The Villalbeto de la Peña meteorite fall: III. Bulk chemistry, porosity, magnetic properties, $^{57}$Fe Mössbauer spectroscopy, and Raman spectroscopy

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Abstract—Detailed mineralogical and chemical studies and measurements of the magnetic properties and porosity of the Villalbeto de la Peña (L6) chondrite are reported. The measured abundances of 36 chemical elements are within the range observed for L6 chondrites for most elements, except for Pd and Os, which are particularly abundant in Villalbeto de la Peña. The specific magnetic susceptibility of the meteorite is $4.85 \pm 0.05 \times 10^{-9}$ m$^3$ kg$^{-1}$ and the porosity is 4.7%. The $\frac{J_{RS}}{J_S}$ ($1.2 \pm 0.2 \times 10^{-3}$) and $H_C$ ($3.3 \times 10^{-4}$ T) values recorded are among the lowest ever reported for a chondrite. $^{57}$Fe Mössbauer spectroscopy of the whole rock indicates that the meteorite faced oxidizing conditions prior to fall. The Mössbauer spectrum of the metal fraction shows the presence of the only ferromagnetic phases kamacite and taenite. No tetrataenite is present, which is in total accordance to magnetic studies. Raman spectra yield compositional values for olivine ($\chi_{Mg} \approx 0.76$), orthopyroxene ($\chi_{Mg} \approx 0.79$), and clinopyroxene ($\chi_{Mg} \approx 0.49$). Raman spectra of phosphate in shock veins indicates that Villalbeto de la Peña was not severely shock-metamorphosed.

INTRODUCTION

The fall of the Villalbeto de la Peña meteorite on January 4, 2004 (Spain) is one of the best documented in history for which atmospheric and orbital trajectory, strewn field area, and recovery circumstances have been described in detail (Llorca et al. 2005; Trigo-Rodríguez et al. 2006). Photometric and seismic measurements during the event, together with radioisotopic analysis of several recovered specimens, suggest an original mass of about 760 kg. About 50 specimens were recovered from a strewn field of nearly 100 km$^2$. Preliminary work by Llorca et al. (2005) revealed that Villalbeto de la Peña is a moderately shocked (S4) equilibrated ordinary chondrite (L6) with a cosmic-ray exposure age of $48 \pm 5$ Myr. In this work we report a study of the mineralogy, bulk chemistry, magnetic properties, and porosity of Villalbeto de la Peña meteorite using a wide variety of techniques in order to fully characterize this genuine meteorite.

BULK CHEMISTRY

Abundances of 36 chemical elements were determined in four different samples from the interior of two meteorite specimens (Table 1). Analyses of trace elements were performed by means of inductively coupled plasma–mass spectrometry (ICP-MS) with a PerkinElmer Elan 6000 apparatus, whereas major and minor elements were analyzed by inductively coupled plasma–optical emission spectroscopy (ICP-OES) using PerkinElmer Optima 3200 RL and a Thermo Jarrell Ash instruments. Two independent methods were used for sample preparation, an acid digestion treatment in a sealed Teflon reactor and an alkaline fusion in a zirconium crucible. The content of Fe (21.3%) and the values of Mg/Si = 0.92, Al/Si = 0.06, and Fe/Si = 1.17 match well with the values of L-group chondrites. For most elements, the measured abundances are within the range observed for L6 chondrites, and values within 20% of the average are found (Kallemeyn et al. 1989; Friedrich et al. 2003). Pd and Os are particularly abundant in Villalbeto de la Peña, but the ratio Os/Pd = 0.83 matches with that of ordinary chondrites (Horan et al. 2003). Some highly volatile elements (such as Te and Ga) are lower in Villalbeto de la Peña than in average L6 chondrites, but others (such as Rb and Zn) have normal abundances. Using the electron microprobe analyses of olivine, pyroxene, plagioclase, chromite, troilite, kamacite, and taenite reported in Llorca et al. (2005) and the...
Table 1. Elemental abundances in the Villalbeto de la Peña meteorite. a.d. = acid digestion; a.f. = alkaline fusion.

<table>
<thead>
<tr>
<th>Element</th>
<th>Unit</th>
<th>Sample preparation</th>
<th>Method</th>
<th>Villalbeto de la Peña</th>
</tr>
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<tbody>
<tr>
<td>Li</td>
<td>μg</td>
<td>g⁻¹</td>
<td>a.d. ICP-MS</td>
<td>2.3 ± 0.2</td>
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<td>Na</td>
<td>mg</td>
<td>g⁻¹</td>
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<td>Mg</td>
<td>mg</td>
<td>g⁻¹</td>
<td>a.d. ICP-ES</td>
<td>164.7 ± 5.0</td>
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<tr>
<td>Al</td>
<td>mg</td>
<td>g⁻¹</td>
<td>a.f. ICP-OES</td>
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</tr>
<tr>
<td>Si</td>
<td>mg</td>
<td>g⁻¹</td>
<td>a.d. ICP-ES</td>
<td>11.2 ± 0.4</td>
</tr>
<tr>
<td>P</td>
<td>μg</td>
<td>g⁻¹</td>
<td>a.d. ICP-ES</td>
<td>224.4 ± 0.9</td>
</tr>
<tr>
<td>S</td>
<td>μg</td>
<td>g⁻¹</td>
<td>a.d. ICP-ES</td>
<td>850 ± 130</td>
</tr>
<tr>
<td>K</td>
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<td>g⁻¹</td>
<td>a.d. ICP-ES</td>
<td>12.0 ± 0.3</td>
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<td>Ca</td>
<td>mg</td>
<td>g⁻¹</td>
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<tr>
<td>Sc</td>
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<td>g⁻¹</td>
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<td>9.6 ± 0.4</td>
</tr>
<tr>
<td>Ti</td>
<td>μg</td>
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<td>Cr</td>
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<tr>
<td>Mn</td>
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<tr>
<td>Fe</td>
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<tr>
<td>Co</td>
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<tr>
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<tr>
<td>Ge</td>
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<tr>
<td>Rb</td>
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<tr>
<td>Sr</td>
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<tr>
<td>Y</td>
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<tr>
<td>Zr</td>
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<td>2.5 ± 0.1</td>
</tr>
<tr>
<td>Mo</td>
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<td>a.d. ICP-MS</td>
<td>5.9 ± 0.1</td>
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<tr>
<td>Ru</td>
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<td>a.d. ICP-MS</td>
<td>2.0 ± 0.2</td>
</tr>
<tr>
<td>Pd</td>
<td>μg</td>
<td>g⁻¹</td>
<td>a.d. ICP-MS</td>
<td>1.15 ± 0.04</td>
</tr>
<tr>
<td>Te</td>
<td>μg</td>
<td>g⁻¹</td>
<td>a.d. ICP-MS</td>
<td>0.84 ± 0.03</td>
</tr>
<tr>
<td>Ba</td>
<td>μg</td>
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<td>a.d. ICP-MS</td>
<td>0.33 ± 0.02</td>
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<tr>
<td>Ce</td>
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<td>g⁻¹</td>
<td>a.d. ICP-MS</td>
<td>4.8 ± 0.1</td>
</tr>
<tr>
<td>Eu</td>
<td>μg</td>
<td>g⁻¹</td>
<td>a.d. ICP-MS</td>
<td>1.2 ± 0.1</td>
</tr>
<tr>
<td>Os</td>
<td>μg</td>
<td>g⁻¹</td>
<td>a.d. ICP-MS</td>
<td>0.10 ± 0.01</td>
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<tr>
<td>Ir</td>
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<tr>
<td>Pt</td>
<td>μg</td>
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<td>a.d. ICP-MS</td>
<td>0.51 ± 0.01</td>
</tr>
<tr>
<td>Th</td>
<td>μg</td>
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<td>a.d. ICP-MS</td>
<td>1.2 ± 0.1</td>
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<tr>
<td>U</td>
<td>μg</td>
<td>g⁻¹</td>
<td>a.d. ICP-MS</td>
<td>0.04 ± 0.01</td>
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</tbody>
</table>

bulk content of Si, Mg, Fe, Al, Ca, Na, S, Ni, and Cr reported in Table 1, it is possible to perform mass balance calculations and derive modal mineralogy. Villalbeto de la Peña is constituted approximately by 51.4% olivine, 25.0% pyroxene, 8.8% plagioclase, 6.1% troilite, 4.5% kamacite, 2.3% taenite, and 1.2% chromite. The olivine/pyroxene ratio is 2.1, typical of L-group chondrites (Rubin 1997).

**MAGNETIC PROPERTIES**

For magnetic measurements, three samples of ~0.3–0.4 g of the Villalbeto de la Peña meteorite were taken from the interior of separate pieces of the fall that were collected just a few days after they fell. Hysteresis loops were run on all samples. From the hysteresis loops the saturation magnetization $J_s$, the remanent saturation magnetization $J_{RS}$, the coercive force $H_C$, and the remanent coercive force $H_R$ were determined (Sugiura et al. 1987). Magnetic susceptibility measurements were made at a low field (0.5 mT). All the magnetic measurements were performed at 300 ± 0.2 K with a Quantum Design MPMS-XL SQUID magnetometer. The magnetic parameters at room temperature are shown in Table 2. The data for the three Villalbeto de la Peña specimens are comparable and indicate the magnetic homogeneity of this meteorite, like most ordinary chondrites (Gattacceca et al. 2003). Specific magnetic susceptibility $\chi$, measured on the three samples, gave a log $\chi$ of 4.85 ± 0.05 (in $10^{-3}$ m$^3$kg$^{-1}$), typical of other L chondrite falls, 4.87 ± 0.10 (Rochette et al. 2003; Consolmagno et al. 2006), and 4.87 ± 0.08 (Smith et al. 2006). Similarly, the log $J_S$ and log $J_{RS}$ values recorded of 4.13 ± 0.02 and 1.2 ± 0.1 (in $10^{-3}$ Am$^2$kg$^{-1}$), respectively, are in the range of other L chondrites (Sugiura et al. 1987) as well as the value of the coercive force of 3.3 ± 0.4 (in 10$^{-4}$ T). Therefore, the Villalbeto de la Peña meteorite has bulk magnetic properties well in agreement with other studied L6 chondrites. However, the $J_{RS}/J_S$ (1.2 ± 0.2 × 10$^{-3}$) and $H_C$ values recorded for Villalbeto de la Peña are among the lowest ever reported for a chondrite, and indicate that tetrataenite is absent. Further, one of the meteorite samples used for this study was heated under Ar at 923 K for 4 h and the hysteresis loop was again recorded. The hysteresis parameters before and after heating (Table 4, sample 3) are unchanged, which confirms that no tetrataenite is present (Nagata et al. 1982; Wasilewski 1988). Then, if kamacite and taenite are the only metal phases present in the meteorite, it is possible to calculate the total metal content of Villalbeto de la Peña from the magnetic susceptibility taking into account the theoretical $\chi$ value for kamacite-taenite spheres of 380 × 10$^{-6}$ m$^3$kg$^{-1}$ (Rochette et al. 2003). The calculated wt% of metal in the Villalbeto de la Peña meteorite from magnetic measurements is 6.6 ± 0.3. This value is in full agreement with the amount of metal calculated from chemical analysis of 6.8 wt%.

**GRAIN DENSITY AND POROSITY**

The grain density ($\rho_g$, density that excludes pores and voids) of Villalbeto de la Peña meteorite was determined with an helium pycnometer and was 3.59 ± 0.05 gcm$^{-3}$. Magnetic susceptibility and grain density are commonly correlated for meteorite falls since both are intensive variables that vary with iron content (Britt et al. 2003; Consolmagno et al. 2006). The values of magnetic susceptibility and grain density of Villalbeto de la Peña plot well within the L chondrite group in a $\chi$ versus $\rho_g$ graph for meteorite falls (Consolmagno et al. 2006). From the grain density determined in this work and the bulk density value reported in Llorca et al. (2005) of 3.42 ±
0.10 g cm$^{-3}$, the porosity of the Villalbeto de la Peña is calculated to be 4.7%.

**MÖSSBAUER SPECTROSCOPY**

About 0.5 g of the interior of a Villalbeto de la Peña meteorite specimen was ground to fine powder and about 50 mg of this powder was sandwiched between adhesive tape in an area of ~1 cm$^2$ to make a Mössbauer absorber. A second sample was also prepared for Mössbauer spectroscopy after mineral separation in order to study the metallic phases of the meteorite, following the procedure described by Kong et al. (1995). The wt% of metal obtained at the end of the separation process was 6.5, which is similar to the amount of metal obtained by chemical analysis and magnetic measurements. Taking into account that no residual silicate and troilite signals appear in the Mössbauer spectrum of the metal separate (see below), the agreement of metal wt% obtained demonstrates the goodness of the separation procedure and, most important, that the metal analyzed is fully representative of the bulk metal composition. Mössbauer spectra were recorded at 300 K using a constant acceleration Mössbauer spectrometer equipped with a $^{57}$Co/Rh source. The parameters of all Mössbauer spectra are listed in Table 3. The Mössbauer spectrum for the Villalbeto de la Peña powdered sample is shown in (a) of Fig. 1. Two well-defined, strong paramagnetic doublets with quadrupole split absorptions of $QS = 2.92$ and 2.10 mm s$^{-1}$ are characteristic for ordinary chondrites and correspond to Fe$^{2+}$ in the ferromagnesian silicates olivine and pyroxene, respectively (Ortalli et al. 1990). In addition to the strong paramagnetic doublets ([b] and [c] of Fig. 1), several other weak absorptions are present, which are attributed to magnetically ordered troilite (Grandjean et al. 1998) and metallic phases ([d] and [e] of Fig. 1). The ratio of relative areas in the Mössbauer spectrum between olivine and pyroxene is 2.44, which is within the range of L-type ordinary chondrites, 1.9 to 2.5 (Verma et al. 2003). While the relative pyroxene area in Villalbeto de la Peña is similar to several other L chondrites (Verma et al. 2002, 2003), the olivine relative area is relatively quite high. The unusually large amount of olivine as well as the low amount of metal in the
whole rock spectrum may indicate that Villalbeto de la Peña
suffered oxidation during metamorphism. Reduced Fe in
metal was likely converted to \( \text{Fe}^{2+} \) which got incorporated in
the silicate olivine phase. This is also supported by the cobalt
enrichment found in kamacite (1.0 ± 0.1 wt%) from
microprobe analysis (Llorca et al. 2005). The average value
for the metallic/total iron in Mössbauer spectra is about 0.3 for
L chondrites (Verma et al. 2002), whereas this value is only
0.05 for Villalbeto de la Peña L6 chondrite. The Mössbauer
spectrum of the metal fraction is depicted in (a) of Fig. 2 and
consists of two six-line patterns due to the presence of
ferromagnetic phases kamacite ([b] in Fig. 2) and taenite ([c]
in Fig. 2). The presence of kamacite is reflected by the
magnetic hyperfine field of \( H_{hf} \approx 33.7 \) T for the strong sextet.
This assignment is consistent with near zero isomer shift and
quadrupole splitting (Table 3). The \( H_{hf} \) value recorded for
kamacite in Villalbeto de la Peña is well within the range
recorded for other ordinary chondrites of 33.2–33.7 T (Verma
et al. 2003). Taenite is identified in the spectrum of the
magnetic separate by the presence of a sextet with a magnetic
hyperfine field of \( H_{hf} \approx 31.4 \) T (Verma et al. 2003). The
observed line widths of \( W \approx 0.52 \) mm s\(^{-1}\) plot in the upper
region of the values reported for taenite in chondrites and
document local disorder in the environment of Fe atoms in the
taenite structure. The ratio of relative areas in the Mössbauer
spectrum of the metal fraction between kamacite and taenite is
3.3, which is similar to other L-type ordinary chondrites
(Abdu et al. 1997). The misfit in the central part of the metal
fraction spectrum is attributed to some minor Fe\(^{3+}\) species
formed by metal oxidation during sample manipulation.

**RAMAN SPECTROSCOPY**

Raman spectroscopy was performed both in micro and
macro mode with a Jobin Yvon T64000 instrument using an
Ar ion laser as an illumination source (514.5 nm) and a CCD
detector cooled at 140 K. Raman spectra in macro mode were
obtained separately over powdered samples of three different
meteorite specimens. For microRaman studies a single
polished meteorite chip was used. All Raman spectrum
recorded in macro mode were very similar. Prominent bands
at 820–821 and 850–851 cm\(^{-1}\) correspond to olivine and
result from the fundamental vibrations of \([\text{SiO}_4]\) tetrahedra.
Weak olivine bands are also observed at 915–917 and 954–956 cm\(^{-1}\).
Bands at 230–232, 333–334, 392–395, 661–663,
678–679, and 1007–1008 correspond to pyroxene. No other
bands are observed in macro mode, but a strong fluorescence
at 400–520 cm\(^{-1}\) could hide the most intense feldspar Raman
bands at about 500 cm\(^{-1}\). On the other hand, FeNi metal has
no active modes for Raman spectroscopy and troilite is a
weak Raman scatterer. Numerous spectra were taken from
individual olivine ([a] of Fig. 3) and pyroxene ([b] and [c] of
Fig. 3) grains in microRaman mode in order to determine
molar ratios of the major cations in the silicates, since the
different cations that occupy the octahedral sites affect the
peak positions of the fundamental vibrations. Olivine
grains exhibit bands always at 820 and 851 cm\(^{-1}\). Using the
correlations developed by Wang et al. (2004) to calculate the
\( \text{Mg}/(\text{Mg} + \text{Fe}) \) molar fraction (\( \chi_{Mg} \)) in olivine based on the
peak positions of the strongest doublet in the olivine spectrum,
it is deduced that olivine in Villalbeto de la Peña meteorite has \( \chi_{Mg} \approx 0.76 \). This is in excellent agreement with
microprobe data (\( \text{Fa} = 24.2 \pm 0.2 \) mol\%) (Llorca et al. 2005).
The FWHM value of the olivine Raman line at 820 cm\(^{-1}\) (\( \nu_1 \))
is ~18 cm\(^{-1}\), which is identical to the values recorded in macro
mode for this band of 17–18 cm\(^{-1}\). The FWHM values of the
\( \nu_1 \) olivine band in the Raman spectra of L6 ordinary
chondrites have been related to the degree of crystal-
structural disorder resulting from shock deformation
(Miyamoto et al. 1995), and spans from 10 cm\(^{-1}\) for poorly

**Fig. 2.** Mössbauer spectrum recorded at room temperature of the
metal fraction of Villalbeto de la Peña meteorite. Deconvolution
curves (b) and (c) correspond to kamacite and taenite phases,
respectively.

**Fig. 3.** Raman spectra of olivine (a), orthopyroxene (b), and
clinopyroxene (c) of Villalbeto de la Peña meteorite. (d) Raman
spectrum of merrillite in a shock vein.
shocked to 21 cm\(^{-1}\) for strongly shocked meteorites. The FWHM value of \(\approx\) 18 cm\(^{-1}\) for \(\nu_1\) in Villalbeto de la Peña is in accordance with the shock stage of S4 determined from petrographical studies (Llorca et al. 2005). The Mg/(Mg + Fe + Ca) molar fraction in pyroxene was determined from peak positions in Raman spectra recorded in micro mode ([b] and [c] of Fig. 3) of bands located at 330–337 and 668–682 cm\(^{-1}\) (Wang et al. 2004). For orthopyroxene, \(\chi_{\text{Mg}} \approx 0.79\), and for clinopyroxene, \(\chi_{\text{Mg}} \approx 0.49\). Clinopyroxene was not identified previously in Villalbeto de la Peña. In the Raman spectra recorded in macro mode it is not possible to distinguish bands from orthopyroxene and clinopyroxene, and bands at 333–334 and 678–679 cm\(^{-1}\) are intermediate between those of orthopyroxene and clinopyroxene recorded in micro mode. Therefore, by comparing band positions recorded in macro and micro mode in Raman spectra it is possible to estimate that the relative amount of orthopyroxene/clinopyroxene is about 7–8. Finally, in addition to the major crystalline silicates olivine and pyroxene, accessory minerals such as merrillite, \(\text{Ca}_9\text{MgNa(PO}_4\text{)}_7\), were also identified by Raman spectroscopy in Villalbeto de la Peña meteorite ([d] of Fig. 3). Strong Raman bands at 957–960 and 973–974 cm\(^{-1}\) originate from the symmetric stretching mode of [PO\(_4\)] tetrahedra, whereas bands of low intensity at 1017–1020 and 1080–1084 cm\(^{-1}\) result from antisymmetric vibrations. No evidence of high-pressure polymorph of merrillite was encountered in the shock veins of the Villalbeto de la Peña meteorite, which should exhibit a characteristic Raman spectrum with only one intense band at about 974 cm\(^{-1}\) (Xie et al. 2002). Considering that shock veins in Villalbeto de la Peña are thin, they likely cooled rapidly and should retain shock-induced high-pressure phases if they formed during shock events. A back transformation from \(\chi'\text{Ca}_3(\text{PO}_4)_2\) takes place only in thick shock veins, which are slower-cooling (Xie et al. 2002). The absence of high-pressure polymorph of merrillite in the shock veins of the Villalbeto de la Peña meteorite indicates that it was not severely shock-metamorphosed.

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