Carbon sequestration and dating - the potential of earthworms and calcium carbonate

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“It may be doubted whether there are many other animals which have played so important a part in the history of the world, as have these lowly organized creatures.”

Darwin, 1881
…several small, or two or three larger, or a single very large concretion of carbonate of lime as much as 1.5 mm in diameter…they are often found in the gizzard, intestines and in the castings of worms…

Darwin, 1881
Canti and Piearce, 2003 after Darwin, 1881 and Robertson, 1936

Morgan, 1981

Gago-Duport et al. 2008
Why study earthworm calcite?

Role in C biogeochemistry

$\text{CaCO}_3$
Why study earthworm calcite?

Dating potential

$\text{CaCO}_3$

$\text{U} / \text{Th}$ $^{14}\text{C}$
Why study earthworm calcite?

Palaeoindicators?

\[
\text{CaCO}_3 \quad \delta^{13}\text{C} \quad \delta^{18}\text{O}
\]
What I’m going to talk about

• What is the function of granules?
• At what rate are granules produced?
• How long do granules last?
• Role in C cycle
• Can they be used for dating?
What is the function of granules?

- Elimination of excess Ca
- Neutralisation of gut pH
- Fixing metabolic CO$_2$
- Osmoregulation
What I’m going to talk about

• What is the function of granules?
• **At what rate are granules produced?**
• How long do granules last?
• Role in C cycle
• Can they be used for dating?
Production experiment 1: Soil

• 11 contrasting soils
• 1 earthworm per 300 g soil
• 27 days
Production experiment 1: Soil
Production experiment 1: Soil
Production experiment 1: Soil
Production experiment 1: Soil

- pH related to granule production
- No correlation with organic matter content, bulk or exchangeable elements
Production experiment 1: Soil

• Average production rate =
  – 0.75 mg calcite day\(^{-1}\)

• 300 earthworms per square metre

• Average production rate
  – 82 g calcite m\(^{-2}\) yr\(^{-1}\)
  – 98 kg C ha\(^{-1}\) yr\(^{-1}\)
Putting the carbon into perspective

• Average production rate
  – 82 g calcite m\(^{-2}\) yr\(^{-1}\)
  – 98 kg C ha\(^{-1}\) yr\(^{-1}\)

• Typical C sequestration in soil
  – 300 to 800 kg C ha\(^{-1}\) yr\(^{-1}\)

• Typical CO\(_2\) fluxes from soil
  – 600 – 37800 kg C ha\(^{-1}\) yr\(^{-1}\)
Production experiment 1: Soil

• pH related to granule production

• Maybe not production but production + dissolution
What I’m going to talk about

• What is the function of granules?
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Granule dissolution

• Granules are found in Quaternary soils (2Ma BP to now)
• But we are not knee deep in granules
• Need to know dissolution kinetics to model survival
Dissolution experiment 1: Leaching

- Three soils
- Mix granules into soil
- Keep soil moist
- Saturate soil, collect leachate
- Monitor granule mass loss and solution chemistry
Dissolution experiment 1: Leaching

- **Hamble**
- **Soil Science**
- **St Albans**

![Graph showing mean granule weight loss over days for different locations.]

- Day 0 to Day 200
- Mean granule weight loss in %
Production experiment 1: Soil

- pH related to granule production

- Granules don’t dissolve rapidly enough for this trend to be due to dissolution
Dissolution experiment 2: Flow through

- Flow through reactors
- \( \text{NaHCO}_3 \) matrix to buffer alkalinity and pH
- Iceland spar dissolved as a “control”
Dissolution experiment 2: Flow through
Dissolution experiment 2: Flow through

Dissolution rate = \[
\frac{\text{Ca concentration} \times \text{flow rate}}{\text{surface area available for dissolution}}
\]

But also, empirically

Dissolution rate = k(1-Ω)^n
Dissolution experiment 2: Flow through

Dissolution rate = \[ \frac{Ca \text{ concentration } \times \text{ flow rate}}{\text{surface area available for dissolution}} \]

But also, empirically

Dissolution rate = k(1-\Omega)^n
Dissolution experiment 2: Flow through

- Fit to the empirical rate equation

\[ \text{dissolution rate} = k(1-\Omega)^n \]

![Graph showing dissolution rates for different samples. Spar BET and Spar Geom have \( n = 2.7 \) and Granule BET and Granule Geom have \( n = 3.8 \).]
Dissolution experiment 2: Flow through

\[
\text{Dissolution rate} = \frac{\text{Ca concentration} \times \text{flow rate}}{\text{surface area available for dissolution}}
\]

But also, empirically

\[
\text{Dissolution rate} = k(1-\Omega)^n
\]
Dissolution experiment 2: Flow through

- Fit to the empirical rate equation

\[ \text{dissolution rate} = k(1-\Omega)^n \]
Dissolution experiment 2: Flow through

Fig. 8. Comparison of some published calcite dissolution rates with rates calculated in the present study.
Dissolution experiment 2: Flow through

- Use constants in SLIM model
- Model predicts dissolution of calcium carbonate in soil
- Model parameters:
  - Dissolution constants
  - pH
  - Flow rate
  - Cation exchange capacity
  - Ca on exchange sites
  - Solution chemistry

Fig. 4, Calculations carried out with Eq. [22] for particle sizes of 1.28 mm, 0.60 mm ○, 0.28 mm △, and 0.14 mm □ together with data (Biphick, 1955). By adjusting the mass transfer rate coefficient $k_t$, the model could be fit to all sets of data.

Warfvinge and Sverdrup, SSMJ 53 (1989) 44 – 51
Dissolution experiment 1: Leaching
Steady state experiment

- Look at production over time
- 42 reps.
- Sample 6 reps after 7, 14, 28, 63, 91, 126 days

Production = dissolution

mg calcite vs. time
Steady state experiment

- Hamble
- Soil Science
- St Albans
Steady state experiment
Steady state experiment

![Graph showing the mass of granules produced over time for different locations: Hamble, Soil Science, and St Albans.](image-url)
Steady state experiment

![Graph showing the mass of granules produced over time for different locations: Hamble, Soil Science, and St Albans. The graph illustrates the relationship between time (in days) and the mass of granules produced (in grams). The data points are connected by lines, and error bars indicate the variability in the measurements.]
Steady state experiment

- Steady states of 0.1 g calcite per earthworm
- 1 m\(^{-2}\) of soil could contain 30 g of earthworm derived calcite
- This is equivalent to 3.6 g of carbon
- In context 1 m\(^{-3}\) of soil might contain
  - 1400 kg of soil
  - 70 kg of organic matter
  - 35 kg of organic C
- Earthworms aren’t going to save us from global warming!
- N.B. fluxes
What I’m going to talk about

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• At what rate are granules produced?
• How long do granules last?
• **Role in C cycle**
• Can they be used for dating?
Role in C cycle

Fig. 2. Soil organic matter - atmospheric CO$_2$ - water three-way component concentration weighted stable isotope mixing diagram for earthworms using our preliminary experimental data. The solid triangle in the centre is the mean value for earthworm granules allowing a quantification of the relative proportions of the end member components to be assessed. In this case, CO$_2$ from air makes up c. 50% of the C and O in the granule and is one of the main dominant features. Model after Phillips & Koch$^{11}$. 
What I’m going to talk about

• What is the function of granules?
• At what rate are granules produced?
• How long do granules last?
• Could they play a role in controlling metals?
• Role in C cycle
• Can they be used for dating?
Dating potential

Fig 3. U-series isochron plot of multiple analyses of earthworm granules from Silbury Hill. The earliest date for this is circa 4400 ca. B.P. which is consistent with the U-Series age for the carbonate granules, indicating they are contemporaneous with the soil formation.
Summary: Granule....

• ...production rate is influenced by soil pH and earthworm weight

• ...production rates account for significant fluxes of C in soil systems - 98 kg C ha\(^{-1}\) yr\(^{-1}\)

• ...account for a small pool of soil carbon – 36 kg ha\(^{-1}\)

• ...dissolution is similar to inorganic calcite

• ...dissolution is governed by pH (and flow rates, exchange sites etc.)

• ...can last in soils for 10 000s years and record appropriate dates

• ...contain a significant proportion of “atmospheric” C and O
Where next?

- Palaeotemperature indicators
But no one knows what they are for!