Comparative micro-Raman study of the Nakhla and Vaca Muerta meteorites

F. Rull,1,2* J. Martinez-Frias,1,2 A. Sansano,1 J. Medina1 and H. G. M. Edwards3

1 Unidad Asociada al Centro de Astrobiología, Universidad de Valladolid–CSIC, 47006 Valladolid, Spain
2 Centro de Astrobiología CSIC–INTA, Carretera de Ajalvir, Torrejón de Ardoz, Madrid, Spain
3 Chemical and Forensic Sciences, University of Bradford, Bradford BD7 1DP, UK

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A comprehensive micro-Raman spectroscopic analysis of the Nakhla and Vaca Muerta meteorites is reported. The major and minor mineral components were identified from comparison with mineralogical standards and literature databases. The compositions of pyroxenes and olivines were obtained using only this technique and correlation data between band parameters and the chemical composition of reference materials existing in the literature. The presence of calcite in both meteorite specimens was noted; its identification inside eucrite grains in the Vaca Muerta meteorite is particularly noteworthy. Their spectral parameters show strong similarities. Aragonite associated with calcite is reported for the first time in Vaca Muerta meteorite. Spectra of siderite, which appears associated with clinopyroxenes, are also reported in Nakhla meteorite. Iron oxides were analysed in detail in both meteorites. Magnetite is the main oxide phase observed in Nakhla and goethite, lepidocrocite and magnetite in Vaca Muerta. In both cases haematite was not observed. A comparison of the spectral parameters of these mineral phases observed in both meteorites was made and their possible origin as secondary minerals is discussed. This study stresses the potential of Raman spectroscopy in the mineralogical characterization of meteorites on a very small scale and also the potential applications of Raman spectroscopy for use on landers or rovers on the surface of Mars or other planetary bodies. Copyright © 2004 John Wiley & Sons, Ltd.

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INTRODUCTION

The SNC meteorites are igneous rocks, named after the type specimens of the three original sub-groups (Shergotty, India, 25 August, 1865; Nakhla, Egypt, 28 June 1911; Chassigny, France, 3 October 1915). They fall into four main groups: shergottites, nakhlites, chassignites and orthopyroxenites. The age range and mineral compositions of the SNCs both suggest that they formed on a planetary body larger than the known asteroids. During the last 25 years there has been increasing evidence that the SNC group of meteorites originated on Mars.

Since the first work of Walker et al.,2 Nyquist et al.,3 Wood and Ashwal4 and Bogard and Johnson,5 different geochronological, cosmochemical and isotopic criteria have been proposed to verify the Martian origin of the SNCs, and also to find clues which additionally identify differences with respect to terrestrial igneous rocks and asteroidal and Moon meteorites.6–8 The radiometric ages of the Martian meteorites spread over a wide range of time. While ALH84001 is the oldest at about 4.5 billion years, shergottites are fairly young at about 180 million years. Nakhlites have an estimate age of 1.37 billion years from the geochronological study carried out by Papanastassiou and Wasserburg9 using the rubidium–strontium dating method. In addition, most Martian meteorites have higher contents of volatiles than typical igneous meteorites derived from asteroids. However, the most important and conclusive evidence that the SNC meteorites originated on Mars comes from the measurement of gases trapped in one meteorite’s interior which matched the data measured by the Viking lander in the Martian atmosphere.5,10–12

The Nakhla meteorite can be described as an olivine-bearing clinopyroxenite consisting mostly of augite with less abundant Fe-rich olivine, plagioclase, K-feldspars, Fe–Ti oxides, FeS, chalcopyrite and a hydrated alteration phase that resembles ’iddingsite’.11,13 Nakhla is also the signature meteorite for the nakhlite subgroup of the SNC meteorites.

*Correspondence to: F. Rull, Unidad Asociada Centro de Astrobiología Universidad de Valladolid–CSIC, 47006 Valladolid, Spain. E-mail: rull@fmc.uva.es
Mesosiderites are mixtures of metal and silicate melting products that appear to have formed when the impact ejecta from the collision of differentiated asteroids reaccreted. Mesosiderites formation can be considered as analogous to the impact that is believed to have formed the Earth's moon.

The Vaca Muerta mesosiderite was originally found in 1861 in Taltal in the Atacama Desert (Chile). The Vaca Muerta mesosiderite is a differentiated silicate and metal-rich meteorite containing many eucrites and other silicate inclusions. Eucrites are basaltic igneous rocks which are mainly composed of plagioclase–pigeonite which were probably formed through the eruption of basaltic lavas on the surface of their parent body (a differentiated asteroid, possibly 4 Vesta). Nevertheless, many of them have experienced post-crystallization processes such as brecciation, impact melting and, particularly, recrystallization, as a result of being subjected to variable degrees of thermal metamorphism.

The Vaca Muerta mesosiderite has been widely studied hitherto: geochronological dating, petrogenetic characterization, noble gas and metal analysis and NIR reflectance spectroscopy have been carried out previously but no detailed Raman spectroscopic studies have been reported.

Raman spectroscopy has been specifically applied to meteorite analysis over the last 25 years. In the last decade, the application of micro-Raman spectroscopy to meteorites has attracted interest because of the possibility of identifying individual mineral grains and to study aspects such as phase transformations and impact effects. This interest is increasing now in parallel with the development of mini-Raman spectrometers as analytical tools for future missions to Mars.

A previous Raman study of the Nakhla meteorite was performed by Edwards et al. in which some of the main minerals species were identified. The Raman analysis of weathering processes and secondary mineral formation in this meteorite have also been undertaken. The first preliminary comparative analysis using Raman spectroscopy between the Nakhla and Vaca Muerta meteorites was reported by Rull et al. and Raman spectra of calcite globules in the latter have been reported recently for the first time. Nevertheless, a detailed spectral analysis of these meteorites has not been undertaken at our knowledge and it constitutes the main purpose of the present work.

Micro-Raman spectroscopy could be used to analyse in a completely non-destructive way individual minerals grains, which offers some unique capabilities as an analytical method in the study of meteorites prior to or in parallel with other complementary microscopic analytical techniques. The Raman spectrum is mainly sensitive to short-range effects in the mineral structure. Other transformations experienced by the meteorites such as partial recrystallization, crystal size and micro-morphological alterations would induce only subtle changes, mainly bandwidth and asymmetry modifications of the band profile.

Hence cation substitution or structure deformations affecting locally the internal vibrations of the anionic groups would have an important effect on the spectrum. Establishing correlations between bands parameters and chemical compositions represents an important goal for the precise crystallochemical characterization of meteorites on the microscopic scale and at the same time for in situ analysis of planetary bodies in space missions.

Moreover, it is important to stress that another feature of interest in the combined study of these two meteorites is the potential identification of the existence of eucrite inclusions in the Vaca Muerta mesosiderite which could permit the comparison of mineral phases which were formed from possible 'lava flows' of basaltic igneous rocks from a differentiated asteroid (possibly 4 Vesta) and those which originated from possible lava flows on Mars.

**EXPERIMENTAL**

In the case of the Vaca Muerta mesosiderite, Raman spectra were taken from the interior of a freshly cut flat section. Samples were kindly donated by Dr Canut de Bon of the Universidad de la Serena. The Nakhla sample consisted of one small piece (100 mg) from the Natural History Museum Collection, London (courtesy Dr Monica Grady). Raman spectra were taken directly from different parts of the specimen without any preparation.

The spectrometer used was a HoloLab 5000 (Kaiser Optical Systems) with a 256 × 1024 CCD detection system. The spectral resolution used ranged between 2 and 4 cm⁻¹. Illumination was performed with two different lasers at wavelengths of 632.8 and 785 nm in order to analyse the possible induced fluorescence and thermal effects and to compare the signal-to-noise ratio between the two cases.

To avoid thermal degradation effects which affect mainly oxide and hydroxide minerals, the laser power on the samples was kept below 10 mW in all cases.

For micro-Raman measurements the spectrometer was coupled to a Nikon microscope through a Mark II holographic Raman probe head using optical fibres. Microscope objectives of ×50 and ×100 were mainly used, which produced a laser spot on the samples 10 and 5 μm in diameter, respectively.

**RESULTS AND DISCUSSION**

**Nakhla**

Nakhla mineralogy mainly comprises the clinopyroxenes, augite and pigeonite with average composition Wo₄₀En₄₀Fs₂₀. Although the composition at the cores was found to be fairly homogeneous, some zoning was observed at the rims with Fe enrichment. Also Nakhla contains olivine, with minor feldspar, ilmenite and chlorapatite. Their paragenesis and textural relationships are consistent with formation
either as (1) a sill or dyke situated close to the Martian surface where the slow cooling gives the pyroxene crystals time to sink and accumulate to high concentrations (70–80% of the rock) or (2) as a surficial lava flow. Fine-grained areas between the pyroxene crystals and high concentrations of calcium in the olivine usually suggest the formation in a rapidly cooled body, such as a lava flow, perhaps similar to the terrestrial Theo’s flow in Ontario, Canada. In addition to these characteristics, nakhlites also display secondary features resulting from the interaction between the magma and liquid water either during emplacement or through later alteration following crystallization. The alteration products which have been detected in nakhlites include sulfates, clay minerals and carbonates, which are $^{13}$C-enriched.

The Raman spectra obtained are consistent with these descriptions. Augite clinopyroxenes are the major mineral phases identified in Nakhla meteorite, followed by olivines. Clinopyroxenes show, in general, fairly quite homogeneous spectra with few exceptions (Fig. 1). The most intense bands at 1010 and 668 cm$^{-1}$ have been assigned to the stretching $\nu$Si-O$_{ab}$ and $\nu$Si-O$_b$–Si, respectively, where O$_{ab}$ and O$_b$ mean non-bonded oxygen and the chain-bonded oxygen of the SiO$_4$ tetrahedron, respectively, in the two oxygen-shared SiO$_4$ tetrahedra of inosilicates.

Also, medium intensity bands are found at 390, 359 and 322 cm$^{-1}$. The assignment of this triplet at low wavenumbers is difficult because strong mixing between cation translations and SiO$_4$ librations may occur. Nevertheless, it is accepted that the 322 cm$^{-1}$ band arises mainly from translations of the cations. These observed bands, and also the presence of weak bands at 556, 531 and 509 cm$^{-1}$, match fairly well with the spectrum of diopside.

The SiO$_4$ vibrations are sensitive to cationic substitution, particularly the Si–O$_b$–Si stretching vibration and also the external modes. On this basis, several correlation charts have been established between Raman band parameters (mainly band positions) and chemical compositions of pyroxenes obtained by complementary macro- and micro-analytical methods. Using these correlation charts between the band positions of the 660 and 330 cm$^{-1}$ bands (see Fig. 1) and the ratio Mg/(Mg + Fe + Ca), a value of about 0.3–0.4 is found for the Mg/(Mg + Fe + Ca) ratio in Nakhlite meteorite. This value is consistent with the value obtained from the average chemical composition of these clinopyroxenes.

The Raman spectra of olivines also show great homogeneity in composition (Fig. 2). The band position and the relative intensities of the characteristic SiO$_4$ stretching doublet are also sensitive to the cation substitution. In this case the components appear at 816 and 844 cm$^{-1}$, respectively. Using the correlation chart established by Chopelas between the band position of the doublet and the Mg/Fe ratio in the forsterite–fayalite series, a high Fe content (about 80%) is obtained for olivines in Nakhla. This result is also confirmed by microprobe analysis.

Additionally, several other minerals have been identified in this study, most of which were not reported in our previous studies. Spectra of plagioclases are shown in Fig. 3. They show similar spectral features and can be closely related with anorthite. Quartz was also identified.

Oxides are shown in Figs 4 and 5. They correspond to magnetite (Fe$_3$O$_4$) and probably ilmenite, although in this last case the possibility that the spectrum corresponds to magnetite with a high content of Ti, as has been reported for the Nakhla meteorite, cannot be ruled out. Nevertheless, the absence of pure haematite in our measurements is noteworthy. Magnetite is known to undergo phase transition to haematite at about 400°C and this transformation is possibly expected from the impact history of the meteorite. In Fig. 6, the Raman spectra of siderite are presented. Siderite appears as a fine deposit on the rims or in the veins.
between clinopyroxene crystals. Their precise identification was performed using detailed deconvolution and band-fitting procedures (Fig. 7). Calcite is rare in Nakhla and appears as globules of about 10 µm diameter. The $v_1(\text{CO}_3)$ bands of calcite and siderite appear at the same spectral position, 1086 ± 1 cm$^{-1}$, but with very different bandwidths (FWHM ∼6 cm$^{-1}$ for calcite and ∼14 cm$^{-1}$ for siderite). The librational external modes appear at 282 and 294 cm$^{-1}$ for calcite and siderite, respectively, but in this case the bandwidths are similar.

There is general agreement that siderite in Nakhla is not a terrestrial alteration product. Carbonates in Mars meteorites are thought to be the major products of percolation and evaporation of brines under pressure of carbon dioxide. Nevertheless, their precise origin is still controversial. Bridges et al. suggest the most plausible models for secondary mineral formation in SNC meteorites involve
the evaporation of low-temperature brines. Harvey and McSween\textsuperscript{42} proposed that the carbonates were formed from a high-temperature interaction between CO\textsubscript{2}-rich fluids and pyroxenes, although in a different model\textsuperscript{43} they proposed that carbonate globules formed at low temperatures.

From the Raman spectra shown here it is not possible to decide unambiguously the possible origin of carbonates found in Nakhla meteorite. Nevertheless, comparison of the spectral characteristics of siderite with those of terrestrial analogues seems to support the low-temperature evaporation processes. Also, the association of siderite and magnetite suggests thermal decomposition and oxidation probably during subsequent impacts events.

**Vacca Muerta**

The Vaca Muerta mesosiderite mostly comprises pyroxene (pigeonite, augite) and plagioclase (Ab\textsubscript{3} 9 to Ab\textsubscript{9} 4) as major components with some silica grains and minor components such as troilite, metallic Fe–Ni, ilmenite, merrillite and chromite.\textsuperscript{17,18} Limonite, formed by terrestrial weathering, has also been described. Recently, as mentioned above, small calcite grains have been identified in the interior of the eucrite inclusions.\textsuperscript{31}

In Fig. 8 are plotted the micro-Raman spectra obtained from pyroxene grains, which represent the major part of the minerals found in the Vaca Muerta mesosiderite.

The pyroxenes are clearly identified as orthopyroxenes and using the same correlation charts\textsuperscript{36–38} between the Mg/(Mg + Fe + Ca) ratio and the band positions of the Si–O–Si band at 676 cm\textsuperscript{-1} and the band at 335 cm\textsuperscript{-1}, a value of the Mg/(Mg + Fe + Ca) ratio between 0.6 and 0.7 is obtained. This value indicates a composition close to that of hipersthene and is fairly homogeneous among the different grains analysed.

Figure 9 shows the spectra of plagioclases and olivines. Plagioclases show a relatively high content in anorthite, as deduced from the position of the doublet of the SiO\textsubscript{4} internal vibrations at 505 and 485 cm\textsuperscript{-1} in comparison with appropriate reference spectra.

Olivines were found in the mesosiderite external crust. Their composition, as deduced from the doublet observed at 524 and 856 cm\textsuperscript{-1} using the previously mentioned correlation charts, is consistent with a low Fe content, in agreement with the chemical analysis.

In Fig. 10, the micro-Raman spectra of Fe oxides and hydroxides are shown. Goethite (α-FeOOH) and lepidocrocite (γ-FeOOH) are relatively abundant minerals in the Vaca Muerta mesosiderite. Magnetite is less abundant. In some cases weak and broad bands around 680–700 cm\textsuperscript{-1} were also observed, which tentatively can be associated with maghaemite (γ-Fe\textsubscript{2}O\textsubscript{3}). However, hematite was not found.
in our study. Haematite shows strong bands at 226 and 396 cm\(^{-1}\) and some medium to weak bands at 410, 612 and 659 cm\(^{-1}\). As mentioned above, magnetite undergoes a phase transformation to maghaemite at about 200 °C and this mineral then transforms to haematite at about 400 °C.\(^{40}\) The absence of haematite could support the idea that the meteorite sample has not been subjected to high temperatures during its long history of impacts and weathering processes. Nevertheless, these facts can be also consistent with a terrestrial weathering process after the fall.

Calcite was observed in Vaca Muerta as small globules 5–10 µm in diameter generally situated in the interior of the eucrite inclusions and their spectra were reported for the first time in previous papers.\(^{31,32}\) A detailed analysis was performed here in a different sample in which also several globules have been observed. Some of the obtained spectra are shown in Fig. 11.

In some cases these globules appear associated with oxides. In a few cases the spectra show notable differences depending on the position. In the centre is clearly calcite and at the rims is aragonite (Fig. 12).

Although calcite is trigonal (space group \(R\)-3\(c\)) and aragonite is orthorhombic (space group \(Pmcn\)), both show similar spectral positions for the totally symmetrical carbonate stretching mode (1086 and 1084 cm\(^{-1}\), respectively). Nevertheless, they differ substantially for the low-wavenumber external modes which are more sensitive to structural changes. For identification purposes the librational modes of carbonate at 282 cm\(^{-1}\) in calcite and 207 cm\(^{-1}\) in aragonite are useful (see Fig. 12). The carbonate bending mode is also different but the typical doublet shown in aragonite around 704 cm\(^{-1}\) is not observed in Vaca Muerta sample.

The precise origin of aragonite is not clear. As calcite can transform in aragonite at low temperature and high pressure, a possible explanation may be related to this pressure transformation undergone during the long impact history of the mesosiderite. Other possibilities, such as a biogenic origin after the fall, can be ruled out considering its spatial distribution (i.e. calcite in the centre and aragonite at the edges). If aragonite globules were formed under biogenic conditions they normally should transform with time into calcite owing to the instability of aragonite. Hence calcite would appear at the rims. Moreover, biogenic aragonite is generally amorphous and the narrow observed bandwidths are not consistent with that.

**CONCLUSIONS**

A detailed comparative micro-Raman spectroscopic study of two meteorites, Nakhla and Vaca Muerta, with fairly well established different origins has been performed. The results obtained confirm the previous conclusions obtained by complementary analytical techniques about the general mineralogy of the meteorites. Nevertheless, by using only this technique and correlation data between band parameters and the chemical composition of reference materials existing in the literature for pyroxenes and olivines, very valuable mineralogical information has been obtained.

Thus, Raman spectroscopy provides a unique opportunity to perform relatively fast semi-quantitative analyses of most minerals in a non-destructive way and on a very small scale, which, emphasizes the potential applications of Raman spectroscopy on landers or rovers on the surface of Mars or other planetary bodies.

Moreover, micro-Raman spectroscopy has permitted mineralogical information to be obtained through the identification of new spectral features in the meteorites.

Siderite and calcite carbonates were analysed in Nakhla meteorite. Calcite appears as rare isolated globules whereas
siderite appears associated with clynopyroxene. These spectra seem not to have been reported previously in Naklha meteorite, to our knowledge. Also, calcite and aragonite have been found in Vaca Muerta mesosiderite. The spectrum of this last mineral is also reported for the first time, to at our knowledge.

The comparative analysis of the Raman spectra between the calcite globules shows strong similarities in the band parameters from the two meteorites including very similar intensity ratios among the different internal and external bands.

Their measured bandwidths also suggest a high crystalline order in calcite compared with those of the siderite found in Naklha meteorite.

The fact that Naklha was recovered very soon after the fall and the fact that the spectra of Vaca Muerta were observed in the interior of the meteorite suggest that calcite was formed from alteration processes other than the terrestrial ones.

Also, the presence of aragonite at the edges of calcite globules in Vaca Muerta can be related to the presence of calcite before some impact event, which presumably have happened before the fall.

Nevertheless, the composition of iron oxides in Vaca Muerta such as magnetite, goethite and lepidocrocite, and the absence of haematite, are indicative of a low-temperature weathering exposure in which the possible contribution of the terrestrial post-fall weathering is difficult to assess from the Raman spectra. Work is in progress to investigate these aspects more precisely.

**REFERENCES**