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Non-destructive spectrometry methods to study the distribution of archaeological and geological chert samples

Maitane Olivares^{a,*}, Andoni Tarrío^b, Xabier Murelaga^c, Juan Ignacio Baceta^c, Kepa Castro^a, Nestor Etxebarria^a

^a University of the Basque Country, Faculty of Science and Technology, Department of Analytical Chemistry, P.O. Box 644 E-48080, Bilbao, Basque Country, Spain

^b National Research Centre on Human Evolution (CENIEH), E- 09004, Burgos, Spain

^c University of the Basque Country, Department of Stratigraphy and Paleontology, P.O. Box 644 E-48080, Bilbao, Basque Country, Spain

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ABSTRACT

The study of lithic raw materials recovered from archaeological sites offers relevant data on source catchment areas. Additionally, it can provide first hand information on artefact displacement, interchange networks and it can reflect the way in which the artefacts were employed. In order to characterize geological and archaeological chert samples and with the aim of finding an analytical fingerprint infrared and Raman spectroscopies were used for molecular analysis and X-ray Fluorescence spectrometry for elemental analysis.

In this work, different chert samples coming from several localities with geological and archaeological importance from the Basque Country have been collected and analysed. As a consequence, Raman spectroscopy allowed to distinguish between α -quartz and moganite in chert samples without organic matter and it is suggested that the ratio of those two components is related to the source of the chert. In addition, the impurities that appear in the samples (CaCO_3 , iron oxides and organic matter) can open new features to distinguish the samples and in this way, it would be possible to discuss the use and transport of the lithic artifacts from the sources to the final settlements.

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1. Introduction

Chert has been one of the most used mineral resources in the prehistory. The characterization of the raw materials from a chemical, mineralogical and petrologic point of view allows to know the provenance of the source of the archaeological artifacts. In this sense, the provenance studies allow archaeologists to investigate such diverse topics as mobility patterns or prehistoric migrations and also, know possible commerce routes.

By the time of characterizing chert, chemical characterization is one of the most versatile and powerful approaches for sourcing artefacts. From an analytical point of view, several techniques have been used in routine analysis, such as X-ray Diffraction (XRD), X-ray Fluorescence (XRF), Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) or Instrumental neutron activation analysis (INAA) among others [1–3]. XRD has been widely used to distinguish different mineralogical phases and thus, crystallographic information can be obtained. On the other hand, when elemental analysis is required, especially in the case of trace and rare-earth analysis, ICP/MS technique can be one of the most used.

Generally, almost all employed techniques require a pre-treatment of the samples, therefore they are invasive and besides, in situ analysis cannot be performed. However, sometimes, the use of non-destructive or non-invasive analysis is needed in order to analyse historical archaeological samples or when microanalysis is required. In this sense, the spectroscopic techniques allow to carry out molecular and elemental analysis without needing any type of sample pre-treatment [4]. From all of them, infrared and Raman spectroscopy should be highlighted since they allow to carry out molecular analysis of the sample, whereas the elemental analysis can be achieved by X-ray Fluorescence.

When these spectroscopic techniques are combined with microscopic techniques more available information can be obtained above all when the analysis of different zones of a sample is required. In this sense, Scanning Electron Microscopy coupled to Energy-Dispersive X-ray analysis (SEM-EDX) as well as a micro-Raman spectrometer coupled to SEM have very promising features in the analysis of valuable samples. On the other hand, neutron diffraction, PIXE and techniques based on neutron activation have to be mentioned due to their powerful characteristics in this topic [5], although they require very costly investments.

However, for the characterization of chert samples, basically destructive techniques have been used in order to know the total composition. In general, chert is composed by two polymorphs

* Corresponding author. Tel.: +34 946015551.

E-mail address: maitane.olivares@ehu.es (M. Olivares).

Table 1
Characteristics of the samples collected in different sites of Basque Country.

| Sites | Depositional settings | Geologic time | | | |
|------------------------------|--------------------------------|---------------|------------|-------------------|-----------------------------|
| | | Miocene | Eocene | Paleocene | Late cretaceous |
| Geological sites of chert | Continental (lacustrine) | Treviño (TRV) | Loza (LOZ) | – | – |
| | Shallow-marine (open platform) | – | – | Bioitza (BTZ) | Portillo de Techa (PDT) |
| | Deep-marine (Flysch) | – | – | Artxilondo (ART) | Barrika (BRK) Kurtzia (KTZ) |
| Archaeological site of chert | Shallow-marine | | | Mugardua Sur (MS) | |

of SiO_2 , α -quartz and moganite [6]. Nevertheless, their proportions as well as the presence of impurities (calcite, iron oxide or organic matter among others) in lithic material, makes its characteristics and the archaeological value vary. The principal aim of this work has been the characterization of different chert samples coming from several localities of the Basque Country using spectroscopic techniques. Based on this spectroscopic characterization our main objective is to establish a procedure to classify the different geological and archaeological samples according to their provenance.

2. Experimental

2.1. Selected samples

The geologic samples analysed in this study were collected from different rock formations of Cretaceous to Cenozoic age cropping out across the *Vasco-Cantabrian* region, in the western Pyrenees. All units are of sedimentary origin and were formed in continental, shallow-marine and deep-marine depositional settings, mostly characterized by the dominance of carbonate lithologies (different types of fossiliferous limestones, marly limestones and marls). Among the chert samples of Cretaceous age, the group named as “Cretaceous” comes from shallow-marine limestones of Coniacian to Santonian age cropping out in the *Portillo de Techa* gorge (Araba province), while those named *Barrika* and *Kurtzia* come from Cenomanian to Maastrichtian deep-marine hemipelagic limestone–marl alternations exposed along sea cliffs near the village of *Sopela* (Bizkaia province). The chert samples of Cenozoic age are more varied with respect to type and origin of the host lithologies. Chert samples coded as *Treviño* occur within lacustrine limestones of Miocene age around *Treviño* (*Treviño* county, Burgos province). The group *Loza* is also from lacustrine limestones of probably early Eocene age forming a distinct syncline around the village of *Loza* (Araba province). The group *Urbasa-Bioitza* comprises samples from early late Paleocene shallow-marine limestones exposed along the northern flank of the *Urbasa* syncline, to the west of

Navarra province. Finally, the samples *Artxilondo* are also of early Late Paleocene age but came from deep-marine limestone–marl cropping in the *Irati* forest area (north of Navarra province). Almost all the chert studied from all above-mentioned localities occurs as elongated nodules oriented parallel to the bedding planes of the host limestones, eventually forming almost continuous levels up to 15–20 cm thick. According to this arrangement, the sedimentological features and relationships with respect to the encasing host limestones, all the chert studied was formed during early diagenetic stages. The analysed chert samples have been characterized in a previous work using destructive techniques: XRD and ICP/MS among others, where detailed information about all formations containing the studied chert and particular features of each geologic site is given [7]. The geological characteristics of the collected samples are summarized in Table 1 and they try to resemble real situations at the time of performing chert analysis.

2.2. Instrumentation

2.2.1. Raman spectroscopy

The molecular and mineralogical analysis of the different chert samples were carried out using a Renishaw System 100 Raman Spectrometer coupled to a fibre optic micro-probe. The equipment has a 785-nm excitation laser, a Peltier-cooled CCD detector and a mobile diffraction grating of 1200 lines mm^{-1} . The laser has a nominal output power of 150 mW at the source and some filters allow to work at 1%, 10% or 100% of that power. Laser power at source has been less than 50 mW in order to avoid thermal decomposition of the samples. The micro-probe is equipped with different objectives (4 \times , 20 \times , and 50 \times) which allows to focus between 10 μm and 200 μm at the sample.

According to the measures, the spectra were collected between 200 cm^{-1} and 2200 cm^{-1} with a spectral resolution of 1 cm^{-1} . The time of integration were between 1 s and 200 s and the number of accumulation was variated in order to achieve the best signal to noise ratio. The software used to collect spectra was WIRE (Renishaw,

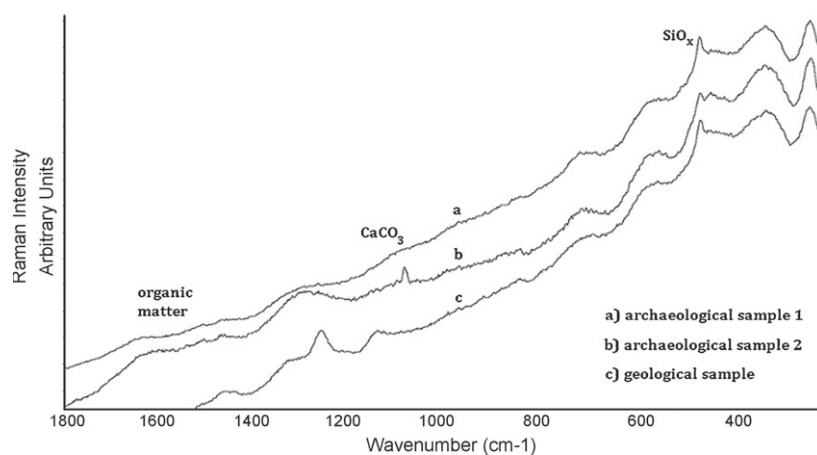


Fig. 1. Comparison of Raman spectra of archaeological (a and b spectrum) and geological (c) chert collected in Basque Country.

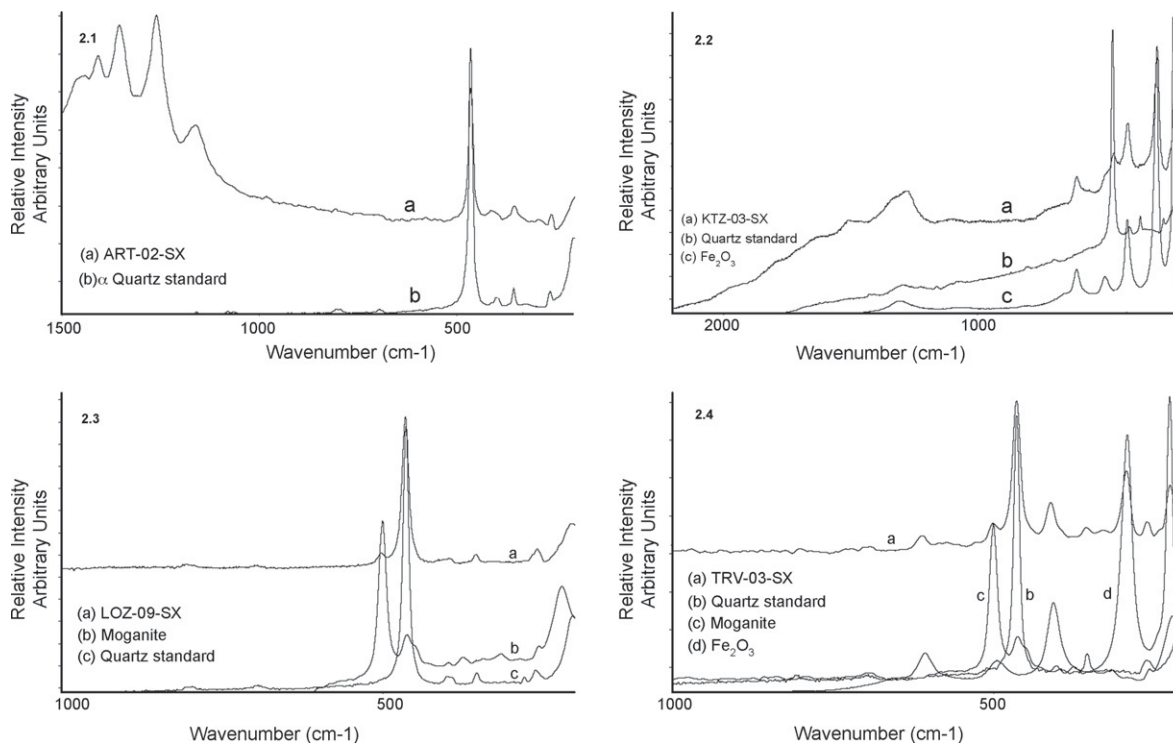


Fig. 2. Raman spectra of chert samples. 2.1(a) Raman spectra of a chert sample collected in *Artxilondo* and (b) α -quartz. 2.2(a) Raman spectrum of a chert sample of *Kurtzia*, (b) α -quartz and (c) iron oxide. 2.3(a) Raman spectrum of a chert of *Loza*, (b) moganite and (c) α -quartz. 2.4(a) Raman spectrum of a chert of *Treviño*, (b) α -quartz, (c) moganite and (d) iron oxide.

UK) and Omnic (Nicolet, Madison, WI, USA) was used to process them.

2.2.2. Infrared spectroscopy

The infrared equipment used in this work was Jasco-6300 spectrometer (Jasco, Japan). This spectrometer can perform transmittance FT-IR and also Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) and Attenuated Total Reflectance (ATR).

In this work transmittance FT-IR and ATR measurements were carried out. ATR spectroscopy allows measuring directly the sample without any pre-treatment. The measure conditions were 4 s, 40 accumulations and a resolution of 4 cm^{-1} in the spectral range of $600\text{--}4000\text{ cm}^{-1}$. In the case of FT-IR, measurements require the preparation of pellets mixing approximately 0.5 mg of sample and 150 mg KBr (Spectroscopic grade) in a agatha mortar and then applying a total pressure of 10 tons. The samples in pellet form were measured in the same operating conditions as in ATR in the range of $400\text{--}4000\text{ cm}^{-1}$. The software used to collect spectra in both cases was GRAMS (Galactic Industries, Salem, NH, USA) and Omnic (Nicolet, Madison, WI, USA) was used to process them.

2.2.3. μ -ED-XRF

Elemental measurements directly on the surface of the chert samples were carried out to complete molecular results. To this aim a portable Röntec (at the moment Bruker AG) ArtTAX μ -ED-XRF with a X-ray tube with molybdenum anode working at a maximum voltage of 50 kV and a maximum current of 0.6 mA was used. The equipment has a thermoelectrically cooled Si-drift (Xflash) detector which has an active area of 5 mm^2 and $8\text{ }\mu\text{m}$ beryllium window. The X-rays are collimated by a tantalum collimator with a diameter of 0.65 mm and the beam diameter in the sample's surface is $200\text{ }\mu\text{m}^2$. A CCD camera integrated in the measuring head gives an image of the sample surface ($8\text{ mm} \times 8\text{ mm}$) and a motor driven XYZ positioning unit allows focusing on different parts of the sam-

ple. According to the measures, the samples were analysed directly without any pre-treatment and the operating conditions were fixed at 1800 s, at a voltage of 50 kV and a current of 0.5 mA.

3. Results

3.1. Raman spectroscopy

The Raman spectrum of archaeological chert samples are illustrated in Fig. 1. In these spectra only two different peaks can be distinguished. As can be seen in spectra of Fig. 1, the most intense band is centered at 465 cm^{-1} (Fig. 1a) corresponding with the symmetric stretching band of SiO_2 , and the second band, centered at 1082 cm^{-1} (Fig. 1b) corresponding with the symmetric stretching band of calcium carbonate, CaCO_3 . Due to the fluorescence effect it is not possible to see the other characteristic peaks of both compounds. This fluorescence effect could be attributed to the presence of organic matter in the samples. Since, two weak and broad bands can be observed above 1300 cm^{-1} and 1500 cm^{-1} (Fig. 1), characteristic of the presence of carbon or organic carbon in the sample. It is supposed that the origin of chert is directly relatedated with organic matter [7], consequently these results can indicate the presence of organic matter in archaeological samples.

On the other hand, analysing some geological chert samples, the obtained results were similar to the archaeological ones as can be seen in Fig. 1. The spectrum obtained from an archaeological sample and a geological sample (Fig. 1c) are practically the same, where only SiO_2 , CaCO_3 and the Raman bands associated with organic matter can be observed.

However, as it is indicated in Table 1, apart of archaeological samples, different kind of geological chert samples were also collected, and in this case, it was possible to eliminate the organic matter (nearly 2% according to the results of a previous work [7]) present in the samples by a thermal treatment. As the mineral composition of chert is stable in a wide range of temperatures and

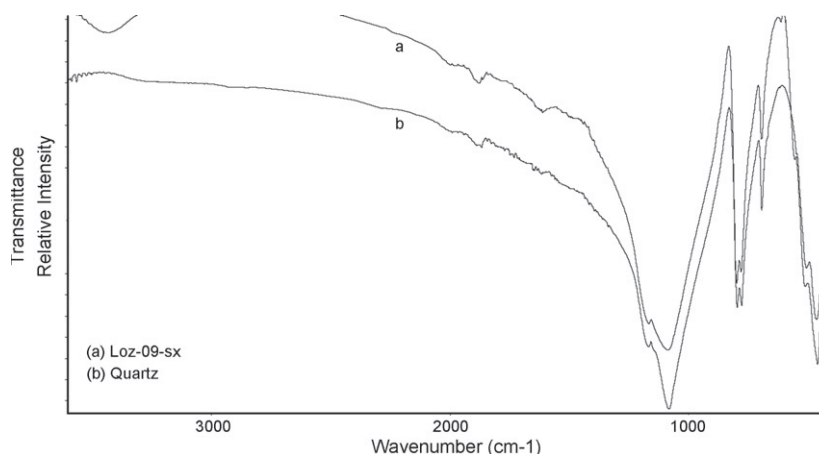


Fig. 3. A FT-IR spectrum of (a) Loza's chert compared with the spectrum of a standard of (b) quartz measured in the same experimental conditions. All the infrared bands observed correspond with the characteristic bands of SiO_2 .

there are not microcrystalline phase transformations [8], the samples were heated below 800°C during 30 min in a muffle furnace (Heraeus, Thermo Fischer Scientific, USA). As a consequence of this procedure, together with the organic matter, calcium carbonate was also eliminated. As can be seen in Fig. 2, analysing geological samples without organic matter it was possible to distinguish different compounds of chert and also differences between the geological samples.

The Raman spectrum of a sample of *Artxilondo* is plotted in Fig. 2.1 and it is compared with the spectrum of α -quartz. Almost all the Raman bands (464 cm^{-1} , 395 cm^{-1} , 355 cm^{-1} and 262 cm^{-1}) present in the spectrum can be identified with this mineral. Furthermore, several intense bands can be observed between the region of 1500 cm^{-1} and 1000 cm^{-1} which can belong to any type of silicate present in the sample. The second figure, Fig. 2.2, is the Raman spectrum of another chert sample, specifically a chert of *Kurtzia* (Fig. 2.2a). In this case, in addition to α -quartz (464 cm^{-1}) impurities of Fe_2O_3 (607 cm^{-1} , 404 cm^{-1} , 288 cm^{-1} and 220 cm^{-1}) can be identified.

In order to characterize chert samples, usually the determination of different microcrystalline phases of silica are required. As it is stated before, α -quartz and moganite are the most common ones. In *Flysch* samples, we do not find moganite, however, in other type of chert samples as *Loza* or *Treviño*, both types of polymorphs have been observed. In this sense, in the Raman spectrum of chert collected in *Loza* (see Fig. 2.3a) two polymorphs of silica have been easily identified (see Fig. 2.3b and c). In contrast to the difficulties

that can be found with XRD to distinguish between both crystallographic polymorphs, with Raman spectroscopy both can be identified, due to the characteristic Raman band at 501 cm^{-1} of moganite. Finally, in the case of *Treviño's* chert, α -quartz (464 cm^{-1}) and moganite (501 cm^{-1}) and also the presence of impurities of Fe_2O_3 (607 cm^{-1} , 404 cm^{-1} , 288 cm^{-1} and 220 cm^{-1}) have been observed as can be seen in the Raman spectra of Fig. 2.4.

3.2. Infrared spectroscopy

Infrared spectroscopy measures were carried out in order to confirm the results obtained with Raman Spectroscopy. To this aim, transmittance FT-IR analyses were carried out. As an example, an infrared spectrum of a chert of *Loza* is plotted in Fig. 3. As can be seen, all the characteristic Si–O vibrational bands are present: SiO_4 asymmetric stretching band (1085 cm^{-1} and 1150 cm^{-1}), Si–O–Si bending bands (798 cm^{-1} , 780 cm^{-1} and 695 cm^{-1}) and finally SiO_4 bending bands (464 cm^{-1} and 514 cm^{-1}). These findings were generally observed in all the samples studied. Moreover, ATR measures were done in order to carry out measures without any pre-treatment and thus, direct measures onto the sample's surface were possible.

In Fig. 4 the ATR spectra of different kind of chert samples are collected. Making a comparison of the results, two types of chert samples can be identified. On one hand, those that contain a higher proportion of calcite (calcium carbonate, CaCO_3) and on the other hand, those that are more pure and thus, only the band of quartz can

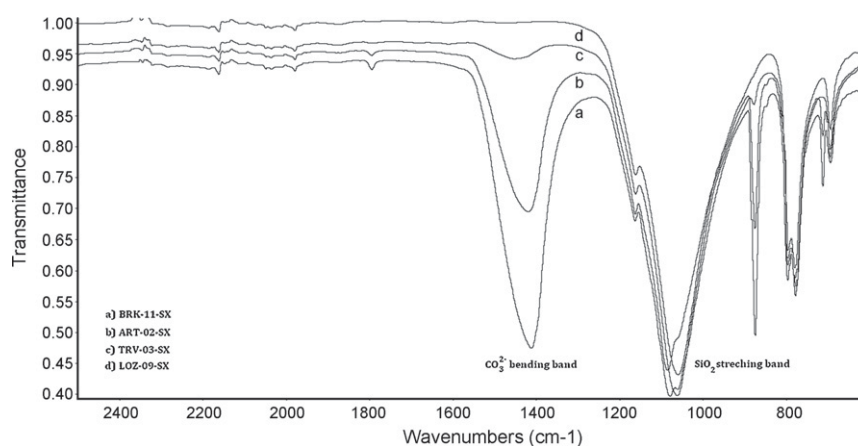


Fig. 4. A comparison of the obtained ATR spectra of different chert samples collected in different locations: (a) collected in *Barrika*, (b) in *Artxilondo*, (c) in *Treviño* and (d) in *Loza*.

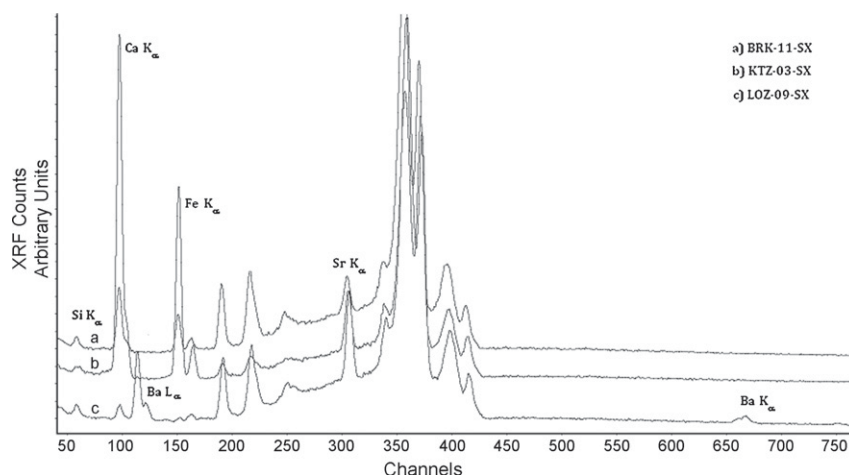


Fig. 5. μ -ED-XRF spectra of geological chert samples. (a) *Barrika's* chert, (b) *Loza's* chert and (c) *Kurtzia's* chert samples.

be distinguished. In the former case, we can see the infrared spectra of a chert of *Barrika* (Fig. 4a) and a chert of *Artxilondo* (Fig. 4b) where the characteristic infrared bands of calcite are clearly observed: the strong CO_3^{2-} bending bands (1450 cm^{-1}), out-of-plane bending band (874 cm^{-1}) and in-plane bending band (710 cm^{-1}). On the other hand, there are chert samples that only present the characteristic infrared bands of quartz (1085 cm^{-1} , 1150 cm^{-1} , 798 cm^{-1} , 780 cm^{-1} , 695 cm^{-1} , 514 cm^{-1} and 464 cm^{-1}), as is the case of *Treviño* and *Loza* chert samples (see Fig. 4c and d). Furthermore, the intensity of the infrared bands is clearly different, thus, it is possible to make a classification of chert samples depending on their percentage of calcite and α -quartz.

3.3. μ -ED-XRF

The aim of the measures with μ -ED-XRF is to complement the molecular results obtained by means of vibrational spectroscopic techniques and thus, to obtain a complete analytical information without any pre-treatment of the sample.

The μ -ED-XRF spectra of different kind of chert samples are illustrated in Fig. 5. In all of them appear the $\text{K}\alpha$ emission line of Si and also the $\text{K}\alpha$ lines of Fe corresponding to α -quartz and Fe_2O_3 respectively. In addition to these elements, $\text{K}\alpha$ emission line of Ca can be identified above all in sample collected in *Barrika* and this fit with the results obtained by means of infrared spectroscopy. With this elemental technique another trace elements have been identified, as is the case of the $\text{K}\alpha$ and $\text{L}\alpha$ emission lines of Ba and the $\text{K}\alpha$ emission line of Sr. The presence of these elements can be directly related with the presence of Ca in the samples as this correlation is frequent in the nature [9]. By means of vibrational spectroscopic techniques, neither Sr nor Ba have been found, so it is possible that both elements can be impurities of chert samples or they are present in trace levels.

4. Conclusions

As can be seen the vibrational spectroscopic techniques with the combination of another elemental techniques as μ -ED-XRF could be powerful techniques when the characterization of chert or similar geological materials is required. All these methods allow non-destructive chemical analysis and in this way allow the characterization of valuable archaeological samples.

Finding the different patterns of chert samples, it would be possible to identify and also to know the origin of the archaeological samples. In this sense, the presence of moganite in chert samples could be a criterion of classification. X-ray Diffraction allows to

characterize moganite in chert samples but it is not easy and it is destructive. By means of Raman spectroscopy, in contrast, the characterization of moganite without any pre-treatment of the sample is possible. In this work, it has been observed two types of chert samples, a group without moganite (*Flysch type*) and other group (*Loza and Treviño*) which have moganite. The first ones belong to cretaceous age, thus it is possible that in these samples the structure of moganite had been altered due to the larger period of ageing. On the other hand, ATR technique allows to carry out measures without any pre-treatment of the sample too. By means of this technique it is not possible to distinguish between different polymorphs of silica, but it is a powerful technique to determine the purity of the sample without any pre-treatment.

According to the impurities, above all calcite and Fe_2O_3 have been found in almost all chert samples. However, in chert collected in *Artxilondo*, *Barrika* and *Kurtzia* their presence is quite representative, so it is possible that this material has not been used in the prehistory age in order to manufacture lithic artifacts.

The only disadvantage that we found is with those chert samples with organic matter. Although as maximum level of organic matter is nearly 2%, it is a considerable interference when Raman spectroscopy analysis are required. However, in the nature there is a link with the presence of organic matter and the origin of chert. In this sense, analysing the impurities present in chert samples and also the characterization of the organic matter included in chert would be a new analytical key in order to determine the origin of geological and archaeological chert samples.

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