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Radiocarbon dating of thin pedogenic carbonate laminae from Holocene archaeological sites

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Abstract: Radiocarbon dating has been previously suggested to be applicable to pedogenic carbonate. However, until now the validity of radiocarbon dates from pedogenic carbonate remained poorly understood because of the relatively low resolution of chronological controls. In this study we compared the radiocarbon dates (a total of 21) of thin (0.2–0.3 mm in thickness) laminae of pedogenic carbonate coatings on clasts from Holocene archaeological sites in the eastern Mediterranean and south Siberia with independently estimated age-ranges for these sites. We obtained a high correlation between the oldest laminae of coatings with the site ages. The ^{14}C ages of pedogenic carbonate were systematically younger by *c*. 0.3–1.6 ka (mean *c*. 0.75 ka) compared with archaeological sites. This finding suggests that pedogenic carbonate – despite potential complicating factors – can be dated more accurately with ^{14}C than has been generally appreciated.

Key words: Pedogenic carbonate, radiocarbon dating, Mediterranean, Siberia, Holocene.

Introduction

Pedogenic (soil-formed) carbonate commonly occurs in soils and palaeosols of arid regions. There are several reasons why pedogenic carbonate is of interest to Earth sciences. First, it can serve as a palaeoenvironmental indicator in arid regions where other proxy records are limited or unavailable (Cerling, 1984; Amundson *et al*., 1989, 1996; Cerling *et al*., 1989; Cerling and Quade, 1993; Quade and Cerling, 1995; Wang *et al*., 1996, 1997, 2000; Monger *et al*., 1998; Buck and Monger, 1999; Deutz *et al*., 2001; Khokhlova *et al.,* 2004). Second, it represents a considerable sink of carbon in terrestrial ecosystems (Adams and Post, 1999; Lal and Kimble, 2000; Landi *et al*., 2003). Third, it provides a record of past atmospheric CO_2 concentrations (Cerling, 1992; Royer *et al*., 2001 and references therein). Fourth, it can contribute to solving geochronological problems. Dating techniques applicable to pedogenic carbonate include the radiocarbon method (Bowler and Polach, 1971; Williams and Polach, 1971; Chen and Polach, 1986; Amundson *et al*., 1989, 1994; Courty *et al*., 1994; Wang *et al*., 1996; Pustovoytov, 1998; Monger *et al*., 1998; Buck and Monger, 1999; Deutz *et al*., 2001), U/Th (Ku *et al*., 1979; Sharp *et al*., 2003; Candy *et al.,* 2004, 2005; Durand *et al.,* 2007) and luminescence (Singhvi *et al*., 1996) dating, as well as measuring thickness of secondary carbonate coatings on clasts (Vincent *et al*., 1994; Pustovoytov, 2003; Amoroso, 2006). Although of these three methods radiocarbon dating provided the majority of numerical data, the validity of ^{14}C ages of soil carbonates remains poorly known. In this paper we present a comparison of radiocarbon dates from pedogenic carbonate coatings on clasts with the ages of related archaeological sites, which suggests that pedogenic carbonate can be accurately dated with ^{14}C.

^{14}C dating of pedogenic carbonate: uncertainties and the study goal

Pedogenic carbonate forms in equilibrium with soil CO_2 in terms of carbon isotopes (Cerling, 1984; Cerling *et al*., 1989). In theory this implies that the ^{14}C content in inorganic carbon of secondary carbonate accumulations in soils should approximate the atmospheric $^{14}CO_2$ level at the time of the secondary carbonate formation, and therefore be a substrate suitable for radiocarbon dating (Amundson *et al*., 1994). However, in practice this assumption is difficult to directly verify because of several potential problems.

(1) The ^{14}C content at the moment carbonate crystallizes in a soil may be lower than that in the atmosphere and result in radiocarbon ages that are too old. Before the late 1980s this had been attributed to the 'limestone-dilution effect' (Williams and

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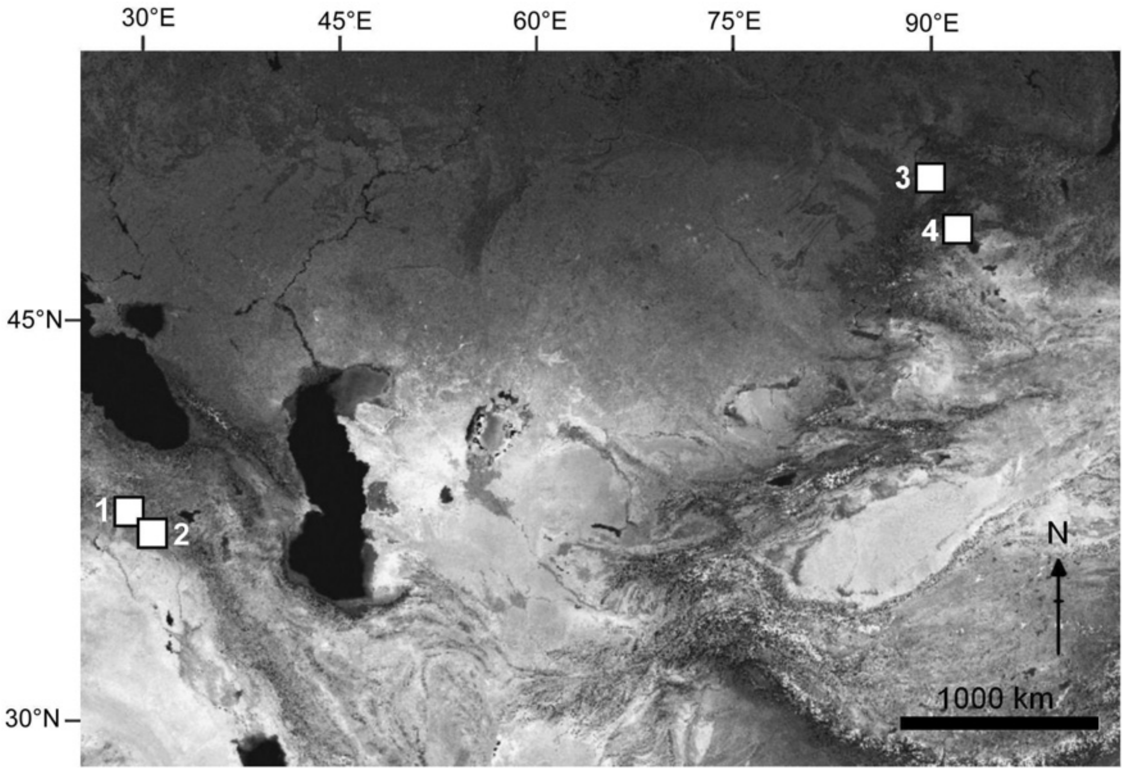

Figure 1 Map of the central part of Eurasia showing locations of the sites studied: 1, Göbekli Tepe; 2, Tell Mozan; 3, Sukhanikha and Bratsky Most; 4, Arzhan-II

Polach, 1971; Chen and Polach, 1986). After the development of the diffusion-reaction model (Cerling, 1984) alternative explanations were preferred, such as respiration of ^{14}C-depleted CO_2 by micro-organisms utilizing old fractions of soil organic matter (Wang *et al*., 1994) or mechanical admixtures of primary limestone particles (Amundson *et al*., 1989; Monger *et al*., 1998).

(2) The accumulation of soil carbonate may proceed non-linearly in time, especially in soils that experienced periods of dramatic climatic change, such as the Pleistocene–Holocene transition. This was possibly one of the reasons why the measured ^{14}C ages of pedogenic carbonate coatings deviated from their modelled ages (Amundson *et al*., 1994; Wang *et al*., 1996).

(3) Pedogenic carbonate may represent a non-closed system if it undergoes diagenetic alteration and re-equilibration in soils and paleosols (Pendall *et al*., 1994; Budd et al., 2002; Pustovoytov and Leisten, 2002; Kuzyakov *et al*., 2006) or if carbonate precipitation continues at the clast-coating contact (Brock and Buck, 2006).

These potential problems suggest that an independent chronological control is required to test the validity of radiocarbon measurements on pedogenic carbonate. As references, researchers use, as a rule, absolute-age estimations for relief forms or parent materials, which are of relatively low chronological resolution (Bowler and Polach, 1971; Williams and Polach, 1971; Chen and Polach, 1986; Amundson *et al*., 1989, 1994; Wang *et al*., 1996; Monger *et al*., 1998; Buck and Monger, 1999; Deutz *et al*., 2001).

The goal of this study was to test the validity of ^{14}C dates from pedogenic carbonate by enhancing the resolution of chronological control. We applied the radiocarbon method to secondary carbonate coatings on clasts from well-preserved Holocene archaeological contexts. To reduce the uncertainty connected with non-linear coatings growth, thin laminae of the coatings were sampled and dated.

Materials and methods

We collected pedogenic carbonate coatings on solid clasts from archaeological sites in the eastern Mediterranean and in southern Siberia (Figure 1). Climatic conditions in both study regions were semi-arid but had pronounced differences in the mean annual temperatures (below). At both Mediterranean sites the Mesopotamian steppe vegetation type (*Artemisietea herbae-albae mesopotamica*) prevailed (Zohary, 1973), whereas the sites in Siberia were covered by steppe plant associations dominated primarily by *Stipa capillata, Artemisia frigida* and *Carex duriuscula* (Koroleva, 1976). In selecting the study objects particular attention was given to finding essentially intact archaeological contexts, most of which were well-preserved stone constructions. Samples were taken at the following sites (coordinates, mean annual temperature (MAT), and mean annual precipitation (MAP) (Alex, 1985; retrieved 27 May 2007 from http://worldclimate.com) are given in parentheses).

Göbekli Tepe (37°13′N, 38°55′E, MAT 18°C, MAP 447 mm): a monumental Pre-Pottery Neolithic (PPN) site in southeastern Turkey, representing a complex of buildings consisting of stone walls and megalithic elements, the so-called T-shaped pillars (Schmidt, 2001, 2003). The function of the architectural constructions was presumably exclusively ritual; no signs of a settlement have been identified at the site. Immediately on their use the buildings were artificially covered with a mixture of stones and fine earth (Schmidt, 2002).

Chronologically, the PPN period consists of two main parts, PPNA and PPNB, the latter of which is broken down further into the early (EPPNB), middle (MPPNB) and late (LPPNB) phases (Aurenche *et al*., 2001).

Two building phases have been found at the site, a PPNA/EPPNB and a MPPNB (Schmidt, 2001), corresponding to approximately 11 750–10 250 and 10 250–9450 cal. yr BP, respectively, in terms of numerical chronology (Aurenche *et al*., 2001) A post-MPPNB and a

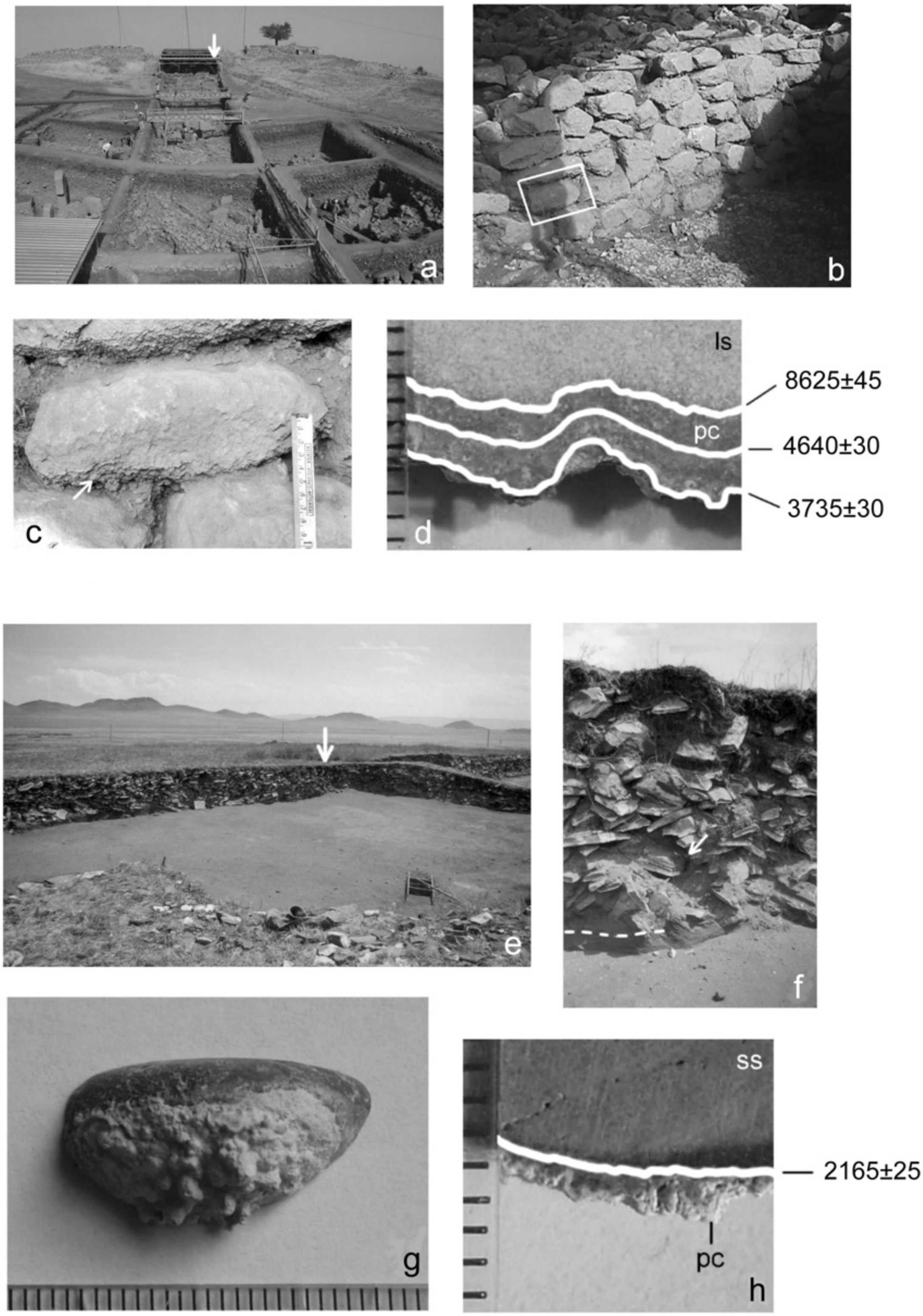

Figure 2 Pedogenic carbonate coatings on stones from two archaeological sites – Göbekli Tepe (a–d) and Arzhan-II (e–h). (a) General view of the excavated area at Göbekli Tepe; stone constructions with megalithic pillars are visible in the foreground; note dark pigmented Ah horizons *in situ* which can be seen on the vertical walls of excavation trenches; in a local depression (to the right of the picture centre) there are redeposited colluvial derivatives of Ah horizons; arrow indicates the position of one of the stone wall contexts studied. (b) A stone wall, location of which is shown in (a); scale length on the upper stone raw 24 cm; prior to excavation the soil surface was about 20–30 cm above the uppermost boundary of the wall. (c) A boulder marked by framework in (b); pronounced pedogenic carbonate accumulations cover the stone underside (arrow); scale in centimetres. (d) A cross-section of the pedogenic carbonate coating shown by arrow in (c); the white lines indicate the laminae sampled for ^{14}C dating; radiocarbon ages are given uncalibrated in years BP; ls, limestone; pc, pedogenic carbonate; scale in millimetres. (e) Overview of the excavated area at Arzhan-II; arrow indicates the profile studied. (f) Soil profile position of which is shown in (e); an Ah horizon with strongly developed root systems is distinctly seen in the upper part of the profile, immediately below there is a Bk horizon with secondary carbonate on the stone undersides; dotted line shows the buried soil surface; arrow points to the sampling location of one of the pebbles studied; a total thickness of the sandstone-plate layer is about 1.2 m. (g) Pebble taken a from the soil profile as indicated by arrow in (f); the stone underside is covered with a pronounced pedogenic carbonate coating; scale in millimetres. (h) A cross-section of the pebble shown in (g); the white line marks the lamina sampled for ^{14}C dating; ^{14}C age is given uncalibrated in years BP; ss, sandstone; pc, pedogenic carbonate; scale in millimetres

post-LPPNB context of unknown age have also been identified (Schmidt, 2003).

The soils at the site surface show a pronounced continuous Bk (*c*. 40–150 cm below the surface) horizon with secondary carbonate pendants on the undersides of stones of architectural structures, pillars and the stones of the fill. Five coating samples were collected from the PPNA/EPPNB constructions, two from the MPPNB constructions, one from a post-MPPNB wall and one from a stone of the post-LPPNB context (Pustovoytov *et al.,* 2007). A higher number of samples of the oldest coatings were taken to clarify the degree of representation of ^{14}C ages yielded from coatings on limestone with our sampling procedure. Carbonate coatings on the stone tops rarely occurred at the site. The position of coatings on the upper sides of stones suggested that they formed before the stones were used as building material. One such sample was collected from approximately the same depth as the majority of coatings on the undersides taken for dating.

Sukhanikha (53°52′N, 91°28′E, MAT 0.5°C, MAP 326 mm): a barrow of Afanas'evo culture off Minusinsk, south Siberia. The central burial was surrounded by a stone wall ring (Leontjev *et al*., 1996), which served as parent material to the soil examined. The secondary carbonate accumulations on stones were identified between 20 and at least 60 cm (pit bottom) below the soil surface. The chronology of the Afanas'evo culture, established on the basis of over 20 radiocarbon dates on wood, bone and charcoal, is constrained to about the end of the fourth to the beginning of the second millennia cal. BC (Vadetskaya, 1986; Görsdorf *et al*., 2001).

Tell Mozan (37°4′N, 40°59′E, MAT 18.8°C, MAP 430 mm): a Bronze Age site in northern Syria. This is the only site in this study where pottery shards, covered by pedogenic carbonate, rather than stone construction were examined. The site represented a city during the early to late Bronze Age (Pfälzner, 1998). Two samples of pedogenic carbonate on the undersides of pottery shards were collected from the Bk horizon, lying 30–120 cm below the surface of soil developed in a redeposited cultural layer. On the basis of ceramic typology the age of the shards is younger than *c*. 4700 cal. BP (P. Pfälzner, personal communication, 2006).

Arzhan-II (52°03′N, 93°35′E, MAT–5.6°C, MAP 303 mm): a barrow from the early Scythian epoch (Tagar-culture) in Tuva, southern Siberia. The soil studied was developed on the stone construction that was stacked up over a burial and consisted of several layers of sandstone plates with a total height of *c*. 1.2 m (Figure 2e, f). The depth interval of the Bk horizon was 20–130 cm below the soil surface. Radiocarbon dates on wood and bone, combined with dendrochronological estimations from larch stems excavated from the burial, suggest that the burial took place in the seventh century cal. BC (Zaitseva *et al*., 2004).

Bratsky Most (53°39′N, 91°33′E, MAT 0.5°C, MAP 326 mm): a barrow of the Chaadas culture in Abakan, southern Siberia. As in Sukhanikha and Arzhan, the soil formation occurred at the surface of a stack of stones overlying the burial. The Bk horizon was located below 20 cm of the soil surface and was observed down to the bottom of the excavation (*c*. 0.6 m below the soil surface). The chronology of the Chaadas-culture is restricted essentially to the ninth to tenth centuries cal. AD (Azbelev, 1994). The barrow at Bratsky Most came into being probably in the tenth century cal. AD (Grachev, 2003; personal communication, 2005).

Prior to collecting secondary carbonate coatings, the integrity of architectural structures was checked. Locally disturbed or problematic contexts were avoided. The soils at the surface of the sites were inspected regarding the degree of development of soil features *in situ,* such as Ah and Bk horizons (Birkeland, 1999). Soil profiles that were obviously eroded were not taken into consideration. Pedogenic carbonate coatings covered the undersides of stones and occurred with variations within 30 to 150 cm below the soil surface. Since the coating thickness varies considerably throughout a soil profile (Vincent *et al*., 1994; Amoroso, 2006), its vertical distribution was examined. In every case the coatings from the zones of Bk horizons where their thickness was regularly at its maximum, were collected. Exceptionally thick coatings, which were likely to have begun their formation prior to their use as building material, were rejected.

The collected stone fragments with coatings were sawn with a diamond saw into a series of slabs 3–5 mm in width. The oldest (innermost) laminae were drilled out from the coating cross-sections with a goldsmith drill under continuous control with a binocular microscope. In sampling the oldest thin laminae from limestone fragments, particular attention was given to avoid admixtures of the limestone to the sample to be dated. Fortunately, the limestone was distinctly lighter in colour than the pedogenic carbonate coatings (Figure 2a). In some rare cases the boundary between the oldest coating laminae and the limestone was not sharp, and those laminae species were not sampled. This sampling procedure allowed for a minimal sampled microlayer thickness of 0.2–0.3 mm, depending on the microstructure, density and other parameters of the coating carbonate. In two of the thickest coatings (Göbekli Tepe) the middle and the outer laminae were also drilled out. Since the youngest coatings (Bratsky Most) were about 0.3 mm thick, the entire coating material was collected through milling the coating with a goldsmith drill. Similarly, the sample of the outer laminae, about 0.1 mm in thickness from 'too old' coatings on the top of a stone at Göbekli Tepe, was gathered through careful milling of the coating surface. The ^{14}C ages and the $\delta^{13}C$ values of the carbonate fraction were determined by the AMS facility at the Leibniz-Laboratory at the University of Kiel, Germany, and the Ångstrom Laboratory of the University of Uppsala, Sweden. The carbonate fraction of samples was reacted with 0.5M HCl to release CO_2, which was graphitized with a Fe-catalyst. The ^{14}C ages were normalized to $\delta^{13}C = -25‰$. The $\delta^{13}C$ values are affected by graphitization and therefore do not correspond directly to those determined with a mass-spectrometer. The measured ages were calibrated with the OxCal v3.5 program (Ramsey, 2001).

Results and discussion

The results of ^{14}C dating and additional data are presented in Table 1. The coating thickness increases from the older to the younger sites, indicating progressive carbonate accumulation with time. The $\delta^{13}C$ values of carbonate laminae, though influenced by graphitization, are characteristic of pedogenic carbonate in C3-dominated biomes (Cerling, 1984). The exceptionally high positive $\delta^{13}C$ values for coating laminae from Tuva might reflect an enhanced concentration of an atmospheric CO_2 component in soil air resulting from the early annual onset of negative temperatures (Cerling, 1984).

There are three main tendencies in the radiocarbon ages of the oldest coating laminae to be emphasized (Table 1, Figure 3, Figure 4a): (1) the calibrated ^{14}C age-intervals for the oldest laminae of pedogenic carbonate coatings are systematically younger than the age constraints of corresponding archaeological sites with a high degree of correlation, (2) the laminae from the same sites show very similar ^{14}C ages and (3) differences in climatic conditions and lithology of parent materials exert no pronounced influence on radiocarbon ages. These regularities can be best explained by the formation of pedogenic carbonate in carbon isotope equilibrium with soil CO_2 and indirectly with atmospheric $^{14}CO_2$. Although the contributions of radiometrically 'too old' inorganic carbon and diagenetic radiocarbon contamination to the final carbonate are unknown, it seems unlikely that the strong correlation between the radiocarbon ages of pedogenic carbonate and the age-constraints of cultural periods (Figure 4a) is a result of accidental combinations of ^{14}C-depleted and ^{14}C-enriched carbonate fractions.

Table 1 Radiocarbon ages of thin laminae of pedogenic carbonate coatings

Site/country	Age constraints of cultural periods (cal. BP)	Depth of the sample below the soil surface (cm) / average coating thickness (mm)	Lithology of clasts covered by pedogenic carbonate	Lamina dated	^{14}C-age, uncal. BP, of $CaCO_3$ fraction of the innermost 0.2–0.3 mm thick lamina of coating	Delta $^{13}C_{carb}$	^{14}C-laboratory index	^{14}C-age, cal. BP (2 sigma)	Probability (%)	^{14}C-age, cal. BP, mean weighted	Difference between the mid-points of site age-ranges and the mean weigthed values for ^{14}C ages of coating laminae (yr)[a]	Difference between the youngest limits of site ages and the oldest limits of 2-sigma intervals of cal. ^{14}C ages (yr)[a]
Göbekli Tepe/ Turkey	11 750–10 250	100/5	limestone	innermost	9290 ± 70	−19.49	KIA-25467	10680–10610	6.8	10 436	564	–430
								10 600–10 240	88.6			
		90/5	limestone	innermost	9020 ± 30	−12.50	KIA-26021	10 240–10 150	95.4	10 195	805	10
		115/5	limestone	innermost	8430 ± 80	−11.00	Ua-19561	9550–9260	93.9	9401	1599	700
								9170–9150	1.5			
		90/5	limestone	innermost	8895 ± 55	−14.27	KIA-25373	10 210–9770	95.4	9990	1010	40
		105/5	limestone	innermost	8960 ± 85	−12.00	Ua-19562	10 250–9750	95.4	10 000	1000	0
				middle	5450 ± 35	−11.92	KIA-23389	6310–6170	95.4	6240		
				outermost	4045 ± 35	−14.21	KIA-23388	4790–4760	3.6	4525		
								4620–4410	91.8			
	10 250–9450	90/5	limestone	innermost	8440 ± 40	−14.05	KIA-26169	9540–9400	90.5	9463	437	-90
								9350–9320	4.9			
		85/5	limestone	innermost	8625 ± 45	−13.31	KIA-26168	9730–9520	95.4	9625	275	-280
				middle	4640 ± 30	−12.37	KIA-26274	5470–5350	76.8	5392		
								5340–5300	18.6			
				outermost	3735 ± 30	−10.92	KIA-26273	4230–4200	2.4	4074		
								4160–3980	93.0			
	younger than 9450	90/5	limestone	innermost	7180 ± 40	−13.63	KIA-28033	8120–8080	9.0	7994		
								8050–7930	80.2			
								7900–7870	6.1			
	younger than 8350	100/3	limestone	innermost	6405 ± 70	−10.80	Ua-21416	7440–7180	95.4	7310		
	older than 10 250	85/6	limestone	outermost	10210 ± 50	−7.14	KIA-28405	12 350–11 600	95.4	11 975		
Sukhanikha/ Russia	4950–3950[b]	30/2	sandstone	innermost	2905 ± 40	−7.55	KIA 21661	3210–3180	3.3	3048	1402	740
								3170–2920	90.8			
								2910–2890	1.3			
Tell Mozan/ Syria	younger than 3300	95/1.5	ceramic shard	innermost	2625 ± 25	−10.55	KIA-28162	2780–2738	95.4	2759		
		105/1.5	ceramic shard	innermost	2815 ± 45	−14.54	KIA-29318	3061–3049	1.0	2917		
								3035–3010	2.9			
								3003–2837	83.0			
								2833–2784	8.6			
Arzhan-II Russia	2650–2550[c]	80/1	sandstone	innermost	2165 ± 25	6.45	KIA 21141	2210–2060	40.9	2212	388	340
								2310–2230	54.5			
					1830 ± 30	2.49	KIA 22806	1870–1840	2.5	1759	841	680
								1830–1690	90.2			
								1650–1630	2.7			
Bratsky Most/Russia	1050–950[d]	40/0.3	sandstone	total coating carbonate	735 ± 40	−6.70	Ua-23056	740–640	90.1	684	316	210
								590–560	5.3			
					670 ± 35	−10.61	KIA-24725	680–620	46.1	614	386	270
								610–550	49.3			
										mean	752	183

[a]Calculated only for the innermost laminae of coatings from archaeological contexts with both oldest and yongest known age limits.
[b]The limits 3000 and 2000 cal. BC were used for calculations.
[c]The barrow is dated to seventh century BC, 700 and 600 cal. BC were used for calculations.
[d]The limits 900 and 1000 cal. AD were used for calculations.

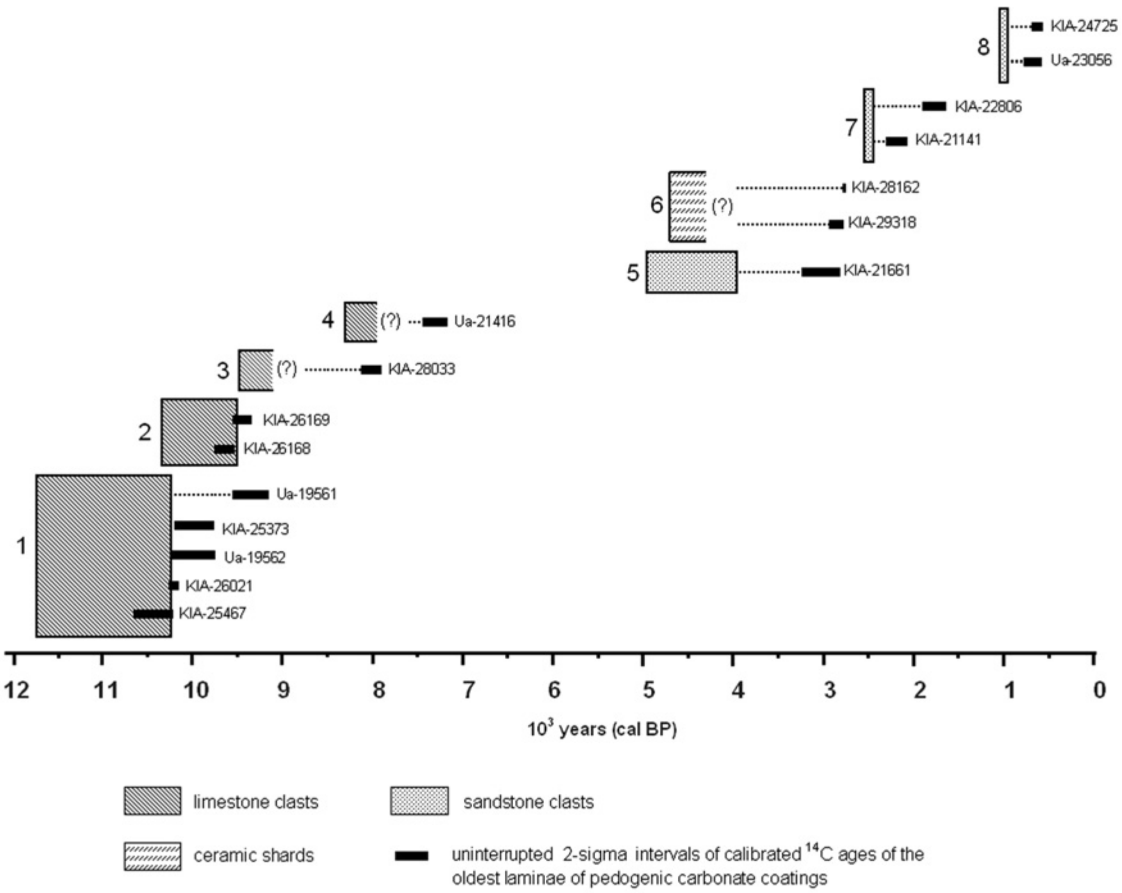

Figure 3 Diagram illustrating the relationship between ^{14}C ages of the oldest laminae of pedogenic carbonate coatings on clasts (black bars) and age-constraints for archaeological sites (rectangles): 1, Göbekli Tepe (PPNA); 2, Göbekli Tepe (PPNB); 3, Göbekli Tepe (post-PPNB); 4, Sukhanikha; 5, Tell Mozan; 6, Arzhan-II; 7, Bratsky Most; for ^{14}C ages uninterrupted calibrated 2σ-intervals are given; corresponding laboratory indexes are given to the right of the age-intervals of the laminae

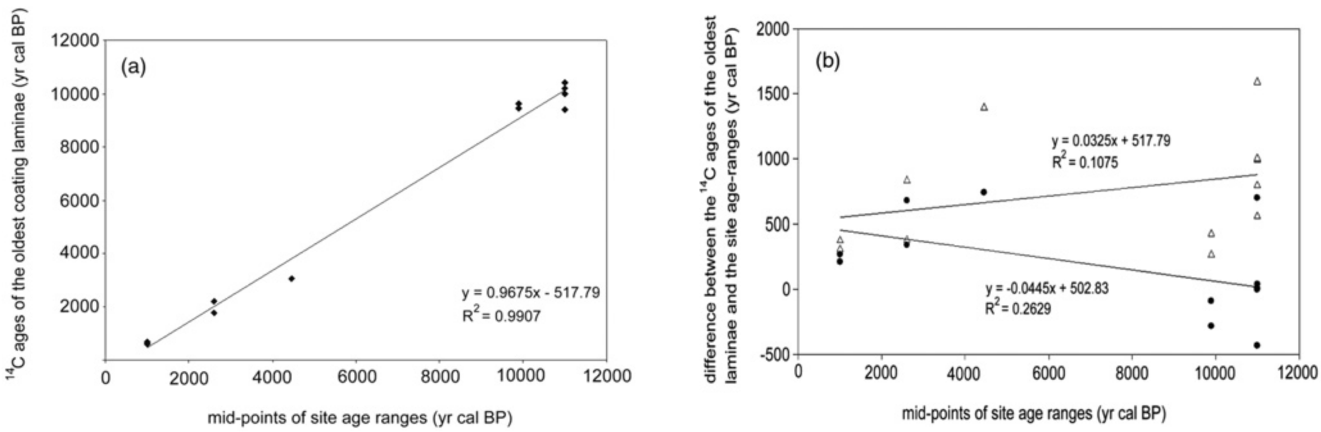

Figure 4 Correlation of the mid-points of age-constraints for archaeological sites with (a) the mean weighted ^{14}C ages of the oldest laminae of pedogenic carbonate coatings on clasts and (b) with the age-differences between site age-constraints and ^{14}C ages of the laminae; open triangles, differences between the mid-points of site age-constraints and the mean weighted ^{14}C ages (cal. BP, 2σ) of pedogenic carbonate laminae; closed circles, differences between the oldest limits of the calibrated 2σ-intervals for ^{14}C ages of the laminae and the youngest limits of the site age-constraints

Furthermore, additional observations lend support to the validity of the measured ^{14}C ages. First, the oldest laminae in coatings on limestone from Göbekli Tepe showed a close agreement of dates that are younger than the site (Table 1, Figure 3). Although we cannot rule out that the minor variations in radiocarbon ages reflect some small mechanical admixtures of limestone carbonate, in general these dates demonstrate that radiocarbon ages are not effectively influenced by radiometrically dead inorganic carbon. Alternatively, the insignificant age variations can be explained by the dynamics of building activities at the site. Second, in two samples of coatings from the same site, the middle and the outermost laminae showed comparable and successively decreasing ^{14}C ages (Table 1). The youngest laminae did not provide modern dates; however, they were in good agreement with each other, suggesting that pedogenic carbonate accumulation ceased at a certain time in the past. The reason for this is unknown, but it might have been associated with generally drier climatic conditions in the late Holocene compared with the early and the mid Holocene in the region (Roberts *et al*., 2001; Wick *et al*., 2003; Robinson *et al.,* 2006 and references therein). We address the paleoenvironmental aspects of this question elsewhere (Pustovoytov *et al.,* 2007). Additionally, the radiocarbon age of the outermost laminae of the coatings covering the tops of stones from Göbekli Tepe is older than the age range of the site (Table 1). This attests to a relatively low level of potential diagenetic radiocarbon contamination, which clearly should be still weaker in the innermost laminae of coatings and on the stone undersides not exposed to direct attack of percolating soil solutions enriched in carbon dioxide.

As a whole, based on the above consideration, we conclude that the ^{14}C ages of individual laminae of pedogenic carbonate coatings on clasts in this study closely approximate the time of their formation.

Quantifying the difference between the age-ranges of cultural periods and the measured radiocarbon ages of the oldest laminae of pedogenic carbonate is of theoretical and practical importance. For the mid-points of age-intervals for sites and laminae this value varied from *c*. 0.3 to 1.6 ka with a mean of *c*. 0.75 ka (Table 1). The latter might be overestimated because a relatively high number of dates were determined on coatings from the oldest site compared with younger sites. Given the correctness of the radiocarbon clock in pedogenic carbonate, the age differences of several hundred years between sites and lamina involve presumably two factors: (1) the time lag between the stabilization of the surface of the site and the beginning of carbonate accumulation on stones, and (2) the time necessary to form a carbonate microlayer 0.2–0.3 mm in thickness. The precise minimum time required for the start of pedogenic carbonate accumulation on stones remained uncertain in this study. However, this time obviously can be shorter than *c*. 1 ka because the stones from the youngest site (Bratsky Most) were already covered by appreciable secondary carbonate coatings on their undersides.

In addition, we also observed two weak, statistically insignificant regularities. One was an increase in the difference between the site ages and the ^{14}C ages of thin coating laminae with increasing site age (Table 1, Figure 4b). We have no ultimate explanation for this effect. The chronology of the PPN time is not elaborated on as much as the younger periods considered in our study, and operates with comparatively long time intervals. If the stone constructions came into being at relatively late stages of the PPNA and PPNB periods, the mid-points of the age-constraints taken for calculation should indicate ages that are too old for the sites and thus increase the calculated age difference between the sites and the oldest coating laminae. Alternatively, the relationship between the age difference and the site chronology may reflect a more complex formation history in older coatings. For example, the coatings from Göbekli Tepe may have experienced some climatic instability in the early Holocene Near East (see above). The second regularity was represented by the fact that the difference between the youngest limits of the site ages and the oldest limits of calibrated intervals for ^{14}C ages of the coating lamina decreased with increasing site age (Table 1, Figure 4b). This may reflect slightly larger calibrated-age intervals for the older dates. It is notable that our measurements revealed a significantly lower age difference between the age-limits for parent materials and the ^{14}C ages of the oldest coating laminae (of the order of 1 ka), compared with the data of Sharp *et al*. (2003), 5 ± 5 ka, obtained with the Th/U method. This fact is attributable to the following factors or their combinations: (1) larger uncertainties in estimation of the parent material ages, (2) formation of secondary carbonate studied by Th/U in Pleistocene environments that were presumably more variable than those of the Holocene, (3) more thick laminae sampled in the latter work (0.5 mm) than in the present study and (4) methodological differences between ^{14}C and Th/U dating techniques.

Conclusions and implications for geological and archaeological work

The central finding of this study is that pedogenic carbonate coatings, if thin-layer sampled, can be accurately dated with ^{14}C. We suggest that it may have some important implications for geosciences. First, radiocarbon dates on the oldest thin laminae of coatings can indicate – at least for the Holocene – well-approximated minimum ages of soils or deposits. In addition to previous research (Amundson *et al*., 1994; Wang *et al*., 1996), our data specify the difference between mean deposit ages and mean ^{14}C ages of the oldest pedogenic carbonate lamina, which can range from 0.3 to 1.6 ka. Second, a set of ^{14}C ages from a succession of coating laminae may reflect the dynamics of carbonate accumulation rates, which in turn is of importance to understanding the formation of Bk horizons and the changes of the carbon sink in arid ecosystems. Third, dating individual coating laminae can contribute to enhancing the resolution of palaeoenvironmental records based on pedogenic carbonate (primarily stable isotopic fingerprints). Also, archaeologists can benefit from dating secondary carbonate accumulations in cases where other chronological indicators (such as ceramics, texts or common datable materials such as charcoal, bone, etc.) are lacking.

Several limitations of our data have to be emphasized. (1) Since our results are restricted to the Holocene, further investigations are required to test the validity of radiocarbon ages of late-Pleistocene pedogenic carbonates. (2) Although the resolution of chronological control in the study objects was higher than in previous works, it was still not high enough to precisely detect the time-lag between the start of pedogenesis and the formation of first portions of pedogenic carbonate on clasts. For this purpose, as well as for examining the contributions of radiometrically old and modern fractions of inorganic carbon, more detailed chronosequences of archaeological sites, including those younger than 1 ka old, should be explored. (3) We studied samples from one depth interval of soil profiles, whereas the radiocarbon content in pedogenic carbonate may appreciably vary throughout a soil profile, usually showing a decrease of ^{14}C with depth (Chen *et al*., 1986; Amundson *et al*., 1994; Pendall *et al*., 1994; Wang *et al*., 1996). Pedogenic carbonate coatings from greater depths should therefore be more suitable for minimum age estimations for soils or deposits. It should be taken into account that in natural sediments and soils and in artificial stone constructions, there are unknown admixtures of coatings that began their formation prior to redeposition or becoming part of a construction. Therefore, if trying to assess a minimum age of a deposit, a soil or a site, care should be taken to avoid coatings in the field that are too old by analysing the distribution of their thickness in a profile. Furthermore, several samples of the oldest lamina should be analysed to clear up the variance and to reduce the risk of dating specimens that are too old.

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