

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

Bidisha Dey¹, Supriyo Kumar Das^{2*}, Kaushik Gangopadhyay³, Tomoyuki Shibata¹,
Masako Yoshikawa¹, Supriya Nandy⁴, Arati Deshpande Mukherjee⁵

¹*Earth and planetary system science program, Hiroshima University, Hiroshima, Japan.*

²*Department of Geology, Presidency University, Kolkata, India.*

³*Department of Archaeology, University of Calcutta, Kolkata, India.*

⁴*Zoological Survey of India, M Block, New Alipore, Kolkata, India.*

⁵*Deccan College & PG Research Institute, Pune, India*

*Corresponding Author.

Email- sdas.geol@presiuniv.ac.in

**This is an article accepted for publication at the Journal of Radioanalytical and
Nuclear Chemistry**

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

Bidisha Dey¹, Supriyo Kumar Das^{2*}, Kaushik Gangopadhyay³, Tomoyuki Shibata¹,
Masako Yoshikawa¹, Supriya Nandy⁴, Arati Deshpande Mukherjee⁵

¹*Earth and planetary system science program, Hiroshima University, Hiroshima, Japan.*

²*Department of Geology, Presidency University, Kolkata, India.*

³*Department of Archaeology, University of Calcutta, Kolkata, India.*

⁴*Zoological Survey of India, M Block, New Alipore, Kolkata, India.*

⁵*Deccan College & PG Research Institute, Pune, India*

Abstract

We present the first measurement of bioavailable strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) and lead ($^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$) isotope ratios from five cattle bones and one soil sample from Erenda, a chalcolithic site in coastal east India. Bioavailable $^{87}\text{Sr}/^{86}\text{Sr}$ of bones differ from that of the soil. A similar Pb isotope ratio of bones to the soil indicates an insignificant diagenesis and local origin of the cattle. Our result suggests a potential influence of marine Sr in modifying the bioavailable $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, although the current coastline is 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) consists of four stable isotopes: ^{84}Sr , ^{86}Sr , ^{87}Sr and ^{88}Sr . The radiogenic ^{87}Sr is derived from the decay of radioactive rubidium (^{87}Rb). The abundance of ^{87}Sr in rocks is determined by the age and original rubidium (Rb) content of the parent material. Higher abundance of Rb in crustal rocks compared to that in mantle leads to high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (near 0.715) of old metamorphic rocks. In contrary, recent volcanic rocks show lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (near 0.704). The $^{87}\text{Sr}/^{86}\text{Sr}$ of marine sedimentary rocks is determined by the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater at the time of sediment deposition and varies between 0.707 and 0.710 [1, 2, 3]. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of soils, plants growing on the soil and animals feeding on the plants in a given locality reflect the composition of underlying bedrock and mirror the variability in local geological substrates [4, 5]. Strontium, although not an essential nutrient [6], enters the body of living animals through food and water intake, and is deposited as hydroxyapatite in bones by substituting calcium (Ca) in mineral lattices due to its chemical similarity to Ca [4]. Lead (Pb), being a heavy metal, is toxic to the body. However, trace amounts of Pb enter the body through food intake and deposit in bones as phosphates [4]. ^{206}Pb and ^{207}Pb is derived from the radioactive decay of ^{238}U and ^{235}U respectively. ^{208}Pb is derived from the decay of ^{232}Th . Lead isotope ratios ($^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$) also vary in the mantle and crustal rocks depending on U/Pb and Th/Pb fractionation. Due to the relatively small difference of masses, the Sr and Pb stable isotopes are not measurably fractionated through the food web. Studies suggest that environmental or anthropogenic sources with different Pb isotope ratios have an insignificant influence on bone isotope ratios compared to the food sources [7].

Bioavailable Sr ($^{87}\text{Sr}/^{86}\text{Sr}$) and Pb ($^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$) isotope ratios have been used as useful tools for investigating ecological and archaeological mobility and migration. Applying Pb and Sr isotope ratios in archaeology assumes that an animal consumes only locally grown food products and that there is sufficient geologic homogeneity to reconstruct the $^{87}\text{Sr}/^{86}\text{Sr}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, and $^{208}\text{Pb}/^{204}\text{Pb}$ range of a locale. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in archaeological faunal remains has been used to determine pastoral migration and mobility worldwide [8, 9]. Strontium isotope values of the domesticated animals of Indian Harappan sites (Figure S1) at Kotada Bhadli and Bagasra

in Gujarat have been used to reconstruct pastoral habits of Harappans [10, 11]. Using the average Sr isotope values of tooth enamel (0.7093 to 0.7096) and comparing it to modern-day biogenic $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7091 to 0.7099) of the region [12], it has been interpreted that cattle and buffalo were raised locally and consumed at Kotada Bhadli [10]. On the contrary, cattle/buffalo were acquired from a region outside Bagasra [13]. The Sr and Pb isotopes in faunal and human dental enamel from Harappa and Farmana have been used to decipher migration patterns in the Indus Valley Civilization [14]. 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, contrary to the widespread application of bioavailable $^{87}\text{Sr}/^{86}\text{Sr}$ ratios on the Harappan archaeological sites, such research is rare in the Indian coastal archaeological sites. The application of the Pb isotope in archaeological faunal remains is rare all over India, although it has been used to determine ancient migration patterns worldwide [4, 15–17]. The objective of this research is 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, by analysing $^{87}\text{Sr}/^{86}\text{Sr}$, $^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios in cattle bones and soil excavated from a protohistoric-historic coastal site, Erenda, in eastern India.

Site and sample description

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 [18]. 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 [19, 20]. Evidence of faunal usage came from bones collected from the site.

The cultural periods of the site are divided into two phases, namely periods I and II. While it is safe to assume that 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 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) [20]. The AMS ¹⁴C dates confirm the cultural periods [18].

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

Trench	Dig	Depth (cm)	Sample type	Taxonomic classification	Cultural association
ZA1	1	10	Bone fragment	Class-Mammalia Order-Artiodactyla Family- Bovidae Genus- <i>Bos</i> .	Medieval- modern.
ZA1	4	59	Bone fragment	Class-Mammalia Order-Artiodactyla Family- Bovidae Genus- <i>Bos</i> .	Early medieval/ medieval
ZA1	5	60	Bone fragment	Class-Mammalia Order-Artiodactyla Family- Bovidae Genus- <i>Bos</i> .	Early medieval/ medieval
ZA1	5	60	Soil		
ZA1	11	92	Bone fragment	Class-Mammalia Order-Artiodactyla Family- Bovidae Genus- <i>Bos</i> .	Early medieval
ZA1	18	130	Bone fragment	Class-Mammalia Order-Artiodactyla Family- Bovidae Genus- <i>Bos</i> .	Chalcolithic

Experimental

Sampling

The archaeological site is a mound measures approximately 30 m east to west and 30 m north to south. Human artefacts are 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 [19]. 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 [19]. 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. Based on their preservation, five representative cattle bones and one soil sample were selected from digs 1, 4, 5, 11 and 18 in trench ZA1 (Table 1) for the present study. Details of the trench positions and digs are described by Gangopadhyay et al. (2017) [20] and Das et al. (2021) [19].

Sample preparation

Bone fragments were transported to the Presidency University in Kolkata and cleaned using a nylon brush. A low-speed stainless steel dental drill was used to remove the soil from uneven bone surfaces 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 HNO₃ and ultrapure grade HClO₄ and H₂O₂ 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 vessels made of PFA (Savillex). 20-40 mg of bone powder were digested with HCl, H₂O₂ and HClO₄ before dilution in 0.6 mL 3 mol/L HNO₃. About 20 mg soil sample was baked at 700 degrees for one day to break down organic material before digesting with HF, HClO₄ and HCl [21], and finally diluted in 3 mol/L HNO₃. 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) [22]. The sample solutions in 3 mol/L HNO₃ 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 3 mol/L HNO₃, and Sr was collected in a 7 mL PFA beaker (Savillex) using 1 mL 0.05 M HNO₃. Pb was collected subsequently using 3 mL 6 mol/L HCl in a 7 mL PFA beaker with round bottom (Savillex). 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 HNO₃ for isotopic analysis. Pb was loaded on a single U-shaped Re filament using colloidal silica and H₃PO₄. 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 $^{88}\text{Sr}/^{86}\text{Sr} = 0.1194$ [23] and the double spike method for Pb [24]. Isotope standards measured alongside samples, NIST SRM 987 for Sr and NIST SRM 981 for Pb, yielded $^{87}\text{Sr}/^{86}\text{Sr} = 0.710255 \pm 0.000017$ ($2\sigma_m$) for Sr; and $^{206}\text{Pb}/^{204}\text{Pb} = 16.9425 \pm 0.0006$ ($2\sigma_m$), $^{207}\text{Pb}/^{204}\text{Pb} = 15.4994 \pm 0.0006$ ($2\sigma_m$), and $^{208}\text{Pb}/^{204}\text{Pb} = 36.7279 \pm 0.0014$ ($2\sigma_m$) for Pb. External reproducibility for isotope ratios in this lab was determined [22] and yielded $^{87}\text{Sr}/^{86}\text{Sr} = 0.710264 \pm 0.000014$ (2σ , $n = 10$) for NIST SRM 987 and $^{87}\text{Sr}/^{86}\text{Sr} = 0.703699 \pm 0.000018$ (2σ , $n = 7$) for reference rock JB-2. Pb isotope ratios yielded $^{206}\text{Pb}/^{204}\text{Pb} = 16.9397 \pm 0.0013$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.4972 \pm 0.0014$, and $^{208}\text{Pb}/^{204}\text{Pb} = 36.7187 \pm 0.0024$ (2σ , $n = 5$) for NIST SRM 981 and $^{206}\text{Pb}/^{204}\text{Pb} = 18.3223 \pm 0.0097$, $^{207}\text{Pb}/^{204}\text{Pb} = 15.5575 \pm 0.0064$, and $^{208}\text{Pb}/^{204}\text{Pb} = 38.2442 \pm 0.0162$ (2σ , $n = 7$) for reference rock JB-2.

Results and discussion

Pb isotope ratios

The Pb isotope ratios of soil (Table 2) are less radiogenic compared to River Ganga sediments, which show $^{206}\text{Pb}/^{204}\text{Pb}$ ratios ranging from 19.77 to 22.16 [25], but more radiogenic than the Bay of Bengal water [26] and aerosols from Kolkata, Bandel and Sagar Island [27] (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).

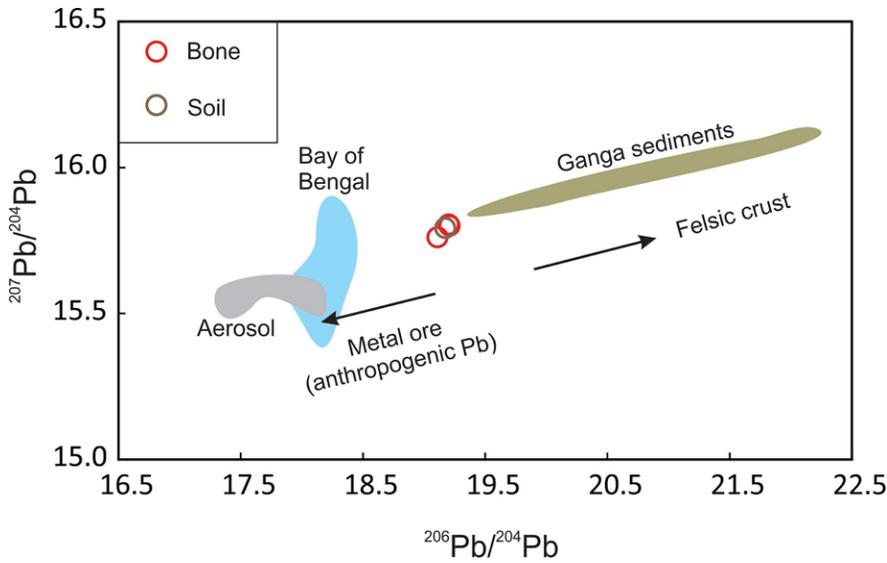


Fig. 1 $^{206}\text{Pb}/^{204}\text{Pb}$ vs $^{207}\text{Pb}/^{204}\text{Pb}$ data from measured samples compared to River Ganga sediments [25], seawater from Bay of Bengal [26] and aerosol from south Bengal (Kolkata, Bandel and Sagar Island) [27].

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

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

The minor difference between the soil and bone isotope ratios may result from Pb isotope ratios in the insoluble silicate fractions in soil and bioavailable/exchangeable Pb taken up by plants. Archaeological bones are considered susceptible to diagenetic alteration due to their high organic matter content, high porosity, and poor preservation of the crystalline structure, especially in the humid tropical coast of eastern India [28]. Nonetheless, it has been observed that even 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 the surrounding environment [4, 29]. Hence, possible influence of diagenesis in the distribution of bioavailable Pb isotopes is unlikely because Pb is incorporated in the bone hydroxyapatite crystals, which are not soluble under natural soil pH conditions [29]. Thus, 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

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the local soil is 0.722706 ± 0.000012 ($2\sigma_m$). The excavation site lies 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 $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios similar to the sediment load for nearby rivers like Subarnarekha, Ganga and its tributaries. The $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios reported from Ganga sediments show $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios ranging from 0.75 to 0.84 [30, 31], which are higher than the measured soil sample. Water from the Ganga and its tributaries also show higher $^{87}\text{Sr}/^{86}\text{Sr}$ (0.73 to 0.79) [32]. The $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios from Subarnarekha sediments are not available. An $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.718 to 0.805 of River Subarnarekha water [33] suggests the rived sediments are likely to be the source of the local soil.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in five cattle bones from Erenda ranges from 0.715561 to 0.715785, all of which are significantly lower than the local soil. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio within cattle bones (Table 2) shows a minor 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 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, while other samples from digs 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 $^{87}\text{Sr}/^{86}\text{Sr}$ for locally raised cattle may have changed over time.

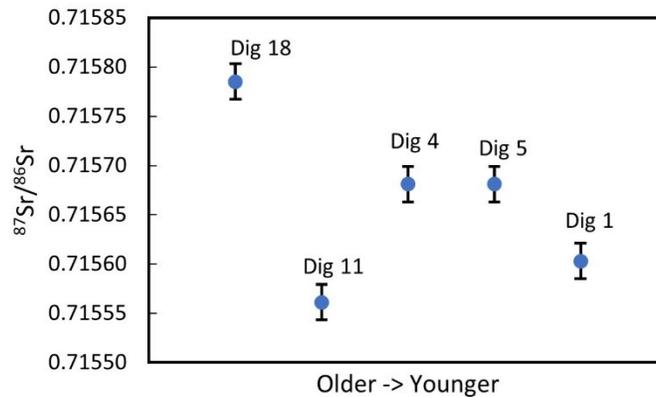


Fig. 2 $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of five cattle bones from archaeological dig site Erenda. Error bars represent external reproducibility (2σ) for natural samples. Samples show a variation in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio with time which is larger than the external reproducibility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

The average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of bones (0.71566 ± 0.00015) is significantly lower than the local soil ($^{87}\text{Sr}/^{86}\text{Sr} = 0.722706 \pm 0.000012$, Table 2). This may have several explanations. Assuming that the initial $^{87}\text{Sr}/^{86}\text{Sr}$ was similar to that of the local soil, contamination from a source (e.g., groundwater) bearing a lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratio may have caused the bone $^{87}\text{Sr}/^{86}\text{Sr}$ to reduce. However, this is unlikely as the reported groundwater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Fig. 3, Table S1) are generally higher than the measured bone isotope ratio. Nearby river sediments and surface water are also higher than measured ratios [30–32], and are unlikely to be the source for contamination.

Sr isotope ratio in cattle bones may differ from dietary sources such as grass and that of the local soil [7]. Cattle bone $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, lower than the local soil and grass, and similar to local rainwater has been reported by Scott et al. (2020) [7]. The authors suggested that the variation of $^{87}\text{Sr}/^{86}\text{Sr}$ due to the isotopic fractionation during biological processes after

ingestion of food as one possibility. However, mass-dependent $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic fractionation in the animal body can be ruled out because internal normalization [23] is used to correct mass-dependent fractionation during analysis. This correction would initialize any mass-dependent isotopic fractionation in the animal body after ingesting food and water, considering both instrumental and biological processes produce mass-dependent fractionation according to Rayleigh law.

Considering these factors, we may conclude that the difference in average bone $^{87}\text{Sr}/^{86}\text{Sr}$ ratio from that of the local soil is due to the local bioavailable $^{87}\text{Sr}/^{86}\text{Sr}$ being different from that of the local soil. Previous research, such as Maurer et al. (2012) [34], 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 [35, 36] and cannot be used for comparison with archaeological samples. The relatively uniform Sr isotope ratios from five bone samples with ages spanning over two thousand years [18] suggest that the bioavailable Sr isotope ratio has not changed significantly over time.

Source of bioavailable Sr

Unlike Harappan sites [11–13] in Gujarat, the baseline value of bioavailable strontium, which is an important parameter for determining pastoral migration patterns, is unavailable in eastern India. The analysed bone samples present only bioavailable $^{87}\text{Sr}/^{86}\text{Sr}$ ratios from eastern India. We attempt to deduce the source of bioavailable Sr for Erenda in this section.

Bioavailable $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios may be influenced by surface water, rainwater and groundwater. Rainwater in coastal areas is likely to show $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios equivalent to seawater ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7092$) due to the dissolution of aerosol particles derived from seawater [37, 38]. Modern-day seawater Sr isotope ratios are uniform with negligible spatial variation [39]. Groundwater $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios may vary depending on the bedrock and source of groundwater. A compiled data set (Supplementary Table S1) showing $^{87}\text{Sr}/^{86}\text{Sr}$ from river water and groundwater of nearby areas is constructed to observe the variability in the Ganga-Brahmaputra plain [33, 40, 41].

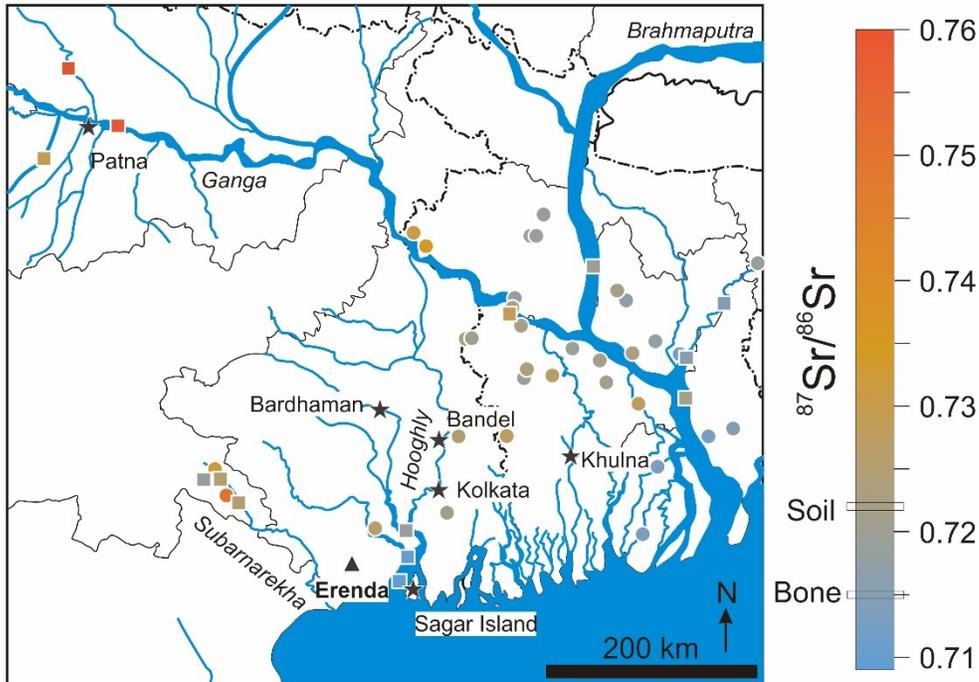


Fig. 3 Spatial distribution of $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios from surface and groundwater showing gradual lowering in $^{87}\text{Sr}/^{86}\text{Sr}$ along the course of Ganga, Brahmaputra, Hooghly and Subarnarekha. Most data from surface and groundwater near the excavation site, except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

A visual interpretation (Fig. 3) of the compiled dataset suggests that surface water generally shows higher $^{87}\text{Sr}/^{86}\text{Sr}$ than groundwater near the Ganga and Brahmaputra Rivers. The groundwater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of an area, closer to the rivers, also becomes higher. The opposite behaviour is seen near the Subarnarekha River (Fig. 3), which shows an $^{87}\text{Sr}/^{86}\text{Sr}$ signature higher than surface water in the groundwater. However, both surface and groundwater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for Subarnarekha changes seasonally with lower $^{87}\text{Sr}/^{86}\text{Sr}$ in the monsoon compared to the dry seasons [31], which may be due to the addition of rainwater with lower $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios. Some of the highest $^{87}\text{Sr}/^{86}\text{Sr}$ distribution is seen in

Ganga water which incorporates Sr with enriched ^{87}Sr from the Himalayan region [32]. The suspended sediment load is usually more radiogenic than the dissolved load in the Ganga and Brahmaputra [30, 32]. An increase in the groundwater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with depth in places around the excavation site indicates that the deeper sediments are richer in radiogenic Sr [40]. Unfortunately, surface or groundwater data in the coastal areas near the excavation site are unavailable. Coastal groundwater from Bangladesh (Burir char) shows less radiogenic ratios than their inland counterparts [41]. River water from Hooghly estuary [43] also indicates a gradual decrease in $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios due to the tidal effect and mixing of seawater with river water.

Most surface and groundwater, except for a few samples from major river estuaries, show higher $^{87}\text{Sr}/^{86}\text{Sr}$ than the measured bone samples. As the excavation site is not near any major river estuary, a different source bearing a lower $^{87}\text{Sr}/^{86}\text{Sr}$ 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 [38]. Aerosol deposition may introduce marine Sr signature to the soil. Precipitation of rainwater with low $^{87}\text{Sr}/^{86}\text{Sr}$ (~ 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) [44]. A similar effect would likely occur near the excavation site, shifting the bioavailable Sr isotope ratios towards the marine signature. Notably, the excavation site is situated in a middle Holocene fluvio-tidal sediment deposit (Panskura formation) covered with mid to late Holocene tidal sediments [19], indicating that the neo- chalcolithic coastline was much nearer compared to today. Sea salt and marine Sr would be more soluble and bioavailable than 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 an 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 indicates a possible marine influence.

Acknowledgements

We thank the anonymous reviewer for providing helpful comments and suggestions in improving the manuscript. We thank the Department of Archaeology, Calcutta University, for the excavation and providing the samples. We thank the Zoological Survey of India and the Archaeozoological Laboratory in Deccan College PG and Research Institute, Puna, for identifying bone samples. We are grateful for the resources and facilities provided for isotopic analysis by the Laboratory for Igneous Rock Geochemistry, Hiroshima University. This work was partially supported by HiPeR, which was selected and supported by Hiroshima University.

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. Dasch EJ (1969) Strontium isotopes in weathering profiles, deep-sea sediments, and sedimentary rocks, *Geochimica et Cosmochimica Acta* 33: 1521-1552.
2. Faure G, Powell JL (1972) *Strontium isotope geology*, Springer-Verlag, New York.
3. Palmer MR, Elderfield H (1985) Sr isotope composition of sea water over the past 75 Myr, *Nature* 314: 526–528.
4. 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. [https://doi.org/10.1016/S0048-9697\(98\)00347-7](https://doi.org/10.1016/S0048-9697(98)00347-7)
5. Slovak NM, Paytan A (2012) *Handbook of Environmental Isotope Geochemistry*. Springer Berlin Heidelberg, Berlin, Heidelberg
6. Nitzsche KN, Wakaki S, Yamashita K, et al (2022) Calcium and strontium stable isotopes reveal similar behaviors of essential Ca and nonessential Sr in stream food webs. *Ecosphere* 13:1–19. <https://doi.org/10.1002/ecs2.3921>
7. Scott SR, Stanton N V., Gorski PR, et al (2020) The effects of a known exposure source on Pb isotopes in bones from Pb-dosed cows. *Appl Geochemistry* 121:104699. <https://doi.org/10.1016/j.apgeochem.2020.104699>
8. Bentley RA (2006) Strontium isotopes from the earth to the archaeological skeleton: A review. *J Archaeol Method Theory* 13:135–187. <https://doi.org/10.1007/S10816-006-9009-X/FIGURES/21>
9. 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. <https://doi.org/10.1002/oa.1157>
10. Chakraborty KS, Chakraborty S, Le Roux P, et al (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. <https://doi.org/10.1016/j.jasrep.2018.06.031>

11. 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.
<https://doi.org/10.1016/j.jaa.2020.101173>
12. 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 ($^{87}\text{Sr}/^{86}\text{Sr}$) variation. *J Archaeol Sci* 92:1–12. <https://doi.org/10.1016/j.jas.2018.01.007>
13. 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. <https://doi.org/10.1016/j.jas.2014.06.013>
14. Valentine B, Kamenov GD, Kenoyer JM, et al (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.
<https://doi.org/10.1371/journal.pone.0123103>
15. 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. <https://doi.org/10.1016/j.apgeochem.2006.07.009>
16. 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. <https://doi.org/10.1177/1461957109355040>
17. 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. <https://doi.org/10.1016/j.jas.2007.10.016>
18. Naskar N, Gangopadhyay K, Lahiri S, et al (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.
<https://doi.org/10.1017/RDC.2021.111>
19. Das SK, Gangopadhyay K, Ghosh A, et al (2021) Organic geochemical and palaeobotanical reconstruction of a late-Holocene archaeological settlement in coastal eastern India. *The Holocene* 31:1511–1524.
<https://doi.org/10.1177/09596836211025970>
 20. 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
 21. 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
 22. Dey B, Shibata T, Yoshikawa M (2023) Sequential Pb-Sr-LREE separation from silicates for isotopic analysis. *Geochem J* 57:73–84.
<https://doi.org/https://doi.org/10.2343/geochemj.GJ23006>
 23. Nier AO (1938) The Isotopic Constitution of Strontium, Barium, Bismuth, Thallium and Mercury. *Phys Rev* 54:275–278.
<https://doi.org/10.1103/PhysRev.54.275>
 24. Compston W, Oversby VM (1969) Lead Isotopic Analysis Using a Double Spike. *J Geophys Res* 74:4338–4348. <https://doi.org/10.1029/JB074i017p04338>
 25. Garçon M, Chauvel C, France-Lanord C, et al (2013) Removing the "heavy mineral effect" to obtain a new Pb isotopic value for the upper crust. *Geochemistry Geophysics Geosystems* 14: 3324–3333. doi: 10.1002/ggge.20219
 26. Lee JM, Boyle EA, Gamo T, et al (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. <https://doi.org/10.1016/j.gca.2015.08.013>

27. Das R, Bin Mohamed Mohtar AT, Rakshit D, et al (2018) Sources of atmospheric lead (Pb) in and around an Indian megacity. *Atmos Environ* 193:57–65. <https://doi.org/10.1016/j.atmosenv.2018.08.062>
28. Kendall C, Eriksen AMH, Kontopoulos I, et al (2018) Diagenesis of archaeological bone and tooth. *Palaeogeogr Palaeoclimatol Palaeoecol* 491:21–37. <https://doi.org/10.1016/j.palaeo.2017.11.041>
29. Traina SJ, Laperche V (1999) Contaminant bioavailability in soils, sediments, and aquatic environments. *Proc Natl Acad Sci U S A* 96:3365–3371. <https://doi.org/10.1073/pnas.96.7.3365>
30. 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. <https://doi.org/10.1016/j.chemgeo.2017.11.029>
31. 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. <https://doi.org/10.1029/2007JF000909>
32. Krishnaswami S, Trivedi JR, Sarin MM, et al (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 $^{87}\text{Sr}/^{86}\text{Sr}$. *Earth Planet Sci Lett* 109:243–253. [https://doi.org/10.1016/0012-821X\(92\)90087-C](https://doi.org/10.1016/0012-821X(92)90087-C)
33. Négrel P, Lemiére B, Machard de Grammont H, et al (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. <https://doi.org/10.1007/s10040-007-0227-4>
34. Maurer AF, Galer SJG, Knipper C, et al (2012) Bioavailable $^{87}\text{Sr}/^{86}\text{Sr}$ in

- different environmental samples - Effects of anthropogenic contamination and implications for isoscapes in past migration studies. *Sci Total Environ* 433:216–229. <https://doi.org/10.1016/j.scitotenv.2012.06.046>
35. Holt E, Evans JA, Madgwick R (2021) Strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) mapping: A critical review of methods and approaches. *Earth-Science Rev.* 216:103593
 36. Thomsen E, Andreasen R (2019) Agricultural lime disturbs natural strontium isotope variations : Implications for provenance and migration studies. *Sci Adv* 5:1–12
 37. Chatterjee J, Singh SK (2012) $^{87}\text{Sr}/^{86}\text{Sr}$ and major ion composition of rainwater of Ahmedabad, India: Sources of base cations. *Atmos Environ* 63:60–67. <https://doi.org/10.1016/J.ATMOSENV.2012.08.060>
 38. Kulkarni MR, Adiga BB, Kapoor RK, Shirvaikar V V (1982) Sea Salt in Coastal Air and its Deposition on Porcelain Insulators. *J Appl Meteorol* 21:350–355
 39. Chakrabarti R, Mondal S, Acharya SS, et al (2018) Submarine groundwater discharge derived strontium from the Bengal Basin traced in Bay of Bengal water samples. *Sci Rep* 8:1–10. <https://doi.org/10.1038/s41598-018-22299-5>
 40. Dowling CB, Poreda RJ, Basu AR (2003) The groundwater geochemistry of the Bengal Basin: Weathering, chemisorption, and trace metal flux to the oceans. *Geochim Cosmochim Acta* 67:2117–2136. [https://doi.org/10.1016/S0016-7037\(02\)01306-6](https://doi.org/10.1016/S0016-7037(02)01306-6)
 41. Yoshimura T, Wakaki S, Kawahata H, et al (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. <https://doi.org/10.3389/feart.2021.592062>
 42. Singh SK, Kumar A, France-lanord C (2006) Sr and $^{87}\text{Sr}/^{86}\text{Sr}$ in waters and sediments of the Brahmaputra river system : Silicate weathering , CO_2 consumption and Sr flux. *Chem Geol* 234:308–320.

<https://doi.org/10.1016/j.chemgeo.2006.05.009>

43. 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. <https://doi.org/10.1016/j.gca.2022.03.002>
44. Alonzi E, Pacheco-forés SI, Gordon GW, et al (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. <https://doi.org/10.1016/j.jasrep.2020.102462>