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Mineral magnetism and archaeomagnetic dating of a mediaeval oven from Zlatna Livada, Bulgaria

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Abstract

Archaeomagnetic palaeodirectional and palaeointensity results are presented from a domestic oven at the mediaeval site of Zlatna Livada. Archaeological evidence suggests that the site was occupied in the 11th or 12th C. AD, with the oven dating to the beginning of this period. The samples are dominated by magnetite and maghaemite. In some samples thermally unstable maghaemite occurs with unblocking temperatures between 300 °C and 400 °C, while in others maghaemite is stable to inversion until >600 °C. The mineral magnetic analyses, Thellier results and sample heterogeneity suggest that the oven was not heated to a very high or consistent temperature in antiquity (<320–<400 °C). Hysteresis measurements show a mixture of single and multi-domain grains, which may account for the variability in the success of the Thellier experiments. Water glass, the material used to physically stabilize unconsolidated samples, does not appear to react with the samples' mineralogy until above 500 °C, and thus does not affect the Thellier results. The oven has a mean palaeointensity determination of 72.13 μT, a mean declination of 15.8° and a mean inclination of 61.9°. The archaeomagnetic age estimate for the site using all three parameters is between 826 and 1004 AD and using only palaeodirectional data is 777–967 AD. Based on these archaeomagnetic age assessments and the archaeological evidence, the site is best dated to the very end of the 10th C. AD or first few years of the 11th C. AD. This confirms that the oven dates to the early period of site use, although the date is perhaps slightly younger than expected. This paper highlights a number of problems encountered during archaeomagnetic studies and emphasises the need for more reference curve data to increase the precision of the dating method, particularly during the mediaeval period in Bulgaria.

Keywords: Archaeomagnetism; Mineral magnetism; Mediaeval oven; Bulgaria; Palaeointensity; Palaeodirection

1. Introduction

Archaeomagnetic studies can reveal information about the long-term behaviour of the Earth's geomagnetic field and, when an adequate reference curve exists, can date archaeological sites and burnt structures (Aitken, 1978; Lanos et al., 1999). Zlatna Livada is located close to the town of Chirpan in south central Bulgaria (lat. = 42.2°, long. = 25.4°; Fig. 1A). The settlement is preliminarily dated by archaeological finds to the 11th–12th C. AD. Based on stratigraphic evidence the oven should date to the beginning of this period and a slightly earlier date is possible (Koleva, personal communication). The oven was constructed by digging into the northern side of a partially sunk domestic dwelling. It was most likely used for domestic purposes such as baking bread, although perhaps for more than one family. The oven is domed and has a diameter of between 1.32 and 1.40 m at its base. The oven has a sandy clay floor that consists of two layers of construction up to 0.40 m thick. Two stones flank the oven mouth, in front of which, a large trapezium-shaped pit and a smaller and deeper square pit occur. These were dug for the removal of ash from the oven.

The aim of this study was to date the site based on the palaeointensity (PI) and palaeodirectional (PD) data

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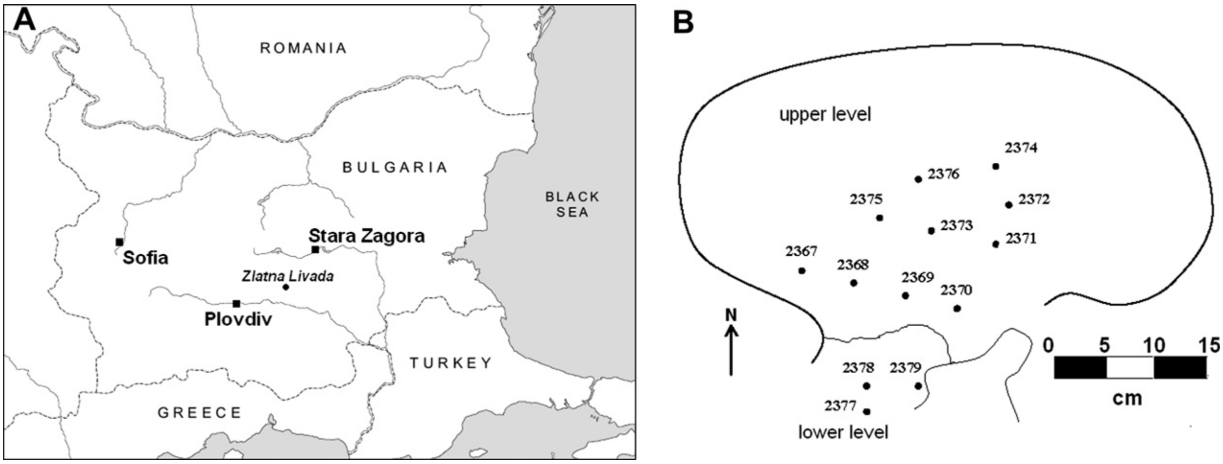

Fig. 1. (A) Location of Zlatna Livada in central Bulgaria. (B) Distribution of samples collected from the Zlatna Livada domestic oven.

recovered from this oven. The magnetic mineralogy has a profound effect on the suitability and reliability of different samples for PI analysis using the Thellier method (Thellier and Thellier, 1959; Jordanova et al., 2003). Despite many studies (e.g. Jordanova et al., 1997) there is still no unambiguous set of experiments for the pre-selection of suitable samples for PI determinations. As such, a second aim was to undertake a suite of mineral magnetic tests for identifying samples suitable for PI measurements and to enable a greater understanding of the behaviour of samples during Thellier analysis.

2. Sampling

A series of 13 independently oriented hand samples of baked clay were removed from the plaster floor of this oven (Fig. 1B). The samples were oriented with a magnetic compass due to the lack of sunlight for sun compass measurements. Declination has been corrected on the basis of the contemporary value (3.9°E) obtained from the Bulgarian geomagnetic field survey. Samples 2377, 2378, 2379 came from a lower, sloping level of the oven (14° slope for 2377, 12° for 2378, 13° for 2379; Fig. 1B). The samples are quite friable, consisting of blackened, coarse grained sand and a fine-grained clay matrix. Consequently, the samples were consolidated in a water-glass solution ($Na_2SiO_3 \cdot nH_2O$). Kostadinova et al. (2004) suggest that while magnetic susceptibility shows a range of behaviours on heating when samples are impregnated with water glass, the remanence parameters are not influenced significantly. The lack of solidification and/or vitrification of quartz grains in the samples suggest a low intensity and short duration of heating. The impregnated samples were then set in oriented blocks of plaster and cut into 8 cm^3 specimens (cubes) for measurement. Between 5 and 13 specimens (cubes) were cut from each hand sample and they all came from the same 2 cm depth layer of material. Very little physical variation (e.g. colour) was noted between individual hand samples.

3. Experimental methods

Thermal demagnetisation was undertaken using a Magnetic Measurements (Ltd.) thermal demagnetiser at the University of Liverpool Geomagnetism Laboratory (ULGL). Alternating field demagnetisation was undertaken at the Bulgarian Academy of Science Laboratory in Sofia (BASS) on a Molspin (Ltd.) tumbling demagnetiser. Remanence measurements (Natural Remanent Magnetisation [NRM] and Isothermal Remanent Magnetisation [IRM]) were undertaken on a Molspin (Ltd.) Minispin magnetometer at BASS and ULGL. IRM curves, backfields, hysteresis loops and Curie curves were undertaken in air on a Magnetic Measurements (Ltd.) Variable Field Translation Balance (VFTB) at ULGL. Data was analysed and paramagnetic signal removed using the RockMagAnalyzer 1.0 software written by Leonhardt (2006). This programme was also used for the removal of the paramagnetic signal from thermomagnetic curves and hysteresis loops. Bulk magnetic susceptibility (K) measurements were undertaken on a KLY-2 Kappabridge at BASS, where the high temperature behaviour of magnetic susceptibility was performed using a CS-23 attachment (AGICO, Brno). Stepwise thermal demagnetisation at BASS was undertaken in a home-made shielded oven with a residual field of less than 5 nT inside the cooling chamber. IRMs were induced in a pulse magnetiser (Max field = 2 T; Min field = 0.23 T). Low temperature magnetic susceptibility measurements, hysteresis loops, thermomagnetic curves, and IRM acquisition curves and backfields were conducted on samples that had not been solidified with water glass. All other tests were performed on water glass impregnated specimens.

A series of mineral magnetic tests were conducted on sister specimens to those used for the PI determination. The entire collection was first subjected to an evaluation of the samples' magnetic viscosity, applying the zero field method (Banerjee, 1981). The specimens' initial NRM was first measured and the specimens placed into μ-metal boxes for three weeks. After this period the samples were removed from the boxes and their stable, viscous free NRM (NRMst) was measured and the viscosity coefficient $\{Sv\% = [(\mathrm{NRM} - \mathrm{NRMst})/\mathrm{NRM}]^{*}100\}$ was calculated. Representative samples of the collection were both thermally demagnetised and alternating field demagnetised to aid as a check that the NRMst value was a true representation of the primary direction of the sample. A mixture of zero field (NRMst; method described above), alternating field and thermally cleaned NRM directions were used in calculating the final sample means using Fisher (1953) statistics. Characteristic Remanent Magnetisations (ChRM) were calculated for these samples using principal component analysis (Kirschvink, 1980).

Lowrie–Fuller tests were initially undertaken on a number of specimens (Lowrie and Fuller, 1971) followed by a 3-axes IRM (3IRM) test (as per Lowrie, 1990) on sister specimens. This involves inducing three different strengths of IRM (0.23 T. 0.46 T and 2 T) along three different axes of a specimen. The specimen was then thermally demagnetised in set temperature steps. At each step the IRM left in each axis is measured. Saturation isothermal remanent magnetisation tests (SIRM test) similar to those undertaken by Van Velzen and Zijderveld (1992) and Jordanova (1996) were used to look at the alteration of the specimens used for Lowrie–Fuller tests during laboratory heating. An initial 2 T IRM is induced in the sample. A new 2 T IRM is induced after each thermal step and both the SIRM remaining after each thermal demagnetisation step (SIRMleft) and the newly induced 2 T SIRM (SIRM) imparted after this measurement are measured. K is also monitored. A comparison is made between the 3IRM (thermal demagnetisation of 3-axes IRMs in the sister samples) and the SIRMleft and this should identify samples where new magnetic minerals are formed. The 3IRM demagnetisation curve shows the original mineralogy. By imparting a new 2 T SIRM after each heating step, magnetisation will be induced into any new minerals created by the previous thermal demagnetisation. K, SIRM and SIRMleft will be affected by any new minerals created. When the thermal decay of 3IRM and SIRMleft is identical the test is positive and when a substantial difference is observed it is negative. Negative SIRM tests are usually associated with unsuccessful Thellier experiments and vice versa (Jordanova et al., 1997, 2003). AF demagnetisation of SIRM(2 T) was additionally performed after heating to certain temperatures during the SIRM test to look at changes in coercivity more closely.

Classic-style Thellier experiments (Thellier and Thellier, 1959) were performed in the Vitosha Mountain laboratory. Samples were heated in a nonmagnetic oven in the presence of the Earth's field, which is fairly stable at the site. The natural laboratory field was measured daily during the experiment with a fluxgate magnetometer (mean laboratory intensity $[F_{\mathrm{lab}}] = 37\ \mu\mathrm{T}$, inclination $[I_{\mathrm{lab}}] = 70^{\circ}$ and declination $[D_{\mathrm{lab}}] = 0^{\circ}$). Samples were heated and measured twice, with a 180° vertical rotation of the sample so that the field was directly opposite during each heating. pTRM checks were conducted after heating to 200 °C (120 °C heating), 300 °C (150 °C heating), 420 °C (320 °C heating) and 460 °C (320 °C heating). Because the samples were hardened in water glass, the magnetic susceptibility could not be used as a reliable indicator of mineralogical change during PI experiments (Kostadinova et al., 2004). Remanence stability and pTRM checks were instead used exclusively with an 8% acceptance criteria for the upper limit of pTRM checks. Remanence measurements for this experiment were made using a computerised astatic magnetometer with an optical feedback system (Boroc Geomagnetic Laboratory, Russia).

4. Results

4.1. Mineral magnetism

Mineral magnetic data for selected samples is shown in Table 1. Mean S_v for the majority of samples is below 10% (mean of 6.19%) and shows that they contain little viscous material. Volume specific magnetic susceptibility (K) is lower than expected for burnt material (mean 24.5×10^{-5} SI) and values for samples 2377–2379 are lower than the rest of the collection (below 10×10^{-5} SI). As shown in previous studies (e.g. Moringa et al., 1999; Jordanova et al., 2001), an increase in K during heating is dependent on the sample initial mineralogical composition and is caused by the formation of new magnetic material, often in the single domain to superparamagnetic grain size. The formation of new ferro-oxides depends on the iron supply, the temperature and surrounding atmosphere (reducing or oxidizing) during heating. Thus, the three samples from the lower levels of the oven (Fig. 1B) have probably not been extensively heated. The Koeningsberger ratio ($Q = \mathrm{NRM}/(K \times H)$), where K is the magnetic susceptibility and H the strength of the ambient geomagnetic field (Dunlop and Özdemir, 1997), was also calculated. In spite of relatively low values of Q, the remanent magnetization is greater than the induced one ($Q > 1$, mean 4.05) and suggests the samples are suitable for archaeomagnetic analysis.

Hysteresis loops (Fig. 2A–D) all show a high paramagnetic component in the samples. On removal of the paramagnetic signal the curves indicate that the samples are all dominated by low coercivity minerals (Fig. 3). This is confirmed by IRM acquisition curves, which almost completely saturate between 100 and 200 mT (Fig. 2A–D), with only a small anti-ferromagnetic contribution suggested (B-ratio; Table 1). Accordingly, curves from 3IRM tests (Fig. 3) are dominated by the soft (0.23 T) component, with only very small medium (0.46 T) and hard (2 T) components evident. Lowrie and Fuller (1971) tests (Fig. 4) have IRM curves with a lower coercivity than the NRM component at low fields. The opposite occurs at high fields with cross-over of the curves at low to medium field strengths. The samples fit Bailey and Dunlop (1983) Type 3, modal

Table 1
Mineral magnetic data for selected Zlatna Livada sample

Sample	K	S_v%	Q ratio	H_{cr}	H_c	H_{cr}/H_c	M_s	M_{rs}	M_{rs}/M_s	SIRM	B-ratio	Paramag	T_c	RS	SIRM test
2367	34.2	5.59	5.23	38.8	11.46	3.39	12.09	2.34	0.19	2.27	0.8	0.0031	600	0.9	
2368	39.2	2.94	4.42												
2369	18.3	5.2	3.67	38.3	9.73	3.94	5.19	0.79	0.15	0.84	0.86	0.0021	620		
2370	32.50	5.74	5.27												
2371	25.70	4.25	4.93	38.8	10.46	3.71	12.09	2.34	0.19	2.27	0.8	0.0031	587	1.6	
2372	22.00	5.51	3.43												Negative
2373	33.10	7.66	3.89	35.8	11.1	3.23	13.1	2.75	0.21	1.47	0.84	0.0037	580	1.53	Positive
2374	22.90	8.41	3.24												
2375	24.20	8.61	3.86	30.21	9.71	3.11	12.21	2.15	0.18	2.26	0.81	0.0029	580	1.12	Negative
2376	42.30	6.68	2.68	40.62	12.05	3.37	8.04	1.14	0.14	1.37	0.86	0.0023	610	1.58	
2377	9.70	2.54	5.51												
2378	6.80	3.97	3.68												
2379	8.10	13.32	2.79	39.06	9.33	4.19	2.28	0.36	0.16	0.61	0.79	0.0044	620	2.42	
Mean	24.5	6.19	4.05												

K = average volume specific magnetic susceptibility (10^{-5} SI), S_v = viscosity coefficient, Q = Koeningsberger ratio, H_{cr} = coercivity of remanence (mT), H_c = Coercivity (mT), M_s = saturation magnetisation (10^{-3} Am^2/kg)], M_{rs} (10^{-3} Am^2/kg)] and SIRM = saturation isothermal remanent magnetisation (10^{-3} Am^2/kg)], B-ratio = SIRM$_{200mT}$/SIRM, paramag = paramagnetic content, T_c = Curie point (°C), RS = K−196 °C/K25 °C.

pseudo single domain (PSD) or mixed dingle domain (SD)/multi-domain (MD) character.

Low temperature magnetic susceptibility curves (K_{LT}) can be separated into three Groups on the basis of their RS ratios (the ratio of magnetic susceptibility at −196 °C and +25 °C; Table 1) and shape (Fig. 5): Group 1 samples (2367 and 2375) show hardly any change in K_{LT} with decreasing temperature; Group 2 samples (2371, 2373 and 2376) show a 150–180% increase in K_{LT}. Group 3 samples (2377 and 2379) have very high RS values. The high RS ratios of the Group 3 and Group 2 samples is probably due to a high paramagnetic fraction to the mineral assemblage (Oldfield, 1991), also noted in the hysteresis loops. Such behaviour may also represent the presence of superparamagnetic haematite or goethite (Dekkers, 1988; De Boer et al., 2001), but this is not the case here. The samples from Group 3 have the highest RS values (also suggestive of MD particles; Thomas, 1992) and show a change in slope angle around −140 °C, perhaps representing a suppressed Verwey transition (Özdemir et al., 1993). These samples also have the lowest K values, suggesting that this behaviour may be related to low levels of heating in antiquity (Table 1). In contrast, the K_{LT} Group 1 samples have a curve more suggestive of SD grains (Oldfield, 1991).

Thermomagnetic curves (Fig. 2A–D) indicate a high paramagnetic content, also suggested by K_{LT} curves and hysteresis loops. On removal of the paramagnetic signal the curves suggest that the samples contain both magnetite ($T_c \sim 580$ °C; Table 1; Fig. 3) and some maghaemite, which is thermally stable up to temperatures of between 600 °C and 620 °C with a small drop in magnetisation after heating. The presence of a second variety of maghaemite that alters at lower temperatures is shown by high temperature magnetic susceptibility measurements with inflexion between 300 °C and 400 °C (samples 2373, Fig. 2D). The presence of maghaemite may explain the possible suppression of the Verwey transition in weak (Group 3) K_{LT} curves.

Fig. 6 shows the hysteresis parameters of the Zlatna Livada samples (Table 1) when compared to Dunlop (2002a,b) curves for synthetic mixtures. All the samples fall between the SD–MD curves and SP–SD curves. Data that falls in this region cannot be interpreted unambiguously (Dunlop, 2002a). However, the data is similar to that of Parry (1982); in Dunlop (2002a), consisting of a mixture of SD and MD grains. The data is also similar to pottery samples of Carvallo (2000; in Dunlop 2002b) which are similarly interpreted. The samples show a rough trend from sample 2373, with the highest M_{rs}/M_s and almost the smallest H_{cr}/H_c ratio, to sample 2379 with the opposite. Samples with low ratios of H_{cr}/H_c have a greater contribution from SD grains and Curie temperatures suggestive of magnetite. Those samples with high H_{cr}/H_c ratios have a higher paramagnetic content and a greater contribution from MD grains and Curie points indicating maghaemite that is thermally stable to temperatures >600 °C. Based on the curves of Dunlop (2002b) the samples have between 50% and 70% contribution from MD grains.

In summary, the samples are all dominated by a mixture of SD and MD grained magnetite and maghaemite that is stable to inversion until varying temperatures (300–400 °C and 600–620 °C). Different quantities of paramagnetic minerals also occur in all samples. There is some suggestion that MD grains may have been oxidised and undergone partial maghaemitisation. Negligible fine-grained ferrimagnetic material and anti-ferromagnetic material is present. Samples from the lower layers (2377–2379) are much weaker with higher MD and paramagnetic content. This is thought to be due to lack of heating in antiquity and as such the samples were not used for PI determinations.

4.2. Palaeodirectional data

Samples 2377, 2378 and 2379 were collected from a sloping surface and show departure from the rest of the data. Therefore, they were also not used in the final calculation

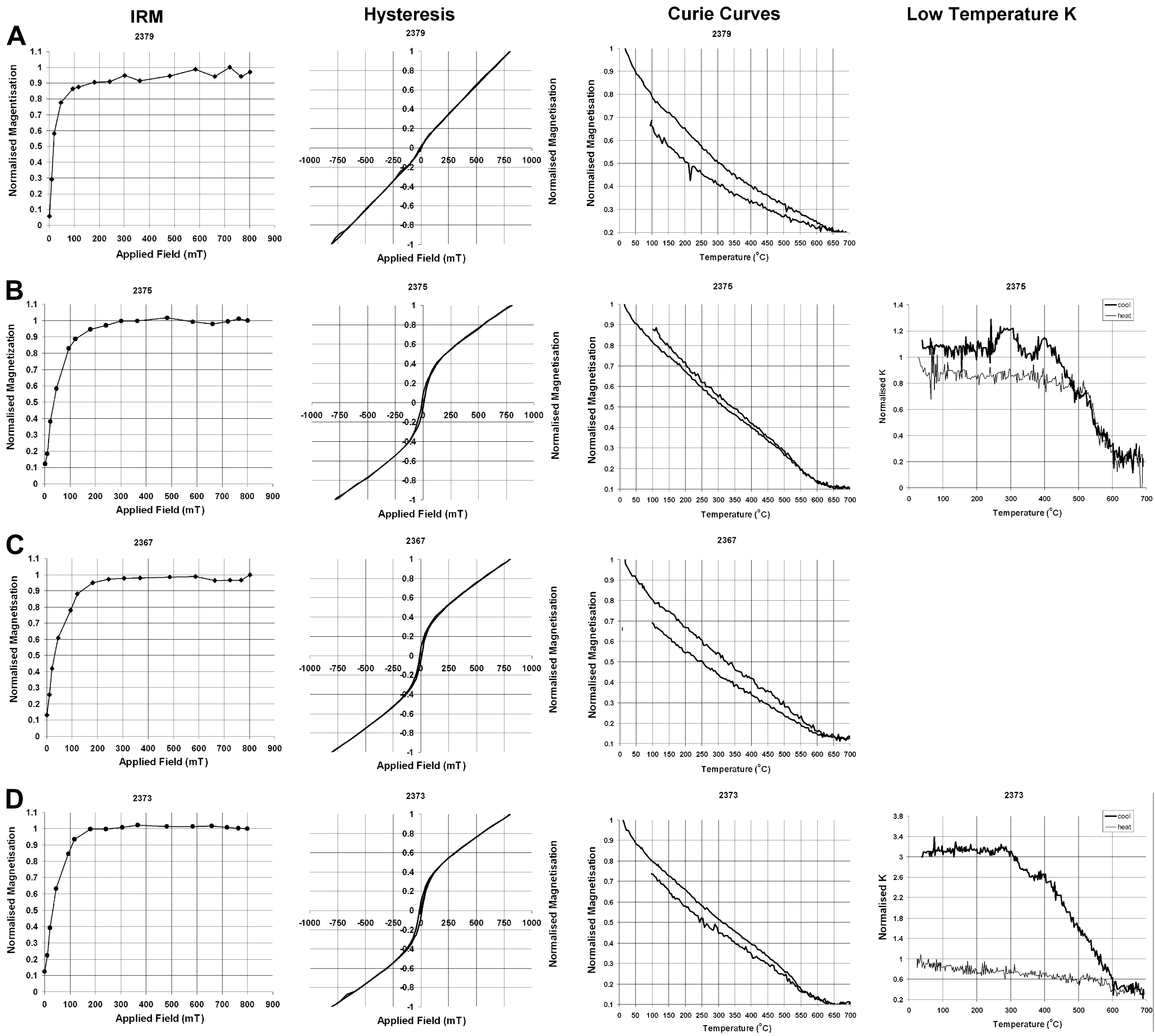

Fig. 2. IRM acquisition curves, hysteresis loops, thermomagnetic (Curie) curves and (K_{HT}) high temperature magnetic susceptibility curves for samples (A) 2379, (B) 2375, (C) 2367 and (D) 2373.

of PD. As with samples 2377–2379, samples 2367 and 2373 also show less consistent declination values but are consistent in inclination and magnetic mineralogy with the other samples and so are included in the final data. The mean PD of samples from the Zlatna Livada is 15.8° declination and 61.9° inclination (Table 2). Fig. 7 shows a comparison of thermal and alternating field (AF) demagnetisation for sample 2373. Specimen 2373v was thermally demagnetised before using the zero field cleaning method (Banerjee, 1981) and shows a secondary viscous component. The other specimens are AF demagnetized after the zero field cleaning. This shows that the zero field method removes any viscous component as seen in sample 2373v (Fig. 8). All the zero field cleaned samples show good correlation and a single component of magnetisation with no VRM evident. Samples show low coercivity behaviour during demagnetisation but the directions are stable up to fields of 100 mT.

4.3. Heating alteration tests

During thermal demagnetisation remanence instability occurs above 480 °C and this may roughly represent the temperature of ancient heating. In 3-axes IRM and SIRM tests remanence is removed and alteration occurs at around 480–520 °C, and again, suggests that the ancient temperature of heating was roughly in this range. During SIRM tests all the samples showed a similar behaviour with a small change (10–30% drop or increase) in SIRM (2 T) and *K* between 120 °C and 520 °C (Fig. 9). Above 520 °C

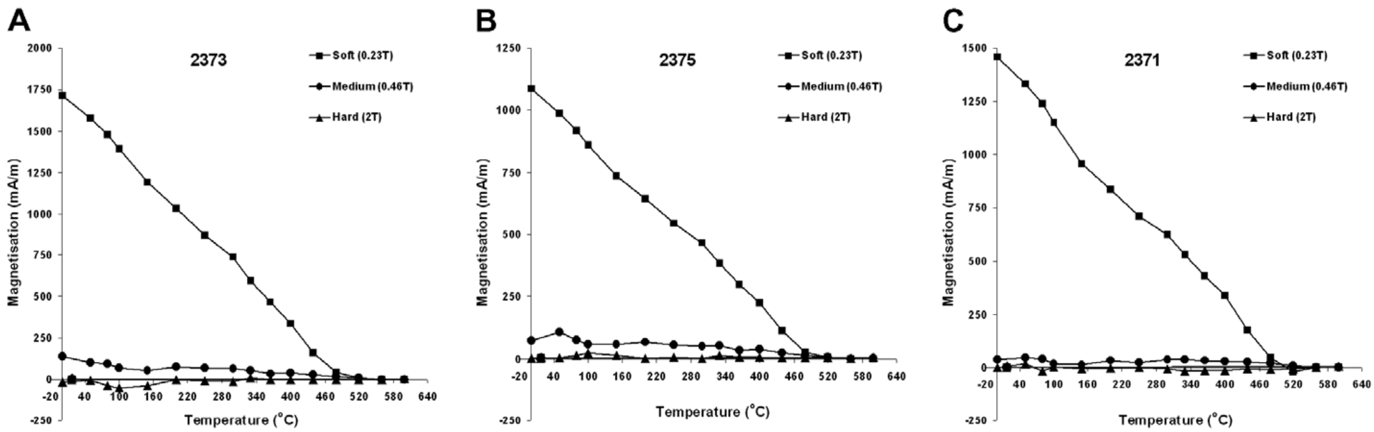

Fig. 3. 3-Axes IRM thermal demagnetisation as per Lowrie, 1990 for samples (A) 2373, (B) 2375 and (C) 2371. This test shows a dominance of lower coercivity ferrimagnetic minerals.

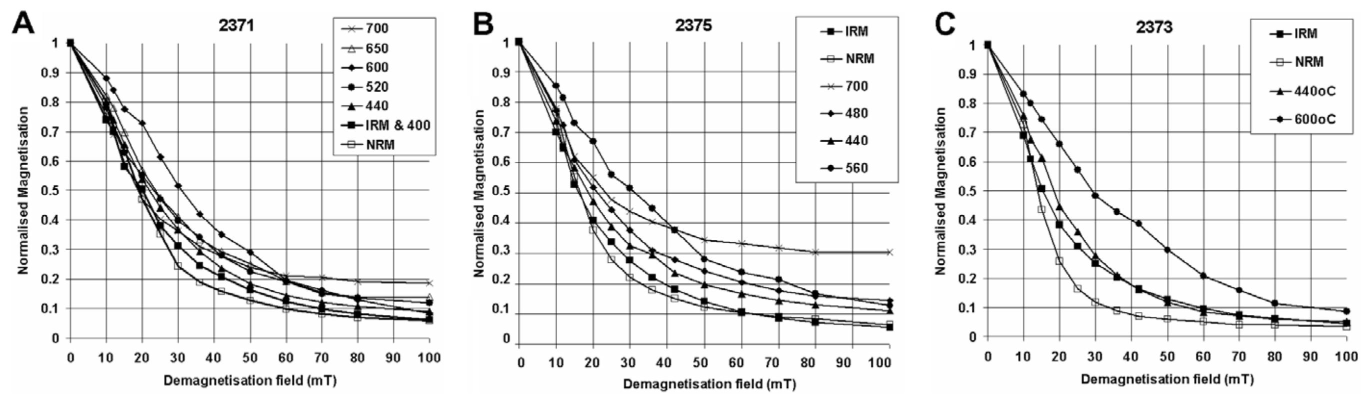

Fig. 4. Lowrie and Fuller (1971) tests for samples (A) 2371, (B) 2375 and (C) 2373. Alternating field demagnetisation of newly induced SIRM (2 T) during the SIRM tests is also shown for different temperatures to show the change of coercivity spectra with heating.

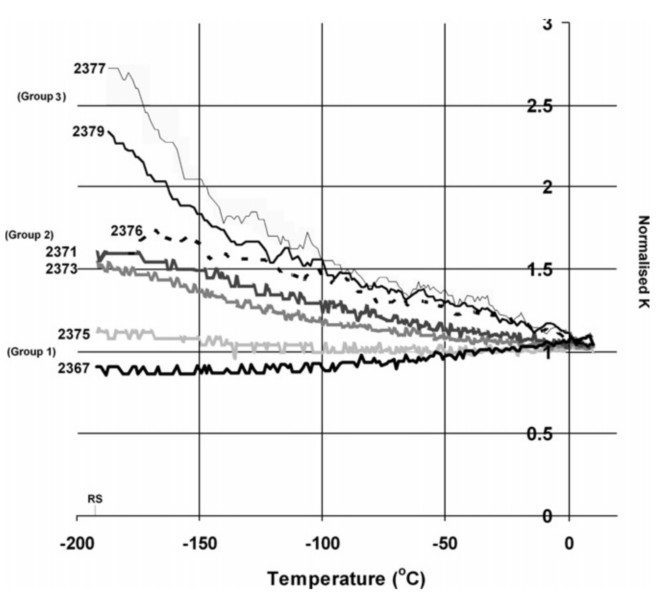

Fig. 5. Low temperature magnetic susceptibility curves (K_{LT}) showing Group 3 (steep curve and RS > 2), Group 2 (shallow curve and RS close to 1.5) and Group 1 (flat curve and RS close to 1) samples. (RS = K at −196 °C/K at +25 °C).

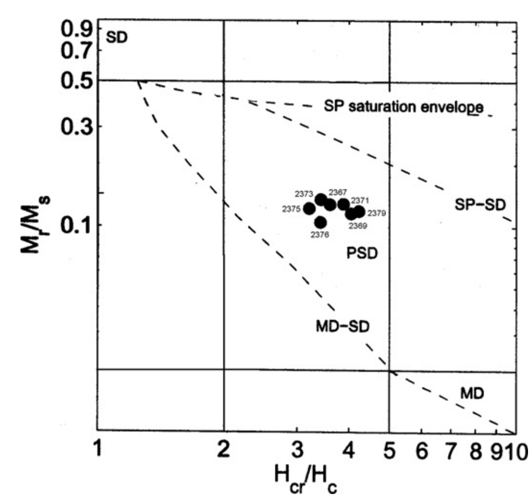

Fig. 6. Hysteresis parameters plotted against Dunlop's (2002a,b) curves for synthetic mixtures.

both SIRM (2 T) and *K* increase rapidly in all samples due to the fact that the samples have been impregnated with water glass, which reacts with the sediment and causes the formation of large quantities of new, strong magnetic

Table 2
Directional archaeomagnetic data for Zlatna Livada

Sample	No/N	Dec (°)	Inc (°)	α_{95} (°)
2367	5/6	**8.8**	**60.7**	**2.6**
2368	5/5	**15.9**	**59.6**	**3.5**
2369	4/10	**16.1**	**64.1**	**1.6**
2370	6/6	**17.6**	**64.6**	**1.8**
2371	9/9	**16.9**	**61.5**	**1.7**
2372	5/6	**16.3**	**62.4**	**1.7**
2373	8/13	**13.9**	**60.5**	**1**
2374	6/7	**17.7**	**61.4**	**1.7**
2375	8/9	**15.5**	**62.5**	**1.3**
2376	12/14	**18.1**	**60.9**	**1.6**
2377	6/6	**10.2**	**68.8**	**8.3**
2378	6/6	**12.3**	**65.9**	**9.1**
2379	7/7	**13.8**	**65.9**	**10.6**
Mean	10	**15.8**	**61.9**	**1.1**

No/N = number of specimens accepted/measured, α_{95} is a precision parameter, Inc = inclination, Dec = declination. Mean values conducted applying weighted Fisher (1953) statistics using a mixed average of specimens results from viscous cleaning of NRM, alternating field and thermal demagnetisation.

mineral phases. Thermal demagnetisation curves of 2 T SIRM (induced only once during the 3IRM experiment) and SIRMleft after each 2 T SIRM induction show close similarity for some samples (2373, Fig. 8A). This constitutes a positive SIRM test. In contrast, other samples (2375 and 2371; Fig. 8B and C) show an evident difference between the two curves and SIRM (2 T) increases with heating. These samples have a higher SIRMleft than the 3IRM curve. This suggests the production of new magnetic mineral phases during heating and constitutes a failed SIRM test. AF demagnetisation of SIRM (2 T) confirms this formation of new minerals in these samples with an increase in coercivity up to 600 °C (Fig. 4). The same happens in samples that have a positive SIRM test (Fig. 4C), but this new mineral formation occurs at higher temperatures.

4.4. Palaeointensity data

Classic Thellier (Thellier and Thellier, 1959) PI experiments, with an additional heating to perform the pTRM checks, were applied on nine specimens from the collection. The selection of specimens was based on the calculated viscosity index (S_v), mineral magnetic characteristics (Table 1) and consolidation. Despite failed SIRM tests for some samples (e.g. 2371 and 2375), a range of samples from across the oven were used. This was done in part to test the evaluation criteria. The results of the PI experiments are presented in Fig. 9 and Table 3. The majority of samples show a consistent behaviour and altered at temperatures between 300 and 400 °C (Figs. 8 and 9).

Based on supposedly favourable mineral magnetic data three specimens from sample 2373 were used. Specimen 2373d has a curved Arai plot with no linearity and specimen 2373j also has a curved Arai plot along with instability of remanence directions. Specimen 2373z gave the only usable PI determination (Table 3). Of two specimens from sample 2376, 2376d gave a poor result with bad pTRM checks, while 2376a gave acceptable results up to 320 °C and had a PI consistent with other accepted samples. Specimens 2371v and 2375v appeared to provide the most reliable PI values despite the fact that their sister specimens failed the SIRM test (Fig. 9). From nine PI experiments the results of only five were accepted (56%, Table 3). This was due to failure of pTRM checks and nonlinearity and curvature of the Arai plot that is indicative of MD behaviour. PI estimates are recorded between 67.90 and 80.05 μT. The weighted (Kovacheva and Kanarchev, 1986) mean is 72.13 μT.

5. Discussion

There are five basic factors that can cause the estimated PI to be different from the true ancient field: (1) mineralogical change can occur during the experiment.; (2) magnetic anisotropy; (3) cooling rate dependence of the imparted TRM in the laboratory; (4) the relationship between the laboratory field direction and the direction of the NRM; and (5) the MD state of the magnetic carriers.

Problem one can be diminished by monitoring mineralogical change through the pTRM checks. Pre-selection is also attempted based on mineral magnetic studies. Kovacheva et al. (in press) show that the effect of anisotropy of TRM on the value of PI is negligible for baked plaster from such ovens. As far as the cooling rate dependence is concerned, the PI experiment is performed without a fan and the specimens are left to cool naturally, which takes between 2 and 4 h depending on the temperature step. Thus, we consider that the cooling rate was essentially the same in both antiquity and the laboratory. According to the recent study of Yu et al. (2004), the direction of F_{lab} is not a problem because the classical Thellier method is the only method which is not influenced by the F_{lab} orientation. Therefore, the greatest problem in this analysis is the presence of MD grains in the Zlatna Livada samples, as shown by mineral magnetic measurements (Figs. 4 and 5).

Dunlop and Özdemir (1997) have shown that if MD grains are the major carriers of the TRM, lower unblocking temperatures (T_{ub}) called low-T_{ub} tails are observed. A low-T_{ub} spectrum results in a large demagnetisation of NRM during the low-temperature heating steps. On the other hand, MD carriers of TRM can also show higher T_{ub} up to the Curie point (Shcherbakova et al., 2000). Besides the possible presence of MD grains, mineralogical changes may also occur during the Thellier experiment. Both the formation of magnetic phases and the lower and higher T_{ub} act in the same direction and increase the visual appearance of the concave NRM–TRM relationship (Arai diagram) (Levi, 1977). Similar features are observed to a greater or lesser extent in our results (Fig. 9). For this reason the regression line calculation fraction "f" of the carried NRM is listed in Table 3 (Coe, 1967; Biggin and

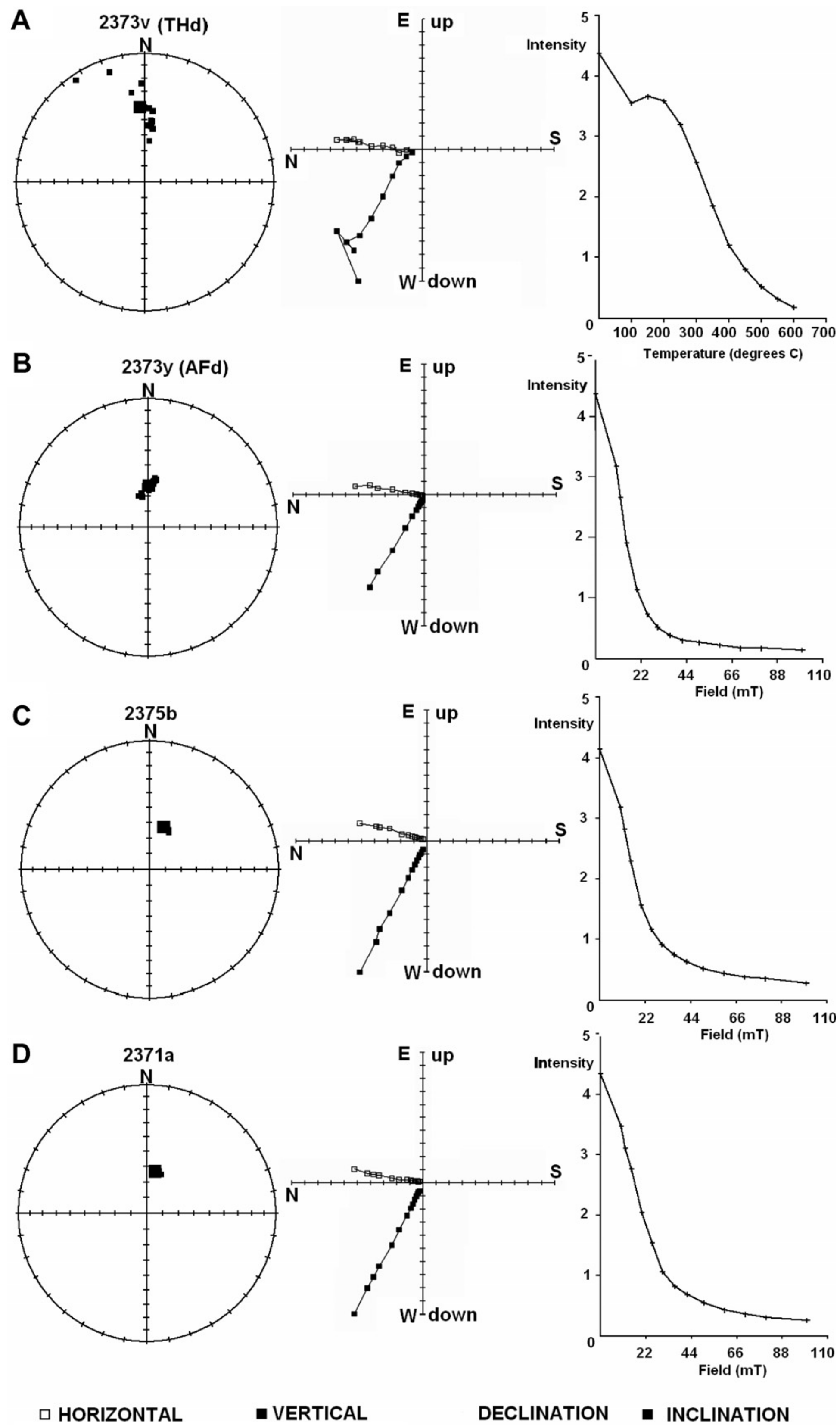

Fig. 7. Comparison between (A) thermal and (B) alternating field demagnetisation plots for specimens from sample 2373. Specimen 2373v (A) was thermally demagnetised before the application of zero field cleaning method. The AF demagnetisation of the other specimens (C–D) was performed after the application of zero field cleaning method.

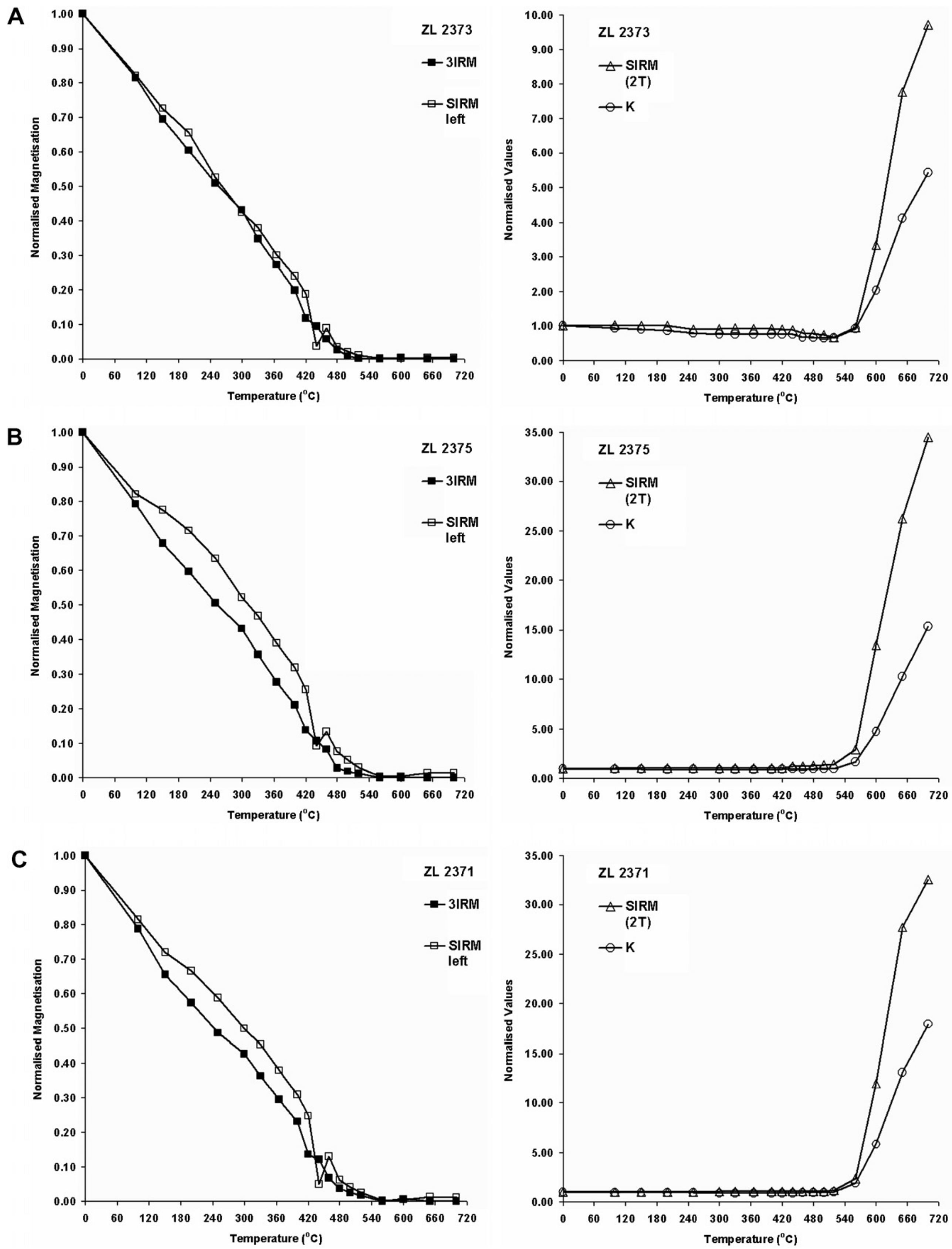

Fig. 8. SIRM tests for samples (A) 2373, (B) 2375 and (C) 2371. SIRM tests show a comparison of stepwise thermal demagnetisation of 2 T SIRM induced at each step (SIRMleft), stepwise thermal demagnetisation of SIRM from 3-IRM test (3IRM of sister specimen). SIRM (SIRM2T) induced after each demagnetisation step and *K* is also shown.

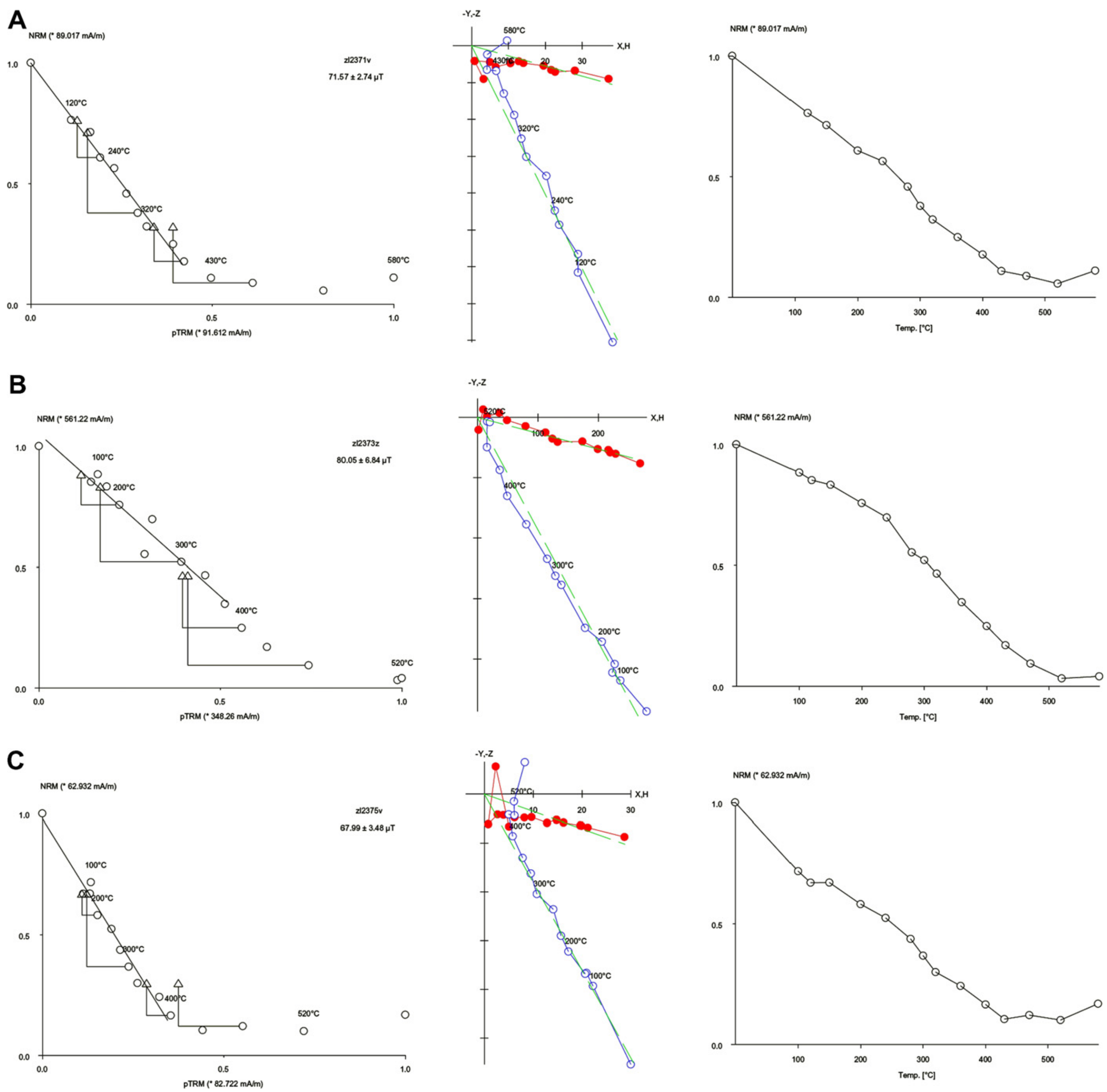

Fig. 9. Examples of Arai diagrams for samples (A) 2371v, (B) 2373z and (C) 2375v, with pTRM checks (on the left), Zijderveld plots (central) and NRM (on the right) demagnetisation curves from the Thellier experiments. Thellier tool (Leonhardt et al., 2004) was used to plot the data.

Thomas, 2003; Chauvin et al., 2005). In spite of the relatively low upper limit of the temperature intervals used, most of the "*f*" values are much higher than 60% of NRM with only one marginal value (45% for 2369b, a sample which fractured into pieces at the 320 °C temperature step). Obviously, the studied material is only carrying a partial thermoremanence (p-TRM) due to the lower heating in the antiquity.

Mineral magnetic studies show that the samples studied contain both SD and MD carriers. One favourable circumstance in a case like this is that even a small SD fraction in the material will carry the greatest part of the formed TRM (McClelland et al., 1996), despite the predominant MD grains. Of course, this depends on the volume relation between SD and MD grains. The hysteresis data suggests that there may be between a 50% to 70% contribution from MD grains in different samples when compared to Dunlop (2002a,b) data. This suggests that SD grains may represent a significant portion of the magnetic grain population in some samples. Alternating field demagnetisation curves undertaken during Lowrie–Fuller and SIRM tests (Fig. 4) do not demonstrate an initial flat portion up to 10 mT, as would be expected if the main carriers are single domain like particles. The same shape is not reflected in the

Table 3
Palaeointensity data for the Zlatna Livada oven

Samples	F_a (μT)	S (μT)	Temperature interval (°C)	N	f (%)	q	PTRMCheck (%)	MAD (°)	Reason for rejection
2369b	75.95	6.81	100–320	8	45	4.1	4.8	4.8	
2371v	71.57	2.74	20–400	10	83	18.7	4	3.0	
2372b	–	–	–						No linearity. MD shape of NRM(T) curve
2373d	–	–	–	–					No linearity. Typical curved MD behaviour
2373z	80.05	6.84	20–360	10	64	6.4	7.9	3.1	
2373j	–	–	–						No linearity. Bad remanence direction
2375v	67.90	3.47	20–400	11	85	13.7	6.2	2.5	
2376a	74.99	4.32	20–320	8	79	10.5	2.5	4.7	
2376d	–	–	–						Bad pTRM checks
w. Mean	72.13	3.49							

Missing values mean that the experimental result was rejected for not fulfilling the laboratory acceptance criteria; N is the number of experimental points included in the regression line calculation; S, the standard error; f denotes the part of NRM included in the regression (in percentage); q, quality factor; MAD, maximum angle of deviation; w. mean, the mean site palaeointensity value calculated using the weighted statistics (Kovacheva and Kanarchev, 1986) with its standard deviation.

NRM lost curves from the PI experiments (Fig. 9). There is an abrupt decrease in NRM with heating to 100 °C during the PI experiment, which reflects the unblocking of unstable parts of the remanence. NRM is removed between 400 °C and 500 °C and this reflects the lower temperature of heating in antiquity.

The presence of multi-domain remanence carriers is best indicated by the hysteresis properties (Fig. 6). The problem that remains is to elucidate how much the Arai plots are influenced by the MD carriers. The fact that Zijderveld plots (Fig. 9) lose remanence stability in the high temperature spectrum simultaneously with failed pTRM checks suggests that the increasing concave nature of the Arai plots is mostly influenced by mineralogical change (Fig. 9) rather than by the predominant MD carriers. McClelland et al. (1996) demonstrated that grains larger than 20 μm show MD-like behaviour during thermal demagnetisation. A comparison of IRM backfields with Thompson and Oldfield (1986) reference curves (not shown) suggests that the grain size of the samples is likely fall below this range.

Table 4
The Zlatna Livada oven data with its archaeological date when compared to Bulgarian palaeosecular variation data for the period from 900 to 1200 AD

Region/site	Site/feature	Lower age	High age	Mid age	Dec.	Inc.	Int.
Melnik	Despot Slav fortress St. Nikola place	1180	1210	1195	×	51.70	61.88
Assenovgrad	St. Jane church	1180	1210	1195	×	55.30	56.43
Kovachevo	Destructions	1180	1180	1180	12.16	57.26	62.46
Novi Pazar	Djurdjevi stupove	1170	1170	1170	×	55.78	57.71
Kurshumlja	St. Nikola church	1150	1180	1165	13.04	63.79	×
Assenovets	Markova water mill	1100	1200	1150	×	54.89	60.64
Pazardjik	Tzepina Fortress	1100	1200	1150	×	52.00	58.72
Patalentiza	Church	1100	1180	1140	×	54.81	51.10
Assenovgrad	Assenov fortress St. Bogor. Petr. Church	1100	1150	1125	×	62.16	52.64
Veliko Tarnavo	St. Dimitar church	1100	1150	1125	×	54.86	55.64
Iskritza	Kiln	1100	1150	1125	8.22	60.68	52.03
				Mean	11.14	56.66	56.93
Krakra_Pernik	Burnt earth from ancient fire	1080	1110	1095	2.63	61.65	59.09
Patlejna	Ceramic centre in monastery estate	1050	1100	1075	−0.60	62.28	60.20
Lubimec	Orta Burun kiln 2	1040	1060	1050	−2.00	63.80	×
Bachkovski Mon	Ossuary	1000	1050	1025	×	×	62.02
				Mean	0.01	62.58	61.61
Petrich	Ancient fire	1014	1014	1014	19.35	59.42	65.14
Pliska	Kings estate	950	1030	990	2.88	64.68	74.08
Balchik	Protobulgarian dwellings	950	1020	985	7.42	69.86	80.11
				Mean	10.32	65.60	73.30
Chirpan	Zlatna Livada oven	1000	1300	1200	15.75	62.10	72.13
Preslav	Inner fortress wall	900	950	925	×	58.20	78.06
Garvan	Slav settlement	900	950	925	×	67.30	74.73
Preslav	Monastery estate	900	950	925	×	66.18	88.53
Vinitsa	Cermanic centre kings estate	900	920	910	22.95	67.95	79.41
Preslav	Cermanic centre kings estate	900	920	910	21.20	71.40	69.03
				Mean	22.08	66.21	77.95

(Dec. = Declination [deg.], Inc. = Inclination [deg.] and Intensity [μT]). Original data from Kovacheva (1997).

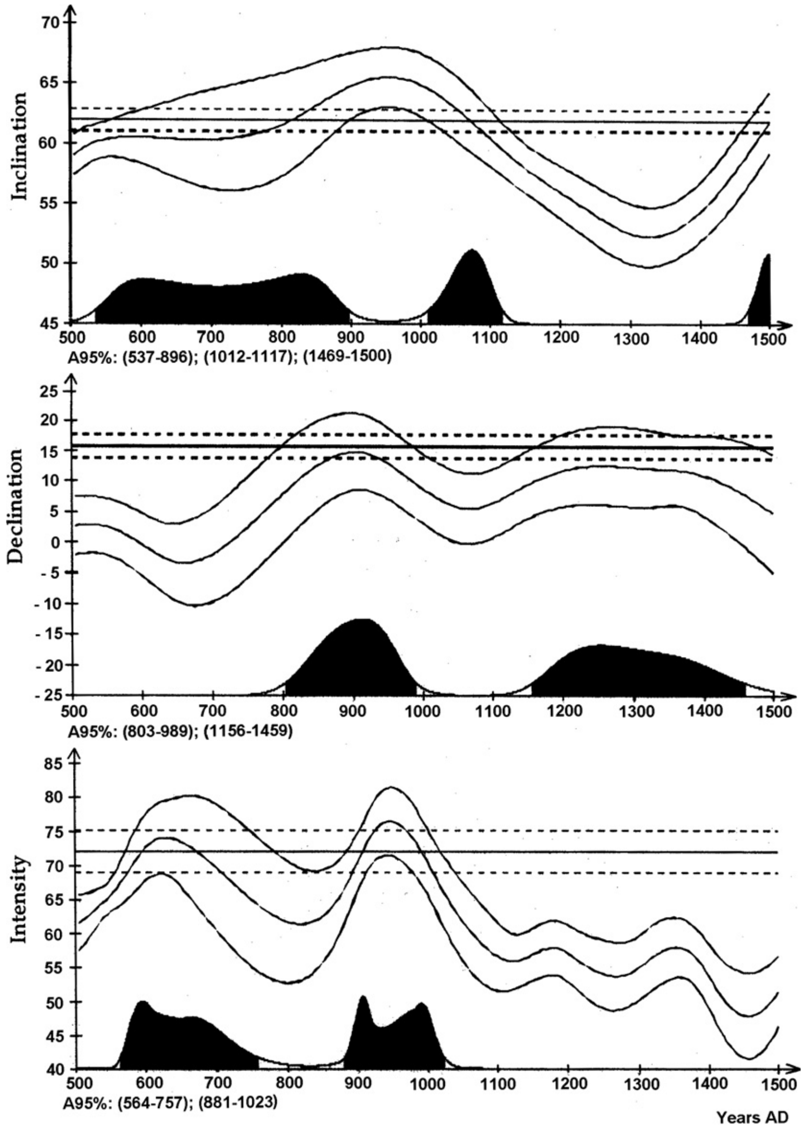

Fig. 10. Concordant age intervals obtained by different archaeomagnetic elements (inclination, declination and intensity). The experimental results from the collection of Zlatna Livada are compared against part of the Bulgarian secular variation curves (500–1500 AD). The RENDATE program was used to define the archaeomagnetic age for the site (Lanos, 2001, 2004; Lanos et al., 2005).

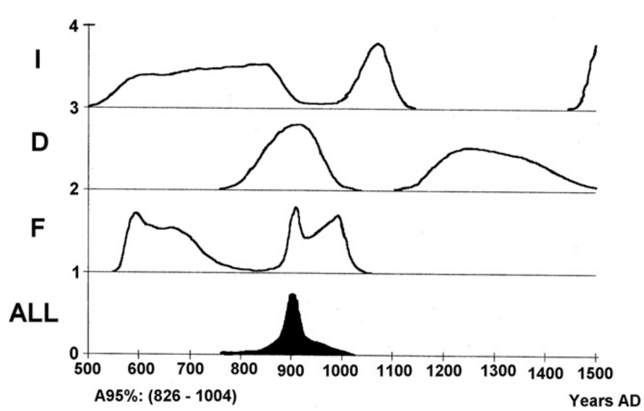

Fig. 11. Final archaeomagnetic dating combining multiple solutions on the basis of the three archaeomagnetic elements (inclination, declination and intensity) from the collection of Zlatna Livada.

Because the PI of the Zlatna Livada collection has been performed using the classical Thellier experiment we are lacking the pTRM-tail tests during the experiment itself. On the other hand, it is shown by Yu et al. (2004) that the calculated pTRM tails can be overestimated or underestimated during Coe (1967) version of the PI experiment. This is dependent on the magnitude and direction of the laboratory field. Therefore, the lack of this check in our study is not considered to be a major problem. An attempt was made to use the thermomagnetic criterion of Shcherbakova et al. (2000) calculating the pTRM tail of laboratory-induced partial thermoremanence from 300 °C to room temperature (T_r) on sister specimens to those used for PI determination. However, because of the heterogeneity of the material, the result cannot be directly transferred to each individual specimen of interest and the thermal instability of the material also means that the data does not reflect the real tail (Shcherbakov et al., 2001). This variability in the behaviour of specimens from the same sample is thought to be due to the heterogeneous heating in antiquity and the heterogeneous base material that was heated.

The heterogeneity of specimens is also an obstacle for using different rock magnetic tests for real pre-selection of specimens for PI experiments. Nevertheless, without them, the samples' behaviour during the PI experiment remains much more obscure. Unfortunately, it is nearly impossible to make a perfect pre-selection of samples for PI experiment. The Thellier experiment itself is quite diagnostic and that is why the internal consistency of values for a studied collection is important. Unfortunately for this small collection, in spite of good internal consistency, the mean PI value can be altered from the true ancient PI due to the presence of MD grains.

6. Archaeomagnetic estimates

The proposed archaeological date for the Zlatna Livada settlement is sometime in the 11th–12th C. AD. The oven is thought to date to the early phase of the site (11th C. AD), although an earlier date is possible (Koleva, personal communication). While large amounts of archaeomagnetic field data exist for the 10th and 12th C. AD, little data exists for the 11th C. AD (Kovacheva, 1997). Palaeosecular variation data for Bulgaria in the 10th to 12th C. AD is shown in Table 4 (Kovacheva, 1997). The missing declination values are from sites represented only by bricks used to determine the palaeoinclination and palaeointensity. Archaeomagnetic data for this period are obviously not sufficient to form more precise reference curves which would constrain the dating intervals obtained (Table 4; Fig. 10). The RENDATE program was used to define the archaeomagnetic age for the site (Lanos, 2001, 2004; Lanos et al., 2005). In Fig. 10, the Zlatna Livada archaeomagnetic values (horizontal lines with their error limits) are compared with the current Bulgarian secular variation curves. Multiple solutions obtained on the basis of different geomagnetic elements are given on the horizontal axis of time, where the black areas represent the probability density. The combined definitive age is given in Fig. 11 where the dating interval is 826–1004 AD. The archaeomagnetic data confirms that the oven dates to the early period of site use, although the date is perhaps slightly younger than expected. Based on both the archaeomagnetic age assessment and the archaeological evidence the site is optimally dated to the very end of the 10th C. AD or first few years of the 11th C. AD.

Because of the extreme difficulties encountered during the Thellier experiments and the remaining doubt about the true value of PI, let us consider what the archaeomagnetic age estimate would be using only the directional results. The application of the RENDATE software using only directional results (not shown) leads to an interval of 777–967 AD. This date overlaps with the estimate including PI results and is even younger than suggested by the archaeological data. If our PI determination is overestimated and the true value is lower, the suggested age for the site is even further from the estimated archaeological age. At present, the Bulgarian reference curve has a low density of data points between the 7th to 9th centuries. These are "dark" ages in our archaeological discoveries and this is reflected in the archaeomagnetic studies. Thus it is suggested that the archaeomagnetic age estimate obtained using both palaeo-directional and -intensity data is the most reliable based on current field data. Only the future accumulation of independently dated archaeological materials will refine the geomagnetic reference curves for this period and other low density periods.

7. Conclusions

Archaeomagnetic palaeo-directional and -intensity and mineral magnetic results from an oven at the mediaeval site of Zlatna Livada reveal a number of different conclusions.

1. The oven was not heated to high temperatures in antiquity (<320–400 °C) and some areas were heated more than others. This is shown by the heterogeneity of the samples, lack of consolidation and mineral magnetic characteristics.
2. Magnetite and two forms of maghaemite (the first thermally stable to around 620 °C and the second which is unstable and inverts between 300 and 400 °C) are the main minerals present.
3. Negligible fine-grained ferrimagnetic material and antiferromagnetic material are present. This again points to a low temperature of heating in antiquity.
4. The samples from the upper level show a mixture of SD and MD ferrimagnetic grains, while those from the lower levels appear to have a greater proportion of MD grains.
5. Consequently, samples with higher MD fractions failed the PI experiments. Those that gave consistent pTRM checks, good remanence stability and a linear Arai plot are considered to have been successful.
6. The oven has a mean PI determination of 72.13 μT, a mean declination of 15.8° and a mean inclination of 61.9°. The archaeomagnetic dating for the last usage of the oven suggests a date between 826 and 1004 AD. The archaeological evidence suggests an early 11th C. AD date and this is partly confirmed by the archaeomagnetic estimate, although the site might be earlier than expected.

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