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Flux balance models for the oxygen and carbon isotope compositions of land snail shells

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Abstract—A simple flux balance model with a diffusive, evaporative boundary layer indicates that the time constant (characteristic time) for approach to oxygen isotope steady state in the body fluid of land snails is ~19 min or less. These comparatively short times support an assumption that the snail's aragonitic shell is commonly precipitated from a body fluid that is at, or near, isotopic steady state. The model indicates that the steady-state $\delta^{18}O$ value of snail shell carbonate depends upon the temperature, relative humidity, $\delta^{18}O$ of the input liquid water, and $\delta^{18}O$ of ambient water vapor. Model shell $\delta^{18}O$ values were calculated for the warm, wet months corresponding to times of snail activity at some European sites. Linear regression of these predicted values against published, measured values yielded the expression: $\delta^{18}O_{calc} = 0.93(\pm 0.13)\ \delta^{18}O_{meas} - 0.9(\pm 0.2)$, with $r^2 = 0.65$. As indicated by the value of r^2, there is scatter in the relationship, but the slope and intercept are close to one and zero, respectively, which lends credence to the model. Therefore, temporal or spatial changes recorded in the $\delta^{18}O$ values of land snail shells appear to be selectively seasonal—commonly the warm, wet months—and include the effects of relative humidity.

For carbon, the time constant for approach to isotopic steady state in the bicarbonate dissolved in the body fluid of land snails is predicted to be ~16 min or less. New and published $\delta^{13}C$ measurements of aragonite shell and associated organic matter exhibit an overall correlation, but with considerable scatter. As noted by previous workers, ^{13}C-rich dietary "limestone" may account for some of the scatter. Additional scatter, according to the model presented herein, could arise from changes in the proportion of total oxidized carbon that is expelled by the snail as bicarbonate dissolved in body fluid (i.e., effects of relative changes in metabolic rates). These results affirm the need for caution in the interpretation of $\delta^{13}C$ values of land snail aragonite shells solely in terms of dietary proportions of C_3 and C_4 plants.

1. INTRODUCTION

The significance of the carbon and oxygen isotopic compositions of the aragonitic shells of land snails as environmental indicators has been studied for over two decades (Yapp, 1979; Magaritz and Heller, 1980, 1983; Magaritz et al., 1981; Lécolle, 1985; Goodfriend and Magaritz, 1987; Goodfriend, 1988, 1991, 1992; Goodfriend and Ellis, 2000). In an extensive study of land snails from sites in Europe (principally France; Fig. 1), Lécolle (1985) found a systematic relationship between the $\delta^{18}O$ values of average annual precipitation and the $\delta^{18}O$ values of the aragonite shell. This correlation included the effects of altitude on the $\delta^{18}O$ of precipitation (Rozanski et al., 1993) in which $\delta^{18}O$ of the shells decreased with increasing altitude (Lécolle, 1985). However, this relationship with altitude broke down at elevations ≥1200 m (Lécolle, 1985).

The aforementioned correlation exists in conjunction with the fact that calculated/observed $\delta^{18}O$ values of snail body fluid are more positive than that expected from equilibrium with associated meteoric water (Yapp, 1979; Magaritz et al., 1981; Lécolle, 1985; Goodfriend and Magaritz, 1987). Yapp (1979) found that the degree of ^{18}O enrichment of the body fluid was linearly related to the inverse of relative humidity, which suggested that isotopic steady-state evaporation of body fluid and exchange with ambient water vapor were important factors in the evolution of body fluid $\delta^{18}O$ values. Successive studies, however, have discounted the role of relative humidity in controlling the $\delta^{18}O$ of the body fluid and hence that of the aragonitic shells of snails (Magaritz et al., 1981; Goodfriend and Magaritz, 1987; Goodfriend et al., 1989). Goodfriend et al. (1989) attributed the relative ^{18}O enrichment of water in the body fluid to metabolic water that incorporated relatively ^{18}O-rich oxygen from atmospheric O_2.

Observed values for the $\delta^{13}C$ of snail shell range from −11.9‰ to 0.5‰ (Yapp, 1979, Magaritz et al., 1981; Goodfriend and Magaritz, 1987). Although there was no discussion of possible causes, Yapp (1979) noted a systematic difference in $\delta^{13}C$ values of shell aragonite from two distinct habitats in a single locale. Magaritz and Heller (1980) observed that analyzed snails from desert regions were systematically enriched in ^{13}C relative to those from mountainous regions. Magaritz et al. (1981) and Magaritz and Heller (1983) were of the view that the variations in $\delta^{13}C$ values of the snail shell aragonite reflect variations in the $\delta^{13}C$ and P_{CO_2} at the surface of the Earth which in turn were governed by the proportions of isotopically distinct soil CO_2 and background atmospheric CO_2 in the mix. Francey (1983) suggested that differences in the $\delta^{13}C$ values of organic matter in snail diets are recorded in the $\delta^{13}C$ values of the shell aragonite, and that an enrichment of the shell carbonate in ^{13}C relative to the organic matter is a consequence of equilibrium fractionation with respect to metabolic gaseous CO_2. The metabolic CO_2 was presumed to have the same $\delta^{13}C$ value as the organic matter from which it was derived.

Here, we present models which incorporate kinetic isotope effects associated with diffusive loss of water vapor and metabolic CO_2 from snails. The predictions of our oxygen isotope flux balance model are compared with a European land snail

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data set published by Lécolle (1985). The calculated outcomes of the carbon isotope flux balance formulation are evaluated with published and some newly analyzed data.

2. EXPERIMENTAL PROCEDURES

$\delta^{13}C$ values of modern snail shells and associated litter from six sites were analyzed to augment published data on carbon isotopes in snails and to test the model. "Grab" samples of commingled snail and litter were obtained for this study from Dr. James Theler of the University of Wisconsin, La Crosse, and formed part of a larger gastropod survey from the Southern Plains of the US (Wyckoff et al., 1997). Multiple shells were used from each of the six sites to approximate an average of the existing conditions. *Vallonia* and *Gastrocopta* species, which represented the majority of the population, were used for the analyses.

The shells were rinsed with de-ionized water then treated ultrasonically in de-ionized water to remove any adhering particles of organic matter or other debris that might affect the results. The shells were crushed gently and treated with 5% reagent grade sodium hypochlorite at room temperature for ~7 to 8 h to remove organic matter. They were then rinsed thoroughly with deionized water and dried in air at ~40 to 50°C. The shell fragments were subsequently reacted overnight in vacuum with 100% H_3PO_4 at 25°C following the method of McCrea (1950).

Each organic litter sample was comminuted in an attempt to homogenize it. Aliquots were then weighed and oxidized in the presence of clean copper oxide and reduced granular copper in organic free vycor combustion tubes (Boutton, 1991). Combustion was carried out initially at 900°C for 2 h, followed by cooling and maintenance at 650°C for 2 h. During this time the copper system eliminates halogens and converts CO and oxides of nitrogen and sulfur to CO_2, N_2 and $CuSO_4$, respectively. The tubes were subsequently cooled to room temperature. The CO_2 gas is separated from the other combustion products by cryogenic distillation under vacuum (Boutton, 1991). CO_2 recovered from shell aragonite and organic litter was analyzed for $\delta^{13}C$ and $\delta^{18}O$ on a Finnigan MAT 252 mass spectrometer. Analytical precision is about ±0.1‰. The δ values are defined in the usual manner:

$$\delta^{13}C \text{ or } \delta^{18}O = [(R_{sample}/R_{standard}) - 1] \times 1000‰$$

where, $R = {}^{13}C/{}^{12}C$ or ${}^{18}O/{}^{16}O$. The standard is PDB for ${}^{13}C/{}^{12}C$ (Craig, 1957). For ${}^{18}O/{}^{16}O$, the standard is PDB for carbonate, but SMOW for water (Gonfiantini, 1978).

3. FLUX BALANCE MODELS

3.1. Previous Work

Oxygen isotope variations in higher animals were characterized with flux balance models that quantitatively incorporated physiologic adaptations (Bryant and Froelich, 1995; Kohn, 1996). The principal oxygen inputs in these models were drinking water, inhaled atmospheric oxygen, and chemically bound oxygen in food. The principal outputs included CO_2 and respiratory and transcutaneous H_2O vapor. Kohn (1996) also incorporated oxygen output through fecal water, urine and sweat. Bryant and Froelich (1995) used empirical scaling functions to estimate the fluxes as a function of body mass. Their model is restricted to herbivorous mammals and their assumptions are mostly valid for large body sizes. The model of Kohn (1996) was applied to different genera of vertebrates including fishes, amphibians, reptiles, birds and mammals by using specific physiologic and observational data.

Kohn (1996) noted that a relationship between bone phosphate $\delta^{18}O$ and relative humidity is observed in drought-tolerant mammalian herbivores and that such a relationship is approximated reasonably well by his model. Kohn (1996) used values of relative humidity to quantify input parameters such as the $\delta^{18}O$ of the plant water (in the food) and the amount of water vapor taken into the lungs. The transcutaneous water vapor loss was assigned a constant value for all thermoregulating animals. $\delta^{18}O$ values of bone phosphate measured by Ayliffe and Chivas (1990) for red kangaroos that live in hot, dry areas were more positive than predicted by the model of Kohn (1996) and more positive than the phosphate $\delta^{18}O$ values of grey kangaroos that live in wetter areas. The effect of humidity on transcutaneous water vapor loss was discussed as a possible cause, with model calculations that incorporated an increase in the transcutaneous output showing some improvement in the model fit (Kohn, 1996).

3.2. Land Snail Physiology

Land snails are pulmonate gastropods and secrete a protective shell of aragonite around themselves. External respiratory gas exchange takes place primarily through the lung (by diffusion through the breathing pore, the pneumostome; Krogh, 1941). Terrestrial snails are highly susceptible to dehydration as they continuously lose water by evaporation from their integument, evaporation through the lung when the pneumostome is kept open, and slime secreted by the body (Howes and Wells, 1934; Prior, 1985; Barnhart, 1986). The amount of water lost by evaporation is dependent upon the ambient relative humidity (Howes and Wells, 1934) with increases in the rate of evaporation as relative humidity decreases. To minimize water loss, snails prefer moist habitats with high relative humidity (Van der Schalie and Getz, 1961, 1963). It has also been observed that most terrestrial gastropods rest during the daytime (called "homing") and forage at night (Edelstam and Palmer, 1950; Newell, 1966; Gelperin, 1974; Cook, 1979).

The main activity phase of a snail appears to be during and immediately following a rain event (Wells, 1944; Heatwole and Heatwole, 1978; Ward and Slotow, 1992). Hence rainwater would be the main source of water for land snails that are wholly subaerial (as opposed to semiaquatic). Water uptake is accomplished by contact rehydration through the integument of the foot (Riddle, 1983; Prior, 1985). During their intervals of activity, most terrestrial snails feed mainly on dead or decaying organic matter. Metabolic production of oxidized carbon from this organic matter is a principal contributor to the dissolved bicarbonate in body fluid (Goodfriend, 1992).

Under conditions of stress, the snails go into a period of dormancy (Howes and Wells, 1934; Yom-Tov, 1971; Cowie, 1984). Snails aestivate at temperatures above 27°C, or when the environmental conditions become dry (Cowie, 1984; Thompson and Cheny, 1996). Snails also become inactive and cease to grow at temperatures below 10°C (Thompson and Cheny, 1996). At these times, the snail body retracts into its highly impermeable shell and secretes the epiphragm to cover the shell aperture, followed by suppression of metabolic rate and gas exchange, to minimize water loss from the body (Barnhart, 1986). It has been shown that body growth, measured in terms of shell growth, ceases at the onset of hibernation and aestivation (Cowie, 1984). Therefore, it seems reasonable to assume that the secretion of the shell takes place during periods of snail activity—usually at times of relatively warm, moist conditions. Exceptions to these general observations about times of land snail activity are found in the carnivores of the genus *Vitrina*