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Magnetism of cigarette ashes

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Abstract

Mineral composition of cigarette ashes is well studied in the literature, but no reports are available about the magnetic fraction. Our study presents an investigation of the basic magnetic characteristics of ashes from several commercially available cigarette brands and a wood ash. Magnetic susceptibility, which is a concentration-dependent parameter in case of uniform mineralogy, shows that cigarette ashes contain relatively high amount of magnetic iron minerals, similar to that in wood ash from our study and other literature data. Magnetization data suggest that cigarette ashes contain some 0.1 wt% or lower quantity of magnetite, depending on the brand. Analyses of magnetic mineralogy imply that the main magnetic minerals in ashes from higher quality cigarette brands are magnetite and iron carbide cementite, while in ashes from lower quality brands without additives magnetic minerals are pure and substituted with foreign ions magnetic particles, as well as coarser (up to several microns), magnetically stable grains. Thus, the magnetic study of cigarette ashes proved that these plant ashes possess non-negligible magnetic properties. The results could serve for better elucidation of mineralogy of cigarette ashes as a whole, as well as for future investigation on the presence of magnetic ultra fine particles in cigarette smoke, which may be inhaled in lungs during smoking.

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1. Introduction

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In magnetism studies, and especially in environmental magnetism, it is well known that during

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fires (like forest fires) and combustion of organic matter, a strong enhancement of the content of iron oxides occurs [1,2]. Significant concentration of magnetic fraction is found also in the fly ashes-a product of high temperature combustion of coal in the thermal power plants (e.g. Ref. [3]). Thus, the magnetic response of the burned matter rich in organic content (e.g. soil, coal, etc.) increases and this feature is easily recorded by magnetic measurements, like magnetic susceptibility determination. The most common magnetic minerals, found in different products of fire and combustion, are maghemite and magnetite [2]. Depending on the firing conditions (maximum heating temperature, firing atmosphere, etc.), the end product may be also hematite. Thus, the application of magnetic methods to investigate the mineral magnetic properties of cigarette ashes is reasonable although in this case we are dealing with particular "artificial" burning process of multicomponent organic material. The aim of our study was to check whether cigarette ashes also contain enhanced magnetic fraction, to determine the kind of the magnetic mineral responsible for it and the grain size of the ferromagnetic particles. The latter has practical implication in respect to the presence of very fine grains, which from magnetic point of view behave as 'superparamagnetic' (SP) or stable single domain and may be present in the smoke and thus be inhaled in lungs. We have investigated the magnetic properties of several cigarette ashes, obtained from three commercially available cigarette brands.

Processes, occurring during cigarette smoking are well studied in specialized investigations [4–6]. According to the latter, two burn modes are envisaged to occur during smoking—smolder and puff burn. During the puff burn several processes are involved—combustion, pyrolysis, condensation and filtration. Temperature profiles of puff burn indicate that in the periphery of the burning line of the cigarette temperature might exceed 1000 °C. When the puff stops, a sudden cessation of airflow occurs and a burn rate becomes about ten times slower than during the puff. During smolder burn, physical processes include combustion, pyrolysis and distillation, while maximum temperature achieved is about 800 °C [4]. A number of papers deal with chemical and morphological characterization of the products from cigarette smoking [6,7]. The main elements detected in different regions of the cigarette coal are: sodium, phosphorous, sulfur, potassium, calcium, carbon, hydrogen, nitrogen and oxygen. Iron is mentioned as present only in trace amounts, but no systematic investigation is available concerning iron and the presence of ironcontaining minerals and their concentration in tobacco and in the different products from cigarette smoking. Thus, our study on the magnetism of cigarette ashes aims to contribute to understanding of the processes and products of cigarette smoking in this aspect.

2. Experimental section

2.1. Samples description

We have studied ashes (whole products residue) from smoked by different smokers cigarettes from three different commercially available on the market brands, labeled as follows: Camel (CM)—three varieties: Camel filter normal (CM), Camel Light (CML) and Camel 100s (CM100); Marlboro (MR) and the Bulgarian brand Shipka (SH). Ashes were collected in glass pots and used for magnetic measurements without further treatment.

In addition, we carried out control magnetic measurements on flue-cured tobacco from non-smoked cigarette from the SH brand. The material was taken from several cigarettes, leaving out the filter and the paper. In order to compare the effects of the firing atmosphere on the composition and properties of the magnetic fraction, we have performed free-air burning of SH cigarettes (sample 'SH-burnt') on a plate. Magnetic properties of cigarette ashes and wood-ash are investigated as well in order to compare the two types of vegetation-ash (wood and tobacco).

2.2. Methods

Different rock-magnetic methods were applied for the identification of the magnetic minerals, their concentration and grain size. The following set of experiments was carried out: measurements of magnetic susceptibility at low and high frequency of the AC field for determination of the concentration of magnetic minerals and presence of very fine nm-sized (SP) grains; hysteresis cycles for determination of the saturation magnetization (J_s) , remanent saturation magnetization (J_{rs}) and coercive force H_c (concentration- and grain-sizedependent characteristics) and back-field DCremagnetization curves for determination of the coercivity of remanence (H_{cr}) ; thermomagnetic analyses of magnetic susceptibility in the hightemperature range (from room temperature up to 700 °C) for determination of Curie/Neel temperatures of the magnetic minerals present; thermal step-wise demagnetization of three-component saturation remanence [1,8].

Samples from magnetic separates from MR, CM and SH ashes were prepared with carbon coating for scanning electron microscope (SEM) observations with qualitative EDX analysis.

2.3. Apparatuses

Magnetic susceptibility and its high-temperature variations were measured with KLY 3 kappa bridge equipped with CS3 temperature attachment (AGICO, Brno, Czech Republic); frequency-dependent magnetic susceptibility at two different frequencies (0.47 and 4.7 kHz) was measured with Bartington susceptibility meter (Bartington Ltd, UK); hysteresis loops were obtained with translation inductometer within an electro-magnet (maximum applied field of 1T), developed at the Paleomagnetic laboratory in St. Maur, Paris. Step-wise thermal demagnetization was done in a shielded mu-metal furnace with residual field inside less than 5 nT; measurements of the remanent magnetization signal were done on a spinner magnetometer JR-4 (Agico Ltd., Czech Republic). Scanning electron microscopy was done on JEOL T300 with electron probe for X-ray microanalysis (EPXMA).

3. Results

3.1. Magnetic susceptibility and its frequency dependence

Magnetic susceptibility is a parameter, which reflects the 'response' of the material when placed in a weak magnetic field (the strength comparable to the Earth's magnetic field) (e.g. Ref. [9]). This magnetic characteristic depends on the kind of the magnetic mineral, or in case of uniform mineralogy, on the concentration of the strongly magnetic iron oxides, although certain grain-size dependence is also evidenced for magnetites and titanomagnetites in the size range $\sim 0.01-0.03 \,\mu m$ [10,11].

Magnetic susceptibility data for the studied cigarette ashes are shown in Table 1. The values are mass-normalized (mass-specific magnetic susceptibility γ), so that comparison can be made among the different materials. It is obvious that ashes from CM and MR brands show the highest γ values, suggesting the highest iron oxide concentration. SH ash shows lower γ and burnt SH cigarettes exhibit the lowest magnetic susceptibility (Table 1). Wood ash possesses relatively low χ compared to cigarette ashes, but higher than the burnt SH cigarettes. Some literature data are also shown in Table 1 for comparison of susceptibility of cigarette ashes with the fly ashes from several Bulgarian coal-burning power plants [12] and wood ash from archaeological sites in UK [13]. It is clear that cigarette ashes show an order of magnitude lower susceptibility values as compared to the fly ashes, and comparable magnetic susceptibility values to these for wood ashes.

Frequency-dependence of magnetic susceptibility is widely used characteristic in environmental magnetism for evidencing the presence of submicrometer ferromagnetic grains (SP grains). It is shown that grains with such sizes react to the low frequency magnetic field, while they do not contribute to χ at high frequency magnetic field [14,15]. Thus, a widely used parameter—frequency dependence of magnetic susceptibility χ_{fd} % defined as $(100 \times (\chi_{lf} - \chi_{hf})/\chi_{lf})$, where χ_{lf} and χ_{hf} are the values for magnetic susceptibility measured at low- and high frequencies of the AC field,

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Sample	Magnetic susceptibility, χ ($\times 10^{-8}$ m ³ /kg)	χ _{fd} %	SIRM/ χ (kA/m)	Tar (mg)	Nicotine (mg)	Additives (%)
Tobacco-SH brand	2.4			14.0	0.9	No
СМ	143.7		0.215	10.0	0.9	8.8
CM100	114.7	8.5	0.165	12.0	1.0	Not indicated
CML	143.9	8.2	0.174	8.0	0.7	Not indicated
MR	142.5	6.8	0.209	10.0	0.8	9.0
SH	71.9	7.5	0.159	14.0	0.9	No
SH-burnt	24.8	3.4	0.173			No
Wood ash from domestic oven	62.7	5.0	0.139			
 Fly ashes from Bulgarian coal-bu. Bulgarian lignitic coals Bulgarian sub-bituminous coals Ukrainian bituminous and anthracitic coals 	rning power plants [$\chi_{average} = 1990$ $\chi_{average} = 1108$ $\chi_{average} = 1887$	12]				
Fireplace ashes from single burnin	ng [13]					
• Bark ash	119		0.11			
• Heartwood ash	87		0.22			
• Heartwood ash	146		0.17			
• Wood ash	178		1.81			
• Wood ash	1/8		1.81			

Magnetic characteristics of the studied ashes and literature data for other types of ashes

Table 1

Magnetic characteristics: mass-specific magnetic susceptibility (χ), frequency-dependence of magnetic susceptibility (χ _{fd}%), ratio of saturation remanence (SIRM) to magnetic susceptibility (χ), tar, nicotine and additives content of the studied cigarettes, as indicated on the corresponding boxes.

respectively, is calculated for determination of the relative amount of SP grains in the studied environmental materials.

Frequency-dependent magnetic susceptibility was measured on Bartington dual frequency sensor MS2B, which however has lower sensitivity than the Kappabridges KLY2 and KLY3. As it is shown by Dearing [16], since the highest precision is +0.1 on each reading, the smallest significant difference between low- and high-field readings is 0.4 units. In order to check the reliability of our χ_{fd} % data, we have performed 10 repeated measurements at each frequency and calculated the corresponding standard deviations. Results are shown in Table 2 together with the calculated difference $K_{\rm lf}-K_{\rm hf}$, and a comparison between mass-specific magnetic susceptibilities measured with Bartington and KLY2 instruments. As it is evident from Table 2, the difference $K_{\rm lf}-K_{\rm hf}$ is greater than 0.4 SI units for all cigarette brands except SHB. On the other hand, $K_{\rm lf}-K_{\rm hf}$ for all the samples is much greater than the calculated standard deviation values, even for SHB. Therefore, we consider the obtained χ_{fd} % values as reliably determined and reflecting the real variations in the concentration of the SP fraction. The material available from CM ash was not enough, so that reliable χ_{fd} % calculation was not possible. That is why only susceptibility measured with the kappabridge KLY2 is given in Tables 1 and 2 for CM ash. Table 2 further demonstrates quite good agreement between the calculated mass-specific χ values, obtained from the measurements by the two instruments in spite of the different working frequencies and measuring accuracies.

Wood ash and SH-burnt ashes show the lowest χ_{fd} % values, while CM and CM100 ashes have the highest χ_{fd} %. In general, χ_{fd} % for the studied

Table 2

Magnetic susceptibility measurements at two working frequencies (low frequency (LF): 0.47 kHz and high frequency (HF): 4.7 kHz) of Bartington dual-frequency sensor with the corresponding std. dev. values, calculated from 10 repeated measurements at each frequency; difference K_{lf} - K_{hf} ; mass-specific magnetic susceptibility, obtained through Bartington susceptibility meter (Bartington Ltd., UK) and Kappabridge KLY 2 (AGICO, Czech Republic)

Sample	$K \times 10^{-5} \mathrm{SI}$		$\chi (\times 10^{-8} \mathrm{m^3/kg})$				
	Bartington MS2B du	al-frequency sensor; $N = 1$					
	$K_{\rm lf}\pm$ std. dev.	$K_{\rm hf}\pm$ std. dev.	Bartington MS2B-LF	KLY 2			
SH	16.885 ± 0.139	15.615 ± 0.131	1.270	74.38	71.90		
SH-burnt	4.47 ± 0.079	4.322 ± 0.067	0.148	21.18	24.76		
СМ				_	143.80		
CML	24.155 ± 0.089	22.175 ± 0.109	1.980	139.60	143.90		
CM100	9.79 ± 0.133	8.955 ± 0.187	0.835	105.30	114.70		
MR	9.52 ± 0.140	8.875 ± 0.181	0.645	126.90	142.50		
W	19.47 ± 0.167	18.495 ± 0.126	0.975	60.09	62.70		

cigarette ashes varies between 7% and 8.5%, which suggests the presence of relatively high amount of SP grains.

3.2. Thermomagnetic analysis of magnetic susceptibility

Heating and cooling experiments were performed in air and Argon atmosphere from room temperature up to 700 °C. Fig. 1 shows the results for the studied cigarette ashes with indication of the heating conditions—in air or in Ar. It can be seen that for all cigarette ashes the main decrease in magnetic susceptibility signal occurs in the temperature range (400-560) °C but the most convex heating curve is obtained for MR sample. For the sample from CML brand a bend at around 300 °C on the heating run can be seen, as well as at 270 °C for CM and at ~350 °C for SH-burnt ash. The high-temperature $T_{\rm c}$'s are in the range 520-560 °C (Fig. 1), as determined by the straight-line approximation of $1/\chi$ vs. T dependence at high temperatures (Curie-Weiss law). The cooling run from 700 °C to room temperature is used often as an indicator about the mineralogical/ phase changes in the material during heating. Reversible heating/cooling cycle suggests no transformations. Cigarette ashes all show irreversible thermomagnetic behavior and the cooling curve is

below the heating one (Fig. 1), except for SHburnt ash and wood-ash, which show almost reversible behavior. In order to check if the transformations during heating are due to the differing heating atmosphere (mostly reducing during cigarette smoking and oxidizing upon heating in air), thermomagnetic analyses in inert atmosphere (flowing Ar gas) were done for two cigarette ashes (CML and SH) (Figs. 1a and d). The cooling curves in both cases lie below the heating ones, thus suggesting that changes should be due to transformations which are not related to the heating atmosphere.

3.3. Thermal demagnetization of three-component isothermal remanent magnetization (IRM)

Step-wise thermal demagnetization of threecomponent IRM was carried out in order to obtain the unblocking temperatures (T_{ub}) of the different coercivity fractions of IRM, imparted along the three orthogonal axes of the cubic samples [8]. Samples were prepared by mixing cigarette ash with gypsum. Control blank gypsum sample was also prepared, magnetized along the three orthogonal axes and subjected to thermal demagnetization. Afterwards, its signal was subtracted from the signal obtained for the cigarette ash samples.



Fig. 1. Thermomagnetic analysis of magnetic susceptibility for determination of Curie points of ferromagnetic minerals. Thick line represents heating run, thin line—cooling run. Susceptibility values are not mass-normalized.

The common characteristic for all ashes is the predominance of magnetically soft fraction (magnetization acquired after application of a DC field of 0.23 T), while the intermediate (0.23-0.47 T field interval) and hard (0.47-2 T interval) components make only minor contribution to the overall signal (Fig. 2). That is why only the soft and intermediate components are shown in Fig. 2. Inflection points again mark the unblocking temperatures of the corresponding IRM component. All cigarette ashes show the presence of one $T_{\rm ub}$ in the range of the medium temperatures, as follows: 210 °C for all three CM varieties; ~350 °C for SH brand, 190 °C for MR (Fig. 2a-e). Wood ash also shows very clearly the presence of T_{ub} in this temperature range—~350 °C (Fig. 2g). Two ashes display a second $T_{\rm ub}$ in the range (400–450) °C: 450 °C for SH-burnt; 450 °C for MR. For all but SH-burnt sample, a high-temperature maximum $T_{\rm ub}$ is also obtained: 560 °C for SH; 580 °C for CM, MR and wood ash; 620 °C for CML and CM100 (Fig. 2).

Magnetic susceptibility (*K*) was also monitored after each heating step, thus giving rough information about the occurrence of mineralogical changes during heating. Results for the normalized to the room temperature susceptibility values are shown in Fig. 3 for all the samples. It can be seen that *K* does not change significantly during the heating experiment, suggesting that the determined T_{ub} are most probably due to the real presence of different magnetic phases rather than a result of mineralogical alterations.

3.4. Hysteresis measurements

Hysteresis curves up to 0.8 T maximum applied field were measured for bulk loose material of the studied samples. Afterwards the loops were corrected with the curve measured for the empty holder, so that its signal is eliminated. Hysteresis parameters (J_s , J_{rs} , H_c , H_{cr}) were calculated from the corrected hysteresis curves and the data are



Fig. 2. Step-wise thermal demagnetization of composite IRM. Full dots denote magnetically soft fraction (0-0.23 T), empty diamonds—intermediate fraction (0.23-0.47 T). IRM values are not mass-normalized and depend on the amount of material used for preparation of each sample.

summarized in Table 3. Coercive force (H_c) and the coercivity of remanence (H_{cr}) are similar for all cigarette ashes and are slightly higher than these for wood ash. However, the saturation magnetization J_s , which is concentration-dependent characteristic, varies significantly among the different cigarette ashes (Table 3). The highest values are measured for CM and MR ashes, while wood ash and the SH-burnt ash show lower values. The same dependence is valid also for the remanent saturation magnetization (J_{rs}), but MR ash shows the highest value of J_{rs} .

The grain-size dependence of the ratios $J_{\rm rs}/J_{\rm s}$ and $H_{\rm cr}/H_{\rm c}$ is well-documented property of magnetite/titanomagnetite grains [17,18] and is commonly used to deduce the magnetic grain size of the iron oxide particles. These ratios are also calculated for the studied ashes and results are shown in Table 3.

3.5. Laboratory-induced remanences (anhysteretic remanent magnetization (ARM) and saturation isothermal remanent magnetization (SIRM))

ARM is a laboratory-induced magnetic remanence, which is widely used in environmental magnetism for determination of the magnetic grain size. It is imparted by applying simultaneously an alternating magnetic field (AF) with



Fig. 3. Normalized to the room-temperature value magnetic susceptibility measured after each heating step during step-wise thermal demagnetization of composite IRM.

Table 3 Hysteresis parameters obtained for bulk cigarette ash material

peak amplitude decreasing to zero and a constant weak DC field. The results obtained for synthetic and natural iron oxide minerals of well-defined grain size show a strong dependence of the ability of the different grain size fractions to acquire ARM [18,19]. SIRM is a strong-field remanence, which mostly depends on the concentration of the magnetic grains, but also on the grain size [18,20]. Thus, a combination of these two remanences can give insight on the relative abundance of the different magnetic grain size fractions in the studied environmental materials.

In our study, ARM was induced by applying AF with peak amplitude of 100 mT and a DC field of 0.1 mT, while SIRM was induced in a DC field of 2T. Cubic samples of 8 cm³ volume were prepared with gypsum, as described before. The so-called "anhysteretic susceptibility" ($K_{arm} = ARM/h$, where h is the strength of the weak DC field during ARM acquisition) was calculated and the ratio K_{arm}/K_{lf} (K_{lf} —volume low-frequency magnetic susceptibility) was used as a grain-size indicator. The ratio SIRM/ K_{lf} is also calculated and shown in Table 1, since it is used by many authors also as a grain-size indicator and comparison of our data with the published ones for wood ashes can be done (Table 1).

The combined bi-plot, including the ratio SIRM/ $K_{\rm lf}$ and the percent frequency-dependence (Fig. 4c) shows in general an increase in SIRM/ $K_{\rm lf}$ with increasing the content of fine SP grains (e.g. $\chi_{\rm fd}$ %), but a certain scatter in the data suggests also differences between the two fractions in the different ashes. More complicated pattern is observed in the bi-plot between SIRM/ $K_{\rm lf}$ and $K_{\rm arm}/K_{\rm lf}$ (Fig. 4d). Generally, both ratios reflect the presence of stable (single-domain (SD)) grains,

Sample	$H_{\rm c}~({\rm mT})$	$H_{\rm cr}~({\rm mT})$	$J_{\rm s}~(10^{-3}{\rm A}{\rm m}^2/{\rm kg})$	$J_{\rm rs}~(10^{-3}{\rm A}{ m m}^2/{ m kg})$	$J_{ m rs}/J_{ m s}$	$H_{ m cr}/H_{ m c}$
СМ	11.2	40.5	93.2	16.8	0.18	3.62
MR	13.6	31.1	86.0	18.4	0.21	2.30
SH	12.1	33.1	62.6	10.2	0.16	2.74
SH-burnt	12.3	39.1	18.5	3.4	0.18	3.18
Wood ash from domestic oven	9.7	25.2	43.0	6.9	0.16	2.60

 H_c —coercive force; H_{cr} —coercivity of remanence; J_s —saturation magnetization; J_{rs} —saturation remanent magnetization.



Fig. 4. Bi-plots of different magnetic characteristics: (a) saturation remanence (J_{rs}) vs. saturation magnetization (J_s); (b) percent frequency dependence χ_{FD} % vs. mass-specific magnetic susceptibility χ ; (c) ratio SIRM/ K_{lf} vs. percent frequency dependence χ_{FD} %; and (d) SIRM/ K_{lf} vs. K_{arm}/K_{lf} .

but K_{arm} exhibits stronger affinity for such grains [11,20].

3.6. SEM

Magnetic extracts from the cigarette ashes were used for SEM observations in order to examine the chemical composition of the material used for the magnetic measurements. Pictures from MR ash are shown in Fig. 5. The particles, having significant Fe content are of irregular shape with rough edges. Qualitative elemental analysis shows that the main constituents except Fe, are Ca, Mg, Si, K, and smaller amounts of Al, P, Ti and Mn (Table 4). A tendency of an increased complexity of the chemical composition of larger particles



15 µm





5 µm

 $5 \, \mu m$

Fig. 5. SEM pictures of magnetic extract from MR cigarette ash: (a) conglomerate of calcium particles; (b) group of Fe-rich particles with irregular shapes and sharp edges (gray and bright particles); (c) Fe-rich particle (element composition in row 5 from Table 6) bound to non-magnetic matter; and (d) poly mineral Fe-rich particle (element composition in row 6 from Table 6).

Table 4 Integral EDX spectra of magnetic extracts (element content in wt%)

Sample	Mg	Al	Si	Р	S	Cl	K	Ca	Ti	Fe
Shipka Marlboro	3.74 2.51	1.66 2.89	5.93 5.88	1.37 2.13	4.83 2.57	5.97 0.14	16.89 4.25	23.17 40.35	0.23 0.42	1.64 2.81
Camel	0.72	—	4.36	0.91	3.46	7.35	17.76	34.55	_	—

 $(>10\,\mu\text{m})$ is observed, based on further analytical data (not shown in Table 4). In order to illustrate the different habitus of the Fe-containing and

other mineral particles in the ashes, a picture of the observed Ca-conglomerates is shown in Fig. 5a. Their presence in the magnetic extract is probably

Brand	Particle dimensions (µm)	Mg	Al	Si	Р	S	Cl	K	Ca	Ti	Mn	Cr	Fe
MR	1 × 1	_	_	_	_		_	_	_	_	_	_	69.94
	1×1	5.69		2.67	2.20	1.72	0.82	1.02	9.69	2.38	0.42	_	38.64
	2.5×3	_		_				_	0.51	_	_	_	69.44
	4×4.5	_	_	1.65	_	_	_	0.38	0.73	_	_	_	66.45
	5×6	4.25	5.39	2.94	1.56			3.03	10.22	0.43	0.39	_	37.58
	10×12	3.57		0.97	2.72			0.58	4.97	_	_	_	54.64
	15×15	2.3	1.81	2.34	0.68	0.51	—	1.79	1.69	—	0.23	0.29	55.74

Table 5 EDX spectra of single magnetic particles (element content in wt%)

due to the low efficiency of the magnetic separation and electrostatic interactions between particles. The data in Table 5 represent the integral spectra taken from the areas of about $500 \times 500 \,\mu\text{m}$ for the different cigarette brands and again suggest the significant amounts of Ca, K, as well as other elements within the separates. The weight percent Fe is not representative for the raw ash material used for susceptibility measurements, so further comparisons with the estimated iron content are not possible.

4. Discussion

4.1. Magnetic susceptibility and mineralogy of cigarette ashes

Magnetic susceptibility measurements of different materials are very sensitive to the presence of strongly magnetic particles and even 1 ppm of magnetite can be easily detected [20]. Another advantage of the magnetic techniques is that they are non-destructive to the material, and samples are prepared in a very simple way (usually just powder material is suitable), without any need for application of special reagents or other treatment.

Magnetic susceptibility is a property of the matter, which reflects mainly the concentration of the different iron-containing minerals, mostly iron oxides and sulfides in natural systems [20], provided that mineralogy does not vary. Many studies are dealing with the processes, which lead to the enhancement of the magnetic properties of different materials as a result of heating. Commonly soils and clays are investigated in order to

explain the enhanced magnetic signal of top soils [2,21] or burned clays from pottery and archaeological remains [22-24]. The main point in these studies is the source and availability of iron during burning of the material, which determines the degree of magnetic enhancement and the kind of the magnetic mineral which is formed as a result of heating. Other key factors determining the concentration and kind of the resultant product are the maximum temperature reached and the firing atmosphere (oxidizing or reducing) [23]. The enhanced magnetic properties of the soils are usually considered as a result of authigenic formation of strongly magnetic minerals (magnetite, maghemite) during the pedogenesis [21,25] or ancient fires [2]. However, few studies also consider the contribution of plant ash magnetism to the magnetic properties of soils [13]. In our study, we focus on the magnetic properties of different cigarette ashes, which are plant ashes as well.

There is very limited information available on the iron content in tobacco. This element is generally mentioned as present in only trace amounts [7]. Few studies report different quantities of Fe, found in tobacco: $(0.5-2.0) \mu mol$ Fe/g (dry weight) [26] and 440–1150 μ g Fe per gram [27], but the mineral phases in which Fe is involved are not specified. Several studies are investigating the phase changes and iron minerals occurring during catalysis by an iron oxide and possible implications for the removal of carbon monoxide in a burning cigarette [28,29]. There is no information about the presence of catalytic iron oxides among the additives of the studied cigarettes (Table 1), however ferric oxides are mentioned among the list of permitted additives [30]. On the other hand, recent investigations report the discovery of nanocrystalline botanical magnetite [31] in grass plant cells. McClean et al. [32] studied also grass material (Normal Festuceae Ness leaf/stem clippings) and identified several forms of iron oxides in plant-magnetite (Fe₃O₄), ϵ -Fe₂O₃ and hematite (α -Fe₂O₃), all present in vivo. McClean and Kean [13] in their study of wood ash magnetism considered as a source of magnetic iron oxides in ash plant phytoferritin. However, it is uncertain whether the iron in phytoferritin is in crystalline or amorphous form, and few studies, available to us, fail to identify unambiguously the form of iron in biological tissues. Kilcovne et al. [33] in a Moessbauer study of rice roots and leafs detect SP iron particles and suggested that Fe is in the form of oxyhydroxide ferrihydrite, although they prefer to speak only about "iron oxide components".

Another source of magnetic signal in vegetation is due to deposition of atmospheric dust particles of different origin on plant leafs. Dust itself contains strongly magnetic iron oxide particles [34] and can be a reason for enhanced magnetic properties of vegetation [35,36]. This feature is recently used in environmental magnetism for fast and cost-effective detection of atmospheric pollution [3].

Mineral magnetic methods are therefore suitable for identification of the form of iron in burnt tobacco material, since the iron content in ash is strongly enhanced as compared to that in nonburned cigarette [37], probably as a result of both significant weight loss during heating [5] and creation of new strongly magnetic minerals during burning. The magnetic enhancement of cigarette ash in respect to unburned tobacco is also confirmed by our magnetic susceptibility measurements. Magnetic susceptibility of ash from SH brand is 30 times higher than that of unburned cigarette (Table 1) and magnetic susceptibility of ash from burnt SH cigarettes is 10 times higher than that of tobacco (Table 1). Thus, the magnetic enhancement is most probably due to a combined effect of both processes, mentioned above, since the reported density loss (up to 80% [5]) is not sufficient as a single explanation for the observed

enhancement of magnetic susceptibility of cigarette ashes as compared to unburned tobacco.

Magnetic susceptibilities of cigarette ashes in the present study are compatible with the literature data for wood ashes [13,38] (Table 1), although, χ for the wood ash in our study is lower than the reported values for fireplace ashes [13]. A possible reason could be the relative availability of oxygen and different temperature during burning, since our wood ash was taken from domestic oven with closed burning chamber, while in a fireplace more oxygen is flowing during the burning process. This probably causes the formation of higher amount of strongly magnetic minerals in the fireplace ashes, as compared to the wood ash from the domestic ovens.

In contrast, the magnetic susceptibility of Bulgarian coal-burning power plant fly ashes (Table 1) shows one order of magnitude higher values, suggesting significantly higher iron oxide concentration. The difference arises from several factors: higher initial Fe concentration in coals; different technological conditions during coal combustion, leading to different solid-phase reactions (as compared to burning cigarette); higher maximum temperatures reached in power plant boilers (1600-1700 °C according to Vassilev and Vassileva [39]), and different initial mineralogy of tobacco and coals. Another important difference is in the parameter χ_{fd} %—as it is seen in Table 1, cigarette ashes show quite high values, indicating the presence of more than 50% SP particles in the ferromagnetic fraction of the ash, according to the empirical model [21]. On the other hand, literature data for χ_{fd} % for power plant fly ashes all show values, varying between 1% and 4% [40,41], indicative of low relative proportion of very fine (nanometer size) strongly magnetic grains.

The mass-specific magnetic susceptibility shows variations among the studied cigarette ashes of different brands as well. CM and MR brands, for which the presence of additives is explicitly indicated on the cigarette box (Table 1), exhibit the highest χ values. However, no information is available about the nature of the additives, so that we cannot do more definite conclusions, related to this fact. The magnetic susceptibility of burnt SH cigarettes is the lowest one, indicating most

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probably significantly lower maximum temperature reached during the free burning in air.

The determination of magnetic mineralogy of the cigarette ashes requires careful consideration of the magnetic phases, involved in the initial unburned tobacco and the possible secondary magnetic phases, formed during burning. For better clarity, the obtained data on the Curie/ unblocking temperatures of the studied ashes and literature data on the main ferri/ferromagnetic minerals in concern are summarized in Table 6.

As it was discussed above, biological iron minerals, recently found in plant tissues, include magnetite (Fe₃O₄), ϵ -Fe₂O₃ and hematite (α -Fe₂O₃) [32]. Of these, ϵ -Fe₂O₃ is a mineral with structure and properties, intermediate between hematite and maghemite (γ -Fe₂O₃) [42] and it is

Table 6

List of the Curie points (T_c) and unblocking temperatures (T_{ub}) determined from thermomagnetic analysis K(T) and step-wise thermal demagnetization of composite IRM

Sample/ mineral	$T_{\rm c}$ (°C)		Maximum T_{ub} (soft comp.) (°C)				
СМ	270,	560	210,	330–380,	580		
CM100	300,	540 (Ar)	230,	400,	620		
CML	520,	650	210,		620		
MR	560		190,	450,	580		
SH		520 (Ar)		330–380,	560		
SH-burnt	350,	540	230,	300,	450		
Wood ash	470,	560		330–380,	580		
Iron carbides ^a							
Fe ₃ C	210-212						
ε-Fe ₂ C	347-350		Decom	poses to χ-	Fe ₂ C		
χ -Fe ₂ C	247		above $\sim 240 ^{\circ}\text{C}$ Converts to Fe ₃ C at $\sim 550 ^{\circ}\text{C}$				
Iron oxides ^b							
Fe ₃ O ₄	580						
α-Fe ₂ O ₃	675						
γ -Fe ₂ O ₃	645		Conver	ts to α -Fe ₂	O3 in		
ε-Fe ₂ O ₃	197		the range Transfe the range	ge (300–35 orms to α-I ge (500–75	0 °C) Fe ₂ O ₃ in 0 °C)		

Literature data on T_c 's of the most common Fe-oxides and carbides are given in addition.

^aData according to Hofer and Cohn [46] and Chikazumi [45].

^bData according to Dunlop and Ozdemir [18] and references therein.

not found in natural rocks or soils/sediments. This mineral has a Curie point of 197 °C, but it is not stable and transforms to hematite upon heating in the temperature range (500-750) °C [42]. Thus, in cigarette ashes, this mineral is not probable to survive, since the temperatures, reached during smoking are usually significantly higher. Magnetite and hematite do not transform during heating up to their Curie points (580 and 680 °C, respectively), except some possible oxidation of magnetite [18]. Therefore, we can expect magnetite and hematite as possible magnetic minerals, present in the cigarette ashes. We assume that some small amount of fine (?biogenic) magnetite particles is present in non-burnt tobacco, based on the low positive γ -value for the tobacco (Table 1), because pure organic matter is diamagnetic (i.e. showing negative magnetic susceptibility) [18]. We do not suppose the presence of pollution particles (which are often strongly magnetic), because we did not find any large spherical magnetic grains (SEM results discussed later) in the magnetic fraction of cigarette ash. The presence of such ferrospheres is indicative for most atmospheric particulate pollutants [3]. Moreover, another argument in support of our supposition is that magnetic susceptibility value for the tobacco ($\chi =$ $2.4 \times 10^{-8} \,\mathrm{m^3/kg}$) is consistent with the background susceptibility, measured for non-polluted leafs of ryegrass and two broad-leaf trees (χ varying between 3.3 and $7.6 \times 10^{-8} \text{ m}^3/\text{kg}$) in an environmental magnetic study in Bulgaria [36].

Chemical reactions involved during burning the cigarettes and the corresponding processes when an iron oxide is involved are well studied [29,28,43]. In general, increasingly reducing conditions with increasing temperature, provoked by the organic matter transformations, determine series of reduction reactions of an iron oxide (maghemite) [28,29]. As a result, Fe₂O₃ first reacts with CO to form magnetite (Fe₃O₄) and CO₂, and further reactions lead to formation of iron carbides (mainly Fe₃C) at temperatures higher than $\sim 750 \,^{\circ}\text{C}$ [28,43]. The composition of the cigarette ash however depends on the specific conditions during burning-air flow, duration of puff and smolder burn, maximum temperature reached during smoking, etc. Since we have

studied cigarette ashes obtained from different smokers and different brands, the composition of each ash could be different. This is confirmed by the results of thermomagnetic analyses for determination of the Curie temperatures and the unblocking temperatures (Figs. 1 and 2 and Table 6). The high-temperature behavior of magnetic susceptibility reveals the main magnetic phase with $T_{\rm c}$ between 520 and 560 °C (Fig. 1 and Table 6), corresponding to the iron oxide magnetite (Fe_3O_4), either almost pure or with foreign-ions substitutions in its lattice [18,44]. The well-expressed peculiarity in the temperature range \sim 270–300 °C for CM ashes (Fig. 1) can be caused by the presence of maghemite, which transforms to hematite in this interval. The presence of unstable maghemite may be due to the very different temperatures existing in the different parts of the burning cigarette (e.g. Ref. [43]). The main contribution to the magnetic susceptibility behavior, however, has magnetite-like phase (Fig. 1), which probably transforms to hematite on heating to 700 °C. We suppose that this transformation does not occur during burning cigarette because of significantly higher heating rate during smoking (up to 100–500 °C/s during puff and 2 °C/s during smolder [4,5]) as compared to the heating rate during the laboratory thermomagnetic analysis ($\sim 10 \,^{\circ}$ C/min). However, magnetic susceptibility is a bulk property which reflects the contribution of all minerals present in the material. Studying the

unblocking temperature spectra of magnetic remanence can give detailed information solely on the ferrimagnetic fraction capable to acquire remanence, eliminating para- and SP fractions. We investigated the thermal demagnetization behavior of three-component IRM, thus involving in the signal only remanence carrying (SD, pseudo-single-domain (PSD) or multidomain) grains. The unblocking temperatures determined show the presence of magnetite Fe₃O₄ (or oxidized magnetite with higher T_c of ~620 °C), commonly observed on the soft component for all the samples (Fig. 2 and Table 6). The lower-temperature magnetic phases with $T_{\rm ub}$'s 210 and 300–380 °C (Fig. 2) make a significant contribution in all ashes, thus it is important to identify their origin as

well. There are several magnetic minerals having

 $T_{\rm c}$ or transformation temperature in this range. Among the natural materials, these are maghemite $(\gamma - Fe_2O_3)$ which transforms to hematite between 300 and 350 °C, some iron sulfides (monoclinic pyrrhotite, greigite), titanomagnetites with significant Ti content; hemoilmenites, magnetite with foreign ion substitutions [18]. However, cigarette ashes are not 'natural' materials and we have to consider also some minerals, which are usually synthesized under specific technological conditions, like combustion, catalysis, etc. Since iron carbides are reported to form often during burning cigarettes, we have to take into account these data. Commonly reported iron carbide cementite (Fe₃C) is ferromagnetic with T_c of about $210 \,^{\circ}\text{C}$ [45,46]. Thus, we suppose that the observed $T_{\rm ub} \sim 190-210 \,^{\circ}{\rm C}$ (Table 6) is due to the presence of iron carbide (Fe₃C) in the studied cigarette ashes. The fact that this phase is observed on the thermal demagnetization of magnetic remanence implies also that carbide particles are of sizes, capable to carry remanent magnetization-e.g. of SD or PSD size range. For SH cigarette ash, SHburnt and wood ash samples, a clear $T_{\rm ub}$ \sim 300–350 °C (Fig. 2 and Table 6) can be related to the presence of magnetite with significant foreign ions substitutions, which leads to a large decrease in T_c (and T_{ub} , respectively) [18]. Considering the qualitative microprobe analysis (Tables 4 and 5), these substitution ions could be Ti, Al, Mg, Mn. The substituted magnetite phase is the main remanence carrier (Fig. 2) for these three samples, and smaller contribution is due to magnetite.

The above conclusions about the magnetic mineralogy are supported also by the magnetization data, obtained from the hysteresis measurements. Saturation remanent magnetization $(J_{\rm rs})$ as a function of saturation magnetization $(J_{\rm s})$ shows positive linear relationship (Fig. 4a), implying an increased concentration of magnetic minerals. According to the literature data, $J_{\rm s}$ for pure magnetite is 92 A m²/kg [18,19]. If we consider magnetite as the main mineral, present in our samples, then we can suppose that CM and MR ashes contain some 0.1 wt% magnetite, while in the other ashes magnetite concentration is lower. This is evident from the thermal demagnetization

of three-component IRM (Figs. 2e and g) obviously in SH and wood ash samples the main mineral is highly substituted magnetite. It is well known that substitutions in the crystal lattice of magnetite cause significant lowering not only in the T_c (as discussed above), but also a decrease in J_s (and J_{rs} , respectively) [44]. Thus, magnetization data shown in Fig. 4a confirm our conclusions drawn from the Curie temperature determinations.

Considering the obtained magnetic mineralogy of cigarette ashes, it is possible to infer several possible sources of iron enhancement of ashes as compared to un-burnt tobacco: (a) effect of density change (as discusses above); (b) magnetic transformation of plant magnetic minerals during burning; (c) appearance of new strongly magnetic phases during burning. The main ferromagnetic minerals found in plant tissues are nanocrystalline magnetite and hematite [32], which will be influenced in different ways during burning tobacco. According to the set of reactions, established during catalysis by an iron oxide [29], hematite $(\alpha - Fe_2O_3)$ will be first reduced to magnetite. From magnetic point of view, this transformation leads to significant magnetic enhancement, since magnetite is characterized by much stronger magnetization, as compared to hematite [18]. The third mechanism relates to formation of new magnetite during heating. Sources of iron for this process are non-magnetic iron minerals in plant tissues, as iron phosphates, silicates, etc. [43]. During burning liberated iron ions form ferromagnetic iron minerals depending on the prevailing atmosphere (oxidizing or reducing).

4.2. Magnetic grain size

The magnetic grain size is evaluated in environmental magnetic studies by using a number of magnetic parameters, which are known to display grain size dependence. Such relations are established for the commonest natural magnetic minerals by studying well defined (by means of physical grain size) synthetic and/or natural materials. The best known is the grain size dependence of magnetite and titanomagnetites [47,48] since these are the most abundant magnetic minerals in nature. Grain-size dependence of the ratios of hysteresis parameters J_{rs}/J_s and H_{cr}/H_c , established for magnetite/titanomagnetite is often used in magnetic studies [49]. However, this relation is strict in cases when one grain size fraction dominates in the samples, while for a mixture of different fractions (e.g. large and fine grains, very fine nm-sized (SP) and coarser (SD) grains, MD and SD grains, etc.), the ratios give an 'effective' grain size, which is not related to the real grain sizes. In case of cigarette ashes, there are several factors, restricting the application of this approach for evaluation of the grain size. The most important factor impeding application of the hysteresis ratios as grain-size indicators is the presence of significant amount of very fine SP grains, as evidenced by the measured high χ_{fd} % (Table 1). Magnetization behavior of these grains bias the hysteresis loop so that effectively lower coercivities are measured [50]. The obtained hysteresis ratios for cigarette ashes would suggest the presence of PSD grains in all ashes [49]. However, taking into account the above considerations, this is an indication only of the 'effective' grain size in our samples. Magnetic mineralogy is indeed dominated by magnetite and substituted magnetite, but certain fraction of iron carbides is detected in some of the ashes (Fig. 2). Rockmagnetic data on the grain size dependence of magnetic iron carbides is not available to our knowledge, only some magnetic properties of nmsized (SP) iron carbide particles are reported [51,52]. For carbon encapsulated Fe nanoparticles (among them cementite is also identified) of average sizes 20 and 16 nm [51] the ratio J_{rs}/J_s is found to vary between 0.25 and 0.3. Our ratios are much lower (Table 3) and most probably influenced by the SP fraction, as well as by the magnetite fraction. The positive relationship between χ and χ_{fd} % (Fig. 4b) also proves that the SP fraction dominates magnetic susceptibility values of the cigarette ashes.

Grain size dependence is well-documented property also for the ratios SIRM/ $K_{\rm lf}$ (or SIRM/ χ) and $K_{\rm arm}/K_{\rm lf}$ [53]. In case of uniform mineralogy, dividing $K_{\rm arm}$ and SIRM by $K_{\rm lf}$ the concentration dependence is eliminated. Both ratios show higher values for stable SD grains, which acquire most effectively remanent magnetization [47]. As mentioned earlier, the affinity of SD magnetite particles is stronger for ARM (resp. $K_{\rm arm}$). Bi-plots shown in Fig. 4c and d can be interpreted in terms of both mineralogical and grain size variations. SIRM/ $K_{\rm lf}$ vs. $\chi_{\rm FD}$ % suggests that for most ashes the concentration of the stable grains (as represented by SIRM/ $K_{\rm lf}$) varies stronger than the concentration of SP grains (as represented by χ_{fd} %). On the other hand, the range of SIRM/ $K_{\rm lf}$ values are relatively restricted (compared to the obtained variations for different natural minerals-e.g. Ref. [19]), indicating similar domain state of the grains among the different cigarette ashes. The obtained SIRM/ χ values are in a very good agreement with the literature data for wood ashes (Table 1, [13]).

The bi-plot of SIRM/ $K_{\rm lf}$ vs. $K_{\rm arm}/K_{\rm lf}$ shows two different trends. The first one holds for samples CM (the three varieties) and MR. The observed direct linear relation suggests that more stable SD grains are present in ashes from CM and MR and coarser grains-in CML and CM100 (Fig. 4d). In contrast, an inverse relation is obtained—SIRM/ $K_{\rm lf}$ decreases as $K_{\rm arm}/K_{\rm lf}$ increases—for samples SB, SH and W. This specific behavior cannot be related to grain size dependence, since both ratios display similar properties related to grain size [53]. Therefore, we suppose that the obtained relation reflects different mineralogy. Indeed, as it was discussed in Section 4.1, SH and wood ashes contain a significant fraction of highly substituted magnetite. According to the obtained $T_{\rm c}$ ($T_{\rm ub}$), the substitutions should be the highest in SH-burnt ash, since the $T_{\rm c}$ for it is the lowest one (Fig. 2f). SH and wood ashes contain magnetite fraction as well (Fig. 2), which is probably of finer grain size, so that they acquire more effectively ARM than SIRM.

5. Conclusions

Magnetic mineralogy analysis shows that Marlboro (MR) and Camel (CM) cigarette ashes contain pure magnetite and iron carbide, while ash from lower-quality Shipka (SH) brand, as well as wood ash contain substituted and non-substituted magnetite. The difference in magnetic mineralogy might be related to the different additives contained in MR and CM brands, which influence the chemical reactions during burning. On the other hand, magnetic mineralogy of ash from SH brand (no additives) is similar to that one of wood (e.g. pure vegetation) ash.

Magnetic grain size analysis showed the presence of generally two distinct fractions—very fine grained (SP) and coarse (stable SD to PSD) one. The presence of large particles is directly evidenced also by the SEM pictures, showing that the biggest magnetic grains are of irregular shape. Sub-micron SP and SD particles, which significantly contribute to the total magnetic fraction, are in the respirable size and thus can be inhaled during smoking into lungs. A further magnetic study therefore can be designed to evaluate the amount of the magnetic particulates passing through cigarette filter during smoking and going to the lungs.

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