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Search for early traces of fire in the Caune de l'Arago at Tautavel (Eastern Pyrenees, France), combining magnetic susceptibility measurements, microscopic observations, and Raman analysis

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Abstract. The Caune de l'Arago is an important Middle Pleistocene archaeological site, consisting of a cave with a sedimentary infilling deposited between 700 and 100 ka. Excavations have revealed traces of the use of fire in the layers formed between 400 and 100 ka, but no earlier traces have been recorded in the underlying levels. These potential older traces may have undergone various processes of weathering, and could have been degraded or considered nonexistent. This study combines magnetic susceptibility measurements, microscopic examination, Raman analyses, and elemental analyses by scanning electron microscopy to look for traces of fire activity such as combustion residues preserved among the sediments. This approach has led to the discovery of a zone in the Q4 level, whose age is estimated at 560 ka, which is rich in magnetic minerals and charcoal. The anthropic or natural origin of these materials is discussed.

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Keywords. Caune de l'Arago cave, Fire, Charcoal, Magnetic susceptibility, Raman spectroscopy, Magnetic minerals, Middle Pleistocene.
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1. Introduction

The Caune de l'Arago is situated near the village of Tautavel (Pyrénées-Orientales, France). It is a major Middle Pleistocene archaeological site [de Lumley et al., 2014, de Lumley, 2015], located in a cave opening into the Corbières massif 88 m above the bed of the Verdouble river. The cave contains a 16-m thick sedimentary sequence, whose base is dated at around 700 ka [Yokoyama et al., 1982]. The excavated stratigraphic section can be correlated with marine isotopic stages (MIS) 14 to 5 [i.e., 563–95 ka, Lisiecki and Raymo, 2005]. The thick sedimentary deposits are delimited above and below by stalagmitic floors (Figure 1), the most recent of which is dated at ~100 ka [Falguères et al., 2004]. Excavations and archaeostratigraphic studies have identified 55 archaeostratigraphic units rich in thousands of faunal remains, lithic artefacts, and several human remains, including the skull of the Tautavel Man, *Homo erectus tautavelensis* [de Lumley and de Lumley, 1971, de Lumley, 2015], dated at 455 ka [Yokoyama et al., 1981], as well as the oldest human fossil found in France, a child's incisor with an estimated age of 560 ka (excavations 2018).

Numerous palaeoenvironmental and palaeoclimatic studies carried out on the Caune de l'Arago infilling have revealed the occurrence of a cold and dry period between 570 and 530 ka, followed by a succession of temperate and cold phases up to about 100 ka [Moigne et al., 2006]. On account of these climatic and environmental fluctuations, Caune de l'Arago is an important site for the study of the adaptation of humans to their environment and, without doubt, the control of fire is an essential step. Prehistorians have long sought to elucidate the circumstances and the date of the first intentional use of fire by Palaeolithic human groups. Many studies have attempted to determine the significant changes this invention brought to their ways of life and thinking. While fire appears above all as a source of heat and light, its mastery broadened the range of techniques, food resources, and social life [de Lumley, 2006]. Archaeological studies dealing with the emergence of fire use during the Palaeolithic suggest that European humans began to control fire between 400 and 300 ka [Roebroeks and Villa, 2011, Shimelmitz et al., 2014]. However, it is during MIS 5 (130 ka–80 ka) that evidence indicates a more perennial use, although there are several sites with good examples of pre-MIS 5 fire mastery, such as in Bruniquel cave (176 ka) [Jaubert et al., 2016]. Based on the absence of any clear archaeological evidence at several sites occupied before MIS 11 (420 ka), fire does not seem to have been part of the usual technological repertoire of European humans until the second half of the Middle Pleistocene [Roebroeks and Villa, 2011, Shimelmitz et al., 2014].

Archaeological sites with a long sedimentary sequence are suitable places to discover traces of the use of fire through time. Caune de l'Arago is a remarkable example with its excavated stratigraphic sequence spanning a significant part of the Pleistocene, from MIS 14 to 5 (563 to 95 ka). So far, some traces of the use of fire have been found in the Top and Upper Complexes, in sedimentary layers formed between 400 and 100 ka ago [de Lumley, 2006]. These traces include charcoals, burnt bones, and flints with thermal impacts, proving the use of fire, at least occasionally [Barbetti, 1986, Roebroeks and Villa, 2011]. In particular, the traces are located in Archaeostratigraphic Unit C [de Lumley, 2015] and in the RFB level (Figure 1), formed of sediments from the Top Complex, younger than 260 ka, those are intrusive into the upper part of the Middle Complex [de Lumley et al., 2020]. In the layers formed from 100 ka onwards, there is an abundance of burnt bones, charcoals, ashes, and heated flint. The current chronological distribution of traces of fire inventoried at Caune de l'Arago thus corroborates the hypothesis that the general principles of fire use were established from 400 ka onwards. Indeed, the first combustion areas—and sometimes even fire structures—appear around 400 ka at several European sites such as Terra Amata (France) [de Lumley, 1969], Orgnac III (France) [Moncel et al., 2005], Beeches Pit (UK) [Preece et al., 2006], Gruta da Aroeira (Spain) [Sanz et al., 2020], and Menez Dregan (France) [Monnier et al., 2016], with probable combustion areas dated at around 500 ka. However, older traces could have existed, with no hearth structure and less concentrated, but may have also undergone

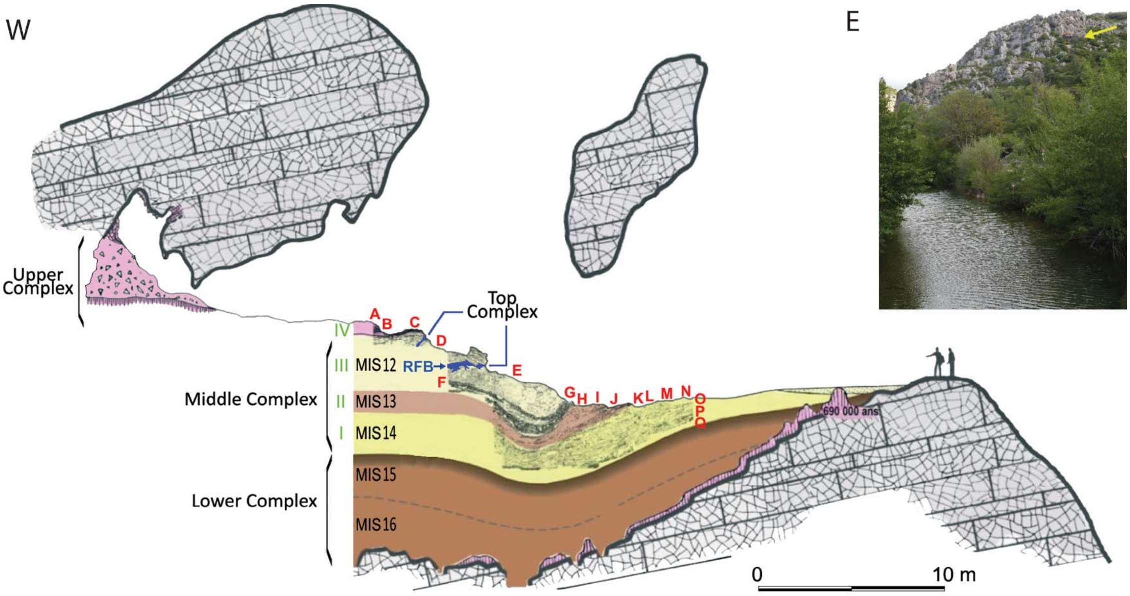

Figure 1. Synthetic section of the Caune de l'Arago infilling. Upper, Middle, and Lower Complexes, stratigraphic subdivisions ("Ensembles" I to IV, in green), and Archaeostratigraphical Units (in red). Correlations with MIS are based on sedimentological, palynological, palaeoecological, biostratigraphical, magnetostratigraphic, and geochronological data [de Lumley et al., 1984, Falguères et al., 2004, 2015]. RFB (in blue), Top Complex "intrusive" sediments in Ensemble III. The yellow arrow on the photo shows the location of the cave above the Verdouble river.

extreme alteration, to the point that they are currently unrecognizable.

Indeed, several phenomena can contribute to obliterate any traces of the use of fire. After a fire has been extinguished, the residues can be quickly dispersed by water and wind, trampling, or reuse. Charcoals are brittle and friable, as well as being oxidizable [Ascough et al., 2011] and sensitive to alkaline environments [Braadbaart et al., 2009], which leads to a decrease in their preservation capacity. The fragility of burnt bones increases with the temperature to which they have been subjected, becoming easily reduced to powder when calcined [Stiner et al., 1995]. The colour of burnt bones is a parameter that needs to be carefully considered. Van Hoesel et al. [2019] show that the colour of experimentally burnt bone varies with the heating temperature under oxidizing conditions, that is, brown between 200 and 300 °C, black between 300 and 350 °C, grey between 350 and 600 °C, and white above 700 °C, temperatures commonly attained in fireplaces [Aldeias et al., 2016, Ferrier et al., 2017]. The black colour of a modern burnt bone is related to the amount of carbonized organic matter it contains, which tends to disappear if combustion is complete. In addition, the black colour of ancient bones can also be due to a mineral coating of manganese dioxide [Shahack-Gross et al., 1997]. Ashes generally consisting of calcium carbonate are not always preserved, especially if there has been leaching or partial decarbonation of the sediments [de Lumley, 2006, Canti, 2003]. Post-depositional physico-chemical processes can therefore dilute the combustion residues among the sediments and make their detection a delicate task.

Thus, when fireplaces or traces of fire use are altered and are no longer easily recognizable, archaeological soils can be examined at high magnification to detect preserved combustion residues. Microscopic analysis is suitable for the detailed micromorphological study of sediments contained in soils. Traces of combustion, such as ashes, vegetal chars, carbonized flesh and fat can be characterized by their morphology and optical properties [Canti, 2003, Goldberg et al., 2009]. Plant cells can be identified on thin polished sections, while carbonized matter appears white in reflected light and dark in transmitted light, and carbonized fats have a globular appearance. However, when uncertainty remains about the colour and/or shape of a structure, it is possible to characterize carbonized organic matter by Raman microspectrometry analysis, which can be performed on micrometric or even smaller objects.

Raman microspectrometry is a technique that involves coupling an optical microscope and a Raman spectrometer. It is often used in archaeology [Smith and Clark, 2004] to analyse the chemical environment and crystalline structure of materials, based on their inelastic scattering of light. Chars are solid residues derived from the carbonization of organic matter. They are identifiable by the presence of two characteristic bands in their Raman spectra called D (vibrations of sp2 bonds in aromatic structures) and G (vibrations of polyaromatic units), located respectively at 1350 cm^{-1} and 1584 cm^{-1} [Rouzaud et al., 2015]. Thus, plant, bone, flesh, and fat chars share these features and can be unambiguously distinguished from their non-carbonized precursors. The contribution of Raman microspectrometry has already been used to characterize prehistoric charcoals and soot in the Chauvet cave in France [Ferrier et al., 2017], in the Nerja cave in Spain [Medina-Alcaide et al., 2019], and on partially burnt bear bone in the Bruniquel cave in France [Jaubert et al., 2016]. In addition, when applied to charcoals, the Raman palaeothermometer developed by Deldicque et al. [2016] can be used to determine temperature, an essential parameter in the phenomena of combustion and thermal alteration. This palaeothermometer is based on the evolution of the relative intensities of the D and G bands as a function of the carbonization temperature. The height ratio (H_D/H_G) of the D to the G band is correlated with the carbonization temperature of the vegetal precursor and increases irreversibly and monotonically between 500 °C and 1200 °C. In this way, the Raman spectra of charcoals combined with microscopic examination provides us with a true palaeothermometer. This method has been used, for example, to determine the maximum temperatures reached during the fire at Notre-Dame Cathedral in Paris on 15 April 2019, using the charcoals produced by this tragic event [Deldicque and Rouzaud, 2020].

After the identification of charred material by Raman microspectrometry, scanning electron microscopy (SEM) coupled with energy dispersive analysis (EDS) can be used to specify the nature of the organic precursor at the origin of the Raman signal. Indeed, semi-quantitative elemental analyses confirm the presence of carbon present by definition in all chars, but also other elements which differ according to the nature of the organic precursor. The ash content of wood is mainly composed of calcium, magnesium, potassium, and aluminum, with a dominance of calcium [Pettersen, 1984]. On the other hand, the ash content of animal flesh is made up of calcium, phosphorus, sulphur, potassium, and magnesium with a dominance of phosphorus and potassium [Horbańczuk and Wierzbicka, 2016]. Thus, when the morphology of a char prevents a clear identification of its precursor, the presence of phosphorus and potassium helps to clarify its animal or vegetal origin. The coupling of micromorphology–Raman microspectrometry–SEM is thus a powerful tool in the identification and characterization of ancient fire residues in sediments. However, this micrometric to millimetric analytical method cannot be realistically applied to all the sediments of a given archaeological site, especially in the case of a cave with a sedimentary infilling 16-m thick as found at Caune de l'Arago. The prior localization of areas of interest becomes necessary and can be performed by magnetic susceptibility measurements.

Magnetic susceptibility, a dimensionless value, is the ability of a material, for example, soil, to become magnetized under the action of an external magnetic field. Its value depends on the type and quantity of magnetic minerals present, most often iron oxides. Le Borgne [1960, 1965] shows that heating at high temperatures, such as those produced by a fire, significantly increases the magnetic susceptibility of soils. This increase depends directly on the quantities of iron oxides and organic matter initially present before the heating, as well as the temperature reached in the fireplace. Thus, a high magnetic susceptibility in cave soils and sediments can reveal traces of human activities such as fires [Barbetti, 1986, Brodard et al., 2012, de Sousa et al., 2018, Herries, 2009, Tite and Mullins, 1971]. Several studies of the magnetic susceptibility of the Caune de l'Arago sediments were conducted by Hedley and Djerrab on block samples, vertical sections, and drill cores to specify the individualization of stratigraphic levels in the cave [Djerrab, 2002]. These studies reported in de Lumley et al. [2020] revealed high magnetic susceptibility values in the RFB level (Figures 1 and 2), correlated with the presence of hearth residues.

At Caune de l'Arago, a seven-meter thick decarbonated pocket formed in the centre of the cave, caused by a massive accumulation of bat guano. In the lower part of the Middle Complex, the deposits are dark brown in colour, rich in organic matter, and decarbonated. This formation named "black earth" is currently interpreted as the result of an invasion of roots that came to draw nutrients after the collapse of the original entrance of the cave [de Lumley et al., 2020].

The objective of the present study is to assess the potential of combining magnetic susceptibility measurements, micromorphological analyses, Raman spectroscopy, and SEM to search for traces of fires, in the absence of preserved hearth structures, and in a long sedimentary sequence several meters thick that has undergone significant post-depositional geochemical evolution over time. New magnetic susceptibility measurements were performed to locate sediments in the excavated archaeological section likely to contain traces of fires. These measurements were used to select sediment samples from levels with the highest magnetic susceptibility, which were then analysed by optical, Raman, and SEM microscopy. Raman microscopy was also used to identify indirect traces of heating, such as the different magnetic minerals responsible for the increase in magnetic susceptibility in sediments. In order to provide new elements for discussion and comparison, laboratory heating experiments were carried out on the cave sediments.

2. Materials and methods

2.1. *In situ magnetic susceptibility measurements*

Magnetic susceptibility measurements were carried out *in situ* on parts of the longitudinal and transversal sections, with a 10 cm sampling step. The studied profile crosses Archaeostratigraphic Units Q to D (Figure 1), located in the Middle Cave Complex and thus covers a period from MIS 14 to MIS 12. Measurements could not be made in certain parts of the section which were either not attainable or lacked homogeneity, that is, G level, where the sediment is almost absent. The lowest point of the profile is located at the base of the archaeological section in the Q4 level, 1110 cm below the zero level of excavations, in the longitudinal section F/G, and in the transversal band 15. The instrument used in the field was an Agico KT5 kappameter, with a sensitivity of 2×10^{-6} SI. The measurements were made on flat parts of cleaned sediments so that no curvature correction was necessary.

2.2. *Sampling*

Twenty-seven sediment samples, about 200 g each, were collected from the stratigraphic sections along the magnetic susceptibility profile with a stainless-steel laboratory spatula and stored in plastic containers. The samples are prefixed by the letters CA (Caune Arago) followed by the sampling height under the zero level of excavations, in cm.

2.3. *Magnetic susceptibility measurements in the laboratory*

The magnetic susceptibility of the collected samples was measured in the laboratory using an Agico KLY 3S susceptibility metre with a sensitivity of 2×10^{-7} SI. Five to ten grams of naturally dried sediment are used for each susceptibility measurement. The accuracy of absolute calibration is ±3% and the diameter of the detection coil is 43 mm. The operating frequency is 875 Hz and the applied field intensity is 300 $A{\cdot}m^{-1}$.

2.4. *Heating experiments*

To simulate the effect of the presence of a fire on the magnetic susceptibility of the cave soil, a sediment sample, unprocessed and with a low magnetic susceptibility was heated in a controlled atmosphere tubular furnace, according to the procedure indicated by Tite and Mullins [1971]. The sediments were heated for 40 min in a neutral atmosphere under continuous argon flow, then 20 min with an air inflow just before and during cooling, to reproduce the oxygen supply when the fire intensity decreases until extinction. Five to ten grams of sediments were heated up to different temperatures, between 450 °C and 600 °C. Magnetic susceptibility was measured at each step of the heating experiments to monitor the evolution of weakly magnetic iron oxides towards highly magnetic forms or *vice versa*.

Mineralogical studies, in particular, measurements on cores collected inside the cave, show that the sediments making up deposits of the Middle Complex of the cave consists mainly of sands, clays, and silts, in variable proportions [de Lumley et al., 2020]. The iron oxides goethite and haematite, which are likely to be transformed into magnetic oxides by experimental heating, are already oxidized, and therefore very stable. Hence, they have probably not undergone much transformation over time. It is therefore reasonable to consider that samples with a low magnetic susceptibility can be used for experiment heating since they are representative of the rest of the sediments in the Middle Complex, as well as soils that have not been heated. Furthermore, the post-depositional geochemical evolution in the seven-meter thick decarbonated pocket in the centre of the cave does not appear to have significantly modified the magnetic susceptibility of sediments [de Lumley et al., 2020]. This suggests that the minerals contributing to the magnetic susceptibility signal have not been severely altered either.

2.5. *Search for heated material in the collected samples*

Three instruments were combined to characterize traces of heating (i.e., minerals having undergone a thermal event such as iron oxides, charcoal, fat, or flesh chars) in the samples with the highest magnetic susceptibility: a photonic microscope, an SEM coupled to an energy dispersive spectrometer, and a Raman microspectrometer. All analyses were performed at the Geology Laboratory of the Ecole Normale Supérieure de Paris, France.

2.5.1. *Search for charred material*

The sediments were first examined by optical microscopy with a Keyence VHX5000 microscope with a magnification ranging from ×20 to ×200. Particles showing vegetal structures and black grains that may have been carbonized were isolated, deposited on a thin slide, and analysed with a Renishaw Invia Raman microspectrometer equipped with a Cobolt laser with a wavelength of 514 nm. No additional preparation was necessary. The acquisition time was 3 min and the laser power was set at 0.5 mW. The spectra were recorded between 600 and 2000 cm^{-1} in order to observe the first-order Raman scattering of carbonized materials. The fluorescence signal was subtracted with a linear baseline, or quadratic when significant. The charcoal formation temperatures were determined based on the Raman palaeothermometer developed by Deldicque et al. [2016]. However, since the palaeothermometer (H_D/H_G ratio) is not only sensitive to the temperature but also to the heating time, calibration curves for heating durations of 1 and 6 h were used. Some chars were imaged by SEM and elemental analyses by EDS were recorded. To avoid elemental contamination of the isolated char grains by sediments, the grains were polished after induration in epoxy resin. Only the grain cores were analysed.

2.5.2. *Characterization of iron oxides*

To identify the magnetic minerals accounting for the high magnetic susceptibility values in the cave sediments, magnetic grains were extracted from the samples using a neodymium magnet. The magnetic grains were weighed, impregnated in epoxy resin and polished. Magnetic minerals were characterized by Raman microspectrometry with the same instrument as above. Raman spectra were recorded between 200 and 1600 cm^{-1} to observe the characteristic peaks of iron oxides. The power of the laser was set at 0.1 mW to avoid altering the iron oxides [de Sousa et al., 2018, Hanesch, 2009]. The magnetic grains were then imaged by SEM with a ZEISS Zigma Field Emission Gun model, coupled to an Oxford Instruments energy dispersive spectrometer.

In principle, the iron oxides contained in the cave sediments with a low magnetic susceptibility are characteristic of unheated samples. These iron oxides cannot be extracted with a magnet because of the weakness of their magnetization. Thus, to help investigate the minerals that could be at the origin of the magnetic minerals after heating, polished sections were prepared from the low magnetic susceptibility samples and iron oxides were localized by SEM using the backscattered electron imaging mode. This mode facilitates the detection of heavy minerals such as iron oxides because of their brighter shades. They were then identified by Raman microspectrometry.

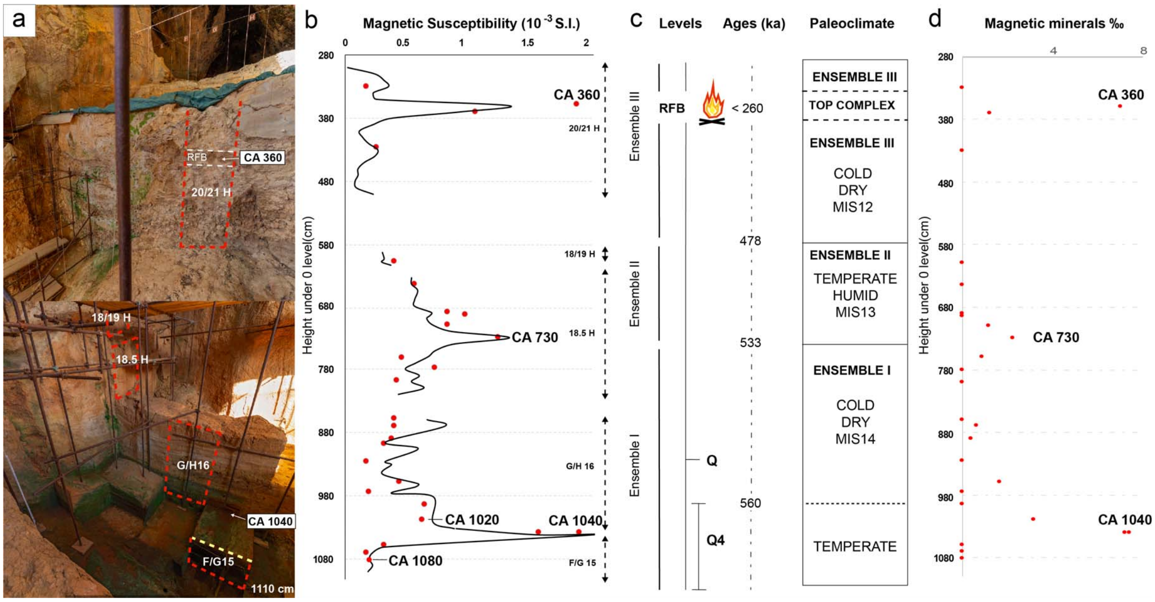

Figure 2. (a) Sections (red dashes) where the magnetic profile was measured in the cave. (b) Field and laboratory magnetic susceptibility measurements: black curve and red dots, respectively. Both graphs show three peaks of high susceptibility centred at 360 cm, 730 cm, and 1040 cm under the zero level of excavations. Letters F, G, and H refer to the grid coordinates of the longitudinal sections used for the excavation plan [de Lumley et al., 1984]. (c) Correlations of archaeostratigraphic units (levels Q to D) with palaeoclimatic conditions and MIS 14–12. RFB, corresponds to intrusive younger sediments trapped in the fissures of MIS 12 deposits, where fire use residues are reported. Unit Q4 is a subdivision of the base of the Q level. (d) Abundance (‰) of magnetically extracted fraction.

3. Results

3.1. *Magnetic susceptibility profile*

Figure 2b shows the magnetic susceptibility measurements, with the curve and points representing *in situ* and collected samples, respectively. The values are in good agreement. Three peaks of high magnetic susceptibility can be distinguished: between samples CA 1060 and CA 1020, between samples CA 770 and CA 680, and between samples CA 380 and CA 350. The relative abundance of magnetic minerals (Figure 2d) shows a correlation with both the *in situ* and laboratory susceptibility measurements (Figure 2b). Samples CA 1040, CA 770, and CA 360 are representative of the three susceptibility peaks and are located in the Archaeostratigraphic Units Q4 (CA 1040), J (CA 730), and RFB (CA 360), which are dated at ~560 ka, ~500 ka, and ~260 ka, respectively [de Lumley et al., 1984, Falguères et al., 2015].

3.2. *Combustion residues*

Several charcoals (Figure 3) identified by optical microscopy, and characterized by Raman microspectrometry (Figure 4) are found in samples CA 360 and CA 1040. The uppermost sample, CA 360, corresponds to the RFB level, while sample CA 1040 is within the Archaeostratigraphic Unit Q4. The charcoals have sizes that vary from 0.2 to 1.2 mm and are sometimes embedded by mineral fractions from the cave soil sediments (Figure 5). SEM–EDS analysis shows that carbon is the most abundant element (41%), followed by oxygen (37%), calcium (3%), and magnesium and potassium (1%). Anthracological analysis links these charcoals to the pine species. The height ratio H_D/H_G ranges between 0.55 and 0.70. Temperatures derived from the calibration curves of Deldicque et al. [2016] indicate that carbonization occurred between 600 and 750 °C for one

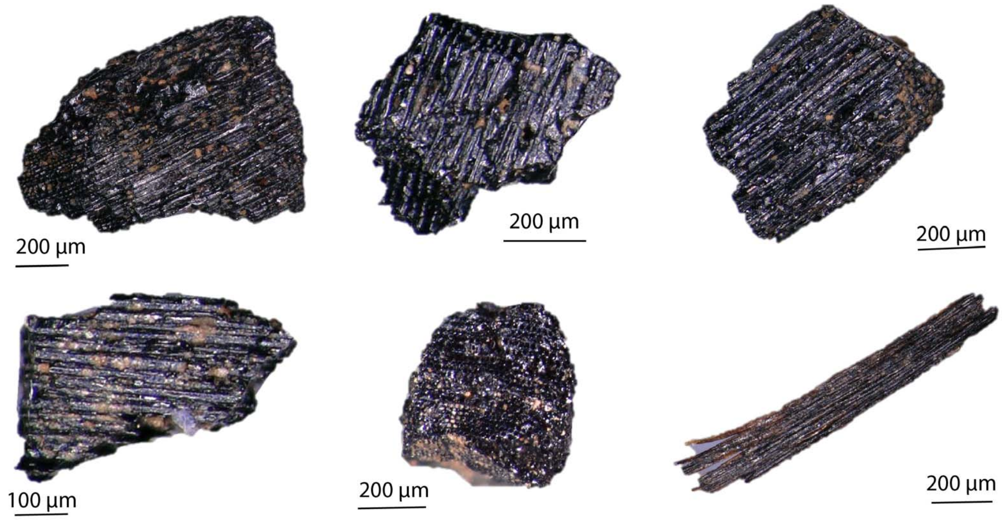

Figure 3. Charcoals found in sample CA 1040.

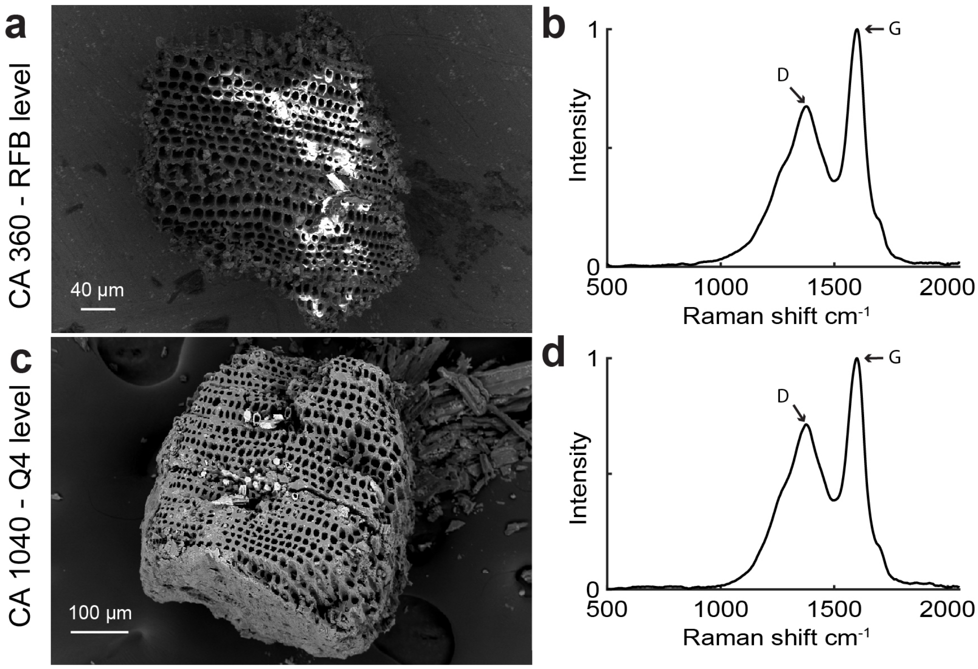

Figure 4. Scanning electron microscopy images of charcoals and their Raman spectra, showing the typical Raman bands of charred materials, D (around 1350 cm^{-1}), and G (around 1584 cm^{-1}). (a, b) Sample CA 360. (c, d) Sample CA 1040.

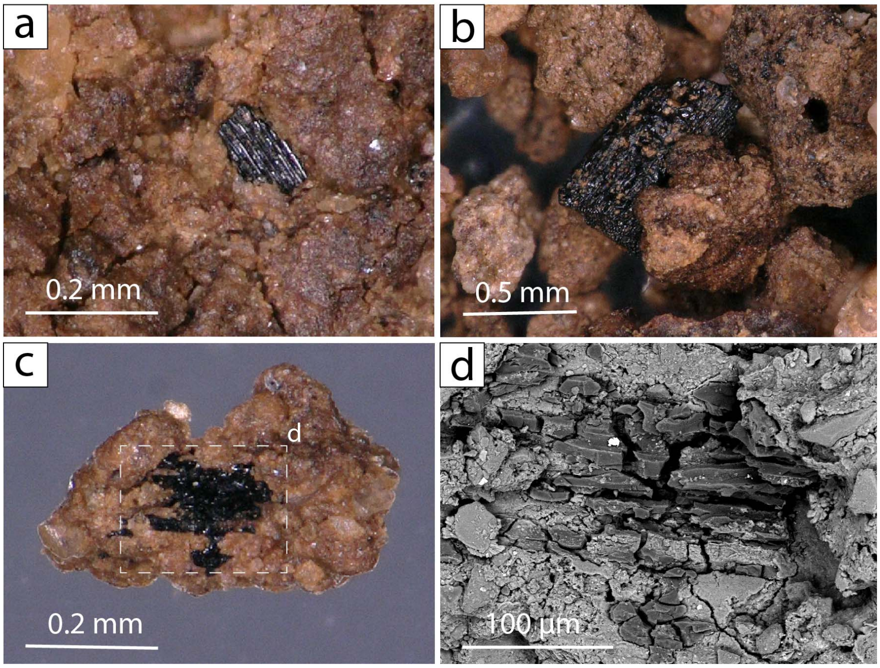

Figure 5. (a, b, c) Charcoals found in sample CA 1040, embedded by sedimentary minerals. (d) Detail of (c), imaged by scanning electron microscopy, highlighting the vegetal morphology.

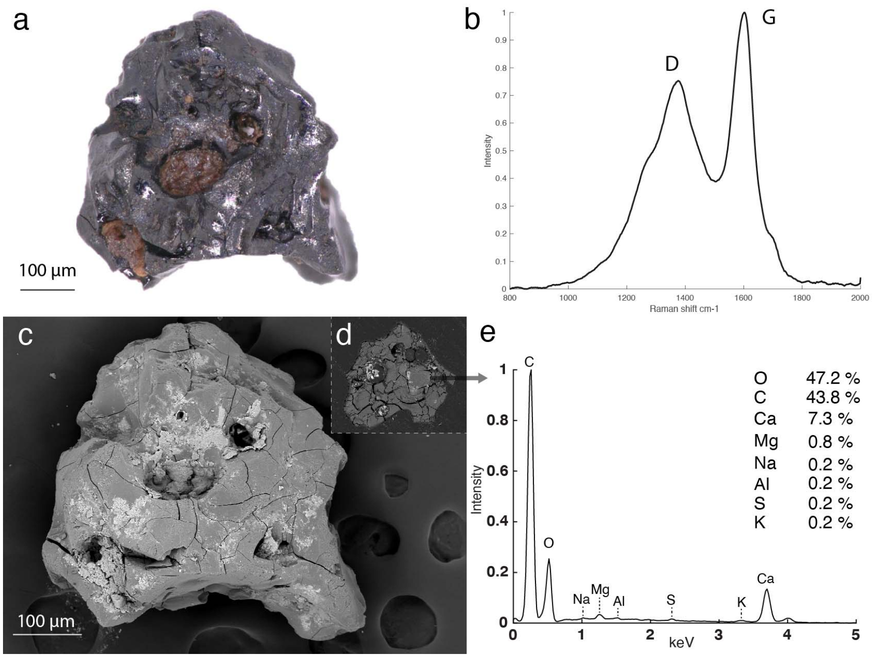

Figure 6. Identification of a char devoid of vegetal structures. (a) Black grain found in sample CA 1040, located in level Q4. (b) Raman spectrum of the grain in (a) showing the D and G bands, characteristic of chars. (c) Scanning electron microscopy image of the same grain, showing cracks on its surface. (d) Polished section of the char on which the EDS analysis was recorded. (e) EDS spectrum of the grain, showing its elemental composition, in atomic percent.

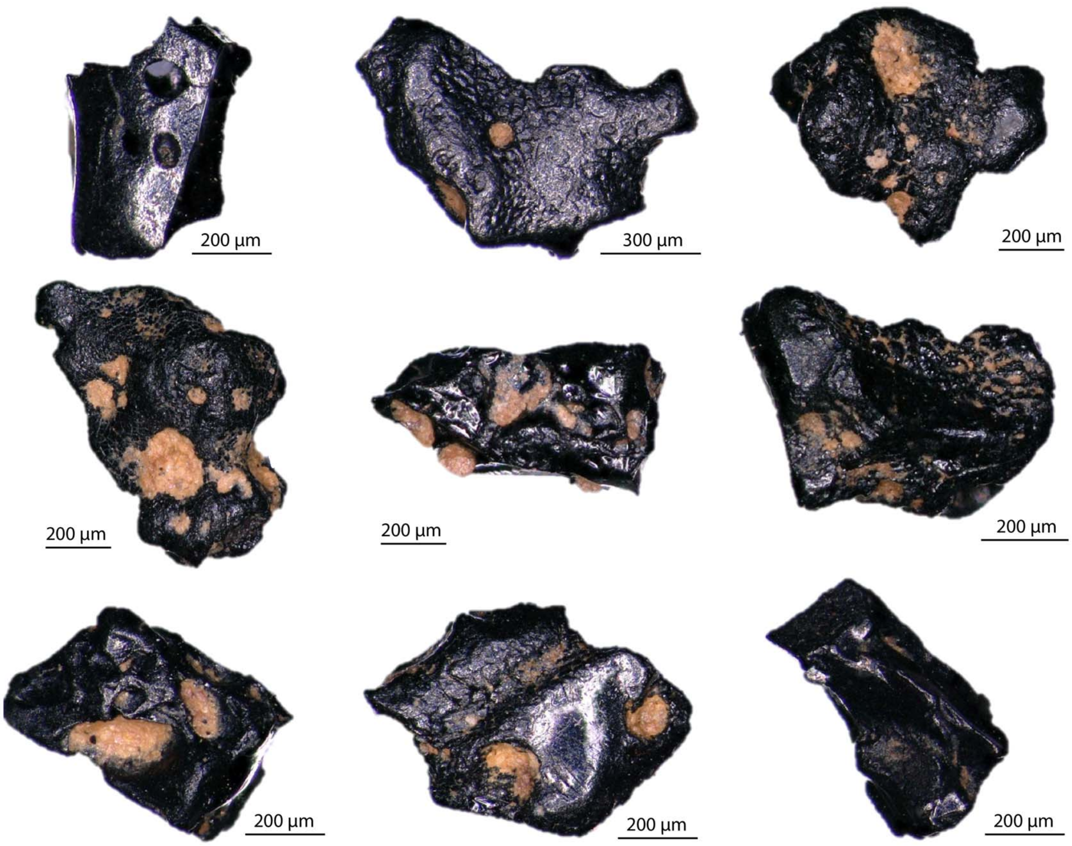

Figure 7. Vitrified Charcoals found in sample CA 1040 in Q4 level.

hour of heating or between 500 and 650 °C for six hours of heating.

About 15 black grains (Figure 6) without any apparent vegetal structure were found in samples CA 1040, representing the magnetic susceptibility peak in level Q4. They have a vesicular and sometimes vitreous appearance, showing cracks (Figures 6c–7). The presence of the D and G bands in their Raman spectra confirms that they are chars. In general, elemental analyses (Figure 6e) indicate the presence of carbon (44%), oxygen (47%), calcium (7%), and magnesium (0.8%), aluminum (0.2%), potassium (0.2%), sodium (0.2%), and sulphur (0.2%). This composition corresponds to that of charcoal and suggests that these black grains are of vegetal origin. Indeed, chars of animal origin would have higher contents of phosphorus and potassium [Horbańczuk and Wierzbicka, 2016]. All these characteristics are those of vitrified charcoals often found in charcoal assemblages of archaeological sites, but their formation process is currently unexplained [McParland et al., 2010].

3.3. *Heating experiments on sediments*

Sample CA 1080 is representative of a level of the cave characterized by low magnetic susceptibility, located just below the high-susceptibility CA 1040 peak (Figure 2a), and of similar composition according to field characteristics and sedimentological analyses [de Lumley et al., 2020]. We therefore chose sample CA 1080 to carry out experimental heating runs designed to evaluate the effects of a fire on the sedimentary minerals contained in the cave soil. Figure 8a shows the evolution of magnetic susceptibility as a function of the heating temperature. The susceptibility increases rapidly from 450 °C to reach, around

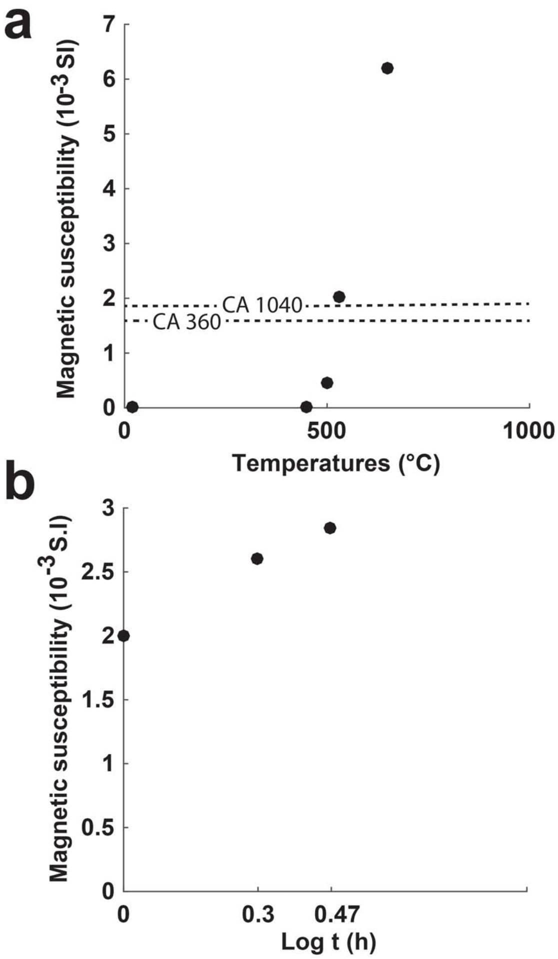

Figure 8. (a) Susceptibility increase of sediment from sample CA 1080, due to experimental heating as a function of temperature. The value obtained from sample CA 1080 after being heated to 530 °C is close to those measured in the sample CA 360, representative of a soil where fire use is attested. (b) Logarithmic law of increase of susceptibility as a function of the heating time.

530 °C, values comparable to those measured in samples CA 1040 and CA 360. The effects of the heating time are shown in Figure 8b, where the increase in susceptibility follows a logarithmic law as a function of heating time.

3.4. *Identification of magnetic minerals*

Two ferrimagnetic minerals, magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) were identified by Raman microspectrometry (Figure 9) in natural high magnetic susceptibility samples: CA 1040, CA 730, and CA 360. Magnetite is identifiable by its peak at 670 cm^{-1}, and maghemite by its main peak at 725 cm^{-1}. Sometimes the maghemite is associated with haematite (Fe_2O_3), which has characteristic peaks at 225, 291, 412, and 1320 cm^{-1}. Magnetite is present in sample CA 1080 after experimental heating at 530 °C for one hour under argon. Sample CA 1080 also contains maghemite after heating at 650 °C under argon for 40 min and then for 20 min in air before cooling according to the procedure of Tite and Mullins [1971]. Magnetite and maghemite are thus the two magnetic minerals responsible for the increase in magnetic susceptibility in the RFB level, in the CA 730 level, and in the Q4 level, as well as in the experimentally heated samples.

The SEM observations (Figure 10) show that magnetic minerals appear as millimeter-sized aggregates, made up of mixtures of iron oxides and other minerals from sediments. These aggregates are systematically present in the high magnetic susceptibility samples CA 360, CA 1040, and in sample CA 1080 heated to 530 °C. Similar aggregates are present in the unheated CA 1080 natural sample, but the iron oxides have very low magnetic susceptibility and they have been identified as haematite α-Fe_2O_3 and goethite α-FeO(OH) by Raman spectroscopy (Figure 9).

However, Raman spectroscopy does not identify magnetite and maghemite superparamagnetic nanoparticles that contribute to the magnetic susceptibility signal. Indeed, these particles are too small to be analysed and cannot be extracted with a magnet. Therefore, we estimated their contribution by measuring the magnetic susceptibility of the residual part of the sorted samples. We estimated this contribution at about 30% in sample CA 360, representative of the RFB level where the use of fire is attested, and about 10% in sample CA 1080, heated in the laboratory at 530 °C. We interpret this discrepancy as due to a difference in heating time between the cave sample and the experimentally heated sample Cairanne et al. [2003].

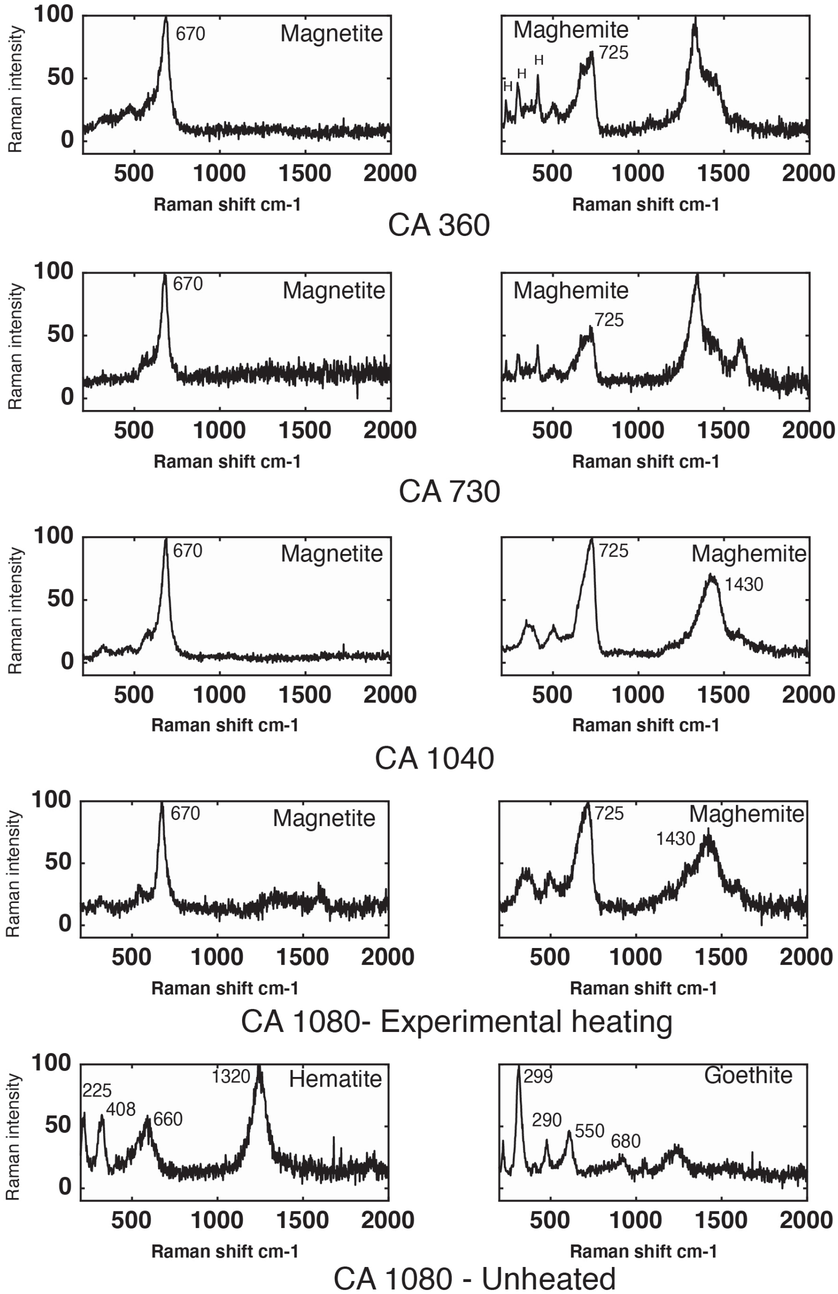

Figure 9. Raman spectra of iron oxides found in experimentally heated and *in situ* samples. Samples CA 360, CA 730, and CA 1040, which correspond to the high-susceptibility levels, contain maghemite and magnetite. Sample CA 1080, located below the magnetic susceptibility peak (CA 1040), contains haematite and goethite before heating, and maghemite and magnetite after being experimentally heated in the laboratory.

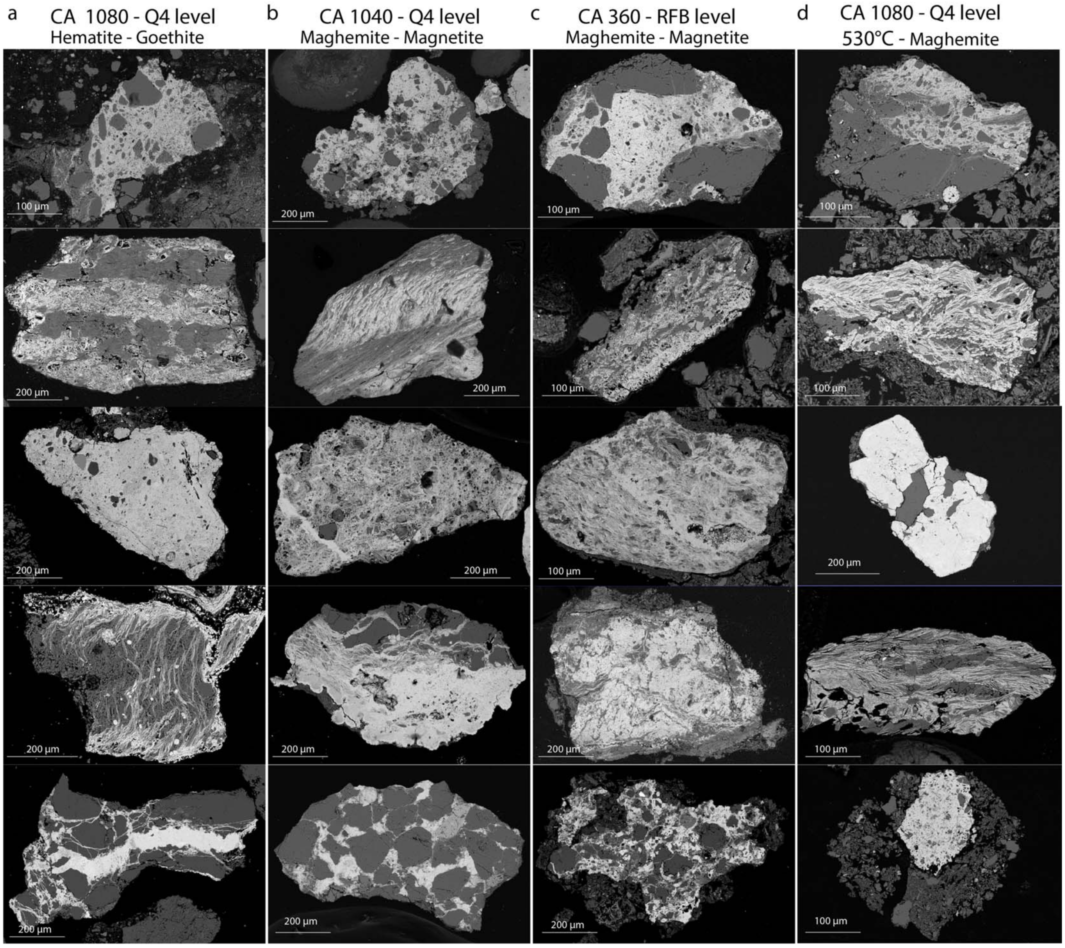

Figure 10. Aggregates composed of iron oxides (bright phases) and sediments (clay minerals, quartz) imaged by SEM in backscattered electron imaging mode. (a) Sample CA 1080 located 40 cm below CA 1040 sample in the Q4 level. The iron oxides are haematite and goethite. (b, c) Samples CA 1040 and CA 360 contain magnetite and maghemite. (d) Sample CA 1080 heated at 530 °C under argon for 40 min then 20 min in air before cooling. The haematite and goethite grains present in sample CA 1080 are transformed into maghemite grains.

4. Discussion

At Caune de l'Arago, no traces of combustion have been identified in levels older than 400 ka. However, if residues of fires had been produced or introduced into the cave during these distant periods, the various processes of alteration would have erased any record, and at the very least, diluted the traces among the sediments. The objective of this study was to search for traces of fires that could have been preserved in the oldest parts of the sedimentary infilling, using a combination of independent methods, prior location with magnetic susceptibility measurements followed by optical microscopy examination and mineralogical characterizations by micro-Raman and SEM–EDS.

4.1. *Summary of the magnetic susceptibility signal-guided search for combustion residues*

Magnetic susceptibility measurements highlight two levels with a strong signal (the RFB level and Archaeostratigraphic Unit Q4), where the examination of the sediments by optical microscopy reveals numerous black vegetal residues, as well as black grains, with vesicular shapes, cracks, and sometimes a vitreous aspect. Raman measurements and SEM–EDS elemental analyses confirm that these vegetal remains are charcoal, and that the black grains without any vegetal structures are vitrified charcoals. Without the Raman analyses, these glassy-like chars could have been discarded because of their morphology suggesting a black mineral or a glass. Moreover, the EDS elemental analyses allow us to distinguish between an animal or vegetal origin. Charcoals in the RFB level are known to be of anthropogenic origin [de Lumley, 2015] and their rediscovery guided by magnetic measurements validates the approach used here. Indeed, the identification by magnetic susceptibility measurements has led us on the track of combustion residues, characterized by Raman and SEM–EDS microscopy.

4.2. *Formation of magnetic minerals*

Magnetite and maghemite are the magnetic minerals associated with the charcoals found in samples CA 1040 and CA 360, corresponding to the magnetic susceptibility peaks of the Q4 and RFB levels, respectively. These two minerals can be formed at the temperatures produced by fires (hearth or natural); if the soils initially contained iron oxides such as haematite or goethite. Haematite can be reduced to magnetite above 500 °C following the reaction:

$$3\,Fe_2O_3 + C \rightarrow 2\,Fe_3O_4 + CO, \qquad (1)$$

where carbon is supplied by the organic matter present in the cave soil [de Sousa et al., 2018]. The magnetite produced can then be oxidized to maghemite by the maghemitization process [Özdemir and Dunlop, 2010] when the fire decreases in intensity and extinguishes [Marmet et al., 1999, Tite and Mullins, 1971]. If goethite is also present in the soil, it can dehydrate into haematite between 350 and 600 °C [Till and Nowaczyk, 2018], and can therefore serve as a source of haematite for reaction (1). Our investigations show that the low magnetic susceptibility sediments of sample CA 1080, located 40 cm below the CA 1040 magnetic susceptibility peak (Figure 2b), contained haematite and goethite (Figure 9) and nanoparticles of haematite and goethite, which are convertible into magnetite and maghemite and nanoparticles of magnetite and maghemite after heating [Till et al., 2015]. This is corroborated by our experimental heating runs carried out on sample CA 1080, which produce maghemite and magnetite grains and nanoparticles of magnetite and maghemite. Moreover, the magnetic susceptibility of the sediments increases to values equivalent to the magnetic susceptibility peaks located in the RFB (CA 360) and Q4 levels (CA 1040) after being heated at 530 °C. This temperature can be reached at the surface and in the topmost few centimeters in the soil, under a combustion area. Indeed, Aldeias et al. [2016] show that the temperature of a charcoal fire can reach 790 °C at the surface and 517 °C at 2 cm depth, in soil composed of a mixture of limestone sand containing quartz.

4.3. *Implications in Caune de l'Arago*

The presence of charcoals was already known in the RFB level [de Lumley et al., 2020]. In contrast, the presence of charcoals in the Archaeostratigraphic Unit Q4, with an estimated age of 560 ka, is an unprecedented finding. The question is whether the magnetic minerals and charcoals found in this level were created inside the cave, or whether they were created outside by natural fires and then transported into the cave. The potential allochthonous origin of these traces of fire is to be taken seriously since the sedimentary infilling was mainly transported into the cave through two processes. First, during wet periods, by runoff from the plateau forming the limestone massif in which the cave is set, and second, during cold and dry periods, by winds from the Tautavel plain. It has been demonstrated that a northwesterly wind (palaeotramontane), blowing at more than 130 km/h, could generate turbulent flows able to transport alluvium into the cave from the plains of Verdouble, sometimes located 60 m below the cave [Perrier et al., 1989].

4.3.1. *Hypothesis of a natural and external origin*

Levels K to Q are located in Ensemble I of the Middle Stratigraphic Complex, which is made up of bedded sands with silty–clayey interbeds. These sediments were mainly transported by winds from the Tautavel Plains during MIS 14 corresponding to a cold and dry climate and steppe-like vegetation [de Lumley et al., 1984]. However, the magnetic susceptibility peak associated with charcoals is located in the Archaeostratigraphic Unit Q4, a subdivision of the base of the Q level. According to the fauna observed, this level appears to show the characteristics of a more temperate climate and a wooded environment, differentiating it from the other levels of Ensemble I in the Middle Complex [Lebreton et al., 2016]. If natural fires had occurred outside the cave, they could have produced the temperatures required to transform the iron oxides initially present in the soil into magnetic minerals in the same way as a hearth fire would have done [Clement et al., 2011]. The charcoals and iron oxides found in the Archaeostratigraphic Unit Q4 are millimetric to submillimetric in size and are therefore easily transported by runoff and wind. In addition, submillimeter-sized charcoal produced during fires can be transported several kilometers by air [Tinner et al., 2006]. For these reasons, it cannot be ruled out that magnetic minerals and charcoals, formed by natural fires outside the cave, are present among the sediments in the Q4 level.

4.3.2. *Hypothesis of an in situ origin*

Several questions arise from the close association of charcoals, vitrified charcoals, and magnetic minerals in the same level, 30 m away from the original entrance of the cave. The transport by wind or water of low-density charcoal particles and much denser magnetic minerals would probably have led to sorting by density. However, we observe light charcoals in the same level as heavier magnetic minerals. Even if these results are currently based on isolated measurements, no charcoal or char is observed in the samples above and below sample CA 1040, for example, in samples CA 1080 and CA 1020, also located in the Q4 level (Figure 2b). Indeed, a temperate climate and woody vegetation could favour the supply of fuel and the necessary conditions for its replenishment. This would have allowed natural fires to occur frequently during infilling of the Q4 level. Wind and runoff would then have distributed charcoals over the entire sedimentary interval Q4, and not just in a single level centred at 1040 cm. In addition, other indications of wet, temperate, and wooded conditions are found in levels H, I, and J, over a thickness of about 80 cm, and excavations have not encountered any microcharcoal or microchar.

Up to now, our investigations and excavations do not reveal any burnt bones in the Q4 level (CA 1040). Their presence is often associated with a human origin. However, the charcoals and magnetic minerals are found in the so-called "black earth", an area with particular features located in the lowest levels of Ensemble I of the Middle Complex. These black earths are characterized by a high organic matter content (1.2 to 3.3%) and by a rarefaction of bones and calcareous lithic objects due to post-depositional decarbonation of the sediments. Thus, if burnt bone fragments were present, they would have undergone a similar degradation. This may also explain the absence of ash remains.

5. Conclusion

The approach developed here allows us to characterize combustion traces in the RFB level in the Caune de l'Arago at Tautavel, already known to contain traces of fire use. In this way, we show the effectiveness of combining magnetic susceptibility investigations, optical microscopy, Raman spectrometry, and SEM in the search for ancient traces of combustion. This study reveals new traces of combustion, charcoals, and vitrified charcoals, in the Archaeostratigraphic Unit Q4, whose age is estimated at 560 ka. Even though the origin of these traces, anthropogenic or natural, is still to be investigated, the method applied here is useful in focusing research on areas within an archaeological site likely to contain preserved ancient fire traces when no macroscopic evidence is observed. Although the excavation methods used at the Caune de l'Arago are extremely meticulous, the traditional processes of sieving (0.8 mm) and flotation of the sediments did not allow the detection of microcharcoal in the lower levels. Evidence of fire use is rare in the first half of the Middle Pleistocene. If combustion traces had been produced, they would likely have undergone strong alteration over time, making them difficult to recognize today. Thus, the method employed in this study could be used to search for combustion residues at other sites lacking any obvious hearth structures in order to expand our current knowledge on the emergence of fire use during the Palaeolithic, so important in the adaptation of humans to their environment and, consequently, in their discovery of the world.

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