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USE OF CHEMICAL COMPOSITION OF FRESHWATER CLAMSHELLS AS INDICATORS OF PALEOHYDROLOGIC CONDITIONS

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Abstract. The feasibility of using the Ca, Mg, and Sr content of freshwater clamshells as indicators of paleohydrologic conditions has been investigated. The Sr/Ca ratio varies with the discharge of Mill Creek, Iowa. The Sr/Ca ratios of clamshells excavated from American Indian midden sites near the Big Sioux River in Plymouth County, Iowa (Kimball Site 13 PM 4), and the Phipps site (13 CK 21) located near Mill Creek in Cherokee County, Iowa, show significant changes that can be related to changes in climate in the period 900 to 1400 A.D. Based on the results of this investigation, the alkaline earth composition of freshwater clams probably can be used as an indicator of paleohydrologic conditions.

Freshwater clams have been reported to incorporate Ca, Mg, and Sr in their shells in proportion to the concentration of these elements in their environment. Also, some streams have been shown to demonstrate marked changes in the ratios of these elements with stream discharge. If the above conditions are met, the clamshells from American Indian middens represent a historical record of the discharge of the stream from which the clams were collected. In some cases, midwestern Indian middens represent several hundred years of occupation, and, therefore, this study could give some insight into the relative discharge of the streams near the village over long periods of time. Long-term changes in the discharge of a stream represent long-term changes in the climate of its watershed.

This study examined the reliability of the relationships between shell and water composition, water composition and stream discharge, and the alkaline earth composition of clamshells from midwestern Indian middens and midden stratigraphy. The relationship between water and shell composition is reported elsewhere.

The chemical composition of many midwestern streams is determined by the relative contributions of ground and surface water. For many streams, ground water represents a relatively stable base flow of essentially constant chemical composition. Flows above this base flow are derived from surface water of highly variable composition. The composition of surface runoff is dependent on frequency and intensity of rainfall, season, and the geology-geomorphology of the watershed. The quantitative aspects of the relationships that govern the chemical composition of streams as a function of stream discharge are poorly known and will require much additional study before suitable models can be developed that can be used for quantitative prediction. Previous studies have shown that, in general, the concentration of the various elements decreases with increasing discharge.

One of the conditions that must be fulfilled in this study is a marked change in the ratios of the alkaline earth metals with a change in discharge. For example, the strontium-calcium ratios must vary with discharge. Durum (1960) and Durum and Haffty (1961) have shown that some rivers show marked changes, while others show little or no change in element ratios with discharge. They report that in some streams the ratio increases with a decrease in discharge, while with others, the opposite is true. The mouth of the Mississippi River shows significant changes in various element ratios with discharge. Skougstad and Horr (1963) found no general relationship between the Sr/Ca ratio and stream discharge. However, their small samples indicated that the James River in South Dakota and the Red River of the North in North Dakota, both in the general area of the prehistoric Indian village sites examined here, show decreasing Sr/Ca ratios with increased discharge. From the limited amount of literature available, possibly the streams from which the midden clams were derived may have been classed with the streams that did show changes in elemental ratios during the time the site was occupied. If the middens under study are located on streams that did show marked changes in element ratios, then the average composition of the streams should reflect wet and dry years.

Another condition that must be satisfied is that the clams deposit the alkaline earth metals in their shell in proportion to the composition of the water. There have been numerous studies on the factors that influence the relationship between mollusk shell and water composition. The majority of these studies have been devoted to marine mollusks. However, Nelson (1963, 1964) has investigated the strontium-calcium content of freshwater clams. He found that the Sr content of the shell was not homogeneous. Marked differences in composition were observed between prismatic, peripheral, and laminar layers. He also noted individual as well as species differences. The annual laminar layers showed significant changes in Sr content as a function of the age of the layer. Odum (1957) observed a higher Sr/Ca ratio in the aragonitic inner layer than in the calcitic prismatic layer of a marine mollusk.

Turekian (1955) reports that the ratio of Sr to Ca in carbonate shells is a function of several variables: 1) the Sr/Ca ratio in the liquid phase from which the solid phase was derived; 2) the particular polymorph (calcite or aragonite) into which the Sr is incorporated; 3) vital effects of the organism; 4) temperature; and 5) salinity of the liquid phase.

He concludes that several interrelationships of these factors are possible. For example, the Sr/Ca ratio is a function of polymorph while the amount of aragonite is a function of temperature. However, Thompson and Chow (1955) reported for certain marine organisms constant Sr/Ca ratios within certain taxonomic groups and stated that temperature, salinity, locality and age of shell had no effect on the ratio. In contrast, Swan (1952) proposed an inverse relationship between growth rate and strontium deposition in bivalve mollusk shells.

Turekian and Armstrong (1960, 1961) examined the composition of fossil and recent molluscan shells and reported that the fossil shells may have been altered from their original composition and that the fossils may not be reliable indicators of paleoecological conditions. Their studies on recent marine molluscan shells show that "the most important parameter controlling the concentration of these elements (Mg, Sr, Ba) in calcium carbonate shells appears to be generic association rather than water temperature or the calcite-aragonite ratio of the shell." Pilkey and Hower (1960) and later Harriss and Pilkey (1966) in their studies on the marine sand dollar, *Dendraster,* showed that Mg appeared to be directly related to temperature and salinity, while Sr was inversely related to temperature and Mn was directly related to temperature, but there were no significant relationships for Na or Fe. Lerman (1965a) found that the concentration of strontium in oyster shells increases with temperature and with increasing Sr/Ca molal ratio in water. Pilkey and Goodell (1963) reported "weak correlations" between Fe, Mg, Mn, Sr, and Ba concentrations of marine mollusk shells, and water temperature and salinity.

Rucker and Valentine (1961) have related trace element composition of oyster shells to water temperature and salinity. Rosenthal, Nelson and Gardner (1965) have found that the deposition of strontium in freshwater snail shells is related almost directly to the concentration of Sr in their environment. However, Krinsley (1960) studied the composition of littoral gastropod shells and found no correlation between magnesium and calcite content on modern locality populations. Pilkey and Harriss (1966) have shown that intertidal oysters and barnacles exhibit linear relationships between composition and piling level for a number of trace elements especially Sr and Mn. However, Mg did not follow this relationship. Curtis and Krinsley (1965) in a paper on the detection of minor diagenetic alteration in shell material, conclude, "any relationship between composition (shell) and ecology must stem from statistical analysis of large populations."

Based on the literature, the chemical composition of freshwater clamshells may possibly be an indicator of paleohydrologic conditions and deserves study.

Experimental Procedures and Results

Analytical procedures

The calcium, magnesium, and strontium content of clamshells and natural waters was determined by atomic absorption spectrophotometry (AAS).

Aqueous samples.—Bentley and Lee (1967) have noted that the calcium concentration of water samples, as determined by AAS, is pH dependent. Therefore, all samples are filtered to remove particulate matter, acidified to pH 1.8 to 3.8 with hydrochloric acid, and analyzed by AAS. A Perkin-Elmer Corporation model 303 atomic absorption spectrophotometer was used with manufacturer's recommended instrument settings (Perkin-Elmer 1966).

Shells.—The determination of Ca, Mg, and Sr in shells requires pretreatment prior to dissolving the shell. This pretreatment involves separating the clamshell into its morphological components, that is, separating the central prismatic or laminar layers from the outer periostracum and inner nacreous or mother-of-pearl layers. A modification of the procedures developed by Nelson (1964) is an adequate pretreatment for AAS.

The shell is cut, using a bandsaw, into ¼- to ½-in. (6–12 mm) wide sections from either side of the umbo along its longest radius. The cut surfaces are then polished with No. 120 C garnet cloth which reveals in cross-section the morphological components of the shell and also guards against differential burning. The section is cleaned with water and brushed and placed in a drying oven at 105°C for several hours. The shell section is ashed, in an oxidizing atmosphere, in a muffle furnace for 6 hr at 600°C. This ashing destroys the organic matter and allows for the separation of the shell into its various parts. The shell ash is weighed and recorded as ash weight. All data reported for parts of a shell, e.g., laminar layers, are based on the ash weight of the part. The shell ash is covered with distilled water, dissolved in boiling hydrochloric acid, filtered, and analyzed by AAS.

The reliability of the above procedure was determined on a single live clamshell from Lake Nashota, Wis. This shell was cut into three equal sections and treated as described above. The data show that laminar layers Ca, Mg, and Sr could be analyzed in this shell with an error of less than 5%. Thereafter, duplicates were run at regular intervals to check reproducibility.

Relationship of stream discharge and water composition

The determination of changes in the chemical composition of streams owing to discharge was initiated on two midwestern streams. A collecting station was established at Mill Creek in northwestern Iowa adjacent to a U. S. Army Corps of Engineers gaging station. This is also located near the Phipps site (13 CK 21), one of the two prehistoric villages used in the study of pre-Columbian clamshells.

The data for the Sr/Ca and Mg/Ca ratios for Mill Creek are presented in Figures 1 and 2, respectively. Lenz and Sawyer (1944) found that during extended dry periods alkalinity was a highly variable function of discharge. However, during periods of change or increased discharge, alkalinity decreased in proportion to the increase in discharge. The same pattern is evident from the Mill Creek data. Both the atomic ratios of Sr/Ca and Mg/Ca at Mill Creek are highly variable below flows of less than 2.5 cfs (71 liters/sec). Above this flow there is a good negative correlation, where the atomic ratio of Sr/Ca has a correlation coefficient (r) with discharge of —0.85. The same distribution is shown with the Mg/Ca ratio as against discharge, with the values below a flow of 2.5 cfs being more erratic than the Sr/Ca ratios. The Mg/Ca values above this flow yield an r of —0.8.

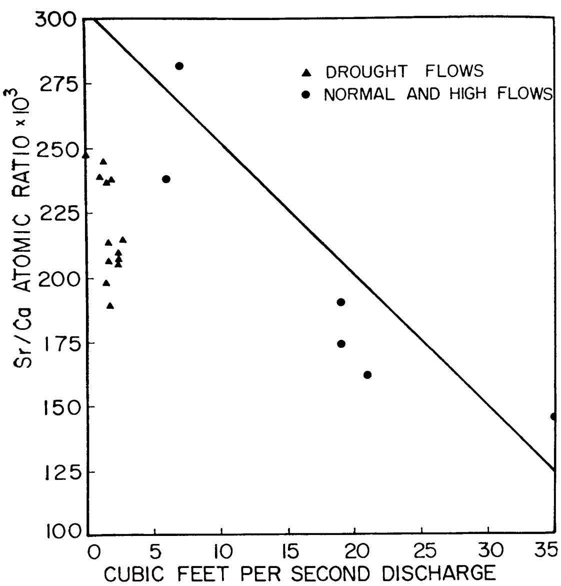

FIG. 1. Sr/Ca atomic ratios versus discharge, Mill Creek, Iowa.

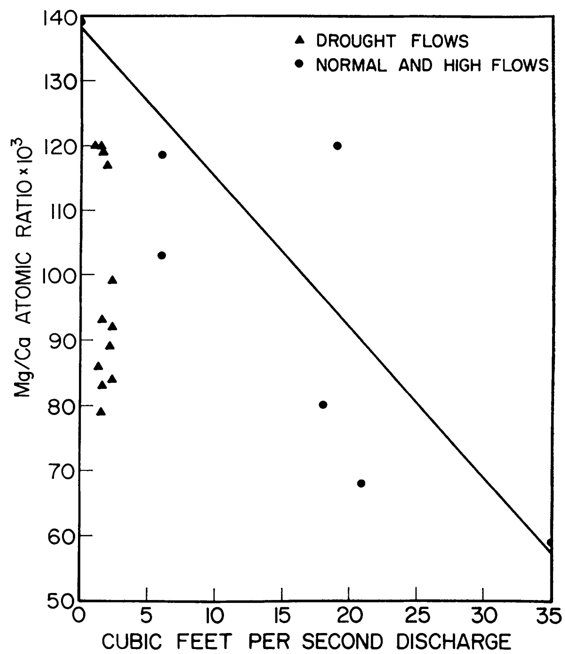

FIG. 2. Mg/Ca atomic ratios versus discharge, Mill Creek, Iowa.

The Mill Creek stream data indicate that there are linear changes in the Sr/Ca and Mg/Ca atomic ratios with stream discharge. Although pre-Columbian agriculture was not as extensive in land usage as is practiced today, which may affect run-off patterns, the basic geomorphology of the area cannot be considered to have changed in any appreciable manner in the last 600 yr. Therefore, the relationship between stream discharge and chemical composition for Mill Creek has probably changed through time only as precipitation has affected the watershed of this stream. This would fulfill the necessary prerequisite for the utilization of the chronological chemical record of pre-

Columbian clamshells as indicators of paleohydrology.

Midden shell composition

Pre-Columbian freshwater clamshells made available for the study of paleohydrology came from selected Indian village sites. These sites, located in northwestern Iowa, were selected specifically to study various aspects of paleoclimatology and ecology within a particular cultural grouping. As stated by Baerreis and Bryson (1967), "Our objective was to cut a limited number of stratigraphic pits in a series of Mill Creek sites that would permit the collection of such additional information relative to the questions of climatic change and thus supplement or enrich the earlier and more extensive work on this culture."

The Mill Creek peoples were part of a movement of primarily agricultural people out of the Old Village complex of Mississippi culture in the St. Louis area to locations near the northern limits of effective maize agriculture and then later providing evidence for withdrawal from the region as a probable consequence of climatic deterioration (Griffin 1961). The character of the settlement pattern of the Mill Creek peoples was such that there developed large and deep midden deposits. This made it possible for the archaeologists, in a controlled stratigraphic excavation, to develop discrete chronological units covering an extended period of time. This allowed for the separation of the various species of clamshells into small units which represented a chronological record of the changes in elemental composition through time. Thus, an internal check could be made against the other evidence from the excavations as to the reliability of using freshwater clamshells as indicators for climatic change.

Previous studies have been involved with long-term changes of a paleontological nature. Turekian (1955), Turekian and Armstrong (1961), and Harriss (1965) made comparisons of grab samples of pre-Columbian clamshells with contemporary clamshells (Nelson, 1967). This study was formulated to set up a situation where a definite chronology existed in order to find out if changes in the elemental composition of clamshells took place when expected climatic changes occurred.

The clamshells from two sites were utilized in this study. The Kimball site (13 PM 4) is located on the banks of the Big Sioux River in Plymouth County at the western border of the state of Iowa, north of Sioux City, Iowa. The second site, Phipps (13 CK 21), is located on Mill Creek, a tributary of the Little Sioux River, in Cherokee County north of Cherokee, Iowa. The radiocarbon dates available for these sites indicate that the Kimball site (13 PM 4) was occupied from about AD 1000 to AD 1400 and the Phipps site (13 CK 21) shows an approximate time range of AD 900 to AD 1400.

The freshwater clamshells from these sites were sorted into groups based on shell morphology, according to Baker's classification (1928). The identifications were later confirmed by H. Van Der Schalie of the University of Michigan Museum of Zoology. The three largest groups, *Quadrula quadrula, Lampsilis ventricosa, Leptodea frasilis,* were segregated as to site and excavation level and then were subjected to chemical analysis for Ca, Sr, and Mg. This included only usable clams, i.e., those that were complete enough to identify and capable of being sectioned so that a sufficient amount of the growth layers could be recovered for chemical analysis. Among the largest group, *Quadrula quadrula,* the laminar layers from one and, for some levels, two shells were analyzed individually. The trace element distribution among the laminar layers of each shell shows a typical heterogeneous pattern. (A complete set of data obtained in this study is available upon request). If diagenesis had taken place through solution and redeposition, then the heterogeneous distribution of trace elements would not be evident. Numerous studies have been concerned with changes in shell composition due to local diagenetic history (Curtis and Krinsley 1965, Lerman 1965a, 1965b, Turekian and Armstrong 1960, 1961). In all these cases the shell, at the death of the organism, remained within an aqueous environment while being slowly buried by sedimentary deposition. This chemically wet environment would remain unchanged until epeirogenic movements had occurred to uplift the bottom strata.

Clams were an integral part of the diet of the Mill Creek peoples, who gathered them live from adjacent streams or rivers, the shell being discarded among the refuse of the village. This in turn was buried, with depositional material, with refuse accumulating on the site area at a maximum rate of 60 cm every 100 yr. Therefore, the clamshells were removed to a dry environment which, unlike a natural depositional site, allows for the recovery of shell material in such a condition that there is very little probability that diagenesis could have taken place. Further a comparison between contemporary *Lampsilis ventricosa* from Mill Creek (see Table 1) and the pre-Columbian *Lampsilis ventricosa* from the Kimball site show little mean difference. The mean Sr/Ca ratio for 14 contemporary specimens was $453 \pm 63 \times 10^{-6}$, which is in the middle of the range for the pre-Columbian clamshells. The Mg/Ca ratio for the

TABLE 1. Contemporary Mill Creek, Iowa, clams

Taxon clam	Concentrations				Atomic ratios		
	Ca (mg/g)	Sr (μg/g)	Mg (μg/g)	Na (μg/g)	Sr/Ca × 10^6	Mg/Ca × 10^6	Na/Ca × 10^3
Lampsilis ventricosa							
1	415	406	62	2,310	447	247	97
2	412	457	53	2,694	507	213	114
3	416	408	71	2,126	448	282	89
4	437	389	77	2,307	407	291	92
5	425	300	52	2,292	323	202	94
6	408	441	43	2,168	494	174	92
7	385	462	58	2,074	548	249	94
8	372	357	38	2,284	439	168	107
9	398	483	47	2,065	555	195	90
10	385	327	47	2,328	388	201	105
11	419	453	57	2,531	494	224	105
12	397	380	34	2,207	437	141	97
13	435	398	42	2,499	418	159	100
14	401	377	63	2,549	430	259	111
Avg ± SD					453 ± 63	215 ± 46	99 ± 8
Amblema costata							
1	397	349	44	1,758	402	183	77
2	398	394	53	1,813	452	220	79
3	400	373	41	2,141	426	169	93
4	385	321	79	2,325	381	339	105
5	403	331	40	2,021	375	164	87
6	413	353	38	2,285	391	152	96
Avg ± SD					405 ± 29	205 ± 70	90 ± 11

contemporary clamshells ($215 \pm 46 \times 10^{-6}$) was also well within the range of the mean for pre-Columbian clams. This implies that diagenesis has not been a factor in the history of these pre-Columbian clamshells.

The Na/Ca atomic ratio in clamshells from Mill Creek appears to be remarkably constant and independent of environmental conditions. A sample of 14 *Lampsilis ventricosa* (see Table 1) from Mill Creek, Iowa, a hard-water stream, had a Na/Ca ratio of $99 \pm 8 \times 10^{-3}$. This conformity is probably related to the biological usage of sodium in water regulation within living tissue. Further evidence of biological conformity is shown by a group of 6 clamshells from Mill Creek of the species *Amblema costata* with a Na/Ca ratio of $90 \pm 11 \times 10^{-3}$. Therefore, it can be suggested that the Na/Ca atomic ratio is a constant factor of freshwater clamshells.

The three species of clams used in this study consisted of two thick-shelled varieties and one thin-shelled type. The thin-shelled type, *Leptodea fragilis,* presents a translucent appearance in prehistoric as well as contemporary specimens. Even after ashing it was impossible to separate the laminar, or growth layers, from the peripheral layers and the mantle. Therefore, the *Leptodea fragilis* specimens were subjected to what was essentially a whole shell analysis. The results of the analysis of 36 *Leptodea fragilis* shells show a random distribution through all levels of the site with overlapping standard deviations for the atomic ratios of Sr/Ca and Mg/Ca. The differences in morphology and preparation of this species would indicate from the results that it is not possible to utilize all species of freshwater clams in this type of study.

The distribution of the other two types consisted of 72 *Quadrula quadrula* and 43 *Lampsilis ventricosa* from the Kimball site and in addition 25 *Quadrula quadrula* from the Phipps site. Before discussing the results of this study, it would be best to examine the other lines of evidence as to climatic changes as detailed by Baerreis and Bryson (1967) so that comparisons can be made with the clamshell analysis.

The arboreal pollen profile from the Phipps site shows a rapid transition from oak dominance below a depth of about 104 cm to cottonwood, elm, and willow dominance above that level. Since the total arboreal count changes little throughout the occupation of the Phipps site, it would seem that the inhabitants were not drastically reducing the forest.

In the nonarboreal pollen profile the composites are more important than the grasses in the lower levels, as might be expected for tall grass prairie, but above the 117-cm level the grasses dominate, giving the nonarboreal spectrum a more steppe-like character. The uppermost levels suggest a return to conditions somewhat like the lower levels. Once again, there appears to be increased desiccation starting at the 102–127 cm level.

Oak pollen is present at the Kimball site, and the nonarboreal pollen assemblage at all levels resembles the upper part of the Phipps profile. Of course, the Kimball location is further west and the uplands are more steppe-like today than the uplands near the Phipps site.

The analysis of the faunal remains as carried out by W. D. Frankforter shows at the Phipps site a gradual increase in the importance of bison reaching a peak at a depth of about 76 cm and then essentially maintaining this level in the upper 60 cm of the deposit. It may be interpreted as a decline in the available forest-edge habitat and an increase in grassland habitat. At the Kimball site, deer, occupying a dominant position throughout the site history, are most numerous in the earliest level, decrease in the middle levels, and become more numerous again in the uppermost levels. Thus, whereas grassland conditions would seem to expand at the expense of the deciduous forest-edge, there is a reversion toward the latter conditions at the end of the occupation.

The chemical analysis of the clamshells is most definitive for the Sr/Ca atomic ratios in light of the previously discussed pollen and faunal data.

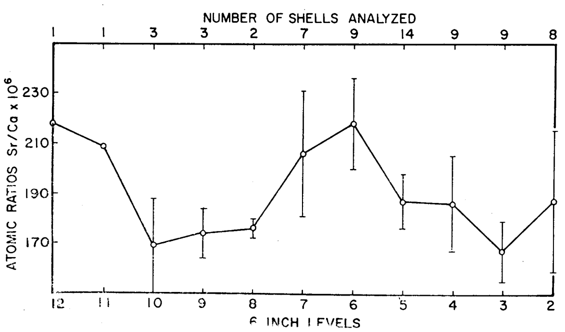

FIG. 3. Composition of prehistoric clamshells (*Quadrula quadrula*), Kimball site 13 PM 4. The mean and standard deviation indicated by point and bar.

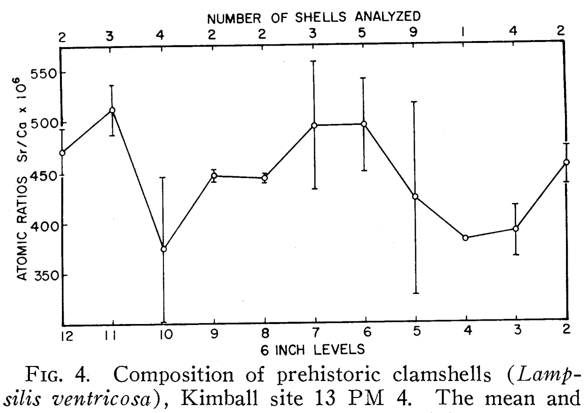

FIG. 4. Composition of prehistoric clamshells (*Lampsilis ventricosa*), Kimball site 13 PM 4. The mean and standard deviation indicated by point and bar.

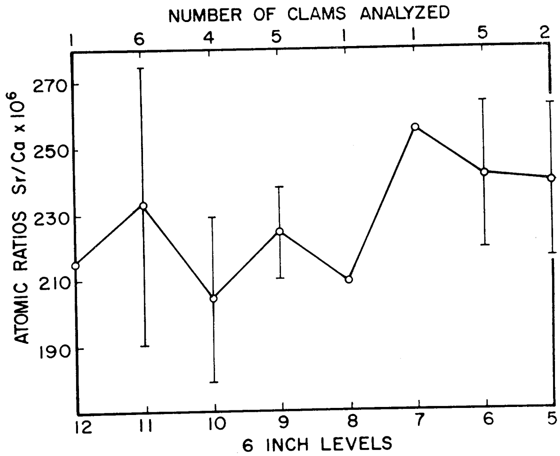

FIG. 5. Composition of prehistoric clamshells (*Quadrula quadrula* rafinesque), Phipps site 13 CK 21. The mean and standard deviation indicated by point and bar.

Figures 3, 4, and 5 display the results of this analysis from the Kimball and Phipps sites and are arrayed stratigraphically, with each level equal to 15.2 cm of excavation. The figures exhibit minima in levels 8–10, then an elevation of the Sr/Ca ratios in the middle levels of the excavation, and a return to the previous minima in the upper levels. The pollen suggests that climatic deterioration with increased dessication occurred below 117 cm or depending on the sample grouping in the 102–127 cm zone. This is equivalent to the break shown in the graphs between levels 7 and 8. The upper levels of the sites are not as clear, but pollen data for the grasses at the Phipps site and the faunal evidence for deer at the Kimball site do suggest that there is a return to previous conditions in the upper levels of the sites. The figures for Sr/Ca exhibit a much more rapid return to previous minima. It may be that there is a time lag between return to a forest-edge environment complementary to deer.

The Mg/Ca atomic ratios, although showing a minimum in the lowest levels, do not present a consistent picture and do not fit with any of the other evidence from the sites, although, all the other data considered have been related primarily to changes in precipitation and do not directly indicate changes in temperature or other factors that might affect changes in the Mg/Ca ratio.

DISCUSSION

In relatively recent years world-wide changes in climate, lasting only a few centuries, have taken place that are different from the modern climate. These changes, documented by Lamb (1963), Baerreis and Bryson (1965), and others, agree on certain periods that vitally affect this work.

The Secondary Climatic Optimum (Lamb 1963) or Neo-Atlantic (Baerreis and Bryson, 1965) began about AD 900 and ended about AD 1200. This episode provided a much warmer climate than today's over much of the northern hemisphere and of particular importance the Great Plains of North America had abundant summer rain. This provided the necessary climatic conditions for the spread of a maize-based agriculture into this area. Following this period there was an irregular deterioration of climatic conditions culminating in what is called the Little Ice Age (Lamb 1963) or Neo-Boreal (Baerreis and Bryson 1965) beginning about AD 1500 and lasting until about AD 1880, when there was a gradual return to the present climatic regime.

The occupation of the sites in northwestern Iowa follow this pattern with initial occupation about AD 900 and terminate as sedentary village sites about AD 1400. The end of the Mill Creek culture was brought about apparently by their inability to sustain their previous agricultural pattern. The climatic changes, as mentioned before, are further evidenced by the changes in the flora and fauna, as recovered chronologically from the sites. It follows then that these climatic changes should have affected the watersheds of Mill Creek and the Big Sioux River. As shown previously, the elemental composition of Mill Creek does change with discharge, and further, there should have been a marked change at the end of the Neo-Atlantic period (AD 1200). The atomic ratio of Sr/Ca in freshwater clamshells can be used as indicators of paleohydrological conditions if they are part of a controlled chronological sequence.

The Sr/Ca ratio of Mill Creek decreases with increased discharge. The changes in this ratio of the prehistoric clamshells coincides with climatic changes in this geographical area. There is an elevation of the Sr/Ca ratio between levels 7 and 8 for both sites and for the two species of clams, which would be expected if, as the floral and faunal evidence indicate, there was a change to more arid conditions. It does appear that there is a return to previous conditions in the upper levels of the site, and this is accompanied by a depression of the Sr/Ca values.

The overall study, as originally conceived, was a pilot program with limited excavations of archaeological sites where climatic factors appeared to be important. Therefore, the recovered samples were very limited in quantity from any one level, and as stated previously, it is desirable because of the intrinsic variability to use large samples. However, the midden shell analysis does indicate that the Sr/Ca atomic ratio of freshwater clamshells is a feasible indicator of paleohydrologic conditions.

Acknowledgments

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