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Determining the Fuel Constituents of Ancient Hearth Ash Via ICP-AES Analysis

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Documenting variation and change in the use of particular plants and plant parts for fuel in ancient households contributes to an understanding of settlement location, local and regional abandonments and resource depletion. Chemical analysis of ash surviving in hearths and other thermal features to determine the kinds and relative amounts of fuels consumed may be less biased by formation processes than the macrofossil record currently employed to document ancient fuel use. Our studies indicate that it is possible to distinguish, chemically, ash of common fuel taxa and tissue types (bark, wood, etc.) in both modern and ancient samples of fuels found in the northern Colorado Plateau region of the American Southwest. However, the chemical signatures of the ancient and modern material of the same taxon differ, indicating possible alteration by post-depositional processes. Although multiple regression performs well in determining the relative contributions of different fuels to modern ash mixtures, possible post-depositional alterations and incomplete characterization of the range of within-taxon variation, currently limit our confidence in applications of this approach to ancient ash from Pueblo III settlements in south-west Colorado.

Keywords: ASH, CHEMICAL COMPOSITION, FUEL WOODS, ICP, AMERICAN SOUTHWEST, PUEBLO III.

Introduction

Patterns of fuel use and depletion have played an increasingly important role in studies of ancient land use, resource depletion, settlement location, and settlement and regional abandonment (e.g. Minnis, 1978; Johannessen, 1988; Kohler & Mathews, 1988; Johannessen & Hastorf, 1990; Kohler, 1992). Reconstructions of ancient fuel use are currently based on microscopic recognition of anatomical features of preserved charred wood fragments at least 4 mm^2 in size (Minnis, 1987: 122). Unfortunately, taxonomic identifications are not always secure when pieces are minute or distorted by burning. In addition, cooking and heating activities commonly result in complete consumption of most fuel used, leaving only ash. Variation among woody taxa and tissue types of the same taxon in their propensity to distort, break into small fragments, and reduce to ash (Jordon, 1965; Stewart, 1994) creates a strong potential for bias in the macrofossil record of fuel use.

Because most fuel is burned to ash, a more complete picture of ancient fuel use might be obtained through chemical analysis of ash surviving in hearths, roasting pits, kilns and other locations where ash accumulates. Analyses of sediments from cave sites in Israel indicate that ash continues to be chemically recognizable even in contexts of great antiquity (Schiegl *et al.*, 1994). In addition, chemical studies of plant tissues demonstrate that different taxa and tissue types of the same taxon vary in their elemental composition (Kollmann & Cote, 1968; Hillis, 1987; Dunn, 1992; Durand, Rose & Shelley, 1993). These results support the potential for using chemical analyses to identify the kinds and relative amounts of fuel taxa and tissue types in ash recovered in archaeological contexts. However, three conditions must be satisfied for this approach to be feasible: (1) we must know the chemical composition of

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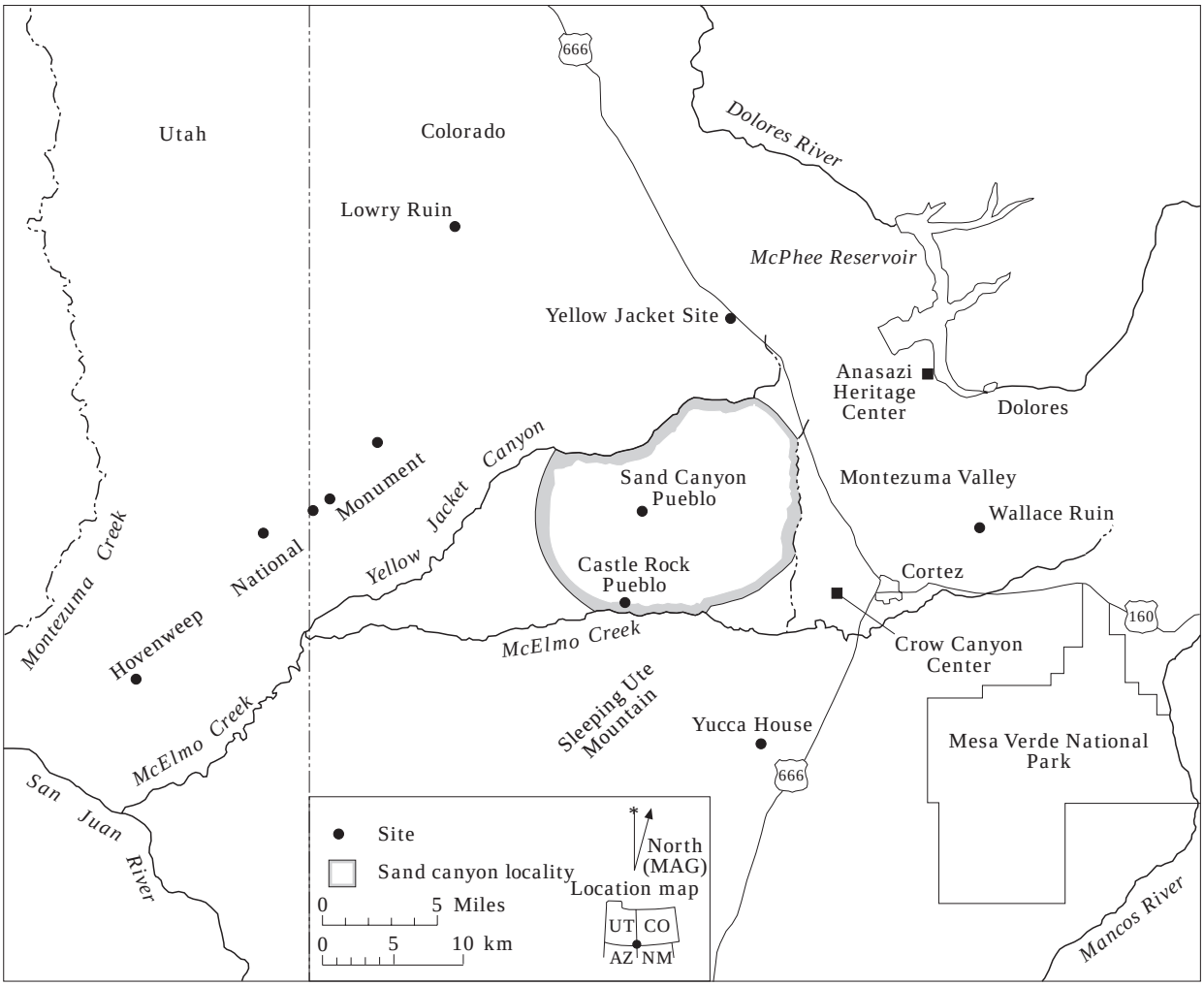

Figure 1. Locations of Sand Canyon study area and sites within the study area from which samples were analysed.

potential fuel taxa and tissue parts and these must be chemically distinguishable; (2) if extended post-depositional weathering significantly alters chemical signatures, such alteration must be systematic and measurable; and (3) it must be possible to distinguish the relative amounts of different taxa and tissue types in mixed ash samples.

Using inductively coupled plasma atomic emission spectrometry (ICP-AES), we analysed (1) modern potential fuels, (2) ancient charcoal that was reduced to ash in the laboratory, (3) ancient hearth ash, and (4) modern ash mixtures, to investigate the potential for chemically identifying the presence and relative abundance of fuel taxa and tissue types in ancient hearth ash. The samples analysed for this study were collected from settlements in south-western Colorado occupied in the final decades before the migration of Pueblo people out of the San Juan Basin near the end of the 13th century AD (Lipe, 1995). By developing the technique of ash chemical analysis, we hoped to obtain a more complete picture of fuel use during the late Pueblo III period in south-west Colorado, and of any role that fuel depletion may have played in the subsequent abandonment of the region.

Materials and Methods

The study area from which samples were collected is located on the north-eastern edge of the Colorado Plateau at the base of the Rocky Mountains, and ranges in elevation from 1500 to 2000 m, while receiving around 32 cm of precipitation annually (Figure 1). Plant taxa belonging to the Great Basin Desertscrub (Turner, 1982) and the Great Basin Conifer Woodland (Brown, 1982) biotic communities occur within the region. Major woody taxa commonly found as macrofossils in ancient hearths include pinyon pine (*Pinus edulis*), Utah juniper (*Juniperus osteosperma*), and a variety of shrubs including sage (*Artemisia tridentata*), mountain mahogany (*Cercocarpus montanus*), and Utah serviceberry (*Amelanchier utahensis*). In addition to these woody taxa, corn (*Zea mays*) cobs with kernels removed were also used as tinder or fuel. All ancient

Table 1. Samples analysed for elemental chemistry

Sample ID No.	Taxon or type	Tissue type	Age	Provenience
1	*Pinus edulis*	Wood & bark	Modern	Dakota sandstone at 5MT765
2	*Pinus edulis*	Bark	Modern	Dakota sandstone at 5MT765
3	*Pinus edulis*	Wood	Modern	Dakota sandstone at 5MT765
4	*Pinus edulis*	Wood & bark	Modern	Navajo sandstone at 5MT1825
5	*Pinus edulis*	Bark	Modern	Navajo sandstone at 5MT1825
6	*Pinus edulis*	Wood	Modern	Navajo sandstone at 5MT1825
7	*Juniperus osteosperma*	Wood & bark	Modern	Dakota sandstone at 5MT765
8	*Juniperus osteosperma*	Bark	Modern	Dakota sandstone at 5MT765
9	*Juniperus osteosperma*	Wood	Modern	Dakota sandstone at 5MT765
10	*Juniperus osteosperma*	Wood & bark	Modern	Navajo sandstone at 5MT1825
11	*Juniperus osteosperma*	Bark	Modern	Navajo sandstone at 5MT1825
12	*Juniperus osteosperma*	Wood	Modern	Navajo sandstone at 5MT1825
13	*Zea mays* (Hopi Blue)	Cob	Modern	Mesa top garden near 5MT765
14	*Zea mays* (Chapalote)	Cob	Modern	Provided by Native Seed search
15	*Artemisia tridentata*	Wood	Modern	Dakota sandstone at 5MT765
16	*Amelanchier utahensis*	Wood	Modern	Dakota sandstone at 5MT765
17	*Cercocarpus montanus*	Wood	Modern	Dakota sandstone at 5MT765
18	Unknown A	Ash	Modern	Lab mixture of modern ash
19	Unknown B	Ash	Modern	Lab mixture of modern ash
20	*Pinus* type	Uncharred wood	Ancient	5MT765, Struc. 1008, Strat. 2
21	*Juniperus*	Charred wood	Ancient	5MT765, Struc. 1004, Strat. 2
22	*Juniperus*	Uncharred wood	Ancient	5MT1825, Struc. 105, Surf. 5
23	*Juniperus*	Charrred wood	Ancient	5MT1825, Struc. 105, Surf. 5
24	*Juniperus*	Charred wood	Ancient	5MT1825, Struc. 105, Strat. 3
25	*Zea mays*	Charred cob	Ancient	5MT765, Struc. 1204, Strat. 3
26	*Zea mays*	Charred cob	Ancient	5MT765, Struc. 1204, Strat. 2
27	*Zea mays*	Charred cob	Ancient	5MT765, Struc. 1204, Strat. 2
28	*Zea mays*	Charred cob	Ancient	5MT765, Struc. 808, Strat. 1
29	*Zea mays*	Charred cob	Ancient	5MT1825, Struc. 105, Surf. 5
30	*Zea mays*	Charred cob	Ancient	5MT1825, Struc. 105, Strat. 1
31	Hearth ash		Ancient	5MT765, Struc. 1005, Fea. 2
32	Hearth ash		Ancient	5MT1825, Struc. 304, Fea. 6
33	Sediment			5MT765, Struc. 808, A horizon
34	Sediment			5MT765, Struc. 808, Strat. 1

and modern samples were collected from in or around two relatively large late Pueblo III (*c.* AD 1250–1280) settlements investigated by Crow Canyon Archaeological Center—Sand Canyon Pueblo (5MT765) and Castle Rock Pueblo (5MT1825). Sand Canyon Pueblo is a large aggregated settlement with over 500 structures that lies in a dense pinyon and juniper woodland at the head of Sand Canyon (Bradley, 1992, 1993). Castle Rock Pueblo is also an aggregated settlement consisting of approximately 60 structures built around a small sandstone butte in a less densely wooded region near the mouth of Sand Canyon.

Several ICP-AES runs using modern and ancient samples were conducted to determine the best preparation and analysis procedures for these kinds of samples. Once appropriate procedures were selected and standardized, the elemental chemistry of 34 samples was analysed for this study, including; (1) 17 modern examples of six known ancient fuel wood taxa, (2) 11 samples of ancient fuel wood charcoal of known taxon identified via anatomical criteria and then reduced to ash, (3) two ancient hearth ash samples, (4) two samples of archaeological sediments, and (5) two mixtures of modern ash created in the laboratory (Table 1). Most of the modern samples were obtained from the bark and wood of *Pinus edulis* and *Juniperus osteosperma* trees rooted in slightly different substrates to obtain data on potential effects of soil differences on chemical composition. We included the ancient charcoal and sediment samples to provide data on the effects of post-depositional weathering. The two mixtures of known quantities of different kinds of modern ash were created to test the methods used to identify the taxonomic composition of mixtures that were likely to make up the ancient hearth ash samples. In addition, two blanks (containing only the chemicals used to process the samples), two machine standards (in-house samples with known element concentrations) and two US National Institute of Standards and Technology pine needle standards (Standard Reference Material 1575) were run with the other samples to check for instrument ''drift'' and to aid in identifying unreliable element concentration data.

Preparation and chemical analysis of all samples followed five steps:

(1) samples were oven-dried at 100°C for 20 h and weighed to the nearest 0·0001 g;
(2) samples (including ash, charcoal, sediment, and pine needle standards) were burned to ash in a muffle furnace at 600°C for 12 h and weighed to the nearest 0·0001 g;

Table 2. Estimated element concentrations (%) from SEM-EDS analysis of digestion residues

Sample	Al	Ca	Cl	Fe	K	Mg	Na	S	Si	Ti	Zn
Ancient *Pinus*	5·49	0·62	0·55	0·98	3·38	0·16	1·03	0·41	85·2	1·85	0·35
Modern *P. edulis*	2·39	0·48	0·16	0·80	4·85	0·32	0·34	0·10	83·7	2·49	0·42
Ancient *Juniperus*	6·23	0·53	0·36	1·02	3·44	0·54	0·97	0·80	83·9	1·43	0·82
Modern *Juniperus*	7·49	0·46	0·10	0·69	3·89	1·08	1·94	0·35	82·2	1·86	0
Ancient *Zea mays*	5·07	0·99	1·01	0·34	3·20	0	1·93	0·56	86·0	0·17	0·77
Modern *Zea mays*	1·58	0	0·51	0·12	1·18	0	0	0·37	95·2	0·13	0·94
Ancient Ash	8·28	0·38	0·31	1·69	3·78	0·64	1·39	0·28	81·5	1·31	0·45

(3) ash was digested to a liquid analyte by soaking at room temperature for 24 h in 100% reagent quality aqua regia (HNO_3:HCl, 1:3) followed by heating of this mixture at 125°C until the volume was reduced to 3 ml. Solids remaining after digestion were recovered in filter paper for analysis;
(4) the liquid analyte produced by the digestion process was then diluted with deionized distilled water to a volume of 100 ml except for six smaller samples (ID Nos. 3, 6, 9, 12, 14, 27) which were diluted to a volume of 50 ml;
(5) the concentrations (ppm) of 30 elements were measured simultaneously for each analyte sample using a Jarrell Ash ICAP 9000 inductively coupled plasma atomic emission spectrometer located at the Lakehead University Instrumentation Laboratory.

Eleven samples of solid digestion residue from the samples reported in this paper were analysed to determine the percentage of original ash not digested and the elemental composition of this residue. These were all derived from ancient archaeological specimens and included three replicate samples of ancient uncharred *Pinus* wood (sample ID No. 20), three replicate samples of ancient charred *Juniperus* wood (sample ID No. 21), two samples of different ancient charred corn (*Zea mays*) cobs (sample ID Nos. 25 & 26) and three replicate samples of ancient hearth ash from Sand Canyon Pueblo (sample ID No 31). Five modern specimen residue samples from an earlier ICP run were also analysed. Although problems with that run led to the exclusion of the ICP results from this study, the residues provide useful comparisons to those from the archaeological samples. The five modern samples include one modern *Zea mays* cob supplied by Native Seed Search and wood from two *Pinus edulis* trees and two *Juniperus osteosperma* trees at Sand Canyon Pueblo. Each wood type includes samples collected from trees growing on two different sandstone formations present in the collection area. To avoid contamination of the sample from surface sediment, we snipped the specimens from dead branches on the trees.

The percentage not digested and thus remaining as residue was measured by dividing the weight of the residue by the total weight of the ash before digestion. The semi-quantitative elemental composition of seven of these residue samples (one of each sample type) was determined through energy dispersive spectrometry coupled with a scanning electron microscope (SEM-EDS). The X-ray data were acquired by rastering the electron beam over between one and three areas of each sample for 100 s.

Treatment of the raw ICP-AES data involved calibrating and standardizing all values, and selecting elements for inclusion in quantitative analyses. Concentration determinations for each element were calibrated by subtracting the values obtained for the blank samples. All sample values were then standardized by dividing by the weight of digested ash and correcting for dilutions. The ICP analysis produced high and low measurements for four elements (Ca, Fe, Mg and Na). Selecting the most accurate measurement depends on the element's concentration in a given sample. In samples with relatively high concentrations, the high values were selected, while in samples with low concentrations, we used the low values.

We eliminated elements from inclusion in subsequent quantitative analyses based on three criteria. Eliminated were: (1) elements for which most samples yielded values below reliable instrument detection limits (IDL); (2) elements whose values for pine needle standards compared poorly to certified concentrations; and (3) elements comprising a large proportion of residue remaining after digestion of the ash as determined by SEM-EDS of residue samples. The accuracy of concentration measurements near the IDL varies among elements. As a general rule of thumb, we considered elements for elimination from quantitative analyses if their concentrations were less than three times their IDL. Only Si was eliminated due to high concentrations in the digestion residue, and it also yielded inconsistent results for the pine needle standard samples. To avoid the problem of digestion residues in future analyses, digestion should be forced to completion by heating samples during digestion and possibly by using other chemicals such as nitric and hydrofluoric acid.

Results

Analyses of digestion residues

The percentages of digestion residues of the digested ash for the ancient wood and charcoal samples range

Table 3. Concentrations (ppm of digested ash) of selected elements from ICP-AES analysis

Sample ID No.	Chemical Elements													
	Al	Ba	Ca	Cd	Cu	K	Mg	Mn	P	Sr	Ti	Tl	Y	Zn
1	15,500	515	234,000	3·61	60·3	11,400	13,000	471	2270	637	370	88·5	8·27	231
2	30,600	675	164,000	5·31	71·3	9420	8080	635	2670	421	604	120	15·6	145
3	454	587	203,000	5·99	77·2	51,400	34,500	722	5860	829	21·3	49·1	0·53	297
4	18,600	785	245,000	4·84	63·1	9550	13,000	476	4080	703	397	80·9	9·5	150
5	30,300	865	196,000	5·04	84·1	10,200	9530	610	3630	558	628	120	14·4	155
6	7500	1160	216,000	7·59	114	18,900	37,800	886	3220	1130	233	69·1	3·51	183
7	4830	730	348,000	3·05	40·4	7000	4350	371	2480	942	117	42·9	5·23	36·4
8	15,700	812	266,000	2·99	62·1	6500	4870	458	3870	958	345	75	9·66	147
9	768	1010	222,000	4·44	173	60,000	16,100	369	8970	3000	53·2	30·0	ND	287
10	7340	1040	311,000	2·81	43·7	23,300	9120	511	4540	2220	216	61·8	5·29	204
11	22,700	925	229,000	5·41	54·5	9150	7340	457	2500	968	553	84·1	10·2	103
12	755	2830	296,000	12·7	209	67,300	25,300	2840	10,400	7050	42·3	127	0·69	277
13	76·8	81·3	6560	1·57	73·6	419,000	9470	116	29,400	78	14·3	36·7	ND	84·6
14	215	23·7	3010	7·71	149	338,000	20,200	581	32,300	76·4	20·1	96·0	ND	563
15	24,600	583	88,000	9·9	137	125,000	16,500	769	12,400	525	695	109	11·8	326
16	2910	1780	349,000	4·61	32·6	7480	10,200	186	3170	1580	94·6	39·7	4·52	120
17	2760	755	266,000	3·1	60·2	24,500	7510	222	5780	1690	90·3	35·3	3·8	205
18	27,200	924	204,000	5·06	64·3	9810	8800	570	2920	673	533	104	13·8	139
19	14,000	635	232,000	4·08	59·1	14,300	10,900	539	2740	1030	341	74·2	7·23	172
20	4990	507	350,000	3·73	87·3	1070	8370	154	1600	1180	91·2	53	9·15	93·2
21	3120	1880	324,000	6·09	23	10,300	39,200	120	765	2980	84	54	6·21	21
22	257	337	280,000	8·84	57·1	40,200	82,600	205	1060	2160	13·7	60·2	2·25	24·9
23	16,100	497	260,000	8·31	53·2	33,500	57,200	232	1690	3040	174	96	5·36	83·7
24	2940	1190	260,000	7·52	45·3	41,600	61,500	126	1140	3250	71·8	66·4	3·33	26·9
25	7480	205	255,000	ND	136	40,500	128,000	402	13,900	2340	455	127	6·09	403
26	9220	173	310,000	ND	168	25,000	84,100	256	3730	2700	464	43·9	6·35	145
27	5970	879	288,000	12·0	193	21,800	105,000	907	10,500	3390	296	103	5·23	223
28	24,600	6810	300,000	4·65	76·4	4070	14,200	261	5780	1790	341	122	11·1	81·2
29	10,400	891	219,000	7	45·5	25,700	42,600	208	12,100	2800	185	83·7	4·36	269
30	11,900	304	248,000	9·54	74·7	39,000	60,600	193	21,700	2940	178	92	5·94	194
31	26,000	771	71,200	3·14	49·1	8190	5840	783	407	627	655	96·8	10·2	116
32	18,300	1310	154,000	2·25	52·3	16,200	12,600	496	4800	1670	530	89·1	7·18	374
33	23,800	159	4170	3·62	13·1	5310	4830	371	411	36·2	663	92	9·24	49·9
34	25,400	192	5990	4·33	14·3	5140	5140	432	368	43·8	665	93·2	10·4	59·6

Values are adjusted by subtracting blanks and rounding to significant figures. ND = not detected. See Table 1 for descriptions of samples.

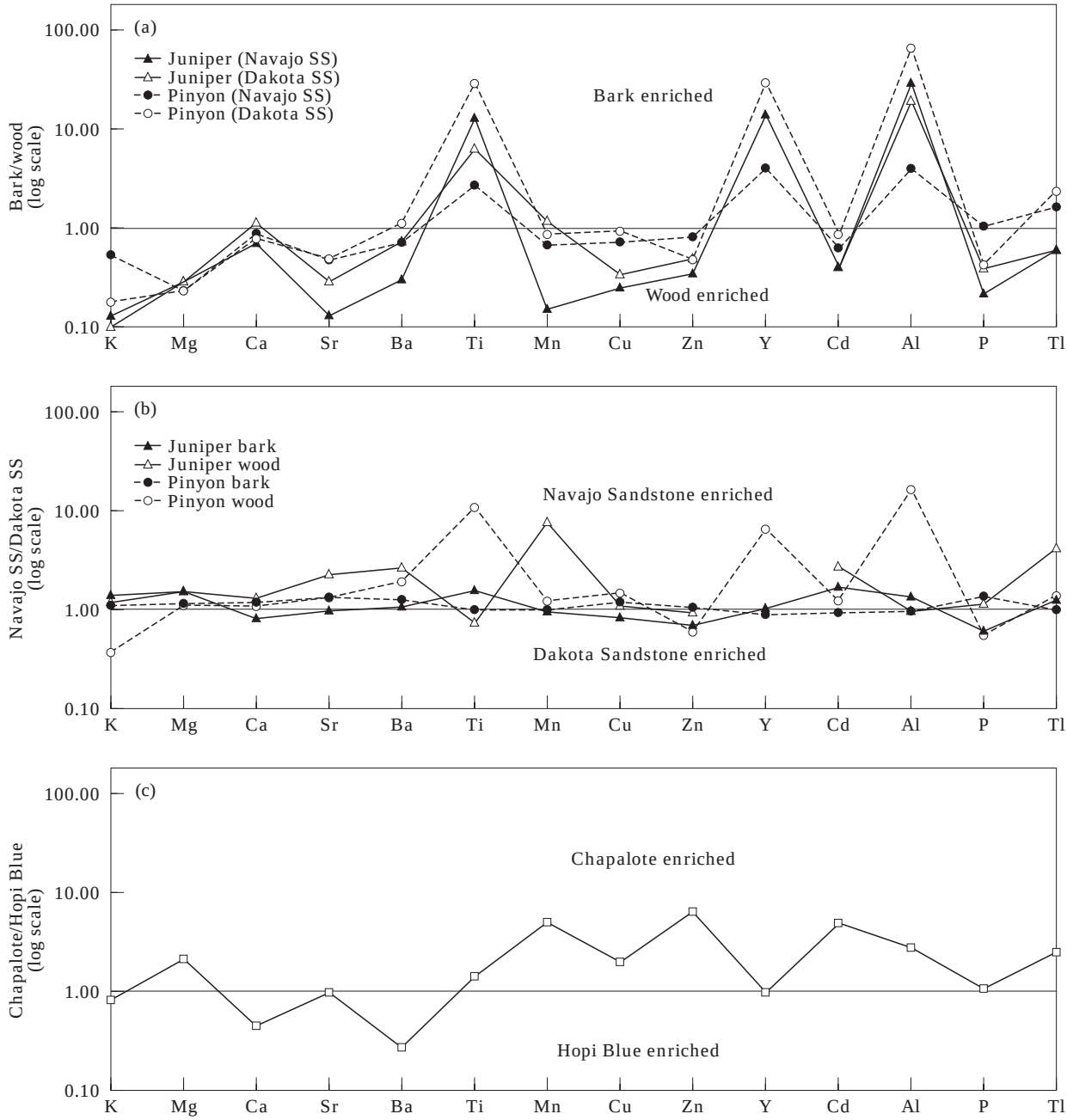

Figure 2. Ratios of element concentrations in: (a) bark and wood from Juniper (*Juniperus osteosperma*) and Pinyon (*Pinus edulis*); (b) samples of the same taxon and tissue types from different sandstone (SS) substrates; and (c) different varieties of corn (*Zea mays*) cobs grown in separate locations. Values above 1·0 indicate greater concentrations of the element in the dividend and values below 1·0 indicate greater concentrations in the divisor.

between 11 and 49%, with an average of 34·5% for the eight ancient samples. The modern samples range from 14·3% to 53·4%, averaging 34·9%. Among the archaeological samples, *Pinus* consistently produced less residue than *Juniperus* samples with *Zea mays* cobs intermediate. Results from the modern samples were similar to the ancient specimens except that *Zea mays* produced the least residue. Digestion residues for the ancient hearth ash were considerably higher with an average of 76·7% for the three samples weighed. The higher values for the ash samples probably result from mixture of the ash with sediment from the enclosing deposits, which may also account for the greater amount of residue from the archaeological *Zea mays* cobs than the modern cob samples. However, some of the variation in undigested residues may result from differences among tissue types. For example, one *Pinus* specimen produced 23·4% of residue when the wood

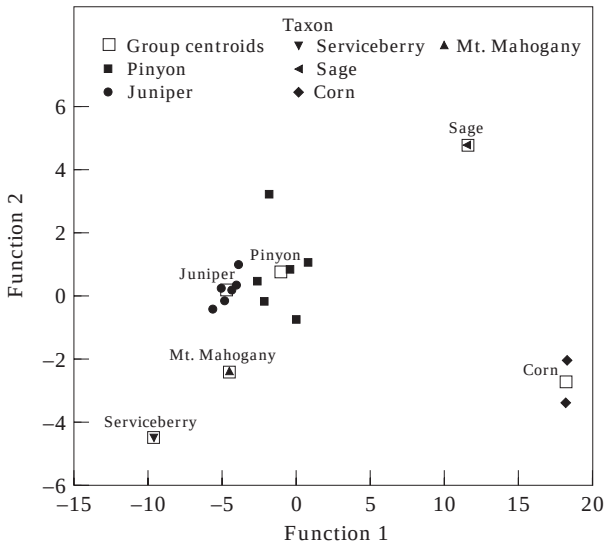

Figure 3. Scatter plot on the first two discriminant functions of element concentrations in modern samples from common fuel wood taxa including: Pinyon (*Pinus edulis*); Juniper (*Juniperus osteosperma*); Mt. Mahogany (*Cercocarpus montanus*); Serviceberry (*Amelanchier utahensis*); Sage (*Artemisia tridentata*); and Corn (*Zea mays*).

and bark were digested together, but wood and bark digested separately produced <0·1% and 35·3% of residue respectively.

Table 2 shows the percentage element concentrations (averaged from the multiple rasters) for the seven sample types. In all samples, Si constitutes over 80% of the residue, with Al and K making up most of the remaining residue. Fortunately, element concentrations are fairly consistent across sample types.

It is possible that the residues are derived, at least in part, from inorganic nutrients in the tissues. Temperate zone woods contain 0·1–1·0% inorganic nutrients (Hillis, 1987: 83). To investigate this possibility, we conducted brief SEM-EDS examinations of the various structures and cell types in heartwood, sapwood and bark across radial sections of *Pinus edulis* and *Juniperus osteosperma* specimens. Some apparently crystalline substances containing some elements found in the digestion residues were observed, suggesting a possible area for future investigation.

In summary, our digestion method produced undissolved residue, primarily of a siliceous nature, the amount varying among taxa and among tissue type within a taxon. Hence, we eliminated Si from the ICP-AES data set of elements in the analyte solutions to reduce the impacts of variation among samples in digestion residue.

ICP-AES analysis

Table 3 shows the calibrated results in ppm of digested ash from the ICP-AES analyses of the 34 samples included in this study. Although data were generated for 30 elements by the ICP-AES instrument, only the elements considered reliable for quantitative analyses are included in Table 3. Using the criteria stated earlier, we eliminated 16 elements from consideration (As, B, Co, Cr, Fe, Mo, Na, Nb, Ni, Pb, S, Se, U, V, Z, Zr). Most of these elements were eliminated due to inconsistent results in comparison to the pine needle standard. Five of the elements (Nb, Pb, Tl, V and Zr) were eliminated due to concentrations near or below the detection limits of the ICP instrument at Lakehead University and three elements (As, Se, Mo) were eliminated based on multiple criteria.

Most of the data were generated in a single run of the instrument. Only two samples (ID Nos. 25 and 26) were analysed in a separate run which did not include the pine needle standard. However, the samples were included in this study because they appear to be reliable, based on consistency in the blank and the machine standards run with the samples. Close correspondence between the measured values and major element concentrations reported for other temperate wood species (Hillis, 1987) indicate that the data generated for this study fall within an expected range.

Discussion

The quantitatively reliable element concentration data can now be used to evaluate the three issues critical to distinguishing the fuel constituents of ash: taxonomic and tissue type variability; post-depositional alteration; and sorting out taxonomic/tissue type ash mixtures.

Taxonomic and tissue variability

If variation in elemental composition is consistently greater within than between taxa and tissue types, the potential for using elemental concentrations in hearth ash to identify the fuel sources of the ash would be limited. Potential sources of variation within taxa include different growing conditions (mainly substrate), and varietal, age and health differences within taxa that can affect element uptake (Hillis, 1987; Dunn, 1992).

Figure 2 presents graphs of the ratios of the concentrations of the 14 selected elements in different kinds of samples. In these graphs, values around 1·0 indicate little or no difference in element concentrations in the particular samples being compared. Values greater than 1·0 indicate enrichment of the sample element in the numerator, while values less than 1·0 indicate depletion. Figure 2(a) shows the element concentration ratios of bark to wood for *Pinus edulis* and *Juniperus osteosperma* samples grown on the same substrates with paired samples from two different substrates (Navajo and Dakota sandstone) included. These data show that the composition of wood and bark varies considerably for some elements suggesting that it should be possible to distinguish between these two

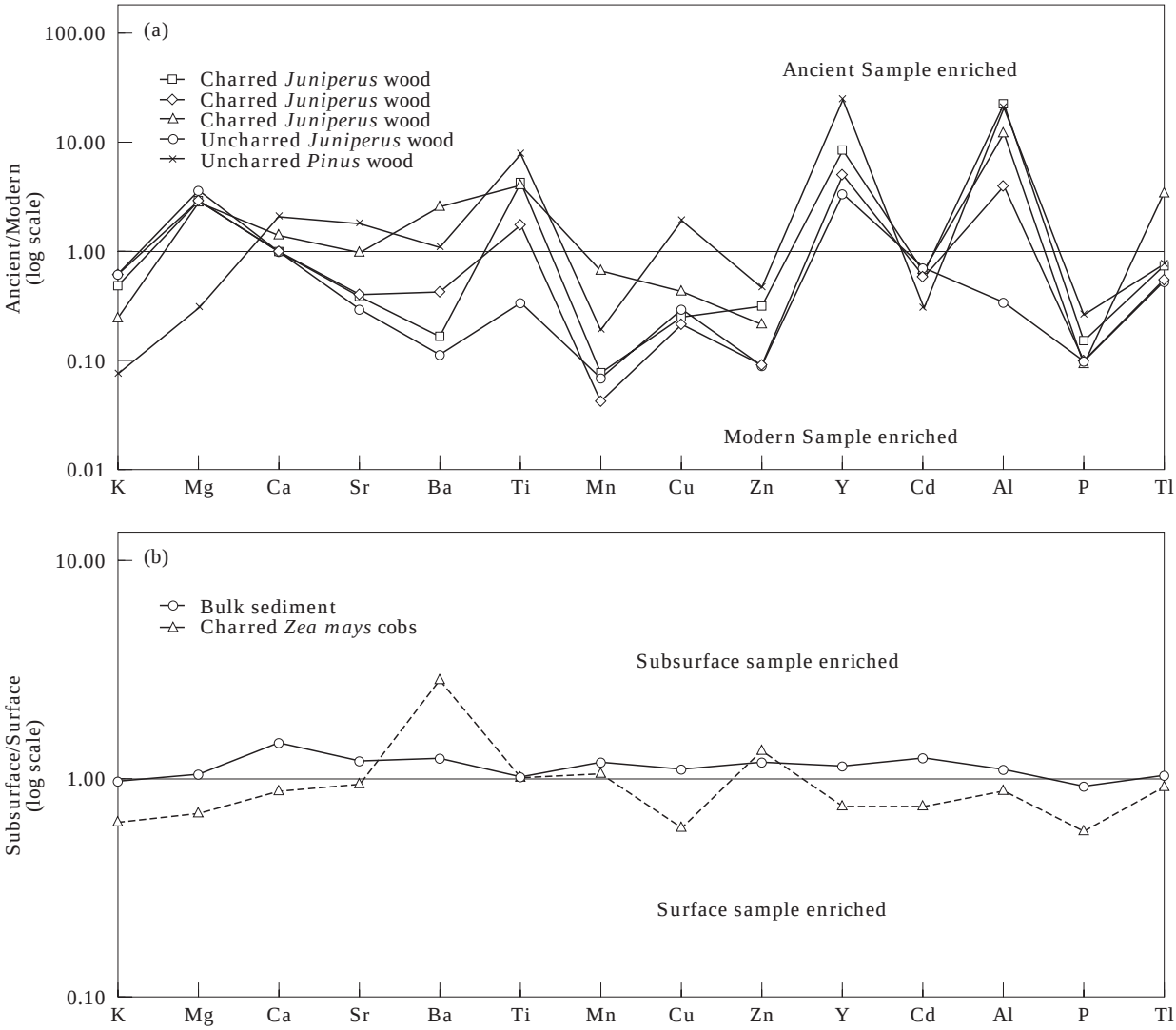

Figure 4. Ratios of element concentrations in: (a) modern and ancient samples of the same taxon; and (b) surface and subsurface samples from Structure 808 at Sand Canyon Pueblo. Values above 1·0 indicate greater concentrations of the element in the dividend and values below 1·0 indicate greater concentrations in the divisor.

tissue types using element concentration data. In addition, the patterns of bark/wood element concentration ratios are very similar for the two different taxa and substrates compared. Figure 2(b) compares the same taxa and tissue types grown on the two different sandstone substrates. Although some variation is evident, most values fall close to 1·0, indicating that substrate plays a minor role relative to taxon and tissue type in determining element concentrations in these samples. Figure 2(c) displays the element concentration ratios for the two different varieties of *Zea mays* cobs (Hopi Blue and Chapalote) analysed. Chapalote *Zea mays* has greater concentrations in several of the elements compared. Although this graph may indicate the potential for varietal variation in element concentrations, the meaning is complicated by the growth of the two cobs in two different locations.

Figure 3 depicts in a scatter plot the results of a discriminant function analysis of selected element concentrations in modern samples of different taxa. We selected a subgroup of seven elements (K, Mn, Sr, Ti, Tl, Y and Zn) to minimize violations of the linear model assumptions that underlie discriminant analysis, particularly the problems introduced through strong correlations among elements (Tabachnick & Fidell, 1983: 299–301). The first two discriminant functions used in the graph encompass 97% of the variation within the modern data set and produced a perfect discrimination of all six taxa. Despite the potential for within-taxon variation documented in Figure 2, there appears to be more between-taxon variation than within-taxon variation when considered in a multivariate fashion. For example, striking differences between bark and wood tissue types did not confound our

ability to distinguish taxa regardless of tissue type in the discriminant analysis.

Post-depositional alteration

Weathering in the soil can lead to accumulation and leaching of elements that might significantly affect our ability to discriminate taxa in ancient samples of ash. Figure 4 shows ratios of element concentrations in ancient and modern samples of the same taxon and tissue type and surface and subsurface samples of sediment and of ancient *Zea mays* cobs. The comparison of ancient and modern samples (Figure 4(a)) shows differences in concentrations of some elements. No discernable differences were found in concentration ratios between elements that are more soluble (K, Mg, Ca, Sr, Ba, Cu) and those that are less soluble (Ti, Mn, Zn), indicating that post-depositional leaching or enrichment may not be responsible for the differences between ancient and modern samples. This conclusion is reinforced by Figure 4(b) comparing element concentration ratios in sediment from the surface (ID No. 33) and 100 cm below the surface (ID No. 34, taken at the same depth as sample No. 28) in Structure 808 at Sand Canyon Pueblo, and charred *Zea mays* cob samples recovered from Stratum 1 (ID No. 30) and from 150 cm below the surface on the floor of structure 105 (ID No. 29) at Castle Rock Pueblo. In both sets of samples, the upper samples were recovered from the zone of leaching while the lower samples came from the zone of accumulation. Almost all values are very close to 1·0, indicating that the migration of elements through post-depositional soil formation processes has not been a significant factor in these samples.

Figures 5 and 6 respectively depict the results of discriminant analyses in which the ancient samples are classified using functions generated for the modern samples, with the ancient samples considered by themselves. Figure 5 shows that the ancient and modern samples of the same taxon differ substantially. Using the discriminant functions derived from data on the modern samples to classify the ancient material, none of the ancient charcoal samples is classified to the correct taxon. However, the three taxa represented in the samples of ancient material shown in Figure 6 discriminate perfectly when treated by themselves. These results indicate that if some form of post-depositional alteration is responsible for the compositional differences between the ancient and modern samples, this alteration has not impaired our ability to distinguish taxa in the ancient samples chemically.

Taxonomic and tissue mixtures

Being able to discriminate samples of individual taxa and tissue types offers no guarantee that the particular plant fuels contributing to mixed ash samples can also be distinguished. To evaluate this issue, we created two

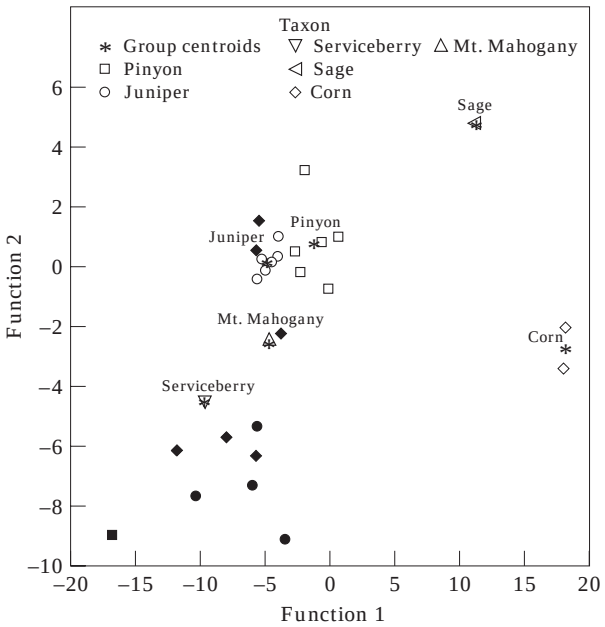

Figure 5. Scatter plot comparison of element concentrations in modern samples (open symbols) and ancient samples (solid symbols) of the same taxon and classified using the discriminant functions derived from the modern samples.

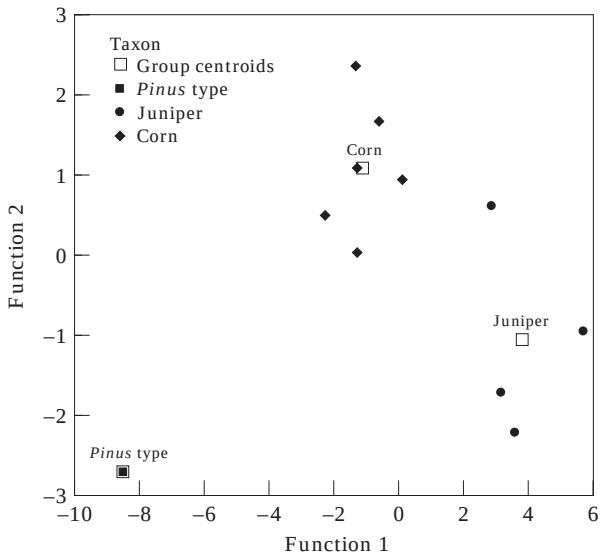

Figure 6. Scatter plot on the first two discriminant functions of element concentrations in ancient samples showing perfect discrimination of taxa.

samples (Unknowns A and B in Table 1) composed of known amounts of ash from modern samples. We then used multiple linear regression in an attempt to ''unmix'' these mixtures. In this analysis, dependent variables (the different samples of known taxon) remain in the regression equation only if their slope coefficients are positive and they result in a significant change ($P<0{\cdot}1$) in r^2. Standardized slope coefficients

Table 4. Multiple regression results for unmixing of prepared modern ash samples

Actual composition			Estimated composition		
Taxon	Tissue type	Percentage	Taxon	Tissue type	Percentage
Unknown A					
Pinus edulis	Bark	80*	*Pinus edulis*	Bark	49
			Juniperus osteosperma	Bark	35
Amelanchier utahensis	Wood	20	*Amelanchier utahensis*	Wood	9
			Sediment	Subsurface	7
Unknown B					
Pinus edulis	Bark & wood	61	*Pinus edulis*	Bark & wood	66
Juniperus osteosperma	Bark & wood	29	*Juniperus osteosperma*	Bark & wood	26
Sediment	Subsurface	10	Sediment	Subsurface	8

Percentage by dry weight of ash.

Table 5. Regression analysis of ancient hearth ash data from Sand Canyon Pueblo in comparison to identified macrofossils recovered from the same feature through flotation

Macrofossils identified		Estimated composition		
Taxon	Tissue type	Taxon	Tissue type	Percentage
Pinus type	Wood			
Pinus type	Cone			
Pinus type	Bark			
Juniperus	Wood	*Juniperus*	Wood	13
Zea mays	Cob			
Zea mays	Kernel			
Rosaceae type	Wood	*Cercocarpus*	Wood	46
Unknown	Wood			
Opuntia (prickly pear)	Seeds			
Phaseolus (bean)	Cotyledon			
		Sediment	Surface	41

indicate the proportional contribution of each dependent variable (See Kohler & Blinman, 1987, for use of the same approach to unmix ceramic assemblages).

Table 4 shows the results of the regression analysis of the two ''unknowns'' prepared in the laboratory. In Unknown A, the regression analysis properly identified *Pinus edulis* bark and *Amelanchier utahensis* wood, but also included *Juniperus osteosperma* bark and subsurface sediment which were not parts of the prepared mixture. However, Pinyon bark was the first dependent variable entered into the regression model and accounts for 80% of the actual mixture. Perhaps the elemental differences between Pinyon and Juniper bark are too subtle for distinguishing with multiple regression as additional dependent variables were added. We cannot currently account for why sediment was included in the regression model. The results for Unknown B are much more favourable. Not only were the proper taxa and tissue types accurately identified, but the estimated proportions almost exactly match the actual proportions in the prepared samples. Encouraged by the results of the regression analysis of the prepared mixtures, we employed the same procedure on the two samples of ancient hearth ash. Table 5 shows the results of this regression analysis of the ash from Feature 2 at Sand Canyon Pueblo (sample ID No. 31) and a list of the types of plant macrofossils identified from the same feature. Although a wide variety of macrofossil remains was present in the hearth, the regression analysis distinguished only *Cercocarpus montanus* wood, surface sediment, and *Pinus* bark in the ash. We can imagine three possible reasons for the poor match between the ash and macrofossil data. Firstly, the taxa and tissue types present as macrofossils, but not distinguished in the ash, actually may not have been used as fuel and thus did not contribute much to the ash in the hearth. Secondly, post-depositional processes altered the hearth ash chemistry such that the chemical data from modern samples are not adequate for unmixing the ancient ash. Thirdly, the small data set on modern samples generated for this study does not adequately document the range of variation in composition of important fuel taxa and tissue types, making it difficult to match and unmix samples drawn from outside the data set. We currently do not have enough information to distinguish among these possibilities. The regression analysis of the hearth ash from Castle Rock Pueblo (sample ID No. 32) identified *Pinus* wood and bark as the only material contributing to the ash. Unfortunately, no comparable macrofossil data exist for this feature.

Conclusions

The results of this study indicate that there is enough variation in elemental composition of fuel materials to allow us to distinguish taxa and different tissue types within taxa through chemical analysis of ash. Post-depositional alteration could be a confounding factor, but the small number of samples analysed for this study proved inconclusive on this point. Although clear differences exist between modern and ancient samples, we are not able to determine if these differences result from post-depositional alteration, or because we have thus far included too few samples to document the range of chemical variation in modern materials adequately. If the post-depositional alteration issue can be resolved, multiple regression may offer a powerful tool for resolving problems with mixed-taxon ash samples, but other approaches should be investigated as well.

Further work is needed before the method can be used with confidence. Adequate characterization of the chemical variation within and between modern taxa and tissue types will require multiple determinations of elemental chemistry over a wider range of taxa than was accomplished for this study. Resolving the issue of post-depositional alteration will require a more thorough analysis of ancient materials and their chemical contexts, and possibly analyses of modern material weathered under controlled conditions. Researchers at Crow Canyon Archaeological Center have collected some of the necessary samples for these additional studies.

If the problems we identified can be resolved, chemical analysis of ash appears to offer an important adjunct to the macrofossil record in studies of fuel use. In addition to the problem of fuel selection and depletion that inspired this work, the technique could be used to investigate the composition of ash recovered from ceremonial contexts, the use of ash as fertilizer in fields, environmental changes that affect fuel resource availability, and functional differences in fires composed of fuels with distinct combustion qualities.

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