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ASSESSING OPEN-SYSTEM BEHAVIOR OF ^{14}C IN TERRESTRIAL GASTROPOD SHELLS

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ABSTRACT. In order to assess open-system behavior of radiocarbon in fossil gastropod shells, we measured the ^{14}C activity on 10 aliquots of shell material recovered from Illinoian (~190–130 ka) and pre-Illinoian (~800 ka) loess and lacustrine deposits in the Midwestern USA. Eight of the 10 aliquots yielded measurable ^{14}C activities that ranged from 0.25 to 0.53 percent modern carbon (pMC), corresponding to apparent ^{14}C ages between 48.2 and 42.1 ka. This small level of open-system behavior is common in many materials that are used for ^{14}C dating (e.g. charcoal), and typically sets the upper practical limit of the technique. Two aliquots of gastropod shells from the Illinoian-aged Petersburg Silt (Petersburg Section) in central Illinois, USA, however, yielded elevated ^{14}C activities of 1.26 and 1.71 pMC, which correspond to apparent ^{14}C ages of 35.1 and 32.7 ka. Together, these results suggest that while many fossil gastropods shells may not suffer from major (>1%) open-system problems, this is not always the case. We then examined the mineralogy, trace element chemistry, and physical characteristics of a suite of fossil and modern gastropod shells to identify the source of contamination in the Petersburg shells and assess the effectiveness of these screening techniques at identifying samples suitable for ^{14}C dating. Mineralogical (XRD) and trace element analyses were inconclusive, which suggests that these techniques are not suitable for assessing open-system behavior in terrestrial gastropod shells. Analysis with scanning electron microscopy (SEM), however, identified secondary mineralization (calcium carbonate) primarily within the inner whorls of the Petersburg shells. This indicates that SEM examination, or possibly standard microscope examination, of the interior of gastropod shells should be used when selecting fossil gastropod shells for ^{14}C dating.

INTRODUCTION

Gastropod shells are preserved in a wide range of Quaternary deposits. They are found in lacustrine, wetland, alluvial, loess, and glacial deposits, and occur within archaeological strata worldwide (Evans 1972). Their common occurrence within a variety of depositional environments makes them a potentially important material for radiocarbon dating. However, gastropod shells have long been avoided for ^{14}C dating because some taxa incorporate ^{14}C-deficient (or "dead") carbon from limestone when building their shells (Frye and Willman 1960; Leighton 1960; Rubin et al. 1963; Tamers 1970; Evin et al. 1980; Goodfriend and Hood 1983; Goodfriend and Stipp 1983; Goslar and Pazdur 1985; Yates 1986; Goodfriend 1987; Zhou et al. 1999; Quarta et al. 2007; Romaniello et al. 2008). This phenomenon, referred to as the "Limestone Problem" by Goodfriend and Stipp (1983), can cause ^{14}C ages of gastropod shells to be as much as ~3000 yr too old. Recent work on terrestrial gastropod taxa in North America, however, has demonstrated that taxa within a number of genus- or family-level clades do not ingest limestone even when it is readily available (Brennan and Quade 1997; Pigati et al. 2004, 2010). Gastropods that do not ingest limestone thus have the potential to yield reliable ^{14}C ages and, therefore, can provide age constraints for a wide range of Quaternary deposits, as long as they remain a closed system with respect to carbon after burial.

A few studies have examined closed-system behavior in fossil gastropods. Brennan and Quade (1997) dated co-occurring terrestrial gastropod shells and carbonized plant fragments recovered from late Pleistocene spring deposits (14–9 ka) in the American Southwest. They found that the majority of terrestrial gastropod ages fit within the stratigraphic age window permitted by ^{14}C ages obtained from the plant fragments. Brennan and Quade also determined the ^{14}C content of 1 aliquot

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of *Succinea* shells from pre-Wisconsin spring deposits, which returned a ^{14}C age of 40.3 ± 0.8 ^{14}C ka, or ~0.7 pMC, indicating a small amount of open-system behavior. Pigati et al. (2004, 2009) dated terrestrial gastropod shells from late Pleistocene spring deposits in southeastern Arizona and found stratigraphically consistent ^{14}C ages for shells that ranged from ~25–11 ^{14}C ka. Finally, Pigati et al. (2010) dated 18 aliquots of fossil gastropod shells and 5 aliquots of plant macrofossils from a 5-cm-thick organic silt within glacial deposits from the Midwestern USA. Calibrated ^{14}C ages of the gastropod shells and plant macrofossils averaged 24.86 ± 0.32 and 24.93 ± 0.30 ka, respectively, which are statistically indistinguishable from one another.

These studies suggest that fossil gastropod shells are not subject to major ^{14}C open-system behavior problems and, therefore, gastropods that do not incorporate carbon from limestone in their shells should yield reliable ^{14}C ages in deposits that are less than ~25 ka old. Open-system behavior, however, is a much more serious concern in older samples (25–60 ka) where small amounts of contamination cause very large errors in ^{14}C ages (Figure 1). For example, contamination of a 20,000-yr-old shell with the equivalent of 0.25 and 0.5 pMC will cause measured ^{14}C ages to be only 240 and 470 yr too young, respectively. Contamination equivalent to 1 and 2% pMC will cause errors of 920 and 1740 ^{14}C yr, respectively. In contrast, a 35,000-yr-old shell that was subjected to the same levels of modern contamination (0.25, 0.5, 1, and 2%) would yield measured ^{14}C ages that are 1430, 2650, 4640, and 7550 ^{14}C yr too young, respectively.

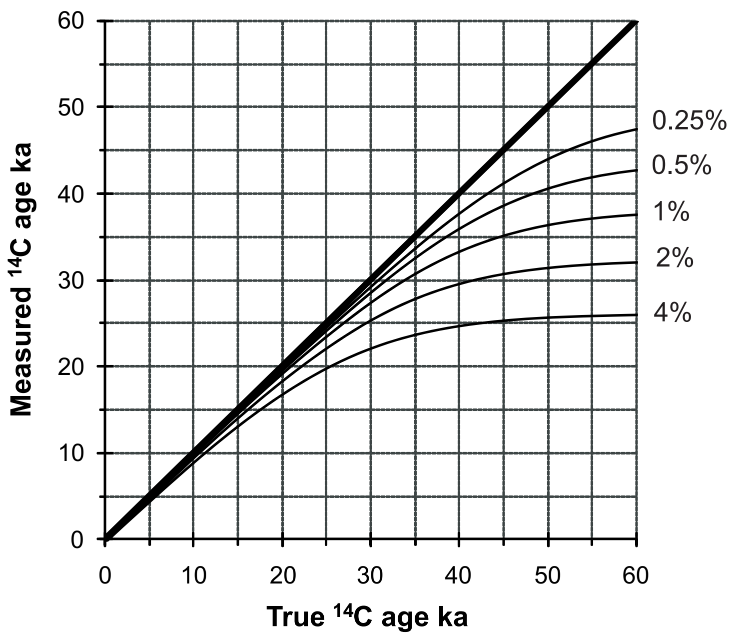

Figure 1 Effect of various levels of open-system behavior with modern carbon on measured ^{14}C ages.

In order to assess small levels of open-system behavior in terrestrial gastropod shells, we measured the ^{14}C activities of 10 aliquots of Illinoian and pre-Illinoian shells from deposits in the Midwestern USA. We then examined the mineralogy, trace element chemistry, and surface texture of fossil gastropod shells to see if we could find mineralogical, chemical, or physical evidence of open-system behavior and determine the best method for selecting shells that are suitable for ^{14}C analysis.

METHODS

We sampled fossil terrestrial gastropod shells that are >130 ka, and therefore should not contain detectable concentrations of ^{14}C, from collections at the Illinois State Geological Survey (ISGS). We selected shells of *Discus macclintockii* and *Hendersonia occulta* recovered from Illinoian-aged (~190–130 ka) proglacial lacustrine deposits at 2 localities in Illinois, the Petersburg Section (Leonard et al. 1971; from ISGS A.B. Leonard Collection) and the Ogles Creek Section (Geiger 2008), respectively. These localities contain a fossiliferous unit known as the Petersburg Silt (Willman and Frye 1970) that occurs immediately below Illinoian glacial till. We also selected pre-Illinoian shells from lacustrine or depressional deposits at 2 other localities in Illinois. The Harmattan Strip Mine (a former coal mine near Danville), contained *Discus macclintockii* (from ISGS A.B. Leonard Collection) in the pre-Illinoian Belgium Silt Member (Leonard et al. 1971) with an estimated age of 700 to 800 ka (Johnson 1986), but possibly as young as 450 ka. The County Line Section in western Illinois (Miller et al. 1994) contains *Pomatiopsis* sp. and assorted gastropod shell fragments. The pre-Illinoian County Line Silt is magnetically reversed and also contains mammalian fossil and amino acid ratios on gastropods, which constrain it to the late Matuyama Chron (~830–780 ka) (Miller et al. 1994). Finally, we examined full glacial aged fossil gastropods from the Oxford locality in southwestern Ohio (Ekberg et al. 1993; Pigati et al. 2010) and several modern gastropods collected from the Midwestern USA (Nekola 2005).

Terrestrial gastropod shells were processed for AMS ^{14}C dating at Miami University using standard methods. Fossil shells were broken and adhering detritus was physically removed. Samples were then treated with 6% NaOCl for 18–24 hr at room temperature to remove all organic material. Shells were not powdered during pretreatment to minimize the potential for adsorption of atmospheric ^{14}C. Shells were then washed repeatedly in 18.2M (hereafter "ultrapure") water, sonicated for a few minutes to remove adhered solution, washed again with ultrapure water, and dried in a vacuum oven overnight at ~70 °C. Shell aragonite was converted to CO_2 using 100% H_3PO_4 under vacuum at 75 °C. Water, SO_x, NO_x, and halide species were removed using passive traps and the resulting CO_2 was split into 2 aliquots. One aliquot was converted to graphite by catalytic reduction of CO (modified after Slota et al. 1987) and submitted to the Arizona-NSF Accelerator Mass Spectrometry (AMS) facility for ^{14}C analysis. The second aliquot was submitted for $\delta^{13}C$ analysis in order to correct the measured ^{14}C activity of the shell carbonate for isotopic fractionation (Pigati 2002). All AMS ^{14}C samples were corrected for sample processing background levels.

X-ray diffraction (XRD) was used to determine the mineralogical composition of gastropod shells. Single shells were broken and cleaned in ultrapure water, powdered, and then mounted on a zero background smear mount plate. Shell mineralogy was determined on a Scintag XGEN-4000 X-ray diffractometer between 23° and 33° 2θ at 0.24° per minute by step scanning. Illinoian and pre-Illinoian shells were also scanned between 31.2° and 33.2° 2θ at a rate of 0.12° per minute to more precisely detect the possible presence of calcite.

Trace element chemistry of fossil and modern gastropod shells was determined using a Varian ICP-MS. Shells were broken and any detrital material was removed, and then shells were cleaned with ultrapure water in an ultrasonic bath repeatedly to remove all detrital material. Approximately 2 mg of shell material was dissolved in 1 mL of ultrapure 0.125N HNO_3 and then diluted to 10 mL with ultrapure water. We analyzed 42 elements, measuring them against 500-ppb external standards prepared from ICP-MS solution standards (Inorganic Ventures, Inc.), using Ge, In, and Re as internal standards. Replicate analyses yielded results within ±3%, and all standards yielded values ±5% of known concentrations.

Gastropod shells that had been cleaned and chemically pretreated for ^{14}C dating were mounted on aluminum stubs and analyzed on a Zeiss Supra 35 VP FEG scanning electron microscope (SEM). Secondary electron (SE) imaging and variable pressure (VP) imaging were used to examine gastropod shell surface features and look for evidence of secondary dissolution and recrystallization. Variation in shell chemistry was initially examined using backscatter electrons (BSE) to locate dense particles within the less dense calcium carbonate. Elemental composition of shell material and secondary minerals was determined using energy-dispersive X-ray spectroscopy (EDS) and the associated analytical program XEDS Genesis 2000.

RESULTS AND DISCUSSION

Radiocarbon Analysis

^{14}C analyses of the gastropod shell samples yielded ^{14}C activities between 0.25 and 1.71 pMC (Table 1, Figure 2). Shells from all localities except the Petersburg Section contained between 0.25 and 0.53 pMC, corresponding to apparent ^{14}C ages between 48.2 and 42.1 ka. These concentrations indicate a small amount (less than ~0.5%) of open-system behavior, which is typical of old (>35 ka) samples of other materials (e.g. charcoal) that are used commonly for ^{14}C dating. The measured ^{14}C activities do not correlate with the size of the shell fragments analyzed, which suggests that increased surface area of smaller samples did not influence the degree of apparent open-system behavior.

Table 1 Radiocarbon results for fossil gastropods. All site locations are in the state of Illinois, USA.

Sample	Lab #	AA #	Taxon	Site	Shells (#)	Mass (mg)	$\delta^{13}C$ (VPDB)	pMC[a]	Apparent ^{14}C age (ka)
1	MU-254	82606	*Discus macclintockii*	Harmattan strip mine	1	16.91	–5.6	0.48 ± 0.16	42.81 ± 2.6
2	MU-255	82607	*Discus macclintockii*	Harmattan strip mine	2	17.05	–5.2	0.34 ± 0.16	45.74 ± 3.7
3	MU-257	82609	*Discus macclintockii*	Petersburg Section (ABL 88)	1	15.95	–8.0	1.71 ± 0.16	32.66 ± 0.8
4	MU-258	82610	*Discus macclintockii*	Petersburg Section (ABL 88)	1	17.99	–9.0	1.26 ± 0.16	35.10 ± 1.0
5	MU-253	82605	*Hendersonia occulta*	Ogles Creek Section	1	13.76	–6.6	0.57 ± 0.16	41.44 ± 2.2
6	MU-249	82601	*Pomatiopsis* sp.	County Line Section	1	22.62	–3.0	0.53 ± 0.16	42.08 ± 2.4
7	MU-250	82602	*Pomatiopsis* sp.	County Line Section	1	13.27	–4.1	0.30 ± 0.16	46.77 ± 4.2
8	MU-251	82603	*Pomatiopsis* sp.	County Line Section	2	16.68	–3.9	0.25 ± 0.16	48.24 ± 5.2
9	MU-247	82599	Shell fragments	County Line Section	16	18.15	–5.8	0.46 ± 0.16	43.31 ± 2.8
10	MU-248	82600	Shell fragments	County Line Section	26	17.59	–6.2	0.48 ± 0.16	42.96 ± 2.7

[a]Uncertainties for measured ^{14}C activities are given at the 1 σ (68%) confidence level.

Shells of *Discus macclintockii* from the Petersburg Section contained ^{14}C activities of 1.26 and 1.71 pMC, which correspond to apparent ^{14}C ages of 35.1 and 32.7 ka. These results indicate significant open-system behavior in these shell samples. Such behavior could be the result of several factors, including secondary precipitation of carbon-bearing minerals (e.g. calcite), inorganic detrital material adhering to the shell, or the exchange of carbon between the shell and the atmosphere after collection.

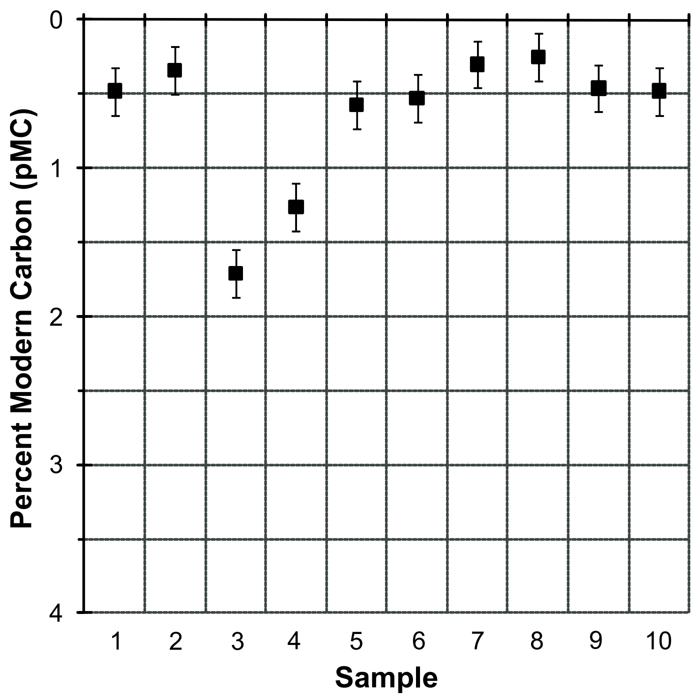

Figure 2 Measured ^{14}C activities of Illinoian (~190–130 ka) and pre-Illinoian gastropod shells. Numbers on horizontal axis refer to sample numbers listed in Table 1.

X-Ray Diffraction

Five gastropod shells (County Line Section, *Pomatiopsis* sp., ~800 ka; Petersburg Section, *Discus macclintockii*, ~150 ka; Harmattan Strip Mine Section, *Discus macclintockii*, ~150 ka; Oxford, *Hendersonia occulta*, ~25 ka; Deer Creek, *Succinea* sp., modern) were analyzed by X-ray diffraction (XRD) to determine if the shell material had altered to calcite and to see if it was possible to detect any secondary mineralization. All shell samples were aragonite and no calcite was detected. A very small quartz peak was identified in the ~800-ka *Pomatiopsis* sp. shell from the County Line Section.

Trace Element Geochemistry

Concentrations of minor and trace elements were determined for Illinoian and pre-Illinoian fossil gastropods to look for open-system behavior. As most XRD analyses have a minimum detection limit of ~5%, trace element analysis with ICP-MS may be more sensitive at identifying secondary mineral phases precipitated on gastropod shells. Illinoian and pre-Illinoian fossil samples of *Discus macclintockii* from the Petersburg Section and Harmattan Strip Mine sites and *Pomatiopsis* sp. from the County Line site were analyzed. The chemical composition was also determined for 19 samples of *Discus chronkheti* and *Hendersonia occulta* from the LGM Oxford outcrops, which yielded identical ^{14}C ages between snail and plant macrofossils (Pigati et al. 2010). Finally, we analyzed the trace element chemistry of 10 modern gastropod shells of *Hendersonia occulta*, *Discus shimeki*, *Discus chronkheiti*, and *Succinea* sp. from localities in Minnesota, Iowa, and Colorado to determine the variability of initial trace element chemistry in terrestrial gastropod shells. Measurable variability between shells was observed in 6 of 42 elements: Mg, Al, Mn, Fe, Sr, and Ba.

Among the Illinoian and pre-Illinoian aged gastropod shells, the trace element chemistry was similar for Fe and Mn, whereas concentrations of Mg, Al, Ba, and Sr varied (Table 2). Concentrations of Mg and Al are greater in samples with high measured ^{14}C activities and younger apparent ages, whereas concentrations of Ba and Sr are lower (Figure 3). The trends of lower Sr and Ba values and higher Mg and Al in samples with higher measured ^{14}C activities are similar to geochemical trends observed in marine fossils with a higher degree of diagenetic alteration (e.g. Bruckshen et al. 1995; Veizer et al. 1999). Full glacial-aged shells from the Oxford outcrops show large variability in trace element chemistries (Table 2). For example, Mg concentrations range from 9 to 1092 ppb and Fe concentrations range from 225 to 1157 ppb. Modern gastropod samples also display a high degree of variability in trace element chemistry (Table 2).

Table 2 Gastropod trace element data.

Sample	Taxon	Location	^{14}C age[a]	Mg	Al	Mn	Fe	Sr	Ba
Pre-Wisconsinan Gastropods									
ABL 88	*Discus macclintockii*	Petersburg Section	33,880	743	81	28	300	80	49
DSL	*Discus macclintockii*	Harmattan Strip Mine	42,125	193	27	12	278	126	66
CLS	*Pomatiopsis* sp.	County Line Section	45,700	61	23	17	269	233	79
LGM Gastropods									
Disc OE-M 1.93	*Discus chronkheti*	Oxford Outcrops	24,860	27	0	46	256	95	204
Disc OE-M 1.5	*Discus chronkheti*	Oxford Outcrops	24,860	206	1	73	225	96	183
Disc OE-M 1.47	*Discus chronkheti*	Oxford Outcrops	24,860	290	40	241	388	75	220
Disc OE-M 1.73	*Discus chronkheti*	Oxford Outcrops	24,860	1092	32	144	328	59	143
Disc OE-M 1.61	*Discus chronkheti*	Oxford Outcrops	24,860	38	0	216	237	101	193
Disc OE R 1.93	*Discus chronkheti*	Oxford Outcrops	24,860	235	17	105	522	57	91
Disc OE R 1.87	*Discus chronkheti*	Oxford Outcrops	24,860	74	10	107	253	78	117
Disc OE R 1.96	*Discus chronkheti*	Oxford Outcrops	24,860	102	17	103	249	67	98
Disc OE R 1.37	*Discus chronkheti*	Oxford Outcrops	24,860	146	33	166	319	67	106
Disc OE-M 0.53	*Discus chronkheti*	Oxford Outcrops	24,860	244	47	1844	1157	123	212
Disc OE R 1.58	*Discus chronkheti*	Oxford Outcrops	24,860	287	47	169	309	72	128
Disc OE R 0.76	*Discus chronkheti*	Oxford Outcrops	24,860	109	26	871	579	93	125
Disc OE R 1.09	*Discus chronkheti*	Oxford Outcrops	24,860	747	118	391	667	67	120
Disc OE R 0.95	*Discus chronkheti*	Oxford Outcrops	24,860	576	66	557	708	73	127
Hend OE-R 1.95	*Hendersonia occulta*	Oxford Outcrops	24,860	14	31	246	255	75	47
Hend OE-R 1.88	*Hendersonia occulta*	Oxford Outcrops	24,860	9	4	184	242	89	67
Hend OE-R 1.94	*Hendersonia occulta*	Oxford Outcrops	24,860	17	6	193	249	63	44
Hend OE-R 1.98	*Hendersonia occulta*	Oxford Outcrops	24,860	26	4	183	239	70	57
Hend OE-R 1.92	*Hendersonia occulta*	Oxford Outcrops	24,860	34	87	264	327	93	76
Modern Gastropods									
Succ Deer 1.77	*Succinea* sp.	Deer Creek Cliff, MN		28	3	1027	908	43	33
Succ Deer 1.87	*Succinea* sp.	Deer Creek Cliff, MN		23	2	37	207	37	26
Succ Deer 1.98	*Succinea* sp.	Deer Creek Cliff, MN		55	0	52	228	34	37
Succ Deer 1.93	*Succinea* sp.	Deer Creek Cliff, MN		19	0	60	214	34	43
Hend Deer 1.55	*Hendersonia occulta*	Deer Creek Cliff, MN		40	12	41	208	23	32
Hend Deer 1.89	*Hendersonia occulta*	Deer Creek Cliff, MN		38	0	85	226	35	13
Hend Deer 1.97	*Hendersonia occulta*	Deer Creek Cliff, MN		22	0	52	201	28	16
Hend Will 1.84	*Hendersonia occulta*	Williams Creeks, IA		30	10	1343	1309	22	13
Disc Ep 1.18	*Discus chronkheti*	Epworth Fen, IA		130	0	1259	663	58	244
Dsic Canon 1.79	*Discus shimeki*	Canon, CO		68	4	484	185	81	566

[a]"^{14}C age" is the average ^{14}C age of gastropod shells from a given location.

The correlation between Mg, Al, Ba, and Sr with the measured ^{14}C activity of Illinoian and pre-Illinoian gastropod shells hints at the possibility of using trace element chemistry to identify open-system behavior among select gastropod samples. However, this success is tempered by the extreme variability in trace element chemistry found in the Last Glacial Maximum and modern terrestrial gastropod shells. This large variability, which is most likely due to local differences in the chemistry of ephemeral surface waters, will complicate efforts to use trace element chemistry to assess open-system behavior.

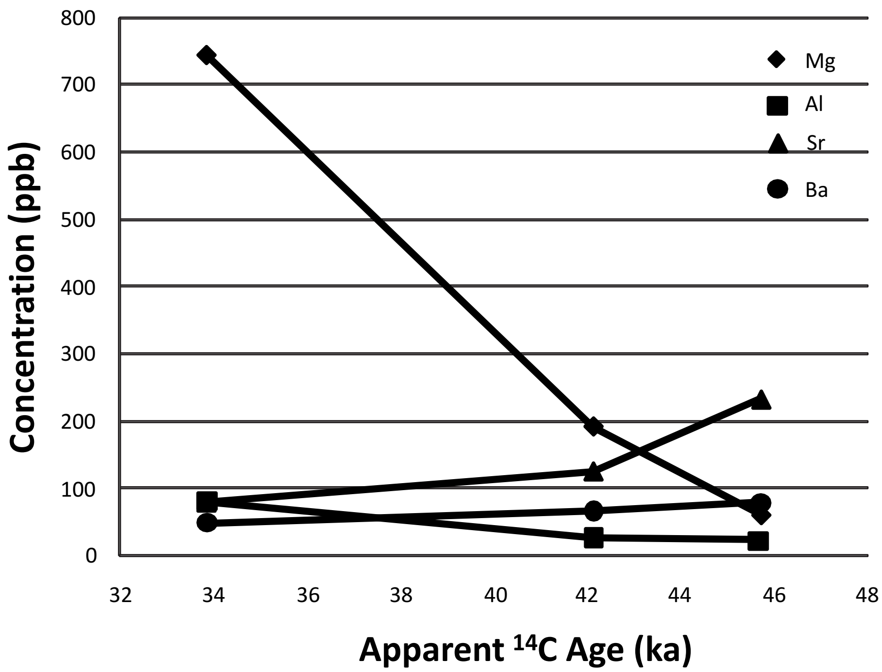

Figure 3 Trace element chemistry versus measured ^{14}C activity for Illinoian and pre-Illinoian gastropod shells.

Scanning Electron Microscopy

Four gastropod shells (*Pomatiopsis* sp., County Line Section, ~800 ka; *Discus macclintockii*, Petersburg Section, ~150 ka; *Hendersonia occulta,* Oxford, ~25 ka; *Succinea* sp., Deer Creek, modern) were analyzed by SEM (Figure 4) to detect possible evidence of open-system behavior, including precipitation of secondary minerals. Clear evidence of secondary mineralization was found only on the gastropod shell from the Petersburg Section (Figure 5), with secondary minerals ~2–15 μm in size visible along external fractures of the shell (Figure 5a). Large clusters (>100 μm in width) of secondary minerals, however, were visible within the interior whorls of the gastropod shell (Figure 5c). EDS analysis of these secondary minerals indicated that they were calcium carbonate (Figures 5b and 5d).

In summary, imaging and elemental analysis with scanning electron microscopy (SEM) identified small (2–15 μm) secondary minerals precipitated on the exterior and large (>100 μm) minerals precipitated within the interior of the shell from the Petersburg Section. These results indicate that SEM analysis is an effective method for identifying the diagenetic alteration of shells. SEM analysis of

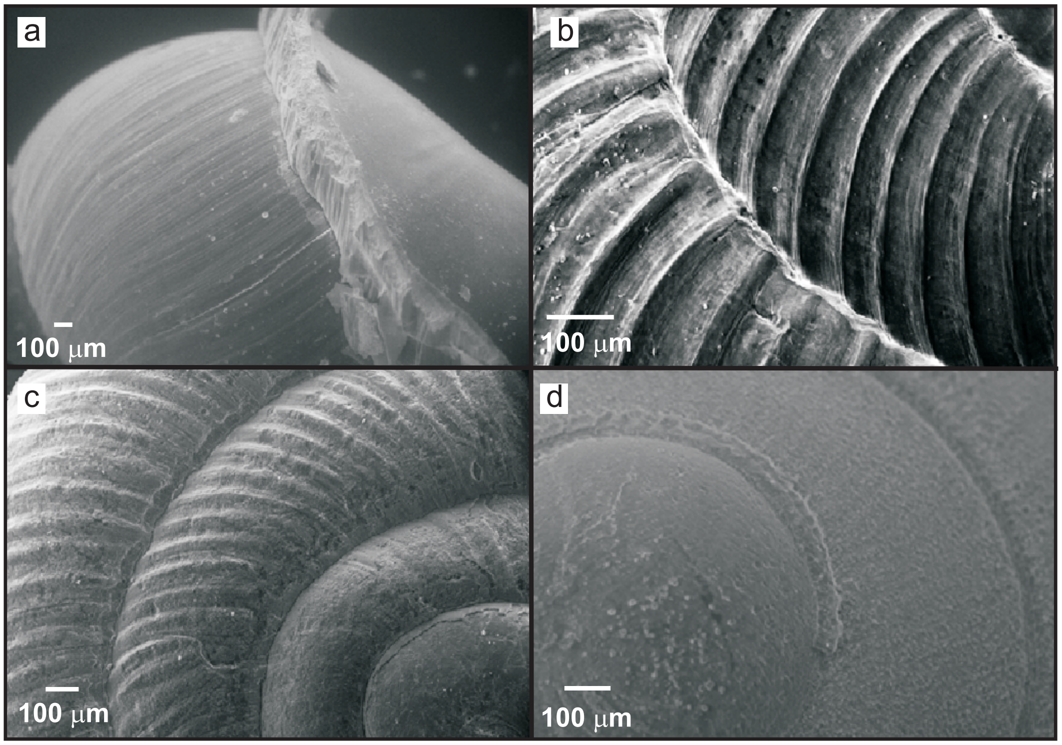

Figure 4 Low-magnification SEM images of gastropod shells: a) modern *Succinea* shell; b) ~25-ka *Hendersonia occulta* shell from the Oxford outcrops; c) *Discus macclintockii* shell from the Illinoian (~190–130 ka) Petersburg Silt (at the Petersburg Section); d) *Pomatiopsis* sp. shell from the ~800-ka County Line Silt (at the County Line Section).

freshwater bivalve shells has been used successfully to screen for diagenetic alteration of shells for ^{14}C dating (Webb et al. 2007), and SEM analyses of marine fossil assemblages have also proven successful for identifying diagenetic alteration prior to geochemical analysis (e.g. Veizer et al. 1999; Wade and Kroon 2002). Shell fragments from the Oxford outcrop and the County Line Site (~800 ka) did not display any evidence of secondary mineralization.

CONCLUSIONS

Gastropod shells are common in a wide variety of Quaternary deposits. Recent studies have demonstrated that some lineages of terrestrial gastropods do not incorporate dead carbon from limestone when building their shells. Thus, their shells have great potential for providing robust ^{14}C ages if they remain a closed system with respect to carbon after burial. To assess this issue, we measured the ^{14}C activity of 10 aliquots of shell material recovered from Illinoian (~190–130 ka) and pre-Illinoian deposits in the American Midwest. Eight of the 10 aliquots yielded ^{14}C activities between 0.25 and 0.53 pMC, corresponding to apparent ^{14}C ages between 48.2 and 42.1 ka. This small level of open-system behavior is common in many materials used for ^{14}C dating and suggests that many fossil gastropods shells do not suffer from major (>1%) open-system problems.

Discus macclintocki shells from the Petersburg Section in central Illinois, however, showed signs of significant open-system behavior. Measured ^{14}C activities of 2 aliquots from this site were 1.26 and 1.71 pMC, which correspond to apparent ^{14}C ages of 35.1 and 32.7 ka, respectively. We examined the mineralogy, trace element chemistry, and physical characteristics of these and other shells to

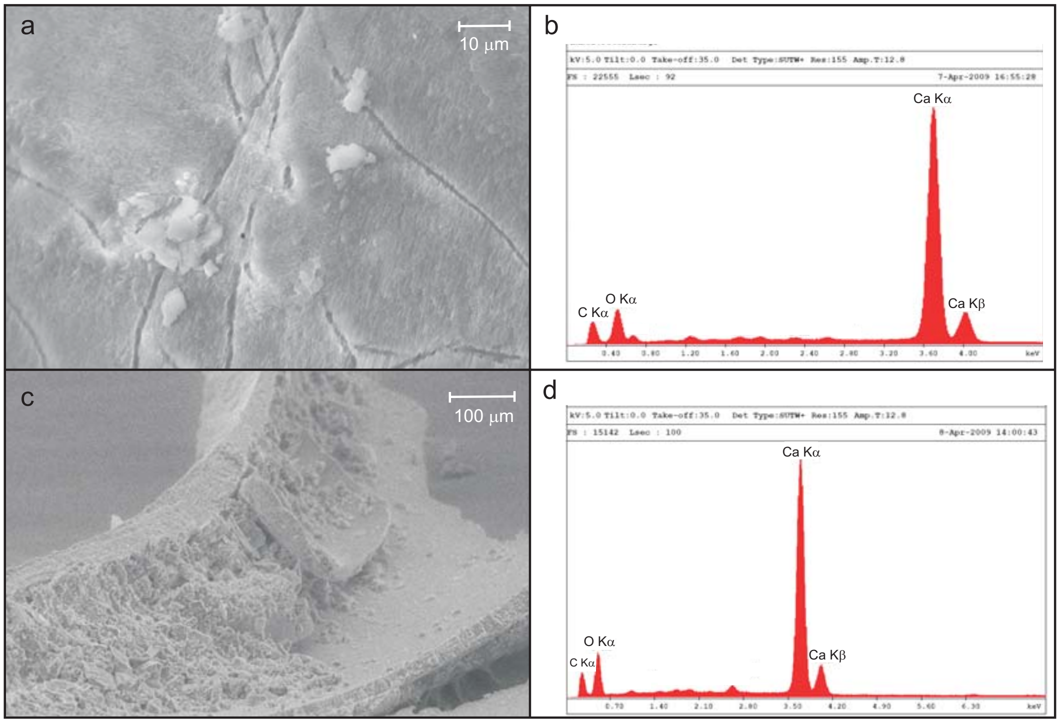

Figure 5 Evidence of secondary mineralization on gastropod shells from scanning electron microscopy analysis: a) secondary mineralization on the outside of gastropod shell from Petersburg Section; b) EDS spectrum of the elemental analysis of secondary minerals in (a), indicating that they are calcium carbonate; c) secondary mineralization within the interior of gastropod shell from Petersburg Section, with mineralization over shell fragment; d) EDS spectrum of the elemental analysis of secondary minerals in (c), also indicating that they are calcium carbonate.

identify the source of contamination and to assess potential screening techniques for selecting fossil gastropod samples suitable for ^{14}C dating.

X-ray diffraction of gastropod shells indicated that all shells were aragonite. Mineralogical analysis of gastropod shells is one of the most common techniques used to identify diagenetic alteration and screen shell material for ^{14}C dating. If all shell material is aragonite, and no calcite is detected, then the shell is thought to be free from significant alteration or contamination. However, the lower detection limit of a few percent for most X-ray diffraction analyses precludes this technique from being very sensitive to open-system behavior. Moreover, secondary precipitation of aragonite is also possible in shells where groundwater has high Mg concentrations (Webb et al. 2007).

We used trace element analysis of the shell material to determine if there was a relationship between shell geochemistry and the degree of open-system behavior with respect to carbon. This technique is commonly employed by marine geochemists to assess diagenetic alteration of shell material. The correlation between Mg, Al, Ba, and Sr with the measured ^{14}C activity of Illinoian and pre-Illinoian gastropod shells indicates the possibility of using trace element chemistry to identify open-system behavior among select gastropod samples. However, the extreme variability in trace element chemistry we found in the full glacial-aged and modern gastropod shells shows the difficulty in using this technique to identify open-system behavior. Trace element analysis may be helpful in selecting specific shells from a fossil assemblage.

We also analyzed the surface of gastropod shells with SEM and BSE (backscatter electrons), and the chemistry of selected areas with EDS (energy-dispersive X-ray spectroscopy). These techniques were highly effective at identifying secondary carbonate mineralization that was predominately within the interior whorls of shells from the Petersburg Section. This was likely the main cause for the elevated ^{14}C activities in the Illinoian shells from the Petersburg Section. SEM analysis can be performed on the same shell material that is used for ^{14}C dating without modifying the material, a key advantage of this technique over XRD analysis. Therefore, we suggest that SEM or other microscopic techniques be employed to examine the surface of shell material, especially the interior whorls, prior to ^{14}C dating of terrestrial gastropod shells.

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REFERENCES

Brennan R, Quade J. 1997. Reliable late-Pleistocene stratigraphic ages and shorter groundwater travel times from ^{14}C in fossil snails from the southern Great Basin. *Quaternary Research* 47(3):329–36.

Bruckshen P, Bruhn F, Meijer J, Stephan A, Veizer J. 1995. Diagenetic alteration of calcitic fossil shells: proton microprobe (PIXE) as a trace element tool. *Nuclear Instruments and Methods Physics Research B* 104(1–4):427–31.

Eckberg MP, Lowell TV, Stuckenrath R. 1993. Late Wisconsin glacial advance and retreat patterns in southwestern Ohio, USA. *Boreas* 22(3):189–204.

Evans JG. 1972. *Land Snails in Archaeology*. New York: Seminar Press.

Evin J, Marechal J, Pachiaudi C. 1980. Conditions involved in dating terrestrial shells. *Radiocarbon* 22(2): 545–55.

Frye JC, Willman HB. 1960. Classification of the Wisconsinan Stage in the Lake Michigan glacial lobe. *Illinois Geological Survey Circular* 285:1–16.

Geiger EC. 2008. Paleoecology of Pleistocene gastropods in glacial lake deposits in southern Illinois/Missouri [Master's thesis]. Southern Illinois University. 138 p.

Goodfriend GA. 1987. Radiocarbon age anomalies in shell carbonate of land snails from semi-arid areas. *Radiocarbon* 29(2):159–67.

Goodfriend GA, Hood DG. 1983. Carbon isotope analysis of land snail shells: implications for carbon sources and radiocarbon dating. *Radiocarbon* 25(3):810–30.

Goodfriend GA, Stipp JJ. 1983. Limestone and the problem of radiocarbon dating of land-snail shell carbonate. *Geology* 11(10):575–7.

Goslar T, Pazdur MF. 1985. Contamination studies on mollusk shell samples. *Radiocarbon* 27(1):33–42.

Johnson WH. 1986. Stratigraphy and correlation of the glacial deposits of the Lake Michigan lobe prior to 14 ka B.P. *Quaternary Science Reviews* 5:17–22.

Leighton MM. 1960. The classification of the Wisconsin Glacial Stage of north central United States. *Journal of Geology* 68(5):529–52.

Leonard AB, Frye JC, Johnson WH. 1971. Illinoian and Kansan molluscan faunas of Illinois. *Illinois State Geological Survey Circular* 461.

Miller BB, Graham RW, Morgan AV, Miller NG, McCoy WD, Palmer DF, Smith AJ, Pilny JJ. 1994. A biota associated with Matuyama-age sediments in west-central Illinois. *Quaternary Research* 41(3):350–65.

Nekola JC. 2005. Geographic variation in richness and shell size of eastern North American land snail communities. *Records of the Western Australian Museum Supplement* 68:39–51.

Pigati JS. 2002. On correcting ^{14}C ages of gastropod shell carbonate for fractionation. *Radiocarbon* 44(3):755–60.

Pigati JS, Quade J, Shanahan TM, Haynes Jr CV. 2004. Radiocarbon dating of minute gastropods and new constraints on the timing of spring-discharge deposits in southern Arizona, USA. *Palaeogeography, Palaeoclimatology, Palaeoecology* 204:33–45.

Pigati JS, Bright JE, Shanahan TM, Mahan SA. 2009. Late Pleistocene paleohydrology near the boundary of the Sonoran and Chihuahuan deserts, southeastern Arizona, USA. *Quaternary Science Reviews* 28(3–4): 286–300.

Pigati JS, Rech JA, Nekola JC. 2010. Radiocarbon dating of small terrestrial gastropod shells in North America. *Quaternary Geochronology* 5(5):519–32.

Quarta G, Romaniello L, D'Elia M, Mastronuzzi G, Calcagnile L. 2007. Radiocarbon age anomalies in pre- and post-bomb land snails from the coastal Mediterranean basin. *Radiocarbon* 49(2):817–26.

Romaniello L, Quarta G, Mastronuzzi G, D'Elia M, Calcagnile L. 2008. ^{14}C age anomalies in modern land snails shell carbonate from southern Italy. *Quaternary Geochronology* 3(1–2):68–75.

Rubin M, Likins RC, Berry EG. 1963. On the validity of radiocarbon dates from snail shells. *Journal of Geology* 71(1):84–9.

Slota Jr PJ, Jull AJT, Linick TW, Toolin LJ. 1987. Preparation of small samples for ^{14}C accelerator targets by catalytic reduction of CO. *Radiocarbon* 29(2):303–6.

Tamers MA. 1970. Validity of radiocarbon dates on terrestrial snail shells. *American Antiquity* 35(1):94–100.

Veizer J, Ala D, Azmy K, Bruckschen P, Buhl D, Bruhn F, Carden GAF, Diener A, Ebneth S, Godderis Y, Jasper T, Korte C, Pawellek, F, Podlaha OG, Strauss H. 1999. $^{87}Sr/^{86}Sr$, $\delta^{13}C$ and $\delta^{18}O$ evolution of Phanerozoic seawater. *Chemical Geology* 161(1–3):59–88.

Wade BS, Kroon D. 2002. Middle Eocene regional climate instability: evidence from the western North Atlantic. *Geology* 30(11):1011–4.

Webb GE, Price GJ, Nothdurft LD, Deer L, Rintoul L. 2007. Cryptic meteoric diagenesis in freshwater bivalves: implications for radiocarbon dating. *Geology* 35(9):803–6.

Willman HB, Frye JC. 1970. *Pleistocene Stratigraphy of Illinois*. Bulletin 94. Champaign: Illinois State Geological Survey. 204 p. 3 plates.

Yates T. 1986. Studies of non-marine mollusks for the selection of shell samples for radiocarbon dating. *Radiocarbon* 28(2A):457–63.

Zhou W, Head WJ, Wang F, Donahue DJ, Jull AJT. 1999. The reliability of AMS radiocarbon dating of shells from China. *Radiocarbon* 41(1):17–24.