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Original paper

Thermomagnetic monitoring of lithic clasts burned under controlled temperature and field conditions. Implications for archaeomagnetism

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Resumen

Se presenta un estudio combinado térmico y magnético sobre un conjunto de clastos líticos de diferentes litologías tallados experimentalmente (sílex, cuarcita, caliza, arenisca y obsidiana), calentados bajos condiciones de campo y temperatura controladas. El objetivo principal de este estudio es evaluar la viabilidad de uso de estas materias primas, comúnmente encontradas en yacimientos arqueológicos prehistóricos, para fines arqueomagnéticos. Los análisis del magnetismo de las rocas comprendieron la medida de la susceptibilidad magnética a bajo campo, curvas de adquisición progresiva de la magnetización remanente isoterma (IRM), ciclos de histéresis y curvas termomagnéticas de los clastos líticos tanto antes como después del calentamiento experimental. Todas las litologías salvo la obsidiana, registraron un incremento de hasta dos órdenes de magnitud en sus parámetros dependientes de la concentración magnética, indicando la formación de nuevos minerales ferrimagnéticos. Las muestras de obsidiana y arenisca son los portadores de la remanencia más fiables, seguidos de caliza, sílex y cuarcita. Los valores de susceptibilidad magnética muestran diferencias significativas entre litologías. La magnetización remanente isoterma demostró ser también altamente discriminatoria así como los parámetros de histéresis a temperatura ambiente. Las principales alteraciones macroscópicas fueron cambios de coloración, rubefacciones, depresiones circulares (potlids) en los sílex y la formación masiva de fisuras internas en los especímenes de obsidiana. La técnica de paleointensidad multiespecimen fue aplicada en muestras representativas proporcionando resultados satisfactorios para las muestras de obsidiana y arenisca. Se discute la aplicabilidad arqueológica de los resultados así como también su relevancia geomagnética.

Palabras clave: Arqueología, arqueomagnetismo, magnetismo de las rocas, paleointensidad, tecnología lítica

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Abstract

We carried out a combined thermal and magnetic evaluation on experimentally knapped clasts of different lithologies (chert, quartzite, limestone, sandstone and obsidian) heated under controlled field and temperature conditions. The main aim of this study is to estimate the feasibility of use of these raw materials, which are commonly found in prehistoric archaeological sites for archaeomagnetic purposes. Rock magnetic analysis included measurements of low-field magnetic susceptibility, isothermal remanent magnetisation (IRM) acquisition curves, hysteresis loops and thermomagnetic curves of lithic clasts both before and after experimental heating. All lithologies, except the obsidian, recorded an increase of up two orders of magnitude in their magnetic concentration-dependent parameters revealing the formation of new ferrimagnetic minerals. Obsidian and sandstone are the most reliable magnetic carriers, followed by limestone, chert and quartzite. Magnetic susceptibility values show significant differences among lithologies. Isothermal remanent magnetisation proved also to be highly discriminatory as well as the room temperature hysteresis parameters. The main macroscopic alterations resulted in colour changes, rubefactions, potlids in cherts and the massive formation of internal fissures in obsidian specimens. The multispecimen palaeointensity technique was applied on selected samples yielding satisfactory results for heated obsidian and sandstone samples. The archaeological applicability of the results is discussed as well as their geomagnetic significance.

Keywords: Archaeology, archaeomagnetism, rock-magnetism, palaeointensity, lithic technology.

Introduction

Combustion structures and burned archaeological materials constitute a valuable source of data to investigate the directional and intensity variations of the Earth's magnetic field in the past. Materials heated to high temperatures (> 600 ºC) are capable, under certain conditions, to acquire a thermo-remanent magnetisation (TRM) recording the direction and intensity of the Earth's magnetic field during the last combustion. Archaeological structures such as kilns, ovens, baths or hearths are particularly suitable for this kind of studies. For that reason, there is a growing interest in the archaeomagnetic community to explore new materials as potential geomagnetic field recorders in order to study the field evolution through time (e.g. Morales *et al*., 2011).

On the other hand, ferromagnetic minerals (*s.l.*) are particularly sensitive to modify their magnetic properties by heating. This makes rock-magnetic methods a very efficient tool with applications ranging from the reconstruction of ecosystem dynamics (e.g. Hallett and Anderson 2010) to identify fire in archaeological sites (e.g. Herries 2009). In forest fires, for example, natural burning produces a magnetic enhancement on topsoils even at moderate temperatures which can be detected with mineral magnetic methods (e.g.: Gedye *et al.* 2000). Regarding archaeological sites, the potential of mineral magnetic methods is of particular interest in palaeolithic contexts where fire identification is not straightforward and thermal alteration evidences (e.g.: ashes, charcoals, etc.) are usually few, ambiguous and generally poorly preserved. Thus, the rock-magnetic information may be useful to evaluate the technological characteristics of prehistoric societies and the cultural interpretation of prehistoric sites. As far as the study of archaeological lithic assemblages is concerned, mineral magnetic analyses have been mostly used to identify source or provenance areas in different parts of the world (e.g.: McDougall *et al.* 1983, Vasquez *et al*. 2001, Thacker and Ellwood 2002, Stewart *et al*. 2003, Zanella *et al*. 2012). However, studies concerning how heating alter the magnetic properties of prehistoric lithic assemblages are relatively scarce and basically restricted to obsidians and cherts (Borradaile *et al.* 1993, 1998; Thacker and Ellwood 2002). It is well known that heat treatment of fine grained siliceous rocks improves their flaking properties in stone tool manufacture (e.g.: Hester 1972; Purdy 1974; Domański and Webb 1992, 2007). Therefore, it would be interesting to extend our knowledge investigating other lithologies commonly found in prehistoric archaeological sites and evaluate their potential as reliable recorders of the geomagnetic field strength.

This work is an experimental study about the variations of magnetic and macroscopic properties induced by heating on an experimental set of lithic clasts from different lithologies commonly found in prehistoric archaeological sites. A collection of experimentally knapped lithic artefacts from five diverse lithologies (chert, limestone, quartzite, sandstone and obsidian) was heated under controlled field and temperature conditions monitored by standard thermocouples. The main objectives of this study are: *i)* characterise the main magnetic and macroscopic properties of these materials induced by heating, *ii)* establish magnetic criteria in order to identify heating processes in analogous prehistoric lithic materials and *iii)* evaluate the magnetic stability and determine the suitability of these lithologies to obtain absolute palaeointensity determinations as well as discuss its methodological implications. Therefore, the interest of this contribution is posed both from a geophysical and archaeological perspective.

Field experiment and sample description

Experimental heating was carried out on a clayish substrate at the locality of Humienta (Burgos, Spain; Figure 1a). A clayish substrate was selected because of the availability to perform the field experiment and because this type of substrates are quite common in archaeological contexts. To avoid possible contaminations the upper 15-20 cm of the superficial soil were removed. Temperature variations during the burning were recorded at 5 minutes intervals with a K-type thermocouple system distributed linearly at 0-1 cm of depth and another one at 3 cm of depth in the centre of the experimental hearth (T3 at quadrant 5; Figure 1b). Burning surface was subdivided in five different quadrants as illustrated in Figure 1b placing two lithic fragments of each lithology per quadrant. Experimental lithic artefacts correspond to the following lithologies: *i)* Neogene chert from Sierra de Atapuerca (Upper Miocene, Villalbal, Burgos); *ii)* Upper Cretaceous limestone from Sierra de Atapuerca (Ibeas de Juarros, Burgos), *iii)* Palaeozoic sandstone from the fluvial terraces of Arlanzón river (Sierra de la Demanda, Burgos), *iv)* Quartzite from Utrilla facies (Olmos de Atapuerca, Burgos) and *v)* Neogene obsidian from New Mexico (USA). Each lithology exhibited predominantly homogeneous texture and colours ranging from black in obsidians to white in cherts. While limestone specimens were mostly grey with reddish mottles, dark light brownish grey and light greyish colours could be distinguished in sandstone and quartzite specimens, respectively. Burning was carried out employing wood fuel (cf. *Quercus sp*.) during 80 minutes. In order to ensure that the pieces undergo the highest thermal impact during the burning, they were dispersed directly on the ground surface. This may guarantee to reproduce the conditions of similar experimental ethnoarchaeological recreations (e.g.: Hester 1972; Domański and Webb 2007).

With the exception of obsidian, this material selection is related to the type of raw materials most frequently identified in the Pleistocene archaeological sites of Atapuerca (Burgos, Spain). For some unknown reason, no evidences of archaeological fire have been yet identified so far in the Pleistocene sites, despite having a record of human occupation virtually spanning the last million years (Rodríguez *et al.* 2011). Obsidian was also included in this study because is a common raw material to manufacture stone tools in volcanic areas and it would be interesting to study the variation of its magnetic properties induced by heating. Besides intending to broadly characterize the magnetic behaviour of these lithologies, this material selection aims to explore the range of variability of their magnetic properties. This can be useful to define a magnetic pattern to detect heat treatment in archaeological lithic assemblages.

Substrate temperatures were completed with temperature readings of the air (T6; Figure 2) and of the embers of the substrate where the lithic pieces were located (T7; Figure 2). It is

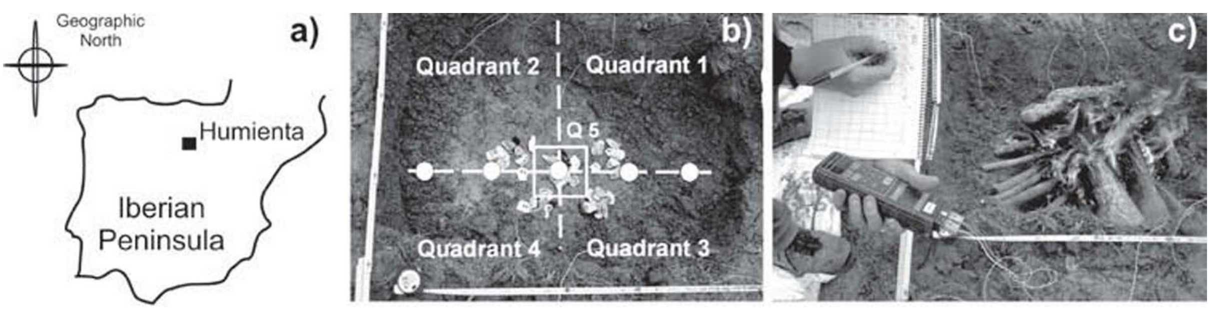


Figure 1. (a) Location of the site where the experiment was carried out. (b) Distribution of pieces by quadrants on the ground surface (Q5 refers to quadrant 5). White circles represent the location of thermocouples (T1-T5) at 0-1 cm of depth. Temperatures of the embers where the lithic pieces were located were recorded with T7 in Q5. (c) Temperature reading during the experiment.

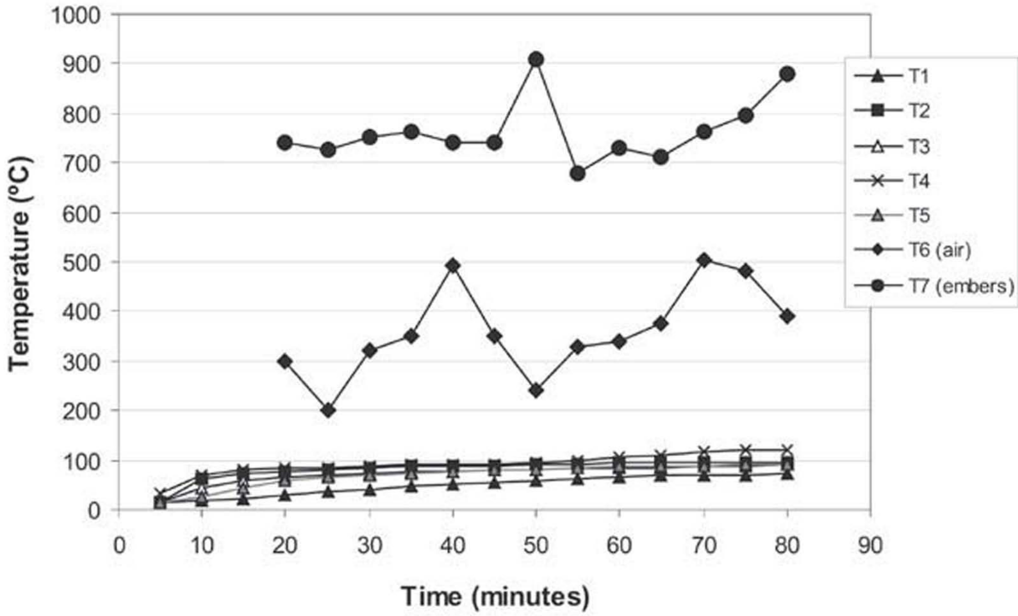


Figure 2. Temperatures recorded by each thermocouple during the experiment. T6 (temperature of the air) and T7 (temperature of the embers where the clasts were located). See text (field experiment section). Note that some temperature variations (e.g.: between min 45 and 60; T7) might correspond to wind variations or alternatively to some fuel addition during burning. More fuel help to increase the temperatures.

worth to point out that the experiment was performed after a rainy day, so the substrate kept a considerable humidity. This fact, together with the low thermal conductivity of the clay, clearly limited heat penetration with depth. This explains why despite heating continuously for 80 minutes, the temperatures of buried thermocouples did not exceed 120 °C (Figure 2). However, the thermocouple of the embers where the artifacts were located (T7; Figure 2), recorded mean heating temperatures of 700 ºC. Therefore, it is reasonable to assume that these samples definitively acquire a full thermoremanent magnetisation (TRM). Following our previous experiments we showed that burning under similar conditions samples acquire a full TRM (Carrancho and Villalaín 2011; Calvo-Rathert *et al*., 2012) and we demonstrate it here studying the magnetic properties (section 4.3). All lithic pieces were measured, photographed and their main macroscopic features described before and after the experimental burning.

Laboratory procedures

As an initial step before performing the field experiment, the low-field magnetic susceptibility (MS) was measured on each sample with a KLY-4 (AGICO, noise level ~ 3 x 10^{-8} S.I.) kappabridge. In order to further constrain the magnetic properties, we selected one pilot sample from each lithology ("pre-burned material") and one piece of each lithology from each quadrant after burning ("post-burned material"), to carry out a series of rock-magnetic experiments with a Magnetic Field Translation Balance (MM_MFTB). These included the measurement on powered sample (~ 450 mg) of progressive isothermal remanent magnetisation (IRM) acquisition curves, hysteresis loops (± 1 T), backfield coercivity curves and thermomagnetic curves up to 700 ºC in air. Heating and cooling rates of thermomagnetic experiments were 10 - 15 ºC min^{-1} applying a field of 38 mT. Curie temperatures of Js-T curves were calculated using the two-tangent method of Grommé *et al.* (1969). Saturation magnetization (M_s), remanence saturation magnetisation (M_{rs}) and coercive field (B_c) were calculated from hysteresis loops after subtracting the dia/paramagnetic contribution. These parameters combined with the coercivity of remanence (B_{cr}) determined from the backfield curves, were used to estimate the domain state distribution of the studied collection in the Day plot (Day *et al.* 1977; Dunlop 2002). All these experiments were carried out at the Laboratory of Palaeomagnetism of Burgos University (Spain).

Results

Macroscopic alterations

Figure 3 illustrates some representative examples of the main macroscopic features observed in the different lithologies after burning. Chert is the raw material from the studied collection which undergoes more changes when heated (Figure 3e). Rubefaction is the most documented alteration (Figure 3b), being observed in all lithologies except in the obsidian. However, 90 % of obsidian pieces have produced internal fissures as the main macroscopic alteration (Figure 3f). The second most documented alteration is colour change which has affected to all lithologies although not in a very evident manner in limestone samples. It is remarkable the appearance of microretouches -which at first glance might be mistakenly confused with wear traces- (Figure 3a) and to a lesser extent, fractures (Figure 3c) and potlids (Figure 3d). The latter are subcircular depressions on the tools surfaces and have been reported in other thermally altered siliceous-rich lithic assemblages (e.g.: Borradaile *et al.* 1998).

Magnetic properties of unburned clasts

The ferromagnetic content of the pre-burned material is very poor, dominating diamagnetic (e.g.: Figure 4a) or paramagnetic behaviour and characterized by noisy curves (Figure 4b). Only obsidian (Figure 4c) and to lesser extent the sandstone samples (Figure 4d) show a higher ferromagnetic content revealing the dominant presence of magnetite as main carrier. Haematite is also present in the sandstone as can be easily distinguished by the wasp-waisted shape of its hysteresis loop (Figure 4d). Moreover, the variation in the intensity of magnetisation among lithologies becomes of up two orders of magnitude according to the progressive IRM acquisition curves of obsidian and sandstone samples (Figure 4e).

Low-field magnetic susceptibility (MS) variations between pre- and post-burned samples of different lithologies are evident as can be observed in Figure 5 and Table 1. Most chert, quartzite and limestone samples (Figure 5a,b and d) exhibit very low pre-burning MS values, even negative, indicating that the matrix is dominated by diamagnetic minerals. Paramagnetic minerals are likely to be also present especially in quartzite since some samples show low positive pre-burning MS values (Figure 5b), and also for limestone (Figure 5d). In contrast, sandstone and mainly obsidian samples exhibit the highest values (mean post-burning MS = 2.03 x 10^{-6} and 2,30 x 10^{-7} m^3kg^{-1} respectively; Table I and Figure 5e and c), indicating that they contain ferromagnetic (*s.l.*) minerals. On average, pre-burning MS values of obsidian samples are around one order of magnitude higher than sandstone ones. Within their variability, all lithologies underwent in general a considerable MS enhancement after burning clearly indicative of mineralogical transformations. This effect is particularly evident in the sandstone. Most likely, heating induced mineralogical changes of the paramagnetic components (i.e.: phyllosilicates) rather common in these lithologies favouring the creation of ferrimagnetic minerals (i.e.: magnetite). Most obsidian samples, however, do not increase the MS values after burning. This is due to the volcanic origin of this material carrying original thermoremanent magnetization

Magnetic properties of post-burning clasts

Progressive IRM acquisition curves of the different lithologies before and after burning are illustrated in Figure 6a and b, respectively.

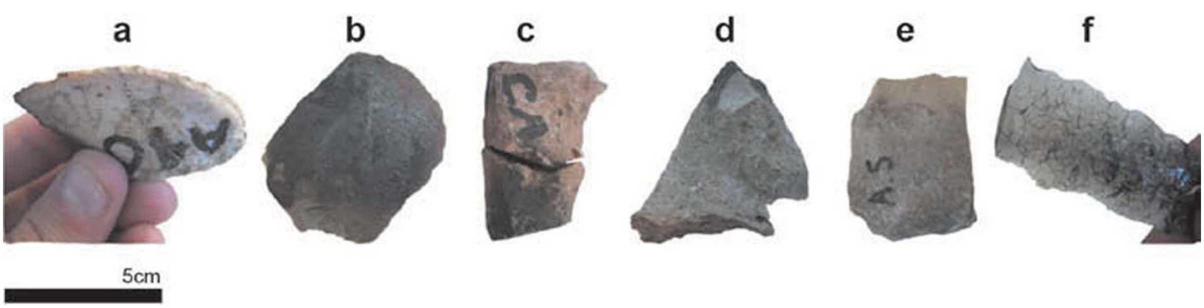


Figure 3. Representative examples of the main macroscopic alterations documented after the burning in the studied lithologies. (a) Microretouches; (b) Rubefaction; (c) Fractures; (d) Potlids; (e) increased lustre; (f) formation of internal fissures.

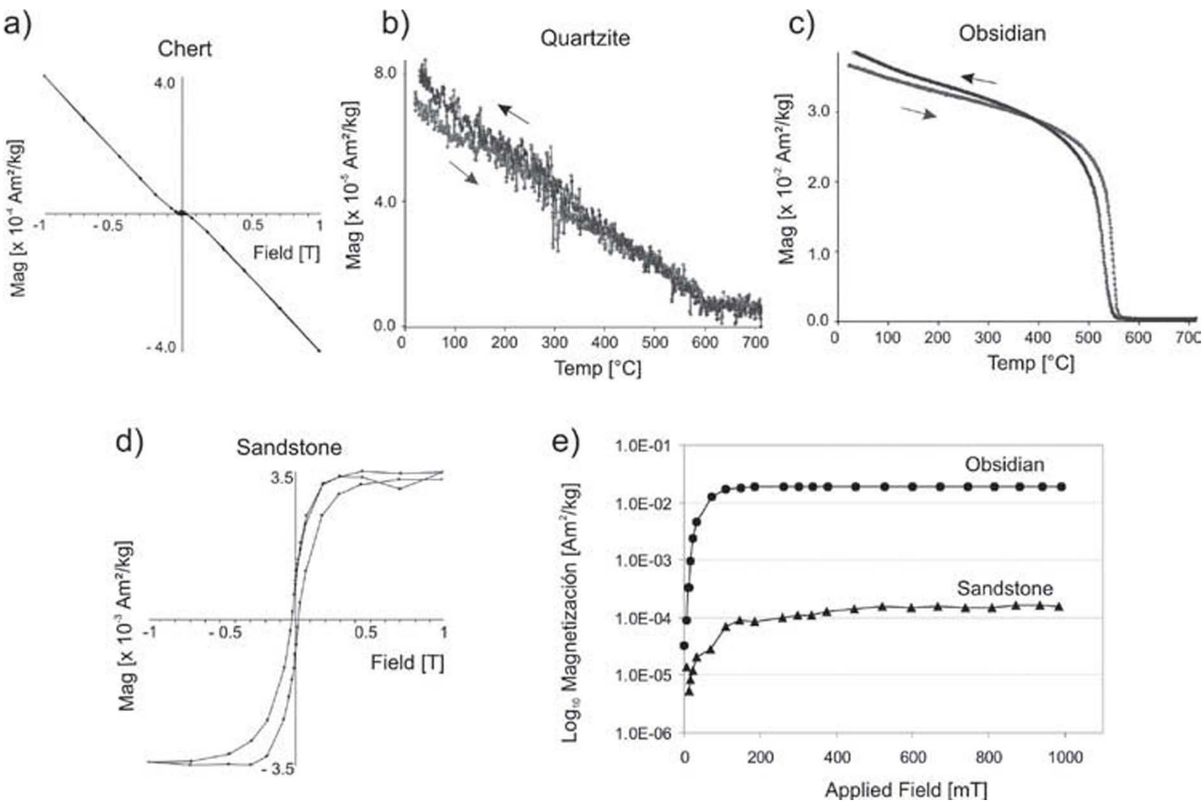


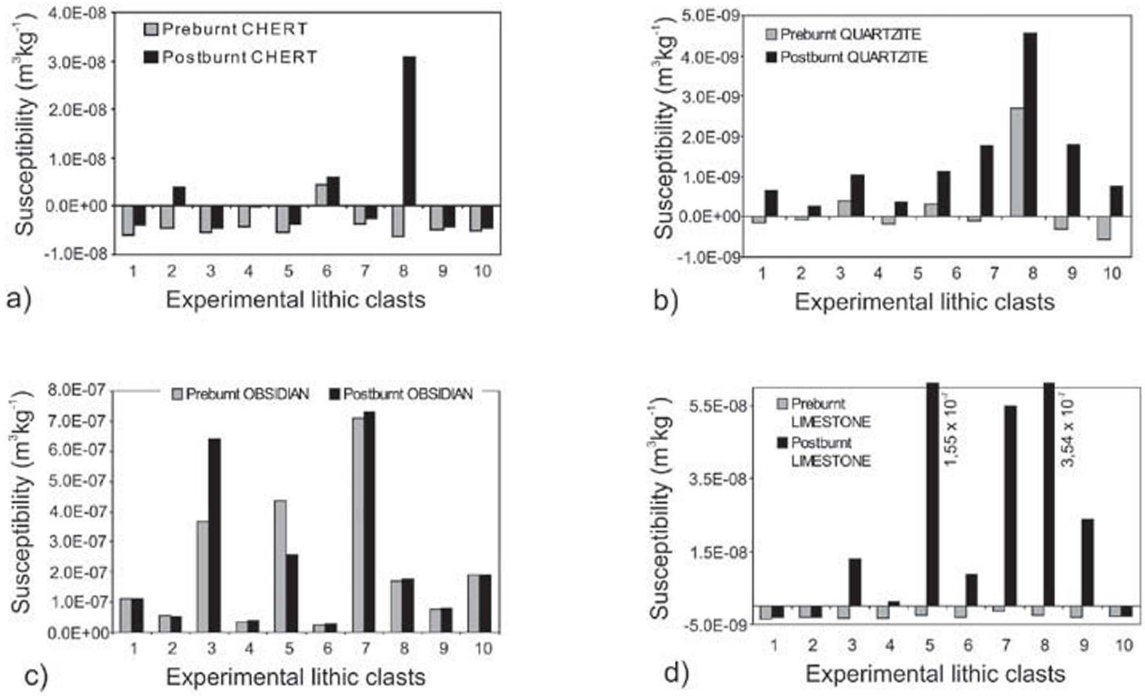
Figure 4. Representative examples of different rock-magnetic experiments carried out on the pre-burning material. (a and d) Hysteresis cycles. (b and c) Thermomagnetic curves and (e) Progressive IRM acquisition curves. Intensity values for each lithology are indicated.

Table 1. Mean magnetic susceptibility values expressed by mass for the pre- and post-burning samples of the different lithologies studied. Standard Deviation is also indicated.

Lithology	Specimens	Pre-burning mean MS (m^3kg^{-1})	St. Deviation (pre-burning)	Post-burning mean MS (m^3kg^{-1})	St. Deviation (post-burning)
Chert	10	-4.09×10^{-9}	3.08×10^{-9}	1.69×10^{-9}	1.08×10^{-8}
Quartzite	9	2.34×10^{-10}	9.71×10^{-10}	1.37×10^{-9}	1.31×10^{-9}
Obsidian	10	2.17×10^{-7}	2.22×10^{-7}	2.30×10^{-7}	2.51×10^{-7}
Limestone	10	-2.83×10^{-9}	6.29×10^{-10}	6.02×10^{-8}	1.14×10^{-7}
Sandstone	10	2.01×10^{-8}	3.88×10^{-9}	2.03×10^{-6}	2.30×10^{-6}

As expected, the studied pre-burning samples show a rather variable ferromagnetic content and thus distinct behaviour (Figure 6a). All IRM curves except the obsidian exhibit in general unstable and noisy behaviours. Most lithologies saturate around 200 mT indicating that a low-coercivity ferromagnetic mineral (magnetite and/or maghaemite) is the main magnetic carrier. Limestone and sandstone specimens do not reach saturation suggesting that some remanence is also carried by a higher coercive phase, most probably haematite (Figure 6a).

Progressive IRM acquisition curves of post-burned lithologies reach saturation around 150 – 200 mT indicating that magnetisation is dominated by a low-coercivity mineral (Figure 6b). The variation in the intensity of magnetisation among lithologies is remarkable, between one and two orders of magnitude.



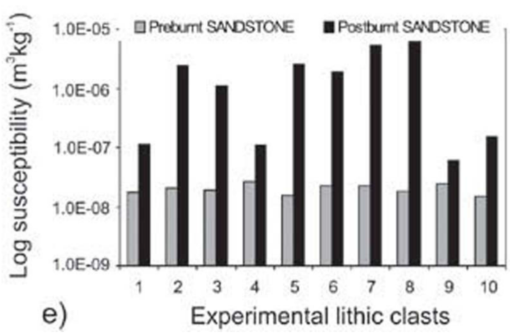


Figure 5. (a-e) Histograms showing the low-field magnetic susceptibility values of all pre- and post-burning samples for each lithology. (a) cherts; (b) quartzite; (c) obsidians; (d) limestone; (e) sandstone. Note that panel "e" is expressed in log-scale.

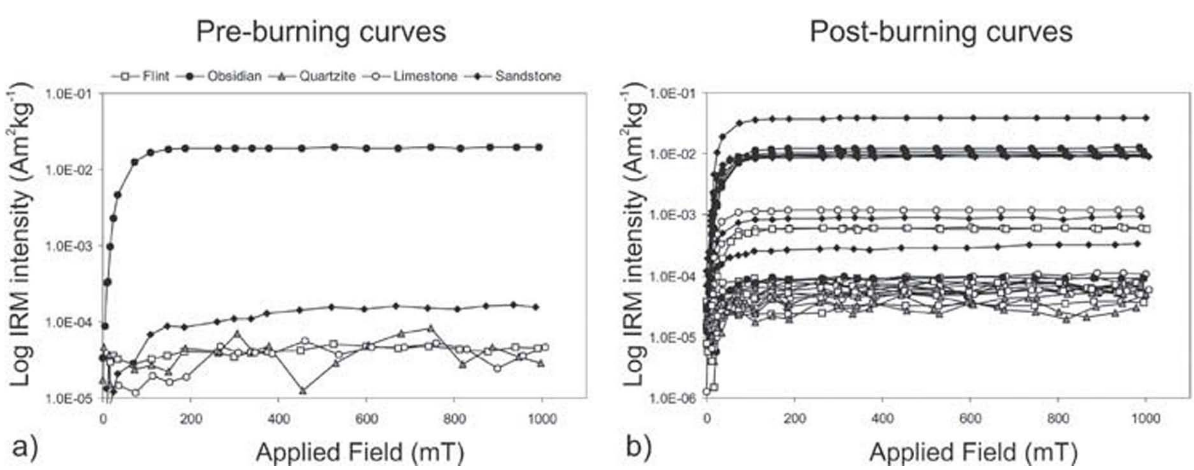


Figure 6. (a-b) Progressive isothermal remanent acquisition (IRM) curves before and after burning, respectively. Lithologies are represented in both graphs according to the legend shown in Figure 6a.

Regardless of the quadrant analysed, obsidian and sandstone are the most stable magnetic lithologies followed in decreasing order by limestone (~ 10 times weaker) and finally by chert and quartzite, which is the weakest one.

The magnetic behaviour after burning can be clearly distinguished by lithologies in Figure 7 which shows examples of progressive IRM acquisition curves, hysteresis loops and their corresponding thermomagnetic curves of representative samples of each lithology studied. The chert, limestone and quartzite exhibit diagrams with the lowest intensity of magnetisation and occasionally very noisy, dominating in all cases the diamagnetic behaviour as denoted by the original (uncorrected) shape of their hysteresis loops (Figure 7b-e-h). The abrupt drop around 580 ºC in the heating cycles of the thermomagnetic curves indicates that the main magnetic carrier of these samples is magnetite (Figure 7c-f-i). This observation is compatible with the progressive IRM acquisition curves which are saturated around 150 – 200 mT (Figure 7a and d). In contrast, the obsidian and sandstone samples exhibit diagrams with the highest intensities of magnetisation (up to two orders of magnitude) and are also probably dominated by magnetite (Figure 7j-ñ).

One aspect that we studied is to see whether there is a relationship between the thermomagnetic behaviour of the sample when heated again in the laboratory and the original heating temperature during experimental burning. In our case, it is noteworthy the high reversibility of thermomagnetic curves –coincidence between heating and cooling cycles-, indicative of high thermal stability of the sample. Those samples fully reversible (Figure 7i-l-ñ) suggest that they underwent heating temperatures of at least 700 ºC, because they do not alter when heated again in the laboratory. In contrast, the absence of thermomagnetic reversibility indicates that the sample did not originally exceed 700 ºC (e.g.: Figure 7f). Some variation in the temperatures reached is not incompatible because heating normally is not totally homogeneous on a hearth-surface (Carrancho and Villalaín 2011). All lithologies from quadrant 4 except the limestone sample (Figure 7f) exhibit a high thermomagnetic reversibility (not shown here), indicating that they most probably reached the temperature recorded by the embers´ thermocouple. The thermomagnetic irreversibility of the limestone sample (Figure 7f) can be due to the fact that this clast was quickly covered by ash causing an insulating effect avoiding heat penetration. This relationship between thermomagnetic reversibility and heating temperature is particularly interesting in the obsidian, which considering its volcanic origin surely exceeded that temperature when it formed. It is striking the similarity between the pre-burning obsidian (Figure 4c) and its respective post-burned sample (Figure 7l) in terms of intensity of magnetisation, mineralogical composition and thermomagnetic behaviour.

Figure 8 (a-b) illustrates the hysteresis ratios of pre- and post-burning samples plotted in the so-called Day plot (*Day et al. 1977*). The same information for the samples after burning differentiated by lithologies is represented in Figure 8b. The hysteresis ratios obtained range from $0.130 < M_{rs}/M_s < 0.234$ and $1.900 < B_{cr}/B_c < 8.210$ for pre-burning samples and $0.082 < M_{rs}/M_s < 0.315$ and $1.658 < B_{cr}/B_c < 6.623$ for the post-burning samples, although with interesting variations among lithologies. These values mostly indicate a pseudo-single domain (PSD) state for the magnetite grains. Pre-burning samples are rather scattered in the Day plot with the sandstone, limestone and quartzite slightly displaced to the right (Figure 8a). This might be due to the contribution of minor amounts of high coercive haematite or alternatively to a significant presence of finest superparamagnetic (SP) grains. Chert sample is in the PSD region while obsidian is nearer to the single domain (SD) area. The main difference between pre- and post-burning samples is that sandstone samples are well grouped in the PSD region closer to the SD (Figure 8b). This fact, together with the high reversibility observed in their thermomagnetic curves (Figure 7ñ) indicated that this lithology could be a good candidate for palaeointensity analysis. In any case the variability in the hysteresis parameters among lithologies is significant (Figure 8b). Quartzite is well grouped in the PSD region with hysteresis ratios relatively similar to chert samples. The latter, however, move to the right and slightly up so they could contain more SP grains on a relative basis (Dunlop 2002, Lanci and Kent 2003). Limestone is with obsidian the lithology which displays the higher dispersion in the grain size distribution which is probably related to relative variations of SP grains in these lithologies. Although is not possible to provide discriminatory values, hysteresis ratios of some lithologies such as sandstone *vs*. chert or quartzite are clearly separated, indicating that their granulometric distribution is distinctive.

Low-field susceptibility vs. SIRM (Saturation of IRM) plot provides interesting information about variations in magnetic mineral concentration (Figure 9). Sandstone and most obsidian samples plot to the right and up indicating that they are the most magnetic. Limestone

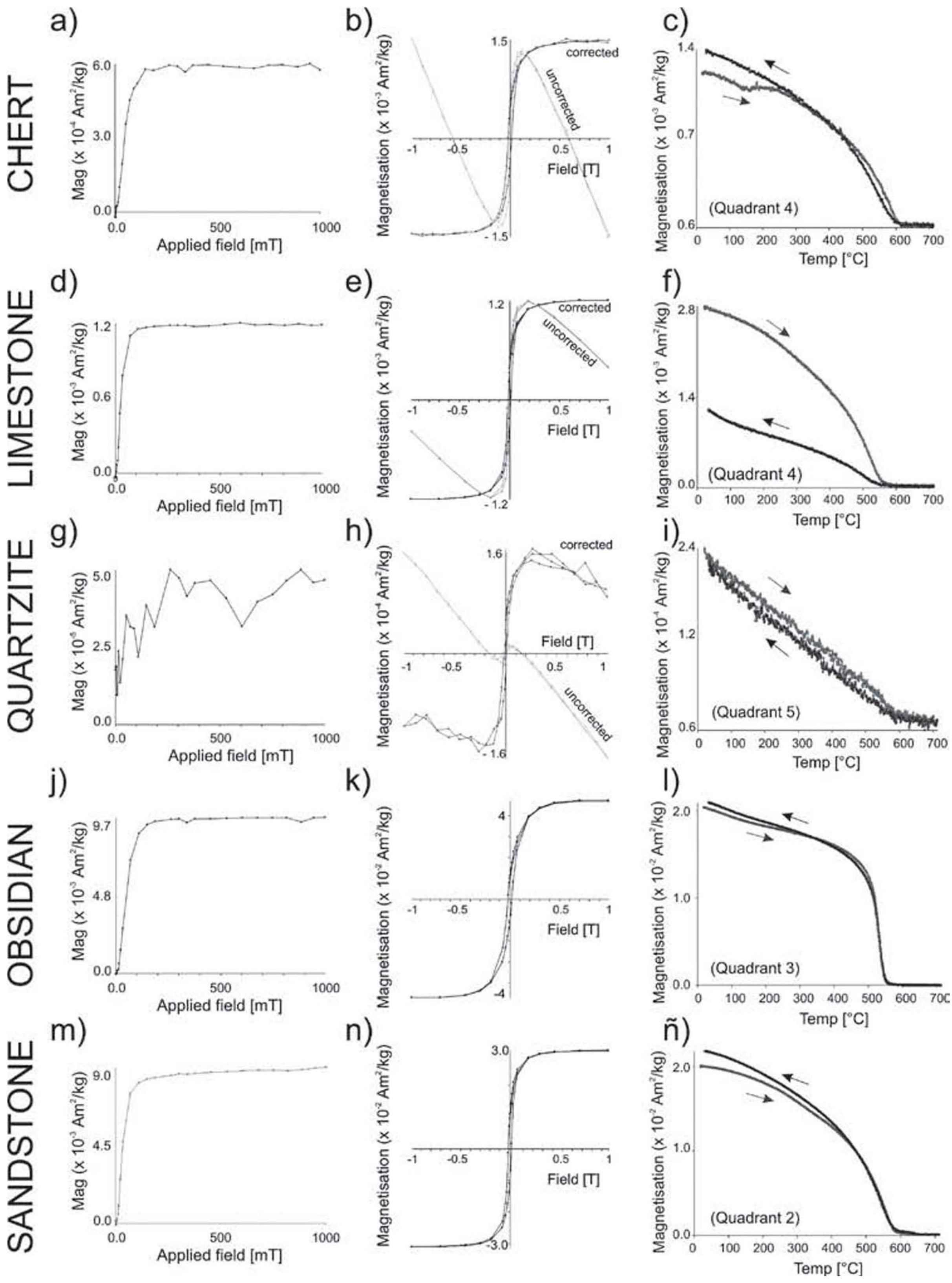


Figure 7. (a-ñ) Representative examples of IRM adquisition curves (left column), hysteresis cycles (central column) and their respective thermomagnetic curves (right column) for representative samples of each lithology after burning. Lithologies, applied field, intensity values and corresponding quadrant are indicated.

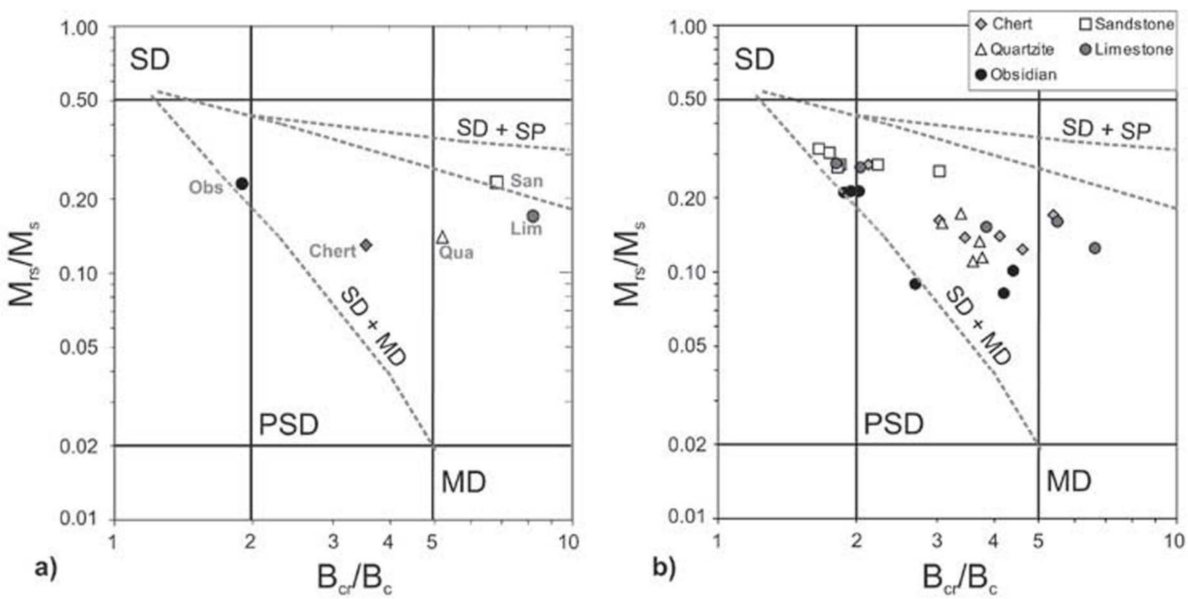


Figure 8. (a) M_{rs}/M_s vs. B_{cr}/B_c logarithmic plot (Day diagram) for pre-burning samples. Lim (limestone), San (sandstone), Qua (quartzite), Obs (obsidian). (b) Post-burning samples differentiated by lithologies according to the legend. The dashed lines represent mixing curves taken from Dunlop (2002) for mixtures of single-domain (SD) with multidomain (MD) or superparamagnetic (SP) magnetite particles.

specimens show a significant variability as it happened in their hysteresis ratios. Quartzite specimens are well grouped in the left hand corner because their ferromagnetic content is very poor. As expected, four of five chert samples do not appear in the plot because of their negative (diamagnetic) MS values. Interestingly, cherts can be characterized because their ferromagnetic content is the lowest one in comparison with the other lithologies which is also a discriminative criterion.

Absolute geomagnetic intensity determinations

Both palaeodirectional and absolute palaeointensity data are essential to define the geomagnetic vector, being the latter generally more difficult to extract from lavas and other baked material due to irreversible magnetic mineralogical changes upon conventional heating experiments (Shaw 1974). Recent studies have demonstrated the usefulness of an

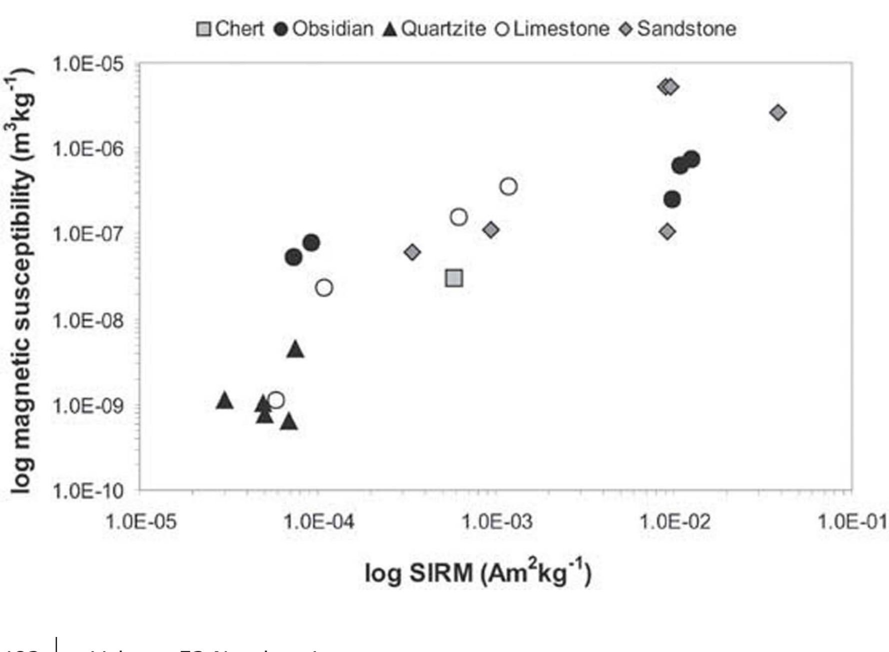


Figure 9. Scattergram of mass magnetic susceptibility vs. SIRM (Saturation isothermal remament magnetisation) for the different post-burning lithologies. Diamagnetic values (five cherts and one limestone) are excluded.

alternative methodology; the multi-specimen parallel differential pTRM method (Dekkers and Böhnel, 2006), in which minimal heating is required, thus increasing probabilities of obtaining accurate data.

Obsidians and sandstone samples showed the most suitable properties to perform absolute palaeointensty experiments. Both lithologies exhibited some features which definitively suggest that they carry a full TRM. First, they show univectorial behaviour upon stepwise thermal NRM demagnetisation with no evidences of p-TRMs (Figure 10 a-b). Note that orthogonal plots show different directions because it was not possible to orientate the small clasts during the experiment. Second, their intensity decay curves have a characteristic convex-shape behaviour where the greater part of the magnetization is removed between 520 – 560 ºC. Exactly the same behaviour is maintained for the laboratory created TRM shown on the same figure. This is typical of SD or small PSD ferromagnetic particles (Dunlop and Özdemir 1997) and is in good agreement with the hysteresis parameters obtained for both lithologies (Figure 8b). Third,

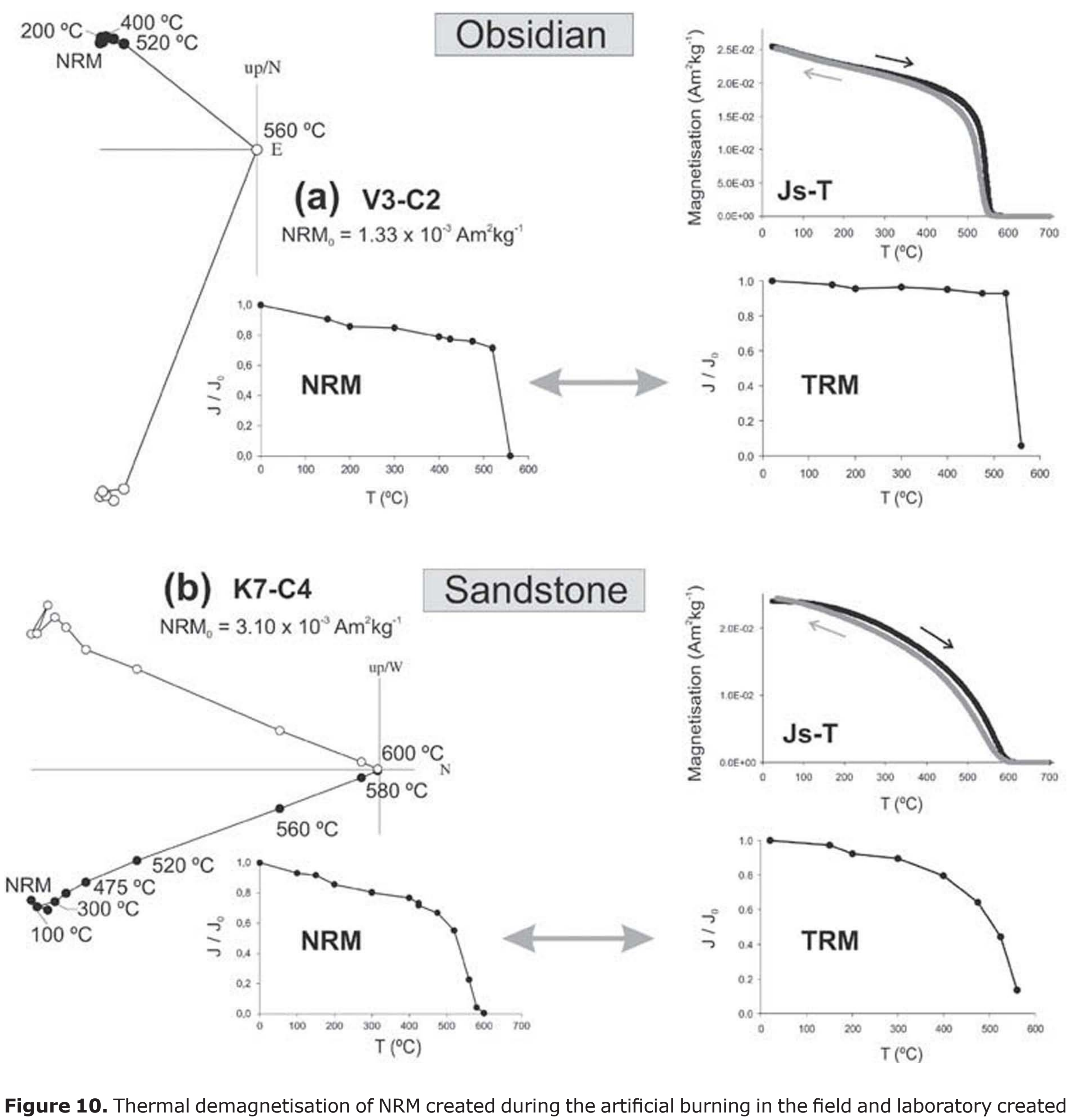


Figure 10. Thermal demagnetisation of NRM created during the artificial burning in the field and laboratory created full TRM for Obsidian (a) and Sandstone (b) samples. Also shown are corresponding continuous thermomagnetic (Js-T) curves. Please note that not exactly same samples were used for NRM and TRM demagnetisation experiements.

their respective thermomagnetic curves are totally reversible (Js-T curves shown on Figure 10) as expected by the temperatures recorded by embers´ thermocouple (T7; Figure2). All these observations agree with our previous results obtained in very similar experiments carried out in the same area showing that a total TRM can be acquired under similar experimental conditions (Carrancho and Villalaín 2011, Calvo-Rathert *et al.* 2012).

Absolute geomagnetic intensity determinations were carried out in the palaeomagnetic laboratory of LIMNA (Morelia, Mexico) using a 'compact version' of the multi-specimen parallel differential pTRM method (see below for an explanation) due to the scarcity and reduced size of available samples. Two samples of obsidians and sandstone from each quadrant were cut using a diamond-disk saw; each fragment was weighted and then pressed into salt pellets in order to obtain standard-dimensions palaeomagnetic samples. In this way, two similar ten-specimen series were formed. The TRM of all 20 specimens was measured using a JR5A spinner magnetometer. Two sets of experiments were performed. First series (even specimens E1 to E19) was heated inside an ASC TD48 thermal demagnetiser up to 475 °C under the influence of a 40 μT magnetic field, while a 50 μT laboratory field was applied for the second series (odd specimens E2 to E20). Here becomes clear the phrase 'compact version' above mentioned; two lab fields used. Since the ambient field was known (and measured) *a priori*, and in order to investigate also possible dependence of the intensity of TRM acquired by samples as a function of the position within the burning (samples heated at different quadrants), just two lab fields were selected; one lower (40 μT) and one higher (50 μT) than the known expected ambient field.

After the completion of the above described experiments the pTRM acquired by each specimen was measured and the relative difference between pTRM (gained in lab) and full TRM (produced during the experimental burning) of specimens coming from the same lithic sample (sister specimens) was calculated. Sister-specimen sets, for both obsidians and sandstones, were plotted and connected by straight lines and its intersections with the horizontal axis (zero difference) were estimated (Figure 11a-b). Mean intensities calculated separately for obsidian and sandstone samples yielded values of 46.0 and 46.7 μT, respectively. Thus, no intensity differences regarding lithologies were observed. Since samples were heated altogether under the same ambient magnetic field we adjusted a best fit line to all the specimens. After the rejection of 1 sister-specimen set showing a significantly high slope, an average ambient field of 46.4 ± 2.4 μT was determined (Figure 11c). We note, however, that in spite of the significantly high slope the rejected sister-specimen pair shows it intersects the horizontal axis at approximately 40 μT.

Discussion and perspectives

The rock-magnetic results reported here show that the experimental heating has produced remarkable alterations in the magnetic properties of the studied lithologies. It is worthy pointing out that each heating event is unique and represents very specific combustion conditions in terms of duration, temperature, etc., which are rarely fully reproducible. However, here we show that high temperature (700 ºC) heating significantly increases the concentration and varies the grain size distribution of magnetic minerals from the studied lithologies in comparison with their unburned counterparts. The intensity of magnetisation and MS values increased between one and two orders of magnitude comparing pre- and post-burning lithologies and similar variations were also observed among different post-burning lithologies. The variability in the mineral magnetic content of these lithologies before burning is certainly an important factor. Obsidian is the only lithology which does not undergo significant magnetic variations, because, as volcanic glass, it is formed at high temperature and generally contain iron oxides (e.g.: titanium-rich magnetites) carrying a stable TRM.

The main magnetic carrier in all lithologies is 'almost pure' magnetite and concentration-dependent parameters (magnetic susceptibility, IRM, saturation magnetisation, etc.) clearly indicate the increase of ferrimagnetic minerals after burning. As far as the weakest lithologies are concerned (chert, limestone and quartzite) the magnetite created after burning most likely come from the alteration of (undetermined) paramagnetic minerals unidentifiable with rock-magnetic methods. At this stage it is not possible determine which specific minerals are involved but a good summary of this type of mineralogical changes can be found in Henry (2007) and references therein. For the purpose of this article, the interesting point is that the rock-magnetic characterization of the pre-burning materials allowed identifying the obsidian and sandstone as the most suitable lithologies for archaeomagnetic analysis. The variations in the domain state of ferromagnetic particles are also notable, particularly in sandstone, which after heating acquired a grain size closer to SD state. For this reason and

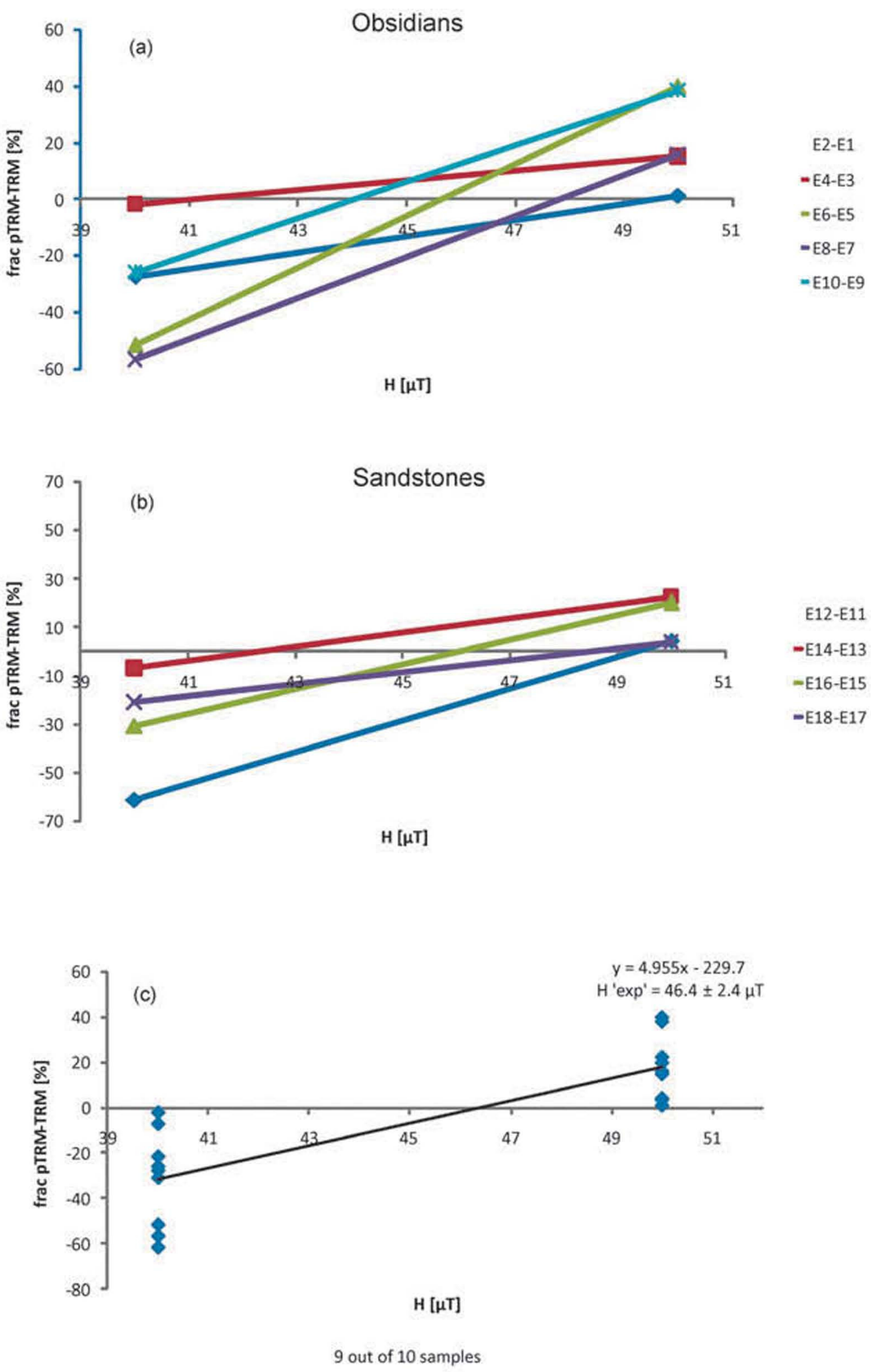


Figure 11. Palaeointensity results obtained in obsidian and sandstone specimens, (a) and (b) respectively, with the multispecimen method. Lines connect sister-specimen of the different lithologies samples. Plots represent the relative percentage differences between the pTRMs acquired at different lab fields (40 and 50 μT) and the total TRM (acquired during burning). Intersection of each line with the horizontal axis (zero difference) determines the intensity of the Earth's magnetic field during the burning. (c) Mean ambient field estimation calculated from both lithologies.

judging from high thermomagnetic stability, sandstone and obsidian were selected to carry out palaeointensity analysis. On the contrary, the chert and quartzite samples studied are not fully ferromagnetic (diamagnetism dominates their behaviour in some specimens even after burning) and their domain state distribution is PSD with a significant contribution of superparamagnetic (SP) particles. Limestone is about ten times more magnetic than chert and quartzite but it does not hold the domain state requirements for palaeointensity analysis and some thermomagnetic curves did not exhibit full reversibility (Figure 7f).

Macroscopic observations are also a valid and complementary argument to detect heat treatment, but not completely diagnostic by themselves. Heating produces a variety of macroscopic alterations in lithic assemblages such as colour changes, increased lustre, or microfractures among others that have been traditionally used as criterion to identify fire in the archaeological record. However, fire is not the only process responsible for colour variations in lithic materials (e.g.: Brown *et al*. 2009) so it is important to combine rock-magnetic and macroscopic observations as Borradaile *et al*. (1993, 1998) already shown. For example, the studied obsidians hardly change their magnetic properties when heated experimentally but in contrast produce very characteristic internal fissures which can be indicative of heat treatment. Obsidian is a volcanic glass with exceptional flaking properties and is unlikely that it was systematically heated in prehistory, so the study of its magnetic properties to identify human-induced heating processes would be probably unsuccessful. It is well-known that variability in the magnetic properties of obsidians may be significant among neighbouring areas (e.g. Zanella *et al.* 2012) and even also from flow to flow (Frahm and Feinberg 2013), which is important in provenance studies. However, the ultimate mechanism responsible of the observed magnetic properties in this study is heating. Any heating of the sample during its history could considerably disturb and reset the NRM and other magnetic properties in general (e.g.: Borradaile *et al.* 1993, 1998). Therefore, for the purpose of identifying heat treatment in archaeological lithic assemblages the provenance is not so a critical factor because it involves a different process. That is not incompatible, and indeed advisable, with the fact that the magnetic properties of a particular set of archaeological obsidians (or any other lithology) are compared with those obtained from the same lithology if the source area is known. Magnetic properties variation not only depends on some specific combustion conditions but also on the previous magnetic mineralogy before the burning. As far as obsidians artifacts are concerned, if the goal is to determine whether they have been heated in the antiquity, macroscopic features (i.e., the internal fissures reported here) seem to be more useful than mineral magnetic analyses themselves. The occurrence of potlids is another macroscopic alteration documented specially in cherts, but some caution needs to be taken here because it is known that in contexts with drastic temperatures changes they can occur without heating (e.g.: Griffiths *et al.* 1985, Borradaile *et al.* 1998).

According to the results reported here for the studied lithologies, in case of heat treatment the contrast between pre- and post-burning magnetic properties is supposed to be distinctive enough in terms of magnetic concentration and grain size distribution. These observations ideally should be accompanied as far as possible by archaeological evidences provided by the context such as charcoals, rubefied substrates or in the best case, by the presence of ashes.

It has been suggested that thermal treatment of siliceous lithologies as cherts causes a consistent marked reduction in fracture toughness as a consequence of recristalization (Domanski and Webb 1992, 2007, Domanski *et al.* 2009). An interesting aspect to consider in similar studies of archaeological lithic materials is the effect of diagenetic processes. Once the artefact -supposedly heated in its manufacture- is abandoned and subsequently becomes buried, weathering processes or recristalization events may produce the removal of para- and/or ferromagnetic minerals (Thacker and Ellwood 2002). Consequently, magnetic-concentration dependent parameters such as magnetic susceptibility or IRM would significantly be reduced hampering the unequivocal identification of heat treatment in that lithic assemblage.

Detailed studies relating the palaeofield strength and the manufacturing processes of archeological artifacts are scarce. Genevey and Gallet (2002) checked their experimental procedure to retrieve the intensity of the geomagnetic field from ancient French pottery by implementing a preliminary test on new ceramic material, obtaining results 3% lower than the expected local field value. Gómez-Paccard *et al.* (2006) carried out an archaeomagnetic study of seven contemporaneous Spanish kilns, which allowed discussing the different factors causing the observed dispersion. Catanzariti *et al.* (2008) conducted a quality control test of the archaeomagnetic method in a modern partially heated structure, obtaining results consistent with the known field value in both direction and intensity. Aidona *et al.* (2006) investigated the spatial distribution of magnetic parameters in the floor-bricks of a test furnace, constructed using similar materials and techniques than during the Roman period, concluding that archaeological kilns may need to be sampled very carefully and at close spacing in order to find the best areas for archaeomagnetic investigations because of the spatial limitation of the fire effect. More recently, Tema *et al*. (2013) performed experiments to monitor the behaviour exhibited during experimentally controlled heating of small brick fragments. Most samples exhibited stable behaviour up to 500-600 C while at higher temperatures important changes on their magnetisation occurred. They also show that they experienced different temperatures depending on their position in the kiln. The suitability of lithic clasts from pyroclastic flows to obtain absolute palaeointensity determinations has been successfully tested by other authors (Roperch *et al.* 2014; Paterson *et al.* 2010; Bardot and McClelland 2000). Yet, no similar experiments were carried out on lithic clasts of archaeological interest. Under similar heating conditions to those obtained in this experiment, we have shown that it is possible to obtain reliable palaeointensity determinations in sandstone and obsidian lithic implements. While it is true that prehistoric fires hardly achieve heating temperatures high enough to acquire a total TRM, the high thermomagnetic stability of obsidian due to its volcanic origin makes it an outstanding candidate for this type of analysis. In volcanic regions obsidian is one of the most frequent raw materials found in prehistoric archaeological sites and it should be kept in mind that these are usually well-dated contexts. Therefore, archaeological obsidians have a considerable potential as recorders of the geomagnetic field strength.

Given the wide variability in the magnetic properties among samples of the same lithology is difficult to extrapolate a characteristic magnetic pattern to unequivocally identify heat treatment in archaeological lithic assemblages. Despite the range overlap in the values of some magnetic parameters among lithologies, sandstone and obsidian consistently recorded higher mean MS values compared to limestone, chert and quartzite samples. These variations in magnetic concentration combined with the granulometric information provided by the hysteresis ratios as well as the macroscopic alterations have diagnostic potential to detect if this type of lithologies were heated in the antiquity or not. Some studies have explored the potential of mineral magnetic methods to detect heat treatment in prehistoric sites (e.g. Brown *et al.* 2009, Herries and Fisher 2010) but much effort remains to be done. This study represents a first step with clear implications for experimental archaeology. Although the geographical provenance of the studied materials is very regional and its archaeological application to detect fire perhaps only makes sense on such a scale, allowed us to magnetically characterize these lithologies when heated.

Conclusions

High-temperature (~ 700 ºC) heating generates remarkable magnetic and macroscopic variations in the five lithologies studied. All lithologies except the obsidian recorded an increase of up two orders of magnitude in their magnetic concentration-dependent parameters revealing the formation of new ferrimagnetic minerals (magnetite). Chert, quartzite and limestone are magnetically weak whereas obsidian and sandstone specimens are the most intense because their ferromagnetic content is higher. Therefore they are the most suitable raw materials for archaeomagnetic purposes. Magnetite formation after burning in the weakest lithologies most probably takes place from the transformation of paramagnetic (undetermined) minerals. Magnetic concentration-dependent parameters (e.g. low-field magnetic susceptibility, IRM, saturation magnetisation) are particularly discriminatory showing significant differences among lithologies compared with their unburnt counterparts. Room temperature hysteresis parameters also revealed a more SD state in sandstone specimens after burning so, under similar combustion conditions, it is a suitable lithology for palaeointensity analysis. The main macroscopic alterations observed (colour changes, rubefaction, potlids and microretouches) are particularly evident in cherts which barely modify their magnetic properties after burning. Alternatively, obsidians hardly change their magnetic properties by heating but the massive formation of internal fissures can be used as macroscopic criterion to detect heat treatment. The multispecimen palaeointensity technique was successfully applied to obsidian and sandstone specimens yielding a field estimation of 46.2 ± 2.4 μT (original field 45,302 μT). Finally, this study has shown how mineral magnetic methods combined with macroscopic observations can readily provide information about the burn history of lithic assemblages as well as obtain geomagnetic field information.

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