

Stable C and O isotope ranges of African land snail shells

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Cenozoic fossil land snails can be found in many continental sections (Pickford, *J. African Earth Sci.*1995). We show how stable C and O isotope ranges of modern land snail shell from various ecosystems in Africa are related to snail genus, climate, and diet. Sequential powdered samples are drilled following growth lines through multiple years of shell growth to document stable isotope response to seasonal environmental variation. Results are summarized as follows: $\delta^{13}\text{C}$: Variation within one specimen is small. Shell $\delta^{13}\text{C}$ primarily responds to differences in diet, i.e. C3 plants, C4 plants, and the ingestion of carbonate from detritus, bedrock or soil.

$\delta^{18}\text{O}$: (1) Snails of the same genus from same ecosystem have similar values. (2) Oxygen isotope ranges from tropical forest, upland forest, coastal steppe, semi-desert and desert are small, with forest values generally lower than desert or semi-desert. (3) Regions with pronounced dry and wet seasonality (savannah, Mediterranean) can have large seasonal variation in $\delta^{18}\text{O}$. Within one climate type, snails of different genus often have similar ranges, although sometimes ranges are different. Habitat/climate has a stronger control on shell chemistry than taxonomy.

The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ ranges of land snail shells reflect ecosystems, diet, and perhaps micro-habitat preference. Land snail fossils are potential targets for paleoenvironmental reconstruction based on a combination of faunal analysis and stable isotope geochemistry. [abbreviation] C: $\delta^{13}\text{C}$ VPDB, O: $\delta^{18}\text{O}$, VPDB.

[Tropical forest: Gabon, Uganda, Tanz.] *Leptocala* C: -11.28 ~ -13.28; O: -0.97 ~ -3.29; *Trochonanina* C: -14.20 ~ -15.56; O: +0.39 ~ -1.74; *Thapsia* C: -11.80 ~ -13.35; O: -1.37 ~ -3.55; *Limicolaria* C: -12.68 ~ -15.36; O: +1.01 ~ -3.85; *Achatina* C: -8.45 ~ -13.02; O: +0.13 ~ -2.83 [Upland forest: Kenya, Ug.] *Limicolaria* C: -9.37 ~ -11.41; O: +1.41 ~ -2.13; C: -7.90 ~ -10.02; O: +3.45 ~ -0.07; C: -8.35 ~ -12.33; O: +2.03 ~ -2.23; *Trochonanina* C: -0.24 ~ -5.22; O: +1.63 ~ -1.25 [Savannah woodland: Namibia, Kenya, Mozambique] *Xeroceratus* C: -6.37 ~ -7.99; O: -2.31 ~ -7.76; *Achatina* C: -5.96 ~ -10.90; O: +5.38 ~ -5.42; C: -4.84 ~ -13.83; O: +5.59 ~ -4.65; C: -8.37 ~ -13.82; O: +1.33 ~ -8.16; *Limicolaria* C: -1.82 ~ -7.92; O: +2.91 ~ -4.64 [Mediterranean: Morocco] *Helicopsis* C: -3.19 ~ -4.62; O: +0.74 ~ -0.99; *Rumina* C: -9.27 ~ -9.80; O: +5.76 ~ -1.08; *Kabylia* C: -5.31 ~ -7.01; O: +3.48 ~ -0.07 [Coastal steppe: Oman] *Rochebrunia* C: -4.49 ~ -7.67; O: +2.95 ~ +0.92; *Euryptyxis* C: -9.28 ~ -10.88; O: +0.80 ~ +0.37; *Obeliscella* C: -7.88 ~ -9.52; O: +1.42 ~ -1.02 [Semi-desert: Nam. Ug.] *Dorcasia* C: -5.91 ~ -8.58; O: +3.89 ~ -0.12; *Bloyetia* C: -5.96 ~ -7.32; O: +2.79 ~ -1.21 [Desert: Nam.] *Dorcasia* C: -0.18 ~ -1.03; O: +3.37 ~ +1.26; *Trigonephrus* C: -0.20 ~ -2.75; O: +5.70 ~ +3.27.

Seasonal methane fluxes and sulfate reduction rates in a eutrophied Baltic estuarine system

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Estuaries and shelves are thought to be the source of 75% of the oceanic CH_4 emissions to the atmosphere, but to date relatively few data are available that report spatial and seasonal variations in production and emission of CH_4 from sediments in eutrophied coastal settings. Himmerfjärden (Baltic Sea, Sweden) is an estuary with a surface area of 174 km^2 . The estuary has a well-described eutrophication gradient from the inner part of the estuary to the opening, which is due to a sewage treatment plant (STP) in the inner estuary that has been discharging treated sewage since 1973. The sediments in the bay consist of organic-rich postglacial mud, sand, and glacial clay. CH_4 fluxes at sediment/water interface, pore water concentrations of SO_4^{2-} , CH_4 , and H_2S , and ^{35}S -sulfate reduction rates were measured in the spring, summer, autumn, and winter in the estuary at two stations, one close to the STP and one at a reference site outside the estuary. Additionally, sea-air fluxes and CH_4 water column concentrations were measured at the two stations.

Benthic methane fluxes were determined from ex-situ incubations and showed seasonal and spatial variations. The lowest CH_4 flux ($0.1 \text{ mmol m}^{-2}\text{d}^{-1}$) was observed in winter at the reference site and the highest CH_4 flux ($8.74 \text{ mmol m}^{-2}\text{d}^{-1}$) was recorded in the summer in Himmerfjärden sediment. For the other seasons, CH_4 fluxes at both stations were between $1 \text{ mmol m}^{-2}\text{d}^{-1}$ and $2 \text{ mmol m}^{-2}\text{d}^{-1}$. Sulfate reduction rates showed spatial variability and were consistently 10-fold higher in Himmerfjärden ($\sim 0.3 \mu\text{mol cm}^{-3}\text{d}^{-1}$) than at the reference site. There was a distinct zone of organoclastic sulfate reduction in both sediments at 3-7 cm depth. In the contaminated sediments near the STP, the sulphate-methane transition zone (SMT) was observed persistently during the year at depths 12-16 cm, indicating the presence of anaerobic methane oxidation, but was not detected above 40 cm depth at the reference site. Water column CH_4 concentration profiles showed that the sediments are the major source of CH_4 in the water column, as there was a pronounced increase in concentrations towards the bottom. Near-bottom water CH_4 concentrations were between 109 and 131 nmol/l . Concentrations at the surface were generally two-fold lower indicating efficient methane oxidation in the water column. Nevertheless, surface waters at both stations were oversaturated with respect to CH_4 throughout the year indicating that Himmerfjärden is an annual net source of CH_4 to the atmosphere.