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The cleaning of burned and contaminated archaeological maize prior to ^{87}Sr/^{86}Sr analysis

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ABSTRACT

Accurate trace-metal and strontium-isotope analyses of archaeological corn cobs require that metal contaminants be removed prior to chemical analysis. Archaeological cobs are often coated with construction debris, dust, or soil which contains mineral particles. In addition, most archaeological cobs are partially or completely burned and the burned parts incorporate mineral debris in their hardened residual structures. Unburned cobs are weak ion exchangers and most metals within a cob are not firmly bound to cob organic matter; therefore, immersing cobs in acids and rinsing them in deionized water to remove mineral contaminants may result in the undesirable loss of metals, including strontium, from the cob.

In this paper we show that some cob metal-pair ratios are not substantially changed when the cob is "cleaned" with deionized water, if the water-cob contact time does not exceed five minutes. Additionally, we introduce a method for eliminating mineral contaminants in both burned and unburned cobs, thus rendering them acceptable for strontium-isotope analysis. However, the decontamination procedure results in the rapid non-stoichiometric leaching of trace metals from the unburned cobs and it is possible that most metals will be extracted from the cobs during the lengthy decontamination process. Trace metals, in particular Al and Ca, should be analyzed in order to determine the presence and level of mineral contamination after cleaning.

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1. Introduction

In recent years, researchers have used strontium isotopes (^{87}Sr and ^{86}Sr) in an effort to determine the sources of timbers used in the construction of Chaco Canyon great houses (English et al., 2001; Reynolds et al., 2005), as well as the sources of maize found in Chaco Canyon and Aztec Ruin, New Mexico (Benson et al., 2003, 2006, 2008, 2009).

The measurement of ^{87}Sr/^{86}Sr ratios in organic archaeological materials requires that the sample be essentially free of inorganic contaminants containing strontium (Sr). This is because acids and mixtures of acids, containing, for example, hydrofluoric acid (HF), which are used to decompose organic matter (Kebbekus, 2003), will also dissolve silicate mineral residue, releasing metal contaminants to the acid solution. Fig. 1 indicates a positive relation between Sr and Al among 16 unburned maize cobs from Gallo Cliff Dwelling, Chaco Canyon, New Mexico (supplementary Table 4 in Benson et al., 2009). These data suggest that the cobs have been contaminated with differing amounts of a Sr-bearing aluminosilicate mineral such as feldspar.

Partially burned organic materials present a particular problem because they often incorporate inorganic material during incomplete combustion of the archaeological cobs. Archaeological maize cobs (hereafter referred to as cobs) are usually found in a burned state. Burned organic materials can act as activated charcoal, adsorbing inorganic metals during their tenure in fire pits, storage caches, or other depositional settings. Additionally, soil mineral particles often are incorporated in the structure of a burned cob.

The objective of the research described in this paper is the development of methods for cleaning contaminated burned archaeological cobs, as well as other organic materials (e.g., burned timbers) used for Sr-isotope sourcing. In the following section, we first assess the presence of mineral contaminants in archaeological cobs and then discuss a series of experiments that were used to develop procedures for the removal of mineral contaminants.

2. Mineral contamination of archaeological cobs

Aluminum (Al) is a major component of aluminosilicate minerals; however, it is a trace component in plant material. Aluminum in five Southwestern Native American maize landraces (100 cobs) analyzed

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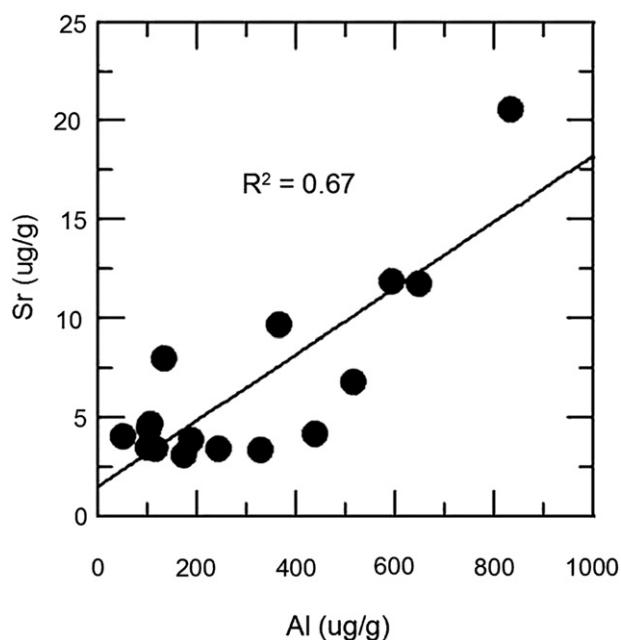
Fig. 1. Sr versus Al in Gallo Cliff Dwelling cobs from Chaco Canyon, New Mexico (data are from supplementary Table 4 in Benson et al., 2009).

Fig. 2. Al distributions in (A) 100 modern Southwestern Native American cobs, and (B) 47 archaeological cobs from Chaco Canyon and Aztec Ruin, New Mexico. Note the difference in horizontal-scale ranges.

by Benson et al. (2008) averaged 4.9 μg/g (Fig. 2A) and two hybrid cobs from a local grocery store yielded Al values of 1.6 ± 0.0 and 1.8 ± 0.1 μg/g (unpublished data of L.V. Benson and H.E. Taylor). On the other hand, 47 unburned archaeological cobs from Aztec Ruin and Chaco Canyon contexts yielded mean Al values of 454 μg/g (Fig. 2B), suggesting the presence of varying amounts of aluminosilicate contamination.

Cobs lose weight during heating, therefore, concentrating nonvolatile metals. To understand the magnitude of this process, we heated three Southwestern Native American cobs on a gas grill for 100 min (Table 1). Indirect heating (two outboard burners) at 220 °C was first applied for 30 min followed by direct heating (all three burners) at 440 °C for 70 min. In one case (cob 3068), the cob began to combust and disintegrate before 100 min had elapsed. In all cases, cobs lost an average of 74% of their mass before they began to disintegrate; therefore, nonvolatile metals are concentrated by a factor of about four during heating. Thus, the magnitude of mass concentration during heating does not account for the elevated concentrations of Al depicted in Fig. 2B.

3. Methods

3.1. Soil sampling and leaching

All soil samples referred to in this paper were collected as part of previously published studies (Benson et al., 2003, 2006, 2009). Eight soil samples were collected by hand auger from floodplain and alluvial fan (orchard) field settings near Salmon Ruin, New Mexico, and nine soil samples were collected from floodplain and alluvial fan settings near Aztec Ruin, New Mexico. At some locations, multiple (2–3) samples were collected from different depths.

In order to produce a synthetic soil water, soils were air dried, homogenized, and a 5-g subsample of each soil was leached for 48 hours (h) with constant agitation, using 500 ml of 1-M acetic acid prepared from distillation-purified glacial-acetic acid. These samples were sequentially filtered through 0.4- and 0.2-micrometer
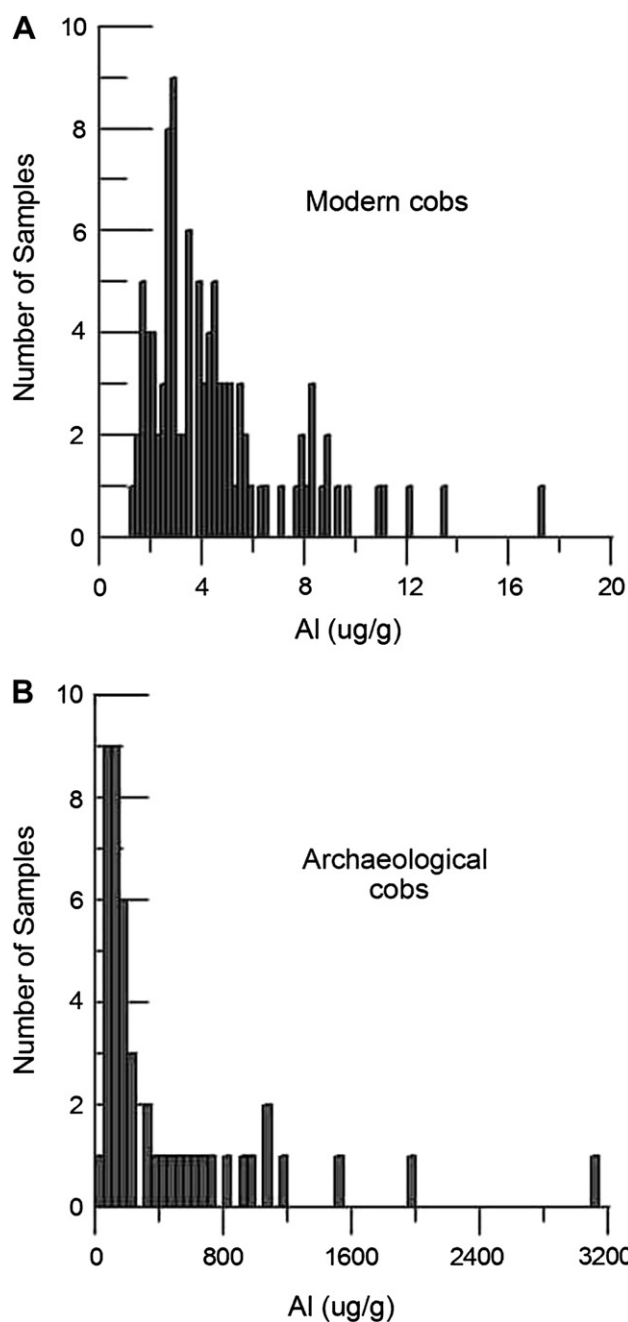
(μm) pore-size membrane filters prior to analysis (see Benson et al., 2003). Trace metals in the synthetic soil waters are listed in supplementary Table 1.

3.2. Trace-metal analyses

Multi-element trace-metal determinations were performed using inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Garbarino and Taylor, 1993; Boss and Fredeen, 1999; Taylor, 2001). All measurements were made on aqueous sample solutions without preconcentration, using direct pneumatic nebulization

Table 1
Weight loss of Southwestern Native American cobs during heating.

Minutes	Cob 3042	Cob 3068	Cob 3089	Cob 3042	Cob 3068	Cob 3089	Cob 3042	Cob 3068	Cob 3089
	Cob weight (g)			Weight loss (%)			Metal concentration multiplier		
	Indirect heating (220 °C)			Indirect heating (220 °C)			Indirect heating (220 °C)		
0	13.64	7.06	5.10	0.0	0.0	0.0	1.00	1.00	1.00
5	13.63	7.00	5.03	0.1	0.8	1.4	1.00	1.01	1.01
15	13.48	6.92	4.97	1.2	2.0	2.5	1.01	1.02	1.03
30	13.28	6.81	4.91	2.6	3.5	3.7	1.03	1.04	1.04
	Direct heating (440 °C)								
45	4.45	2.23	1.72	67	68	66	3.07	3.17	2.97
55	4.37	2.11	1.64	68	70	68	3.12	3.35	3.11
70	4.11	1.85	1.57	70	74	69	3.32	3.82	3.25
100	3.26	0.88	1.45	76	88	72	4.18	8.02	3.52

☐ Indicates sample began to burn and decompose.

with a Perkin–Elmer Elan 6000 instrument (ICP-MS) or a Perkin–Elmer Optima 3300 DV (ICP-AES)[1].

3.3. Strontium-isotope analyses

Strontium chemical separations and isotopic determinations were conducted in a Class 1–10,000 clean room at the University of Colorado, Boulder, Colorado. Strontium separates were obtained using a Sr-specific resin (Sr resin SPS, Eichrom Technologies, Inc.). The total procedural blank for Sr was ~30 picogram (pg). Strontium isotopic measurements were obtained using a Finnigan-MAT 261 thermal-ionization mass spectrometer in 4-collector static mode.

4. Experiments

In order to remove contaminant dust and soil from the burned archaeological cobs, we chose to follow a procedure somewhat similar to that used by palynologists to remove minerals from sediment samples prepared for pollen and charcoal analysis. The pollen cleaning procedure uses potassium hydroxide (KOH) to disaggregate the sediment and remove humic acids, hydrochloric acid (HCl) to remove carbonate minerals, and HF to remove silicate minerals (Faegri and Iverson, 1975). Because KOH contains high levels of metal contaminants we chose not to apply it to our samples.

4.1. Experiment 1

Ten burned cobs from Salmon Ruin were selected for the first experiment. The procedure used to clean the Salmon Ruin burned cobs consisted of the following steps: About 1 cm³ of each cob was weighed, crushed, and homogenized in an agate mortar and pestle. The crushed sample was quantitatively transferred to a 50-ml polycarbonate centrifuge tube using deionized (DI) water. About 20 ml of 10% high-purity HCl was added to the centrifuge tube and the suspension was shaken and allowed to sit overnight. The sample was then centrifuged at 5000 rpm for 10 min and the supernatant liquid was decanted to waste. Water was added to the centrifuge tubes and they were spun at 5000 rpm for 10 min and the rinse solution discarded. The DI rinse was repeated twice more to ensure removal of Ca. Next 20 ml of 50% HF was added to
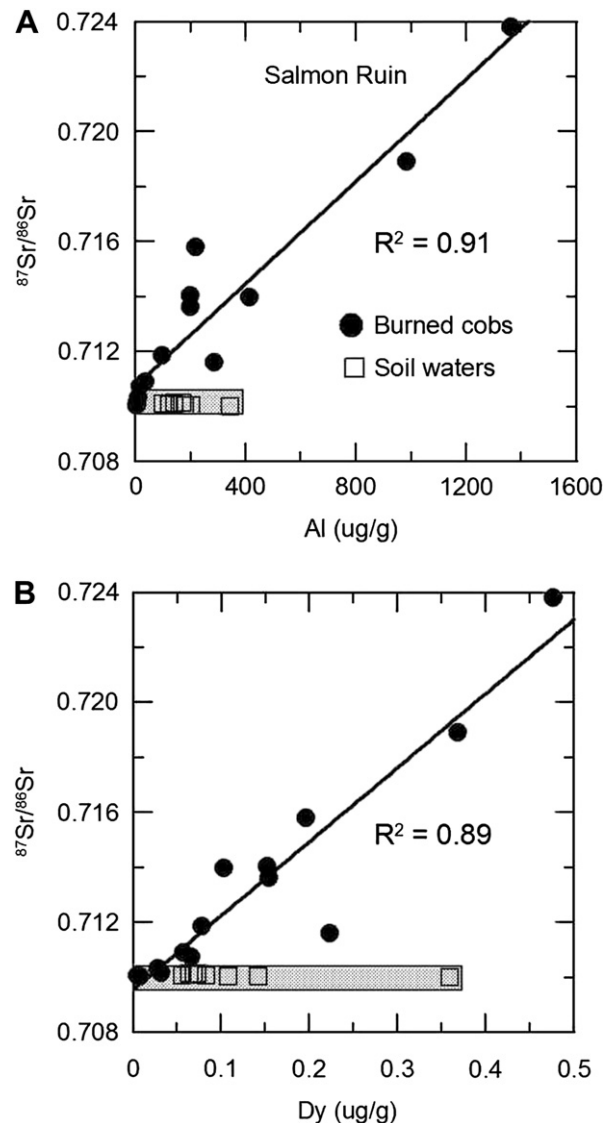
Fig. 3. $^{87}Sr/^{86}Sr$ ratios of partially cleaned burned cobs from Salmon Ruin, New Mexico as a function of (A) Al and (B) Dy. Shaded rectangles enclose soil leachate data. Line through Al and Dy values of burned cobs was created by linear regression of the data.

the sample; the sample was then shaken and allowed to sit for 48 h. The sample was then centrifuged at 5000 rpm for 10 min and the supernatant was decanted to waste. Water was added to the centrifuge tube(s) which were balanced and spun at 5000 rpm for 10 min and the rinse solution discarded. The water rinse was repeated twice more. A weighing boat was then tared and the extracted sample was transferred to the boat and air dried in a laminar flow hood. The weight of the preprocessed dried corn cob sample was then determined and the sample was transferred to a platinum crucible and the weight of the crucible and the sample determined. The sample was then ashed in a muffle furnace by ramping the temperature of the furnace in 50 °C increments every 30 min from a starting temperature of 100 °C to a final temperature of 450 °C at which temperature the sample was held for 16 h. After cooling to room temperature, the sample was transferred to a small Teflon vessel into which 2.0 ml of DI water, 0.5 ml of high-purity HNO_3, 1.5 ml of high-purity HCl, and 1.0 ml of HF were added. The solution was then evaporated to dryness on a sand bath, the residue dissolved in 2 ml of concentrated HNO_3, and the procedure
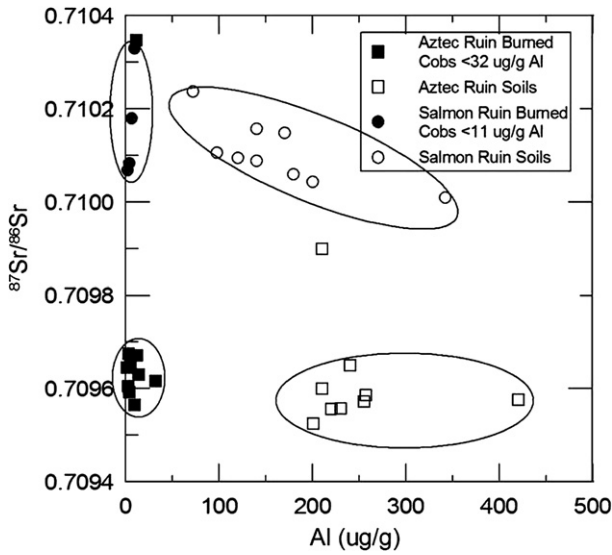
Fig. 4. $^{87}Sr/^{86}Sr$ ratios of cleaned (low Al) burned cobs from Aztec and Salmon ruins, New Mexico compared with $^{87}Sr/^{86}Sr$ ratios of synthetic soil waters from both sites.

repeated. Then 10 ml of DI water and 1 ml of HNO_3 were added to the vessel which was gently heated on the sand bath to near dryness. The residue was then diluted with 100 ml of DI water in a volumetric flask.

Aluminum values of the 10 cobs range from 2.0 ± 0.0 to 1360 ± 20 μg/g (supplementary Table 2), suggesting that some of the cobs remain contaminated with aluminosilicates after cleaning.

4.2. Experiment 2

Because some of the Al values in the first set of Salmon Ruin burned cobs remained elevated after treatment, a second set of four Salmon burned cobs was subsequently processed in an additional experiment. The cleaning procedure applied to the second set of Salmon cobs differed from the procedure described above in the number of rinses after application of HCl (six rinses) and HF (four rinses). This was done to ensure that minerals dissolved by the acids were removed in the rinses. In general, Al values of the second set of Salmon cobs were not substantially reduced, indicating that some silicate particles remained in the ashed burned cobs (supplementary Table 2).

4.3. Experiment 3

A set of 10 burned cobs from Aztec Ruin, New Mexico, was processed in the third experiment. By this time, we had adopted the hypothesis that some aluminosilicate particles were escaping the initial HF treatment, and the multiple rinses, and were still present when the cobs were ashed. Thus, when HF was added to the ashed cob samples, some and possibly all of the residual aluminosilicate(s) were put into solution, yielding the elevated Al values. Therefore, in the third experiment, we increased the rate of centrifugation to 10,000 rpm and we omitted HF from the group of acids added to the ashed sample(s), greatly reducing the dissolution of residual aluminosilicate material. Visible particles in the acidified ashed samples were removed by filtration (0.45 μm). Analyses of the 10 Aztec cobs indicated that Al was present at very low levels (≤ 32 μg/g) and that the great majority of the
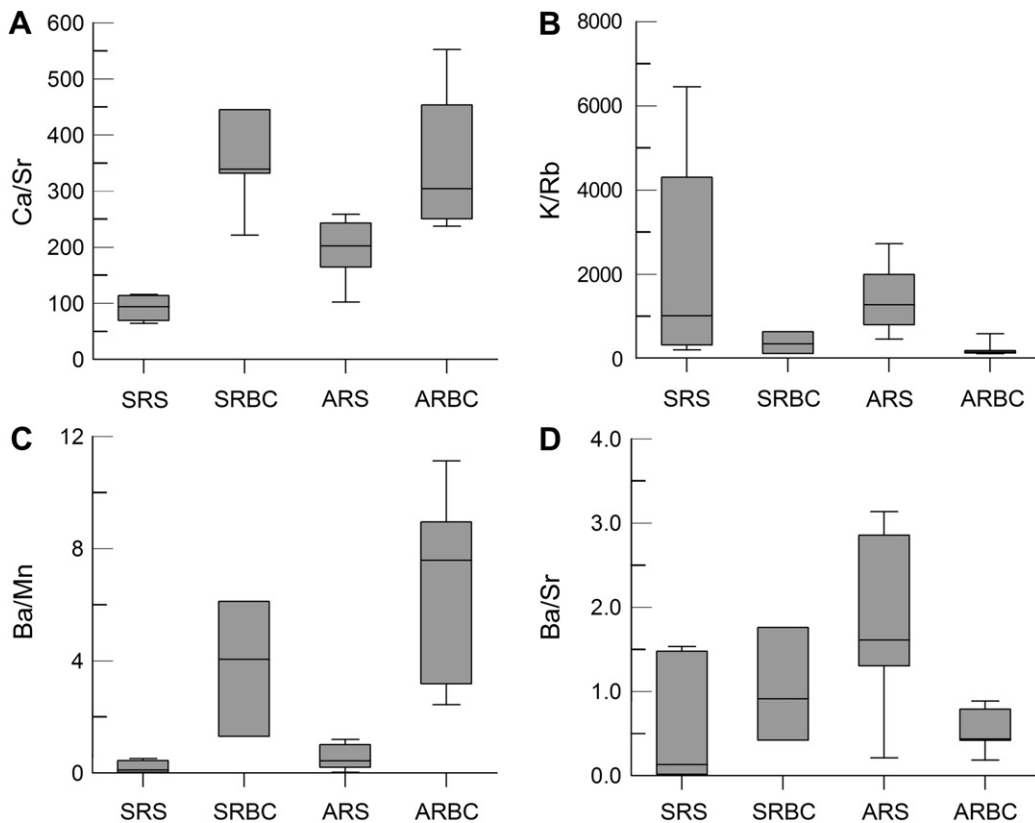
Fig. 5. Box-and-whisker diagrams for (A) Ca/Sr, (B) K/Rb, (C) Ba/Mn, and (D) Ba/Sr ratios in Salmon Ruin synthetic soil waters (SRS), Salmon Ruin soil waters calculated from the metal ratios of burned corn (SRBC), Aztec Ruin synthetic soil waters (ARS), and Aztec Ruin soil waters calculated from the metal ratios of burned corn (ARBC). Plots illustrate the minimum, maximum, upper and lower quartiles (top and bottom of shaded box), and median value (horizontal line in the box) of a group.

Table 2
Cob metal leaching experiments.

Cob Type	Cob Weight g	Al µg in cob		Ba µg in cob		Ca µg in cob		K mg in cob		Mn µg in cob		Rb µg in cob		Sr µg in cob	
		Avg	SD	Avg	SD	Avg	SD	Avg	SD	Avg	SD	Avg	SD	Avg	SD
Hopi Blue	2.95	16.4	0.9	3.76	0.2	462	8	12.4	0.3	18.1	0.2	3.87	0.07	7.52	0.2
Zuni Blue	2.97	7.3	0.0	3.01	0.02	566	0	7.71	0.2	21.2	0.3	2.89	0.07	9.61	0.06
Acoma Orange	8.57	9.8	0.7	4.30	0.2	539	5	24.9	0.1	29.9	0.2	13.8	0.2	11.9	0.06
	Time (min)	Al µg/L in 40 ml sample		Ba µg/L in 40 ml sample		Ca µg/L in 40 ml sample		K mg/L in 40 ml sample		Mn µg/L in 40 ml sample		Rb µg/L in 40 ml sample		Sr µg/L in 40 ml sample	
Hopi Blue	2	2.1	0.2	1.3	0.0	63	3	12.0	0.2	2.1	0.0	3.0	0.0	2.1	0.0
	5	3.6	0.2	2.7	0.0	145	13	26.2	1	5.4	0.1	6.3	0.0	5.6	0.0
	15	5.0	0.4	4.4	0.1	219	11	35.4	1	8.3	0.1	8.9	0.0	9.5	0.1
	60	6.0	0.7	11	0	228	12	37.8	0.3	8.7	0.1	9.4	0.0	11	0
	1440	7.9	0.4	13	1	300	6	49.9	1	11	0	13	0	15	0
Zuni Blue	2	2.0	0.1	0.70	0.01	49	9	6.50	0.1	1.8	0.1	2.0	0.0	1.4	0.0
	5	1.6	0.2	1.5	0.0	93	8	15.5	0.2	3.8	0.0	5.0	0.1	3.4	0.1
	15	1.8	0.5	2.0	0.0	114	12	17.9	0.4	4.1	0.1	5.8	0.1	4.2	0.1
	60	2.4	0.2	2.7	0.003	113	7	20.2	1	4.3	0.1	6.5	0.05	5.1	0.1
	1440	3.1	0.1	5.3	0.1	198	7	29.1	0.3	6.4	0.05	9.7	0.1	8.3	0.1
Acoma Orange	2	1.9	0.03	0.82	0.01	64	3	19.4	0.1	8.1	0.1	8.8	0.002	1.3	0.01
	5	2.4	0.04	1.0	0.004	109	3	37.0	1	12	0.1	17	0.02	2.4	0.02
	15	3.1	0.1	1.5	0.02	128	1	45.9	1	14	0.2	21	0.04	3.1	0.005
	60	4.1	0.3	1.9	0.04	188	3	64.8	0.1	17	0.2	30	0.01	4.7	0.004
	1440	6.9	0.2	12	0.2	859	0.3	141	0.6	37	0.1	76	2	25	0.07
	Time (min)	MTTS (%)	MRIC (µg)	MTTS (%)	MRIC (µg)	MTTS (%)	MRIC (µg)	MTTS (%)	MRIC (mg)	MTTS (%)	MRIC (µg)	MTTS (%)	MRIC (µg)	MTTS (%)	MRIC (µg)
Hopi Blue	2	3.3	15.8	8.9	3.43	3.5	446	24.8	9.32	2.9	17.6	19.5	3.12	7.1	6.99
	5	5.3	15.5	16.8	3.13	7.3	428	49.4	6.27	6.9	16.8	38.1	2.40	17.1	6.23
	15	6.7	15.3	24.9	2.82	10.1	416	62.3	4.67	9.7	16.3	49.9	1.94	26.1	5.55
	60	7.5	15.1	46.5	2.01	10.3	415	64.8	4.36	10.0	16.3	51.4	1.88	28.7	5.36
	1440	8.6	14.9	51.4	1.83	11.8	408	73.8	3.24	11.1	16.1	60.4	1.53	33.4	5.01
Zuni Blue	2	6.9	6.82	5.9	2.83	2.2	554	21.6	6.05	2.2	20.7	18.1	2.37	3.6	9.26
	5	5.7	6.91	11.9	2.65	3.9	544	46.7	4.11	4.2	20.3	39.9	1.74	8.1	8.83
	15	6.4	6.86	14.6	2.57	4.5	540	52.0	3.70	4.5	20.2	44.8	1.59	9.6	8.69
	60	7.5	6.78	17.8	2.47	4.5	541	56.1	3.39	4.6	20.2	48.1	1.50	10.8	8.57
	1440	8.3	6.72	25.7	2.23	5.9	533	66.7	2.57	5.5	20.0	58.3	1.20	13.9	8.27
Acoma Orange	2	4.9	9.31	4.8	4.10	3.0	523	19.5	20.0	6.8	27.9	16.0	11.6	2.8	11.5
	5	5.9	9.20	5.7	4.06	4.7	513	34.3	16.3	9.8	27.0	28.5	9.87	4.6	11.3
	15	7.1	9.08	7.6	3.98	5.3	510	40.5	14.8	10.6	26.7	33.5	9.18	5.7	11.2
	60	8.5	8.95	8.9	3.92	6.8	502	50.3	12.3	12.2	26.3	42.3	7.96	7.5	11.0
	1440	11.0	8.70	29.9	3.02	18.0	442	78.0	5.47	18.0	24.5	72.1	3.85	22.6	9.19

MTTS (%): metal transferred from cob to solution relative to amount in cob.
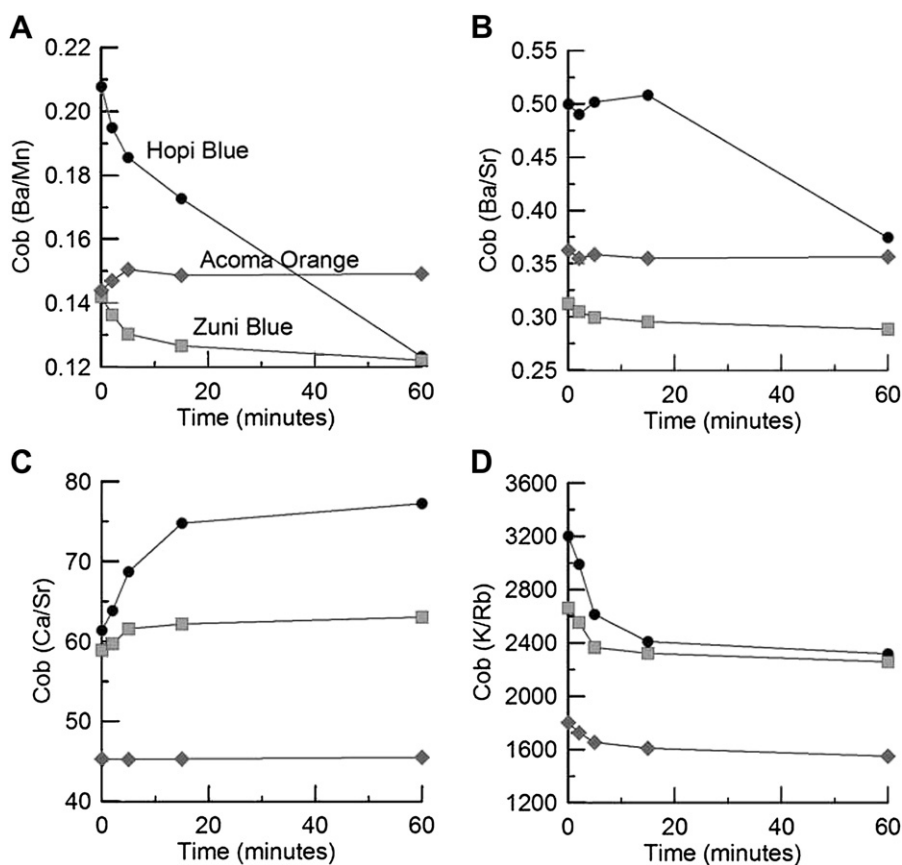MRIC (mass): metal remaining in cob.

Fig. 6. Metal-pair ratios with time for three cob types submerged in DI water.

contaminant aluminosilicate fraction had been eliminated from the burned archaeological cobs (supplementary Table 2).

4.4. Experiment 4

In this experiment we attempted to assess the magnitude of solute loss during initial cleaning of cobs in DI water. Some metal ratios (e.g., Sr/Ba) have been previously used to source cobs using metal-pair distribution coefficients (see, e.g., Benson et al., 2008). If metal loss occurs during rinsing or submersion of cobs in DI water, the use of metal pairs to source archaeological cobs could be invalidated.

Using a titanium-bladed knife, we removed the kernels from three clean Native American (Hopi Blue, Zuni Blue, and Acoma Orange) cobs. The center section of the cob was freeze-dried and then cut into small (<5 mm) pieces. About one-third of the pieces were weighed, secured in a pre-cleaned nylon mesh bag, and put into a pre-cleaned Teflon beaker to which 250 ml of DI water was added. The stirred solution was sampled (40-ml samples) at intervals of 2, 5, 15, 60, and 1440 min, using a syringe with attached filter (0.45 μ). The filtrate was transferred to a sample bottle and acidified with nitric acid. Triplicate ICP-MS and ICP-AES analyses were performed on the 40 ml samples.

An untreated set of cob fragments from each of the three Native American landraces were frozen and freeze-dried. These fragments were treated in the manner detailed in Experiment 3 prior to ICP-MS and ICP-AES analysis. Data resulting from this experiment (supplementary Table 3) were then used to determine the rate of loss of trace metals from the cob over the 24-h

experiment and the total loss of metals from the cob during the experiment.

5. Results

5.1. Strontium-isotope ratios versus aluminum concentrations

Strontium-isotope ratios of "partially cleaned" burned cobs from Salmon Ruin that resulted from Experiments 1 and 2 converge on $^{87}Sr/^{86}Sr$ ratios of synthetic soil waters from that site with decreasing concentration of Al (Fig. 3A). This indicates that as the Sr-bearing aluminosilicate contaminant decreases the $^{87}Sr/^{86}Sr$ ratio of the archaeological cob approaches that of the original uncontaminated cob. The convergence of cob $^{87}Sr/^{86}Sr$ and soil–water $^{87}Sr/^{86}Sr$ with decreasing rare-earth element (REE) values is also apparent (e.g., dysprosium [Dy] in Fig. 3B), suggesting that a REE-containing aluminosilicate mineral is also reflected in the Dy concentration of the contaminant.[2]

Comparison of low-Al (<32 μg/g Al) Aztec Ruin and Salmon Ruin (<11 μg/g Al) burned cobs indicates that they have $^{87}Sr/^{86}Sr$ values similar to the $^{87}Sr/^{86}Sr$ values of synthetic soil waters from those sites (Fig. 4). Therefore, it appears that our burned-cob cleaning procedure (experiment 3) successfully eliminates most of the Sr-bearing contaminants associated with burned archaeological cobs and yields $^{87}Sr/^{86}Sr$ ratios that accurately reflect those of the original clean unburned cobs.

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[2] Because all REEs are highly correlated, other REE such as Ce, La, etc. can be used to check for silicate contamination.

5.2. Trace-metal ratios in cleaned burned cobs and synthetic soil waters

In previous papers (Benson et al., 2003, 2008), the senior author and his colleagues attempted to determine if some trace-metal pairs partition systematically between soil water and cobs grown from those waters. Four metal ratios (Ca/Sr, K/Rb, Ba/Mn, and Ba/Sr) appear to hold some promise in this respect (see, e.g., Benson et al., 2008). Using the distribution coefficients obtained for these metal pairs (Table 2 in Benson et al., 2008), we calculated the soil–water ratios of the trace metals associated with cleaned burned Aztec Ruin and Salmon Ruin cobs. In Fig. 5, we compare box-and-whisker diagrams of the measured and calculated soil–water metal pairs for Aztec Ruin and Salmon Ruin areas.

The calculated and measured Ca/Sr and Ba/Mn ratios show little or no overlap (Fig. 5A and C); however, the calculated and measured K/Rb ratios indicate some overlap, especially in the case of Salmon Ruin (Fig. 5B), and the calculated and measured Ba/Sr ratios indicate a great deal of coherence for Salmon Ruin with some overlap for Aztec Ruin (Fig. 5D). In general, however, it does not appear that our cleaning procedure for burned cobs returns the trace-metal ratios in the cob to their original state.

5.3. Trace-metal ratios

One problem in the use of metals to "source" organic materials is the fact that most metals are not tightly bound to the plant. The surface of cobs is cellulose-based and the part that contacts water is negatively charged (Biermann, 1996). Lignin is available in considerable quantities (26%) in a cob and the hydroxyl and carboxyl groups in lignin exert considerable attractive force on metals. Maize cobs are composed of aligno-cellulosic (composed of lignin and cellulose) material with a large number and array of different functional oxygen groups that have negative charge (Nassar, 2006). Cellulose and hemicellulose make up 50 and 26% of cobs. Cellulose is a polysaccharide (a form of carbohydrate) that makes up the plant cell wall and is composed of glucose. Acid polysaccharides have carboxyl groups. Natural cellulose contains several ionizable functional (carboxyl and hydroxyl) groups; therefore, it acts as a weak ion exchanger. Crude polysaccharides in corn cobs contain two functional groups; the carboxyl group has a strong affinity for cations and the hydroxyl group has a weak affinity (Lehrfeld, 1996).

Thus, if a cob acts as an organic ion exchanger, a laboratory procedure that includes rinsing or submerging a cob in DI water (or a sequence of acids) may result in metal loss to the water. In order to determine the magnitude and stoichiometry of metal loss, we submerged small pieces of three freeze-dried cobs in DI water for up to 24 h (see Section 4.4). The data resulting from that experiment indicate that some fraction of all the metals analyzed were transferred from the cob to the water (supplementary Table 3).

We are particularly interested in the effect of metal loss on the ratios of four metal pairs (Ba/Mn, Ba/Sr, Ca/Sr, and K/Rb) that were previously shown to partition systematically from the soil water to the cob (Benson et al., 2008). We used the data shown in Table 2 to construct residual metal-pair ratios for each of the three cobs during the first hour of cob submergence (Fig. 6). The data indicate that cob submergence for ≤5 min has little effect on the metal-pair ratios of interest and that Ba/Sr values are stable for about 20 min. Thus we conclude that five minutes of rinsing to remove attached sediment will not substantially alter the Ba/Mn, Ba/Sr, Ca/Sr, and K/Rb metal-pair ratios. However, the sequence of steps involving the introduction of HCl and HF to dissolve contaminant mineral particles and the multiple rinses used to eliminate the acids from the sample will most probably result in the non-stoichiometric loss of most metals from unburned archaeological cobs.

6. Conclusions

In this paper we show that some cob metal-pair ratios are not substantially changed when the cob is "cleaned" with deionized water when the water-cob contact time does not exceed five minutes. In addition, we introduce a method for eliminating mineral contaminants in burned cobs, thus rendering them acceptable for strontium-isotope analysis. Unfortunately the cleaning procedure results in the non-stoichiometric leaching of trace metals from the burned sample; therefore, trace-metal pairs cannot be used to determine the areas where the cobs were grown via the application of metal-pair distribution coefficients. In addition, if excessive amounts of strontium are lost during the cleaning of an unburned cob, there may not be sufficient strontium available for a precise strontium-isotope determination. As a check on the effectiveness of the burned-cob cleaning procedure, trace-metal concentrations (in particular, Al and Ca) should be measured in order to determine the absence or presence of residual mineral contaminants. Application of the burned-cob cleaning procedure to unburned cobs will probably result in the loss of most of the cob's metal content, including Sr.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.jas.2009.09.005.

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