RAMAN AND INFRARED REFLECTION SPECTROSCOPIC STUDY OF PRE-COLUMBIAN MESOAMERICAN POTTERY

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Abstract: The research shows the benefits of the combined use of Raman microprobe (RMP) and infrared reflection spectroscopy (IRS) in the analysis of archaeological materials, in particular, to obtain some information about the mineralogical composition of the different ceramics. Taking advantage of the recent development of RMP and IRS techniques, we report for the first time a survey of pre-Columbian Mesoamerican ceramic materials from two sites: Cuanalan (Teotihuacán, Mexico) and Kaminaljuyú area (Guatemala). The Raman spectra obtained from selected areas of the rough fragments from the Cuanalan ceramic materials show that these samples are characterized by the highly heterogeneous body matrix mineralogy due to the presence of a large variety of minerals such as feldspars (alkali polymorph and plagioclase), diopside, magnetite and Ti-magnetite, and one titanium oxide, rutile. This mineralogical assemblage including a confirmed diopside is characterized for the clays that start to crystallize at a temperature near to 800–900ºC. Representative FTIR reflection spectra of the ceramic matrix of Cuanalan pottery in the 1700–400cm^{-1} were indicative of noncalcareous ceramic materials, showing strong SiO vibration of meta-clay. RMP studies of the Mayan ceramics from Guatemala have shown their different mineralogy and chemistry. Due to the presence of calcite (some characteristic Raman CO_3 lines were observed) and the absence of diopside and Ti-oxides in ceramic pottery from the Kaminaljuyú area a firing temperature somewhere between 600-700ºC can be deduced. The IRS spectra indicate a weakly calcareous ceramic matrix with weak CO^2_3 vibration of microcrystalline calcite. The main CO^2_3 reflection bands (at 1530, 1442, and 880cm^{-1}) were obtained in the heterogeneous samples by using an infrared microscope capable of distinguishing small mineral inclusions and eliminating the characteristic bands of the silicate matrix in the range 1047–1055cm^{-1}. The combined application of RMP and IRS improves the identification of the mineralogical phases in the composition of the pottery and makes it possible to analyze the new phases which are formed during the firing of the clayey raw material to pottery.

Cuanalan (Teotihuacán, Mexico)

Kaminaljuyú area (Guatemala)

INTRODUCTION: Raman microprobe (RMP) and infrared reflection spectroscopy (IRS) have been called by researchers methods of mineral "fingerprinting" [1-3] and a combined use of these techniques permits to identify practically all mineralogical and gemological objects. These methods present many comparative advantages in comparison to the majority of well-known traditional mineralogical techniques. First, RMP and IRS are the non-destructive methods, and thus potentially are very important tools for mineralogists, gemologists, archeometrists and geoarchaeologists. Since non-destructive methods at present are preferred in mineralogical, gemological, geoarchaeological and archaeometric identification, these methods are considered to be the appropriate methods for this aim. RMP and IRS are also useful as an alternative to the more traditional methods of X-ray analysis such as XRD, SEM/EDS and EPMA.

EXPERIMENTAL DETAILS: Eighteen archeologically procured plainware pottery fragments from two sites were analyzed for the first time with RMP and IRS. Eight fragments are from the site of Cuanalan, a formative village that predates the beginnings of Teotihuacán, the great pre-Columbian metropolis of central Mexico (Figure 1). The other ten fragments of pottery analyzed in this study are from the Kaminaljuyú area in Guatemala (Figure 2). Their Raman (Figures: 3,5) and IR reflection spectra (Figures: 4,6) were recorded with multi-channel micro-Raman LabRam 300 spectrometer (Horiba Jobin-Yvon) using the λ_L=632.87 nm line of an He/Ne laser, and 20 mW on the sample in the spectral range between 100 and 3500 cm^{-1} and FTIR Spectrometer Bruker Tensor 27. Standard Spectrum software was used for recording. In order to obtain more information about the minerals used in the potteries, the mineralogical composition of studied materials is examined using point-to-point RMP and IRS techniques.

Figure 1. Cuanalan pottery and fragments (Teotihuacán, Mexico)

Figure 2. Kaminaljuyú pottery and fragments (Maya civilization, Guatemala)
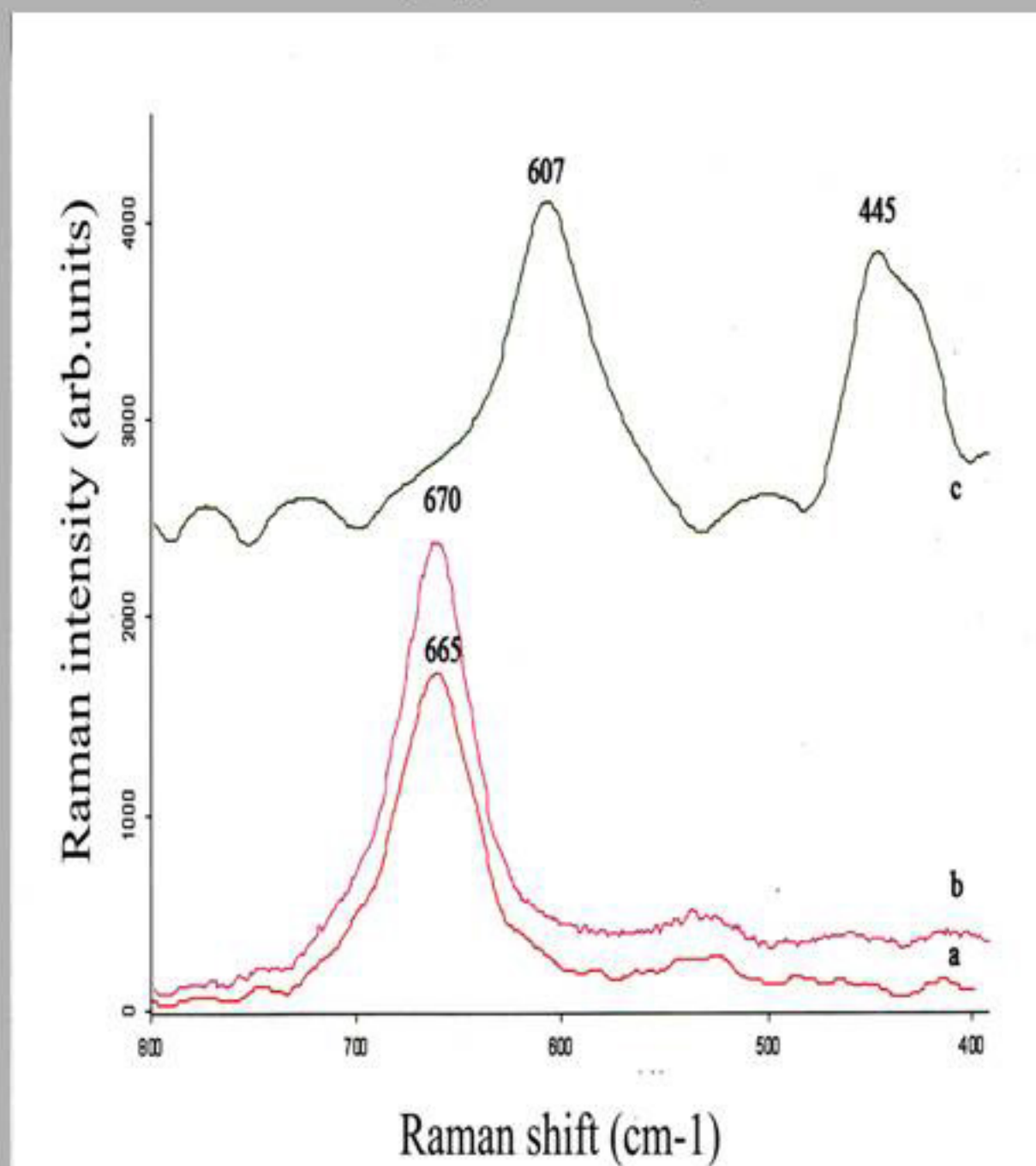
Figure 3. Raman spectra of magnetite (curve a), Ti-magnetite (curve b), and rutile (curve c). Note the major peak position shift (665 to 670 cm^{-1}) that is caused by the substitutional solid solution among Fe and Ti.
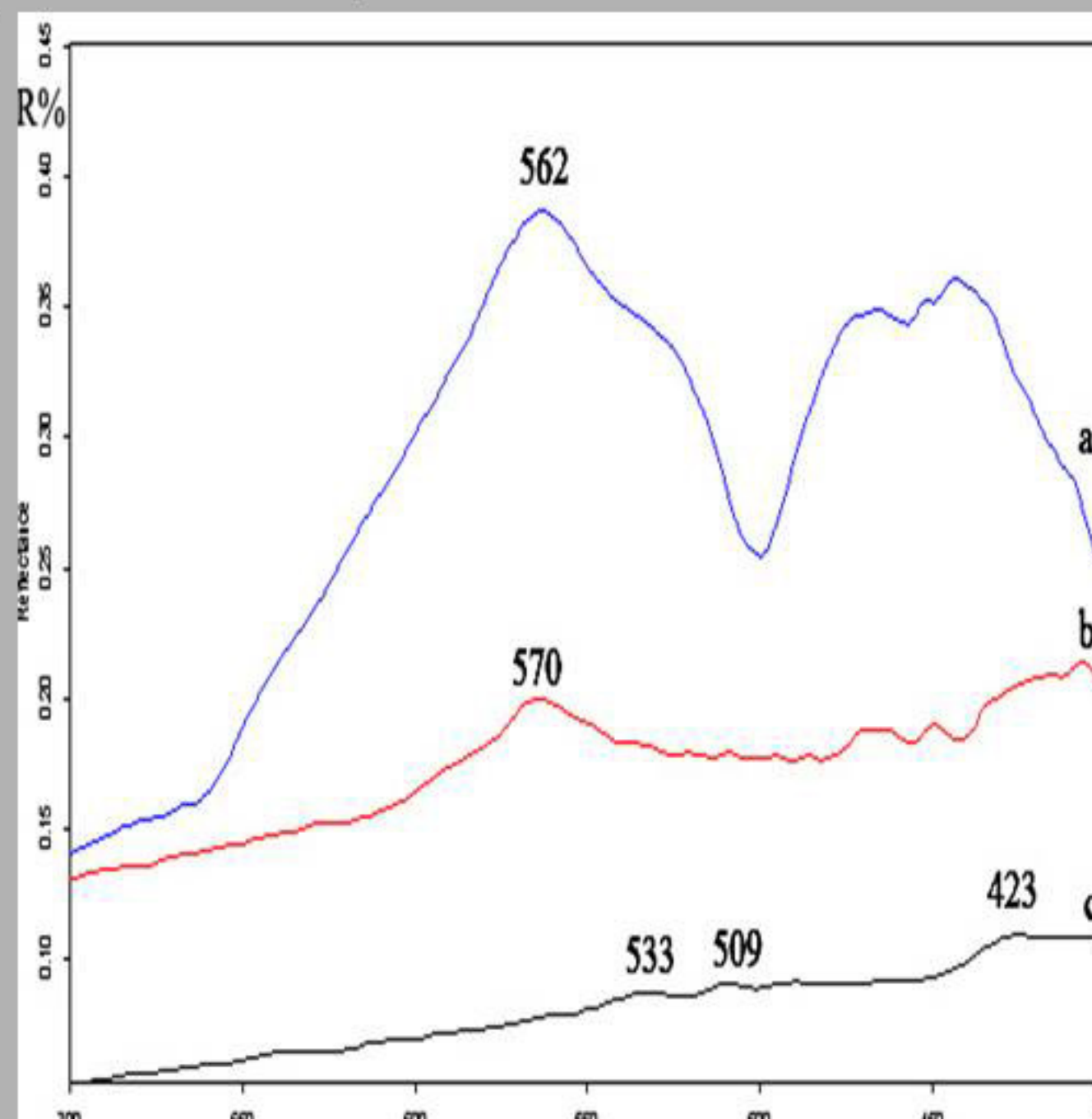
Figure 4. IRS of minerals (a: magnetite, b: Ti-magnetite, c: rutile) within the ceramic matrix from Cuanalan pottery.
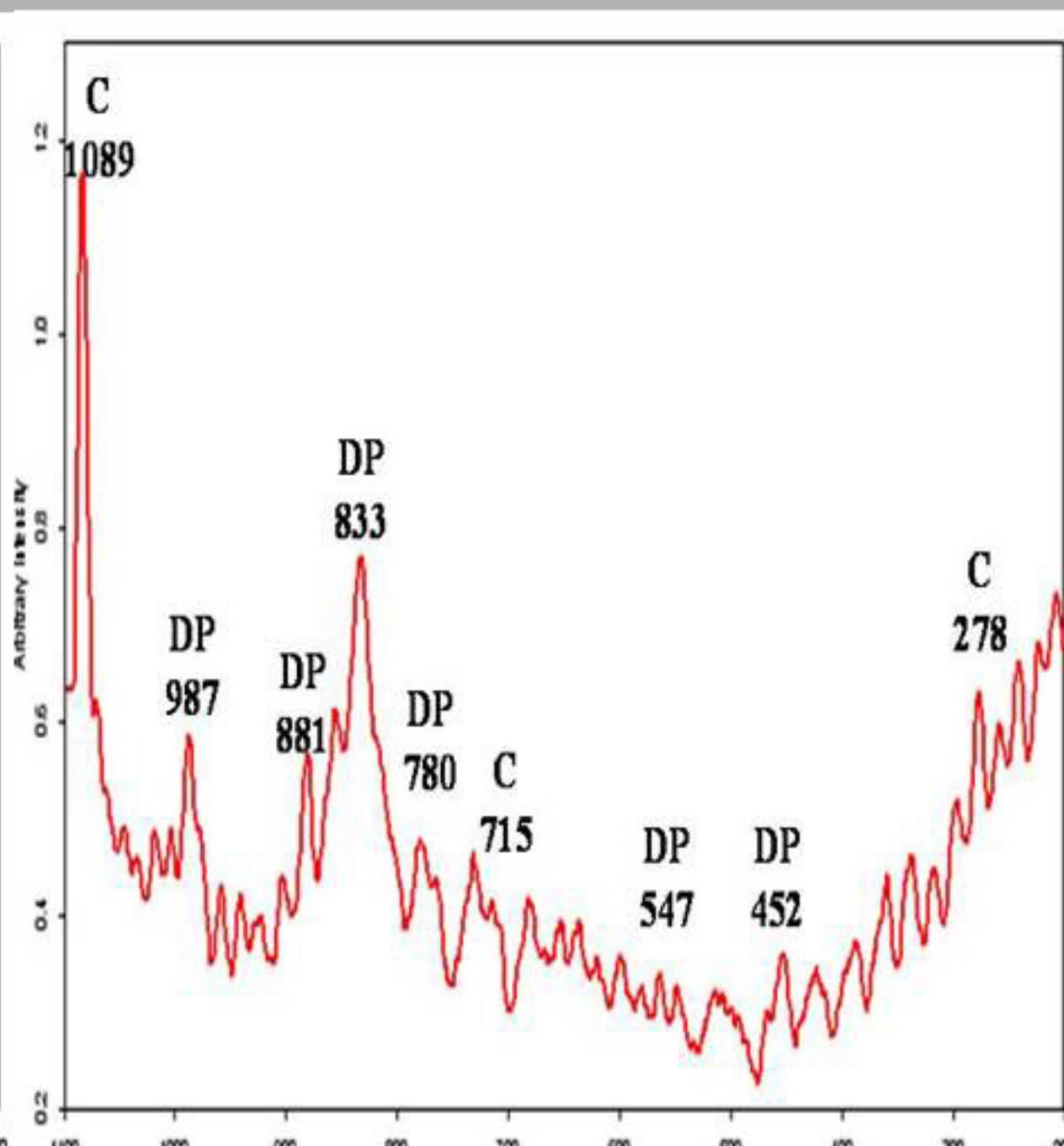
Figure 5. RMP spectra of calcareous Mayan pottery(Kaminaljuyú area, Guatemala) containing disordered phase (DP) and calcite (C).
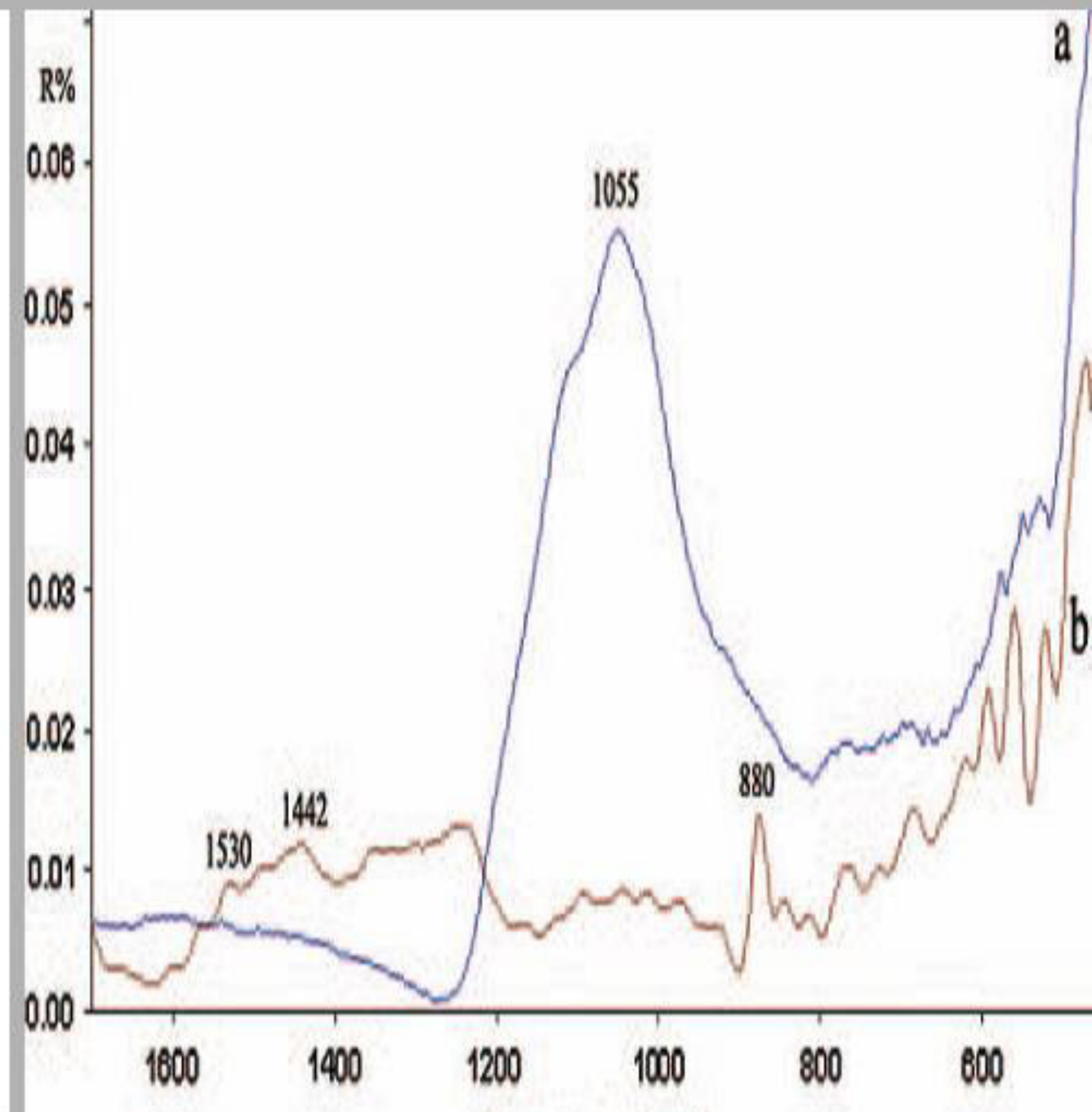
Figure 6. Representative FTIR reflection spectra in the range of 1700–400cm^{-1} of the ceramic matrix of pottery excavated at (a) Cuanalan, a formative village, Mexico, and (b) Kaminaljuyú area, Guatemala.

RESULTS: Taking advantage of the recent development of RMP and IRS techniques, we report for the first time a survey of pre-Columbian Mesoamerican ceramic materials from two sites: Cuanalan (Teotihuacán, Mexico) and Kaminaljuyú area (Guatemala). The Raman spectra obtained from selected areas of the rough fragments from the Teotihuacan ceramic materials show that these samples are characterized by the highly heterogeneous body matrix mineralogy due to the presence of a large variety of minerals such as quartz, feldspars (alkali polymorph and plagioclase), diopside, magnetite and Ti-magnetite, and one titanium oxide, rutile (Figure 3). Crystal chemical features on some mineralogical phases were also detected. In particular, the internal vibration of the $Fe^{3+}O_6$ octahedron has been assigned as the major contributor to the fundamental Raman broad band of magnetite failing around 662-665 cm^{-1} which is typical of the inverse spinel structures. This band shifts towards highly wave numbers (670-675 cm^{-1}) in the Raman spectrum of Ti-magnetite. The phenomenon occurs because there is the solid solution in the magnetite-ulvöspinel structures where the vibrations of $Ti^{4+}O_6$ and $Fe^{3+}O_6$ octahedra control their Raman spectra features. When forming Ti-magnetite the main Raman peak is shifted to upward position, consistent with the increase of $Ti^{4+}O_6$ fractions in their structures. The IRS spectra obtained from selected areas of the Cuanalan ceramic fragments confirm the results of RMP: these samples are highly heterogeneous, containing a large variety of minerals (Figure 4). RMP studies of the Mayan ceramics from Guatemala have shown their different mineralogy and chemistry. Due to the presence of calcite (some characteristic Raman CO_3 lines were observed – Figure 5) and the absence of diopside and Ti-oxides in ceramic pottery from the Kaminaljuyú area a firing temperature somewhere between 600-700ºC can be deduced. A representative FTIR reflection spectrum of the ceramic matrix of Cuanalan pottery (Figure 6) was indicative of noncalcareous ceramic materials showing strong SiO vibration of meta-clay. The IRS spectra of the Mayan ceramics indicate a weakly calcareous ceramic matrix with weak CO_3 vibration of microcrystalline calcite. These results demonstrate that the firing and cementation of ceramics from this area was obtained by low-temperature sintering [4].

CONCLUSIONS

1. The present study demonstrates that the combined use of the non-destructive RMP and IRS techniques is useful for mineralogical analysis, crystal chemical characterization and for the determination of firing temperatures of ancient pre-Columbian Mesoamerican pottery.

2. The combined application of RMP and IRS improves the identification of the mineralogical phases in the composition of the pottery and makes it possible to analyze the new phases that are formed during the firing of the clayey raw material to pottery.

3. With the recent development of RMP and IRS techniques, these spectroscopic methods are emerging as an important tools in mineralogical research and, in particular, in the case of in-situ studies of the mineralogical composition of pre-Columbian Mesoamerican pottery.

References

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