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AGE AND THERMAL STABILITY OF PARTICULATE ORGANIC MATTER FRACTIONS INDICATE THE PRESENCE OF BLACK CARBON IN SOIL

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ABSTRACT. Black carbon (BC) from incomplete combustion of organic materials is abundant in many soils. Its age is often higher than that of thermally unaltered soil organic carbon (SOC) owing to the presence of BC from fossil sources or to a high recalcitrance against microbial decomposition compared to that of plant residues. For a meaningful application of radiocarbon as an indicator for soil carbon age and turnover, the relative contribution of BC needs to be quantified, but BC is difficult to separate physically from soil. However, BC is thermally more stable than SOC, and hence thermal stability may provide a quantitative BC indicator. Here, we analyzed 30 light particulate organic carbon (POC) soil fractions for their thermal stability and for their ¹⁴C signature. POC is particularly sensitive to "contamination" with BC, because it is obtained by combined size and density fractionation. A steady-state "bomb" 14C model was used to derive mean POC ages. Soils from four sample sets, each consisting of six to eight individual POC samples and representing different field sites and POC types, were analyzed. Samples from one of the sets were virtually BC free, and their mean POC ages ranged from 60 to 100 yr. The ¹⁴C signature of samples from the other three sets indicated the presence of very old carbon, with mean POC ages of several hundred and up to 3500 yr. Two indicators for thermal stability-(1) the amount of heat released at temperatures >450°C and (2) the amount of heat released at 500°C (the latter representing the peak temperature of heat released from charcoal isolated from soil)-correlated both significantly and nonlinearly with POC age, indicating that samples with high BC content were older than those with low BC content. It can be concluded that at an individual site with increasing abundance of BC, both the age and the thermal stability of POC increase. However, thermal stability proved to be a reliable predictor for BC in only one sample set, whereas thermal signals of the other two BC-containing sample sets were not significantly different from those of BC-free samples. Thermal stability thus gives no unequivocal indication for the presence of BC in POC across different sites.

INTRODUCTION

Black carbon (BC) from incomplete combustion is ubiquitous in the environment and found in many soils (Schmidt and Noack 2000). It naturally originates from vegetation fires, but fossil sources, such as coal dust, also may contribute to BC in soil (Marschner et al. 2008). BC is not a single compound class but rather a continuum of pyrogenic materials with similar properties (Hammes et al. 2007). With respect to the soil carbon cycle, much BC research has been prompted by the recalcitrance of BC against microbial decomposition and thus the potential of BC to contribute to soil carbon sequestration and climate change mitigation (Lehmann et al. 2006).

The relative recalcitrance against microbial decomposition and the potential content of fossil carbon suggest that the radiocarbon age of BC is on average higher than that of non-BC soil organic carbon undergoing continuous microbial turnover. High ¹⁴C ages of charcoal particles in biologically active mineral soil indicate high BC recalcitrance (Carcaillet 2001; Schmidt et al. 2002; Krull et al. 2006). Also, results from long-term field experiments demonstrated that a high ¹⁴C age of soil carbon was accompanied by substantial amounts of BC (Rethemeyer et al. 2005; Jenkinson et al. 2008). Furthermore, in soil samples from Halle, Germany, a high age was derived not only for bulk soil carbon but likewise for light particulate organic carbon (POC) fractions (Rethemeyer et al. 2005). POC is considered to represent a labile soil carbon fraction with turnover times of a few years to decades (Baisden et al. 2002); therefore, ¹⁴C signatures without signs of bomb carbon may be indicative of the presence of BC.

Thermal methods have been established as rapid tools to scan for the occurrence of BC in soil (Leifeld 2007; Maharaj et al. 2007; Plante et al. 2009). In mineral soils, thermal peaks at around 500°C are indicative of the presence of BC, because most nonpyrogenic soil organic matter is thermally

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less stable (Leifeld 2007). However, it is unknown whether BC is present in soil fractions containing mostly little or moderately decomposed plant residues, such as light particulate organic matter (POM), and whether it could be identified by thermal analysis.

This study tested the hypothesis that the thermal stability of the POM fraction correlates positively with its age, assuming that a high POC age is caused by impurities through old BC. If such a relationship was verified for different samples, thermal stability of POC could serve as a fast and quantitative indicator for the presence of BC in this soil fraction.

MATERIAL AND METHODS

Soil Samples and Soil Fractionation

Thermal stability parameters and ¹⁴C signatures were measured for four different sample sets. Two sets originated from temperate grassland sites on clayey rendzic Leptosols (WRB 2006) sampled in the Spanish Pyrenees. Soils were collected from four different grasslands at depth increments of 0 to 10 and 10 to 20 cm (i.e. eight soil samples). Fine earth samples (i.e. sieved ≤ 2 mm) were separated by density fractionation into free POM (fPOM) and occluded POM (oPOM), representing sample sets 1 and 2, respectively. For density fractionation, samples were centrifuged with 1.8 g cm⁻³ sodium polytungstate (SPT) solution until all the heavy (pellet) material was separated from light (floating) material. All floating material (≤1.8 g cm⁻³) was collected as fPOM in a 63-µm sieve, washed thoroughly, and oven-dried overnight at 60°C. The remaining pellet was resuspended in SPT and treated with ultrasonication (22 J mL⁻¹) to destroy soil aggregates before repeated centrifugation and collection of oPOM ($\leq 1.8 \text{ g cm}^{-3}$). The third sample set was collected during a long-term field trial from a temperate cropland in Groβ-Enzersdorf (hereafter called Grossenz), Austria, 5 km east of Vienna. Here, six soil samples from topsoil and subsoil of a siltic Chernozem (WRB 2006) were taken, and a combined fPOM and oPOM fraction (POM) was obtained after ultrasonication with 22 J mL⁻¹ and density separation at 1.8 g cm⁻³ in SPT as described above but without prior separation of fPOM. The fourth sample set was derived from eight topsoils (0-10 cm) in subalpine mountain grassland on leptic Cambisol (WRB 2006) in the Swiss Alps, canton Grisons. The site is managed as grassland since AD 1350. Here, POM was separated as for sample set 3. None of the four sites was prone to vegetation fires during recent decades. The carbon fraction of POM is hereafter referred to as POC. For sampling depths and site coordinates, please see the Appendix.

Importantly, none of the POM fractions showed macroscopic or microscopic (light microscopy) signs of BC; hence, impurities were caused potentially by finely dispersed or soluble but attached BC. However, visual identification of charcoal particles indicated the presence of BC in some bulk soil samples from sample sets 1 to 3. In contrast, sample set 4 with samples taken from a site located at the tree line lacked any signs of charcoal in the bulk soil and for the current study served as a control with minimum BC content.

Thermal Stability

Bulk soils were ground to less than 63 μ m and subjected to oxidative differential scanning calorimetry (DSC) in synthetic air over a temperature range of 50 to 600°C at a heating rate of 10°C min⁻¹. About 20 mg of sample was measured in open Al crucibles, and an empty pan served as reference. POM fractions were diluted 1:10 with Al₂O₃, ground as above, and oxidized in the same way as bulk soils. The detection limit of the method was around 1 mW, which corresponds to about 0.012 mg carbon for pure BC samples (see Leifeld 2007 for details). In Leifeld's publication and in later studies (Plante et al. 2009; Harvey et al. 2012), a high thermal stability with exothermic thermal peaks at around 500°C could be attributed to BC materials. For comparison, the most dominant exotherms for mineral soils were between 300 and 400°C. This difference enables quantification of BC in mineral soils. Charcoal particles were handpicked from bulk soil, gently rinsed with water, dried, ground, diluted 1:10 with Al_2O_3 , and measured as described above. The height of its peak at 500°C linearly depends on the amount of charcoal and was used for quantifying BC in bulk soils. The method proved reasonable for tracking the fate of biochar applied to soil (Felber et al. 2014). In contrast to thermograms of bulk soil, those of POM showed exotherms also at higher temperatures (Rovira et al. 2008), and these may interfere with the BC signal. Therefore, in addition to peak temperatures and heights, integrated thermal measures may be used as indicator for the presence of BC in POM fractions. Here, we applied two indicators for BC in POM, namely the heat flux at 500°C signal may directly indicate BC, the integrated high-temperature region may indicate both BC and thermally stable non-BC materials, such as lignin-containing cell wall compounds, which are abundant in POM. Hitherto, it is not known whether the integrative measure is diagnostically conclusive for the presence of BC in POM.

Radiocarbon Analysis

All samples were pretreated using acid fumigation with 0.5M HCl to remove carbonates (Agarwal and Bucheli 2011). For sample sets 1, 2, and 4, a POM sample mass equivalent to 0.5 to 1.0 mg of C was combusted and graphitized for accelerator mass spectrometry (AMS) measurements of ¹⁴C content. These were conducted at the AMS facility of the Laboratory of Ion Beam Physics at the ETH (the Swiss Federal Institute of Technology), Zurich, according to the protocol of Synal et al. (2007). For sample set 3 (Grossenz), between 0.9 and 1.3 mg of sample was placed in a quartz vial and covered with copper oxide, following the protocol described in Steier et al. (2004). Silver wire was added to remove halogens. The vial was closed with a PTFE plug valve, and the sample was combusted in a tube furnace at 900°C for 2 hr. The evolved CO_2 was converted to solid graphite for the production of ¹⁴C AMS targets. The ¹⁴C content was measured at the Vienna Environmental Research Accelerator (VERA), an AMS facility with a 3MV Tandem accelerator. All results were expressed as percent modern carbon (pMC):

$$pMC = 100(A_{sn}/A_{abs}) \tag{1}$$

as defined by Stuiver and Polach (1977).

An overview of sites, measured ¹⁴C contents, and time of sampling and measurement can be found in the Appendix.

Calculation of Mean Carbon Age

Calculation of mean ¹⁴C ages using the ¹⁴C signature of POC followed the time-dependent steadystate ¹⁴C turnover model ("bomb model") developed by Harkness et al. (1986) and later applied to POC by Leifeld et al. (2009). The model assumes a continuous exchange of ¹⁴C between the respective carbon pool (here: POC) and the atmosphere. The temporal change in ¹⁴C signature of the carbon pool is calculated at annual time steps and depends on the atmospheric signature and the mean residence time of carbon:

$$A_{t} = A_{(t-1)}e^{-k} + (1 - e^{-k})A_{i} - A_{(t-1)}\lambda$$
(2)

where A_i is the (measured) ¹⁴C activity (pMC) of POC at time t, $A_{(t-1)}$ is the ¹⁴C activity of POC in the previous year, A_i is the atmospheric ¹⁴C activity, k is the exchange rate constant of POC, and λ is the ¹⁴C decay constant (1/8268 yr⁻¹). With this model, we did not consider any time lag between

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C assimilation and transfer to POC. Values for pMC were corrected for radioactive decay between time of sampling and time of AMS measurement. Values for A_i were taken from the recent IntCal13 calibration (Reimer et al. 2013) for the period from 10,000 to 440 cal yr BP (5-yr resolution), from the atmospheric ¹⁴C record of Stuiver et al. (1998) for the period from AD 1511 to 1954, and from Levin and Kromer (2004) for the period from 1959 to 2004. The period between 1954 and 1959 was interpolated linearly. Data for 2004 to 2012 were taken from Levin et al. (2013). The model typically gives *k* (the turnover rate) or its inverse 1/*k* (the mean residence time [MRT] or turnover time). In the following, we will refer to the mean age of POC rather than to turnover time, assuming that the postulated continuous carbon flow through POC is interfered by the presence of BC infrequently incorporated into soil. Depending on the amount and age of BC incorporated, mean ages estimated by the model may be biased by up to 30% (Leifeld 2008). It should also be noted that the mean age resulting from the steady-state turnover model as used here and in other soil science applications differs from the notation usually used for ¹⁴C-dated samples and hence does not refer to calibrated or conventional ¹⁴C age.

RESULTS

Bulk soils from the Spanish Pyrenees and from the Austrian site contained BC indicated by a well-separated thermal exotherm at around 500°C, whereas this exotherm was not present for bulk soils from the Swiss mountain grassland (Figure 1). With the thermogram of physically separated charcoal particles serving as calibration standard (Figure 2), the BC/SOC ratio could be estimated for bulk soils from Spain (13.1 \pm 3.4) and Austria (33.4 \pm 2.0) (percentage mean \pm SD). The thermal picture was less conclusive for POM (Figure 2). Many POM samples from sample sets 1 to 3 showed substantial heat releases at temperatures >450°C, but a distinct BC peak was seldom visible. POM thermograms from sample set 4 tended to have a similar heat release in this temperature region. In contrast, physically separated charcoal particles reflected a typical thermal pattern with most of the heat released at higher temperatures (Figure 2). Thermal stability indices indicated significantly higher thermal stability of POM for sample set 3 than for all other sample sets (Table 1). The samples from set 3 also had the highest mean age as derived from ¹⁴C turnover modeling. Furthermore, samples from sets 1 and 2, which presumably all contained charcoal, had mean ages of several hundred years on average, whereas the BC-free POM from sample set 4 had mean ages of less than 100 yr. Organic carbon contents were higher for POM from sample sets 2 and 3 than for POM from sets 1 and 4.

Table 1 Thermal stability indicators (% heat released >450°C; signal height at 500°C [W g⁻¹ POM], organic carbon [OC] content [%], and mean age [yr]) of particulate organic matter fractions of four different sample sets: 1 (free POM from Pyrenees), 2 (occluded POM from Pyrenees), 3 (POM from Grossenz), and 4 (POM from the Alps). Numbers are means, and standard deviations are given in parentheses. Different letters indicate significant differences at the P<0.05 level (Tukey's test).

Sample set #	% heat >450°C	Signal height 500°C (W g ⁻¹)	OC content (%)	Mean age (yr)
1	13.57 (1.42)a	2.71 (0.47)a	26.5 (4.8)a	522 (583)ab
2	13.10 (2.16)a	2.90 (0.54)a	31.9 (2.3)b	237 (289)a
3	34.57 (8.72)b	9.39 (3.49)b	33.6 (3.4)b	1306 (1138)b
4	13.80 (3.74)a	1.50 (0.65)a	22.6 (2.6)a	79 (12)a

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Figure 2 Differential scanning calorimetry thermograms of POM and charcoal fractions extracted from the bulk soils (same samples as in Figure 1) from Spain (dashed, sample from set 2), Austria (solid, set 3), and Switzerland (dotted, set 4) and of charcoal separated from a sample from a Spanish site (dashed curve with arrow). Note that thermograms are normalized to each sample's organic carbon content to allow comparison of data from Figures 1 and 2.

With the increasing percentage of heat released above 450°C, the mean age of POM fractions increased significantly for samples from sets 1 to 3 (Figures 3, 4; Table 2). In contrast, samples from set 4 showed a significant but negative relationship between heat release and mean age. Results from the regression analysis of signal heights at 500°C and mean age revealed a similar albeit weaker relationship. Again, the slope was negative for samples from set 4. Regression coefficients differed notably between sample sets. However, when all samples were pooled, there was still a positive and highly significant correlation between the two measures of thermal stability and the (log) mean age of the POM fractions (data not shown).

Table 2 Regression coefficients *a* (intercept) and *b* (slope), coefficient of determination R^2 , and error probabilities *P* for slopes of linear regressions depicted in Figures 3 and 4. Values in parentheses are standard errors.

Sample	% heat >450°C			Signal height 500°C (W g ⁻¹)				
set #	а	b	R^2	Р	a	b	R^2	Р
1	-2.43 (0.45)	0.36 (0.03)	0.95	< 0.001	-0.53 (0.21)	1.10 (0.08)	0.97	< 0.001
2	-0.16 (0.61)	0.18 (0.05)	0.71	< 0.01	0.22 (0.60)	0.67 (0.21)	0.64	< 0.05
3	1.83 (0.29)	0.03 (0.01)	0.81	< 0.01	2.26 (0.26)	0.08 (0.03)	0.70	< 0.05
4	2.09 (0.06)	-0.01 (0.01)	0.63	< 0.05	1.99 (0.05)	-0.06 (0.03)	0.38	0.11



Figure 3 Relationship between heat released above 450°C from POM fractions and their mean carbon age (log scale).

Figure 4 Relationship between signal height at 500°C from POM fractions and their mean carbon age (log scale).

DISCUSSION

Our analysis of bulk soil thermal stability showed the presence of BC in samples from two sites of origin (Spain, Grossenz) as indicated by a marked peak at around 500°C. This pattern is in line with previous analyses of BC-containing mineral soils (Leifeld 2007; Maharaj et al. 2007) and with the thermogram of isolated charcoal particles that combusted mainly at this temperature (Figure 2). The contribution of BC to total soil organic carbon of between 13% (samples from Spain) and 33% (samples from Austria) was substantial but well within the range observed in field experiments (Schmidt et al. 1996; Rethemeyer et al. 2005; Leifeld et al. 2006; Marschner et al. 2008) and natural soils in Europe (Schmidt et al. 2002). However, bulk soil measurements do not indicate where in the soil matrix the BC is located. Charcoal and other BC materials, such as biochar, have lower specific densities than soil minerals, and hence an occurrence or even enrichment of BC materials in the light fraction is conceivable and was documented previously for Terra Preta soils (Glaser et al. 2000). The present analysis of the corresponding light POM fractions from the various samples revealed a wide range of thermal stabilities and mean carbon ages. For three out of four sample sets representing two regions of origin and two different POM types, mean carbon ages as derived from ¹⁴C turnover modeling indicated the presence of relatively old carbon moieties. Although no charcoal particles were dated directly, this presence can be inferred from the difference to the age of POC from site 4 containing no or minimum charcoal. Mean ages in the range of decades can be considered as typical for POC from grassland soils of the temperate or subalpine region (Leifeld et al. 2009). The Swiss mountain site was the coldest among all sites, and we assume the mean age of (nonpyrogenic) POC at this site to be the highest.

The comparison of sample sets 1 and 2, representing POM that is either inter-aggregate (i.e. free) or intra-aggregate (i.e. occluded and protected), revealed no significant differences in thermal stability or mean age. However, regression slopes indicated a more steeply increase in mean age with thermal stability for the fPOM fraction and, hence, a higher age of BC located in fPOM than in oPOM. This finding suggests stabilization mechanisms of BC in soil, considering the well-recognized role of aggregation for stabilization of soil carbon (Six et al. 1999) and BC in soil (Liang et al. 2008). For example, in soil of the same age and thermal stability that is exposed to vegetation fires and BC formation, BC is quickly protected physically within aggregates where it ages. After the aggregate lifetime has passed, the remaining, old BC is released as fPOM whereas newly formed, young BC preferentially enters the interior of aggregates. Our data, however, can serve only as an indication for such relationship, and studies addressing this subject in more detail would be required to better understand the mechanisms for BC stabilization via aggregation in soil.

Mean carbon ages (sample set 1 vs. 3) and thermal stabilities (sample sets 1, 2 vs. 3) of POM samples as well as BC/SOC ratios of the corresponding bulk soils from set 3 were significantly higher than those of samples comprising sets 1 and 2, which also contained BC. Does this simply mean that the higher share of BC in samples from set 3 (Grossenz) induced a higher mean POC age? Or was BC in POM of the Grossenz soil also older? Regression slopes (Table 2) indicated that carbon age increased more steeply with increasing BC contents for samples from Spain (sets 1 and 2), suggesting that these samples contained BC of higher age than samples from the Austrian cropland site Grossenz and, hence, that the higher mean POC age in sample set 3 was due to a larger relative amount of BC rather than to a particularly high age of BC.

Our results support the first part of our hypothesis and allow rejection of its second part. First, for POM samples containing old BC, there was a highly significant positive relationship between thermal stability and mean age, owing to the higher thermal stability and presumably higher age of BC than of the nonpyrogenic compounds in the POM fraction. However, this relationship was site specific, and thermal stability as a proxy for mean age could be used only within a narrow, calibrated range of samples. Under these conditions, a large number of samples might be screened without the need for time-consuming and expensive ¹⁴C measurements. BC-free POM fractions showed either no or a negative relationship between mean age and thermal stability, depending on the kind of thermal proxy used. Second, the method could not clearly distinguish BC-containing from BC-free POM fractions due to an overlap in the statistical distribution of thermal parameter values between the respective sample sets. Thus, although a distinct thermal BC peak could be used for BC quantification in mineral bulk soils, DSC had limited applicability regarding BC identification and quantification in POM.

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				Year	Year	Sampling	Site coordi-
Sample ID	Site	pMC	Error	sampled	measured	depth (cm)	nates (N/E)
ETH-40363	fPOM Spain1	109.87	0.37	2008	2010	0-10	42°13′/1°50′
ETH-40364	fPOM Spain2	103.52	0.38	2008	2010	10-20	42°13′/1°50′
ETH-40370	fPOM Spain3	107.70	0.37	2008	2010	0-10	42°13′/1°46′
ETH-40371	fPOM Spain4	91.42	0.38	2008	2010	10-20	42°13′/1°46′
ETH-40377	fPOM Spain5	89.34	0.38	2008	2010	0-10	42°15′/1°41′
ETH-40378	fPOM Spain6	83.24	0.38	2008	2010	10-20	42°15′/1°41′
ETH-40356	fPOM Spain7	109.76	0.37	2008	2010	0-10	42°16′/1°41′
ETH-40357	fPOM Spain8	104.23	0.38	2008	2010	10-20	42°16′/1°41′
ETH-40365	oPOM Spain1	111.25	0.37	2008	2010	0-10	42°13′/1°50′
ETH-40366	oPOM Spain2	98.73	0.38	2008	2010	10-20	42°13′/1°50′
ETH-40372	oPOM Spain3	114.77	0.37	2008	2010	0-10	42°13′/1°46′
ETH-40373	oPOM Spain4	107.75	0.37	2008	2010	10-20	42°13′/1°46′
ETH-40379	oPOM Spain5	106.53	0.37	2008	2010	0-10	42°15′/1°41′
ETH-40380	oPOM Spain6	90.96	0.40	2008	2010	10-20	42°15′/1°41′
ETH-40358	oPOM Spain7	112.96	0.37	2008	2010	0-10	42°16′/1°41′
ETH-40359	oPOM Spain8	103.16	0.38	2008	2010	10-20	42°16′/1°41′
VERA-51123 ^a	POM Grossenz1	95.4	0.4	2012	2013	0-5	48°20′/16°56′
VERA-51124	POM Grossenz1	90.8	0.4	2012	2013	0-5	48°20′/16°56′
VERA-51126	POM Grossenz2	65.5	0.3	2012	2013	40-60	48°20′/16°56′
VERA-51127	POM Grossenz2	72.3	0.3	2012	2013	40-60	48°20′/16°56′
VERA-51129	POM Grossenz3	93.4	0.6	2012	2013	10-15	48°20′/16°56′
VERA-51131	POM Grossenz4	99.1	0.4	2012	2013	0-5	48°20′/16°56′
VERA-51132	POM Grossenz4	98.7	0.5	2012	2013	0–5	48°20′/16°56′
VERA-51134	POM Grossenz5	84.8	0.3	2012	2013	40-60	48°20′/16°56′
VERA-51136	POM Grossenz6	92.2	0.7	2012	2013	10-15	48°20′/16°56′
VERA-51137	POM Grossenz6	86.2	0.4	2012	2013	10-15	48°20′/16°56′
ETH-37230	POM Alp1	108.74	0.41	2003	2009	0-10	46°31′/9°40′
ETH-37227	POM Alp2	109.62	0.41	2003	2009	0-10	46°31′/9°40′
ETH-37229	POM Alp3	109.96	0.41	2003	2009	0-10	46°31′/9°40′
ETH-37228	POM Alp4	110.85	0.42	2003	2009	0-10	46°31′/9°40′
ETH-37231	POM Alp5	112.94	0.42	2003	2009	0-10	46°31′/9°40′
ETH-37232	POM Alp6	111.06	0.42	2003	2009	0-10	46°31′/9°40′
ETH-37233	POM Alp7	111.20	0.42	2003	2009	0-10	46°31′/9°40′
ETH-37226	POM Alp8	111.55	0.42	2003	2009	0-10	46°31′/9°40′

Appendix. List of sample ID (ETH samples measured at ETH facility, VERA samples measured at VERA, Vienna facility), site of origin, measured pMC value with error, years of sampling and ¹⁴C measurement, and sampling depths and site coordinates.

a. VERA samples with the same number in column 2 are independent AMS measurements of the same POM sample. These double samples were pooled for DSC due to the small sample amount. The mean pMC value of these samples was used for regressing thermal stability against age.