

## ON CORRECTING $^{14}\text{C}$ AGES OF GASTROPOD SHELL CARBONATE FOR FRACTIONATION

Jeffrey S Pigati

Desert Laboratory and Geosciences Department, University of Arizona, Tucson, Arizona 85721, USA.

Email: jpigati@geo.arizona.edu.

**ABSTRACT.** Correcting the  $^{14}\text{C}$  age of a sample for fractionation is straightforward if the measured carbon was derived entirely from the atmosphere, either directly or through chemical and/or biological reactions that originated with atmospheric carbon. This correction is complicated in the case of gastropods that incorporate carbon from limestone or secondary carbonate (e.g. soil carbonate) during shell formation. The carbon isotopic composition of such gastropod shells is determined by fractionation, as well as mixing of carbon from sources with different isotopic values. Only the component of shell carbonate derived from atmospheric carbon should be corrected for fractionation. In this paper, the author derives a new expression for correcting the measured  $^{14}\text{C}$  activity of gastropod shells for fractionation, and describe an iterative approach that allows the corrected  $^{14}\text{C}$  activity and the fraction of shell carbonate derived from atmospheric carbon to be determined simultaneously.

### INTRODUCTION

Carbon isotopes ( $^{12}\text{C}$ ,  $^{13}\text{C}$ ,  $^{14}\text{C}$ ) fractionate along biological pathways because of differences in the rates of reaction for different molecular species (Clark and Fritz 1997). Typically, the lighter carbon isotope is taken up preferentially to the heavier isotope and, therefore, the stable and radiogenic isotopic ratios of biological products are lower than that of the reactants. For example, the isotopic composition of carbon in  $\text{C}_3$  plants is nearly 20‰ lower than the atmospheric  $\text{CO}_2$  from which it is derived. If the effects of fractionation were ignored, the  $^{14}\text{C}$  age of material with a low  $\delta^{13}\text{C}$  value would appear older than contemporaneous material with a high  $\delta^{13}\text{C}$  value.

The effect of fractionation on  $^{14}\text{C}$  is about twice the effect on  $^{13}\text{C}$  (Wigley and Muller 1981), and therefore the  $\delta^{13}\text{C}$  value of a sample can be used to correct the measured  $^{14}\text{C}/^{13}\text{C}$  ratio ( $A_{\text{measured}}$ ). The  $A_{\text{measured}}$  value is determined by accelerator mass spectrometry (AMS), and is standardized to a  $\delta^{13}\text{C}$  value of  $-25\text{‰}_{\text{PDB}}$  (by convention) using the equation

$$A_{\text{corrected}} = A_{\text{measured}} \left( \frac{1000 - 25}{1000 + \delta^{13}\text{C}} \right) \quad (1)$$

(Linick et al. 1986; Donahue et al. 1990). Note this equation is the correct form for AMS measurements of the  $^{14}\text{C}/^{13}\text{C}$  ratio. The term in parentheses on the right side of the equation should be squared for AMS measurements of the  $^{14}\text{C}/^{12}\text{C}$  ratio. The corrected ratio ( $A_{\text{corrected}}$ ) is used to calculate the  $^{14}\text{C}$  age of a sample.

Equation 1 is valid only if the measured carbon was derived entirely from the atmosphere, either directly or through chemical and/or biological reactions that originated with atmospheric carbon. For example, carbon fixated in plants by photosynthesis or in skeletal material by metabolic processes originates in the atmosphere. Similarly, carbon in shells of gastropods that do not incorporate limestone during shell formation is derived from the atmosphere, either directly or via consumption of plants. Any difference between the isotopic composition of these materials and atmospheric carbon is due entirely to fractionation, and Equation 1 can be applied.

### CORRECTING FOR FRACTIONATION AND SOURCE MIXING

Correcting the  $A_{\text{measured}}$  value of shell carbonate for gastropods that incorporate limestone or secondary carbonate is more complicated. Stable and radiogenic isotopic values of gastropod shell car-

bonate are determined by fractionation, as well as mixing of carbon from sources with different isotopic values (Goodfriend and Hood 1983). Only the component of shell carbonate derived from atmospheric carbon should be corrected for fractionation. Goodfriend and Hood (1983) previously derived an expression to correct the  $^{14}\text{C}$  activity of this component for fractionation. However, their initial correction equation was in error (Equation 14; Goodfriend and Hood 1983), and, thus, their derived expression was also incorrect. The proper form of the correction equation for shell carbonate is

$$A_{corrected} = A_{measured} \left( \frac{1000 - 25}{1000 + \delta^{13}\text{C}_{nlc}} \right) \quad (2)$$

where the subscript *nlc* denotes the component of shell carbonate derived from non-limestone carbon.  $\delta^{13}\text{C}_{nlc}$  is related to the  $\delta^{13}\text{C}$  value of the shell carbonate ( $\delta^{13}\text{C}_{shell}$ ) by

$$\delta^{13}\text{C}_{shell} = f_{lc} \delta^{13}\text{C}_{lc} + f_{nlc} \delta^{13}\text{C}_{nlc} \quad (3)$$

where *f* is the fraction of shell carbonate derived from limestone (*lc*) and non-limestone (*nlc*) carbon. Goodfriend and Hood (1983) stated that the  $\delta^{13}\text{C}_{lc}$  value for gastropods should be 0‰ (identical to limestone), and, thus, the  $f_{lc}\delta^{13}\text{C}_{lc}$  term could be dropped. This is incorrect because carbon isotopes are fractionated during dissolution of limestone, which is composed of calcite, and the subsequent precipitation of shell carbonate, which is composed of aragonite. Laboratory experiments have shown the  $\delta^{13}\text{C}$  value of synthetic aragonite precipitated from a bicarbonate solution is enriched by ~1.8‰ ( $1.8 \pm 0.2\%$ —Rubinson and Clayton 1969;  $1.7 \pm 0.4\%$ —Romanek et al. 1992) relative to calcite precipitated from an identical solution. The magnitude of enrichment is independent of temperature between 10 and 40°C (Romanek et al. 1992). If these experimental results can be applied to biogenic aragonite, and assuming equilibrium conditions prevail (i.e. no vital effects), the  $\delta^{13}\text{C}_{lc}$  term in Equation 3 equals the  $\delta^{13}\text{C}$  value of limestone (typically 0‰) plus the amount aragonite is enriched relative to calcite (denoted as  $\Delta_{a-c}$ ) during the dissolution-precipitation process, or simply  $\Delta_{a-c}$ . Substituting  $\Delta_{a-c}$  for  $\delta^{13}\text{C}_{lc}$  and  $(1-f_{nlc})$  for  $f_{lc}$  in Equation 3 gives

$$\delta^{13}\text{C}_{shell} = [(1 - f_{nlc}) \Delta_{a-c}] + f_{nlc} \delta^{13}\text{C}_{nlc} \quad (4)$$

which can be simplified and solved for  $\delta^{13}\text{C}_{nlc}$

$$\delta^{13}\text{C}_{nlc} = \left( \frac{\delta^{13}\text{C}_{shell} - \Delta_{a-c}}{f_{nlc}} \right) + \Delta_{a-c} \quad (5)$$

Equation 5 can then be combined with Equation 2 to give

$$A_{corrected} = A_{measured} \left[ \frac{1000 - 25}{1000 + \left( \frac{\delta^{13}\text{C}_{shell} - \Delta_{a-c}}{f_{nlc}} \right) + \Delta_{a-c}} \right] \quad (6)$$

Equation 6 cannot be solved directly because the  $f_{nlc}$  value cannot be determined independently of the  $A_{corrected}$  value. However, an iterative approach described below can be used to solve for both parameters for live and fossil gastropods.

#### Application to live gastropods

The uncorrected  $^{14}\text{C}$  activity of gastropod shell carbonate ( $A_{shell}$ ) is related to the  $^{14}\text{C}$  activity of the non-limestone carbon source by

$$A_{shell} = f_{lc} A_{lc} + f_{nlc} A_{nlc} \quad (7)$$

where the non-limestone component consists of carbon obtained via the atmosphere and live plants (they can be grouped together because their  $^{14}\text{C}$  activities are identical). The  $f_{lc} A_{lc}$  term can be dropped because the  $^{14}\text{C}$  activity of limestone ( $A_{lc}$ ) is zero. Rearranging gives

$$f_{nlc} = A_{shell} / A_{nlc} \quad (8)$$

For gastropods that consume only live vegetation, the  $A_{nlc}$  value can be quantified either through measurement of the atmosphere or live plants. In 2001, the  $^{14}\text{C}$  activity of live plants was  $1.0919 \pm 0.0039$  ( $n = 2$ ; Pigati et al. submitted). Equations 6 and 8 can be solved iteratively as follows:

1. Begin by assuming  $f_{nlc} = 1$  and solve Equation 6 for  $A_{corrected}$ .
2. Substitute the calculated  $A_{corrected}$  value from step 1 for  $A_{shell}$  in Equation 8, and solve for  $f_{nlc}$ .
3. Substitute the calculated  $f_{nlc}$  value from step 2 into Equation 6 and solve for  $A_{corrected}$ .
4. Repeat steps 2 and 3 until the  $A_{corrected}$  and  $f_{nlc}$  terms converge. This is usually achieved in 3–4 iterations.

An additional step is required for gastropods that include plant detritus (decaying leaves, wood, etc.) in their diet. The  $^{14}\text{C}$  activity of plant detritus may be different from that of live vegetation because the  $^{14}\text{C}$  activity of the atmosphere has decreased exponentially since cessation of aboveground testing of nuclear weapons (Manning et al. 1990; Meijer et al. 1995). The  $^{14}\text{C}$  activity of homogenized plant detritus can be measured by AMS, which can then be used to estimate the mean  $^{14}\text{C}$  activity of all plants (live and detritus) consumed by the gastropod by using

$$A_{plants} = A_{liveplants} f_{liveplants} + A_{detritus} f_{detritus} \quad (9)$$

The calculated  $A_{plants}$  value can then be combined with the  $^{14}\text{C}$  activity of the atmosphere ( $A_{atmos}$ ) to calculate the  $A_{nlc}$  value in Equation 8 using

$$A_{nlc} = A_{plants} f_{plants} + A_{atmos} f_{atmos} \quad (10)$$

There is disagreement regarding the relative contribution of plants ( $f_{plants}$ ) and the atmosphere ( $f_{atmos}$ ) toward the carbon isotopic composition of shell carbonate. Goodfriend and Hood (1983) suggested that 25–40% of inorganic carbon in gastropod shells is derived from plants, and 30–60% is derived from the atmosphere. Stott (2002), however, found that atmospheric  $\text{CO}_2$  plays little to no role in determining the isotopic composition of gastropod shell carbonate. Until this is resolved,

Equation 10 may be solved using a range of atmospheric (0–60%) and plant (25–100%) values to determine a range of corrected  $^{14}\text{C}$  activities.

### Application to fossil gastropods

There are 2 approaches for correcting  $^{14}\text{C}$  ages obtained from fossil gastropod shells for fractionation. One is to measure the  $^{14}\text{C}$  activity of live specimens collected from geologic settings that maximize the potential for ingestion of limestone. Equations 6 and 8 can then be solved to determine a species-specific, worst-case  $f_{\text{nlc}}$  value for the live specimens, which is assumed to be invariant through time. This should be done using the same species that are to be used for  $^{14}\text{C}$  dating in the fossil record. Equations 6 and 8 can then also be solved using an  $f_{\text{nlc}}$  value of 1 (i.e. no limestone correction) to determine a range of possible  $A_{\text{corrected}}$  values.

For cases in which measuring the  $^{14}\text{C}$  activity of live specimens is not possible, Equations 6 and 8 can be solved using  $f_{\text{nlc}}$  values of ~0.6 and 1 to calculate a range of possible  $A_{\text{corrected}}$  values. The lower  $f_{\text{nlc}}$  value is the minimum observed by Goodfriend and Hood (1983) and Pigati et al. (submitted). The upper value assumes limestone and/or secondary carbonate are not incorporated by the gastropod during shell formation. The difference in the  $A_{\text{corrected}}$  values between those corrected using a  $f_{\text{nlc}}$  value of 0.6 and those corrected using a  $f_{\text{nlc}}$  value of 1 is 1.1% for gastropods feeding exclusively on  $\text{C}_3$  biomass, and 0.1% for those feeding on  $\text{C}_4$  biomass. These corrections are quite small compared to age anomalies due to incorporation of limestone during shell formation.

### PROPOGATION OF UNCERTAINTIES

The uncertainty associated with the  $A_{\text{corrected}}$  term in Equation 6 is given by

$$\Delta A_{\text{corrected}} = (A^2 + B^2 + C^2 + D^2)^{1/2} \quad (11)$$

where

$$A = \left[ \frac{975}{1000 + \Delta_{a-c} + \left( \frac{\delta^{13}\text{C}_{\text{shell}} - \Delta_{a-c}}{f_{\text{nlc}}} \right)} \right] \Delta A_{\text{measured}}$$

$$B = \left\{ \frac{-975 A_{\text{measured}} \left( 1 - \frac{1}{f_{\text{nlc}}} \right)}{\left[ 1000 + \Delta_{a-c} + \left( \frac{\delta^{13}\text{C}_{\text{shell}} - \Delta_{a-c}}{f_{\text{nlc}}} \right) \right]^2} \right\} \Delta (\Delta_{a-c})$$

$$C = \left\{ \frac{-975 A_{\text{measured}}}{f_{\text{nlc}} \left[ 1000 + \Delta_{a-c} + \left( \frac{\delta^{13}C_{\text{shell}} - \Delta_{a-c}}{f_{\text{nlc}}} \right) \right]^2} \right\} \Delta \delta^{13}C_{\text{shell}}$$

$$D = \left\{ \frac{975 A_{\text{measured}} (\delta^{13}C_{\text{shell}} - \Delta_{a-c})}{f_{\text{nlc}}^2 \left[ 1000 + \Delta_{a-c} + \left( \frac{\delta^{13}C_{\text{shell}} - \Delta_{a-c}}{f_{\text{nlc}}} \right) \right]^2} \right\} \Delta f_{\text{nlc}}$$

where the delta ( $\Delta$ ) symbol at the end of each equation denotes the uncertainty associated with the individual parameter.

The uncertainty associated with the  $f_{\text{nlc}}$  term in Equation 8 is given by

$$\Delta f_{\text{nlc}} = \left[ \left( \frac{\Delta A_{\text{shell}}}{A_{\text{nlc}}} \right)^2 + \left( \frac{-A_{\text{shell}} \Delta A_{\text{nlc}}}{A_{\text{nlc}}^2} \right)^2 \right]^{1/2} \quad (12)$$

where  $A_{\text{shell}}$  is the same as  $A_{\text{measured}}$  in Equation 11. Equations 11 and 12 can be solved iteratively in a spreadsheet simultaneously with Equations 6 and 8. The magnitude of these uncertainties is certainly small compared to other sources of error in the  $^{14}\text{C}$  age calculation, but nonetheless can be propagated for completeness.

## SUMMARY

Correcting the measured  $^{14}\text{C}$  activity of gastropods that incorporate limestone or secondary carbonate during shell formation is complicated by the fact that the isotopic composition of the shell carbonate is a function of fractionation and mixing of carbon from sources with different isotopic values. Only the component of shell carbonate derived from atmospheric carbon should be corrected for fractionation. The equations presented here can be used to determine the corrected  $^{14}\text{C}$  activity of gastropod shell carbonate, as well as the fraction of the carbonate derived from non-limestone sources. For gastropods that do not incorporate limestone during shell formation (i.e.  $f_{\text{nlc}} = 1$ ), Equation 6 simplifies to the standard correction equation (Equation 1).

## ACKNOWLEDGEMENTS

I thank N Lifton for direction on propagation of uncertainties and T Shanahan and J Rech for constructive reviews of this manuscript.

## REFERENCES

- Clark ID, Fritz P. 1997. *Environmental isotopes in hydrogeology*. CRC Press LLC, Boca Raton, FL, 328 pp.
- Donahue DJ, Linick TW, Jull AJT. 1990. Isotope-ratio and background corrections for accelerator mass spec-

- trometry radiocarbon measurements. *Radiocarbon* 32(2):135–142.
- Goodfriend GA, Hood DG. 1983. Carbon isotope analysis of land snail shells: implications for carbon sources and radiocarbon dating. *Radiocarbon* 25(3):810–830.
- Linick TW, Jull AJT, Toolin LJ, Donahue DJ. 1986. Operation of the NSF-Arizona Accelerator Facility for radio-isotope analysis and results from selected collaborative research projects. *Radiocarbon* 28(2a):522–533.
- Manning MR, Lowe DC, Melhuish WH, Sparks RJ, Wallace G, Brenninkmeijer CAM, McGill RC. 1990. The use of radiocarbon measurements in atmospheric studies. *Radiocarbon* 32(1):37–58.
- Meijer HAJ, van der Plicht J, Gislefoss JS, Nydal R. 1995. Comparing long term atmospheric  $^{14}\text{C}$  and  $^3\text{H}$  records near Groningen, the Netherlands with Fruholmen, Norway and Izana, Canary Islands  $^{14}\text{C}$  stations. *Radiocarbon* 37(1):39–50.
- Pigati JS, Shanahan TM, Quade J, Haynes Jr. CV. Radiocarbon dating of minute gastropods and new constraints on the timing of late Quaternary spring-discharge deposits in southern Arizona, USA. *Palaeogeography, Palaeoclimatology, Palaeoecology*, submitted.
- Romanek CS, Grossman EL, Morse JW. 1992. Carbon isotopic fractionation in synthetic aragonite and calcite: effects of temperature and precipitation rate. *Geochimica et Cosmochimica Acta* 56:419–430.
- Rubinson M, Clayton RN. 1969. Carbon-13 fractionation between aragonite and calcite. *Geochimica et Cosmochimica Acta* 33:997–1002.
- Stott LD. 2002. The influence of diet on the  $\delta^{13}\text{C}$  of shell carbon in the pulmonate snail *Helix aspersa*. *Earth and Planetary Science Letters* 195(3–4):249–259.
- Wigley TML, Muller AB. 1981. Fractionation corrections in radiocarbon dating. *Radiocarbon* 23(2):173–190.