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GEOCHEMICAL CHARACTERIZATION OF FLINT ARTIFACTS BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY WITH LASER SAMPLING (LA-ICP-MS): RESULTS AND PROSPECTS

BEATRICE MORONI*
MAURIZIO PETRELLI

Department of Earth Sciences, University of Perugia
Piazza Università I-06100 Perugia, Italy

**to whom all correspondence should be addressed*
fax: + 39 075 5852603 - e-mail: b.moroni@tiscali.it

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ABSTRACT

Inductively Coupled Plasma Mass Spectrometry with laser sampling (LA-ICP-MS) was applied in the chemical characterization of flint artifacts of different geologic and geographic provenance in order to examine the mode and extent of chemical variability inside the pieces, and to find out any key parameters for provenance studies. The chemical variability of flint within the tools was found to be high due to sedimentary and diagenetic processes. However, this variability was low if compared to the variability existing between different geologic formations, and between different stratigraphic levels and outcrops of the same formation. Therefore, despite the chemical variability which requires a representative number of micro-samplings to be performed, LA-ICP-MS may provide a great deal of geochemical information in the field of flint provenance studies.

KEYWORDS: flint lithic industries, Umbria, Central Italy, geochemistry, provenance

INTRODUCTION

Flint is one of the most abundant, utilized, and enduring raw materials used in prehistory. Flint by definition is a rock composed almost entirely of microcrystalline quartz. There are several hypotheses for the mechanisms of formation of different types of flint (*e.g.* Murata and Larson 1975; Kastner *et al.*, 1977; Hein *et al.*, 1981; Isaacs 1982; Williams and Crerar 1985; Williams *et al.*, 1985; Monty *et al.*, 1991). Whatever the process, the evidence is that silicification generally occurs during diagenesis before compaction of the sediments (Knauth 1994). Since the silicification process is generally almost complete, flint is commonly 95% or more SiO_2 and contains only small amounts of minor and trace elements. There are several possible sources for the minor and trace elements contained in a flint. Some elements with high chemical stability may be inherited in the deposited sediments; other elements which can be easily mobilized due to weathering may be adsorbed onto particle surfaces from local seawater. In both cases the type and abundance of chemical elements reflect the chemical composition of the source rocks and the physico-chemical conditions in the sedimentary basin. Further chemical fractionation occurs during diagenetic burial, lithification and cementation. Thus the trace element content of flint is a complex combination of chemical signatures inherited during the processes of transport, deposition and diagenesis. Further chemical changes may occur in the flint detrital formations and, finally, in the flint artifacts after usage due to the weathering conditions. Therefore, the minor and trace element contents of flint provide a great deal of information concerning the petrogenetic history of this rock (Hein *et al.*, 1981; Craddock *et al.*, 1983; McLennan 1989) and may be regarded, hence, as a basic approach in the sourcing of flint artifacts.

In the last decade a significant contribution to the sourcing of archaeological materials has been afforded by inductively coupled plasma mass spectrometry (ICP-MS; Tykot and Young 1996; Tykot 1998; Mallory-Greenough *et al.*, 1999; Kennett *et al.*, 2002) and inductively coupled plasma mass spectrometry with laser sampling (LA-ICP-MS). The higher number of analytes which can be determined simultaneously along with the much lower detection limits and higher sensitivity in respect to most instrumental techniques make ICP-MS and LA-ICP-MS very powerful and well-suited to detect spatial heterogeneities (Durrant 1999; Pillay 2001; Gratuze *et al.*, 2001). In addition, by these techniques objects can be analyzed in a minimally destructive method using the whole object or a very small amount of material removed from it, therefore they represent a good compromise between the requirement of detailed geochemical characterization and the basic demand by archaeologists of preserving the artifacts as much as possible.

In this study we tested the potential of LA-ICP-MS in the chemical characterization of flint artifacts. The starting point was to study the mode and extent of chemical variability of flint for a large number of chemical elements. To attain this purpose a selection of flint tools were analyzed by LA-ICP-MS along transect sections of the tools in order to find out the most stable and least variable elements within the transects. These elements were then applied to the chemical characterization of flints of different geologic and geographic provenance with final aim to assess discriminative geochemical parameters for provenance studies.

MATERIAL AND METHODS

Flint samples

In the sedimentary series outcropping in Central Italy - the so-called *Umbro-Marchigiana Stratigraphic Series* - flint is a typical feature of some Meso-Cainozoic geologic formations of stratified limestones such as *Corniola*, *Calcari Diasprigni*, *Maiolica*, *Scaglia Bianca*, *Scaglia Rossa* and *Bisciaro* (*e.g.* Bonarelli 1967). The origin of flint within these formations is by substitution of carbonate sediments by silica during diagenesis. This is well evidenced by the presence of fossil remnants preserved in the silicified material (Baldanza 2002).

Scaglia Bianca and, especially, *Scaglia Rossa*, are the most widespread geologic formations in Central Italy where they give rise to extensive outcrops in correspondence of the mountain reliefs. Flint from *Scaglia Bianca* is dark grey to black and forms bands and nodules present all over the geologic formation. Flint from *Scaglia Rossa* is pink to dark red and forms bands and nodules present in two distinct flint members, the former Upper Cretaceous and the latter Lower Palaeogenic in age. Flints from the two members are undistinguishable by macroscopic appearance.

This study was carried out on a selection of *Scaglia Bianca* and *Scaglia Rossa* flint artifacts of Palaeolithic to Neolithic industries from the National Archaeological Museum in Perugia, Umbria (Table 1). The artifacts are from two different archaeological districts in Umbria, namely Norcia and Perugia (Fig. 1), both well known and constrained from the palaeoethnographic and techno-typometric point of view (Moroni Lanfredini 1995-96; Moroni Lanfredini 1999). Moreover, they come from ground environments, so the chemical signatures are expected to record the weathering conditions in the period of burial. Provenance of raw material was found to be strictly local, namely from Norcia and Perugia surroundings, in all cases (Moroni 2002).

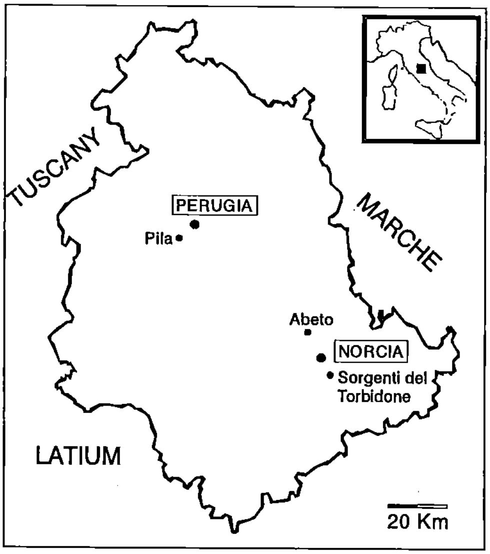

Fig. 1: Location of the sites of provenance of the lithic industries

All the pieces are fine grained with conchoidal fracturing and fresh appearance. Three of them (AB XXXIII, AB II and AB 74) are also characterized by a cortex so evidencing a derivation from secondary pebbles. Two of the artifacts (Pi 336 and PI 85) show homogeneous texture at microscopic scale, whereas the rest of samples show different kinds of macroscopic textural heterogeneities. Namely, three samples (TB 6, AB-C 118 and PI 40) have a patchy appearance, whereas three samples are characterized by the presence of bands (ABII and AB 74) or zones (AB XXXIII) of different colour to the side of the cortex.

Analytical procedure

Samples were cut perpendicular to the external surface of the tools, the obtained fragments were polished and then washed by ultrasonic bath to remove impurities. The samples were finally analyzed for minor and trace elements along transects on the polished surface by LA-ICP-MS at the Department of Earth Sciences, University of Perugia (Italy).

The ICP-MS is a Thermo Electron X7 from Thermo Electron Corporation (Waltham, USA). The instrument is quadruple based and offers a sensitivity of more than $6x10^7$ count per second (cps) for 1 mg ml^{-1} of In when used in the standard solution nebulisation mode. Background intensities are usually a few cps for elements above m/z = 85 (Rb) except Pb which may reach 100-200 cps due to memory effects.

The laser ablation system is a commercial New Wave UP213 (New Wave, UK). The laser source consists of a Q-switched Nd:YAG laser, whose fundamental emission in the infrared (1064 nm) is converted into 213 nm by means of three harmonic generators. Helium is preferred to Argon as a carrier gas to enhance transport efficiency of ablated material. The Helium carrier inside the ablation cell is mixed with argon as a makeup

Sample	*Archaeological site*	*Age of industry*	*Geological formation*	*Age of formation*	*Provenance*
AB II	Abeto	Acheulean	Scaglia Bianca	Middle Cretaceous	Norcia
AB 74	Abeto	Acheulean	Scaglia Rossa	Palaeocene	Norcia
AB XXXIII	Abeto	Acheulean	Scaglia Rossa	Upper Cretaceous	Norcia
AB-C 118	Abeto	Campignan	Scaglia Rossa	Palaeocene	Norcia
TB 6	Sorgenti del Torbidone	Mousterian	Scaglia Bianca	Middle Cretaceous	Norcia
PI 40	Pila	Acheulean	Scaglia Rossa	Upper Cretaceous	Perugia
PI 85	Pila	Acheulean	Scaglia Rossa	Palaeocene	Perugia
Pi 336	Pila	Acheulean	Scaglia Bianca	Middle Cretaceous	Perugia

Table 1: A summary of the analyzed artifacts

gas before entering the ICP torch to maintain stable and optimum excitation condition. A spot size of 100 mm was used throughout this study.

The system is optimized for dry plasma conditions on a continuous ablation of NIST SRM 612 by maximizing the signals from selected masses (La^+ and Th^+) and reducing oxide formation measured by ThO^+/Th^+. For the operating parameters summarized in Table 2 we obtain a ratio ThO^+/Th^+ less than 0.5%. All LA-ICP-MS measurements were carried out using time resolved analysis operating in a peak jumping mode (one point per mass peak with 25 ms of dwell time) and a total of 41 element were quantified (Table 3). Each spot analysis consists in 70 s background acquisition followed by a 70 s data acquisition from the sample. Calibration was performed using NIST SRM 612 as external calibration sample in conjunction with internal standardization using Si, following the method of Longerich *et al.* (1996). The use of an internal standard element of know concentration was used to correct for the mass of material ablated that is function of the incident laser power and absorptivity of the sample.

Limits of Detection, Precision and Accuracy for the LA-ICP-MS configuration adopted in this work are examined in a series of experiments on USGS Columbia River Basalt (BCR-2G) and Icelandic Basalt (BIR-1G) glass reference material. The limits of detection (LOD) are displayed in Fig. 2. LODs decrease with increasing m/z and they range from 0.01 to 1 ppm for elements with m/z $\leq$ 71 except for ^{42}Ca whose LOD is about 50 ppm. Limits of detection for elements with m/z $\geq$ 85 are below 0.01 ppm except for ^{90}Zr and ^{137}Ba which have higher values. Precision is given at one relative standard deviation (RSD). A precision better than 4.1 % is found for all elements that are present in the two standards with concentrations above 0.1 ppm (Fig. 4). Precision drastically decreases (the RSD increases) for the most dilute elements (<0.1 ppm) and in particular the RSD is about 28.6 % for U (0.01 ppm) and 9.4 % for Ta (0.04) within the BIR-1G standard. In order to correlate the RSD with the analyte concentration we parameterize the upper limit for the RSD using the following empirical equation (Fig. 4):

$$RSD = 4.1 + \frac{0.006}{C^2}$$

where C is the concentration of the analyte expressed in ppm. This equation is able to fit well the behaviour of the RSD for concentration below 0.1 and it tends to a constant value of 4.1 for concentration higher than 0.5 ppm. Accuracy is given as relative difference from the reference value. Average values for accuracy are displayed in Fig. 4.

ICP rf power	900-1250 W
Helium	0.7 - 0.8 l/min
Argon gas	Nebuliser: 0.8 - 1.0 l/min
	Auxiliary: 0.8 - 1 l/min
	Cool: 13-14 l/min
Settle time	1.5 ms
Dwell time	25 ms
Laser frequency	10 Hz
Laser beam diameter	120μm
Laser energy density	~ 10 J/cm^2

Table 2: Instrument and analytical parameters

Element concentrations in BCR2-G agree with the reference values of BCR-2 to within 10%; the only exception is the Ta which is 11.5 % higher than the reference values. Accuracy values agree to better than 13.0 % on the BIR-1 reference standards, with the exception of Tb, Ta, Pb and U which have higher values. The low accuracy obtained on U and Ta is likely related to their great dilution (0.01 and 0.04 ppm respectively) in this sample.

RESULTS

Descriptive statistics of representative transects of analysis is reported in Table 3. In the table the number of spot analyses (N), the mean values, the relative standard deviation estimates (RSD, as determined using the empirical equation in Fig. 4), and the coefficient of variation of data for the transects (CV, calculated as the percent ratio of the standard deviation of data on the mean value of data) are reported for each sample. RSDs are from 4.1 to 179.2, and less than 10% for at least 35 on 41 analytes. The highest RSD values are pertinent to some REEs and Ta due to their high dilution. CVs span over a wide range of values from 5% to 267%. It is to note that in most cases the extent of chemical variation, expressed by CVs, significantly or greatly exceeds the analytical precision, expressed by RSDs.

Many chemical elements show significantly high and/or variably scattered CV values in

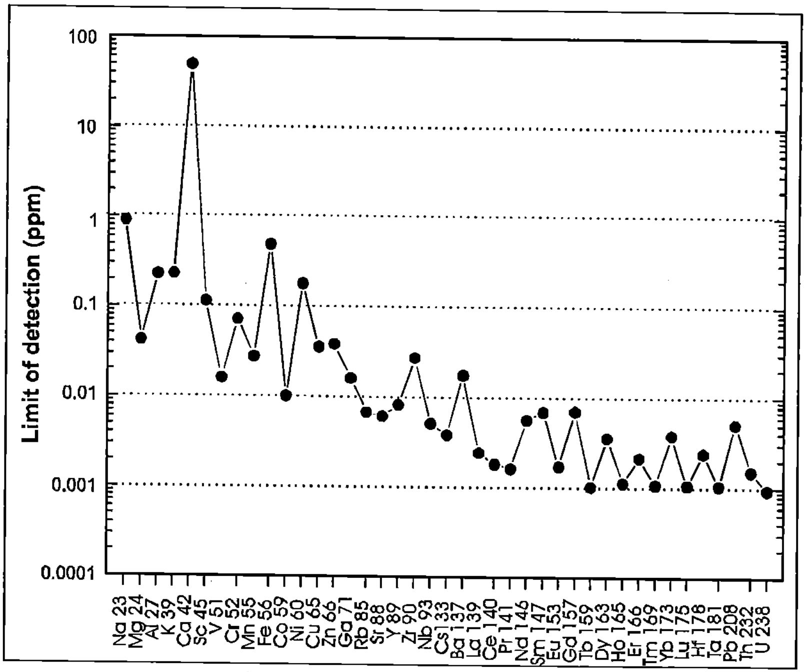

Fig. 2. Plot of the limit of detection for the analytes.

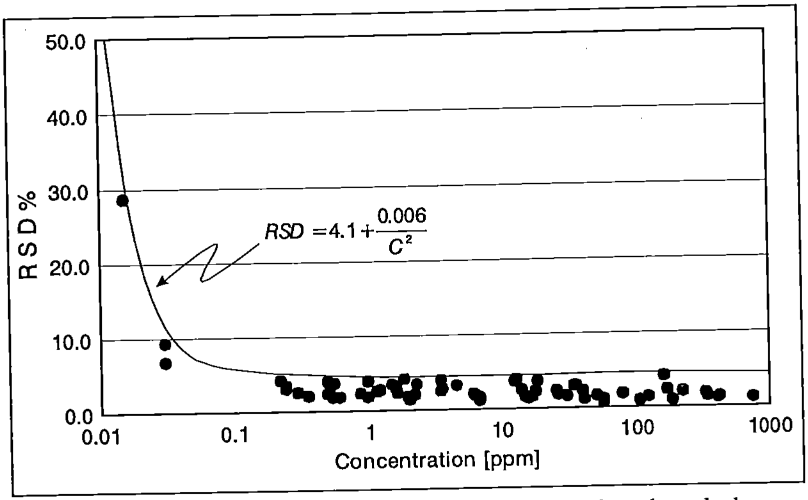

Fig. 3. Relative standard deviation RSD for reference US geological standards.

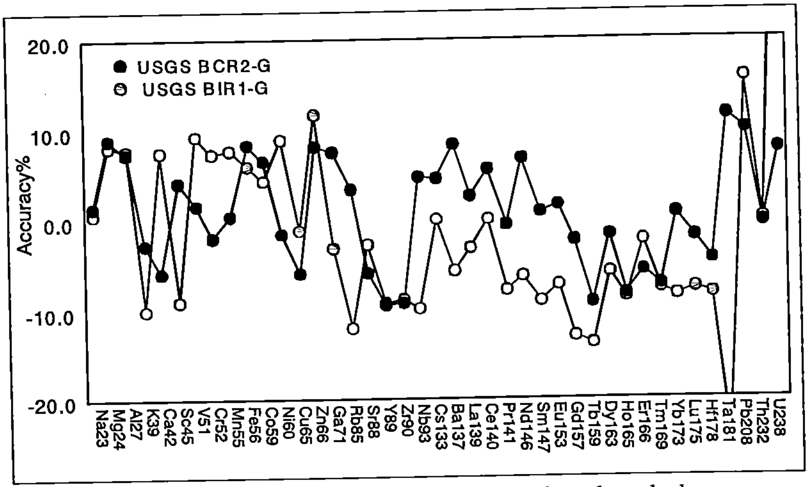

Fig. 4. Accuracy of analysis for reference US geological standards.

the samples. Among them, REEs (La to Lu series) are generally characterized by high CV values, well exceeding 100% (samples ABII, ABXXXIII, PI40 and PI85) and 200% (sample AB74) in some of the samples, and often higher to much higher than the CV values of the rest of elements. In addition, the REEs CV values are quite uniform (sample AB74) or, in most cases, slightly scattered (samples AB-C118, TB6, PI40, PI85 and Pi336). The scattering is, on turn, generally lower than the scattering exhibited by the rest of elements in the same sample. Other elements, such as transition (V, Cr, Zn, Fe, Mn, Co, Ni, Cu), High Field Strength (HFSE; Y, Zr, Nb, Ta, Hf, Th), Large Ion Lithophile (LILE; Cs, Ba, Pb) and alkali (Ca, Mg) elements, are mostly over 20% CV. Only a few elements, namely Na, K,

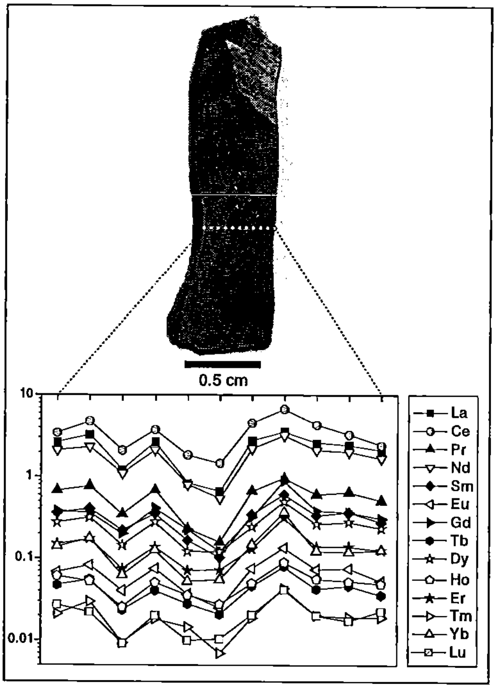

Fig. 5: REEs trends of sample Pi336. Except for Lu and Tm, error bars lie within the symbols.

Sc and, in most samples, Al, Rb, Sr and U, are characterized by CV values lower than 20%. It is noteworthy that the number of chemical elements with CV values lower than 10%, that is in the order of magnitude of RSD, is 1 in sample PI85, 2 in sample ABII, 3 in sample AB74, 4 in sample Pi336, 6 in sample ABXXXIII, and 7 in samples AB-C118, TB6 and PI40. In addition, the CV ranges of variation are 5.9-118.5 in sample PI85, 6.3-44.6 in sample AB-C118, 5.2-221.8 in sample TB6 and 7.1-118.3 in sample PI40.

Since samples AB-C118, TB6 and PI40, exhibiting the highest number of stable elements, have a patchy macroscopic appearance, and sample PI85, showing the lowest number of stable elements and a similar to larger range of variation of CV, is a macroscopically homogeneous sample, this means that the extent of chemical variation is not directly related to the macroscopic appearance. Likely, the scale of chemical variation is smaller than the scale of macroscopic textural features.

When looking to the mode of variation of chemical elements within flint, that is to the patterns of variation of chemical elements within the transect sections, the behaviour of the elements is worth of interest. REEs, in particular, are characterized by up-and-down trends with wide ranges of variation even in the texturally homogeneous samples such as sample Pi336 (Fig. 5). In addition, the REE trends are such similar each other that they may be completely superimposed (Fig. 5). In Fig. 6 the ranges of chondrite-normalized

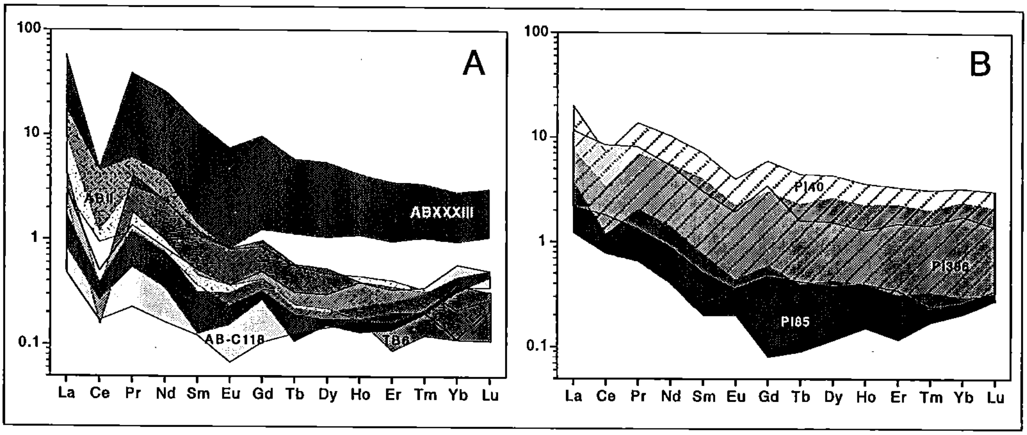

Fig. 6. Chondrite-normalized REE patterns of samples from Norcia (a) and Perugia (b).

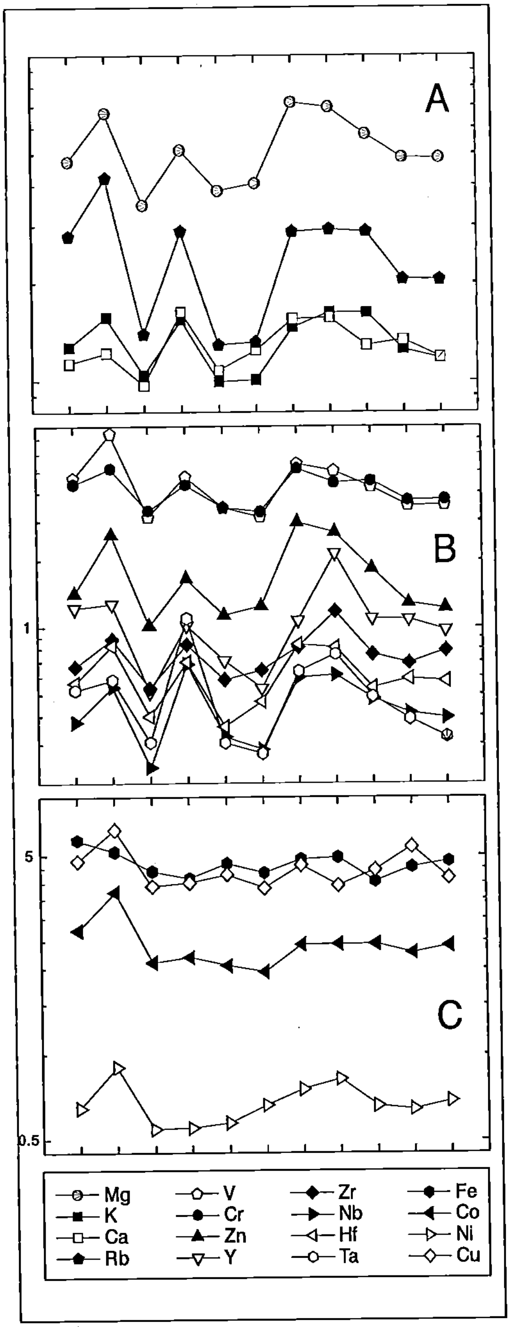

Fig. 7. Trends of alkali (a) and transition (b, c) elements in sample Pi336. Data are normalized to one of the samples (AB74) in order to facilitate the comparison.

REE patterns are reported for the samples from Norcia (Fig. 6a) and Perugia (Fig. 6b). In the graph accentuated negative Ce anomalies are present in all the samples from Norcia, and in one of the samples from Perugia (sample PI40).

Transition, HFS, LIL ad alkali elements are generally characterized by scattered trends in both homogeneous and heterogeneous samples, with general good correlation of alkali elements (*e.g.* Mg, K, Ca and Rb), of transition elements (*e.g.* V, Cr) and of HFS elements (*e.g.* Nb, Ta) (Fig. 7). In a few cases, some transition (Mn, Co, Ni, Fe, V, Zn) and alkali (Ca, Mg, Mn) elements show typical trends of enrichment within the transects. It is the case of sample ABXXXIII, which is characterized by similar convex trends for Mn, Co and Ni (Fig. 8a), sample ABII, which shows typical concave to convex trends for Fe, Co, V, Zn and Mn (Fig. 8b), and sample AB74 which shows, instead, similar trends of enrichment of Ca, Mn and Mg from one side to the opposite side with white coloured band (Fig. 8c).

DISCUSSION

Chemical characteristics and geochemical processes

A main aspect arising from the results of this study is the great chemical heterogeneity of flint from a chemical standpoint. What we found is, in fact, that although samples may appear visually homogeneous, they show a great number of chemical elements with CV values significantly or greatly exceeding the analytical precision, expressed by RSD. This aspect, which was already pointed out by Julig *et al.* (1992) in the source determination of flint artifacts by INAA, has been well evidenced in this study by the use of LA-ICP-MS which is, in fact, a very powerful technique as for the high spatial resolution of the laser probe coupled with low detection limit and high precision of ICP-MS.

Detailed examination of the mode of variation of chemical elements within the flint artifacts by LA-ICP-MS may provide some insight on the possible sources for the chemical signature of flint. Results of this study show that most chemical elements exhibit up-and-down trends within the transects of analysis. Among these elements, REEs are characterized by typical, similar-shaped scattered trends with wide ranges of variation in all the samples and no relationship with the macroscopic appearance of the samples (Fig. 5). It is well known that Rare Earth Elements are insoluble elements which tend to be transferred into flint as part of the original sediment and are quite stable during diagenesis and weathering (McLennan 1989), therefore they reflect the chemistry of the original sediment as derived from primary accumulation. In the case of interest the up-and-down trend of REEs in the flint samples thus reflects the minero-chemical heterogeneity of the original sediment giving rise to flint. While the trend similarity is to be ascribed to the very similar chemical and physical properties of REEs (Rollinson 1993), the wide range of variation of data is likely to be ascribed to the presence of very small grained REE-bearing refractory minerals dispersed in the original sediment.

For what concerns the REE patterns as derived for each spot in the transect sections of analysis (Fig. 6), a main point to be stressed is the negative Ce anomaly characterizing all the samples from Norcia and one of the samples from Perugia. LREE relative fractionations have proven useful environmental indicators in discriminating terrigenous (Ce undepleted) versus seawater (Ce depleted) sources (Murray 1994). Looking to these points, by comparison with data reported by Murray *et al.* (1992), deposition in pelagic sequences in the presence of small terrigenous contribution can be deduced in both Norcia and Perugia sedimentary environments. Notwithstanding, the less negative Ce anomaly in the two

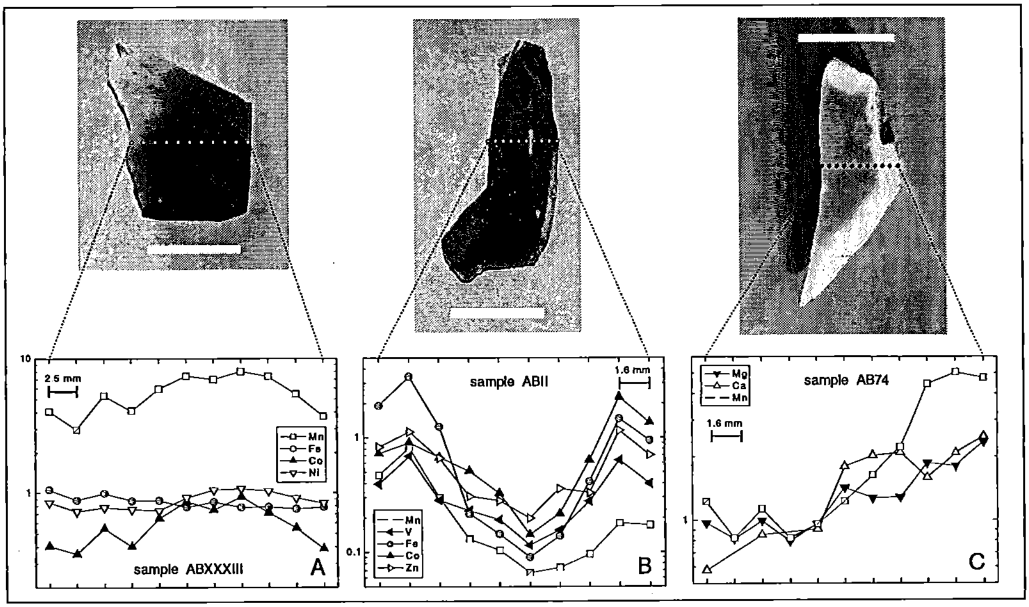

Fig. 8. Trends of alkali and transition elements within sample ABXXXIII (a), ABII (b) and AB74 (c). Error bars lie within the symbols. White bars in the photographs are 2 cm long.

samples from Perugia points to the presence of a less distant terrigenous source in these latter case in respect to the rest of samples.

Along with REEs, a large number of minor and trace elements exhibit scattered trends inside the analyzed flints. In sample Pi336, for example, some alkali (Mg, Ca, K, Rb) and transition (V, Cr, Zn, Y, Zr, Nb, Hf, Ta) elements have trends similar to the trend of REEs (Fig. 5 and Fig. 7a,b). In the same sample other transition elements (Fe, Co, Ni, Cu) exhibit scattered trends as well, but these trends are different from those of REEs (Fig. 7c).

It is not possible, at this stage, to discuss the processes originating these trends, however some considerations may be done based on literature data. It is well known, for example, that Ca, Mg and Mn are clear indicators of the presence of remnant carbonate phase within flint. Diagenetic chemical fractionation is, in fact, dominated by the substitution of the carbonate fraction by silica. Therefore variations in chemistry attributable to diagenesis mainly consist in a depletion of Ca and carbonate-related minor and trace elements such as Mg, Mn, Sr and Ba. On the other hand, some alkali (Na, K) elements may enter the silica framework during diagenesis (Keene and Kastner 1974). In the case of interest the trend similarity between alkali and REEs may reflect the persistence of small undiagenized calcareous plagues along with small refractory minerals within flint. LILE (K and Rb) appear not related to the silica framework but to the carbonate phase or, likely, to the REE-bearing water suspended clay fraction. In this respect they may be regarded as a record of the original chemistry of the sediment. The transition and HFS elements are generally considered immobile elements (Rollinson 1993; Murray 1994) therefore they are likely to be ascribed to the refractory original sediment as well. The different trends of Fe, Co, Ni, Cu in respect to the trends of V, Cr and Zn, these latter being similar to those of REEs, point to a different origin, from metalliferous and terrigenous sources respectively, for the two groups of transition elements.

Some transition (Mn, Co, Ni, Fe, V, Zn) and alkali (Ca, Mg, Mn) elements, which exhibit the already mentioned up-and-down trends, are also characterized by typical trends of enrichment in some of the samples. It is the case of the banded texturally heterogeneous samples ABXXXIII, ABII and AB74 which show, in fact, bipolar (samples ABXXXIII and ABII) and polar (sample AB74) variations of these elements in the transects of analysis (Fig. 8).

Sample ABXXXIII is characterized by similar convex trends for Mn, Co and Ni (Fig. 8a), whereas sample ABII shows typical concave to convex trends for Fe, Co, V, Zn and Mn (Fig. 8b). It is well known from literature (McLennan 1989; Murray 1994) that alteration may change the chemical composition of flint for some elements such as Na, Mn and Fe, which can be easily mobilized, and leave the most stable elements such as REEs practically unchanged. What we can expect as a response to weathering is, thus, a depletion of these elements at variable depth from the exposed surface depending on the weathering conditions. While Na do not show any trace of weathering (the trend for this element is quite flat with no apparent depletion to the external surface of samples), the transition elements Mn, Co, Ni, Fe, V, and Zn are characterized by typical trends of enrichment which could, actually, be related to weathering. When trying to estimate the depth of penetration of presumed weathering, as calculated by measuring the distance between two adjacent spots of analysis, we found a weathering penetration depth of 1.6 mm in sample ABII, and of at least 2.5 mm in sample ABXXXIII (Fig. 8). This kind of weathering profile and penetration depth are a common feature of severely weathered material (*e.g.* desert patinas; Pawlikowski and Wasilewski 2002). In our case, instead, no patina was observed on the flint surface. In addition, no arid conditions are recorded in the archaeological sites of the flint tools. Therefore the observed chemical trends are not to be considered as the result of weathering but, more likely, as a record of the original composition of the sediment.

Sample AB74 is characterized by increasing Ca, Mg and Mn values from the coloured side to the white-banded side of the artifact (Fig. 8c). As already evidenced in the discussion, the distribution and relative abundance of these elements typically related to the carbonate fraction reflect the mode and extent of diagenetic substitution suffered by the original carbonate sediment. Therefore the chemical variation in sample AB74 chiefly reflects the chemical variation of the geological object from which the artifact was obtained. Considering the rounded shape and the presence of a cortex on the white-banded zone of the artifact, it is clear that the tool was obtained from a flint nodule characterized by decreasing diagenetic silicification from the coloured core to the white-banded rim. Since sample AB74 shows a cortex just in the white-banded side of the nodule, a further note is that secondary weathering processes occurring on the flint nodule before employment did not change the original chemical signature induced by diagenetic silicification.

In the light of all these points the chemistry of the analyzed flint artifacts appears to be mainly influenced by the chemistry of the original sediment and, secondly, by the mode and extent of diagenetic processes. In the lack of extreme palaenvironmental conditions, such as in the case of the lithic industries in Umbria, the role of weathering in the secondary and burial environments may be practically neglected.

Sourcing of flint artifacts

In order to obtain archaeometric information on the provenance of a material it is necessary to select first which elements are best suited for the purpose. Results of this study show that only a few elements, namely Ca, Mg and Mn are to be absolutely excluded in provenance studies since they are markedly affected by diagenetic fractionation. Caution is also recommended in the use of Sr and Ba since they can be locally enriched in correspondence of undiagenized carbonate plagues within flint. The rest of elements tend to reflect, more or less, the composition of the original sediment and, thus, can provide information on the sourcing of flint. Among them, the REEs and the HFS elements Y, Zr,

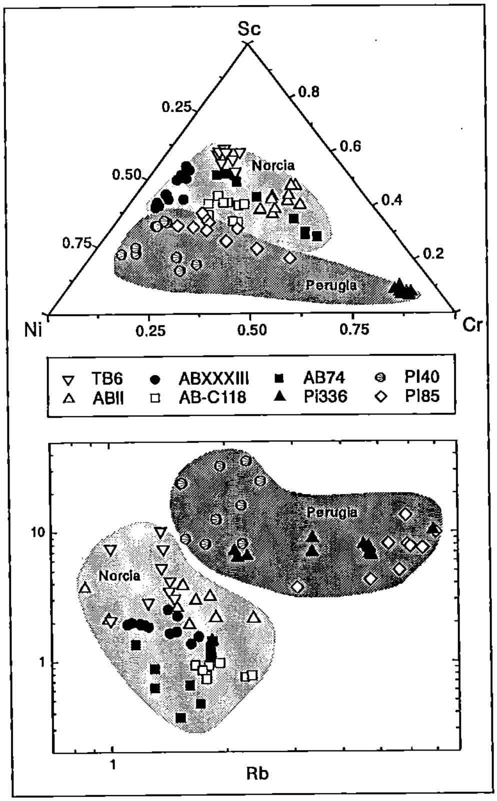

Fig. 9. Ternary diagram Ni-Cr-Sc, and bivariate plot Rb vs Cu.

Hf, Nb and Ta have been proven to be good indicators of the presence of a terrigenous contribution within flint although the extreme dilution and the high CV values in the analyzed samples dramatically restrict the number of useful elements to the light REEs on one end, and to the HFSE Nb, Y and Zr on the other hand. The LILE K and Rb have been found to represent the sedimentary clay fraction as well. Among the transition metals, V, Cr and Zn are likely to reflect the presence of a mafic refractory fraction, whereas Fe, Co, Ni and Cu have been associated to a metalliferous source. Finally, Na, Al and Sc have been proven to be suitable elements in the characterization of flint owing to their quite low and/or uniform CV values in the data set. In the graphs in Fig. 9 samples from Perugia and from Norcia can be readily distinguished, the formers showing higher Ni, Cr, Rb and Cu in respect to the latter samples. Since all these elements tend to be enriched in the presence of terrigenous refractory contents their relative enrichment in the samples from Perugia clearly indicates a 'less pelagic' sedimentary environment with significant contributions from suspended and particulate matter as well. In addition it is possible to discriminate the Scaglia Bianca from the Scaglia Rossa samples and, what's more, the Cretaceous from the Palaeocene level of the Scaglia Rossa formation, the Cretaceous levels (samples PI40 and ABXXXIII) showing lower Cr and higher Cu in respect to the Tertiary levels (samples PI85, AB-C118 and AB74).

CONCLUSION

In this study on a selection of flint artifacts of different geologic formations and geographic provenance we tested the validity of Inductively Coupled Plasma Mass Spectrometry with laser sampling (LA-ICP-MS) in the chemical characterization of flint in order to examine the type and extent of chemical variability inside the pieces, and to find out any key parameters for provenance studies. The obtained results point to the good quality of analysis by LA-ICP-MS which is, in fact, a very powerful technique as for the number of analytes and for the precision of analysis. In addition, the method is sensitive enough to detect the intrinsic chemical variability of material which was found to be generally high due to sedimentary and diagenetic processes.

The fact that flint is a very heterogeneous material is a crucial aspect to be taken into account when sampling flint artifacts, since a necessary premise of sampling, that is that the sample be representative of the object, may be dramatically in contrast in this case with the primary need of preserving the object as much as possible. Work is now in progress in our lab in order to assess the feasibility and the potentials of quasi-non-destructive, statistically representative sampling and analysis by LA-ICP-MS via laser ablation deep drilling of the artifacts. In spite of the great chemical variability, when trying to compare the samples each of them with its own intrinsic chemical variability, samples of different lithology and provenance can be readily distinguished. The obtained results thus enlighten some points of the potentials of LA-ICP-MS in the sourcing of flint artifacts.

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