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Comment

Comment on "Stable carbon isotopes in freshwater mussel shells: Environmental record or marker for metabolic activity?" by J. Geist et al. (2005)

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In a recent analysis of $\delta^{13}C$ in the aragonitic shells of the bivalve *Margaritifera margaritifera*, Geist et al. (2005) argue that variation in the carbon isotope composition of contemporaneous shells from one locality over periods of decades cannot be correlated with one another, and thus do not record environmental signals. Instead, they ascribe the observed fluctuations to respiratory loss of light carbon and consequent enrichment of ^{13}C in the youngest part of the shell. However, we note two significant weaknesses in the study that make it difficult to accept their conclusions. First of all, we note the absence of reliable and long-established sclerochronological techniques in the analysis of their shells needed to determine the timing of shell growth and construct reliable chronologies. Second, the authors do not report relevant environmental and physiological data needed to establish an independent metabolic control on shell $\delta^{13}C$.

One of the key elements of Geist et al. (2005) is the description of a new technique to separate shell growth increments and organic-rich growth layers by heating. While not entirely novel (see Bourgoin, 1988), we feel that the utility and reliability of this method is highly questionable, and their failure to compare their results in detail to well-established, accurate and reliable sampling techniques puts their conclusions into doubt. Micromilling produces records with substantially higher resolution (seasonal, fortnightly and even subdaily sampling is possible), and the operator has complete control over the spatial and temporal scale of sample acquisition (e.g., Jones et al., 1983; Pätzold et al., 1991; Wefer and Berger, 1991; Dettman and Lohmann, 1995; Goodwin et al., 2001; Surge et al., 2001; Wurster and Patterson, 2001; Kobashi and Grossman, 2003; Buick and Ivany, 2004; Watanabe et al., 2004). Manually operated or computer-assisted micromilling devices are simple to operate, widely used by others in the field, and suffer none of the drawbacks that Geist et al. (2005) note for serial drilling.

Routine sclerochronological techniques, namely intra-annual microgrowth patterns (e.g., Dunca and Mutvei, 2001) and intra-annual stable isotope analyses (e.g., Veinott and Cornett, 1998; Dettman et al., 1999; Wurster and Patterson, 2001; Kaandorp et al., 2003; Ricken et al., 2003) are needed to show whether a growth line was formed during winter or summer. As noted by Geist et al. (2005), misidentification of growth lines alter the constructed chronology: years with weak winter bands adhere together using their technique, while years with well-developed summer growth interruptions may be split in two. Thus, less than half of the samples analyzed in Geist et al. (2005) are annually resolved, with no indication whether a given "annual" measurement actually represents growth during the period between a winter and summer growth line, summer and winter shutdown, a whole growth season, or multiple annual increments adhering together. Seasonal fluctuations in the carbon isotope composition of freshwater bivalve shells often exceed mean inter-annual variations (e.g., Veinott and Cornett, 1998; Dettman et al., 1999; Wurster and Patterson, 2001; Kaandorp et al., 2003; Ricken et al., 2003), so this imprecision in sample resolution has significant effects on the resulting $\delta^{13}C$ curve.

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This can be illustrated using intra-annual stable carbon isotope data of the freshwater bivalve, *Elliptio complanata* (Fig. 1), published by Veinott and Cornett (1998, Fig. 3E). Seasonal $\delta^{13}C$ values of this species vary by as much as 4.3‰ during the course of one growing season ('year' 1991), whereas mean values of 1991 and 1992 were −13‰ and −12.5‰, respectively. However, average values of the second half—i.e., summer to winter line—of year 1990 (−11.9‰) and the second half of 1991 (−13.4‰) differed by as much as 1.5‰ and were hence threefold larger than the inter-annual variation between years 1991 and 1992 (Fig. 1). This simple modeling approach indicates that temporal resolution of carbon isotope analyses is a major issue. If sections b and c (Fig. 1) were split by a strong summer growth break, but a weak winter growth break caused a and b to adhere together, the difference in calculated 'annual' means would be exaggerated ($a + b = -12.1$‰; $c = -13.4$‰). Similar results can be achieved when modeling other intra-annual shell carbon isotope data presented by Dettman et al. (1999), Wurster and Patterson (2001), Kaandorp et al. (2003) or Ricken et al. (2003). Before making inferences about inter-annual variations of shell $\delta^{13}C$, the seasonal range must be known. The above model is still oversimplified, because $\delta^{13}C$ values of faster growing shell portions are overrepresented in samples spanning over multiple annual increments. Hence, variable annual growth rates must also be taken into account. Geist et al. (2005), however, failed to do so.

Beyond this, cross-dating (Douglass, 1919; Fritts, 1976) individual chronologies is necessary to evaluate the temporal resolution of each time-series (much less correlate them between animals). Without this information, a precise alignment of $\delta^{13}C$ data cannot be constructed and Fig. 8 of Geist et al. (2005) simply represents a series of sequential measurements. Any attempt to correlate these graphs makes critical assumptions about synchronicity of growth between specimens that are neither supported nor testable with the data collected. The differences observable between results obtained from inner and outer shell layers in specimen Z1 and Z12 illustrate this problem. The data presented indicates that, for samples representing variable time intervals—with a mean of two years in duration—shell carbonate $\delta^{13}C$ can vary by 4‰ over the course of the lifetime of *M. margaritifera*, but more detailed inferences are difficult to sustain.

Some of these problems could have been averted by reporting widths of growth increments measured prior to treatment, disaggregation and analysis. Changes in seasonal and inter-annual growth rates result from variable temperature, amount and quality of food and other environmental parameters (e.g., Dunca and Mutvei, 1996; Aldridge, 1999; Allen et al., 1999; Brockington and Clarke, 2001) and can only be determined with growth curves derived from growth increment width measurements (e.g., Jones et al., 1983; Marsh et al., 1999; Watanabe et al., 2004) or by using the seasonality in high-resolution (= sub-annual) oxygen isotope profiles (Klein et al., 1996; Veinott and Cornett, 1996; Dettman et al., 1999). Without these measurements it is also not possible to correct the $\delta^{13}C$ chronologies for ontogenetic age- and growth rate-related trends which are well documented in marine species (e.g., Borchardt, 1985; Jones et al., 1986; Tanaka et al., 1986; Lorrain et al., 2004). The presence of ontogenetic trends in the $\delta^{13}C$ of freshwater bivalves would be a novel contribution, but the data of Geist et al. (2005) do not demonstrate the claimed age trends (enrichment of younger shell portions in ^{13}C; Fig. 8 in Geist et al., 2005) despite specimens being collected from the same locality. Corrections (=detrending) for kinetic effects on $\delta^{13}C$ of the shell carbonate are critical for correlating records for multiple individuals and are necessary to extract environmental signals. Again, this requires information on the time represented by each sample and the variation of shell growth rates.

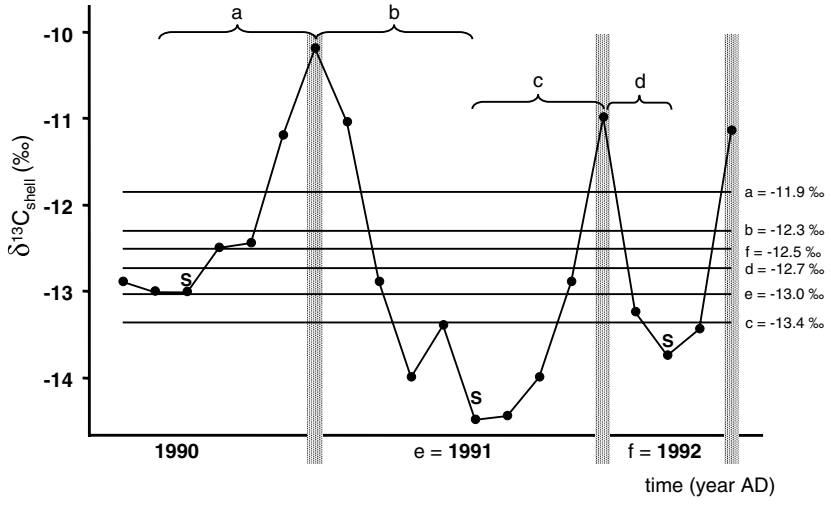

Fig. 1. Intra-annual carbon isotope data of *Elliptio complanata* by Veinott and Cornett (1998) covering almost three years of growth. Horizontal lines indicate mean $\delta^{13}C$ values for different portions of the shell; s, summer; (a) second half of year 1990 (summer to winter line), (b) first half of year 1991, (c) second half year 1991, (d) first half of year 1992, (e) full growing season of year 1991, (f) full growth season of year 1992.

Assuming that Geist et al. had achieved an annually resolved $\delta^{13}C$ time-series and corrected for growth trends and ontogenetic age, the methods they applied were probably inadequate to answer the question raised in the title. Shell carbon isotope composition depends on multiple factors such as dissolved inorganic carbon (DIC), the composition of their food, pH, kinetic effects, growth rate and ontogenetic age (e.g., Mook and Vogel, 1968; Krantz et al., 1987; Andreasson and Schmitz, 1998; Owen et al., 2002; Lorrain et al., 2004). In order to demonstrate metabolic fractionation effects and rule out environmental controls on shell $\delta^{13}C$, relevant variables influencing shell $\delta^{13}C$ need to be accounted for (e.g., Dettman et al., 1999; Stott, 2002). Ideally, combined sclerochronological and isotope analyses in conjunction with detailed monitoring of environmental and physiological parameters, is necessary to evaluate their relative contribution to shell $\delta^{13}C$ variability (e.g., Dettman et al., 1999). Due to the absence of such data, the authors should have compared shell growth rates with shell $\delta^{13}C$ values, because shell growth is directly related to the metabolism of the bivalve. This would have been a strong test of their assumption that metabolism is controlling the carbon isotope composition of the shell carbonate.

Typical values of DIC ($\delta^{13}C_{DIC}$) in freshwater can be as low as $-14‰$ (e.g., Hellings et al., 2000; Kaandorp et al., 2003), or even lower if soil respiration is the dominant source of carbon to the river (Mook, 2000). Alternatively, if the region is carbonate rich, $\delta^{13}C_{DIC}$ may approach $+1‰$ (Mook, 2000). Additionally, DIC consists of CO_2, HCO_3^- and CO_3^{2-}, with the concentration of each dependent on pH and each with their own $\delta^{13}C$ value. Bivalves probably use HCO_3^- for biomineralization and therefore the $\delta^{13}C$ value of HCO_3^- needs to be known to determine what a shell in equilibrium should be (see Kaandorp et al., 2003). If the authors had known the $\delta^{13}C$ value of the bicarbonate, they then could apply the $2.7‰$ aragonite-bicarbonate fractionation factor determined by Romanek et al. (1992). Applying this fractionation factor to their shells, which range from $-15‰$ to $-10‰$, results in a $\delta^{13}C$ value of the bicarbonate ranging from $-12.7‰$ to $-17.7‰$. This range of $\delta^{13}C$ values of bicarbonate is within the range normally recorded in freshwater rivers. Without knowledge of the $\delta^{13}C$ values of the different DIC species, little can be said about the amount of metabolic carbon in the shells or isotopic equilibrium between shells and water.

In comparing changes in shell $\delta^{13}C$ and atmospheric CO_2 (Fig. 6), Geist et al. argued that recent years (post 1960) do not show the pronounced change in slope seen in atmospheric records. This interpretation is faulty simply because a linear regression, by definition, does not display a change in slope. The data presented may indicate that (1) the long term average parallels atmospheric trends (consistent with the Suess effect) with a $-5‰$ offset and (2) considerable noise was introduced based on the authors' methodology. Specifically, much of the signal recorded in the shells could likely be explained by analytical uncertainty related to their unconventional method of isotopic analysis. Aragonite samples were heated to 550 °C converting them to calcite, and then analyzed on an elemental analyzer coupled to a continuous flow isotope ratio mass spectrometer. This procedure likely increased the scatter in the data and can reportedly cause a $-0.5‰$ uncertainty of the $\delta^{13}C$ values. Furthermore, an acceptable level of precision should be better than $0.2‰$ by conventional standards. Additionally, changes in organic matter inputs into the river, as well as organic pollution, might also obscure the atmospheric $\delta^{13}C$ signal in rivers. With the data presented by Geist et al., it is impossible to know if the shells are recording environmental conditions or not.

In summary, the only conclusions about the shell composition of *M. margaritifera* that can be drawn from this work is that undetrended time-series of $\delta^{13}C$ variations, constructed from samples of variable temporal resolution without sclerochronological context, cannot be correlated with one another. The data presented do not support the existence of ontogenetic age trends in isotopic composition, as there is neither a consistent trend according to age nor an attempt to measure the influence of growth on $\delta^{13}C$. Even if metabolic effects influence the $\delta^{13}C$ record in these shells to some degree, the experimental design employed can neither measure that effect, nor correct for known influences of ontogenetic age and growth rate variations to extract environmental signals from the studied shells.

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