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Mössbauer parameters of ordinary chondrites influenced by the fit accuracy of the troilite component: An example of Chelyabinsk LL5 meteorite

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Abstract. The influence of the fit accuracy of the troilite component in the Mössbauer spectra of ordinary chondrites on the parameters obtained for other spectral components was evaluated using the Mössbauer spectrum of Chelyabinsk LL5 meteorite fragment with light lithology as a typical example. It was shown that with respect to the application of a usual sextet component where quadrupole interaction is taken into account in the first-order perturbation limit, substantial improvement of the spectrum fit can be achieved either by using the full Hamiltonian description of the troilite component or by its formal approximation with the superposition of three symmetric doublet components. Parameter values obtained for the main spectral components related to olivine and pyroxene were not sensitive to the fit of troilite component while parameters of the minor spectral components depended on the way of troilite component fitting.

Keywords: Mössbauer spectroscopy; Chelyabinsk LL5 ordinary chondrite; Mössbauer parameters; Troilite

1. Introduction

Ordinary chondrites are the group of stony meteorites the most frequently found on the Earth. These meteorites consist of the main iron-bearing phases such as olivine $(\text{Fe, Mg})_2\text{SiO}_4$, pyroxene $(\text{Fe, Mg, Ca})\text{SiO}_3$, troilite FeS , chromite FeCr_2O_4 , kamacite $\alpha\text{-Fe}(\text{Ni, Co})$, martensite $\alpha_2\text{-Fe}(\text{Ni, Co})$, taenite $\gamma\text{-Fe}(\text{Ni, Co})$, etc. The total amount of iron in ordinary chondrites is in the range of 19–28 wt. %, with 10–18 wt. % of iron in both olivine and pyroxene, 4–6 wt. % of iron in troilite and 2–17 wt. % of iron in metallic phase [1]. Therefore, ^{57}Fe Mössbauer spectroscopy is often used for study of ordinary chondrites. Mössbauer spectra of various ordinary chondrites are very complicated. In the studies using the low velocity resolution (conventional) Mössbauer spectroscopy the authors usually observed two magnetic components related to kamacite and troilite, and two quadrupole doublets related to olivine and pyroxene as well as additional ferric components in the weathered meteorites (see, for instance, [2–5]). However, application of Mössbauer spectroscopy with a high velocity resolution permitted us to reveal larger number of spectral components related to the ^{57}Fe in the M1 and M2 sites in olivine and pyroxene, α , α_2 and γ phases, and chromite [6–10]. It was shown earlier that the Mössbauer spectra of extracted and synthetic troilite cannot be fitted properly by treating the quadrupole interaction as a first-order perturbation (PFO) over the hyperfine magnetic interaction, but consideration of the full Hamiltonian (FH) is required to fit these spectra correctly [11, 12]. Similar approach was applied in the study of ordinary chondrites in [13, 14]. The relative area of troilite component in the Mössbauer spectra of ordinary chondrites may vary in the range of ~10–20%, and the fit of Mössbauer spectra of ordinary chondrites using PFO for troilite component lead to some errors indicated by differential spectra (see [8–10, 15]) and possible misfits of other spectral components. Therefore, we fitted the high velocity resolution Mössbauer spectra of three ordinary chondrites using FH applied for the troilite component [16], which significantly improved the fit quality. Here we consider the effect of different approaches to fit the troilite component in the Mössbauer spectrum of ordinary chondrites on the value of Mössbauer parameters obtained for the remaining spectrum components. For this purpose, as a typical example, we have used the high velocity resolution ^{57}Fe Mössbauer spectrum of a recently fallen Chelyabinsk LL5 ordinary chondrite fragment which was not yet weathered.

2. Experimental

We chose fresh Chelyabinsk LL5 meteorite fragment with light lithology (it was indicated as No 1a in [10]) immediately found after meteorite fall. This fragment was characterized using metallography and X-ray diffraction (Fig. 1). Thin powder of this fragment was glued on alumina foil free from iron with a thickness of $\leq 10 \text{ mg Fe/cm}^2$.

The Mössbauer spectrum was measured using an automated precision Mössbauer spectrometric system built on the base of the SM-2201 spectrometer with a saw-tooth shape velocity reference signal formed by the digital-analog converter using discretization of 2^{12} (quantification using 4096 steps). Details

and characteristics of this spectrometer and the system were given elsewhere [17–19]. The 1.8×10^9 Bq $^{57}\text{Co}(\text{Rh})$ source (Ritverc GmbH, St. Petersburg) was used at room temperature. The Mössbauer spectrum was measured in transmission geometry with moving absorber in the cryostat at 295 K and recorded in 4096 channels. For its analysis, the spectrum was converted into 1024 channels by a consequent summation of four neighboring channels to increase a signal-to-noise ratio for the minor spectral components. The resultant statistics of the spectrum was $\sim 8.5 \times 10^6$ counts per channel and signal-to-noise ratio was 248. The instrumental (systematic) error in the velocity values attributed to the spectrum points and in the hyperfine parameters was taken to be equivalent to ± 0.5 channel and ± 1 channel, respectively. If the statistical error calculated with the fitting procedure (fitting error) for the obtained fit parameters exceeded the instrumental (systematic) error we indicate the larger error instead. Criteria for the best fits were the followings: differential (residual) spectrum, normalized χ^2 , and a physical meaning of the spectral parameters. Values of δ are given relative to $\alpha\text{-Fe}$ at 295 K.

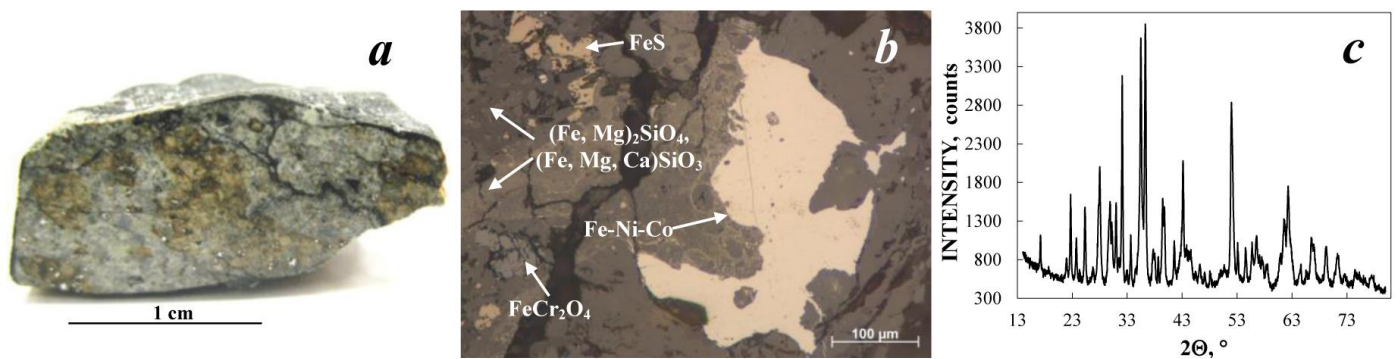


Figure 1 Chelyabinsk LL5 ordinary chondrite, fragment No 1a with light lithology (*a*), representative image of metallographic analysis with the main phases (*b*) and X-ray diffraction pattern indicating the presence of olivine, pyroxene and troilite as the main compounds (*c*).

The magnetic spectrum component of troilite in the Mössbauer spectrum of Chelyabinsk LL5 fragment was computer fitted with Lorentzian peaks via the least squares procedure in the following three ways:

- (a) with the UNIVEM-MS program by using a PFO sextet component,
- (b) with the UNIVEM-MS program by using a formal approximation (referred to as 3DA in the following) of the magnetic component with 3 symmetric doublet components all with equal line widths and with the area ratio of the outer and inner doublet components being fixed to 3, but with the center and separation of the doublet peaks being adjusted independently for the 3 doublets,
- (c) with version 4.0Pre of the MOSSWINN program [20], by using numerical diagonalization of the full static Hamiltonian of the magnetic and quadrupole hyperfine interactions for the excited and ground nuclear states, with the electric field gradient (EFG) tensor asymmetry parameter η and the azimuthal angle α of the hyperfine magnetic field in the EFG eigensystem being fixed to 0.3 and 49° , respectively (on the basis of [13]).

Justification for approximation (b) is provided by Figure 2 showing that considerable improvement of the fit can be achieved when instead of approximation (a) three doublets with equal line widths and with constrained area ratios are used to account for a spectrum component typical for troilite in ordinary chondrites. This may be a viable approximation especially when the most negative velocity peaks of the troilite component (the 1st and the 2nd peaks) do not overlap considerably with other minor components. In this case it is straightforward to fit the left peaks in both doublets with corresponding peaks at positive velocities.

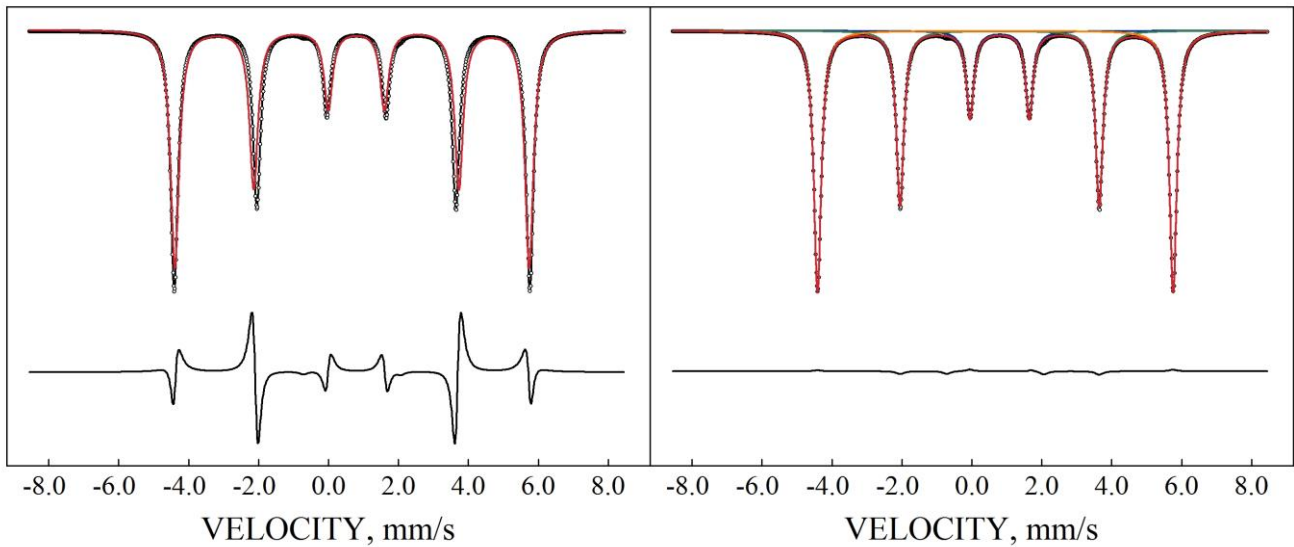


Figure 2 Typical theoretical curve (calculated via the FH method) describing the spectrum component of troilite (connected points), and its best fit achieved with a PFO sextet component (left) and with 3 symmetric doublets all with equal line widths and with their relative area fractions being constrained to 3:2:1 (right). Below the curves the corresponding residual spectra are displayed.

Concerning the remaining spectrum components in the Mössbauer spectrum of the selected chondrite sample, during the fit it was assumed that the line width of the contributing Lorentzian peaks is at least 0.23 mm/s, and for components for which the fit preferred a narrower peak, this minimum value was fixed instead. Doublet components of the fit were assumed to be symmetrical, whereas remaining magnetic components were accounted for by PFO sextets with a relative area ratio of 3:2:1:1:2:3 being fixed for the 1–6 peaks.

The singlet, doublet and sextet components were described by their respective parameters such as area fraction (A), isomer shift (δ), quadrupole splitting (ΔE_Q), effective hyperfine magnetic field (H_{eff}), twice the first order quadrupole shift (2ε), and the line width (Γ) of the contributing Lorentzians. In addition to the corresponding A , δ , H_{eff} and Γ parameters, in fit method (c) the troilite component was determined by the V_{zz} (the main component of the EFG), η , β (the polar angle of \mathbf{H}_{eff} in the eigensystem of the EFG) and α parameters.

3. Results and Discussion

The Mössbauer spectrum of Chelyabinsk LL5 meteorite fragment with light lithology No 1a measured at room temperature is shown in Figure 3 together with the subcomponents identified during the fit. The numerical results of the three different approaches to the spectrum fit are given in Table 1. It was possible to reveal 10 spectral components. On the basis of the corresponding hyperfine parameters magnetic components 1, 2 and 3 were related to martensite α_2 -Fe(Ni, Co), kamacite α -Fe(Ni, Co) and taenite γ -Fe(Ni, Co), respectively, magnetic component 4 was related to troilite FeS, quadrupole doublets 5 and 6 were related to the M1 and M2 sites in olivine, quadrupole doublets 7 and 8 were related to the M1 and M2 sites in pyroxene, paramagnetic singlet 9 was related to paramagnetic taenite γ -Fe(Ni, Co) with Ni concentration in the range of ~29–33 at. % and singlet 10 was related to chromite FeCr₂O₄ (explanation is the same as in ref. [10]). Concerning the PFO approximation (a), the associated differential spectrum (Figure 3a) clearly indicates that this fit is not optimal. This is mainly because the PFO sextet component 4 does not fit the subspectrum of troilite well (see Figure 3a), resulting in a relatively large χ^2 value (see Table 1).

At the same time, Figure 3a reveals that in the present case approach (b) may be a viable approximation for the troilite component because its leftmost two peaks appear clearly in the spectrum, and in addition another of its peaks is also clearly apparent at around the velocity value 1.65 mm/s, which facilitates the correct fit also of the third doublet component of the 3DA approximation. After reaching the best 3DA fit, the approximate values of H_{eff} and averaged δ values for troilite were obtained from the parameters of the doublet components. The results of this fit are also given in Table 1. The corresponding differential spectrum indicates a considerably improved fit of the experimental spectrum points (see Figure 3b) with substantially reduced χ^2 value in comparison with the PFO fit.

The results of the FH-based fit method (c) are displayed in Figure 3c with the corresponding parameters given in Table 1. The differential spectrum indicates an acceptable fit (see Figure 3c) with the χ^2 value being further reduced in comparison with the previous fits.

Comparison of Mössbauer parameters for corresponding spectral components given in Table 1 shows that the Mössbauer parameters of olivine and pyroxene are not sensitive to the type of the spectrum fit applied, with the uncertainty intervals overlapping even for the smallest, Pyroxene M1 component. On the other hand, parameters for the minor magnetic components related to metallic phases obtained using FH and 3DA simulation fits were in general close considering also the errors in the parameter values, whereas results of the PFO fit displayed larger discrepancies in this respect. As for parameters of singlet components, they were in good agreement regarding the isomer shift, but displayed differences regarding the line width and area fraction parameters. The latter differences may in part be due to different constraints (fixed parameter vs. free variation) used to fit the line width of these components.

It should be noted that the value of H_{eff} for troilite turned out to be different beyond the error for the three fits. Therefore, the most reliable H_{eff} value should be obtained using the full Hamiltonian fit while values obtained from the other fits may be considered as a rough result.

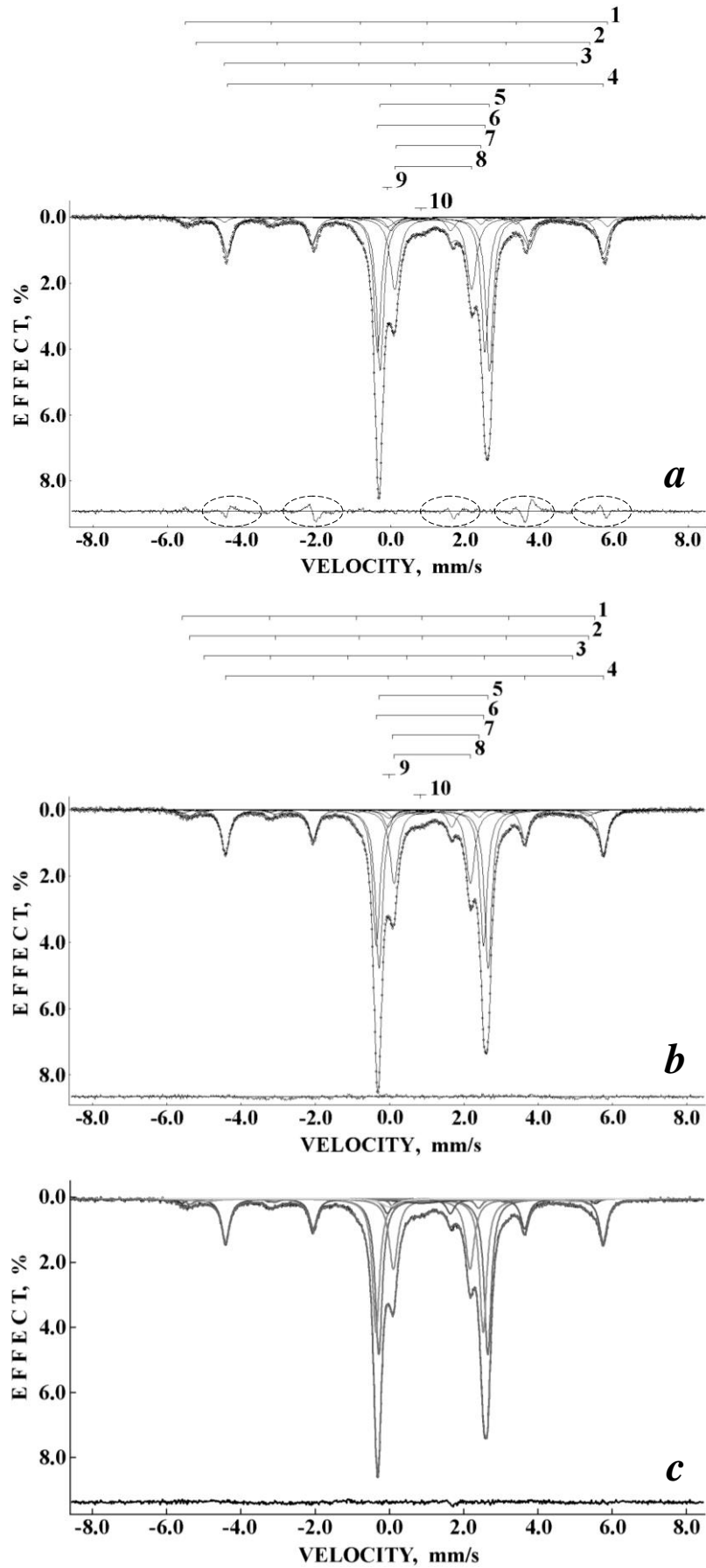


Figure 3 Mössbauer spectrum of the Chelyabinsk LL5 fragment showing the result of the three different fit methods applied to fit the troilite component: PFO (*a*), 3DA (*b*) and FH (*c*). Indicated components are the results of the best fits. Differential spectra are shown below.

Table 1. Mössbauer parameters of Chelyabinsk LL5 ordinary chondrite (fragment No 1a) obtained with different fit methods applied for the troilite component (PFO – fit with sextet component where quadrupole interaction is taken into account in the first-order perturbation limit, 3DA – approximation by using superposition of three symmetric doublets, FH – full Hamiltonian fit). See text for the remaining notations.

Parameter	Fit method applied for the troilite component			Component ^a
	PFO	3DA	FH	
Γ , mm/s	0.273±0.034	0.323±0.076	0.23 ^c	α_2 -Fe(Ni, Co) (1)
δ , mm/s	0.116±0.017	-0.020±0.017	-0.014±0.017	
2ϵ , mm/s	0.077±0.017	-0.017±0.028	-0.010±0.018	
H_{eff} , kOe	352.3±0.5	344.8±2.4	346.1±0.7	
A^b , %	4.09	1.93	1.65	α -Fe(Ni, Co) (2)
Γ , mm/s	0.233±0.034	0.362±0.053	0.310±0.055	
δ , mm/s	0.039±0.017	0.008±0.017	0.013±0.017	
2ϵ , mm/s	0.034±0.017	-0.039±0.017	-0.009±0.017	
H_{eff} , kOe	328.7±0.6	332.9±1.7	334.3±0.9	γ -Fe(Ni, Co) (3)
A^b , %	1.68	3.61	2.62	
Γ , mm/s	0.233±0.034	0.350±0.097	0.806±0.116	
δ , mm/s	0.083±0.017	-0.184±0.017	-0.108±0.039	
2ϵ , mm/s	0.376±0.017	0.292±0.065	0.198±0.071	Troilite (4)
H_{eff} , kOe	294.1±0.6	307.9±2.1	311.4±0.4	
A^b , %	1.93	1.07	3.38	
Γ , mm/s	0.321±0.034	0.267±0.034	0.255±0.034	
δ , mm/s	0.733±0.017	0.737 ^d	0.736±0.017	Troilite (4)
2ϵ , mm/s	-0.150±0.017	–	–	
V_{zz} , 10 ²¹ V/m ²	–	–	-5.13±0.04	
η	–	–	0.3 ^c	
H_{eff} , kOe	313.2±0.5	315.7±0.5	311.5±0.08	Troilite (4)
β , °	–	–	48.2±0.1	
α , °	–	–	49.0 ^c	
A^b , %	18.51	18.74	18.03	
Γ , mm/s	0.233±0.034	0.233±0.034	0.23 ^c	Olivine M1 (5)
δ , mm/s	1.184±0.017	1.184±0.017	1.184±0.017	
ΔE_Q , mm/s	2.937±0.017	2.934±0.017	2.935±0.017	Olivine M1 (5)
A^b , %	28.12	29.13	28.55	
Γ , mm/s	0.233±0.034	0.233±0.034	0.23 ^c	Olivine M2 (6)
δ , mm/s	1.086±0.017	1.085±0.017	1.085±0.017	
ΔE_Q , mm/s	2.885±0.017	2.886±0.017	2.887±0.017	Olivine M2 (6)
A^b , %	24.88	25.00	24.52	
Γ , mm/s	0.233±0.034	0.233±0.034	0.23 ^c	Pyroxene M1 (7)
δ , mm/s	1.282±0.023	1.240±0.017	1.268±0.020	
ΔE_Q , mm/s	2.282±0.035	2.331±0.024	2.279±0.039	Pyroxene M1 (7)
A^b , %	1.24	1.39	1.72	
Γ , mm/s	0.306±0.034	0.275±0.034	0.278±0.034	Pyroxene M2 (8)
δ , mm/s	1.142±0.017	1.148±0.017	1.141±0.017	
ΔE_Q , mm/s	2.064±0.017	2.051±0.017	2.063±0.017	Pyroxene M2 (8)
A^b , %	17.28	15.86	15.58	
Γ , mm/s	0.411±0.046	0.376 ^c	0.471±0.143	γ -Fe(Ni, Co) (9)
δ , mm/s	-0.088±0.042	-0.014±0.027	-0.004±0.034	
A^b , %	1.62	1.24	1.53	Chromite (10)
Γ , mm/s	0.376 ^c	0.769±0.103	1.377±0.238	
δ , mm/s	0.806±0.018	0.814±0.029	0.860±0.078	Chromite (10)
A^b , %	0.65	1.46	2.43	
χ^2	4.476	1.193	1.048	

^aNumbers in parenthesis correspond to numbers of spectral components in Fig. 3a,b. ^bThe values have two decimal digits as it was calculated to keep the total relative area equal to 100 %. ^cFixed parameter. ^dError was not determined.

4. Conclusion

The Mössbauer spectrum of Chelyabinsk LL5 ordinary chondrite fragment with a light lithology was chosen for comparison of the influence of the fit accuracy of the troilite spectral component on the parameters of the remaining components. Three different fit methods were applied to account for the troilite component: PFO and 3DA, both using the UNIVEM-MS program, and FH using version 4.0Pre of the MOSSWINN program. The obtained results show that Mössbauer parameters for the main spectral components related to the ^{57}Fe in the M1 and M2 sites in both olivine and pyroxene were not sensitive to the fit method applied for the fit of the troilite component. Mössbauer parameters obtained for magnetic sextets related to $\alpha_2\text{-Fe}(\text{Ni}, \text{Co})$, $\alpha\text{-Fe}(\text{Ni}, \text{Co})$ and $\gamma\text{-Fe}(\text{Ni}, \text{Co})$ via the 3DA (b) and FH (c) fit methods were in general close to each other, whereas the results obtained via the PFO (a) method displayed larger discrepancies in this respect. Mössbauer parameters for minor singlet components related to paramagnetic $\gamma\text{-Fe}(\text{Ni}, \text{Co})$ and chromite agreed well concerning the isomer shift, but displayed differences beyond error concerning the line width and area fraction parameters. Thus, to obtain Mössbauer parameters for olivine and pyroxene in the spectra of ordinary chondrites the PFO fit of the troilite component may also be suitable, whereas regarding the minor spectral components it appears to be necessary to use the FH (c), or at least the 3DA (b) fit method to observe reliable results.

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