Pb and Sr concentrations and isotopic compositions in prehistoric North American teeth: A methodological study

Citation: Dudás, F.ö. et al. “Pb and Sr Concentrations and Isotopic Compositions in Prehistoric North American Teeth: A Methodological Study.” Chemical Geology 429 (2016): 21–32.

As Published: http://dx.doi.org/10.1016/j.chemgeo.2016.03.003

Publisher: Elsevier

Persistent URL: http://hdl.handle.net/1721.1/106292

Version: Final published version: final published article, as it appeared in a journal, conference proceedings, or other formally published context

Chemical Geology 429 (2016) 21–32

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Pb and Sr concentrations and isotopic compositions in prehistoric North American teeth: A methodological study

F.Ö. Dudás [a],*, S.A. LeBlanc [b], S.W. Carter [a], S.A. Bowring [a]

[a] Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA
[b] Peabody Museum of Archaeology and Ethnology, Harvard University, 11 Divinity Avenue, Cambridge, MA 02138, USA

ARTICLE INFO

Article history:
Received 23 July 2015
Received in revised form 2 March 2016
Accepted 5 March 2016
Available online 7 March 2016

Keywords:
Pb isotopes
Sr isotopes
Teeth
Chaco
Mimbres
Basketmaker

ABSTRACT

We present Pb and Sr isotopic compositions and elemental concentrations for dentin and enamel from 28 human teeth from 10 locations in the southwestern United States. These teeth represent Native American communities that were functioning between 300 BCE and 1200 CE. We wished to assess whether Pb isotopic data can extend the interpretations made from Sr isotopic data alone, and to determine the analytical requirements for doing Sr and Pb analyses from single samples. Pb concentrations in our samples are between 0.06 and 48 ppm, with Sr concentrations between 10 and 3300 ppm. $^{87}Sr/^{86}Sr$ compositions lie between 0.708 and 0.712. Pb isotopic compositions are more variable, with $^{206}Pb/^{204}Pb$ ranging between 17.9 and 21.7. Isotopic compositions and elemental concentrations for both Sr and Pb can be determined on samples smaller than 1 mg, but there is real heterogeneity between samples of this size. Neither concentrations nor isotopic compositions are reproducible to within analytical uncertainty in replicate aliquots from individual teeth. We cannot determine whether this variability is an in-vivo or a diagenetic effect. Combined Pb and Sr isotopic data discriminate most locations, and the inclusion of Pb data provides a stronger basis for archeological interpretations. Our data suggest that Pb is more susceptible to post-mortem exchange than Sr. Background isotopic data are needed to characterize Pb and Sr sources in the study areas. Pb concentration data for enamel samples indicate a blood Pb load of 0.1–0.2 μg Pb/dL for preindustrial Native Americans.

1. Introduction

Isotopic analyses of strontium (Sr), in a range of materials including human remains, are a proven method for ascertaining their origins, and are used in many different disciplines, including archeology and anthropology. By comparison, though lead (Pb) isotopic analyses are important in geological and environmental studies, they are less commonly used in archeology and anthropology. The number of studies that use Pb isotopes with human remains – bones or teeth – is limited (e.g., Chiaradia et al., 2003; Gulson, 1996; Gulson and Gillings, 1997; Gulson et al., 1997; Kamenov, 2008; Turner et al., 2009; Valentine et al., 2008).

Key to the interpretation and value of studying Sr and Pb isotope ratios in human teeth is that enamel forms early in life and retains this isotopic composition, whereas dentin, like bone, remodels and reflects the isotopic composition of food sources over the last 5–7 years of life (Hillson, 1996). If individuals move from where they lived in infancy, their enamel reflects the isotope ratios of their birth locality, and dentin reflects the isotope ratios of where they lived during the last 5–7 years of life. Thus, among other applications, isotopic analyses can potentially track migration and mate exchange in prehistory (e.g., Price et al., 1994; Price et al., 2010).

The primary goals of our methodological study, using both Pb and Sr isotopes, were to determine whether Pb isotopic analyses could provide information beyond that obtained from Sr isotopes, and to assess the minimum sample size required for reliable analyses of both isotopic systems in single samples. Because high precision isotopic analyses are destructive, it is important to minimize sample size and to determine the reliability of information acquired from minimal sample sizes. A methodological assessment is warranted in part because of the difficulties in determining original isotopic compositions, as documented in other studies (Budd et al., 1998, 2000a; Benson, 2010; Trickett et al., 2003). Our work is an adjunct to ongoing studies of Native American remains in the southwestern United States (US), in which a large data set of Sr isotopic analyses of human remains is being generated, supplemented by acquisition of other kinds of data (T.D. Price, pers. comm.).

The main hurdle to the interpretation of isotopic data from archeological materials, including human remains, is that the elements of interest, Sr and Pb in this case, but including also the lighter elements (H, C, O, N, and S), are subject to post-mortem processes – diagenesis –

---

* Corresponding author at: 37 Birchwood Lane, Lincoln, MA 01773, USA.
E-mail addresses: fdudas@mit.edu (F.Ö. Dudás), leblanc@fas.harvard.edu (S.A. LeBlanc), swcarter@mit.edu (S.W. Carter), sabowring@mit.edu (S.A. Bowring).

http://dx.doi.org/10.1016/j.chemgeo.2016.03.003
0009-2541/

that can modify both concentrations and isotopic compositions. Diagenetic processes in wet climates usually involve interaction with groundwater; in arid environments, crystallization of secondary phases is important. Diagenetic effects need to be evaluated independently at each location, and may vary even between burials at the same location.

An additional problem affects Pb data: anthropogenic Pb pollution of the earth's surface is pervasive. No sample can be assumed to be free of Pb contamination that could occur during initial recovery, transport, storage, or sample preparation. Anthropogenic Pb pollution, in some locations, dates back about 7000 years (Lee et al., 2008); global aerosol Pb pollution probably started in Greek or Roman times, and dates back about 3000 years (Dunlap et al., 1999; Hong et al., 1994). In the southwestern US, which is distant from most sources of prehistoric anthropogenic Pb pollution, contamination at the time of burial was unlikely, and subsequent contamination is also minimized by the remoteness of the archeological sites.

We chose the southwestern US study sites because their isolation and arid climate both favor retention, in human teeth, of original compositions. Because most of our samples were collected prior to 1930, the possibility of contamination by gasoline-derived aerosol Pb pollution is minimized. Our study focuses on four geographic areas where previous Sr isotopic analyses did not discriminate at a level necessary to address archeological questions. We report Sr and Pb concentrations and isotopic compositions in dentin and enamel pairs from 28 teeth from 10 different locations.

2. Background and sample selection

Table 1 provides relevant information for the 10 sites, and Fig. 1 shows their approximate locations. We selected 28 teeth from among approximately 300 on which Sr isotopic analyses are being done in another study. These 28 included no Sr isotopic outliers, but included samples for which Sr isotopic analyses overlapped, thus making archeological interpretations ambiguous.

2.1. Archeological background

After initial colonization of the continent, the populations of the US southwest were mobile foragers. Beginning around 3000 BCE, there was a shift to corn (maize) agriculture and populations grew in size and social complexity. There are two models for the shift to farming: local adoption of domesticates by foragers, or migration of farming populations from Mesoamerica (LeBlanc, 2008). In the Four Corners area, it has been proposed that both happened: the westerly populations were migrants and the easterly populations (e.g., Falls Creek near Durango) were indigenous foragers who adopted farming. In this model, we expect a high level of social and mate exchange among the closely related westerly people, but a lower level of interaction with the easterly population that would have been culturally and linguistically different. Because these people did not have pottery and made rather spectacularly decorated baskets, they have been called Basketmakers. The Basketmaker culture sites considered here spanned approximately from 300 BCE to 300 CE. Smiley and Robins (1997) provide a cultural overview and a discussion of the Basketmaker sites.

Table 1
Site locations and background information.

Location	State	Approximate age	Total samples	Sample numbers
Four Corners — Basketmaker				
White Dog	AZ	300 BCE–300 CE	1	TS13
Battle Cave	AZ	300 BCE–300 CE	2	F6233, F6234
Grand Gulch	UT	300 BCE–300 CE	2	F6245, F6246
Cave 7	UT	300 BCE–300 CE	2	F5594, F5600
Durango — Basketmaker				
Falls Creek	CO	300 BCE–300 CE	4	F2513, F2515, F5218, F2519
Chaco Area — Chacoan				
Penasco Blanco	NM	850–1130 CE	4	F5595, F6182, F6185, F6188
Pueblo Bonito	NM	850–1130 CE	5	F5399, F5400, F5403, F6171, F6173
Kin Bineola	NM	850–1130 CE	2	F6248, F6250
SW New Mexico — Mimbres				
Harris	NM	800–1000 CE	1	TS347A
NAN	NM	800–1100 CE	5	F5392, F5393, F5394, F5390, F5391

Population and social complexity reached its peak in the US southwest between 900 and 1130 CE. The greatest concentration of people and the most monumental architecture developed in Chaco Canyon, New Mexico. Lister and Lister (1981) provide a cultural overview and a discussion of these sites. Various models propose that people regularly moved in, that people colonized outward from the center, that women only were brought into Chaco Canyon; there may have been two social groups with little biological interaction among them (Vivian, 1990, and Plog and Heitman, 2010, provide examples of different models).

Around the same time as the events in Chaco Canyon, a unique culture developed in southwestern New Mexico, focused on the Mimbres River valley. These people produced artistically refined, painted pottery bowls that are unprecedented in North America (LeBlanc, 1983). Suddenly, around 1130 CE, the culture and the pottery essentially disappear. Based on pottery, there are hints of considerable population movement within the area, but we have little archeological understanding of the social behaviors or population movements during this cultural florescence, so knowing what types of people moved what distances would be of major significance. Shafer (2003) and Haury (1936) describe the sites studied here. Samples from the Mimbres area were collected in the 1970s and 1980s. The Mimbres area is near the Chino Mine (Hanover, NM) and the smelter complex at Hurley, NM, both of which were active in the 1970s, so that recent anthropogenic contamination of the Mimbres samples is possible.

2.2. Geochemical background

Pb and Sr occur in bones and teeth as substitutions for Ca in the apatite structure (Skinner, 2005), which can accommodate large amounts of both elements. Whereas ^{87}Sr/^{86}Sr compositions are typically between 0.7 and 0.8, a range that is roughly 12% of the value, Pb isotopic variation can be much larger; so, for example, ^{206}Pb/^{204}Pb varies between 16 and 22 in “normal” samples, a range that is more than 25% of the value. This suggests that discrimination with Pb might be more efficient than with Sr. Bentley (2006) provides a comprehensive review of archeological interpretation of Sr isotopic data, but no comparable assessment of Pb isotopic applications is available.

Archeological interpretations of isotopic data hinge on identifying what in-vivo concentrations and isotopic compositions were. The extensive literature that treats diagenesis of archeological samples emphasizes changes that occur in human and animal bones, in light stable isotopes, and in samples from relatively wet environments. There are fewer studies on effects in enamel, and on changes that occur in arid environments.

Bones and teeth consist dominantly of hydroxyapatite, with minor substitutions of carbonate and fluoride for hydroxyl. During diagenesis, increases in carbonate substitution lead to bones that are more soluble, whereas increases in fluoride substitution lead to bones that are less soluble than hydroxyapatite (Sillen and Sealy, 1995). Thus, the preservation of bones and teeth is intimately linked with the chemistry of diagenetic modification. Multiple mechanisms can be involved in diagenesis (e.g., Ericson et al., 1991; Lee-Thorp and Sponheimer, 2003; Michel et al., 1996; Nielsen-Marsh and Hedges, 2000): 1. adsorption of cations onto external surfaces; 2. exchange of anions (CO_3^{2-} for PO_4^{3-}, and substitutions between CO_3^{2-}, OH^-, F^-, and Cl^-), some of which require a coupled cation substitution to maintain charge balance; 3. exchange of cations (Sr^{2+} or Pb^{2+} for Ca^{2+}, among other possible

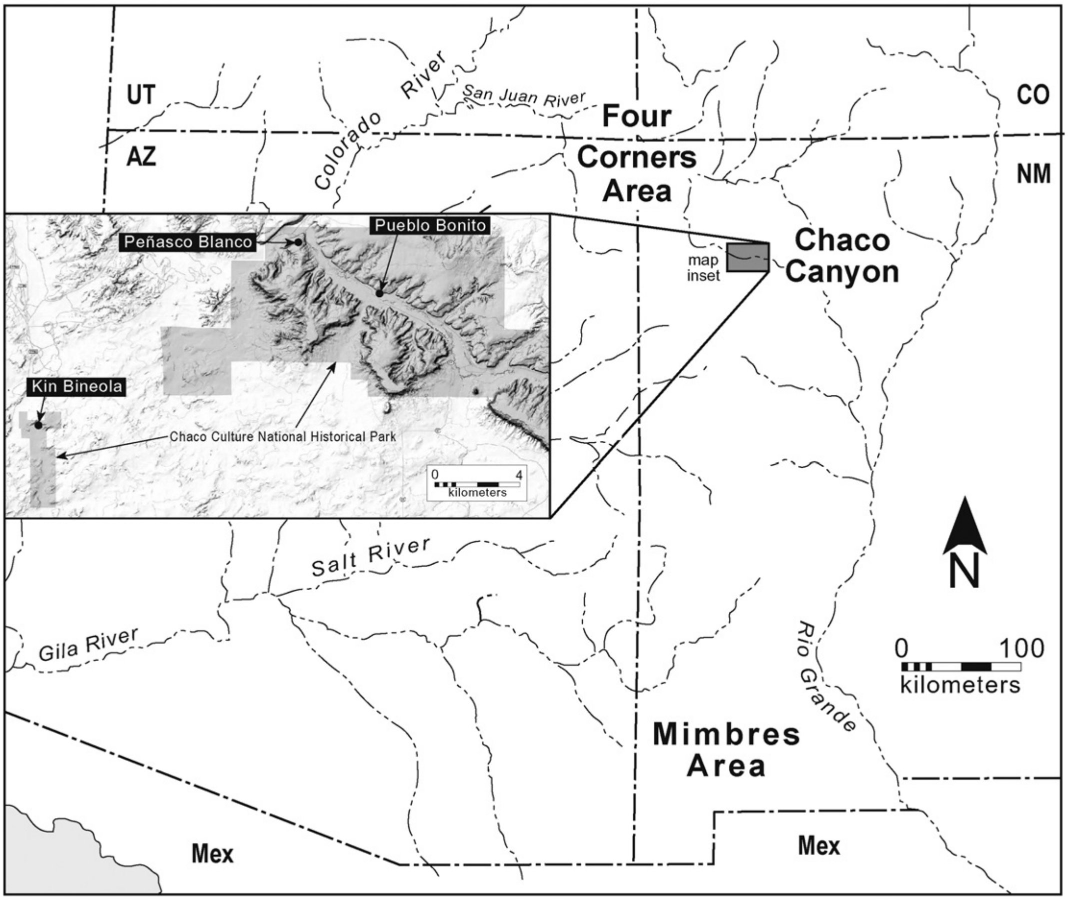

Fig. 1. Samples for this study are from the Four Corners Area (includes samples from Durango, Colorado), the Mimbres Area, and Chaco Canyon. The inset map shows sites within Chaco Canyon National Monument (gray stipple). Detailed maps are in the Supplementary materials.

substitutions); 4. recrystallization with or without ion exchange; 5. diffusion; and 6. precipitation of new phases. All mechanisms are mediated by an aqueous phase: the chemistry of pore solutions that can be quite different from that of their rock host (Trueman, 2004), and the porosity of the sample (Michel et al., 1996; Nielsen-Marsh and Hedges, 2000), a physical property, are important controls on the extent of diagenesis.

The extent of diagenesis can be evaluated by chemical analyses, microscopic observations, porosity measurements, infrared spectrometry, and X-ray diffraction. In this study, our target was to minimize sample size, and these tests of diagenesis, though important, would require samples much larger than our target sample size. Among these, it is only chemical analyses that can evaluate the extent of exchange of Sr and Pb.

Of the mechanisms noted above, the effect of adsorption can be minimized by adequate cleaning prior to analysis. Secondary phases that form in pores of the samples – clays and carbonates, particularly – can also be removed by adequate cleaning; secondary phosphates (Karkanas et al., 2000), potentially less soluble than biogenic apatite, might not be as easily removed, especially if they are formed during recrystallization. The extent of diffusion depends on the concentration contrast, for each element, between the sample and the aqueous fluid that is present in pore spaces, and the duration of exposure. Its effect in bone and enamel has not been adequately studied, but some data indicate diffusion profiles of ≤100 μm thickness (Brenn et al., 1999). In arid environments, where the aqueous phase is likely to be a capillary film lining pore spaces, the size of the reservoir feeding a diffusion profile is small, and exposure is likely to be intermittent. Careful sampling and cleaning can eliminate most external, contaminated layers. Contamination in recrystallized samples, and in samples with cation exchange in crystallographic sites of biogenic apatite, cannot be removed by any known method of treatment prior to analysis (Hoppe et al., 2003), and in-vivo compositions cannot be recovered.

In arid environments, desiccation of bone results in an increase of porosity as the organic component of bone dehydrates and is attacked by microorganisms. In the absence of recrystallization, this leads to embrittlement and physical decomposition. Enamel, because it lacks a significant organic component, is more resistant to both physical and chemical changes than dentin, and the literature on diagenesis clearly documents this (Bentley, 2006).

2.3. Geological background

Isotopic compositions of skeletal materials average those of food and water sources. Because all of the teeth we studied are from sites that depended on agriculture, the isotopic compositions of the teeth are expected to reflect averages of local geology. Elemental concentrations are expected to reflect biological discrimination between Sr and Ca, and Pb and Ca — essentially approximations of generalized distribution coefficients. To a first approximation, all of the sites would have soils with roughly similar Sr and Pb concentrations, and we would expect small differences in in-vivo elemental concentrations. Prehistoric agriculture developed predominantly in valley bottoms filled with sediment derived from nearby rocks. The mixing of sediment from various bedrock sources into colluvium and alluvium in the valley floors results in a first-order averaging of local isotopic compositions. Different types of foods – meats and grains or vegetables, for example – represent the average isotopic compositions of different geographic ranges; variation in food types thus represents a second-order averaging of isotopic compositions. Because there is discrimination of Sr and Pb with respect to Ca in biological systems, higher Sr/Ca and Pb/Ca characterize plant tissue whereas lower Sr/Ca and Pb/Ca occur in tissues from higher trophic levels (Bentley, 2006; Patterson et al., 1991). Thus, biological discrimination modifies the geographic averaging that relates to different types of foods (Burton et al., 1999). There is a third averaging process, because local populations depended to some degree on non-locally sourced foods (Benson et al., 2009; Benson, 2010), so that human remains reflect isotopic averaging of broader geological regions than either plants or animals would.

Water, because it carries only low concentrations of Sr and Pb, is a less significant source, but averages the isotopic composition of drainage basins that are geographically larger than many food source areas. In arid environments, wind-borne dust can also be an important, non-local geochemical source. Its isotopic composition is unconstrained. There is no way of accounting for the in-vivo or post-mortem effects of wind-borne paleo-dust on elemental concentrations or isotopic compositions. For the locations we studied, eolian deposits are minor features that are interpreted to derive mostly from local bedrock. We thus consider water and eolian inputs to be less important.

Geological information relating to our sample sites is presented in the Supplementary material. Background isotopic data are available only for Chaco Canyon.

3. Analytical methods

The Supplementary text presents a detailed description of analytical methods. Our target was to assess whether samples of 10 mg or less could provide reproducible, interpretable information. We determined concentrations by isotope dilution (ID), using ^{84}Sr and ^{208}Pb tracers, and measured isotopic compositions (IC) by thermal ionization mass spectrometry (TIMS). Total procedural blanks for Sr were 50–100 pg, the bulk of which derived from the SrSpec resin used for Sr separation. These blanks are negligible because total Sr content in the samples ranged from 0.1 to 73 μg Sr (except for one sample at 0.009 μg), more than 1000 times the blank. Total procedural blanks for Pb were 5–20 pg, compared to sample sizes of 0.54 to almost 800 ng; at the lowest sample sizes, blank contamination could be significant, since the blank could be almost 4% of the total Pb in the sample. These blank measurements do not include the contamination from metal instruments or abrasive wheels that could occur during initial separation of dentin and enamel samples from the teeth.

4. Results

4.1. Observations on analytical methods

Table 2 presents selected data for all samples; the full data set is presented in the Supplementary materials. We successfully collected combined Sr IC and ID, and Pb IC and ID data from samples over the full range of sample sizes. Dentin samples averaged 13.2 mg, with a range of 0.9–106.6 mg; enamel samples averaged 26.2 mg, with a range of 0.8–212 mg. Dentin samples averaged 3.5 μg Sr (range 0.009–73 μg), whereas enamel samples averaged 2.4 μg Sr (range 0.12–8.4 μg). Total Pb content averaged 41 ng in dentin (range 0.6–270 ng), and 79 ng in enamel (range 0.5–780 ng). For large samples, purification of both Sr and Pb on the ion exchange columns was less consistent, with Ca being the main contaminant in both cases. At small sample sizes (<3 mg), the Pb blank becomes the limiting constraint on accurate measurement of Pb IC. Our experience indicates that the methanol and ammonium acetate cleaning steps are important, particularly for the more porous dentin samples.

4.1.1. Concentration data

Sr content in dentin ranges from 10 to 847 ppm, with one outlier at 3300 ppm (Fig. 2a). Replicate dentin aliquots ($n = 5$) have Sr content within 10–20 ppm of each other. This is outside the analytical uncertainty of the ID method, and suggests that dentin is heterogeneous on the scale of our sampling. There is a break in the distribution of Sr concentrations in dentin above 250 ppm; between about 50 and 250 ppm (Fig. 2a), there is a regular distribution of data, but above 250 ppm, the next values are in excess of 300 ppm. About 35% of all data lie above this break in the concentration profile. Among the 9 dentin samples that contain over 300 ppm Sr, 6 contain much more Sr than their corresponding enamels. Of the 9 high Sr samples, 5 are from Mimbres (all Mimbres dentin samples have Sr > 300 ppm), 3 are from Durango, and one is from Chaco Canyon. About 20% of dentin samples have Sr below 100 ppm.

Sr content in enamel ranges from 98 to 644 ppm (Fig. 2a). Replicate enamel aliquots (10 pairs, and 2 triples) typically have Sr content within 20 ppm of each other, but some are more than 100 ppm apart. As with dentin, this is outside the expected limit of analytical uncertainty, and indicates sampling of material that is heterogeneous. Only two enamel samples have concentrations above 350 ppm.

Pb concentration in dentin ranges from 0.06 to 15 ppm, with one outlier at 48 ppm (Fig. 2b). In neither dentin nor enamel were the Pb concentration data reproducible to the level of analytical uncertainty. For 8 pairs and 2 triplets of dentin aliquots, the average difference between “replicates” was 1.9 ppm, whereas 9 pairs of enamel replicates had an average difference of 0.6 ppm. Our expected reproducibility for Pb ID analyses is 0.5%. Eleven dentin samples contain over 2 ppm Pb; all 8 Mimbres dentin analyses have >2 ppm Pb, two are from Chaco Canyon (Pueblo Bonito), and one is from the Four Corners area. As with Sr, there is a break in the distribution of Pb content in dentin (Fig. 2b), with about 50% of the samples lying above the break at 0.7 ppm. Only 20% of dentin samples have Pb below 0.4 ppm. Enamel Pb concentrations range from 0.07 to 10 ppm. About 30% of enamel aliquots lie above the break in the Pb distribution profile at 0.6 ppm. All enamels containing over 1 ppm Pb also contain high Pb in dentin, and dentin Pb content exceeds enamel Pb content in all but two of these high-Pb samples. All Mimbres enamel samples contain >1 ppm Pb; two enamel samples from Pueblo Bonito and one from Penasco Blanco also contain Pb > 1 ppm. At the low concentration end, there is a regular distribution of Pb concentrations in enamel up to 0.4 ppm, and more than 50% of all enamel aliquots contain less than 0.4 ppm Pb.

There is no correlation between Sr and Pb content in dentin or enamel ($r^2 < 0.3$). However, dentin that contains high Sr also tends to contain high Pb concentrations. Among the 12 dentin aliquots that contain either Sr > 200 ppm or Pb > 2 ppm, 7 are from Mimbres, 2 each are from Chaco Canyon (Pueblo Bonito) and Durango, and one is from the Four Corners. Similarly, of the 9 enamel aliquots that contain either Sr > 200 ppm or Pb > 2 ppm, 7 are from Mimbres, and one each is from Chaco Canyon (Penasco Blanco) and Durango.

4.1.2. Isotopic composition data

Sr IC is highly variable, ranging between 0.708 and 0.712 (Fig. 3a). For both dentin and enamel, the Sr IC data are reproducible to within about twice the reproducibility of our standard analyses, i.e., to within $\pm 0.000030\ 2\sigma$. The average difference for 30 dentin replicates (excluding one value at 0.000400) is 0.000024; the average difference between 20 replicate enamel pairs (excluding one value at 0.000200) is 0.000030. Thus, Sr IC is more reproducible than Sr concentration data, but is not reproducible to within expected analytical uncertainty: it is variable within teeth at the level of our sampling. Sr IC in dentin and enamel are correlated for most samples, but enamel compositions extend over a wider range. In six samples, ^{87}Sr/^{86}Sr in enamel significantly exceeds that in dentin; 5 of these are from Mimbres and one is from Durango.

We have evaluated the Pb data using only ^{206}Pb/^{204}Pb. Though analyses can be done with other ratios, they give results similar to the ^{206}Pb/^{204}Pb analysis. We expect to reproduce values of ^{206}Pb/^{204}Pb on replicate aliquots to within 0.05. For 19 dentin replicates, the average difference between pairs was 0.17; for 11 enamel replicates, the average difference was 0.10. The reproducibility of Pb IC is poorer than we expected, and suggests real heterogeneity within teeth for the sample

Table 2
Isotopic data.

		Dentin	Enamel	Dentin			Enamel		
		^{87}Sr/^{86}Sr	^{87}Sr/^{86}Sr	Pb isotopic ratios			Pb isotopic ratios		
Sample #	Location			206/204	207/204	208/204	206/204	207/204	208/204
F5594	Cave 7	0.709556	0.709610	18.461	15.609	38.493	18.998	15.655	38.656
F5594	Cave 7	0.709532	0.709592						
F5600	Cave 7	0.709577	0.709544	19.159	15.685	38.794	18.816	15.664	38.590
F5600	Cave 7	0.709537	0.709565				18.680	15.646	38.455
F6245	Grand Gulch	0.709683	0.709691	19.288	15.692	38.944	18.846	15.624	38.530
F6246	Grand Gulch	0.709772	0.709788	19.149	15.681	38.876	18.633	15.558	38.329
F6246	Grand Gulch		0.709761				18.702	15.622	38.528
F6246	Grand Gulch		0.709739						
TS13	White Dog	0.709282	0.709548	19.074	15.707	38.831	18.817	15.648	38.606
TS13	White Dog	0.709412							
F6233	Battle Cave	0.709252	0.709380	18.995	15.671	38.701	18.817	15.645	38.501
F6233	Battle Cave		0.709340						
F6234	Battle Cave	0.709593	0.709583	18.591	15.659	38.381	18.736	15.638	38.413
F5218	Falls Creek	0.710197	0.710174	19.068	15.648	38.470	19.199	15.651	38.591
F5218	Falls Creek	0.710158		18.847	15.665	38.440			
F5218	Falls Creek	0.710175		19.190	15.693	38.720			
F5218	Falls Creek	0.710170							
F5218	Falls Creek	0.710173							
F5213	Falls Creek	0.710302	0.710345	18.939	15.670	38.550	19.005	15.638	38.199
F5213	Falls Creek		0.710744	19.466	15.708	38.672			
F5215	Falls Creek	0.710797		19.607	15.716	38.827	20.204	15.740	38.752
F5215	Falls Creek	0.710750	0.711648				19.790	15.716	38.851
F5215	Falls Creek		0.711653						
F5219	Falls Creek	0.710162	0.710263	18.422	15.618	38.088	18.832	15.698	38.573
F5219	Falls Creek						18.786	15.638	38.534
F5403	Pueblo Bonito	0.709093	0.709101	21.060	15.825	39.669	20.318	15.768	39.430
F5403	Pueblo Bonito	0.709091	0.709144	20.954	15.826	39.591	20.450	15.771	39.425
F5403	Pueblo Bonito		0.709047	21.243	15.846	39.746			
F5400	Pueblo Bonito	0.709218	0.709210	21.158	15.822	39.791	20.861	15.816	39.553
F5400	Pueblo Bonito	0.709245	0.709207	20.936	15.808	39.719	20.706	15.779	39.548
F5400	Pueblo Bonito	0.709204	0.709218						
F5399	Pueblo Bonito	0.709289	0.709299	21.596	15.866	39.967	21.264	15.830	39.787
F5399	Pueblo Bonito	0.709296		21.420	15.901	40.024			
F5399	Pueblo Bonito	0.709284		21.689	15.903	40.082			
F6171	Pueblo Bonito	0.709227	0.709230	20.307	15.754	39.249	20.022	15.755	39.212
F6171	Pueblo Bonito	0.709174	0.709236	19.915	15.736	39.225	19.967	15.743	39.173
F6173	Pueblo Bonito	0.709306	0.709288	20.220	15.768	39.291	20.254	15.746	39.337
F6173	Pueblo Bonito	0.709336		20.340	15.735	39.280			
F5595	Penasco Blanco	0.709591	0.709596	19.349	15.684	38.913	18.845	15.647	38.560
F6182	Penasco Blanco	0.708911	0.708981	19.093	15.657	38.864	19.289	15.681	39.035
F6182	Penasco Blanco	0.708707	0.708974				19.260	15.707	39.128
F6188	Penasco Blanco	0.709467	0.709401	19.319	15.696	39.029	19.238	15.694	39.188
F6188	Penasco Blanco	0.709436		19.332	15.689	39.158			
F6188	Penasco Blanco	0.709458		19.267	15.644	39.026			
F6185	Penasco Blanco	0.709196	0.709161	19.179	15.680	39.096	19.120	15.685	39.021
F6185	Penasco Blanco	0.709181							
F6248	Kin Bineola	0.709436	0.709440	19.041	15.692	39.007	19.060	15.693	39.062
F6250	Kin Bineola	0.709508	0.709387	18.941	15.682	38.912	18.960	15.653	38.841
TS347A	Harris	0.708524	0.711998	18.234	15.545	38.722	18.236	15.559	38.701
TS347A	Harris		0.711977						
F5392	NAN, Rm 22	0.708534	0.710653	18.052	15.508	38.349	18.042	15.522	38.328
F5392	NAN, Rm 22		0.710741				18.078	15.524	38.363
F5393	NAN, Rm 22	0.708808	0.709876	18.028	15.517	38.393	18.004	15.495	38.334
F5393	NAN, Rm 22	0.708771							
F5393	NAN, Rm 22	0.708802							
F5394	NAN, Rm 22	0.708278	0.708633	18.002	15.504	38.387	18.031	15.520	38.422
F5394	NAN, Rm 22	0.708292	0.708616	18.042	15.509	38.402			
F5394	NAN, Rm 22	0.708292							
F5390	NAN, Rm 12	0.708297	0.708634	18.001	15.541	38.480	18.007	15.546	38.523
F5390	NAN, Rm 12	0.708280	0.708601	17.975	15.506	38.376	17.996	15.530	38.464
F5391	NAN, Rm 12	0.708603	0.710268	18.001	15.570	38.630	18.002	15.589	38.685
F5391	NAN, Rm 12	0.708575	0.710239	17.951	15.507	38.432	17.998	15.526	38.475

weights we used. The Pb IC of dentin and enamel are correlated (Fig. 3b), with few outliers. Nevertheless, most enamel–dentin pairs have Pb isotopic compositions that do not overlap within analytical uncertainty. The range of Pb IC, from ^{206}Pb/^{204}Pb of 17.9 to 21.7, is remarkably large, with most samples clustering near 19. Even with reproducibility of 0.1–0.2 for replicate aliquots, this large range of ^{206}Pb/^{204}Pb allows discrimination of sample sources.

4.2. Observations on archeological sites: discrimination

Combined Sr IC–Pb IC plots (Fig. 4a and b) illustrate how our data discriminate between sites. Samples from Mimbres and Pueblo Bonito (Chaco Canyon) are clearly distinct, and demonstrate that the combination of Sr IC and Pb IC data is superior to Sr IC alone, by which Pueblo Bonito is not distinguishable. From a purely methodological point of

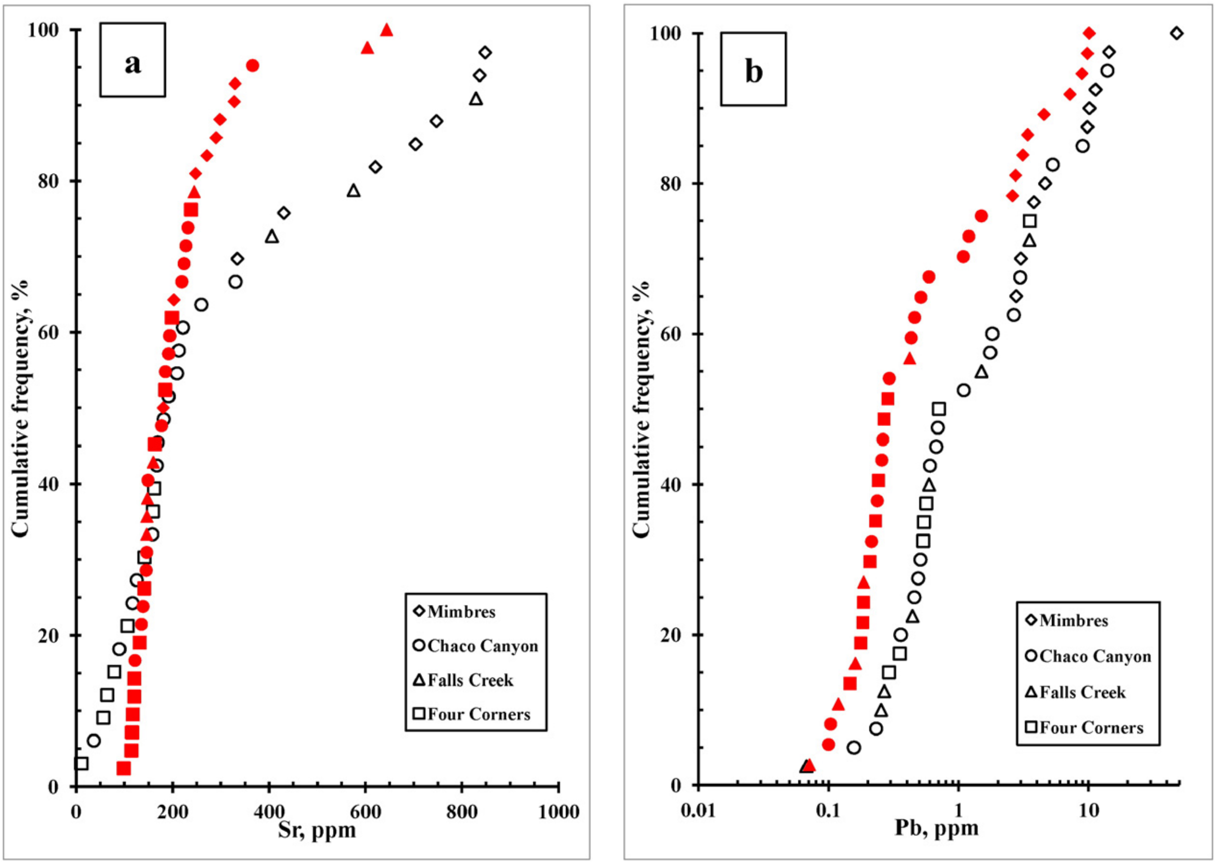

Fig. 2. Cumulative frequency plots of Sr (a) and Pb (b) concentrations in dentin (open symbols) and enamel (filled symbols). All concentration data, including replicates, are shown. Dentin–enamel pairs are not linked in these plots. A dentin sample with 3300 ppm Sr is excluded from panel (a). Panel (b) has a log concentration scale.

view, our approach is successful, despite serious concerns about reproducibility in ID and IC data. Though we can discriminate sites, we do not suggest that this discrimination reflects in-vivo, dietary signals.

Within the cluster of data with $^{206}Pb/^{204}Pb$ near 19, for both dentin and enamel, some discrimination of locations is still possible (Fig. 5). For example, the Durango (Falls Creek; eastern Basketmaker) samples are clearly distinct, with Sr IC above 0.710, whereas other samples have Sr IC < 0.710. Penasco Blanco samples overlap other locations in Sr IC, but the combined Pb IC and Sr IC data separate them for dentin samples, and only one enamel sample overlaps data for other locations. Five locations – the four western Basketmaker sites and Kin Bineola – are not easily distinguishable from each other in our data, though individual sites may be different from each other (e.g., Kin Bineola and Grand Gulch). Discrimination of these sites may be possible with a larger data set.

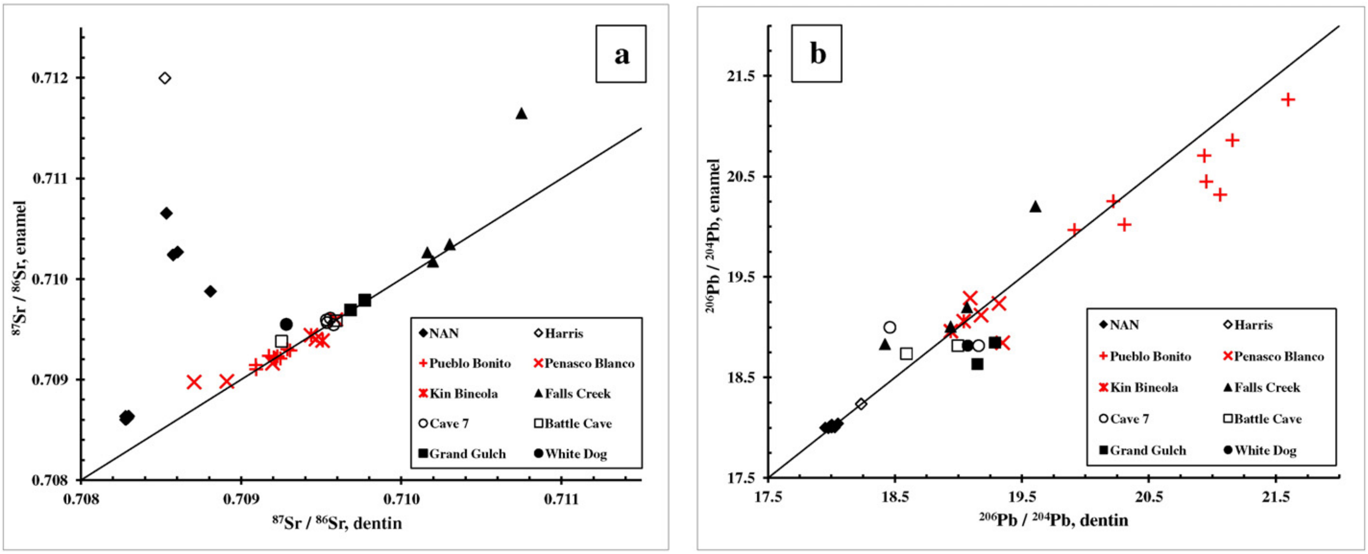

Fig. 3. Isotopic compositions of Sr (a) and Pb (b) in dentin and enamel. All analyses, including replicates, are shown. The diagonal line indicates identical isotopic compositions in dentin and enamel.

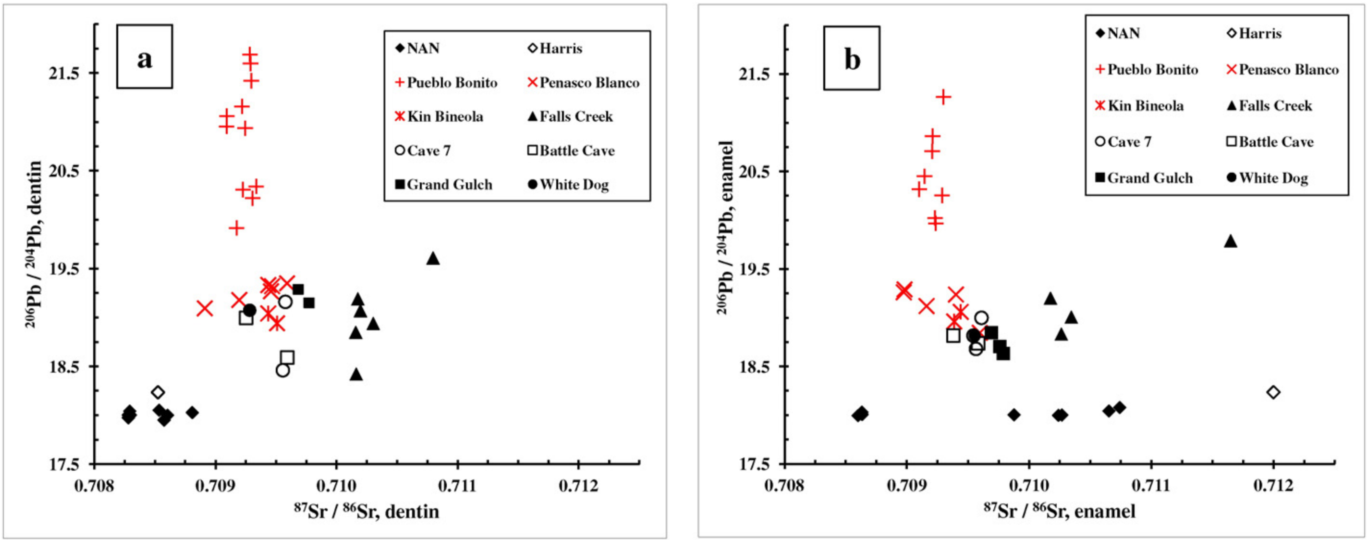

Fig. 4. Sr and Pb isotopic compositions in dentin (a) and enamel (b). All analyses, including replicates, are shown.

5. Discussion

5.1. Post-mortem elemental mobility

The lack of reproducibilty, to within analytical uncertainty, between aliquots from the same sample implies that there is real variability of both IC and ID between aliquots, and that small aliquots make this variability evident. Larger samples, because they tend to average the signal, show better reproducibility. The variability derives either from an original, in-vivo signal (Bentley, 2006, for Sr), or from post-mortem modifications. From our data, we have no definitive way of discriminating between in-vivo and post-mortem signals.

Our assessment of post-mortem effects relies initially on concentration data. For both Sr and Pb, the concentrations in dentin and enamel overlap or parallel each other over a range of concentrations (Fig. 2), a range in which there is potentially an equilibrium distribution of elements between dentin and enamel. We interpret this apparent equilibrium distribution as an in-vivo signal (Montgomery et al., 1999). Sr concentrations in dentin deviate increasingly from those in enamel, being higher in dentin than in enamel in the high range, and being lower in dentin in the low range. Dentin is generally enriched in Pb compared with enamel. These observations, and the widely recognized susceptibility of dentin to post-mortem modification, indicate that dentin in many of our samples has suffered diagenetic modification. The data also indicate that enamel has in some cases been modified, but to a lesser extent.

Dentin and enamel overlap in Sr content between 150 and 200 ppm, and we assume that this “least modified” Sr content approximates the in-vivo Sr content of the teeth. This compares to an average near 100 ppm in bone from modern North American populations, and about 200 ppm in bone from modern populations in the Far East (Schroeder et al., 1972). Diet accounts for this difference in modern populations: because Sr/Ca decreases with increasing trophic level, people who consume higher proportions of meat, like North Americans, tend to have lower Sr in bone. Because Sr/Ca in foods is linked to trophic level, it is difficult to acquire bone Sr content much above 200 ppm in human populations, unless the soils from which a population derives the bulk of its food have exceptionally high Sr, or high Sr material is added to the diet (Kuhnlein and Calloway, 1977). Thus, both elevated (>250 ppm) and depleted Sr (<100 ppm), and a disparity of Sr content between dentin and enamel are signals of diagenetic modification.

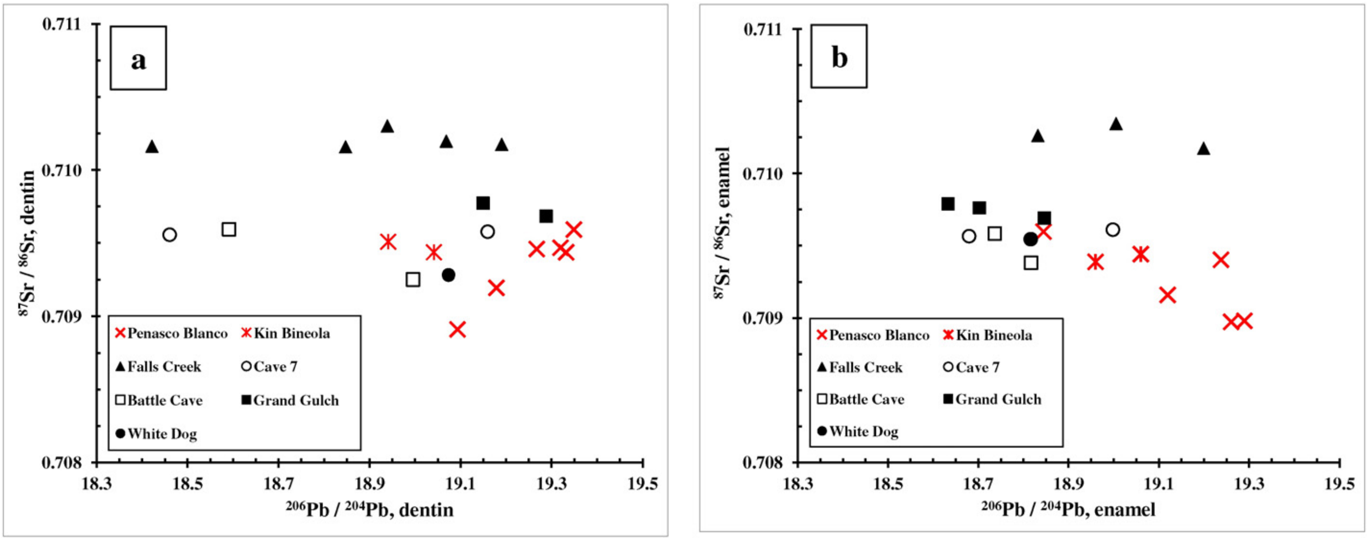

Fig. 5. Detail of Sr and Pb isotopic compositions in dentin (a) and enamel (b).

Based on elevated Sr content, all dentin samples from Mimbres are altered, and all but two enamel samples are also altered. All four dentin and two enamel samples from Falls Creek are altered, and two dentin samples from Chaco Canyon (one from Pueblo Bonito and one from Penasco Blanco) are altered. Low Sr content in dentin indicates that one sample from Chaco Canyon (Kin Bineola) is altered, and that four dentin samples from the Four Corners area (two each from Battle Cave and Grand Gulch) are altered. No enamel samples show Sr content low enough to be suspicious. Based on Sr concentration criteria, 59% of dentin and 21% of enamel samples have been modified by diagenesis. We do not suggest that alteration entails complete replacement of original Sr.

A corresponding analysis is not possible for Pb, because all modern teeth have been affected by pervasive Pb pollution (Patterson et al., 1991). Older data show median values of 10 ppm in both dentin and enamel (Ferguson and Purchase, 1987). More recent data show population means of 4.6 to 8.8 ppm for 19th century teeth, with a range of 0.9–27 ppm in individual teeth, and a range of 0.3–17.3 ppm for 20th century teeth potentially affected by leaded gasoline aerosols (Farmer et al., 2006).

Among our samples, dentin and enamel concentrations parallel each other up to about 0.7 ppm Pb, with a significant offset — dentin contains more Pb than enamel in most cases (Fig. 2b). We treat the range between 0.15 and 0.7 ppm as a "least modified" composition. All Mimbres samples contain over 2.5 ppm Pb, with dentin concentrations typically exceeding those in corresponding enamel. Two dentin samples from Falls Creek contain >1.5 ppm Pb. Chaco Canyon samples show contrasting behavior; at Pueblo Bonito, 7 of 10 dentin analyses exceed 1 ppm Pb, along with 2 of 7 enamel analyses, whereas only one dentin from Kin Bineola and one enamel from Penasco Blanco exceed 1 ppm. Only one dentin sample from the Four Corners sites has elevated Pb content. At the low end, concentrations below 0.15 ppm may reflect Pb depletion, but this is ambiguous, because concentrations below 0.15 ppm are possible as in-vivo concentrations (Patterson et al., 1991). By the criterion of elevated Pb content, Pb exchange has affected all Mimbres samples and most Pueblo Bonito samples. The Pb concentration criteria ("least modified" Pb content between 0.15 and 0.7 ppm) suggest that 52% of dentin and 43% of enamel samples have been altered. If the interpretation of the extent of diagenesis in enamel is correct, our data indicate that Pb is more easily exchanged than Sr. The extent of exchange is matrix-dependent, and is site- and element-specific.

Unfortunately, we have not found a key that allows unambiguous geochemical and archeological interpretation of our concentration and isotopic composition data. The Mimbres and Chaco Canyon data are illustrative.

Elemental concentration data for all but two enamel samples from Mimbres suggest that these samples are diagenetically altered. Five of 8 enamel aliquots have Sr isotopic compositions >0.709, whereas presumably exchanged dentin samples have $^{87}Sr/^{86}Sr < 0.709$. Four of these 5 enamels have Sr concentrations in the "diagenetic" range (Fig. 6a), without "diagenetic" isotopic compositions. All enamel and dentin aliquots from Mimbres have high Pb concentrations and relatively uniform Pb isotopic compositions (Fig. 6b; the sample from Harris is distinct). The simplest interpretation of the data is that Pb, in both dentin and enamel, records exclusively diagenetic features, and that Sr is exchanged in dentin, but only partially exchanged in enamel. This interpretation conflicts with the generally presumed stability of enamel. Yet it is also possible that both Pb concentrations and isotopic compositions reflect systemic, in-vivo exposure to Pb from pottery or other sources: among the locations we studied, the Mimbres culture is known for its exceptional pottery. Pb isotopic data for rocks and ores in southern New Mexico (Stacey and Hedlund, 1983) include compositions similar to those measured in Mimbres teeth ($17.7 < {}^{206}Pb/^{204}Pb < 18.3$ in high-grade, near-surface Pb–Zn vein ores), and can be interpreted either as sources of Pb encountered in-vivo, or as sources for diagenetic Pb. The nearby sources of recent anthropogenic Pb pollution – the Chino and Tyrone mines and Hurley smelter – process ores that have Pb isotopic compositions ($17.4 < {}^{206}Pb/^{204}Pb < 17.7$) different from the Mimbres values. In the absence of Pb isotopic and concentration data on Mimbres pottery, the ambiguity regarding in-vivo or diagenetic Pb cannot be resolved, and archeological interpretations are tentative.

At Chaco Canyon, neither Sr concentrations nor isotopic compositions show patterns that suggest diagenesis; only 5 of 26 aliquots have Sr content <100 ppm or >250 ppm (Fig. 6c). By contrast, 6 of 9 dentin aliquots from Pueblo Bonito contain >1 ppm Pb, as do 2 of 7 enamels; dentin also has generally higher $^{206}Pb/^{204}Pb$ than enamel (Fig. 6d). These patterns can be interpreted either as reflecting prevalent Pb diagenesis in dentin, with a smaller diagenetic imprint in enamel (and no diagenetic effect on Sr), or as a shift, during the lifetime of the Pueblo Bonito individuals, to a lifestyle with increased exposure to Pb having a radiogenic isotopic composition ($^{206}Pb/^{204}Pb \geq 22$). In Pueblo Bonito dentin, the almost linear relation of log Pb content to increasing $^{206}Pb/^{204}Pb$ suggests two-component mixing between a component with low concentration and low $^{206}Pb/^{204}Pb$, and a component with high concentration and radiogenic Pb: this mixing relationship can be interpreted either as an in-vivo or a diagenetic signal.

At other Chaco Canyon locations (we include Kin Bineola among the Chaco Canyon sites), radiogenic Pb isotopic compositions are absent, as are Pb concentrations over 2 ppm. Pueblo Bonito and Penasco Blanco share most geological features, but Pueblo Bonito lies immediately on the edge of Chaco Wash, whereas Penasco Blanco is on a hill above the wash — they may have different diagenetic histories. We are thus left with two options: diagenesis affecting only one of three locations among those we studied at Chaco Canyon, or in-vivo compositions that are distinct at Pueblo Bonito. Either option requires some special pleading, with conclusions that are hard to accept — the conclusion that there was little communication between the Pueblo Bonito and Penasco Blanco communities assumes that all data are in-vivo values and populations were not mobile, whereas the conclusion that the Pueblo Bonito Pb data are due to diagenesis assumes that enamel and dentin have suffered Pb exchange but not Sr exchange, and diagenesis affected only Pueblo Bonito.

Because we have so few data from other sites, similar comparisons or discussions aren't warranted. Better constraint on the extent of diagenesis, from observations that were outside the purview of our study, is necessary for interpretation of our data.

5.2. Sample size

One of our targets was to evaluate the sample size required for combined analyses of Sr and Pb. We were successful in obtaining data (Sr ID and IC, Pb ID and IC) for samples as small as 0.8 mg. However, the lack of reproducibility of concentrations and isotopic compositions to something approaching analytical uncertainty suggests either that there is an unaccounted source of contamination, or that there is real heterogeneity among samples that are smaller than about 10 mg. We can eliminate blank contamination as a source of variability because we have good constraints on the blank in all aspects of sample processing other than the initial, physical isolation of the samples: we are not able to evaluate or quantify the contamination that may come from initial isolation of the sample using diamond- or carbide-tipped saws or burs, nor have we found any study that has addressed this issue. We designed our sample cleaning procedure to minimize the impact of contaminants on the final sample, and it is clear that meticulous cleaning of samples is essential. We conclude that our analyses reveal real variability in small (<10 mg) samples. By comparison, Junior et al. (2003) suggest that 20 mg are required for reproducible sampling of deciduous teeth in modern populations.

To minimize variability between small aliquots, consistent, targeted sampling of enamel (crowns only, or near-root only) is warranted. Enamel forms progressively on individual teeth, and different teeth record different periods during infancy and early childhood (Hillson,

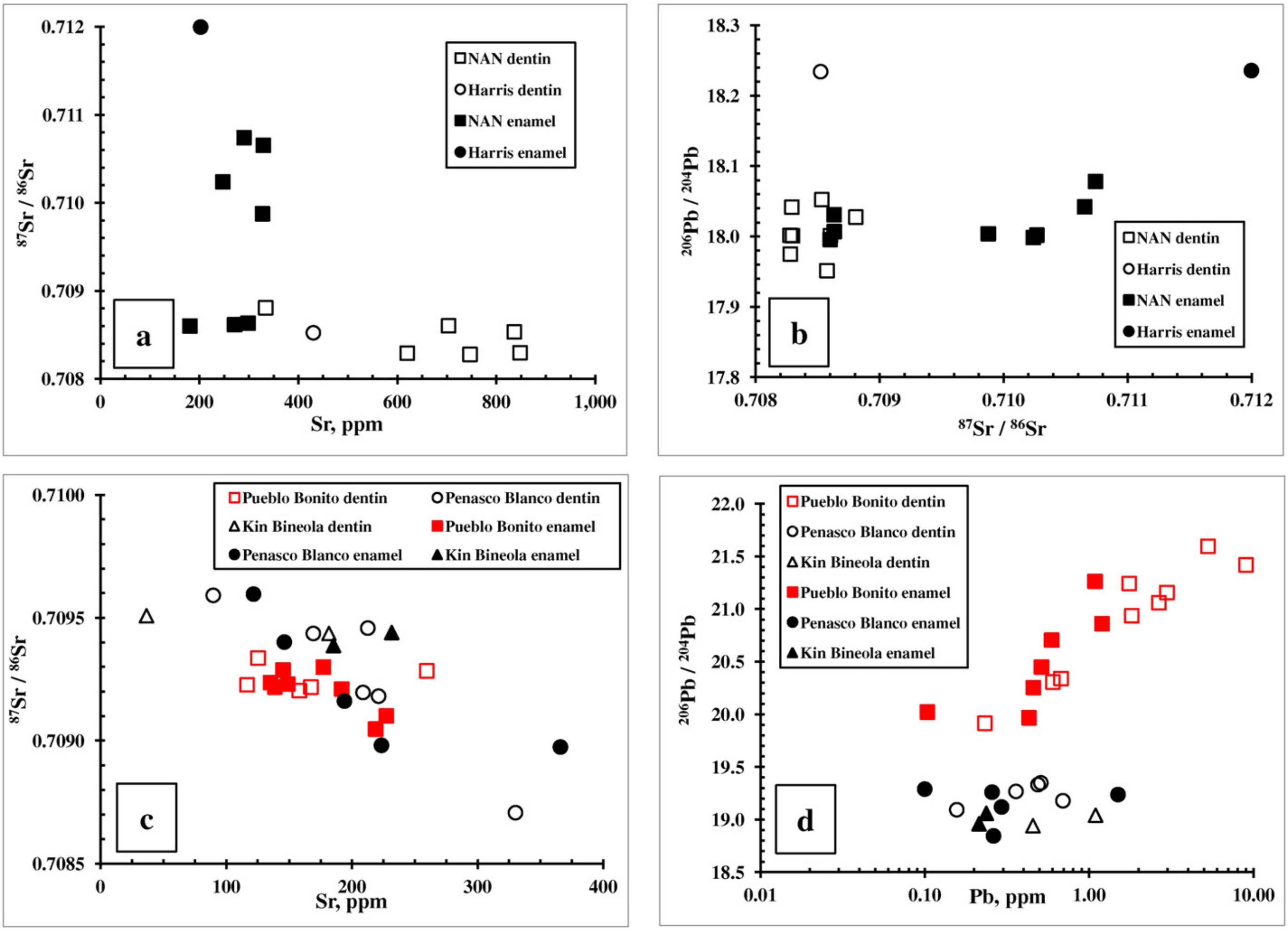

Fig. 6. Sr and Pb concentration and isotopic composition data for samples from Mimbres and Chaco Canyon. Scales on the figures vary. (a) Sr concentration and isotopic composition data for samples from the Mimbres area. Concentrations above 250 ppm are potentially affected by diagenesis. (b) Combined Sr and Pb isotopic compositions for Mimbres samples. (c) Sr concentration and isotopic compositions for samples from Chaco Canyon. (d) Pb concentration and isotopic compositions for samples from Chaco Canyon.

1996). Thus, small aliquots taken from different parts of single teeth might well show in-vivo differences that are outside of analytical uncertainty. Larger samples (≥50 mg), though having the advantage of avoiding blank contamination concerns, have the disadvantage of requiring more careful chemical separation of Ca from both Sr and Pb, and the disadvantage of averaging potentially useful information recorded in teeth during the period of enamel formation. Though laser ablation or secondary ion mass spectrometry has great potential for isotopic analyses that have spatial resolution and are less destructive than our conventional approach (Benson et al., 2013), there remain analytical hurdles for achieving the accuracy and precision that are required for addressing archeological questions.

5.3. Comparisons with other data

In addition to the Pb isotopic data from the area near Mimbres (Stacey and Hedlund, 1983), there are three additional groups of data to which comparisons can be made: Chaco Canyon Sr and Pb data; Pb data for ores from New Mexico; and Sr and Pb data for SW US pottery. There are many Sr isotopic studies of the Chaco Canyon area (Benson et al., 2003, 2006a, 2008, 2009; Benson, 2010, 2012; English et al., 2001; Reynolds et al., 2005), including studies of archeological corn and construction timbers, and present-day deer mice, soils, waters, and evergreens. Benson (2012) also reports Pb concentration and isotopic composition data. Sr isotopic data on recent deer mice (*Peromyscus maniculatus*; Benson et al., 2008) and archeological corn (Benson et al., 2009; Benson, 2010) do not overlap the lowest 20% of the Sr isotopic compositions in teeth, the values below 0.709125 (Fig. 7), most likely because human teeth integrate a broader range of sources than either mice or corn. Chaco Canyon soil data, using the regional subdivisions used in Benson et al. (2009) and Benson (2010), overlap the tooth Sr isotopic data with the exception of a single analysis at the low end (a dentin analysis from Penasco Blanco at 0.708707). Soils from other locations, notably the Chuska Slope, also overlap the Chaco Canyon tooth data. Other nearby sites (Aztec ruin, Salmon ruin) have Sr isotopic compositions that are distinct from those at Chaco Canyon (Benson et al., 2009). Most water samples have Sr isotopic compositions above those measured in teeth. The tooth data overlap with data on archeological timbers from Chaco Canyon, and the data for trees from the Chuska Mountains (Fig. 7), but both of these show a much broader range than the teeth. The overlap of Chaco Canyon tooth data with soils, timber, and foods can be interpreted either as an in-vivo or a diagenetic signal.

Only Benson (2012) presents Pb isotopic data for samples from Chaco Canyon. Benson notes that low Pb contents, contamination of the cobs, and overlap of isotopic compositions between locations compromise the utility of Pb isotopic data. Notably, however, one of the Pueblo Bonito cobs overlaps both Sr and Pb of Pueblo Bonito enamel, including the unusually radiogenic $^{206}Pb/^{204}Pb$ (Fig. 8). Sr and Pb isotopic data for Chaco Canyon and Chuska Slope soils are within the range of the Penasco Blanco and Kin Bineola tooth data: the Pb isotopic approach may have more promise than Benson (2012) suggests.

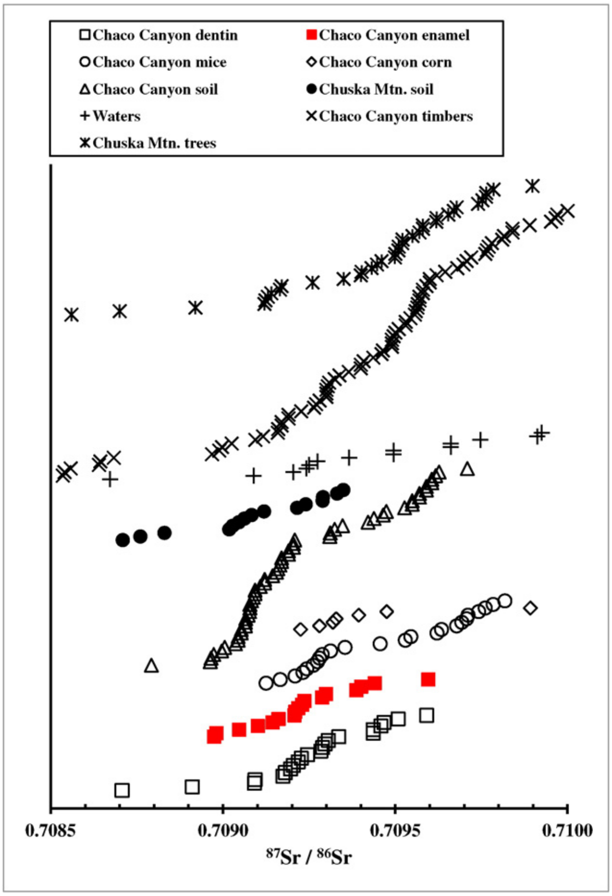

Fig. 7. Comparison of Chaco Canyon tooth data with Sr data from the literature for deer mice, archeological corn, extracts of soil from Chaco Canyon and the Chuska Mtn. areas, river waters, architectural timbers of the Chaco Canyon great houses, and modern trees from the Chuska Mtns. Data for river waters, architectural timbers, and modern trees extend beyond the limits of this plot.

A clear step forward in clarifying our interpretations would be acquisition of a broader range of combined Sr–Pb background data. In the absence of local background data, we can only speculate on the geological sources from which apparent end-member compositions in our data set (e.g., the NAN Pb IC and low Sr IC, or the high Pb IC in the Pueblo Bonito samples) derive. The main cluster of data, around Sr IC ~0.7095 and ^{206}Pb/^{204}Pb ~18.9, indicates that these compositions might be characteristic of a range of geological sources in the Four Corners area, as partly confirmed by the soil and vegetation Sr data in Benson et al. (2003, 2006a, 2006b, 2008, 2009) and Benson (2010, 2012). Though many locations overlap in Sr isotopic composition, it is quite possible that Pb isotopic data would improve our ability to distinguish them.

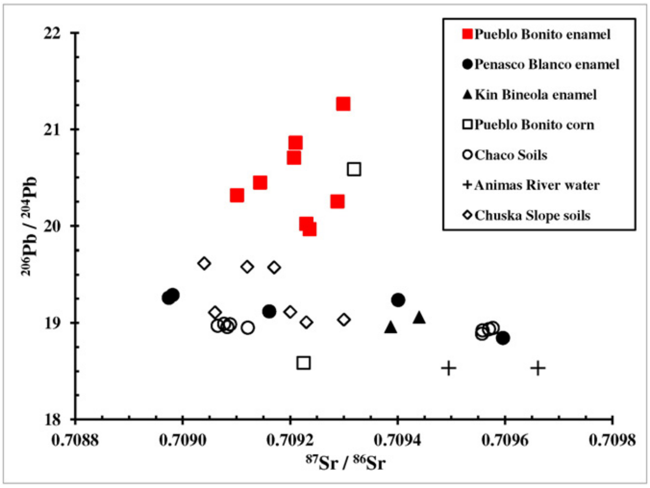

Fig. 8. Sr and Pb isotopic composition data for enamel from Chaco Canyon (this study), and for corn, soils, and river water from Benson (2012).

Combined Sr and Pb isotopic data are available for a variety of igneous rocks in the Four Corners area (see, for example, NAVDat.org), but the bulk of these analyses focus on rocks that are a small proportion of the landscape: they do not provide a realistic picture of average rock or soil compositions. To the extent that ore-forming processes integrate the isotopic compositions of large volumes of the crust, Pb data for ores provide a picture of the range of compositions that might be sampled in food and water. Ore data from Utah and Arizona do not overlap the Pb isotopic compositions of the teeth we analyzed. There is partial overlap with the ore Pb data from Colorado, and essentially complete overlap between the teeth and Pb ores from New Mexico (Fig. 9a).

On Pb isotopic plots, there is consistency between the teeth, Rio Grande glaze paints from younger archeological sites (Huntley et al., 2007), and prehistoric (~800 to 1200 CE) gray ware ceramics from the Grand Canyon area (Carter, 2008), although the latter have slightly lower ^{207}Pb/^{204}Pb (Fig. 9b). This consistency, despite the large range of measured Pb isotopic compositions, suggests that Pb in the teeth may

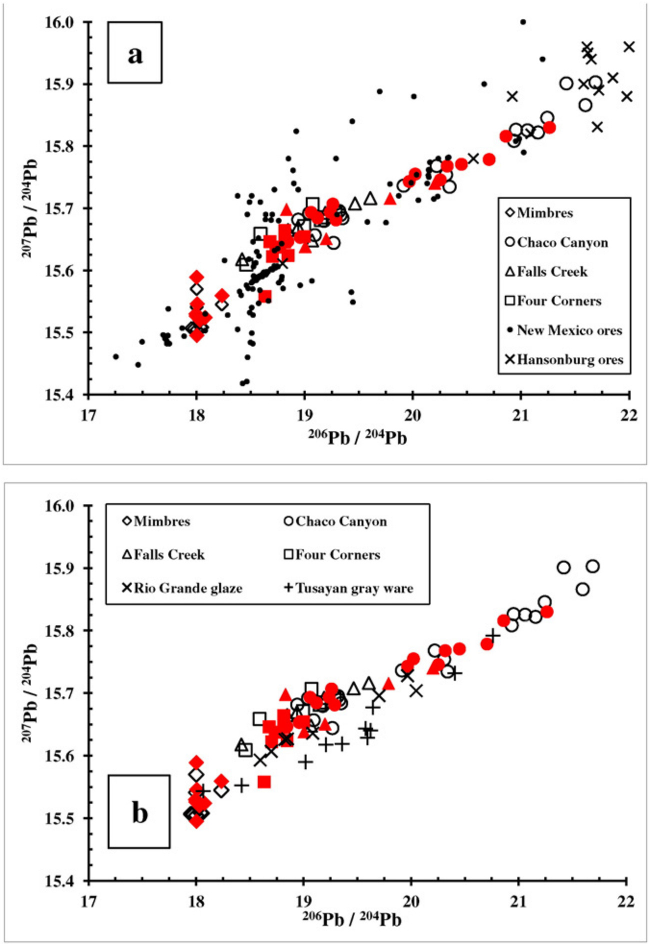

Fig. 9. (a): Pb isotopic data for teeth compared with data for ore samples from New Mexico. Open symbols are for dentin; filled symbols are for enamel. A small number of ore analyses plot outside the limits of the graph. Ore data are from: Brown, 1965; Doe and Rohrbough, 1977; Doe and Zartman, 1979; Ewing, 1979; Gulson, 1986; Huntley et al., 2007; Stacey and Hedlund, 1983; and Thibodeau et al., 2013. (b): Comparison of Pb isotopic data for teeth, Rio Grande glaze paints (1300–1700 CE; Huntley et al., 2007), and Tusayan gray ware ceramics (800–1200 CE; Carter, 2008). Open symbols are for dentin, filled symbols are for enamel.

not be related exclusively to food sources, but may also integrate Pb compositions of other materials (pots, tools, ornaments, or body paint) that individuals used or wore, and that may have been traded between sites. This is particularly true of the high $^{206}Pb/^{204}Pb$ samples from Pueblo Bonito; the only ore that has compositions approaching these is in south-central New Mexico, in the Hansonburg District (Fig. 9a). In the Mimbres area, which is closer to the Hansonburg District Pb mines, this radiogenic Pb component is not evident. That some unglazed and unpainted ceramics have radiogenic Pb isotopic compositions suggests that clay-rich sediments in the southwest US can have such radiogenic Pb compositions, and are a second possible source for the Pb isotopic compositions at Pueblo Bonito.

We can also compare our data to the trace metal concentrations in bones from prehistoric Native American burials (Ericson et al., 1991; Kuhnlein and Calloway, 1977). Neither study used the type of sample cleaning we used. In dentin of deciduous 17th century Hopi teeth, Kuhnlein and Calloway found ~7 ppm Pb and ~478 ppm Sr, and indicated that they had no way of assessing post-mortem effects. By comparison, they found ~28 ppm Pb and 98 ppm Sr in contemporary Hopi teeth, and ascribed the lower Sr content of contemporary teeth to a significantly reduced consumption of corn and other vegetable materials. Ericson et al. clearly show that porous bones have significant surficial contamination, with less contamination of interior fragments. Our results ($<$0.5 ppm Pb in enamel and clean dentin) are consistent with the low range of their measurements.

Our data also allow a comparison to estimates of the blood lead levels of prehistoric populations. Excluding samples with high Pb concentrations (NAN, Pueblo Bonito, and Harris, and outlying concentrations from Penasco Blanco and Falls Creek), the range of Pb concentrations in enamel in this study is 0.07–0.59 ppm, comparable to the range observed in prior studies of pre-industrial populations (0.039–0.68 ppm; Budd et al., 2000b and references therein). Assuming an approximately linear relation between enamel (= bone) Pb and blood Pb (Flegal and Smith, 1992), our data translate to a range of 5–15 nmol/L (0.1–0.3 μg/dL) in blood lead concentration. Our minimum level is above the minimum calculated by Flegal and Smith, which they characterize as the "natural" Pb content of blood. Though Patterson et al. (1991), whose data Flegal and Smith (1992) used for their evaluation of "natural" Pb levels, consider the Pb contents in prehistoric human enamel samples from Arizona (Kayenta-Anasazi) to reflect post-mortem Pb additions, their data and ours could also reflect the beginnings of systemic anthropogenic Pb contamination from ceramics and other implements, even in pre-industrial human populations relatively isolated from early metal production and fabrication.

6. Concluding statement

Our most significant finding from an archeological perspective is the potential value of Pb data. Prior studies show that Sr varies among individuals from the same site, and that some must have been migrants, but there was little ability to determine where they were born based on Sr alone. Even when individuals had similar Sr, it was not clear that all such individuals were local because Sr did not differ much in a particular area. However, the combined results of Sr and Pb give much greater resolving power for both issues. Though we cannot unequivocally distinguish in-vivo and diagenetic effects, combined Pb and Sr isotopic data discriminate locations; if the enamel compositions, particularly, are in-vivo features, the case becomes much stronger that individuals from Pueblo Bonito having similar Sr and Pb were born locally. This would strongly support some models of Chacoan behavior. Similarly, if the differences in isotopic composition between the western (Four Corners) and eastern (Durango) Basketmaker samples are an in-vivo signal, the data support a model of culturally distinct populations. We recommend that archeological studies use both Sr and Pb in combination for migration studies. Our evidence is clear: it is possible and desirable to use both elements in almost all archeological studies, and Sr alone does not provide the same level of information.

Acknowledgments

We acknowledge, first and foremost, the encouragement of T. Douglas Price in initiating this study. He was instrumental in acquiring samples from Harvard University's Peabody Museum and the American Museum of Natural History, which released samples in accordance with those institutions' considerations involving all legal requirements governing research decisions (NAGPRA). We acknowledge three anonymous reviewers who provided thorough, insightful, and constructive comments. The MIT Undergraduate Research Opportunity Program (UROP) supported Liz Santorella during the initial steps of this study, and we acknowledge the contributions of both. Without the assistance of Kerri Schortzmann and Livia Capaldi in the laboratory, this study would not have been completed, and we acknowledge their help. We acknowledge Phil Geib for contributing Fig. 1.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.chemgeo.2016.03.003.

References

Benson, L.V., 2010. Who provided maize to Chaco Canyon after the mid-12th-century drought? J. Archaeol. Sci. 37, 621–629.

Benson, L.V., 2012. Development and application of methods used to source prehistoric Southwestern maize: a review. J. Archaeol. Sci. 39, 791–807.

Benson, L.V., Cordell, L.S., Vincent, K., Taylor, H., Stein, J., Farmer, G.L., Futa, K., 2003. Ancient maize from Chacoan great houses: where was it grown? Proc. Natl. Acad. Sci. 100 (22), 13111–13115.

Benson, L.V., Stein, J., Taylor, H., Friedman, R., Windes, T.C., 2006a. The agricultural productivity of Chaco Canyon and the source(s) of pre-Hispanic maize found in Pueblo Bonito. In: Staller, J.E., Tykot, R.H., Benz, B.F. (Eds.), Histories of maize: multidisciplinary approaches to the prehistory, linguistics, biogeography, domestication, and evolution of maize. Elsevier, San Diego, pp. 290–314.

Benson, L.V., Hattori, E.M., Taylor, H.E., Poulson, S.R., Jolie, E.A., 2006b. Isotope sourcing of prehistoric willow and tule textiles recovered from western Great Basin rock shelters and caves — proof of concept. J. Archaeol. Sci. 33 (11), 1588–1599.

Benson, L.V., Taylor, H.E., Peterson, K.A., Shattuck, B.D., Ramotnik, C.A., Stein, J.R., 2008. Development and evaluation of geochemical methods for the sourcing of archaeological maize. J. Archaeol. Sci. 35, 912–921.

Benson, L.V., Stein, J.R., Taylor, H.E., 2009. Possible sources of archaeological maize found in Chaco Canyon and Aztec Ruin, New Mexico. J. Archaeol. Sci. 36, 387–407.

Benson, A., Kinsley, L., Willmes, M., Defleur, A., Kokkonen, H., Mussi, M., Grün, R., 2013. Laser ablation depth profiling of U-series and Sr isotopes in human fossils. J. Archaeol. Sci. 40, 2991–3000.

Bentley, A.R., 2006. Strontium isotopes from the earth to the archaeological skeleton: a review. J. Archaeol. Method Theory 13 (3), 135–187.

Brenn, R., Haug, C., Klar, U., Zander, S., Alt, K.W., Jamieson, D.N., Lee, K.K., Schutkowski, H., 1999. Post-mortem intake of lead in 11th century human bones and teeth studied by milli- and microbeam PIXE and RBS. Nucl. Inst. Methods Phys. Res. B 158, 270–274.

Brown, J.S., 1965. Oceanic lead isotopes and ore genesis. Econ. Geol. 60, 47–68.

Budd, P., Montgomery, J., Cox, A., Krause, P., Barreiro, B., Thomas, R.G., 1998. The distribution of lead within ancient and modern human teeth: implications for long-term and historical exposure monitoring. Sci. Total Environ. 220, 121–136.

Budd, P., Montgomery, J., Barreiro, B., Thomas, R.G., 2000a. Differential diagenesis of strontium in archaeological human dental tissues. Appl. Geochem. 15, 687–694.

Budd, P., Montgomery, J., Evans, J., Barreiro, B., 2000b. Human tooth enamel as a record of comparative lead exposure of prehistoric and modern people. Sci. Total Environ. 263, 1–10.

Burton, J.H., Price, T.D., Middleton, W.D., 1999. Correlation of bone Ba/Ca and Sr/Ca due to biological purification of calcium. J. Archaeol. Sci. 26, 609–616.

Carter, S.W., 2008. Investigating the Intersections Between the Archaeological and Geological Components of the Grand Canyon Landscape From a Geoarchaeological Perspective on Ceramics and Sources PhD dissertation Stanford University.

Chiaradia, M., Gallay, A., Todt, W., 2003. Different contamination styles of prehistoric human teeth at a Swiss necropolis (Sion, Valais) inferred from lead and strontium isotopes. Appl. Geochem. 18, 353–370.

Doe, B.R., Rohrbough, R., 1977. Lead isotope data bank. US Geological Survey, Open-File Report 77-418.

Doe, B.R., Zartman, R.E., 1979. Plumbotectonics, the Phanerozoic. In: Barnes, H.L. (Ed.), Geochemistry of Hydrothermal Ore Deposits. Wiley, New York, pp. 22–70.

Dunlap, C.E., Steinnes, E., Flegal, A.R., 1999. A synthesis of lead isotopes in two millenia of European air. Earth Planet. Sci. Lett. 167, 81–88.

English, N.B., Betancourt, J.L., Dean, J.S., Quade, J., 2001. Strontium isotopes reveal distant sources of architectural timber in Chaco Canyon, New Mexico. Proc. Natl. Acad. Sci. 98 (21), 11891–11896.

Ericson, J.E., Smith, D.R., Flegal, A.R., 1991. Skeletal concentrations of lead, cadmium, zinc, and silver in ancient North American Pecos Indians. Environ. Health Perspect. 93, 217–223.

Ewing, T.E., 1979. Lead isotope data from mineral deposits of southern New Mexico — a reinterpretation. Econ. Geol. 74, 678–683.

Farmer, J.G., MacKenzie, A.B., Moody, G.H., 2006. Human teeth as historical biomonitors of environmental and dietary lead: some lessons from isotopic studies of 19th and 20th century archival material. Environ. Geochem. Health 28, 421–430.

Ferguson, J.E., Purchase, N.G., 1987. The analysis and levels of lead in human teeth: a review. Environ. Pollut. 46, 11–44.

Flegal, A.R., Smith, D.R., 1992. Lead levels in preindustrial humans. N. Engl. J. Med. 326, 1293–1294.

Gulson, B.L., 1986. Lead Isotopes in Mineral Exploration. Elsevier, Amsterdam (257 pp.).

Gulson, B.L., 1996. Tooth analyses of sources and intensity of lead exposure in children. Environ. Health Perspect. 104, 306–312.

Gulson, B.L., Gillings, B.R., 1997. Lead exchange in teeth and bone — a pilot study using stable lead isotopes. Environ. Health Perspect. 105, 820–824.

Gulson, B.L., Jameson, W., Gillings, B.R., 1997. Stable lead isotopes in teeth as indicators of past domicile — a potential new tool in forensic science? J. Forensic Sci. 42 (5), 787–791.

Haury, E.W., 1936. The Mogollon Culture of Southwestern New Mexico. Gila Pueblo, Globe, Arizona.

Hillson, S., 1996. Dental Anthropology. Cambridge University Press, Cambridge, UK.

Hong, S., Candelone, J.-P., Patterson, C.C., Boutron, C.F., 1994. Greenland ice evidence of hemispheric lead pollution two millenia ago by Greek and Roman civilizations. Science 265, 1841–1843.

Hoppe, K.A., Koch, P.L., Furutani, T.T., 2003. Assessing the preservation of biogenic strontium in fossil bones and tooth enamel. Int. J. Osteoarchaeol. 13, 20–28.

Huntley, D.L., Spielmann, K.A., Habicht-Mauche, J.A., Herhahn, C.L., Flegal, A.R., 2007. Local recipes or distant commodities? Lead isotope and chemical compositional analysis of glaze paints from the Salinas pueblos, New Mexico. J. Archaeol. Sci. 34, 1135–1147.

Junior, D.S., Junior, F.B., de Souza, S.S., Krug, F.J., 2003. Cryogenic sample grinding for copper, lead and manganese determination in human teeth by slurry sampling GFAAS. J. Anal. At. Spectrom. 18, 939–945.

Kamenov, G.D., 2008. High-precision Pb isotopic measurements of teeth and environmental samples from Sofia (Bulgaria): insights for regional lead sources and possible pathways to the human body. Environ. Geol. 55, 669–680.

Karkanas, P., Bar-Yosef, O., Goldberg, P., Weiner, S., 2000. Diagenesis in prehistoric caves: the use of minerals that form *in situ* to assess the completeness of the archaeological record. J. Archaeol. Sci. 27, 915–929.

Kuhnlein, H.V., Calloway, D.H., 1977. Minerals in human teeth: differences between preindustrial and contemporary Hopi Indians. Am. J. Clin. Nutr. 30, 883–886.

LeBlanc, S.A., 1983. The Mimbres People: Ancient Pueblo Painters of the American Southwest. Thames and Hudson, London.

LeBlanc, S.A., 2008. The case for an early farmer migration into the American Southwest. In: Webster, L.D., McBrinn, M. (Eds.), Archaeology Without Borders: Contact, Commerce, and Change in the U.S. Southwest and Northwestern Mexico. University Press of Colorado, Boulder, pp. 107–142.

Lee, C.S.L., Qi, S.H., Zhang, G., Luo, C.L., Zhao, L.Y.L., Li, X.D., 2008. Seven thousand years of records on the mining and utilization of metals from lake sediments in central China. Environ. Sci. Technol. 42, 4732–4738.

Lee-Thorp, J., Sponheimer, M., 2003. Three case studies used to reassess the reliability of fossil bone and enamel isotope signals for paleodietary studies. J. Anthropol. Archaeol. 22, 208–216.

Lister, R.H., Lister, F.C., 1981. Chaco Canyon: Archaeology and Archaeologists. University of New Mexico Press, Albuquerque.

Michel, V., Ildefonse, P., Morin, G., 1996. Assessment of archaeological bone and dentine preservation from Lazaret Cave (Middle Pleistocene) in France. Palaeogeogr. Palaeoclimatol. Palaeoecol. 126, 109–119.

Montgomery, J., Budd, P., Cox, A., Krause, P., Thomas, R.G., 1999. LA-ICP-MS evidence for the distribution of Pb and Sr in Romano-British, medieval and modern human teeth: implications for life history and exposure reconstruction. In: Young, S.M.M., Pollard, A.M., Budd, P., Ixer, R.A. (Eds.), Metals in Antiquity: Proceedings of the International Symposium, Harvard University. Archaeopress, Oxford.

Nielsen-Marsh, C.M., Hedges, R.E.M., 2000. Patterns of diagenesis in bone I: the effects of site environments. J. Archaeol. Sci. 27, 1139–1150.

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.

Plog, S., Heitman, C., 2010. Hierarchy and social inequality in the American Southwest, A.D. 800–1200. Proc. Natl. Acad. Sci. 107 (46), 19619–19626. http://dx.doi.org/10.1073/pnas.1014985107.

Price, T.D., Johnson, C.M., Ezzo, J.A., Ericson, J., Burton, J.H., 1994. Residential mobility in the prehistoric southwest United States: a preliminary study using strontium isotope analysis. J. Archaeol. Sci. 21, 315–330.

Price, T.D., Burton, J.H., Sharer, R.J., Buikstra, J.E., Wright, L.E., Traxler, L.P., Miller, K.A., 2010. Kings and commoners at Copan: isotopic evidence for origins and movement in the Classic Maya period. J. Anthropol. Archaeol. 29, 15–32.

Reynolds, A.C., Betancourt, J.L., Quade, J., Patchett, P.J., Dean, J.S., Stein, J., 2005. ^{87}Sr/^{86}Sr sourcing of ponderosa pine used in Anasazi great house construction at Chaco Canyon, New Mexico. J. Archaeol. Sci. 32 (7), 1061–1075.

Schroeder, H.A., Tipton, I.H., Nason, A.P., 1972. Trace metals in man: strontium and barium. J. Chronic Dis. 25, 491–517.

Shafer, H.J., 2003. Mimbres Archaeology at the NAN Ranch Ruin. University of New Mexico Press, Albuquerque.

Sillen, A., Sealy, J.C., 1995. Diagenesis of strontium in fossil bone: a reconsideration of Nelson et al., (1986). J. Archaeol. Sci. 22, 313–320.

Skinner, H.C.W., 2005. Biominerals. Mineral. Mag. 69, 621–641.

Smiley, F.E., Robins, M.R., 1997. Early farmers in the northern Southwest: papers on chronometry, social dynamics, and ecology. US Department of the Interior, Bureau of Reclamation, Upper Colorado Region, Animas — La Plata Archaeological Project, Research Paper No. 7. Northern Arizona University, Flagstaff.

Stacey, J.S., Hedlund, D.C., 1983. Lead-isotopic compositions of diverse igneous rocks and ore deposits from southwestern New Mexico and their implications for early Proterozoic crustal evolution in the western United States. Geol. Soc. Am. Bull. 94, 43–57.

Thibodeau, A.M., Habicht-Mauche, J.A., Huntley, D.L., Chesley, J.T., Ruiz, J., 2013. High precision isotopic analyses of lead ores from New Mexico by MC-ICP-MS: implications for tracing the production and exchange of Pueblo IV glaze-decorated pottery. J. Archaeol. Sci. 40, 3067–3075.

Trickett, M.A., Budd, P., Montgomery, J., Evans, J., 2003. An assessment of solubility profiling as a decontamination procedure for the ^{87}Sr/^{86}Sr analysis of archaeological human skeletal tissue. Appl. Geochem. 18, 653–658.

Trueman, C.N., 2004. Forensic geology of bone mineral: geochemical tracers for postmortem movement of bone remains. In: Pye, K., Croft, D.J. (Eds.), Forensic Geoscience: Principles, Techniques and Applications. Geological Society, London, Special Publication 232, pp. 249–256.

Turner, B.L., Kamenov, G.D., Kingston, J.D., Armelagos, G.J., 2009. Insights into immigration and social class at Machu Picchu, Peru based on oxygen, strontium, and lead isotopic analysis. J. Archaeol. Sci. 36, 317–332. http://dx.doi.org/10.1016/j.jas.2008.09.018.

Valentine, B., Kamenov, G.D., Krigbaum, J., 2008. Reconstructing Neolithic groups in Sarawak, Malaysia through lead and strontium isotope analysis. J. Archaeol. Sci. 35, 1463–1473. http://dx.doi.org/10.1016/j.jas.2007.10.016.

Vivian, R.G., 1990. The Chacoan Prehistory of the San Juan Basin. Academic Press, San Diego.