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Sourcing and nuclear magnetic resonance: new applications for old materials

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ABSTRACT
Solid-state nuclear magnetic resonance, which enables the characterization of structures of a variety of materials whatever their crystallinity/amorphous state, is used in the present work to determine the provenance of two raw materials, namely marbles and cherts. Regarding marbles, the ^{13}C NMR signal of the carbonate function contains information about both the Fe content in its area and the presence of calcium substitutions in the calcite crystal in its linewidth. Regarding cherts, discriminant information is provided by both ^{29}Si and ^{27}Al NMR: the ^{29}Si area signal depends on the paramagnetic ion content of the material, and the ^{27}Al spectra give information both on the aluminosilicate content and its distribution in tecto- and layer-lattice aluminosilicates. As an application, we use the differences observed from one source to another to determine the provenance of archaeological finds.
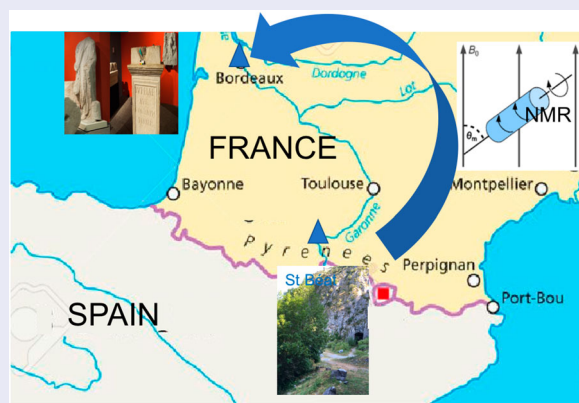
Introduction

Determining the geographical origin of the raw materials used for precious artefacts such as prehistoric tools and ancient monuments/statues is a challenge that allows to get an essential insight to historical aspects of past societies. The analyst looks for some clues, up to traces of some minerals, crystalline phases, fossils while applying more and more statistical tools to analyse the data collected. The aim of the present work was to identify the provenance of two kinds of stone used at very different periods for different purposes: chert tools from the Magdalenian, and marbles, symbols of power and luxury whose prestige reached its apogee during the reign of the emperor Augustus (63 BC–14 AC). In this goal, we used a methodological approach combining traditional analysis methods with Nuclear Magnetic Resonance (NMR). NMR has many advantages for the study of archaeomaterials: it is a non-destructive and versatile technique since it allows to probe the raw material without any previous preparation. While some NMR applications are able to be used in a non-invasive way without any sampling, using portable NMR instruments (mobile NMR), they are currently limited to detect the most sensitive nucleus, ^{1}H, in a liquid state (Baias and Blümich 2018). Alternatively, Solid State NMR spectroscopy permits to obtain detailed structural information of inorganic materials down to a few milligrams of powder, in a non-destructive way since the radiation used for this kind of spectroscopy is non-ionising (Stebbins and Xue 2014) making the collected samples available for further analyses. It also provides invaluable chemical information which cannot be obtained with other techniques since

all nuclei of the periodic table having at least one NMR-active isotope can be analysed, their respective sensitivities being linked to both the natural abundancy of the isotope chosen and its frequency resonance.

The first applications of NMR in the field of Cultural Heritage started less than 10 years ago, and were described in a review (Capitani, Di Tullio, and Proietti 2012), special issue (Capitani and Proietti 2015) and even book chapter (Webb 2018), showing that NMR is a very promising technology capable of investigating liquid, solid or even swollen samples by following isotopes with a non-zero nuclear spin of many different elements (Abragam 1961). Thus, NMR offers a very wide array of techniques for studying the structure and dynamics of organic or inorganic materials. For example, spectra of minerals were recorded soon after NMR development in the late 1940 s, and the progress observed for this technique has advantageously contributed to the Earth Sciences domain (Mackenzie and Smith 2002). Probably more than other spectroscopic methods, NMR gives information on the immediate structural surrounding through the chemical shift values of the resonances observed in the spectrum, on the number of atoms involved in the different resonances through the signal area when the relaxation conditions are respected and the presence of defects in the component observed thanks to the breadth at half-height of the resonance (Engelhardt 1989). At last, the spin–lattice T1 relaxation process can vary in proportion of the paramagnetic impurities content present in natural materials (Goldman 2001) and can be estimated when spectra are recorded under saturation conditions.

Regarding marbles, the target was their major component, calcium carbonate, whose NMR signal response depends on its local environment, such as the presence of secondary elements (Gutiérrez et al. 2019), and its crystallisation state (dolomite vs. calcite) (Pianet et al. 2018). The Carbon nuclide ^{13}C, which is the NMR detectable isotope present at 1% naturally, was targeted. Its signal contains information about both the Fe content in its area and the presence of calcium substitution in the calcite crystal in its linewidth. In a previous work, we successfully used ^{13}C solid-state NMR for white marble provenance, and we were able to distinguish between fine-grained white marbles coming from quarries located in six different countries (France, Italy, Spain, Portugal, Turkey and Greece) and to use the NMR spectrum profile to identify the origin of some archaeologic items (Gutiérrez et al. 2019). In the present work, we focus our analysis on marbles from the district of Saint-Béat (Région Occitanie, Département Haute-Garonne, Pyrénées, France) and try to localize the origin of the marble used for two archaeological items from the Musée d'Aquitaine collection (Bordeaux, Région Aquitaine, Département de la Gironde, France).

Cherts are mainly composed of silicate, and to a lesser extent of aluminosilicate. Thus, the nuclides commonly amenable to NMR measurements for this kind of mineral are ^{29}Si (natural abundance, 4%) and ^{27}Al NMR (natural abundance 100%) (Jakobsen, Jakobsen, and Lindgreen 1988). In the present work, solid-state NMR is used to get information in chert chemical structure, and to see if differences are observed depending on their geographic location. For this purpose, chert was collected from three different deposits of the Pyrénées (France), Montgaillard, Montsaunès and Buala (Sànchez de la Torre, Le Bourdonnec, and Gratuze 2019) and their ^{29}Si and ^{27}Al spectra compared with two archaeologic artefacts found in two different places (Montlléo –Prats i Sansor, Cerdanya, Spain- and Cova del Parco –Alòs de Balaguer, La Noguera, Spain) (Sànchez de la Torre 2015), and their provenances were successfully confirmed.

For the two kinds of lithic materials, marbles and cherts, studied herein, NMR spectroscopy has been successfully used as a tool for supporting decision-making for provenance identification.

Materials and methods

Samples

For marbles, white marbles were collected from four different quarries in the district of Saint-Béat: Boutx, Marignac, Saint-Béat Lavigne and Saint-Béat Château (see Figure 1 for their location). Samples were taken off two artefacts from the Musée d'Aquitaine collection for analyses purposes: a togatus (inventory number 60.2.19) and an altar dedicated to the Tutela Augusta (inventory number 60.1.20, ILA 17), both of them found at Bordeaux (Roman *Burdigala*).

For cherts, experiments were performed on geologic samples from three distinct sources from the Pyrénées (Montgaillard, Montsaunès and Buala) and samples were taken from two archaeologic items found in the Palaeolithic sites of Montlleó and Cova del Parco.

Solid state NMR experiments

NMR experiments were recorded on a Bruker Avance II 400 (magnetic field of 9.4 T) equipped with a 4 mm CP-MAS probe (CESAMO facilities, Bordeaux, France).

For marbles, ^{13}C MAS NMR spectra were recorded on 200 mg powdered samples at 100.6 MHz (9.4 T) and a spinning rate of 8 kHz; Single pulse-MAS spectra were collected with a recycling delay of 300 s, 32 transients and 2 dummy scans for a total experimental time of 170 min per sample.

For cherts, around 170 mg of powdered samples were used to record (i) ^{29}Si at 79.51 MHz (9.4 T) and a rotation rate of 8 kHz, using a single pulse sequence with a recycling delay of 50 s and 256 transients for a total experiment time of 4 h, a Cross-Polarization
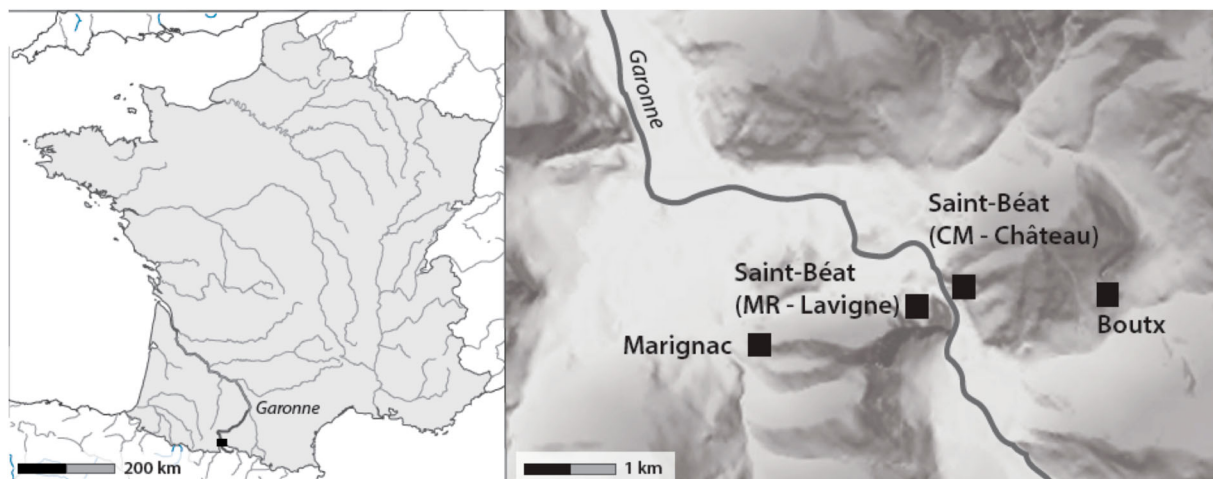
Figure 1. Location of the marble quarries in the district of Saint-Béat (Département Haute Garonne, Région Occitanie, France). Left: the black insert localizes the district of interest; Right: expansion of the geographical area.

pulse sequence using a contact time of 6 ms, a recycling delay of 5 s and 6000 transients for a total experiment time of 10 h and (ii) ^{27}Al at 104.3 MHz (9.4 T) and a rotation rate of 10 kHz, or 3 kHz using a single pulse experiment with a recycling delay of 0.5 s and 5120 transients for a total experiment time of 45 min.

Spectra were analysed using the NMR solid state fitting process (sola) of the Topspin 3.5, pl7 software (Bruker^{TM}).

Results

Marbles

In a previous paper (Gutiérrez et al. 2019), we demonstrated how ^{13}C NMR was useful to determine the

provenance of some archaeologic items: the target is the principal component of marble, calcite, whose ^{13}C NMR signal presents a specific profile (area and full width at half maximum, $\Delta\nu_{1/2}$) depending on its provenance. In this previous work, we demonstrated that the area depends on the iron content, when the linewidth reflects defects in the calcite crystal in

Table 1. Area and full width at half maximum of the ^{13}C resonance of marbles from different geographic origins.

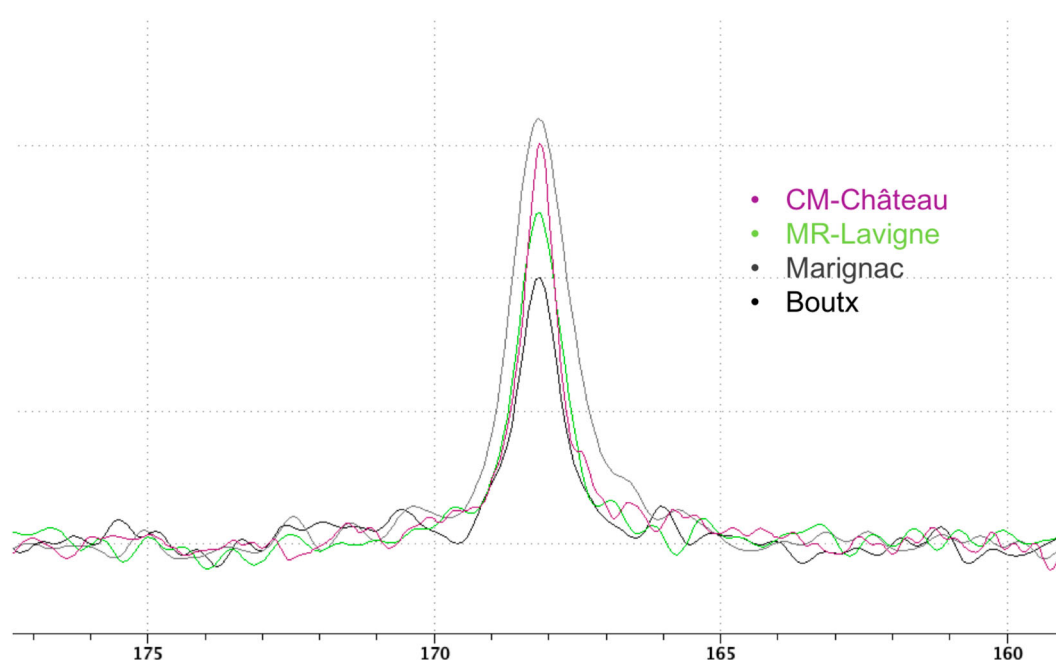| Origin	Area	$\Delta\nu_{1/2}$ (Hz)
Boutx ($n = 3$)	1.1 ± 0.3	84 ± 5
CM-Château ($n = 2$)	2.5 ± 0.2	74 ± 5
Marignac ($n = 2$)	3.5 ± 0.4	95 ± 10
MR-Lavigne ($n = 3$)	3.4 ± 0.4	114 ± 8
Togatus (60.2.19)	2.7	68
Altar (60.1.20)	2.9	62

Figure 2. ^{13}C NMR spectra of white marbles from different quarries in the district of Saint-Béat: quarry "Château" in the Cap de Mont (CM-Château, purple); quarry "Lavigne" in the Mont-Rié (MR-Lavigne, green); quarry "Marignac" (grey); quarry "Boutx" (black).
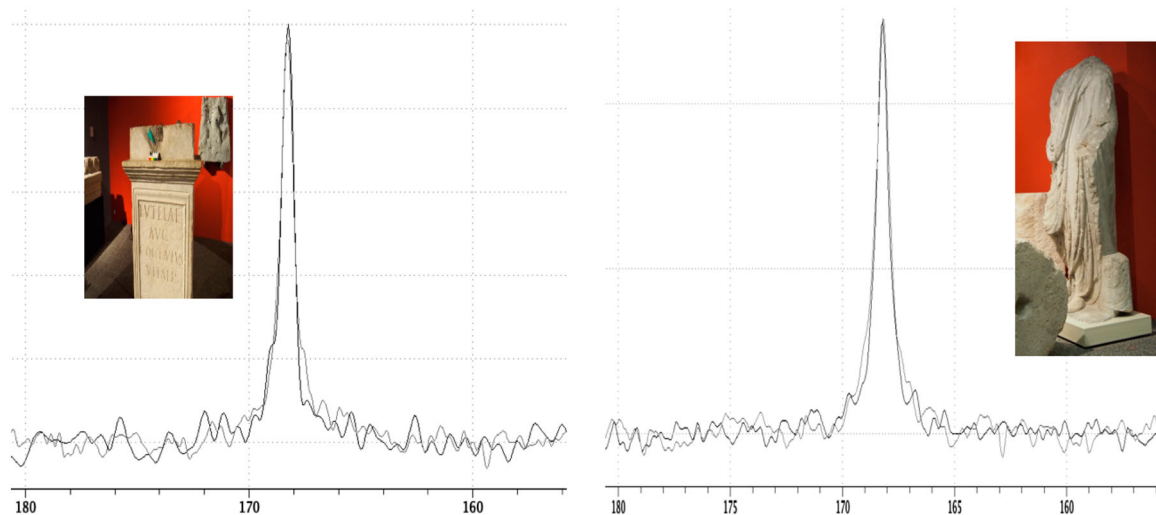
Figure 3. ^{13}C NMR spectra of the altar dedicated to the Tutele Augusta (left, 60.1.20) and of a togatus (right, 60.2.19) in black compared with a spectrum of saint-Béat, from the quarry Château, in grey.

which the calcium is replaced by another atom such as aluminium, strontium or magnesium. Thus, by combining different geochemical methodologies such as ICP-OES, XRD and NMR, with common petrological techniques for the marbles considered (Gutiérrez 2011; Lapuente Mercadal 2014; Gutiérrez et al. 2016; Royo Plumed 2016) we were able to distinguish the marbles depending on their geological source. Also in the present work, focused on the contribution of solid-state NMR as a "decision-making" technique, we extend this analysis to marbles coming from the same region, the district of Saint-Béat (region Occitanie, France, Figure 1), for which further analyses are still under investigation (notably ICP-OES and DRX). Figure 2 presents ^{13}C NMR spectra recorded for four different quarries around the town of Saint Béat: Boutx, Marignac, Lavigne (Saint-Béat, Mont Rié) and Château (Saint-Béat, Cap du Mont). Table 1 displays

the area and linewidth measured for the white marbles obtained in the previously mentioned quarries. Some interesting differences can be outlined, and were used to determine the geographic origin of the two artefacts from the Musée d'Aquitaine of Bordeaux, whose petrographic, cathodoluminescence and ^{13}C/^{18}O isotope signature features are characteristic of marbles coming from this region of the Pyrénées (Royo Plumed et al. 2015; Royo Plumed et al. 2018).[1] The comparison of the ^{13}C spectrum of these artefacts with the different marbles from the district of Saint-Béat permits to propose that they could be made of marble of the quarry Saint-Béat Château (Figure 3).

Cherts

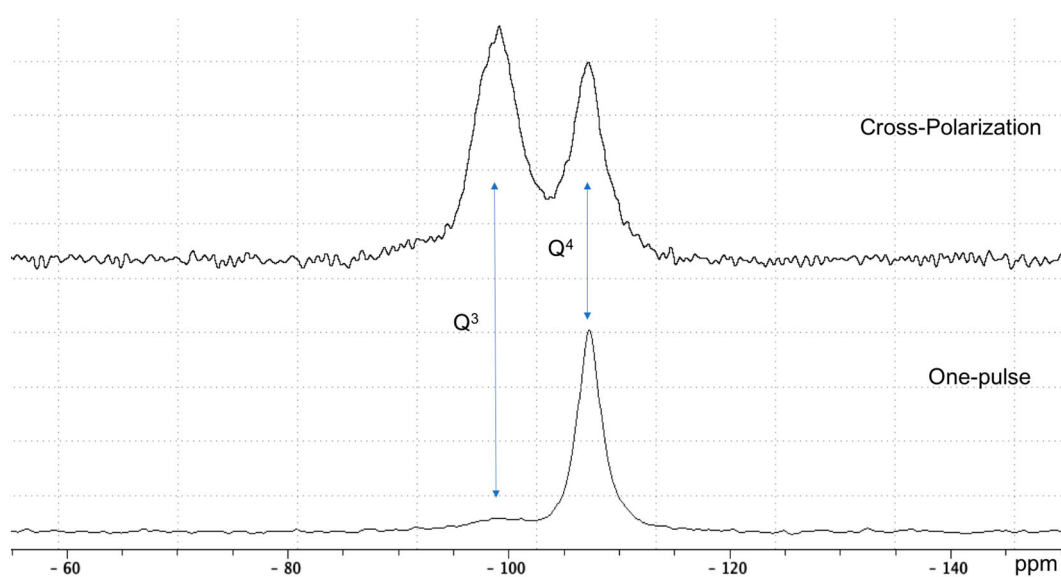Considering the success of solid-state NMR for decision-making purpose concerning marbles

Figure 4. ^{29}Si MAS NMR spectra of Buala chert using a single pulse experiment (down) or a Cross-Polarization pulse sequence with a 6 ms contact time (top).

Table 2. ^{29}Si MAS NMR data obtained for three geologic cherts and two archaeologic items (Cova del Parco and Montlleó).

	Total area	δ Q^4 (ppm)	$\Delta\nu_{1/2}$ Q^4 (Hz)	δ Q^3 (ppm)	$\Delta\nu_{1/2}$Q^3 (Hz)*	Q^3/Q^4
Buala ($n = 5$)	2.0 ± 0.2	−104.5 ± 0.1	169 ± 15	−97.1 ± 0.4	383 ± 28	0.18 ± 0.05
Montsaunès ($n = 6$)	2.6 ± 0.2	−104.5 ± 0.1	189 ± 12	−97.0 ± 0.5	382 ± 15	0.18 ± 0.03
Montgaillard ($n = 5$)	1.1 ± 0.2	−104.5 ± 0.1	165 ± 16	−96.5 ± 1.5	402 ± 18	0.20 ± 0.02
Cova del Parco	1.9	−104.5	181	−97.1	436	0.22
Montlleó	2.8	−104.5	150	−96.8	413	0.24

*Measured from CP-AV experiments.
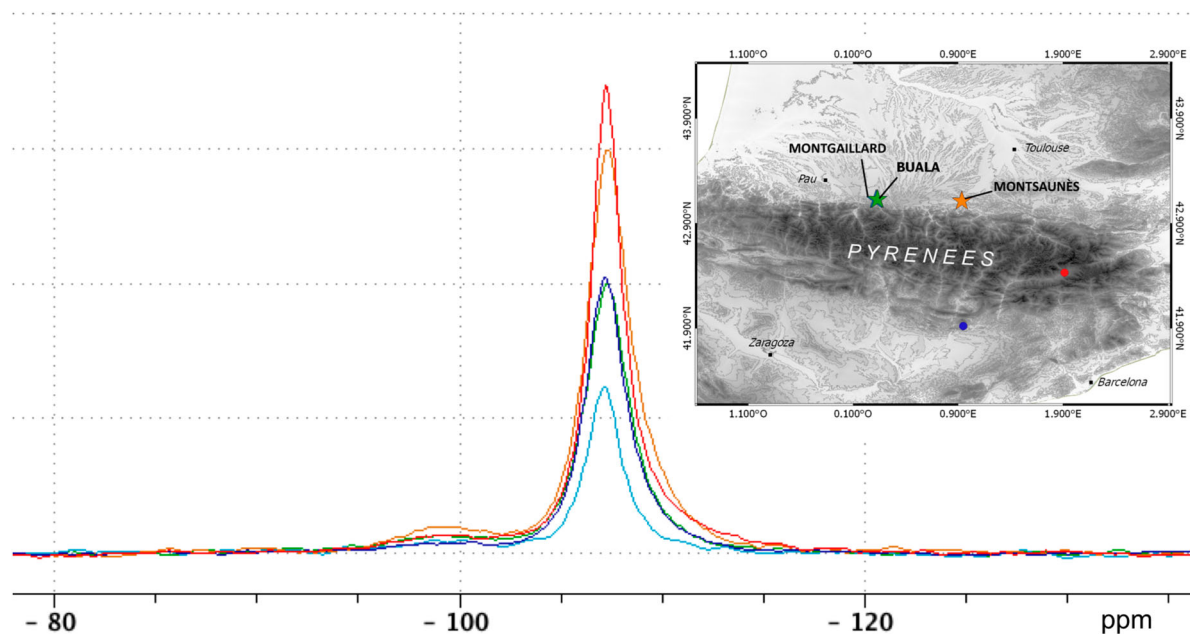
Figure 5. *Left.* ^{29}Si NMR spectra permitting the assignment of the provenance of two archaeologic cherts: one found at Cova del Parco (Blue) coming from Buala (Green) and the second one found at Montlleó (Red) coming from Montsaunès (Orange). *Right.* Map showing the location of the different geological and archaeological samples described in this work.

provenance, we use a similar strategy for cherts. In the present case, ^{29}Si and ^{27}Al magic-angle-spinning (MAS) NMR experiments are used for the identification of the silicate minerals within cherts. The ^{29}Si NMR spectrum (Figure 4) shows two components assigned to the Q^4 framework tetrahedral units – quartz- at −104.5 ppm and the Q^3 silanol units around −97 ppm, whose attribution is consistent with the enhancement of its resonance observed under the Cross-Polarization experiment (Adams, Hawkes, and Curzon 1991). The Q^3/Q^4 ratio is close to 0.2 whatever the sample, highlighting, as expected, the dominance of SiO$_4$ species. The line broadening observed for Q^3 and Q^4 species ($\Delta\nu_{1/2}$, Table 2) mainly reflects overlapping of different silicate structures of varying degrees of polymerization since spectra were recorded at Magic Angle spinning -MAS- with sufficient speed to cancel both dipole–dipole interactions and chemical shift anisotropy (Mackenzie and Smith 2002). Few differences can be observed on the Q^4 resonance notably concerning the Montsaunès sample whose line width is slightly higher than for Buala or Montgaillard. However, the most significant difference observed from one to another geologic chert samples is the signal area: it evolves from 1.1 for the Montgaillard sample to 2.6

for the one of Montsaunès (Table 2, Figure 5). This difference is not the consequence of a variable SiO$_2$ content –that is constant and close to 99.2 ± 0.2% as measured using XRF for each sample – but should be due instead to magnetic susceptibility arising from the presence of magnetic impurities (Oldfield et al. 1983), whose content plays a role in the transversal relaxation T1 of the NMR signal, as for marbles. Their measures were performed for each geological source and were estimated close to 270 s for Montsaunès, 440 s for Buala and 720 s for Montgaillard, confirming the role of T1 in the signal area.

^{29}Si spectra were also recorded for two archaeologic items found in different sites in the south Pyrenean Region (Figure 5). The comparison of their ^{29}Si spectra with those performed for three different deposits permits to propose the following provenances, Buala for the chert coming from Cova del Parco and Montsaunès for the chert found at Montlleó (Figure 5, Table 2).

^{27}Al MAS-NMR experiments were also conducted on the different cherts samples. Despite the low aluminium abundancy in cherts (less than 1% Sànchez de la Torre et al. 2017a), ^{27}Al is a nucleus easy to observe by NMR, its natural abundance being of 100%, its gyromagnetic ratio comparable to one of
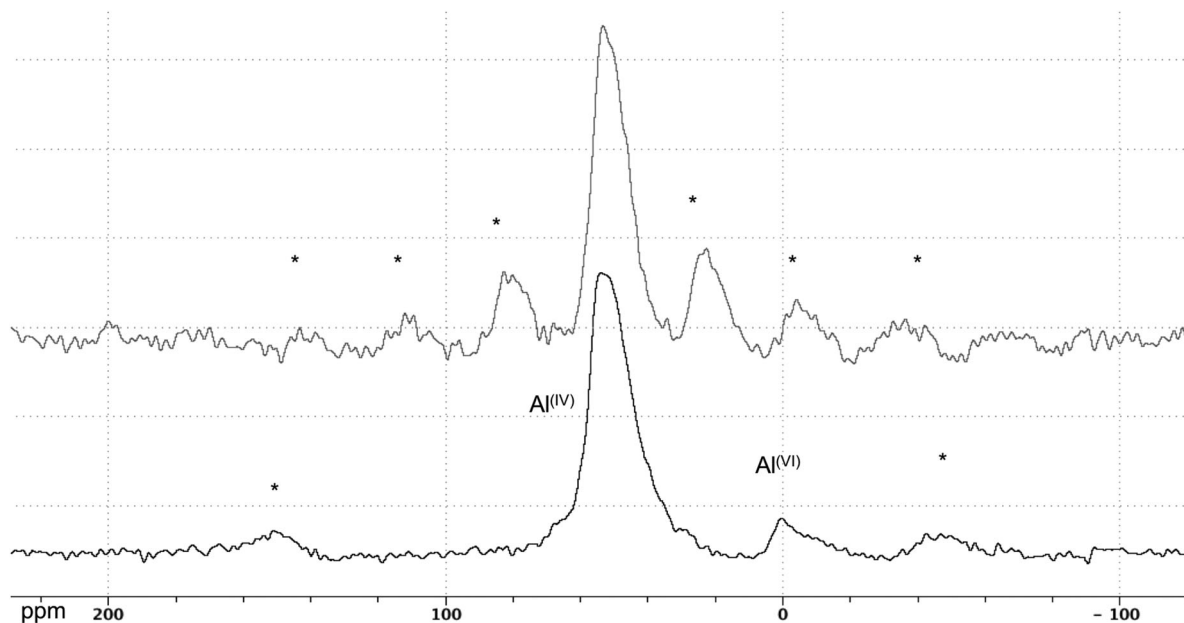
Figure 6. ^{27}Al MAS-NMR spectra of MontSaunes Chert recorded at a 10KHz (bottom) or 3KHz (top) spinning rate. (*) represents the rotation side bands.

^{13}C and short relaxation times. Due to these favourable properties, ^{27}Al MAS-NMR spectra were obtained in a reasonable time (close to 1 h, Figure 6). Interestingly, two resonances are observed: the main one (δ_{iso} 52–54 ppm, see Table 3) assigned to a 4-coordinated Aluminosilicate (Al^{IV}), such as AlO_4 connected to SiO_4 tetrahedra of $Q^4(4Si)$ type, and a minor resonance assigned to a 6-coordinated Al (Al^{VI}) occurring at 4–5 ppm such as AlO_6 (Guarino et al. 1997). The ability to distinguish octahedral and tetrahedral Al in inorganic compounds make possible the semi-quantitative estimate of their amount as shown in Table 3. The quadripolar nature of ^{27}Al nuclei (spin 5/2) also requires the determination of the Chemical Shift Anisotropy (CSA) and the asymmetry parameter (η) that permit the determination of δ_{iso}. To ensure a better estimation of these parameters, spectra were also recorded at a spin rate of 3000 Hz (Figure 6, top). All these values are reported in Table 3. First of all, the total area observed is representative of the content already measured for each sample using XRF as previously reported (Sànchez de la Torre et al. 2017b) (0.55% for Bula, vs. 0.35% for Montgaillard and Montsaunès). Another interesting measure is the Al^{IV}/Al^{VI} ratio that appears to be different in the Montsaunès sample (7.3) compared to the one observed for Buala or Montgaillard (1.7 and 1.8, respectively).

As previously shown, some discriminant elements can be exploited to determine the geographic origin of archaeologic cherts such as the area signal of ^{29}Si or even ^{27}Al spectra combined with the Al^{IV}/Al^{VI} ratio. Using these different data, we are able to assign the chert found at Cova del Parco to the Buala deposit when the Montlleó one appears to come from the Montsaunès place.

Discussion

In the present work, we apply solid-state MAS-NMR spectroscopy for arch-aeometric purposes, notably to identify the provenance of archaeologic artefacts through two examples, Marbles and Cherts. The thread is the same, it consists of looking at the major component of the stone and inspecting the NMR response, which can be extremely sensitive to the chemical environment of the studied nucleus.

For marbles, the target was the calcite $CaCO_3$, and the nucleus tracked the carbon ^{13}C. In a previous work (Gutiérrez et al. 2019), we demonstrate how the ^{13}C nuclide was sensitive to the presence of paramagnetic species such as Fe_2O_3, by the intensity of the calcite signal and to the defects of the calcite crystals in which calcium could be replaced by another atom. This property, which was applied to marbles coming

Table 3. ^{27}Al NMR quantities. δ_{iso}, CSA and $\Delta\nu$ were obtained by fitting the Al^{IV} resonance using the software TOPSPIN 3.5 (Bruker).

	Total Area	Al^{IV}	Al^{VI}	Al^{IV}/Al^{VI}	δ_{iso} (ppm)	η	CSA	$\Delta\nu$ (Hz)
Buala (n = 4)	160 ± 20	157 ± 20	3 ± 1	1.7 ± 0.7	53.4 ± 0.4	0.4 ± 0.1	37 ± 4	1050 ± 50
Montsaunès (n = 6)	128 ± 18	119 ± 18	8 ± 1	7.3 ± 1.3	53.3 ± 0.6	0.3 ± 0.2	34 ± 18	960 ± 100
Montgaillard (n = 5)	121 ± 22	117 ± 23	2 ± 1	1.8 ± 1.1	53.2 ± 0.9	0.8 ± 0.2	41 ± 28	1030 ± 140
Cova del Parco	169	167.5	2.5	1.5	52.1	0.3	30	1300
Montlleó	120	112	8	7.1	52.5	0.3	30	1200

from different quarries of the Mediterranean basin (Turkish, Greek, Italian, Spanish and French quarries), is presently extended to neighbouring quarries from the district of Saint-Béat. Four of them were chosen due to their location regarding the Garonne river: Marignac and the quarry of Lavigne are on the left bank, in the Mont Rié while Boutx and Château on the right bank, in the Cap du Mont (see Figure 1). The ^{13}C NMR spectra recorded are significantly different and thus, they can be used as a help to discriminate between marbles coming from this same district, which is usually very difficult to achieve through the usual archaeometric methods applied to the study of marbles. The two archaeologic items tested were probably made of the same marble, and the comparison of their spectra with those of marbles from studied quarries suggests that they were coming from that of Saint-Béat Château.

Concerning cherts, we target both the main component SiO_4 quartz-like structure – which represents up to 99% of the mineral content – using ^{29}Si NMR and their aluminosilicate contents – less than 1% – using ^{27}Al NMR, since this nuclide is recognized to be easy to observe, and permits the determination of Al(IV)/Al(VI) ratios (Jakobsen, Jakobsen, and Lindgreen 1988; Smith 1993). The ^{29}Si spectra of the three geologic Pyrenean deposits studied in this work present significant differences notably in the peak area of the major component Q^4, that should be used as a discriminant element for provenance purpose. This phenomenon is the consequence of differences in "spin–lattice" or T1 relaxation from one sample to another attributed to different contents of magnetic impurities such as transition metals or rare earth cations. ^{27}Al spectra also present discriminant profiles: the total signal area, which reflects the aluminium-containing minerals and does not depend on the relaxation time since this nuclide is known to have short T1 and the distribution of the signal between two species Al (IV) and Al(VI). These discriminant NMR profiles served previous analyses for decision-making about the provenance of two archaeologic items, found in two different Pyrenean sites, Cova del Parco and Montlleó. In fact, previous studies demonstrated that the Cr, Sr and Th trace elements levels permit to discriminate the Montgaillard flysch and the Montsaunes cherts (Sànchez de la Torre et al. 2017b), however the comparative petrographic and geochemical characterization of the archaeological sample from Cova del Parco does not fit with one or the other geologic site. The discovery of another geological outcrop near Montgaillard, Buala (Sànchez de la Torre, Le Bourdonnec, and Gratuze 2019), and the analysis of these artefacts and the Buala site by Micro-PIXE (Sànchez de la Torre et al. 2019) to determine major, minor and trace elements in cherts demonstrated that this latter site can be distinguished using PCA graphs. However,

some uncertainties still remain to attribute the provenance for the archaeologic chert tools. At this stage, ^{27}Al and ^{29}Si solid-state NMR can help to take a decision: with regards to the spectra profiles, we can propose that the artefact coming from Cova del Parco is made of Buala chert when the one of Montlléo, of Montsaunès demonstrating trans-Pyrenean human circulation on long distance associated to procurement strategies since the Magdalenian (13,700–18,800 BP).

In conclusion, solid-state NMR that is known to be useful for material characterization purpose can be also successfully used for provenance purposes. It supports the approaches commonly used, and helps for decision-making when the identification of the provenance could not be achieved by using them alone. Indeed, the different methods used to give information on the structure of the material under investigation according to different point of view: if NMR probes the ensemble of local environments around the nucleus observed in the material (C for marbles, Si or Al for cherts) whether it is crystalline or amorphous, powder X-ray Diffraction data will inform about the different crystalline components present and elementary analysis will track the content of secondary or trace elements. All these analyses combined with others (notably the isotopic ratio for marbles for which numerous data still exist (Gorgoni et al. 2002)) permit step by step to propose a provenance with confidence.

Note

1. Unpublished data from the analysis undertaken within the framework of the ROMAE project (LaScArBx n°ANR-10-LAB-52).

Notes on contributors

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