

Pedogenic carbonates as a proxy for palaeo-CO₂ in the Palaeozoic atmosphere

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Received 30 April 2004; received in revised form 9 April 2006; accepted 28 May 2006

Abstract

According to a model by Cerling [Cerling, T. E., 1991. Carbon dioxide in the paleoatmosphere: evidence from Cenozoic and Mesozoic paleosols. *Am. J. Sci.* 291, 377–400, Cerling, T. E., 1999. Stable carbon isotopes in palaeosol carbonates. In: Thiry, M., Simon-Coinçon, R. (Eds.), *Palaeoweathering, Palaeosurfaces and Related Continental Deposits*. vol. 27 of *Spec. Publ. Int. Assoc. Sediment.*, pp. 43–60], the carbon isotope composition of calcretes should depend on the soil type and the CO₂-concentration in the atmosphere. We have tested Cerling's model by investigating 14 Palaeozoic sections with soil profiles. A large number of carbonate types of different genetic origin exist in the localities examined. Comparing the Palaeozoic samples with recent and subrecent calcretes, it can be demonstrated that anhedral, cryptocrystalline (<10 μm) and subhedral microcrystalline (10–40 μm) carbonates are clearly of pedogenic origin. Crystals of larger size with a poikilotopic texture are of groundwater or burial diagenetic origin. Macro- and micromorphological features, typical of recent calcretes, occur in several soil profiles, but thin section microscopy reveals a strong diagenetic overprint of most pedogenic carbonates. Time equivalent sections with comparable soil types (protosols, calcisols and vertisols) show large variations in carbon isotope composition. On the other hand, different carbonate generations at one site do not differ much. Therefore Palaeozoic calcretes appear to be unsuitable for a deduction of the Palaeozoic CO₂-concentration.

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Keywords: Palaeoatmosphere; Carbon dioxide; Palaeosols; Palaeozoic; Stable isotopes

1. Introduction

Several approaches have been used to estimate the Earth's atmospheric CO₂-concentrations in the geological past. Among them is the GEOCARB-model of Berner (1991, 1994) the most prominent. Carbon isotopes in calcretes have been used as another tool to estimate the

atmospheric concentration of CO₂ (Cerling, 1991, 1999). The Cerling model is based on differences between ¹³C/¹²C-ratios in atmospheric and plant respired CO₂. It describes the relationship between both types of CO₂ as a function of depth in the soil profile. Below a depth of about 50 cm the δ¹³C value of soil CO₂ is nearly constant (Fig. 1). Assuming that pedogenic carbonates will retain this isotopic signal, the latter can be used to infer palaeoatmospheric CO₂.

Cerling (1991) uses a diffusion–production equation to model the contributions of atmospheric and soil respired CO₂ in the soil atmosphere. Davidson (1995) has simplified

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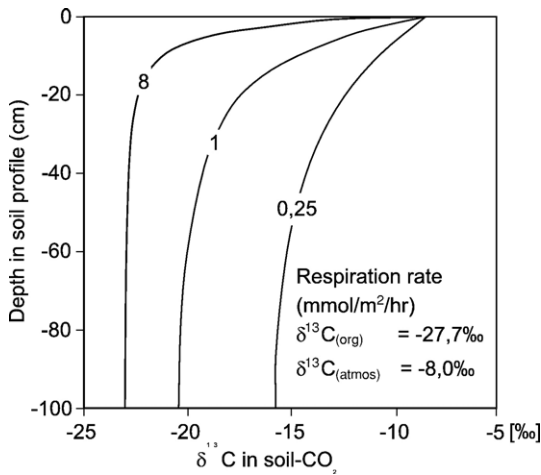


Fig. 1. C-isotope ratio of soil-CO₂ calculated with different respiration rates (after Cerling and Quade, 1993).

the equation to estimate the palaeoatmospheric CO₂ concentration:

$$C_{\text{air}} = S(z) \frac{\delta^{13}C_s - 1.0044 \delta^{13}C_\phi - 4.4}{\delta^{13}C_{\text{air}} - \delta^{13}C_s} \quad (1)$$

where C_{air} is the concentration of atmospheric CO₂, S is the amount of soil respired CO₂ as a function of depth (z) and $\delta^{13}C_s$, $\delta^{13}C_{\text{air}}$, $\delta^{13}C_\phi$ are the isotopic compositions of soil CO₂, atmospheric CO₂ and soil respired CO₂ respectively.

Eq. (1) is suitable as an atmospheric CO₂-palaeobarometer if several assumptions are fulfilled. Isotopic composition of soil CO₂ is reflected by soil carbonates, that precipitate in equilibrium with the soil CO₂ and below a depth of 50 cm (Cerling, 1991, 1999). Assumptions are required for the concentration and isotopic composition of soil respired CO₂ ($S(z)$, $\delta^{13}C_\phi$) and also for the isotopic composition of the atmospheric CO₂ ($\delta^{13}C_{\text{air}}$), which introduces uncertainties in the Cerling model (Ekart et al., 1999; Royer et al., 2001).

For an estimate of palaeoatmospheric CO₂-concentrations calcretes need to be distinguished from other terrestrial carbonates. Palustrine and even lacustrine carbonates, if in nearshore position, can display root traces and micromorphological fabrics similar to pedogenic carbonates (Fig. 2). Soil carbonates used for CO₂ estimates must have precipitated in the vadose zone in exchange with atmospheric CO₂. Carbonates formed in a carbonate hostrock have to be avoided, because of the risk of inherited isotopic signatures.

1.1. Definition and classification of pedogenic carbonates (calcretes) and paleosols

There is no uniform definition of the term calcrete in the literature (e.g. Lamplugh, 1902; Netterberg, 1967; Goudie, 1973; Freydet and Plaziat, 1982; Machette, 1985; Alonso-Zarza, 2003). Netterberg (1967) defined calcretes as carbonates precipitated from supersaturated soil- or groundwaters near the soil surface. We use the term *groundwater carbonate* for all kinds of carbonates precipitated in the phreatic soil zone (Fig. 2). The term calcrete is used exclusively for carbonates from the vadose zone.

Netterberg (1980), Goudie (1983), Machette (1985) provided a classification of calcretes based on morphological features, which also reflects stages of successive calcrete development (Fig. 3). Stages 1 to 6 reflect an increase in maturity. These stages are almost equivalent to calcretes types.

Macro- and micromorphological fabrics are a clue of terrestrial carbonate origin (Wright and Tucker, 1991; Pimentel et al., 1996; Khadkikar et al., 2000). As it is important to distinguish between pedogenic and groundwater derived carbonates some criteria are discussed below:

An *asymmetric vertical distribution* of carbonate within a soil profile is one feature of pedogenic carbonates. In most cases a gradual lower and a sharp

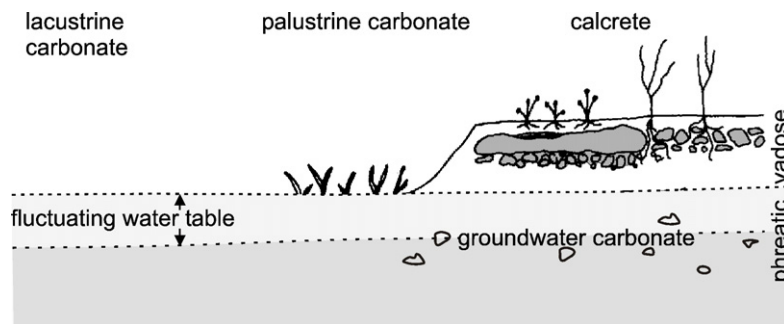


Fig. 2. Different kinds of terrestrial carbonate with similar micromorphology (after Freydet and Plaziat, 1982).

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