

# Pedogenic carbonates as a proxy for palaeo-CO<sub>2</sub> in the Palaeozoic atmosphere.

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## Abstract

According to a model by Cerling (1991, 1999), the carbon isotope composition of calcretes should depend on the soil type and the CO<sub>2</sub>-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 CO<sub>2</sub>-concentration.

**Keywords:** palaeoatmosphere, carbon dioxide, palaeosols, Palaeozoic, stable isotopes

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## 1 Introduction

Several approaches have been used to estimate the Earth's atmospheric CO<sub>2</sub>-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 CO<sub>2</sub> (Cerling 1991, 1999). The Cerling model is based on

differences between <sup>13</sup>C/<sup>12</sup>C ratios in atmospheric and plant respired CO<sub>2</sub>. It describes the relationship between both types of CO<sub>2</sub> as a function of depth in the soil profile. Below a depth of about 50 cm the δ<sup>13</sup>C value of soil CO<sub>2</sub> is nearly constant (Fig. 1). Assuming that pedogenic carbonates will retain this isotopic signal, the latter can be used to infer palaeoatmospheric CO<sub>2</sub>.

Cerling (1991) uses a diffusion-production equation to model the contributions of atmospheric and soil respired CO<sub>2</sub> in the soil atmosphere. Davidson (1995) has simplified the equation to estimate the palaeoatmospheric CO<sub>2</sub> concentration:

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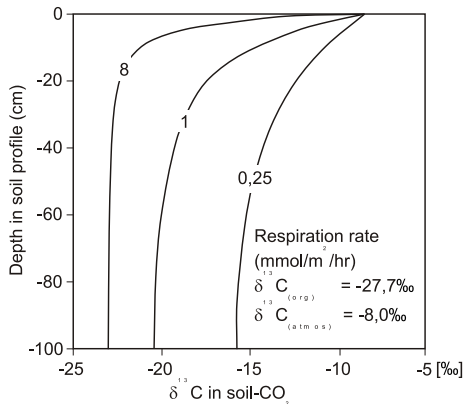


Figure 1. C-isotope ratio of soil-CO<sub>2</sub> calculated with different respiration rates (after Cerling and Quade 1993).

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

where  $C_{\text{air}}$  is the concentration of atmospheric CO<sub>2</sub>,  $S$  is the amount of soil respired CO<sub>2</sub> 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-CO<sub>2</sub>, atmospheric CO<sub>2</sub> and soil respired CO<sub>2</sub> respectively.

Equation (1) is suitable as an atmospheric CO<sub>2</sub>-palaeobarometer if several assumptions are fulfilled. Isotopic composition of soil CO<sub>2</sub> is reflected by soil carbonates, that precipitate in equilibrium with the soil CO<sub>2</sub> and below a depth of 50 cm (Cerling 1991, 1999). Assumptions are required for the concentration and isotopic composition of soil respired CO<sub>2</sub> ( $S(z)$ ,  $\delta^{13}C_\phi$ ) and also for the isotopic composition of the atmospheric CO<sub>2</sub> ( $\delta^{13}C_{\text{air}}$ ), which introduces uncertainties in the Cerling model (Ekart et al. 1999, Royer et al. 2001).

For an estimate of palaeoatmospheric CO<sub>2</sub>-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 CO<sub>2</sub> estimates must have precipitated in the vadose zone in exchange with atmospheric CO<sub>2</sub>. 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, Freytet 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). Stage 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

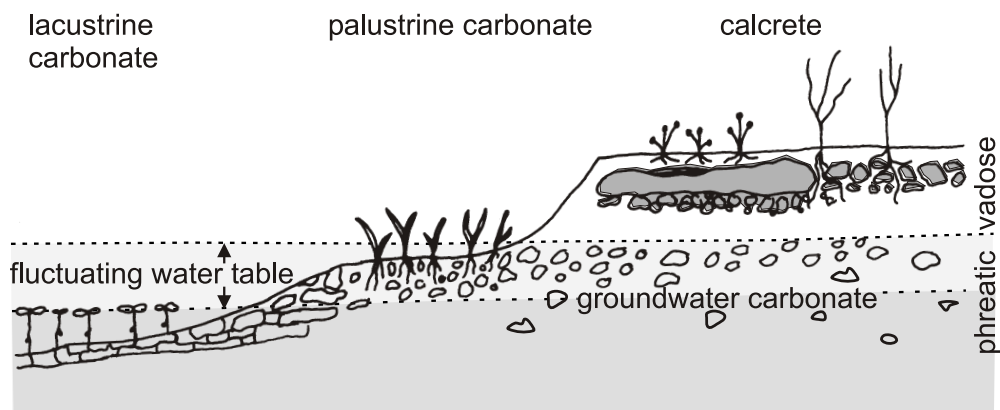


Figure 2. Different kinds of terrestrial carbonate with similar micromorphology (after Freytet and Plaziat 1982)

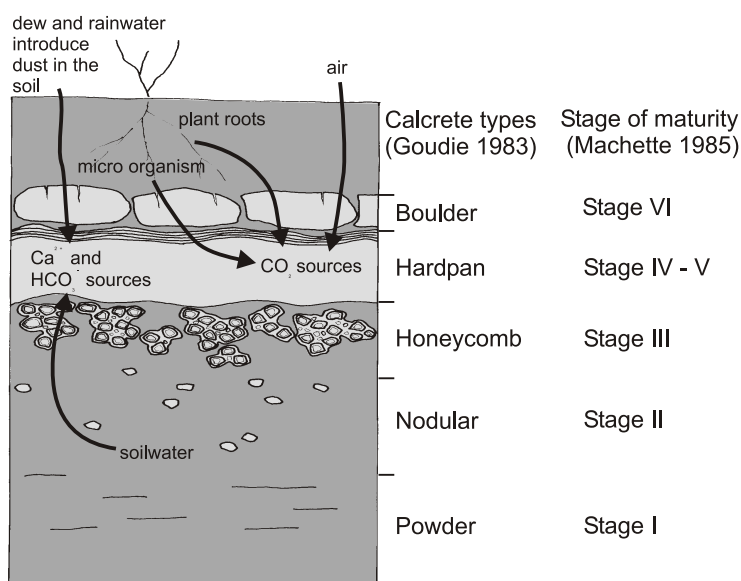


Figure 3. Idealised scheme of calcrete types and stages of maturity, sources of carbonate in soils.

sharp upper boundary of carbonate precipitation is observed. However this criterion does not fit in all cases. E.g. calcretes formed under varying climatic conditions and in association with a repeated soil development normally fail to display an asymmetric profile (Marriott and Wright 1993). If palaeosols are truncated or have experienced repeated soil development, the reconstruction of the original depth of carbonate accumulation is difficult or impossible (Cojan 1999).

*Granular cracks* are fractures in and around carbonate concretions, normally filled with micro- to finely crystalline carbonates. They are thought to reflect alternating wet and dry

conditions during carbonate growth in the vadose soil zone (Khadkikar et al. 2000, Retallack 1990, Wright et al. 1993). Movement and rotation of concretions due to pedoturbation may also lead to granular cracks.

*Clotted textures* are fabrics of dense (cryptocrystalline) concretions in a coarser matrix of microcrystalline carbonates. Clotted textures are very common in mature calcretes (honeycomb to boulder calcretes, Fig. 3) and thought to be formed by coalescence of pre-existing nodules in a vadose environment (Wright and Tucker 1991).

*Floating grains* are isolated clastic grains in a carbonate matrix. They are not in contact with other clastic grains and are formed by dis- and replacement of siliciclastic soil components due to carbonate precipitation (Goudie 1983). Floating grains are typically found in the vadose zone (Freytet and Plaziat 1982, Khadkikar et al. 2000).

*Exploding grains* are clasts brecciated and dispersed by carbonate growth. Often floating grains show such a breakage. Khadkikar et al. (2000) assume that water penetrates grains along microfractures. Repeated wetting and drying in the vadose zone supports carbonate precipitation along microfractures.

Unfortunately, most palaeosols of Palaeozoic age are altered by diagenetic processes and many features are lost during geologic history. Therefore, the nomenclature of recent soils cannot be used without modifications. In this paper the nomenclature of Mack et al. (1993) is applied. It utilizes the most prominent macromorphological features preserved in a palaeosol. The palaeosols in this study are classified as protosols, calcisols and vertisols. According to Mack et al. (1993) all of these classes can provide calcretes. Calcisols therein are soils, which comprise a prominent horizon of carbonate accumulation. Protosols provide evidence of pedogenesis, including root traces or peds, but they lack any prominent pedogenic horizontation. Vertisols may display horizontation but their diagnostic feature is a strong pedoturbation, revealed by deep tracking desiccation cracks and pseudo-anticlines, which are curved and intersected slip and shear planes within the soil profile. They are thought to be formed due to clay shrinking and swelling in seasonally wetted and dried soils and there-

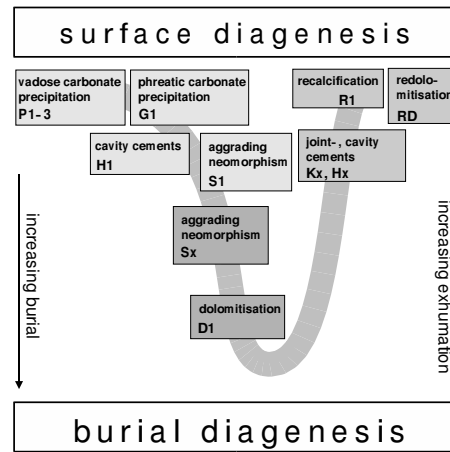


Figure 4. Carbonate types attributed to different diagenetic stages.

fore are features of the vadose soil zone (Yaalon and Kalmar 1978, Soil Survey Staff 1975, Khadkikar et al. 2000).

## 1.2 Diagenesis

The carbonate types at the different localities are described and classified as representing early, burial and very late diagenetic stages, where calcretes and groundwater carbonates are understood as early diagenetic formations from the vadose and phreatic environment respectively. Origin of the different carbonate types at each locality is discussed below (Fig. 4).

### 1.2.1 Carbonate precipitation

*Crypto- and microcrystalline carbonates* Brewer (1964), Knox (1977) and Khadkikar et al. (2000) found that clotted textures formed by microcrystalline carbonates, that enclose small patches of cryptocrystalline carbonates, are a common feature of recent and subrecent calcretes. The cryptocrystalline carbonates are usually anhedral, whereas the surrounding microcrystalline crystals often display remarkable rhombohedral shapes (Folk 1971, Wright and Peeters 1990). A dull brown or grey

occurrence of cryptocrystalline carbonates is attributed to an incorporation of clay minerals during carbonate precipitation in the vadose zone (Wieder and Yaalon 1982). Vadose carbonates usually have low Fe- and Mn-concentrations and variable but low Sr-contents from 60 to 220 ppm (Khadkikar et al. 2000, Morad et al. 1998). For carbonates representing crypto- and microcrystalline carbonates we use abbreviation P1 and P2 respectively in this study.

*Microcrystalline hem-carbonates* Klappa (1983), Wright et al. (1993) and Balin (2000) describe microcrystalline carbonates forming rims around clasts and fingering into surrounding carbonates. Although vadose rim cements usually appear on the downsides of clasts, pedogenic turnover often leads to rim cements that lack orientation (Wright et al. 1993). Microcrystalline hem-carbonates found in the sections are termed P3.

*Poikilotopic calcites* Friedman (1965) describes coarser sized poikilotopic cements that fill spaces between sedimentary grains and also enclose single clasts. Poikilotopic calcites have been found from meteoric phreatic but also from deep burial environments (Folk 1974, Scholle 1979, Beckner and Mozley 1998, Adams and MacKenzie 2001). Low sediment compaction within the cemented parts of rock, indicates an early diagenetic formation of poikilotopic calcites, which precipitate almost without affecting stratification (Beckner and Mozley 1998, Garcia et al. 1998). Garcia et al. (1998) and Morad et al. (1998) found low Fe-concentrations in early diagenetic poikilotopic calcites. Poikilotopic calcites with a uniform appearance under cathodoluminescence, are formed in the phreatic rather than the vadose zone (Beckner

and Mozley 1998). Similar calcites are abbreviated as G1.

### 1.2.2 *Aggrading neomorphism*

Aggrading neomorphism describes the alteration of pre-existing carbonates accompanied by an increase in crystal size, but without changes in overall chemistry (Folk 1965). Neomorphic carbonates have to be separated from mesogenetic cements. They often replace small amounts of carbonate, whereas mesogenetic cements occur pervasively.

*Micro- to coarsely crystalline calcites* Neomorphic formation of micro- to coarsely crystalline carbonates is indicated by the occurrence of concavo-convex crystal contacts and by enclosures of smaller patches of crypto- and microcrystalline crystals (Folk 1965, Bathurst 1975). Corrosive contacts to clastic grains and jagged margins to other crystals rule out a mesogenetic cement origin for these carbonates (Bathurst 1975, Füchtbauer 1988). Abbreviation used is S1 to Sx.

### 1.2.3 *Dolomitisation, dedolomitisation and redolomitisation*

*Micro- to coarsely crystalline, rhombohedral dolomites* Spötl and Wright (1992), Garcia et al. (1998) and Worden and Matray (1998) have demonstrated a burial origin of coarser crystalline, rhombohedral dolomites and ankerites within a sandstone matrix. According to our nomenclature they are D1-dolomites.

*Crypto- to microcrystalline, anhedral calcites* Clark (1980), Judersleben and Voigt (1993), Al-Hashimi and Hemingway (1973) found patches of crypto- to microcrystalline calcites that imitate coarser rhombo-

hedral crystals and therefore indicate a recalcification of former dolomites. Rhombohedral hydroxide rims may indicate a pre-existing dolomite too (Richter 1974, Richter 1985). A late near-surface recalcification is assumed for such carbonates (Al-Hashimi and Hemingway 1973, Morad et al. 1995). Low magnesium calcites (LMC) with low Fe-content are in agreement with late near-surface recalcification. Calcites of similar origin are abbreviated with R1.

*Crypto- to microcrystalline, anhedral and microcrystalline, subhedral dolomites* that imitate coarser rhombs are thought to be redolomites (Clark 1980). Some larger crystals floating within the crypto- to microcrystalline matrix can testify a former presence of coarser euhedral dolomites. Abbreviation for this dolomite type is RD.

#### 1.2.4 Carbonate cements in fractures and caves

*Micro- to coarsely crystalline, subhedral carbonates* Cements in root traces and early solution cavities are often thought to be early diagenetic in origin because of the preservation of the cavity structures (Retallack 1990). Other micro- to coarsely crystalline, subhedral calcites can be found within post burial fractures and caves. Abbreviation for similar carbonates is H1 to Hx and Kx respectively.

## 2 Methods

14 localities with palaeosols from Lower Devonian to Lower Permian age were selected (Fig. 5). The localities are assigned to three time intervals. Each interval comprises of

20 to 30 million years. One or more stratigraphic sections were measured and described from each time interval in order to provide data from Edinburgh comparable paleosol morphologies across the entire time scale studied. Sections were sampled at depths comprising carbonate concretions or horizons. Samples were cut into 2 halves and one piece was polished. Powders for stable isotope measurements (10 to 20 mg) were obtained from the polished half by micro-drilling. A binocular microscope has been used to drill patches of 2 to 5 mm with optically uniform carbonates, which was verified by thin sections taken from the other half of sample (Table 1).

Carbon and oxygen isotope ratios have been measured with a Finnegan MAT 251 by the method of McCrea (1950). Extractions were run 24 hours at 25° C. Carbon and oxygen isotope ratios are given in the standard permil notation with respect to the PDB standard. Inhouse working standard Solnhofen 1 has been used routinely. Analytical uncertainty is 0,1‰ for  $\delta^{13}\text{C}$  and 0,2‰ for  $\delta^{18}\text{O}$ . The phosphoric acid liberation of  $\text{CO}_2$  produces differences in oxygen isotope composition from calcite and dolomite that have to be considered (Rosenbaum and Sheppard 1986, Sharma et al. 2002, Hoefs 2003). Because there is no consensus about the correct fractionation factor and the samples investigated are often mixtures of both carbonates, we give raw data without correction.

A Zeiss Axiolab microscope with a Citl cathode CL8200MK3A is used for cathodoluminescence observations. Element analysis is performed with a Jeol JXA 8900 RL electron microprobe. Measured concentrations were automatically corrected with the software CITAF (Armstrong 1995). Qualitative and quan-

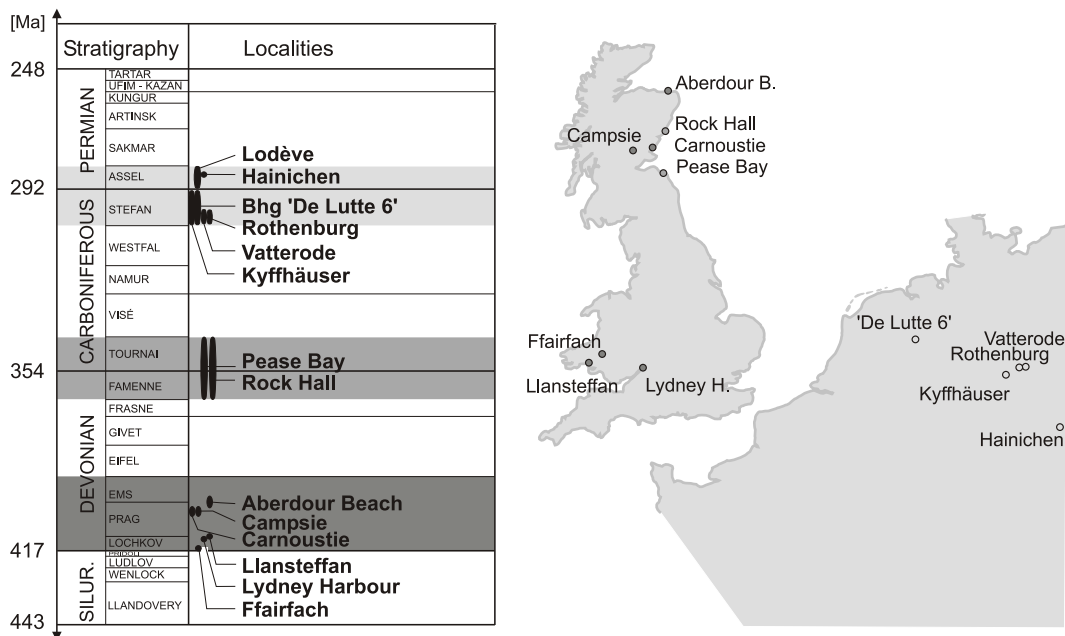


Figure 5. Stratigraphical and geographical position of the examined localities

titative carbonate analyses were performed by staining thin sections with Alizarin-S and potassium ferrocyanid, X-ray diffractometry and coloumetric carbonate content determination (Evamy and Shearman 1962, Dickson 1966, Müller and Gastner 1971). A Philips PW 1800 is used for X-ray diffractometry. Calcite and dolomite contents are determined semiquantitatively by comparison of the (104)-calcite and d(104)-dolomite peaks using laboratory standards (Faupel and Thomson 1989). Ca/Mg-ratio of dolomite is calculated by using the d(104)-dolomite peak (Lumsden 1979).

### 3 Descriptions and interpretations of sites and soils

The investigated localities were selected from recent literature (Table 1). Detailed field work has revealed, however, that some sites provide no suitable calccrete or even palaeosols (Quast 2003). The carbonate types found at the localities are described from the locations where they are best examined. Fig. 6 sum-

Site	P1-3	G1	S1	Sx	D1	R1	RD	Hx, Kx
Llansteffan	○	X	X	X	X	X		X
Lydney	○			X	X			X
Ffairfach	○							
Carnoustie	○							
Campsie	X	X	X					X
Aberdour	○							
Pease Bay	○			X				
Rock Hall	○			X				
Vatterode	X		X					X
Rothenburg	○	X		X	X	X	X	X
Kyffhäuser	○							
Hainichen	X		X					X
Well De Lutte 6	○	X						X
Lodève	○				X	X		

X: carbonate type was found at this site  
○: former occurrence of carbonate type is indicated by sedimentological evidence

Figure 6. Carbonates types found or inferred from sedimentological evidence at each locality. Abbreviations for carbonate types are given in the text. Hx- and Kx-carbonate types are attributed to early and very late diagenetic stages.

marises the carbonate types observed or inferred by sedimentological evidence at each locality.

#### 3.1 Lower Devonian sites

The Welsh sites *Llansteffan*, *Lydney Harbour* and *Ffairfach* contain protosols, vertisols and calcisols within fluvial sediments of a coastal plain (Allen 1964, Friend and Williams 1978). Various soils are developed as indicated by pseudo-anticlines, root traces and an upward loss of strat-

Table 1  
Localities of paleosols and their classification

Locality/ Section	National Grid	Lithostratigraphy	Environment	Soil	Calcrete stages*	Methods	References
Llansteffan	1 SN 350 099	Red Marl Fm.	Coastal-plain	2 Protosols, 2 Vertisols	NC, HC, HP	TS, CL, EMS, XRD	Allen (1964), Friend and Williams (1978)
	2			1 Protosol	NC		
	3			1 Vertisol	NC, HC		
Lydney Harbour	1 SO 512 741	Raglan Marl Group	Coastal-plain	1 Calcisol, 1 Vertisol	NC, HP	XRD	Allen (1964), Friend and Williams (1978)
	2			1 Protosol, 1 Vertisol	NC		
Ffairfach	1 SN 191 610	Red Marl Fm.	Coastal-plain	1 Protosol ?	NC		Quast (2003)
	2			1 Protosol	NC		
Campsie	1 NO 124 328	Garvock Group	Alluvial-fan	2 Calcisols	NC, HP, BC	TS, CL, EMS, XRD	Friend and Williams (1978)
	3	Strath Rory Group	Alluvial-plain	1 Protosol, 1 Calcisol	NC, HP		
Carnoustie	NO 570 345	Garvock Group	Alluvial-fan and -plain	1 Protosol	NC		Friend and Williams (1978), Saigal and Walton (1988)
Aberdour Beach	1 NJ 658 884	Crovie Group	Alluvial-fan and -plain	1 Calcisol	NC, HC	XRD	Friend and Williams (1978) , Trewin and Kneller (1987)
	2			1 Protosol ?	NC		
Pease Bay	3 NT 792 721	Kinnesswood Fm.	Alluvial-fan and -plain	2 Protosols	—		Wright et al. (1993)
	4				NC		
Rock Hall	1 NO 768 647	UORS	Alluvial-fan and -plain	2 Protosols	—	TS, XRD	Trewin (1987), Balin (2000)
	2				NC		
Vatterode	R 44 6039/ H 57 1835	Untere Mansfeld Subgroup	Alluvial-fan and -plain	3 Calcisols, 1 Protosol	NC, HC, HP, BC	TS, CL, EMS, XRD	Gebhardt (1988), Schneider and Gebhardt (1993)
	1 R 44 8294/ H 57 2278	Untere Mansfeld Subgroup	Alluvial-fan and -plain	1 Protosol	NC	TS, EMS, XRD	Gebhardt (1988), Schneider and Gebhardt (1993)
2				2 Calcisols, 3 Protosols	NC, HC		
Kyffhäuser	R 44 3561/ H 56 9844	Untere Mansfeld Subgroup	Alluvial-fan and -plain	1 Calcisol	NC		Paul (2004)
Hainichen	—	Härtensdorf Fm.	Alluvial-fan and -plain	1 Protosol	NC	TS	Schneider and Rößler (1995)
Core De Lutte 6	—	Limburg Fm.	Alluvial-plain	5 Protosols	NC		Pagnier and v. Tongeren (1996)
Lodève	1 —	Viala Fm.	Alluvial-plain	1 Calcisol	—	TS, XRD	Körner et al. (2001)
	2				NC, HP		

\* Abbreviations given for calcrete stages and analytical methods: NC: nodular calcrete - HC: honeycomb calcrete - HP: hardpan - BC: boulder calcrete, TS: thinsections - CL: cathodoluminescence - EMS: electron microprobe analysis - XRD: X-ray diffractometry



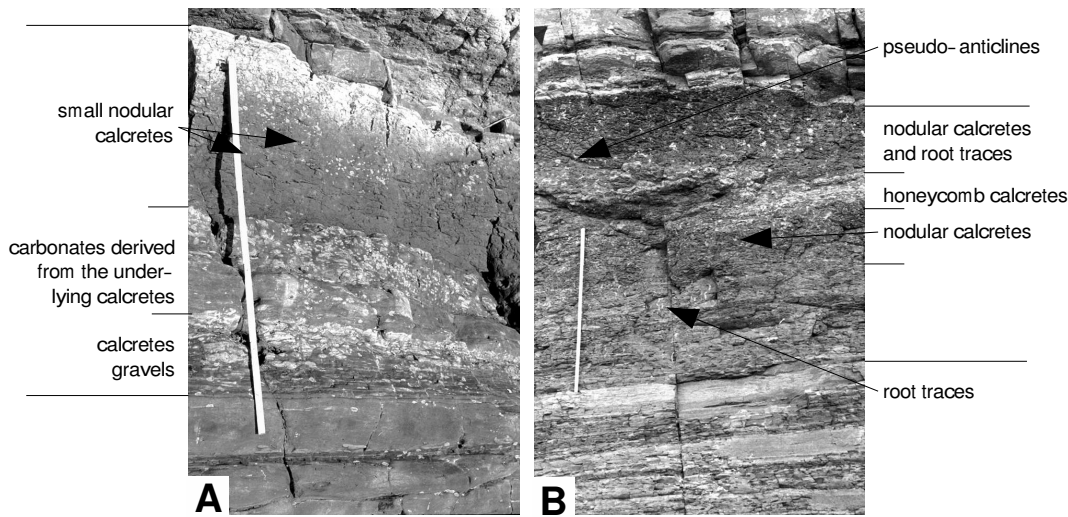


Figure 7. Well developed paleosols A) protosol in section Llansteffan 2 with light brown horizontal aligned calcrete gravels at its base, a horizon comprising carbonates derived by dissolution of the latter and some small in situ calcretes near the top of soil. B) vertisol at the section Llansteffan 3 comprises root traces, pseudo-anticlines and various calcrete stages at different soil levels. Scale is 1 m at each section.

ification. Pedogenic, groundwater, reworked and diagenetic carbonates were found (Fig. 7). Section Llansteffan 2 for example displays carbonates from different origin within a protosol. At the base of the protosol, horizontal and lenticular concretions occur within well bedded sediments (Fig. 7A). Their occurrence and their vertical position in the profile excludes vadose formation within the soil. On the other hand, they display granular cracks, floating grains and sharp margins, often observed in pedogenic carbonates from other sites. Therefore, reworking, abrasion and fluvial transport is suggested for these carbonates, similar to the calcrete gravel Marriott and Wright (1996) have described at this locality. Above the calcrete gravels isometric concretions occur. Upwards, the number and size of concretions decrease rapidly. They were formed most likely by dissolution of the underlying calcrete gravels. Above a zone that lacks any concretions, smaller concretions appear in the upper part of protosol together with root traces. They are sharply bounded to the sediment. Due to their vertical position in the soil pro-

file, a pedogenic origin is suggested. In contrast to section 2 the section Llansteffan 3 provides a vertisol with carbonates exclusively of pedogenic origin. Carbonate precipitation is restricted to the vadose zone, which is indicated by pseudo-anticlines and a loss of stratification.

Although sedimentological evidence for pedogenesis is given for all localities, no P1 to P3 carbonates have been found at these sites. At Llansteffan micro- to finely crystalline Sx-calcites occur near stylolites and reveal a length growth normal to stylolites solution planes. Contemporaneous formation of Sx-calcites and stylolites is therefore postulated. Stylolites indicate a mesogenetic stage with moderate burial (Clark 1980, Bathurst 1983, Langbein et al. 1982). A second type of micro- to coarsely crystalline Sx-calcites enclose patches of pre-existing carbonates. Carbonate staining delineates the coexistence of calcite and dolomite within the patches. Therefore a rather complex carbonate generation is considered for the micro- to coarsely crystalline Sx-carbonate. It is a LMC with minor Fe-content (0.2%, Table 2).

Table 2

Element microprobe analysis results and calculated carbonate compositions

Locality	Carb. type	n	Ca		CaCO <sub>3</sub> (mol%)	Mg		MgCO <sub>3</sub> (mol%)	Fe		FeCO <sub>3</sub>		Mn		Sr	
			(wt%)	$\sigma$		(wt%)	$\sigma$		(ppm)	$\sigma$	(mol%)	(ppm)	$\sigma$	(ppm)	$\sigma$	
Campsie	P1	10	38.7	0.8	97.3	0.5	0.2	1.9	1185	659	0.2	3328	3288	313	222	
	P2	13	40.0	0.7	98.8	0.2	0.1	0.9	441	387	0.1	810	1103	143	227	
	P3	10	39.7	0.8	97.3	0.3	0.1	1.2	717	898	0.1	7793	6256	344	269	
	G1	6	39.5	0.4	98.3	0.2	0.1	0.7	570	258	0.1	4637	2091	1025	1288	
	S1	5	40.4	0.2	99.2	0.1	0.0	0.5	n.n.	–	0.0	1316	893	198	86	
	Hx	4	39.8	0.8	97.7	0.2	0.1	0.9	2024	3163	0.4	6095	2850	197	107	
	Kx	9	39.5	0.9	96.8	0.3	0.2	1.3	2675	3169	0.5	7685	2786	371	270	
	Llansteffan	Sx	3	38.0	0.6	96.9	0.6	0.2	2.5	1114	82	0.2	1685	338	539	72
Hx		1	39.5	–	97.7	0.2	–	0.8	n.n.	–	0.0	8522	–	110	–	
Kx		4	39.5	0.3	98.0	0.2	0.1	0.7	775	752	0.1	5647	3196	1557	1118	
Rothenburg	R1	6	39.4	0.8	98.4	0.3	0.1	1.3	1428	1402	0.3	237	246	172	129	
	Hx	3	40.2	0.3	99.3	0.2	0.1	0.6	176	249	0.0	31	38	175	82	
Vatterode	P1	9	21.8	0.3	50.6	12.5	0.4	47.8	2399	594	0.4	4960	3156	1847	848	
	P2	4	21.8	0.2	51.0	12.5	0.2	48.2	1296	358	0.3	2419	2424	1572	794	
	Hx	2	40.7	0.1	98.4	0.3	0.1	1.0	n.n.	–	0.0	3421	488	64	39	

Although such low Fe-content is unusual for carbonates formed during burial diagenesis, Saigal and Bjørlykke (1987) have found similar calcites from a shallow burial diagenesis. At Lydney Harbour fine to medium crystalline dolomite rhombs have replaced pedogenic and non-pedogenic carbonates. Internal fabrics were destroyed in almost all calcretes, but ghost structures reveal that carbonate originated from pedogenesis. Staining indicates low Fe-dolomites. Similarly low Fe-dolomites from Triassic sandstones have been formed during burial diagenesis (Morad et al. 1995).

*Campsie, Carnoustie and Aberdour Beach (Midland Valley, Orcadian Basin, Scotland)* contain calcisols and protosols from an alluvial-fan and -plain facies. Most sections from these sites lack root traces or peds, but macro- and micromorphological appearance of carbonates suggests a pedogenic origin. At Campsie 1 and 2 thick limestone horizons appear as coalesced carbonate concretions comprising granular cracks and clotted textures. Some floating and exploded grains suggests a strong dis- and replacement of a former clastic

matrix. Vertical arrangement and an increase in size towards the top indicate a pedogenic origin of concretions at Carnoustie and Aberdour Beach.

At section Campsie 3 pedogenic overprint is easier recognizable (Fig. 8). At its base fine grained sediments become increasingly destratified, root traces are found at higher levels. The protosol lacks any carbonate concretions, but is completely cemented by a poikilotopic calcite. Well stratified layers follow above the soil and have cut deep channels in it. A few root traces indicate a weak soil development. Carbonate concretions coalesce laterally into a hardpan. Granular cracks, clotted textures, floating and exploded grains reveal the pedogenic origin of carbonates.

P1, P2 and P3 carbonates are found at all Campsie sections. Thin sections exhibit small patches of cryptocrystalline, anhedral carbonates (P1), which are enclosed by microcrystalline, but subhedral carbonates (P2). Their primary rhombohedral shape is detected by cathodoluminescence (Fig. 9A). A pale orange (Campsie) occurrence of P1 carbonates is attributed to the incorporation of clay-minerals during vadose

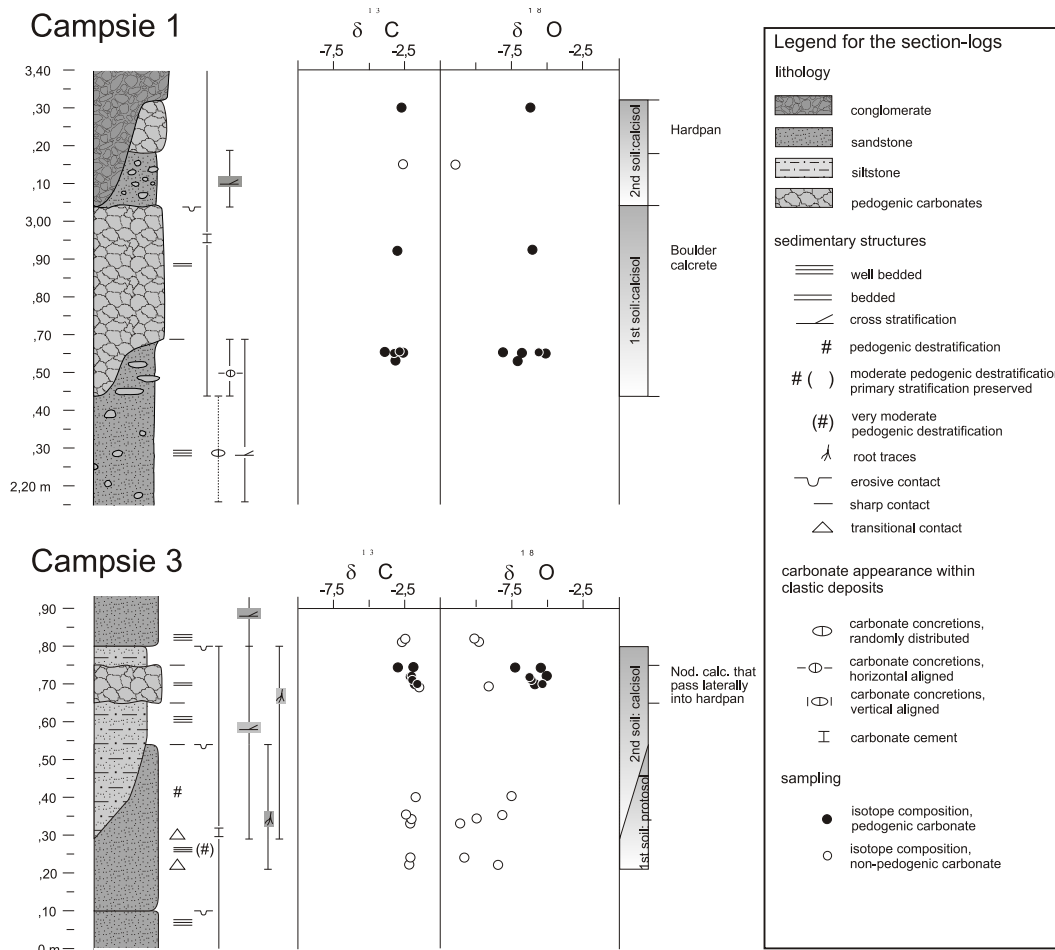


Figure 8. Overview of sections Campsie 1 and Campsie 3

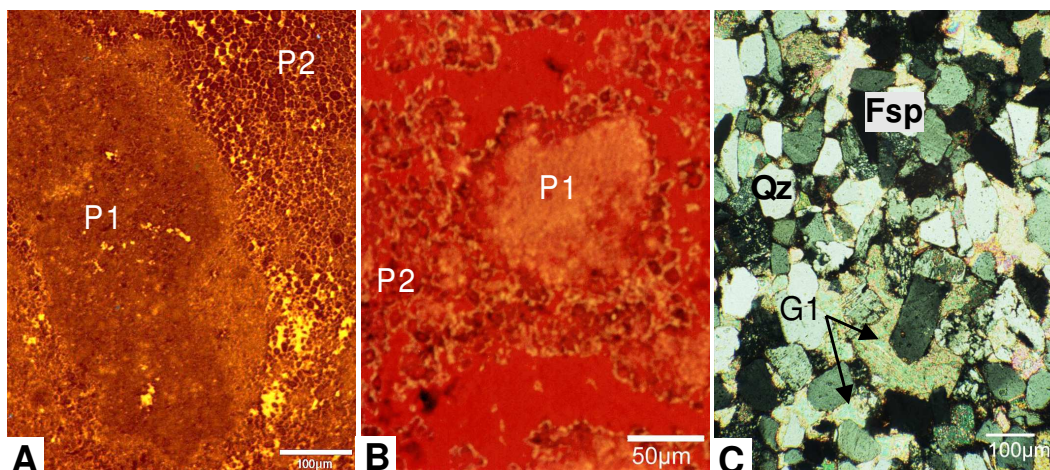


Figure 9. Carbonate types from early diagenetic origin. A) and B) are cathodoluminescence images. A) Patches of cryptocrystalline calcites (P1) are enclosed by microcrystalline calcites (P2) in the calcretes of the Campsie site. The latter reveal rhombic shapes by cathodoluminescence. B) P1 and P2 carbonates similar to those of the Campsie site consist of dolomite in the mature calcretes at Vatterode. C) Sedimentary grains are enclosed by a poikilotopic calcite (G1) at Campsie section 3

carbonate precipitation. P1, P2 and P3 carbonates from Campsie are low-Mg-calcites (LMC) with also low Fe-concentrations. Sr-concentrations range from 200 to 400 ppm, comparable to recent calcitic calcretes. Early diagenetic G1 carbonates have completely cemented the lower part of section Campsie 3 (Fig. 9C). Cathodoluminescence reveals uniform bright orange crystals. Poikilotopic calcites are generally LMC, with less than 1% Mg and less than 0.2% Fe. They generally contain much higher Sr-concentrations than the vadose P1 to P3 carbonates. The non-pedogenic S1, Hx, Kx carbonates from Campsie are LMC with Sr-concentrations that do not differ significantly from the pedogenic carbonates. Iron is below the detection limit within S1 carbonates, whereas Hx and Kx carbonates reveal Fe-concentrations of about 0.4% Fe, and therefore higher than those of pedogenic carbonates.

### 3.2 Upper Devonian to Lower Carboniferous Sites

*Pease Bay* and *Rock Hall* (Midland Valley, Scotland) both exhibit thick carbonate horizons in alluvial-fan and -plain deposits of an intramontane basin. Most carbonate concretions occur within trough cross bedded deposits that lack any evidence of pedogenic overprint (Fig. 10A). The concretions are often arranged parallel to bedding planes and reveal gradual transitions into the sediments. They are formed by poikilotopic calcites and lack internal fabrics like granular cracks or clotted textures. Eventually, concretions coalesced into layers, without affecting significantly the former stratification (Fig. 10B). Only minor displacement of clastic grains is seen in the carbonate concretions and layers. Missing

soil formation and carbonate morphology suggest a groundwater origin for these concretions and layers. Only at the sections *Pease Bay 4* and *Rock Hall 2* some concretions are correlated with weak soil development indicated by desiccation cracks (*Pease Bay 4*), blocky aggregates and root traces. These concretions differ from groundwater carbonates by their sharp margins and a strong displacement of clastic grains.

### 3.3 Permo-Carboniferous sites

Profiles which are increasingly de-stratificated upwards and partly accompanied by root traces and desiccation cracks gives evidence for pedogenic development at the sections from *Rothenburg*, *Kyffhäuser* (*Saale Basin, Germany*), *De Lutte 6* (*Ems-Graben, Netherlands*), *Lodève* (*France*). Micromorphology supports a calcrete origin for most carbonate concretions at these sites and also at *Hainichen* (*Erzgebirge Basin, Germany*). At *Rothenburg* besides some calcretes, layered concretions occur, interpreted as groundwater carbonates.

*Vatterode* (*Saale Basin, Germany*) exhibit three calcisols and a protosol. Calcretes within the soils reveal very well preserved microfabrics (Chap. 1.2). Because of its good preservation a more detailed description is given:

Pedogenic overprint is testified at *Vatterode* by an upward de-stratification and minor root traces. Carbonate contents of the calcisols typically increase towards the top. Calcisol 2, for example, exhibits a siltstone with randomly distributed calcite concretions at its base (Fig. 11). Stratification is generally intact but is destroyed near the concretions. The

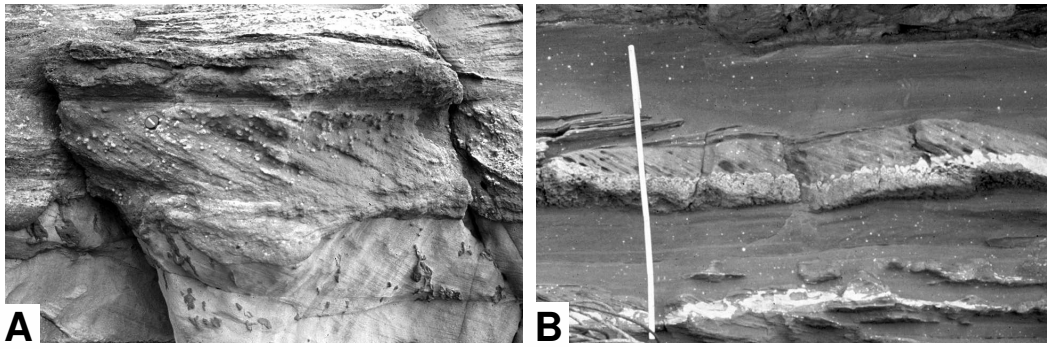


Figure 10. A) Carbonate concretions at Pease Bay are correlated with coarse grained, cross bedded sandstones that lack any evidence of pedogenic overprint. B) Carbonate has cemented several horizons of sandstones without disturbance of cross stratification at the Rock Hall site. Note the concretions are similar to those of Pease Bay, which are fused together at the base of the cemented layer and also carbonate sheets imitating bedding planes at the top of layer. Lens cap in A) is 5 cm in diameter, scale given in B) is 1 m.

amount of concretions increases upward and siltstone passes into non-continuous carbonate layers. Carbonate mineralogy changes from calcite to dolomite. Carbonate concretions coalesce into an overlying 40 cm thick impermeable dolostone horizon. The soil is upward terminated by a second dolostone horizon, where coalesced concretions form well rounded boulders, separated by small joints of clastic material.

The succession very well compares with calcrete stages found in modern calcisols (Machette 1985). It encloses nodular, honeycomb and hardpan calcretes. The uppermost horizon corresponds to a boulder calcrete formed at the beginning of brecciation and dissolution of a former hardpan (Goudie 1983; Wright and Tucker 1991). Carbonate concretions in the calcisol reveal sharp margins to the sediment, granular cracks and clotted textures. Strong re- and displacement of clastic grains, due to carbonate precipitation, is suggested by rare floating and exploded grains. Boulders of the highest horizon partly exhibit laminae at their upside margins, which is often found in mature calcrete profiles (Goudie 1983, Machette 1985)

The large number of calcretes accompanied by moderate pedogenic overprint of surrounding sediments indicates soil formation in an arid climate. This assumption is supported by an early dolomite precipitation and a silcrete horizon, within the fourth soil profile (Fig. 11). The principal carbonate precipitation should be directly below the soil surface at arid climates (McFadden and Tinsley 1985). Therefore the tops of boulder calcrete and hardpans, respectively, represent a palaeosol surface, which is important for the interpretation of stable isotope data (Chap. 4). Carbonate concretions are found directly above the hardpan of the third calcisol, thought to be derived by hardpan dissolution, which occurs when the soil is covered by further deposits. In addition to the soil carbonates the section includes lacustrine limestones.

Cathodoluminescence reveals P1 and P2 carbonates at Vatterode, very similar to those of Campsie (Fig. 9A/B). The carbonates are LMC and stoichiometric dolomites. Both, calcites and dolomites are attributed to formation in the vadose environment. Evaporation accompanied with strong precipitation

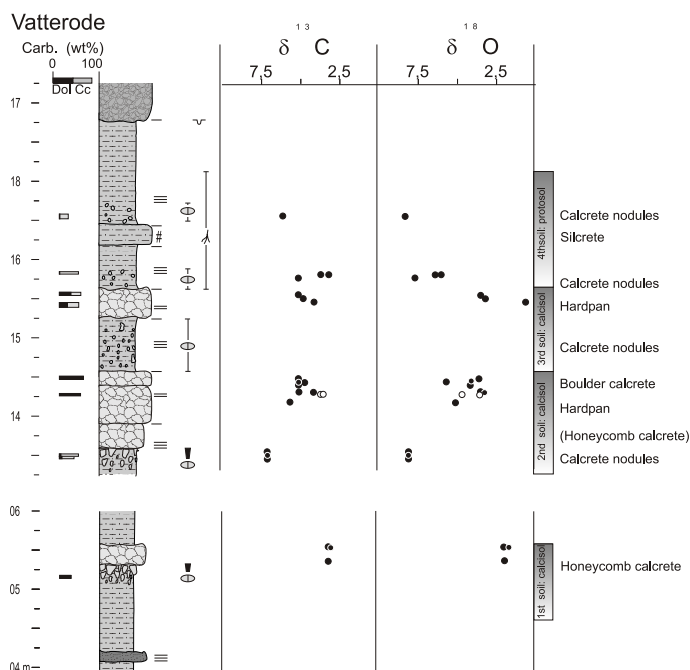


Figure 11. Overview of the Vatterode section (legend see Figure 8).

of LMC leads to an enrichment of Mg in soil water which may trigger dolomite precipitation (Watts 1980). Therefore dolomite is found predominantly in mature calcrete stages at Vatterode (Fig. 8). However, direct dolomite precipitation from pore waters is under debate and formation from a former calcite must be taken into account (Arakel and McConchie 1982). Low Fe- and Mn-concentrations of P1 and P2 carbonates are attributed to carbonate formation in a vadose environment (Morad et al. 1998). High Sr-concentrations of about 1500 and 1800 ppm found in P1- and P2-dolomites, are explained by equilibrium with evaporitic pore waters (Morad et al. 1998). Hx carbonate from Vatterode has no detectable Sr and also lacks Fe.

Micro- to coarsely crystalline, rhombohedral dolomites (D1) occur at the Lodève sections. Similar to those of Lydney Harbour they replace carbonates in a facies independent manner and thought to be formed by deep burial diagenesis. They are enriched in Ca (pers. communication Frank Körner). At the section Rotenburg 1

crypto- to microcrystalline dolomites (RD) imitate coarser rhombs, which are coated by hydroxides in many instances. Some larger subhedral dolomites are floating within the crypto- to microcrystalline matrix, which underlines the former presence of coarser euhedral dolomites. A near-surface fault bound redolomitisation is assumed.

#### 4 Stable isotope compositions

The localities, we examined, contain protosols, calcisols and vertisols. All sites were selected from basins near the palaeo-equator. According to the Cerling model, such palaeosols of nearly the same age, should give comparable carbon isotope ratios from pedogenic carbonates, which is, however, not the case (Fig. 12). At Lower Devonian and Devonian-Carboniferous sites  $\delta^{13}\text{C}$ -values from calcretes differ by 13‰ and 7.5‰ respectively (Fig. 13). Those of the Permo-Carboniferous sites reveal a difference of 6.7‰. Because of the rapid evolution of vascular plants in the Lower Devonian, localities in this

age range perhaps must be divided into shorter time intervals (Berner 1997, 1998). If sections of Lochkovian age are separated from those of Pragian and Emsian age, isotope variations in each interval become smaller, but still have differences of about 5‰. Variations in this range lower the accuracy of CO<sub>2</sub> estimations considerably.

Especially for the Lower Devonian sites, each locality has a distinct carbon isotope composition that does not match any other locality. At all sites, non-pedogenic carbonates reveal a carbon isotope composition close to or identical to soil derived carbonates, although different values might be expected due to the different carbonate origin (Fig. 12).

With some exceptions, O-isotope values for pedogenic and non-pedogenic carbonates are more or less the same at each site. Most sites reveal  $\delta^{18}\text{O}$ -values for pedogenic and non-pedogenic carbonates that match meteoric to shallow burial conditions, whereas high  $\delta^{18}\text{O}$ -values from Lydney Harbour and Rothenburg sites may be derived from dolomitisation (Chap. 1.2). At Ffairfach primary pedogenic carbonates have  $\delta^{18}\text{O}$ -values typical for burial diagenesis, whereas fracture fillings reveal compositions that favor a meteoric-water origin.

By comparison with the microstructures from modern calcretes, pedogenic carbonates of the Campsie and Vatterode sites appear to be nearly unaltered by diagenesis. If original carbon isotope composition is preserved within these calcretes, a clear distinction between carbonates which formed under different conditions maybe delineated, but no significant  $\delta^{13}\text{C}$  differences are observed at Campsie. In contrast,  $\delta^{18}\text{O}$ -values of the different carbonate types show clear differences at this site. Pede-

genic carbonates are enriched in  $^{18}\text{O}$  compared to groundwater carbonates and cavity or fracture fills. This relationship suggests the preservation of carbon isotope compositions of pedogenic carbonates at the Campsie site.

The Vatterode site is the only site, that exhibits an increase of  $\delta^{13}\text{C}$ -values upwards in a soil profile. Isotope data from Vatterode, therefore, obviously match the Cerling assumptions, but the upward change of carbon isotope is associated with a change from calcite to dolomite (Fig. 11). Due to its higher  $\delta^{18}\text{O}$ -values a pedogenic formation of dolomite seems likely (Land 1980). Nevertheless it is not clear if  $^{13}\text{C}$ -values of dolomites represent  $^{13}\text{C}$ -values of soil CO<sub>2</sub> at higher soil levels. A dolomite specific  $^{13}\text{C}$ -enrichment cannot be excluded. In coincidence with most other sites, Vatterode reveals no significant difference in  $\delta^{13}\text{C}$ -values, when comparing the pedogenic carbonates with non-pedogenic carbonates.

In summary, diagenesis appears to be the most important process in affecting the isotope composition of pedogenic and non-pedogenic carbonate. A detailed discussion of the different diagenetic stages appears to be necessary.

## 5 Conclusions

Palaeosols from 14 localities near the palaeo-equator can be classified on the basis of sedimentological features. The carbonates can be characterized by their macro- and micro-morphology. Most carbonates of an early vadose origin appear in asymmetric profiles, which agrees with the observations of Goudie (1983) and Wright and Tucker (1991). In contrast groundwater carbonates pro-



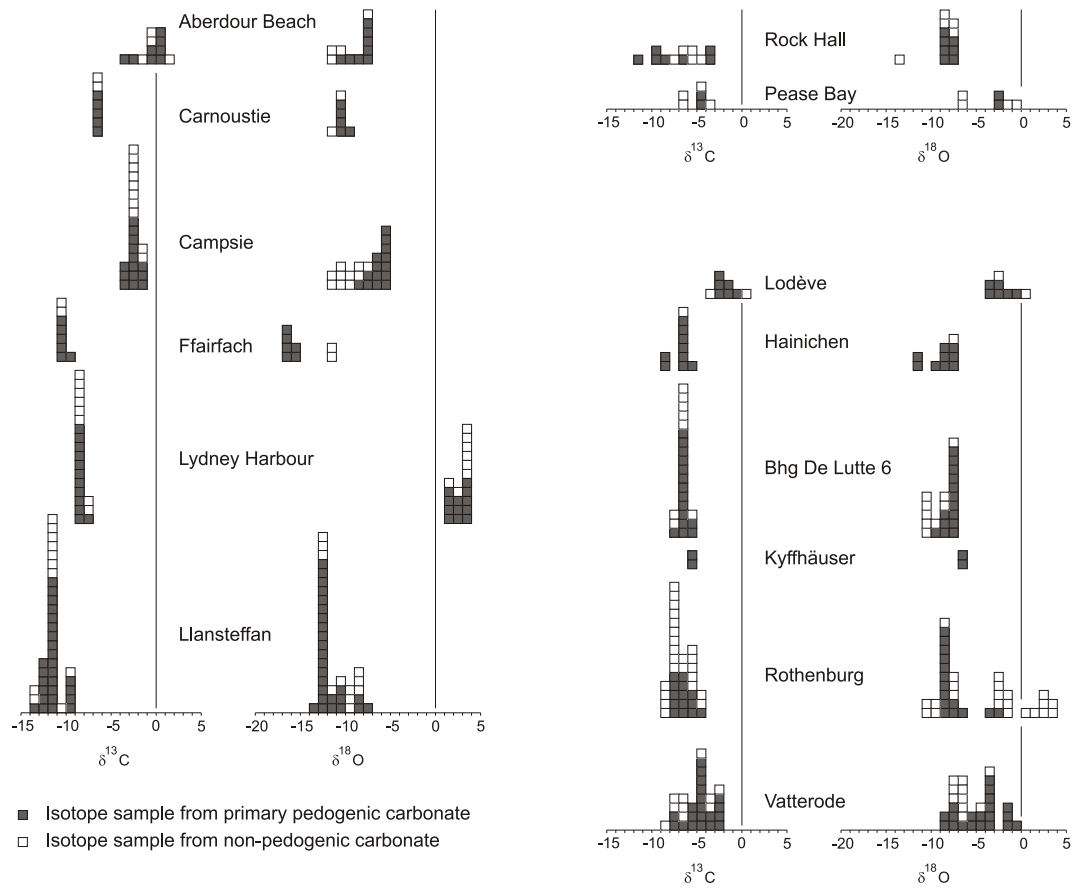


Figure 12. Carbon and oxygen isotope compositions from all localities

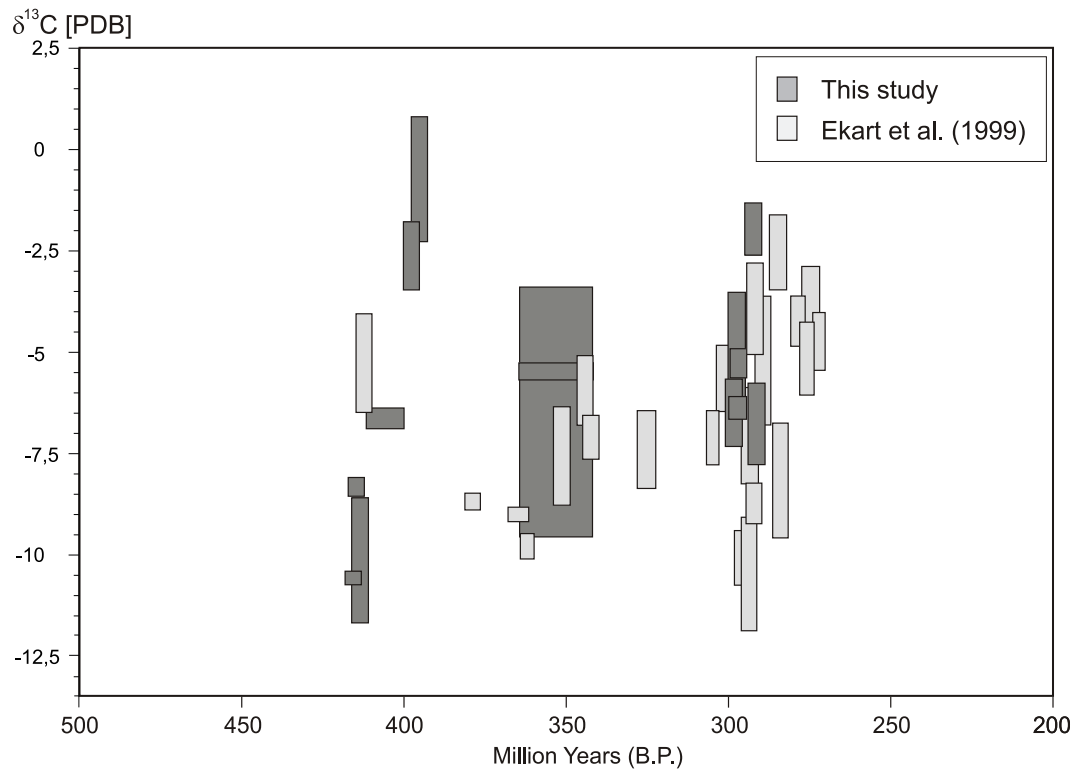


Figure 13. Carbon isotope compositions of calcretes through the Paleozoic. Results of this study compared with compilation given in Ekart et al. (1999).



vide a rather symmetric occurrence in vertical succession. Micromorphological evidence for vadose carbonate growth is given by simultaneous re- and displacement and cracking of clastic grains. Calcrete nodules display sharp margins with granular cracks, whereas phreatic conditions cause a lesser sediment displacement and more continuous margins of concretions. Primary non-pedogenic carbonates are of groundwater, palustrine or lacustrine origin.

Although a rather conservative behaviour of fossil calcretes has been predicted by many workers, thin sections, cathodoluminescence and electron microprobe analyses indicate a complex diagenetic overprint for most sites. Palaeosols from three time-slices, each of which comprise 20 to 30 million years, show large ranges in carbon isotope composition. Large carbon isotope variations in time equivalent calcretes from different sites do not match the assumptions of the Cerling model. Therefore the palaeosols investigated in this study appear unsuitable for estimating the CO<sub>2</sub> concentration in the Palaeozoic atmosphere.

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