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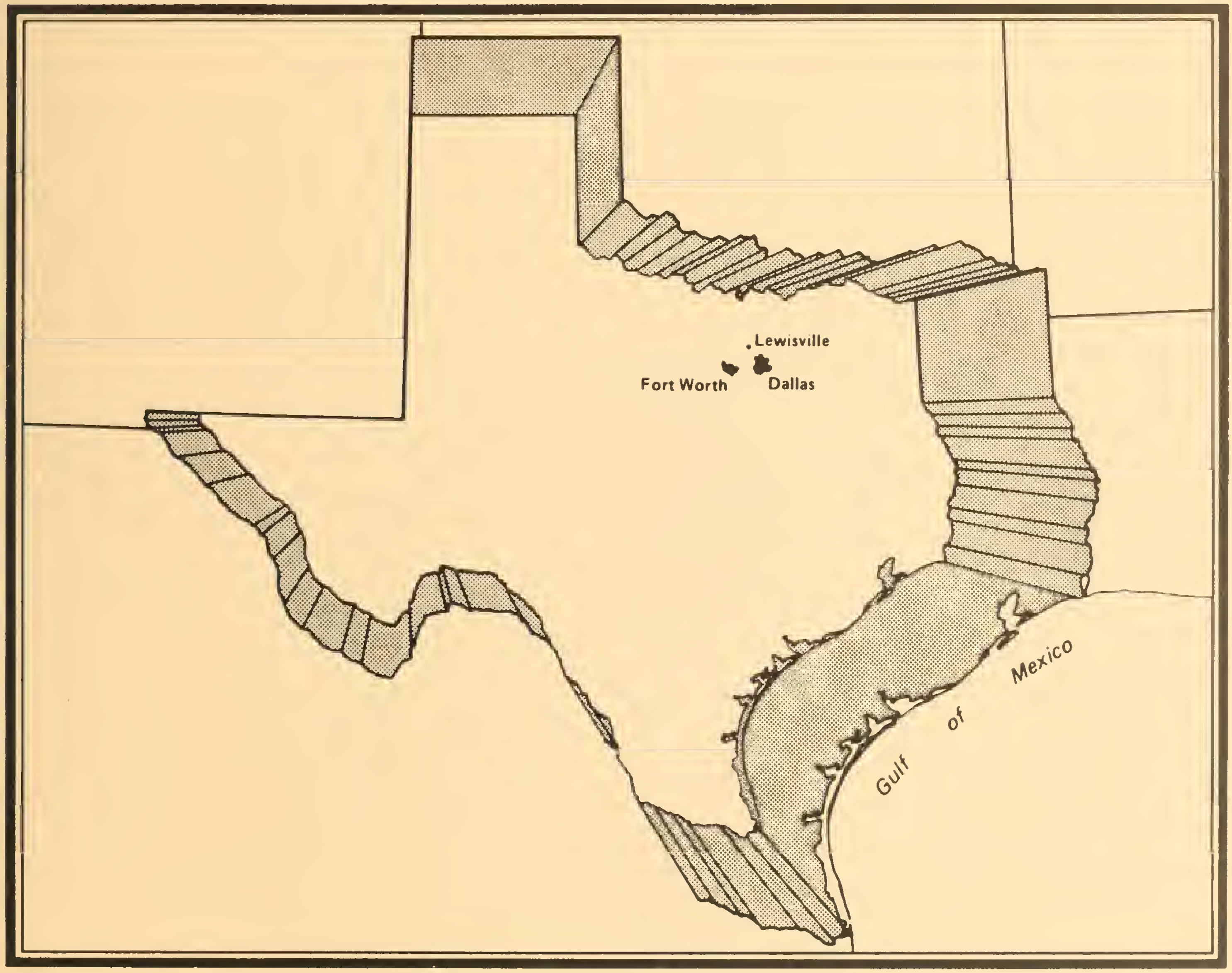

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ABSTRACT

The Lewisville site, located in Denton County on the Trinity River north of Dallas, Texas, was thought to provide evidence of the earliest human activity in the western hemisphere. Radiocarbon dates of 37,000 to 38,000 B.P. determined for the site in the late 1950s conflicted with the presence of a Clovis point, which would fix the age of the site between 11,000 and 11,500 B.P.*

It was hypothesized (Johnson, 1982) that Clovis people were burning lignite from nearby outcrops: lignite in hearth residues would give older than actual ages by radiocarbon dating. X-ray diffraction and instrumental neutron activation analysis proved inconclusive; however, Moessbauer spectroscopy indicated that hematite, a pyrite combustion product, was present in the ash. From this evidence we conclude that there is some support for the hypothesis.

INTRODUCTION

The Lewisville site, located in Denton County on the Trinity River north of Dallas, Texas, was thought by some to provide evidence of the earliest human activity in the western hemisphere (Brannon et al., 1957). The site was originally excavated by W. W. Crook, Jr., and R. K. Harris, members of a team from the Dallas Archaeological Society. The investigators studied 21 fire-oxidized zones that were interpreted to be hearths. A Clovis point, along with the remains of a great variety of extinct and present-day animals, was found associated with hearth 1. All presumed hearths occur in several alluvial layers that form the basal portion of the upper Shuler Formation of late Pleistocene age.

A controversy arose when several radiocarbon dates for the charcoal associated with the hearths gave ages greater than 37,000 and 38,000 radiocarbon years (Brannon et al., 1957; Crook and Harris, 1957, 1962; Fergusson and Libby, 1962). Since the Clovis point defines a narrow range between 11,000 and 11,500 B.P.,* it was possible that the Clovis point had been "planted," and the hearths were produced by some non-anthropic phenomenon (Johnson, 1982).

Damming the Trinity River in 1959-60 created a reservoir that flooded the site, preventing further excavation and research. Twenty years later, a drought caused the reservoir level to fall below the archaeological site. L. Banks and R. Burton of the U.S. Corps of Engineers and D. Stamford of the Smithsonian Institution invited a pedologist experienced with hearths and hearth-like features to investigate the site: D. L. Johnson of the Department of Geography at the University of Illinois, Urbana-Champaign. Feature 22, which resembled a hearth, was chosen for study and identified as Lewisville site 41DN72 (sample TX-2A) (Johnson, 1982). Excavation at this site was already underway, initiated by Stamford, Banks, and coworkers J. Rancier and B. Hesse.

*B.P. = years before present.

Radiocarbon dating was recently run on charcoal from feature 22 (TX-2A) by D. Coleman of the Illinois State Geological Survey. The finite radiocarbon date of 26,610 ± 300 B.P. was younger than the dates obtained two decades earlier, although it was still much older than the 11,000 to 11,500 B.P. age range of other well-dated Clovis camp sites. This suggested the possibility of contamination by materials of different ages.

To explain the disparate radiocarbon dates, a hypothesis was advanced (Johnson, 1982) proposing that the site was of Clovis age and that Clovis people were burning lignite from nearby outcrops of the Woodbine Formation of Cretaceous age. If the origin of the ash in hearth 1 was determined to be from the Woodbine Formation, it would serve as strong evidence that the Clovis people were present at the site and burned lignite in their fires. The presence of lignite would then explain the older-than-expected radiocarbon dates.

In this study, samples of hearth material and the surrounding soil were examined, using Moessbauer spectroscopy, X-ray diffraction, and neutron activation analysis. It was thought that if lignite from the Woodbine Formation had been burned in the hearths, these three analytical methods would show a pyrite-to-hematite transformation due to combustion, traces of authigenic kaolinite, or some type of trace-element fingerprint. This finding would suggest that the Clovis people burned lignite in the hearth and that the Lewisville site was indeed a Clovis camp 11,000 to 11,500 years old.

Eight samples were initially analyzed (DJ-1 through DJ-8) and later augmented by three more (TX-1A, TX-2A, and TX-3A). The sample identification and descriptions are given in table 1.

Table 1. Sample Index

Sample	Description
DJ-1	41 DN 72, hearth 8, carbonized material collected in 1957
DJ-2	Lignite (selected small pieces from the Woodbine Formation)
DJ-3	Lignite and charcoal ash from a modern all-night fire stoked with modern wood and Cretaceous lignite in a hearth dug into the upper Shuler alluvium (fire tended by Banks, Johnson, and others on March 20, 1982)
DJ-4	Hearth 22, sediment, 35 to 40 cm deep
DJ-5	Lignite (large pieces)
DJ-6	41 DN 72, hearth 8, Crook and Harris, selected carbonized material collected in 1957
DJ-7	Surface ash from all-night fire
DJ-8	41 DN 72/N1000E 996, Shuler Formation sediment from surrounding area of hearth 22
TX-1A	Charcoal from feature 22, Rancier photo 3 and 4; F101NW, N1001.95, E1002.65, elev. 99.20 m
TX-2A	Sample used by D. Coleman for dating of feature 22
TX-3A	F106SE; N1010, E1002; elev. 99.45 m; N1010.6, E1003.33; March 13, 1979

EXPERIMENTAL METHODS

Moessbauer Spectroscopic Analysis

Moessbauer spectra were obtained with an Austin Science Associates Spectrometer that utilized a linear acceleration motor to move the source (^{57}Co in Rh). A Nicolet 1070 N Signal Averager with 1024 channels collected the spectra. Two spectra were collected simultaneously and combined to yield a spectrum that was recorded in 512 channels. All the spectra were obtained at room temperature and recorded until approximately 5 x 10^6 counts per channel in the base line had been accumulated.

Moessbauer spectra were analyzed by the least squares fit of Lorentzian-shaped multiplets to the observed spectrum using the computer program MOSFIT (Smith et al., 1978). Each iron absorption is described in terms of one to six Lorentzian curves with these parameters: isomer shift; quadrupole coupling constant; and internal magnetic field (when present). Within each species multiple, line width and intensity parameters were set equal for each absorption. Magnetically split absorptions had intensity ratios of 3:2:1:1:2:3. These constraints were employed because of the large number of components typically found in the spectra.

X-ray Diffraction Analysis

The mineralogical analysis of the samples was performed by X-ray diffraction, using unoriented powders and $<2\mu$ sedimented slides. The samples were scanned at 2° 2Θ/min using a Copper K α radiation source.

Elemental Analysis

The elemental composition of the samples was determined using instrumental neutron activation analysis. The samples were first ground to pass 60 mesh, then analyzed by established procedures (Cahill, 1981).

SAMPLE PREPARATION

- DJ-1 through DJ-8: These original samples were analyzed as received without modification.

- TX-1A: This sample consisted of charcoal from feature 22 (Rancier photos 3 and 4; F101NW, N1001.95, E1002.65, elev. 99.10 m). It contained one moderately sized (1 cm) fragment and a quantity of small broken pieces. The 1-cm fragment was set aside and saved. All smaller pieces were ground in an agate mortar and analyzed by Moessbauer spectroscopy.

- TX-2A: The composite sample used by D. Coleman contained several 1-cm fragments with black inclusions. The black areas, which were scraped from the fragments, had the appearance of clay. The scrapings were ground in an agate mortar and used to obtain the Moessbauer spectrum.

- TX-3A: This sample (F106SE, N1010, E1002; elev. 99.45 m; N1010.5, E1002.22; March 13, 1979) appeared to be clay fragments of various sizes. Some fragments contained a few, widely dispersed flakes of black material. The black materials were segregated from the sample, ground in an agate mortar, and used to obtain the Moessbauer spectrum.

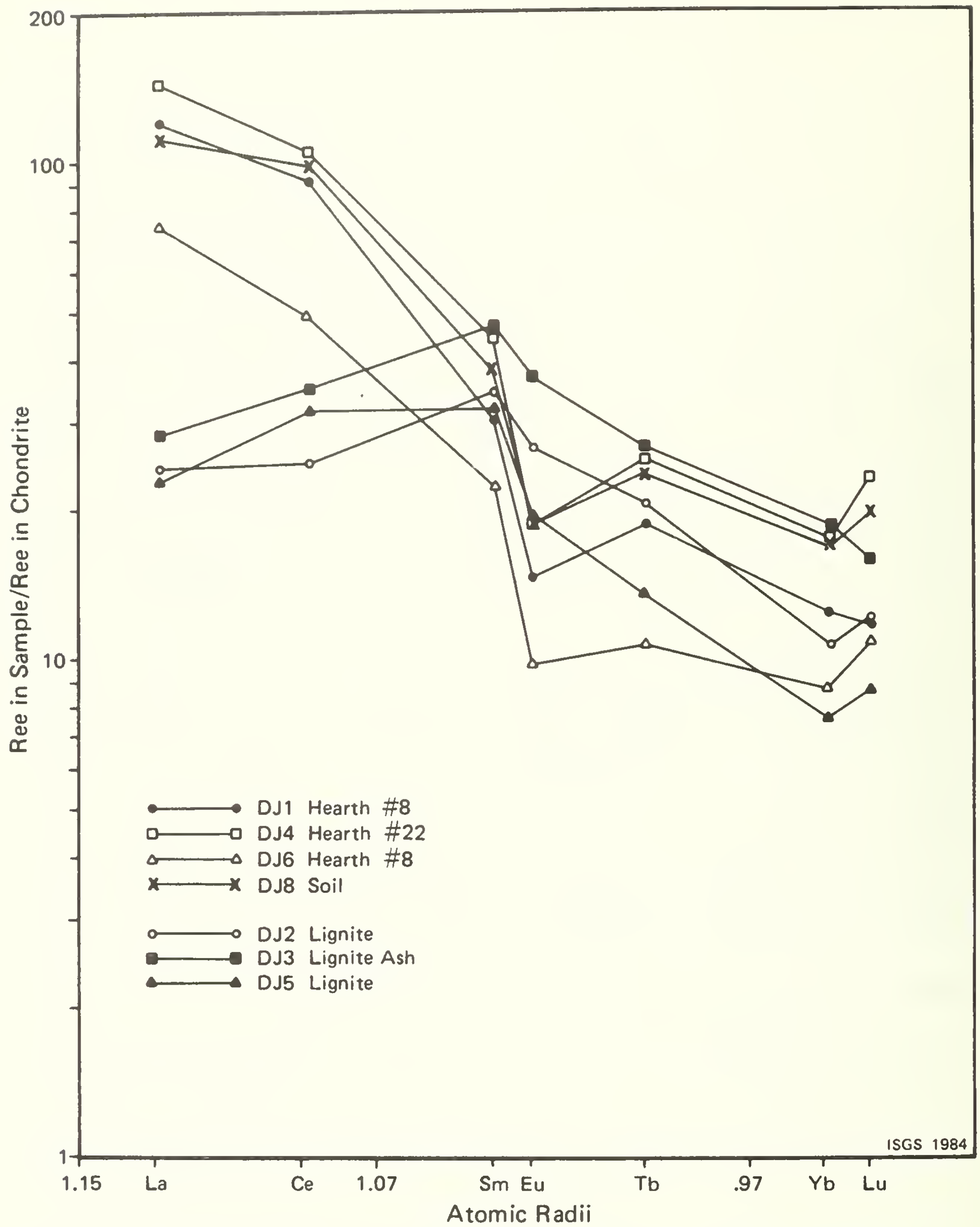

Figure 1. Rare earth elements (REE): abundance pattern at Lewisville site relative to chondrite meteorite (Evenson et al., 1978)

RESULTS AND DISCUSSION

Elemental Analysis

The original eight samples, which included DJ-1 through DJ-8, were analyzed for 23 elements. Percent moisture (110°C) and percent ash (500°C and 750°C) were also determined. The results are shown in table 2. Of the hearth samples analyzed, only the ash from the modern all-night lignite fires prepared by Banks and Johnson showed any appreciable increase in iron over that found in the surrounding soil.

Table 2. Lewisville Lignite Neutron Activation Analyses

Element*	DJ-2 lignite	DJ-5 lignite	DJ-8 soil	DJ-7 top ash	DJ-3 ash	DJ-1 hearth 8	DJ-6 hearth 8	DJ-4 hearth 22
Fe (%)	2.2	2.9	2.1	42.3	23.7	1.9	1.4	2.5
K	137	538	9600	28	172	6800	3400	9700
Na	71	330	1490	155	86	1475	1100	1600
Mn	170	38	540	14000	140	130	71	510
As	1.8	3.7	7.2	146	1	3.3	3.9	7
Br	1.2	4.0	<2	1	1	26	70	1.7
Co	11	7.4	12	160	12	6.4	3.8	11
Cr	11	27	66	22	11	110	175	65
Ni	28	45	23	180	33	21	16	27
Zn	90	10	34	42	48	36	27	48
Ta	0.1	0.3	1.4	0.2	<0.1	0.7	0.4	1.3
Hf	1.1	3	13	1.5	0.8	9	3	15
W	0.2	<0.3	1.7	<0.2	0.9	0.8	0.3	0.9
La	6	6	37	10	7	29	19	36
Ce	16	21	61	<10	23	59	32	69
Sm	54	5.3	6.1	2.7	7.5	4.8	3.6	6.9
Eu	1.6	1.2	1.1	0.7	2.2	0.9	0.6	1.1
Tb	0.8	0.5	0.9	0.4	1	0.7	0.4	1
Yb	1.9	1.3	2.8	0.5	3.1	2.2	1.5	3.1
Lu	0.3	0.2	0.5	0.4	0.4	0.3	0.3	0.6
Th	0.4	1	10	0.5	10	7.3	3.1	10
U	<0.2	0.9	<2	<0.3	3	1.9	3.2	3
Cs	0.2	0.2	4.2	<0.2	<0.1	3.3	1.8	3.8
Rb	<0.2	5	85	58	<2	51	24	65
Sc	2.2	5.1	9.4	12	3.4	7	4.3	9
Ga	4.4	2.5	11.5	2	11	8.7	5.3	12
Sb	0.2	0.4	<0.5	1.8	0.2	0.3	0.2	0.5
H_2O (%) 110°C	6.29	6.83	3.31	2.58	3.88	7.78	12.01	1.86
Ash (%) 500°C	10.46	14.55	–	76.25	6.57	78.90	43.98	97.52
Ash (%) 750°C	9.57	13.62	92.6	71.94	5.81	73.45	36.83	93.88

*Analyses were performed on the samples as received. All values are listed as ppm unless otherwise noted.

The data obtained for the seven rare earth elements, La, Ce, Sm, Eu, Tb, Yb, and Lu (table 2), were plotted in an abundance pattern relative to the abundance of these elements in the standard, the chondrite meteorite. Figure 1, therefore, is a standard abundance plot to determine similarities between any of the hearth, soil, or lignite samples; it dramatically illustrates that the rare earth composition of Woodbine Formation lignite and its corresponding ash are very similar to one another, but are not similar to the soil or the hearth samples. The rare earth composition of the surrounding soil follows the same pattern as that of the hearths. From this data, it is reasonable to provisionally conclude that Woodbine Formation lignite was not burned in the hearths.

Table 3. Mineralogic Composition of Texas Samples (calculated by H. D. Glass method, 1978)

	<2μ clays (%)			Nonclays as X-ray counts					
Sample	Expand-able	Illite	Kaolinite	Quartz	Ortho-clase	Plagio-clase	Calcite	Pyrite	Others
DJ-(1)	57	23	20	370	47	75	135	–	
DJ-(2)*	14	10	76**	10	–	–	–	190	
DJ-(3)*	43	20	37**	8	–	–	–	115	Hematite
DJ-(4)	40	33	27	448	62	77	135	–	
DJ-(5)*	9	8	83**	50	–	–	–	–	
DJ-(6)	40	36	24	165	tr	tr	tr	–	
DJ-(7)	–	–	–						Hematite = 175 †Pyrrhotite (P°) = 33 Graphite C ? = 25
DJ-(8)	35	38	27	365	55	47	220	–	

* chlorox treated
**authigenic kaolinite
† P° = 46.2 Mole % Fe

X-ray Diffraction Analysis

The mineralogical data obtained from X-ray diffraction are listed in table 3 under three headings:

1. nonclays, including quartz, orthoclase feldspar, plagioclase feldspar, calcite, and pyrite;
2. clays, including expandable clay minerals, illite, and kaolinite;
3. other minerals that form during burning, such as hematite, pyrrhotite, and graphitic carbon.

Pyrite decomposition products were only found among the all-night fire samples. An authigenic kaolinite characteristically found in the lignites DJ-2 and DJ-5 and in the all-night fire ash (DJ-3) was not found in any of the hearth samples. This may be a concentration problem, or it may be due to dehydration and structural breakdown of kaolinite caused by repeated heating in the hearths. Therefore, the X-ray data are inconclusive in determining whether lignite ash was present in the samples.

Moessbauer Spectroscopic Analysis

A summary of the mineral composition of the samples determined by Moessbauer spectroscopy and X-ray diffraction is shown in table 4. Examination of these data shows that the first eight samples failed to provide any insight into the problem. Pyrite decomposition products were positively identified only in the samples from the all-night fires and the 35- to 40-cm lining of hearth 22 (DJ-4, table 4).

Table 4. Mineral Composition of Samples as Determined by Moessbauer Spectroscopy and X-ray Diffraction

Minerals	DJ-2 lignite	DJ-5 lignite	DJ-8 soil	DJ-7 top ash	DJ-3 ash	DJ-1 hearth 8	DJ-6 hearth 8	DJ-4 hearth 22 35–40 cm	TX-1A hearth 22	TX-2A hearth 22 Coleman	TX-3A Story
Pyrite	MX	MX	–	M	MX	–	–	–	–	–	–
Pyrrhotite	–	–	–	X	–	–	–	–	–	–	–
Hematite	–	–	–	MX*	MX	–	–	M**	M	M	M
Other iron oxides	–	–	–	M	M	–	–	M	M	M	M
Goethite	–	–	M	–	–	–	–	–	–	–	–
Iron sulfates	–	M	–	–	–	–	M	–	–	–	–
Graphitic carbon	–	–	–	X	–	–	–	–	–	–	–
Quartz	X†	X†	X	–	X†	X	X†	X	–	–	–
Calcite	–	–	X	–	–	X	–	X	–	–	–
Orthoclase	–	–	X	–	–	X	X†	X	–	–	–
Plagioclase	–	–	X	–	–	X	X†	X	–	–	–
Clay minerals											
Illite	X	X	X	–	X	X	X	X	–	–	–
Kaolinite	X††	X††	X	–	X‡	X	X	X	–	–	–
Expandable	X	X	X	–	X	X	X	X	–	–	–
Fe^{+3}	M†	M†	M	M†	M	M	M	M	M	M	M
Fe^{+2}	–	M†	M	–	M	–	–	–	–	–	–

* Abundant.

** Little present; Moessbauer parameters are close to hematite.

† Low level abundance.

†† Authigenic kaolinite.

‡ Authigenic kaolinite but less than DJ-2 and DJ-3 due to dehydration.

Table 5. Moessbauer Parameters for Iron Species*

Assignment	Isomer shift (mm/sec)**	Quadrupole coupling constant (mm/sec)	Internal magnetic field (KOe)
DJ-1, hearth 8			
Clay, Fe^{+3}	0.356(6)	0.554(4)	–
Clay, Fe^{+3}	0.706(1)	1.8(4)	–
DJ-2, lignite (selected small pieces)			
Pyrite	0.302(1)	0.632(2)	–
Fe^{+3} (low level)	0.554(9)	0.930(18)	–
DJ-3, lignite and charcoal ash from all night fire			
Oxides of iron	0.436(8)	0.10(10)	516(1)
	0.606(1)	0.20(4)	518(1)
	0.376(2)	0.04(10)	496(1)
	0.306(2)	−0.06(84)	510(2)
Pyrite or Fe^{+3} clay	0.336(2)	0.624(6)	–
Clay, Fe^{+2}	1.296(2)	2.66(4)	–
DJ-4, hearth 22, 35 to 40 cm deep			
Hematite (small amount close to hematite)	0.306(4)	0.12(8)	503(3)
Clay, Fe^{+3}	0.351(1)	0.570(2)	–
DJ-5, lignite (large pieces)			
Pyrite	0.296(1)	0.620(2)	–
Fe^{+3} (low level)	0.416(1)	0.66(12)	–
Fe^{+2} (low level)	0.906(1)	3.2(2)	–
DJ-6, 41DN72, hearth 8, Crook and Harris (selected pieces)			
Clay, Fe^{+3}	0.359(2)	0.496(10)	–
Clay, Fe^{+3}	0.345(7)	0.96(6)	–
DJ-7, Surface ash from all night fire			
Oxides of iron	0.369(2)	−0.186(4)	514(3)
	0.346(1)	0.06(2)	488(8)
Very low level	0.316(7)	0.22(14)	442(10)
Fe^{+3} low level	0.352(7)	0.676(12)	–
DJ-8, 41DN72/N1000E 996 soil (surrounding area)			
Goethite (Al present?) low level	1.066(3)	0.04(6)	398
Clay, Fe^{+3} (abundant)	0.355(3)	0.544(4)	–
Clay, Fe^{+2}	1.206(6)	2.20(12)	–
TX-1A, charcoal from feature 22, Rancier photo 3 and 4			
Hematite	0.362	0.276	512
Clay, Fe^{+3}	0.359	0.568	–
TX-2A, sample used by D. Coleman for dating feature 22			
Hematite	0.396	0.244	519
Clay, Fe^{+3}	0.358	0.580	–
TX-3A, F106SE; N1010, E1002; elev. 99.45; N1010.6, E1003.33 (Story)			
Hematite	0.317	−3.84	519
Clay, Fe^{+3}	0.360	0.588	–

* Error factors in last digit given in parentheses, as 0.356(6) is 0.356 ± 0.006.
**Shifts reported versus NBS iron foil.

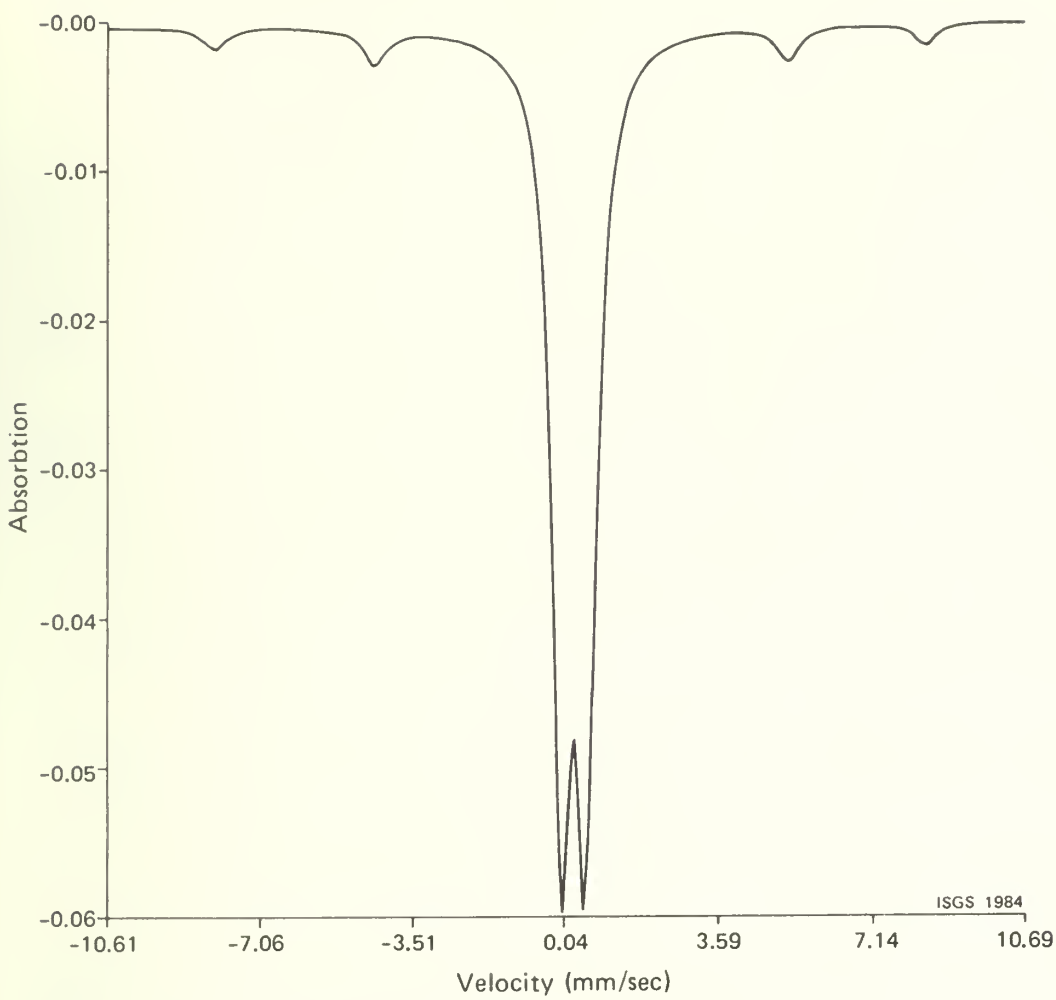

Figure 2. Moessbauer spectra of sample TX-2A

Three additional samples TX-1A, TX-2A, and TX-3A were prepared for analysis by concentrating the obvious carbon materials present. All the Moessbauer analyses for TX-1A, TX-3A, and TX-2A show the presence of iron oxide, identified as hematite; TX-2A has the highest concentration of hematite.

The hematite assignment is based principally upon the internal magnetic field values calculated from the spectrum. Isomer shift and quadrupole coupling constant determination are imprecise for their low intensity spectra. An internal magnetic field of 500 KOe or more indicates hematite. All other oxides have considerably lower values (note the value of geothite in DJ-8, table 5). Hematite is indicated by the low intensity, magnetically split lines found on either side of the center doublet, as shown in the Moessbauer spectra of TX-2A (fig. 2).

Because hematite, a combustion product of pyrite, was found in the samples from hearth 22, which had a controversial radiocarbon date of 26,610 B.P., we found some support for the suggestion that small quantities of Woodbine Formation lignite were burned in this hearth. The result would be a mix of carbon dated > 37,000 radiocarbon years with younger carbon-14 materials.

CONCLUSIONS

This project was based on the assumption that if Woodbine Formation lignite had been burned in Clovis hearths, radiocarbon dating of that ash would indicate ash much older than would be expected from a Clovis hearth. It was also assumed that if lignite had been burned, the pyrite contained in it would be converted to hematite during the combustion process, and would then be found in the hearths. Further confirmation of the presence of lignite ash in the hearths was expected by the use of instrumental neutron activation and X-ray diffraction.

From "fingerprints" obtained from neutron activation analysis of the hearth samples, it was reasonable to provisionally conclude that no Woodbine Formation lignite was burned in the hearths. Furthermore, perhaps because of concentration problems, pyrite combustion products were not detected using X-ray diffraction. This analytical method was inconclusive in determining whether or not lignite ash was present in the hearth samples.

The use of Moessbauer spectroscopy, on the other hand, produced positive results. Hematite, a pyrite combustion product, was found in hearth 22. We conclude that there is some support for the hypothesis that Woodbine Formation lignite was burned in this hearth, thus increasing the apparent age (radiocarbon date) of the hearth material.

Straightforward results were difficult to obtain because of problems with size, uniformity, and number of samples. If further analytical work is done on Lewisville sediments and hearth contents, it is recommended that all analyses be performed on the same sample or riffled aliquots.

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