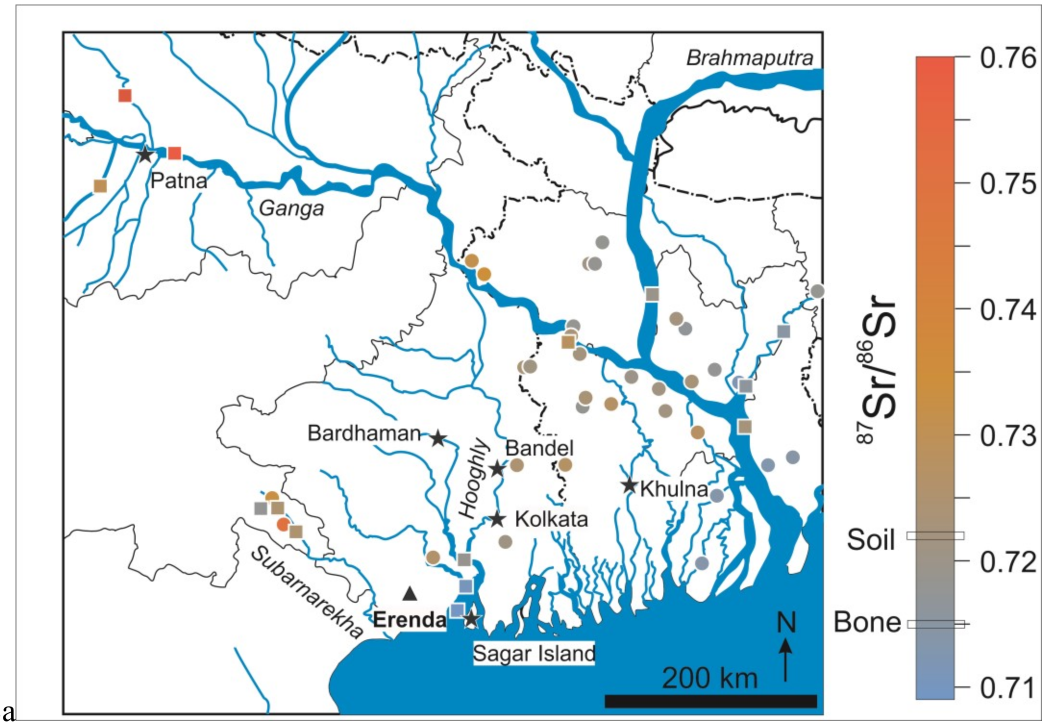

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Fig. 3 Spatial distribution of $^{87}Sr/^{86}Sr$ isotope ratios from surface and groundwater showing gradual lowering in $^{87}Sr/^{86}Sr$ along the course of Ganga, Brahmaputra, Hooghly and Subarnarekha. Most data from surface and ground water near the excavation site, except for Ganga estuary, show higher $^{87}Sr/^{86}Sr$ than measured bones. Circle and squares represent groundwater and river water respectively. Colour scale represents variation of Sr isotope ratios. Stars represent large cities and other relevant locations. Triangle represents excavations site (Erenda). Measured soil and bone isotope data are marked in the linear scale. Data is available in Table-S1.

Source of bioavailable Sr

Unlike Harappan sites [21, 22, 24] in Gujarat, the baseline value of bioavailable strontium, which is an important parameter for determining pastoral migration patterns, is not available in eastern India. The analysed bone samples present the only bioavailable $^{87}Sr/^{86}Sr$ ratios for eastern India. So, we attempt to deduce the source of bioavailable Sr for Erenda in this section.

Bioavailable $^{87}Sr/^{86}Sr$ isotope ratios may be influenced by surface water, rainwater and groundwater. Rainwater in coastal areas are likely to show $^{87}Sr/^{86}Sr$ isotope ratios equivalent to seawater ($^{87}Sr/^{86}Sr = 0.7092$) due to dissolution of aerosol particles derived from seawater [47, 48]. Groundwater $^{87}Sr/^{86}Sr$ isotope ratios may vary depending on the bedrock and source of groundwater. A compiled data set (Supplementary table S1) showing $^{87}Sr/^{86}Sr$ from river water and groundwater of nearby areas are constructed to observe the variability in the Ganga- Brahmaputra plain [43, 49, 50]. A visual interpretation (Fig. 3) of the compiled dataset suggests that surface water generally show higher $^{87}Sr/^{86}Sr$ than groundwater near the Ganga and Brahmaputra rivers. Groundwater $^{87}Sr/^{86}Sr$ ratio of an area also gets higher closer to these rivers. The opposite behaviour is seen near the Subarnarekha River (Fig. 3), which shows $^{87}Sr/^{86}Sr$ signature higher than surface water in the groundwater. However, both surface and groundwater $^{87}Sr/^{86}Sr$ ratio for Subarnarekha changes seasonally with lower $^{87}Sr/^{86}Sr$ in the monsoon compared to the dry seasons [41] which may be due to the addition of rainwater with lower $^{87}Sr/^{86}Sr$ isotope ratios. Some of the highest $^{87}Sr/^{86}Sr$ distribution is seen in Ganga water which incorporates Strontium with enriched ^{87}Sr from the Himalayan region [42]. The suspended sediment load is usually more radiogenic than the dissolved load in the Ganga and Brahmaputra [40, 51]. An increase in the groundwater $^{87}Sr/^{86}Sr$ ratios with depth in places around the excavation site indicates that the deeper sediments are richer in radiogenic Sr [49]. Unfortunately, surface or groundwater data in the coastal areas near the excavation site are not available. Coastal groundwater from Bangladesh (Burir char) shows less radiogenic ratios compared to their inland counterparts [50]. River water from Hooghly estuary [52] also show gradual decrease in $^{87}Sr/^{86}Sr$ isotope ratios due to tidal effect and mixing of sea water with river water.

Overall, most surface and groundwater, except for a few samples from major river estuaries show higher $^{87}Sr/^{86}Sr$ than the measured bone samples. As the excavation site is not located near a major river estuary, a different source bearing lower $^{87}Sr/^{86}Sr$ ratio is needed to explain the measured isotope ratios. Sea salt makes up the majority of aerosol in hot and humid coastal areas which may travel inland due to wind [48]. Deposition of the aerosol on to the ground may introduce marine Sr signature to the soil. Precipitation of rainwater with low $^{87}Sr/^{86}Sr$ (~0.709) may also be a source of bioavailable Sr. An effect of sea spray in changing the bioavailable Sr isotope ratios is reported by Alonzi et al. (2020) [53]. A similar effect is likely to occur near the excavation site, which would shift the bioavailable Sr isotope ratios towards the marine signature. It is to note that the excavation site is situated in a middle Holocene fluvio-tidal sediment deposit (Panskura formation) covered with mid to late Holocene tidal sediments [32], indicating that the neo- chalcolithic coastline was much nearer compared to today. Sea salt and marine Sr in them would be more soluble and therefor more bioavailable compared to the Sr in mineral constituents of the soil. This indicates that bioavailable Sr isotope ratios may be less radiogenic than the soil in this area.

Conclusion

Radiogenic isotopic variation of Sr and Pb have been analysed in five cattle bones and one soil sample for the first time from an archaeological site in coastal eastern India. A lack of variation in Pb isotopes in bones and soil indicates insignificant role of diagenesis in bioavailable Pb isotope distribution and a local origin of the cattle. Strontium, on the other hand, shows complex behaviour, does not reflect local soil Sr isotope ratios, and indicate a possible marine influence.

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Declarations

The authors declare no competing interests.

Authors' contributions

Bidisha Dey: Methodology, Validation, Formal analysis, Investigation, Writing – original draft. Supriyo K. Das: Conceptualization, Investigation, Writing- review and editing, Project administration. Kaushik Gangopadhyay: Conceptualization, Investigation, Resources, Writing- review, Project administration. Tomoyuki Shibata: Methodology, Resources, Validation, Supervision, Writing- review, Funding acquisition. Masako Yoshikawa: Methodology, Resources, Validation, Supervision, Writing- review, Project administration. Supriya Nandy: Formal analysis, Writing- review. Arati Deshpande Mukherjee: Formal analysis.

References

[1] Faure G, Mensing TM (2005) Isotopes: Principles and applications, 3rd edn. John Wiley & Sons, Inc., Hoboken, New Jersey

[2] Clow DW, Mast MA, Bullen TD, Turk JT (1997) Strontium 87/strontium 86 as a tracer of mineral weathering reactions and calcium sources in an Alpine/Subalpine Watershed, Loch Vale, Colorado. Water Resour Res. 33:1335-1351

[3] Probst A, El Gh'mari A, Aubert D, Fritz B, McNutt R (2000) Strontium as a tracer of weathering processes in a silicate catchment polluted by acid atmospheric inputs, Strengbach, France. Chem Geol. 170:203-219

[4] Stewart BW, Capo RC, Chadwick OA (2001) Effects of rainfall on weathering rate, base cation provenance, and Sr isotope composition of Hawaiian soils. Geochim Cosmochim Acta. 65:1087-1099

[5] Kennedy MJ, Hedin LO, Derry LA (2002) Decoupling of unpolluted temperate forests from rock nutrient sources revealed by natural 87Sr/86Sr and 84Sr tracer addition. Proc Natl Acad Sci. 99:9639-9644

[6] Pett-Ridge JC, Derry LA, Kurtz AC (2009) Sr isotopes as a tracer of weathering processes and dust inputs in a tropical granitoid watershed, Luquillo Mountains, Puerto Rico. Geochim Cosmochim Acta. 73:25-43

[7] Åberg G, Fosse G, Stray H (1998) Man, nutrition and mobility: A comparison of teeth and bone from the Medieval era and the present from Pb and Sr isotopes. Sci Total Environ. 224:109-119

[8] Patterson C, Ericson J, Manea-Krichten M, Shirahata H (1991) Natural skeletal levels of lead in Homo sapiens sapiens uncontaminated by technological lead. Sci Total Environ. 107:205-236

[9] Forsyth JE, Weaver KL, Maher K, Islam MS, Raqib R, Rahman M, Fendorf S, Luby SP (2019) Sources of blood lead exposure in Rural Bangladesh. Environ Sci Technol. 53:11429-11436

[10] Lahd Geagea M, Stille P, Gauthier-Lafaye F, Millet M (2008) Tracing of Industrial Aerosol Sources in an Urban Environment Using Pb, Sr, and Nd Isotopes. Environ Sci Technol. 42:692-698

[11] Molofsky LJ, Killick D, Ducea MN, Macovei M, Chesley JT, Ruiz J, Thibodeau A, Popescu GC (2014) A novel approach to lead isotope provenance studies of tin and bronze: Applications to South African, Botswanan and Romanian artifacts. J Archaeol

Sci. 50:440-450

[12] Slovak NM, Paytan A (2011) in: Baskaran M (ed) Handbook of Environmental Isotope Geochemistry, Advances in Isotope Geochemistry. Springer, Berlin, Heidelberg

[13] Chakrabarti R, Mondal S, Acharya SS, Lekha JS, Sengupta D (2018) Submarine groundwater discharge derived strontium from the Bengal Basin traced in Bay of Bengal water samples. Sci Rep.8:1-10

[14] Lee JM, Boyle EA, Gamo T, Obata H, Norisuye K, Echegoyen Y (2015) Impact of anthropogenic Pb and ocean circulation on the recent distribution of Pb isotopes in the Indian Ocean. Geochim Cosmochim Acta. 170:126-144

[15] Nitzsche KN, Wakaki S, Yamashita K, Shin KC, Kato Y, Kamauchi H, Tayasu I (2022) Calcium and strontium stable isotopes reveal similar behaviors of essential Ca and nonessential Sr in stream food webs. Ecosphere 13:1-19

[16] Siegel MD, Bryan CR (2013) In: Holland HD, Turekian KK (ed) Treatise Geochemistry 2nd edn. Elsevier Ltd

[17] Scott SR, Stanton NV, Gorski PR, Dahman C, Overdier JT, Shafer MM (2020) The effects of a known exposure source on Pb isotopes in bones from Pb-dosed cows. Appl Geochemistry 121:104699

[18] Bentley RA (2006) Strontium isotopes from the earth to the archaeological skeleton: A review. J Archaeol Method Theory. 13:135-187

[19] Thornton EK, Defrance SD, Krigbaum J, Williams PR (2011) Isotopic evidence for Middle Horizon to 16th century camelid herding in the Osmore Valley, Peru. Int J Osteoarchaeol. 21:544-567

[20] Chakraborty KS, Chakraborty S, Le Roux SP, Miller HML, Shirvalkar P, Rawat Y (2018) Enamel isotopic data from the domesticated animals at Kotada Bhadli, Gujarat, reveals specialized animal husbandry during the Indus Civilization. J Archaeol Sci Reports. 21:183-199

[21] Chase B, Meiggs D, Ajithprasad P, Slater PA (2018) What is left behind: Advancing interpretation of pastoral land-use in Harappan Gujarat using herbivore dung to examine biosphere strontium isotope (^{87}Sr/^{86}Sr) variation. J Archaeol Sci. 92**:**1–12

[22] Chase B, Meiggs D, Ajithprasad P (2020) Pastoralism, climate change, and the transformation of the Indus Civilization in Gujarat: Faunal analyses and biogenic isotopes. J Anthropol Archaeol. 59:101173

[23] Chase B, Ajithprasad P, Rajesh SV, Patel A, Sharma B. (2014) Materializing Harappan identities: Unity and diversity in the borderlands of the Indus Civilization. J

Anthropol Archaeol. 35:63–78

[24] Chase B, Meiggs D, Ajithprasad P, Slater PA (2014) Pastoral land-use of the Indus Civilization in Gujarat: Faunal analyses and biogenic isotopes at Bagasra. J Archaeol Sci. 50:1–15

[25] Valentine B, Kamenov GD, Kenoyer JM, Shinde V, Mushrif-Tripathy V, Otarola-Castillo E, Krigbaum John (2015) Evidence for patterns of selective urban migration in the greater Indus Valley (2600-1900 BC): A lead and strontium isotope mortuary analysis. PLoS One 10:1–20

[26] Christensen AM, Holm PM, Schuessler U, Petrasch J (2006) Indications of a major Neolithic trade route? An archaeometric geochemical and Sr, Pb isotope study on amphibolitic raw material from present day Europe. Appl Geochemistry. 21:1635–1655

[27] Smits E, Millard AR, Nowell G, Pearson DG (2010) Isotopic investigation of diet and residential mobility in the Neolithic of the Lower Rhine Basin. Eur J Archaeol. 13:5–31

[28] Valentine B, Kamenov GD Krigbaum J (2008) Reconstructing Neolithic groups in Sarawak, Malaysia through lead and strontium isotope analysis. J Archaeol Sci. 35:1463–1473

[29] Kendall C, Eriksen AMH, Kontopoulos I, Collins MJ, Turner-Walker G (2018) Diagenesis of archaeological bone and tooth. Palaeogeogr. Palaeoclimatol. Palaeoecol. 491:21–37

[30] Traina SJ, Laperche V (1999) Contaminant bioavailability in soils, sediments, and aquatic environments. Proc Natl Acad Sci U S A. 96:3365–3371

[31] Naskar N, Gangopadhyay K, Lahiri S, Chaudhuri P, Sharma R, Kumar P, Ojha S, Chopra S, Ghosh A (2021) New AMS ^{14}C dates of a multicultural archaeological site from the paleo-deltaic region of West Bengal, India: cultural and geo-archaeological implications. Radiocarbon 63:1645–1655

[32] Kumar DS, Gangopadhyay K, Ghosh A, Biswas O, Bera S, Ghosh P, Paruya DK, Naskar N, Mani D, Kalpana MS, Yoshida K (2021) Organic geochemical and palaeobotanical reconstruction of a late-Holocene archaeological settlement in coastal eastern India. Holocene 31:1511–1524

[33] Gangopadhyay K, Halder B, Chowdhury S (2017) Chalcolithic Pottery from Erenda (West Bengal): A Preliminary Assessment. Pratna Samiksha A J Archaeol New Ser. 8:125–133 (2017).

[34] Yokoyama T, Makishima A, Nakamura E (1999) Evaluation of the coprecipitation of incompatible trace elements with fluoride during silicate rock

dissolution by acid digestion. Chem Geol. 157:175–187

[35] Dey B, Shibata T, Yoshikawa M (2023) Sequential Pb-Sr-LREE separation from silicates for isotopic analysis. Geochem J. 57:73–84

[36] Nier AO (1938) The Isotopic Constitution of Strontium, Barium, Bismuth, Thallium and Mercury. Phys. Rev. 54:275–278

[37] Compston W, Oversby VM (1969) Lead Isotopic Analysis Using a Double Spike. J Geophys Res. 74:4338–4348

[38] Garçon M, Chauvel C, France-Lanord C, Limonta M, Garzanti E (2013) Removing the 'heavy mineral effect' to obtain a new Pb isotopic value for the upper crust. Geochemistry Geophys Geosystems. 14:3324–3333

[39] Das R, Bin Mohamed Mohtar AT, Rakshit D, Shome D, Wang X (2018) Sources of atmospheric lead (Pb) in and around an Indian megacity. Atmos Environ 193:57–65

[40] Awasthi N, Ray E, Paul D (2018) Sr and Nd isotope compositions of alluvial sediments from the Ganga Basin and their use as potential proxies for source identification and apportionment. Chem Geol. 476:327–339

[41] Singh SK, Rai SK, Krishnaswami S (2008) Sr and Nd isotopes in river sediments from the Ganga Basin: Sediment provenance and spatial variability in physical erosion. J. Geophys. Res Earth Surf. 113:3006.

[42] Krishnaswami S, Trivedi JR, Sarin MM, Ramesh R, Sharma KK (1992) Strontium isotopes and rubidium in the Ganga-Brahmaputra river system: Weathering in the Himalaya, fluxes to the Bay of Bengal and contributions to the evolution of oceanic 87Sr/86Sr. Earth Planet Sci Lett. 109:243–253

[43] Négrel P, Lemiére B, Machard de Grammont H, Billaud P, Sengupta B (2007) Hydrogeochemical processes, mixing and isotope tracing in hard rock aquifers and surface waters from the Subarnarekha river basin, (east Singhbhum district, Jharkhand state, India). Hydrogeol J. 15:1535–1552

[44] Maurer AF, Galer SJG, Knipper C, Beierlein L, Nunn EV, Peters D, Tütken T, Alt KW, Schöne BR (2012) Bioavailable ^{87}Sr/ ^{86}Sr in different environmental samples - Effects of anthropogenic contamination and implications for isoscapes in past migration studies. Sci Total Environ. 433:216–229

[45] Holt E, Evans JA, Madgwick R (2021) Strontium (^{87}Sr/^{86}Sr) mapping: A critical review of methods and approaches. Earth Sci Rev. 216:103593

[46] Thomsen E, Andreasen R (2019) Agricultural lime disturbs natural strontium isotope variations : Implications for provenance and migration studies. Sci Adv. 5:1–12

[47] Chatterjee J, Singh SK (2012) 87Sr/ 86Sr and major ion composition of rainwater of Ahmedabad, India: Sources of base cations. Atmos. Environ. 63:60–67.

[47] Kulkarni MR, Adiga BB, Kapoor RK, Shirvaikar VV (1982) Sea Salt in Coastal Air and its Deposition on Porcelain Insulators. J Appl Meteorol. 21:350–355

[49] Dowling CB, Poreda RJ, Basu AR (2003) The groundwater geochemistry of the Bengal Basin: Weathering, chemsorption, and trace metal flux to the oceans. Geochim Cosmochim Acta. 67:2117–2136

[50] Yoshimura T, Wakaki S, Kawahata H, Zakir Hossain HM, Manaka T, Suzuki A, Ishikawa T, Ohkouchi N (2021) Stable Strontium Isotopic Compositions of River Water, Groundwater and Sediments From the Ganges–Brahmaputra–Meghna River System in Bangladesh. Front Earth Sci. 9:1–17

[51] Singh SK, Kumar A, France-lanord C (2006) Sr and ^{87}Sr / ^{86}Sr in waters and sediments of the Brahmaputra river system : Silicate weathering , CO_2 consumption and Sr flux. Chem Geol. 234:308–320

[52] Damodararao K, Singh SK (2022) Substantial submarine groundwater discharge in the estuaries of the east coast of India and its impact on marine strontium budget. Geochim Cosmochim Acta. 324:66–85

[53] Alonzi E, Pacheco-forés SI, Gordon GW, Kuijt I, Knudson KJ (2020) New understandings of the sea spray effect and its impact on bioavailable radiogenic strontium isotope ratios in coastal environments. J Archaeol Sci Reports. 33:102462