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# Cathodoluminescence Spectroscopy of Quartz Grains as a Tool for Ceramic Provenance

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This paper examines the possibility of differentiating between two ceramic types by using cathodoluminescence (CL) investigation. Ceramics are from two sites (Auvernier-la-Saunerie and Charavines) of the Neolithic civilization of Saône-Rhône (2900–2400 BC). A standard site also was built with a low-calcite clay and a sandstone from south Germany. The method consists of comparing the CL spectra of quartz grains in ceramics. CL can be defined as a visible and near visible light (from 1.4 eV to 4.2 eV) emitted upon the interaction between an electron beam and matter.

For the analysis a scanning electron microscope coupled with an optical detection system was used. Three to six quartz grains were analysed from each sample. Conditions were constant for each acquisition. All the CL spectra of quartz exhibited two components, a blue component centred at  $2.75 \pm 0.04$  eV, and an orange–red centred at  $1.93 \pm 0.03$  eV. To compare all the spectra the ratio (R) between relative intensities of blue and red bands was calculated. The results demonstrated that it is possible to define several types of CL for quartz grains. Using this property, a mean and standard deviation of ratio R was calculated for each ceramic and plotted on a two-dimensional diagram. Samples from Charavines and the standard group were clearly separated. CL spectra of the ceramics from Auvernier were similar to Charavines but did not give clear differentiation. The use of the CL signal from other minerals, such as calcite, gave a better distinction for these ceramics. © 1999 Academic Press

**Keywords:** CATHODOLUMINESCENCE SPECTROMETRY, QUARTZ, NEOLITHIC CERAMICS.

## Introduction

The aim of this paper is to introduce a semi-quantitative procedure to study the provenance of ceramics using cathodoluminescence investigation on quartz grains.

Quartz is one of the most abundant components in ceramics and is a chemically stable phase that is resistant to alteration. There are a few reviews (Zingernagel, 1978; Matter & Ramseyer, 1985; Marshall, 1988; Ramseyer *et al.*, 1988; Owen, 1991; Bruhn *et al.*, 1996) on application of cathodoluminescence (CL) to the provenance of sandstone. These studies have defined a relationship between rock-formation conditions and the luminescence of quartz grains. Zingernagel (1978) classified three types of

luminescence for quartz that relate to their rock-formation condition: a violet luminescence for the plutonic and volcanic rocks, a brown colour for the metamorphic rocks and a non-luminescent type for the authigenic quartz. According to Demars *et al.* (1996), most of the detrital grains have a brown or violet–blue colour.

### *Archaeological problems*

The pottery artefacts examined in this study were found on the sites of Auvernier-la-Saunerie (canton de Neuchâtel, Switzerland) and Charavines (Isère, France). These sites belong to the Neolithic civilization of Saône-Rhône (the terminology of “Rhodanien Final

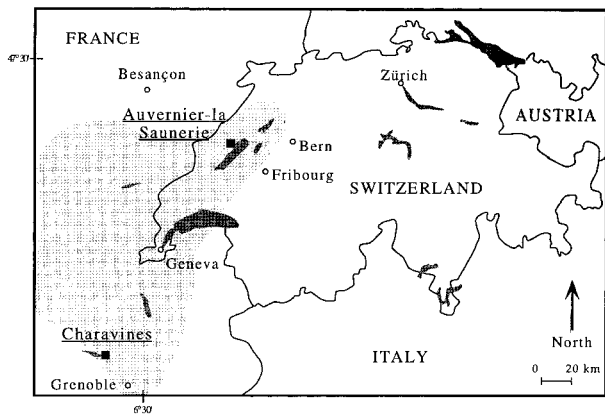


Figure 1. Geographical situation of the studied Neolithic sites and the area of the Saône-Rhône civilization (Thévenot *et al.*, 1976). ■, Archaeological sites; □, the area of the Saône-Rhône civilization.

Neolithic Civilization” is also used). This civilization (Thévenot *et al.*, 1976) occupied the northern part of the Alps between France and Switzerland (Figure 1), starting at the beginning of the 3rd millennium BC and continuing for five to six centuries (Ramseyer, 1988; Bocquet, 1995). Each site exhibited two different pottery types, a “coarse” ceramic (ordinary ceramic) and a “fine” ceramic. The prevailing coarse ceramics are assumed to be of local production. Fine ceramics represent only 2.5% of the total (2286 pieces) in Auvernier-la-Saunerie, the rest being coarse ceramics (Ramseyer, 1988). Fine ceramics were interpreted as possible imported products, because they seem to have been produced with a better technology than the coarse ceramics. This hypothesis was reinforced by the fact that some flints from the site of Grand-Pressigny (western France) were found in the same stratigraphic context as the fine ceramic group in Switzerland.

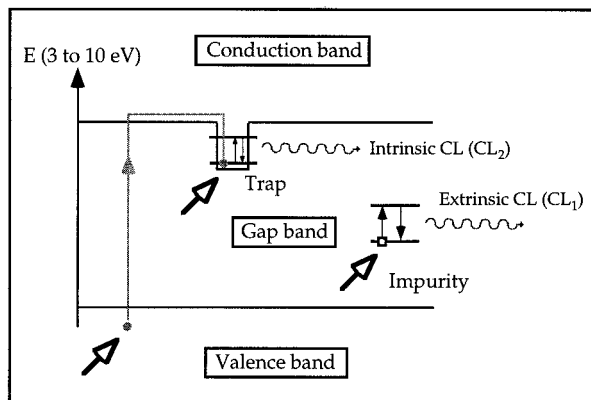
A detailed study of mineralogy, petrography and chemistry on a total of 302 sherds from nine sites was made at the Institute of Mineralogy and Petrography of Fribourg (Switzerland) by Benghezal (1994). She concluded that: (a) there is no difference between coarse and fine ceramics from the same site, and (b) the majority of the fine ceramics were relatively local in origin. Only few fine ceramics have an unknown origin.

However, due to the overlapping of the reference groups it was tempting to see if another method, i.e., CL, would give more precise information about the question of the origin of these ceramics.

### Sampling

For this study 52 archaeological samples were studied:

Auvernier la Saunerie: 15 samples of fine ceramics and 14 samples of coarse ceramics (seven ceramics were studied by Benghezal, 1994).



↗ : Electronic Bombardment

Figure 2. Electron beam excites electrons from the valence band to conduction band and traps vacancy. At the same time the electronic bombardment excites electrons in the traps which return to a lower energy level thus emitting photons (intrinsic CL). Also impurities are excited by the bombardment and create radiation (extrinsic CL with an impurity-associated centre).

Charavines: 14 samples of coarse ceramics and nine samples of fine ceramics (all samples of this site were studied by Benghezal, 1994).

A standard group (nine samples) corresponding to an artificial production site was made by mixing a low calcite clay (CaO < 1 wt%) from Rafz quarry (Switzerland) with quartz grains from South Germany (quarry unknown because location is an industrial secret).

## The Cathodoluminescence of Quartz Grains

### Cathodoluminescence (CL)

CL may be defined (Yacobi & Holt, 1990) as a visible and near-visible light emitted upon the interaction between an electron beam and matter (the sample must be an insulator). Figure 2 shows a schematic model of CL. At first an electron of the valence band is excited to the conduction band and trapped at a low energy level near the conduction band (atomic lacuna). Radiative transition is created by the relaxation of the trap centre (intrinsic CL).

Impurity associated centres like transition metals or rare earths are also excited and the loss of excitation energy creates a radiation specific to the impurity (extrinsic CL).

### Defects in quartz

In quartz and other siliceous materials two kinds of defects occur: intrinsic and impurity-associated defects. There are several types of intrinsic defects of which the most common is the E<sub>1</sub>' centre, electron at oxygen

vacancy in the polyhedral  $\text{SiO}_4$  (Ikeya, 1993). Other intrinsic defects are oxygen vacancy, interstitial oxygen ( $\text{O}^{2-}$  centre) and oxygen-associated trapped-hole centres called peroxy centre for dry quartz and NBOHC (non-bonding oxygen hole centre) for wet quartz (Griscom, 1990; Ikeya, 1993). Impurities in quartz are iron (Fe), titanium (Ti), aluminium (Al), potassium (K), sodium (Na), lithium (Li), hydrogen (H) (Heaney, 1994) and germanium (Ge) (Ikeya, 1993). They can form impurity-associated defects like  $[\text{TiO}_4/\text{M}^+]$ , where  $\text{M}^+$  is  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{H}^+$  (Ikeya, 1993).

#### Research equipment

Analyses were made with a JEOL 820 scanning electron microscope (SEM) coupled with an optical detection system and an electronic system to control data acquisition. An ellipsoid mirror collects the signal inside the analysis chamber and sends it to a HRS2 Jobin-Yvon monochromator with 1200 grooves/mm. A Hamamatsu R943-02 photomultiplier (PM) records the signal and gives the acquisition to the computer. The result is a spectrum in the energy range of 1.38 to 4.13 eV. For our acquisition a range of 1.55 to 3.54 eV (from 350 to 800 nm) was used. The system started at 350 nm with a ramp of 1.667 nm/s, time acquisition being 300 s. The experimental conditions were almost constant for each measurement. The acceleration voltage was 20 kV, probe current 0.15  $\mu\text{A}$ , magnification  $\times 1000$  which gives an analytical surface of 0.013  $\text{mm}^2$ , and a working distance of between 14 and 16 mm. All spectra were corrected by the efficiency curve of the detection system. Samples were polished thin sections coated with carbon.

#### Origin and evolution of the cathodoluminescence signal

Figure 3 shows the CL-spectra of four quartz grains, which exhibit two principal components; a small blue one centred at 2.70–2.82 eV (440–460 nm) and a pronounced orange-red centred at 1.94–2.00 eV (620–640 nm).

As shown in Table 1 and Figure 3, each component is a combination of two or three emission bands; for the blue component there are bands at 3.3, 2.8, 2.5 and the last one near 2.2 eV. For the red component there is a principal emission band near 1.9 eV and another band at 2.0 eV. At least a band in the deep-red at 1.8 eV is sometimes necessary to deconvolve correctly the red component. According to publications (Luff & Townsend, 1990; Munekuni *et al.*, 1990; Ramseyer & Mullis, 1990; Remond *et al.*, 1992; Stevens-Kalceff & Phillips, 1995; Stevens-Kalceff *et al.*, 1997), red emission bands at 1.88 and 2.00 eV are associated with NBOHC defects. The blue emission band near 2.77 eV is associated with a radiation recombination of a  $\text{E}_1$  centre. The green band at 2.21 eV can be related to a germanium (Ge) impurity-associated

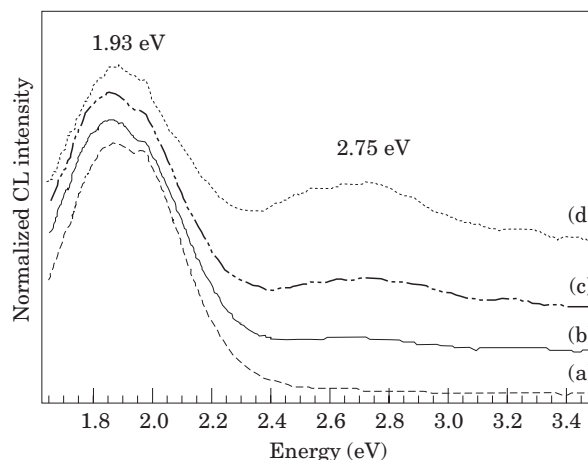


Figure 3. CL spectra of four quartz grains. (a) Grain no 4 ( $R_4=0.04$ ) from the sample of Auvergnier BDX4881. (b) Grain no 3 ( $R_3=0.18$ ) from the sample of Charavines AB-245. (c) Grain no 6 ( $R_6=0.39$ ) from the sample of Charavines AB-246. (d) Grain no 7 ( $R_7=0.62$ ) from the sand BDX4818.

centre. The ultraviolet band near 3.28 eV should be related to an aluminium (Al) impurity associated centre.

To summarize, the CL spectra of quartz grains are combinations of several emission bands from intrinsic and impurity defects created during physical and chemical processes of rock formation. In accordance with published papers (Ramseyer & Mullis, 1990; Remond *et al.*, 1992; Stevens-Kalceff, Phillips & Moon, 1996), the experiments described above show that the luminescence of quartz changes with beam exposure time (Figure 4). Evolution is not symmetric; intensity of the blue component decreases rapidly during the first 10–20 s after which it is stationary. For the red component, intensity increases rapidly during the first 20 s and then it becomes stationary. Due to these changes, measurements were made in the stationary area; the blue intensities are measured in the area between 57 and 63 s and the red intensities are measured between 165 and 171 s.

CL experiments on fired German quartz sand show that there are no CL changes with temperature (Picouet, 1997).

#### Semi-quantitative Comparison Procedure

All studied grains present a typical spectrum as shown in Figure 3, the only difference between the spectra being the relative intensity of the blue and red components. All quartz grains analysed in this study have more or less the same dimensions, between 150  $\mu\text{m}$  and 1 mm. To compare all the spectra, the ratio ( $R$ ) between the relative intensity of blue and red components was established. For all spectra the relative intensity of the blue band was calculated in a range of 2.71–2.79 eV, for the red band between 1.95–1.98 eV. This yields a ratio,  $R$ , which is characteristic for each

Table 1. The mean (of 32 spectra) of the CL emission positions of quartz grains and their origin, according to the literature. First emission band is not present on all spectra (18 spectra)

Energy (eV)	Intensity (a.u.)	Luminescence interpretation
1.80 ± 0.02	(52)	impurity associated centre of [Fe <sup>3+</sup> - M <sup>+</sup> ] where M <sup>+</sup> can be Li <sup>+</sup> , H <sup>+</sup> §
1.88 ± 0.01	(874)	non-bridging oxygen hole centre (NBOHC)*‡ or associated with oxygen vacancies†
2.00 ± 0.02	(62)	non-bridging hydroxy precursor third type of NBOHC precursor?*
2.21 ± 0.08	(17)	radiative recombination of a self trap exciton‡ or Germanium impurity*†
2.48 ± 0.04	(23)	extrinsic emission†‡
2.77 ± 0.04	(82)	radiative recombination of an exciton associated with E <sub>1</sub> ' centre‡
3.28 ± 0.05	(39)	impurity associated centre of [Al <sup>3+</sup> - M <sup>+</sup> ]. M <sup>+</sup> can be Li <sup>+</sup> , H <sup>+</sup> †‡

\*: Munekuni *et al.*, 1990; †: Luff & Townsend, 1990; ‡: Stevens-Kalceff & Phillips, 1995; §: Stevens-Kalceff *et al.*, 1997.

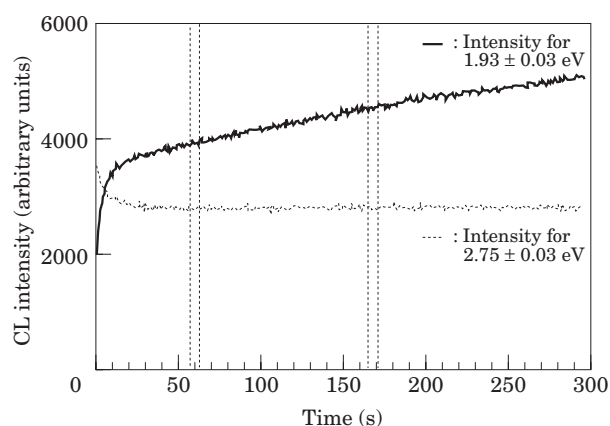


Figure 4. Evolution of quartz grain CL signal, with beam exposure time, for the main two components.

spectrum. For each grain  $i$ , at least two spectra were recorded to establish the reproducibility of the signal and to calculate the average ratio  $R_i$  and the relative standard deviation of the acquisition  $\sigma_i$ . Three to five quartz grains were analysed for each sample. The ratio  $R_m$  and the relative standard deviation of the mean  $\sigma_m(\%)$  are defined by the formulae:

$$R_m = \sum_{i=1}^N \frac{1}{N} \times R_i \quad \text{and} \quad \sigma_m(\%) = \frac{\sqrt{\left( \sum_{i=1}^N \frac{1}{N-1} (R_i - R_m)^2 \right)}}{R_m}$$

where  $N$  is the number of quartz grains analysed in each sample.

### Results

Results of all acquisitions were converted to a histogram (Figure 5), which gives the frequency of the values of the ratio  $R_i \pm \sigma_i$ . Using the smoothed curve of the histogram, it is possible to define three principal types of CL:

(1) type one, the “red” quartz grains with  $0.00 < R_i < 0.11$ ;

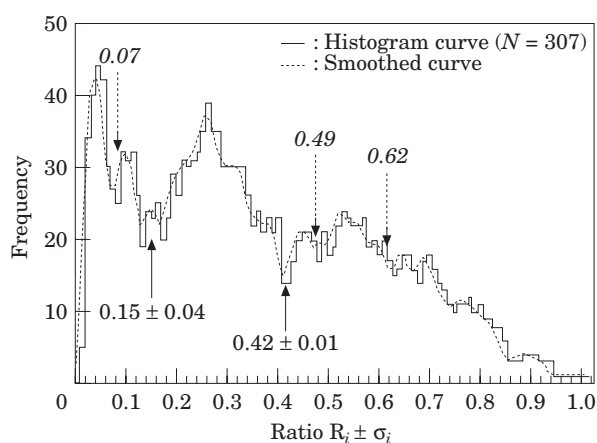


Figure 5. Histogram of the frequency of the ratio  $R_i \pm \sigma_i$  for 307 quartz grains.

- (2) type two, the “purple” quartz grains with  $0.19 < R_i < 0.41$ ;
- (3) type three, the “blue” quartz grains with  $0.43 < R_i$ .

Due to the fact that experimental conditions are important in the cathodoluminescence of quartz grains, it is not possible to compare these results directly with the literature (Zingernagel, 1978; Matter & Ramseyer, 1985; Ramseyer *et al.*, 1988; Owen, 1991; Demars *et al.*, 1996). Figure 6 presents the distribution of quartz grains based on the classification of different CL types. Variations in the frequency of the ratio  $R_i$  presented in Figure 5 and 6 show that the 279 quartz grains analysed in the ceramics do not have the same geological origin. This condition implies that  $R_i$  may be used for the differentiation of archaeological ceramics. The determination of  $R_m$  and  $\sigma_m(\%)$  for each sample allows two parameters to classify ceramics in a bi-variable diagram where  $R_m$  is the abscissa and  $\sigma_m(\%)$  the ordinate. The comparison between the results of ceramics from different sites is shown in Figure 7(a) and (b).

### Comments

The analysed 99 quartz grains of the samples from Charavines (34 in fine ceramics and 65 in coarse

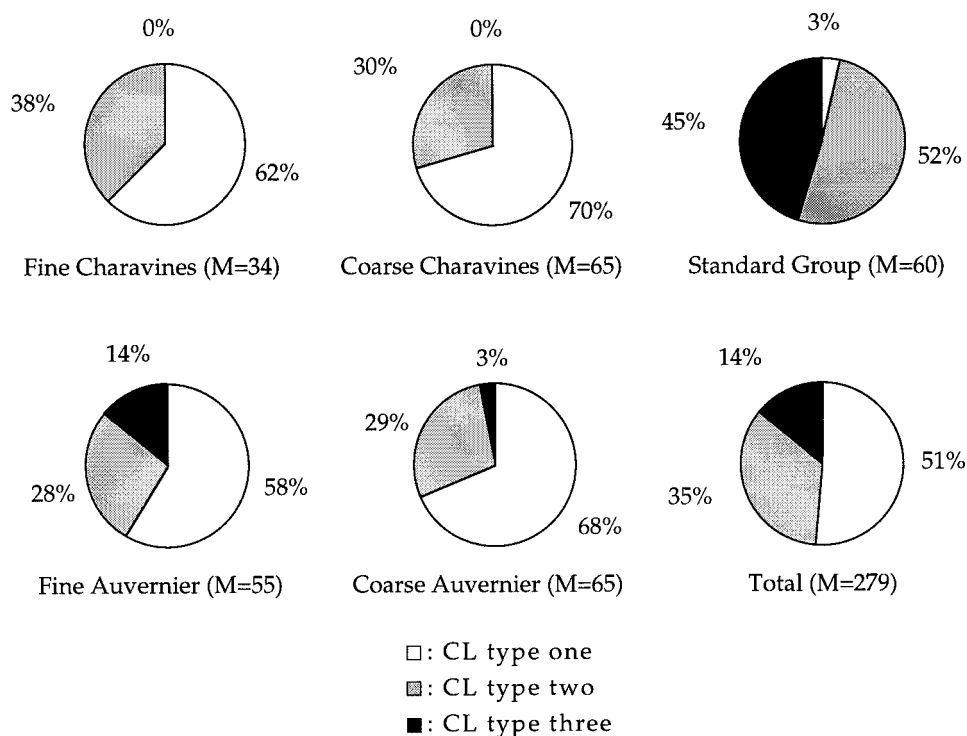


Figure 6. Pie diagrams of quartz grains distribution based on different CL types. The distribution of the CL types of the Charavines samples is almost the same for fine and coarse ceramics. The distribution of the CL types in the samples from Auvernier is close to Charavines with the exception of the presence of CL type three. The standard group differs markedly from the others. M represents the number of quartz grains.

ceramics) belong to CL types one and two (Figure 6), i.e., 67.5% of red and 32.5% of purple quartz. Some samples have only “red” quartz grains while others have only “purple” quartz grains, but the majority of fine and coarse ceramics have a mixture of the two. As shown in Figure 7(a) and (b), samples from Charavines form a homogeneous group. For the samples from Auvernier, the majority of the 120 analysed quartz grains belongs to CL type one (64.1%) (CL type two, 28.3% CL type three 7.6%). This distribution is valuable for the distinction between fine and coarse ceramics from Auvernier, as shown in Figure 6. As in the case of Charavines ceramics, some samples from Auvernier have only “red” and others have a mixture of “red” and “purple” quartz grains. But at this site, three fine ceramics and two coarse ceramics contain a mixture of “red”, “purple” and “blue” quartz grains. Ceramics from Auvernier therefore occupy a large area in Figure 7(a). Samples of the standard group contain quartz (Figure 6) of CL type two (52%), CL type three (45%) and CL type one (3%), forming a distinct and homogenous group (Figure 7(b)).

Based on these results, it is possible to distinguish the artificial ceramics of the standard group from the archaeological samples from Charavines (Figure 6 & Figure 7(b)). A distinction between Auvernier and the other two is impossible due to the large “cloud” in Figure 7(a).

## Conclusions

The aim of this study was to test whether it is possible to use the cathodoluminescence spectrometry of quartz to differentiate ceramics. According to our results it is possible to characterize individual quartz grains using the ratio of the relative intensities between their CL blue and red components. The sherds from Charavines and the standard group form two homogeneous, very distinct groups, but samples from Auvernier spread over the whole  $R_m/\sigma_m$  diagram and cannot be differentiated from the sherds of the other two groups. In comparison, according to Benghezal (1994), chemical data show a clear distinction between the CaO-poor (mean content=1.2 wt %) Charavines and the CaO-rich (mean content=6.8 wt %) Auvernier group. There is no separation between fine and coarse ceramics from Charavines, based on CL-data; if the coarse ceramics are of local production (Bocquet, 1995), then the fine ceramic must also have a local origin, a deduction which is in agreement with the conclusion based on petrographic and chemical data (Benghezal, 1994). Neither can fine and coarse ceramics be distinguished by CL-measurements. If, as Ramseyer (1988) suggests, the coarse ceramics are of local production, then the fine ceramics must also have a local derivation. The spread of the Auvernier data could be partially explained by quartz contributions from two sources,

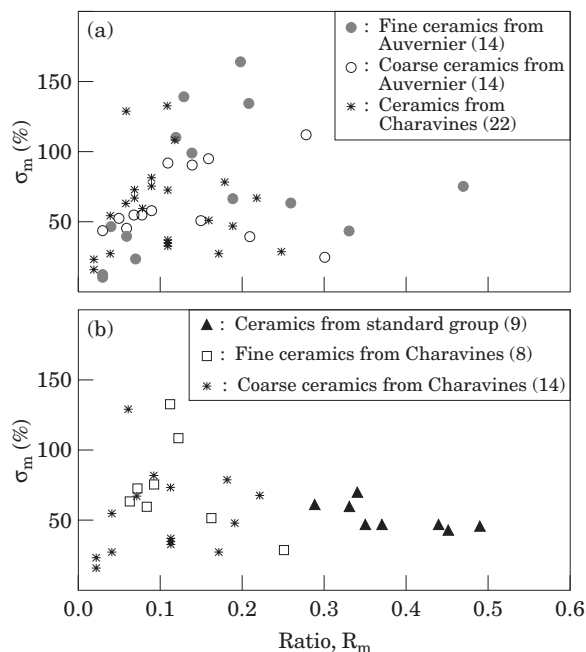


Figure 7. Diagram of the ratio  $R_m$  versus  $\sigma_m$  (%) for the studied samples.

the Alps and the Jura, while the greater homogeneity of the Charavines data may reflect the fact that the area received sediments only from the Alps. More research with other luminescence methods is required to differentiate unequivocally between the samples from Charavines and Auvernier. Cathodoluminescence imaging of all minerals (feldspar, calcite, etc.) of the ceramic body could be a promising approach. In this case CL imaging of Auvernier samples gives four different luminescence colours: an intense blue and a yellowish green for the feldspar grains, an intense orange for the calcite included in the matrix, and a weak purple for quartz grains (Picouet, 1997). CL imaging of Charavines samples shows only three different colours: an intense blue and a yellowish green for the feldspar grains and a weak purple for quartz grains. Ceramics of this site do not show orange-red colours in the matrix (Picouet, 1997). Because the firing temperatures were less than 800°C (Benghezal, 1994), cathodoluminescence of calcite permits differentiation of most of the samples from both sites.

Although not an easy method, the cathodoluminescence spectroscopy of quartz grains, in combination with others methods, shows considerable promise as a means of ceramic provenance determination in archaeometry.

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