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The ^{57}Fe hyperfine interactions in the iron-bearing phases in some LL ordinary chondrites

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Abstract The study of several LL ordinary chondrites such as NWA 6286 LL6, NWA 7857 LL6 and Chelyabinsk LL5 fragments with different lithology was carried out using scanning electron microscopy with energy dispersion spectroscopy, X-ray diffraction and ^{57}Fe Mössbauer spectroscopy with a high velocity resolution at 295 K. Small variations in the ^{57}Fe hyperfine parameters were revealed for the M1 and M2 sites in olivine, orthopyroxene and clinopyroxene as well as for α-Fe(Ni, Co), α_2-Fe(Ni, Co) and γ-Fe(Ni, Co) phases, and for troilite in different samples of studied LL ordinary chondrites.

Keywords Mössbauer spectroscopy · LL ordinary chondrites · Hyperfine interactions

1 Introduction

Ordinary chondrites are stony meteorites consisted of olivine (Fe, Mg)$_2$SiO$_4$, orthopyroxene (Fe, Mg)SiO$_3$ clinopyroxene (Fe, Mg, Ca)SiO$_3$, troilite FeS, α-Fe(Ni, Co), α_2-Fe(Ni, Co) and γ-Fe(Ni, Co) metallic phases, chromite FeCr$_2$O$_4$, etc. There are three groups of ordinary chondrites (H, L and LL) which characterized by the content of: (i) total iron, ~25–28 wt.% (H), ~20–25 wt.% (L) and ~19–22 wt.% (LL), and (ii) metallic iron, 15–19 wt.% (H), 4–10 wt.% (L) and 1–3 wt.% (LL) [1]. Therefore, it is not too easy to detect metallic iron in the Mössbauer spectrum of LL ordinary chondrite (see, for instance, [2]). Recently

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we have started the study of Chelyabinsk LL5 ordinary chondrite fragments (fall in 2013) using Mössbauer spectroscopy with a high velocity resolution and revealed the minor magnetically split components related to α-Fe(Ni, Co), α_2-Fe(Ni, Co) and γ-Fe(Ni, Co) phases as well as components related to crystallographically non-equivalent M1 and M2 sites in silicate phases and to chromite [3–5]. For further investigation of LL ordinary chondrites we studied two other LL ordinary chondrites found recently in the Northwest Africa named as NWA 6286 LL6 (found in 2010, Meteoritical Bulletin, No. 99, 2012) and NWA 7857 LL6 (found in 2013, Meteoritical Bulletin, No. 102, 2014). These meteorites were not analyzed by Mössbauer spectroscopy yet. Therefore, we compared the ^{57}Fe hyperfine parameters for Chelyabinsk LL5 fragments and samples of NWA 6286 LL6 and NWA 7857 LL6 ordinary chondrites.

2 Experimental

Two samples of NWA 6286 LL6 and NWA 7857 LL6 and four Chelyabinsk LL5 fragments with different lithology (No 1a with light lithology, No 2 and No 2a with mixed light and dark lithology and No 3 with black lithology) were chosen for comparative study. These samples were polished for the investigation using scanning electron microscopy (SEM) with energy dispersion spectroscopy (EDS). Then powdered samples were prepared from the polished surfaces for X-ray diffraction (XRD). Then powdered samples were glued on aluminum foil free from iron with a thickness of 6–10 mg Fe/cm^2 for Mössbauer spectroscopy.

X-ray diffraction patterns were measured using XRD–7000 powder diffractometer (Shimadzu) operated at 40 kV and 30 mA with Ni-filtered CuK$_\alpha$ radiation. For detailed X-ray line profile analysis, step-scan data were recorded for these samples in the 2Θ range of 14–100°. 2Θ steps were of 0.026° or 0.030° and counting time was of 25 s. SEM analysis was carried out using ΣIGMA VP electron microscope (Carl Zeiss) with an X-max (Oxford Instruments) energy dispersion spectroscopy device, Auriga CrossBeam scanning electron-ion microscope (Carl Zeiss) with EDS device X-max 80 (Oxford Instruments) and AMRAY 1830 scanning electron microscope equipped with EDAX PV9800 energy dispersive spectrometer.

Mössbauer spectra of NWA 6286 LL6, NWA 7857 LL6 and four Chelyabinsk LL5 fragments were 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) and temperature variable liquid nitrogen cryostat with moving absorber. Details and characteristics of this spectrometer and the system can be found in [6–8]. The 1.0×10^9 Bq ^{57}Co(Rh) source (Ritverc GmbH, St. Petersburg) was used at room temperature. The Mössbauer spectra of ordinary chondrites were measured in the cryostat with moving absorber at 295 K in transmission geometry and recorded in 4096 channels. These spectra were converted into 1024 channels by a consequent summation of four neighboring channels to increase a signal-to-noise ratio for the minor spectral components. Statistical count rates in the 1024-channel Mössbauer spectra of NWA 6286 LL6, NWA 7857 LL6 and four Chelyabinsk LL5 fragments were in the range $7.7 \times 10^6 - 19.2 \times 10^6$ counts per channel and signal-to-noise ratio for these spectra ranged between 209 and 607.

The Mössbauer spectra of NWA 6286 LL6, NWA 7857 LL6 and four Chelyabinsk LL5 fragments were computer fitted with the least squares procedure using UNIVEM-MS program with a Lorentzian line shape. We used a new approach to fit the Mössbauer spectra of ordinary chondrites using the simulation of the full static Hamiltonian required to fit a troilite magnetic spectral component (details were given in [9, 10]). The spectral parameters such as: isomer shift, δ, quadrupole splitting (quadrupole shift for magnetically split components), ΔE_Q, magnetic hyperfine field, H_{eff}, line width, Γ, relative area of spectral components, A, and statistical criterion, χ^2, were determined. The Mössbauer spectrum of standard absorber of α-Fe foil (7 μm) demonstrated Lorentzian line shape with the values of $\Gamma_{1-6} = 0.238 \pm 0.031$ mm/s, $\Gamma_{2-5} = 0.232 \pm 0.031$ mm/s and $\Gamma_{3-4} = 0.224 \pm 0.031$ mm/s. An instrumental (systematic) error for each spectrum point was ± 0.5 channel (in mm/s), the instrumental (systematic) error for the hyperfine parameters was ± 1 channel (in mm/s or kOe). If statistical error calculated with the fitting procedure (fitting error) for these parameters exceeded the instrumental (systematic) error we used the larger error instead. Estimated relative error for A usually did not exceed 10 %. Criteria for the best fits were differential spectrum, χ^2 and a physical meaning of the spectral parameters. Values of δ are given relative to α-Fe at 295 K.

3 Results and discussion

SEM analysis with EDS demonstrated that NWA 6286 LL6 and NWA 7857 LL6 contained metal grains with different Ni and Co concentration. It is well-known that Ni content in α-Fe(Ni, Co), α_2-Fe(Ni, Co) and γ-Fe(Ni, Co) phases varies in the ranges ~3–7 at.%, ~8–25 at.% and ~26–50 at.%, respectively (in the latter case 50 at.% of Ni is in γ-FeNi phase). For instance, there were no α-Fe(Ni, Co) phase observed in NWA 6286 LL6 while many metallic grains contained γ-Fe(Ni, Co) phase were found. In contrast, both α-Fe(Ni, Co) and γ-Fe(Ni, Co) phases were observed in NWA 7857. Various metallic phases were found in four Chelyabinsk LL5 fragments No 1a, No 2, No 2a and No 3. All samples contained troilite with some slight variations in stoichiometry (50–53 at.% S), chromite associated with hercynite $FeAl_2O_4$ while ilmenite $FeTiO_3$ was found in Chelyabinsk LL5 fragment No 2a only.

An analysis of XRD data for NWA 6286 LL6, NWA 7857 LL6 and four Chelyabinsk LL5 fragments revealed the presence of olivine (~50–59 wt.%), orthopyroxene (~19–26 wt.%), anorthite $CaAl_2Si_2O_8$ (~6–12 wt.%), troilite (~3.6–7.4 wt.%), clinopyroxene (~3.6–6.2 wt.%), chromite (~0.6–1.7 wt.%), α-Fe(Ni, Co)/α_2-Fe(Ni, Co) phases (~0.2–1.8), hercynite (~0.5–1.2 wt.%) and γ-Fe(Ni, Co) phase (~0.3–0.9 wt.%) while ilmenite (~0.1 wt.%) was determined in Chelyabinsk LL5 fragment No 2a only.

Mössbauer spectra of ordinary chondrites NWA 6286 LL6, NWA 7857 LL6 and Chelyabinsk LL5 fragments No 1a and No 3 are shown in Fig. 1. These spectra demonstrate similar spectra shape with several magnetic and paramagnetic components. The best fits of these spectra using new approach described in [9, 10] permitted us to minimize the misfits. On the basis of the Mössbauer hyperfine parameters and relative areas of obtained components these components were related to the following iron-bearing phases. In the spectrum of NWA 6286 LL6 component 1 was associated with α_2-Fe(Ni, Co) phase while components 2 and 3 were related to γ-Fe(Ni, Co) phase with some variations in Ni concentration (here and further these assignments were done on the basis of EDS analysis and the values of hyperfine fields); component 4 was related to troilite while components 5 and 6 were associated with non-stoichiometric troilite $Fe_{1-x}S$ with possible variation of x; pairs of components 7 and 8, 9 and 10, and 11 and 12 were related to the M1 and M2 sites in olivine, orthopyroxene and clinopyroxene, respectively; components 13, 14

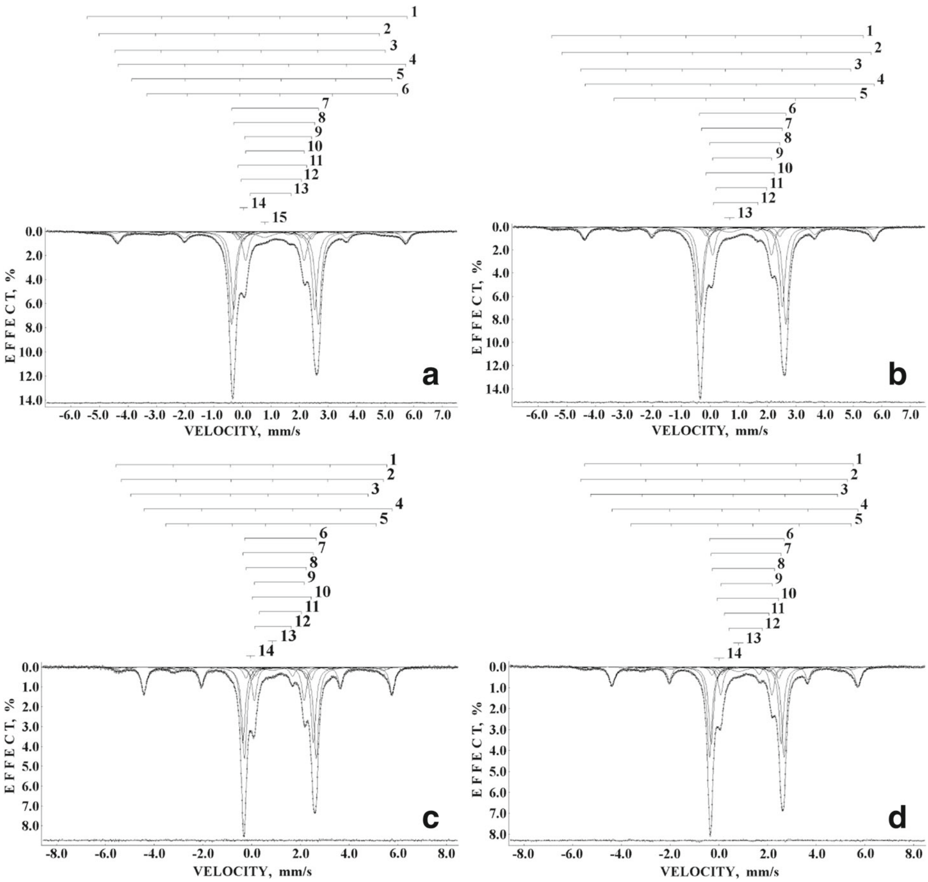


Fig. 1 Mössbauer spectra of ordinary chondrites NWA 6286 LL6 (**a**), NWA 7857 LL6 (**b**) and Chelyabinsk LL5 fragments No 1a (**c**) and No 3 (**d**) measured at 295 K. Indicated components are the results of the best fits (see explanation in the text). Differential spectra are shown below

and 15 were associated with hercynite, chromite and paramagnetic γ-Fe(Ni, Co) phase, respectively. In the spectrum of NWA 7857 LL6 components 1 and 2 were associated with α-Fe(Ni, Co) phase with some variations in Ni concentration while component 3 was related to γ-Fe(Ni, Co) phase; component 4 was related to troilite while component 5 was associated with non-stoichiometric troilite $Fe_{1-x}S$; pairs of components 6 and 7, 8 and 9, and 10 and 11 were related to the M1 and M2 sites in olivine, orthopyroxene and clinopyroxene, respectively; components 12 and 13 were associated with hercynite and chromite, respectively (no paramagnetic γ-Fe(Ni, Co) phase was revealed). Components for Chelyabinsk LL5 fragments No 1a and No 3 were related to the same phases: component 1 and 2 were associated with α-Fe(Ni, Co) and α_2-Fe(Ni, Co) phases while component 3 was related to γ-Fe(Ni, Co) phase; component 4 was related to troilite while component 5 was associated with non-stoichiometric troilite $Fe_{1-x}S$; pairs of components 6 and 7, 8 and 9, and 10 and 11 were related to the M1 and M2 sites in olivine, orthopyroxene and clinopyroxene, respectively; components 12, 13 and 14 were associated

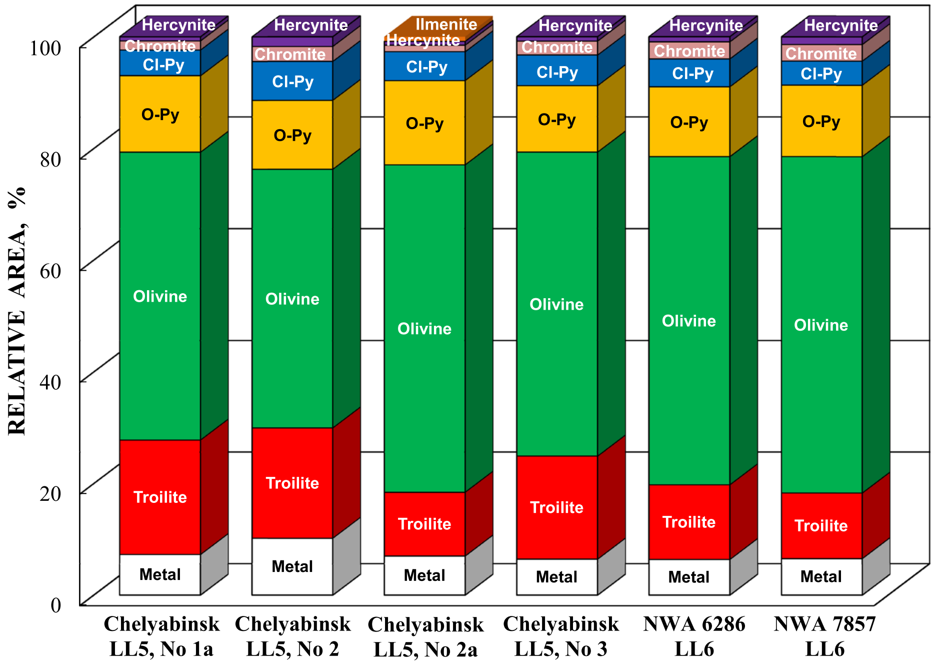


Fig. 2 Comparison of the relative areas of Mössbauer spectra components associated with corresponding iron-bearing phases in LL ordinary chondrites: NWA 6286 LL6, NWA 7857 LL6 and Chelyabinsk LL5 fragments No 1a, No 2, No 2a and No 3; O-Py is orthopyroxene, Cl-Py is clinopyroxene

with hercynite, chromite and paramagnetic γ-Fe(Ni, Co) phase, respectively. However, the number of spectral components in the Mössbauer spectra of Chelyabinsk LL5 fragments No 2 and No 2a was different. For instance, in the latter spectrum component associated with ilmenite was revealed. The relative areas of spectral components associated with corresponding phases for NWA 6286 LL6, NWA 7857 LL6 and Chelyabinsk LL5 fragments are shown in Fig. 2. These relative areas reflect roughly the phase composition in these ordinary chondrites.

A comparison of the ^{57}Fe hyperfine parameters (ΔE_Q and δ) for the M1 and M2 sites in olivine, orthopyroxene and clinopyroxene in NWA 6286 LL6, NWA 7857 LL6 and Chelyabinsk LL5 fragments is shown in Fig. 3. It was interesting to observe the same ΔE_Q and δ values as for the M1 sites as for the M2 site in olivine for NWA 6286 LL6 and NWA 7857 LL6 while these parameters for different fragments of Chelyabinsk LL5 demonstrated small variations. The similarities or differences of the ^{57}Fe hyperfine parameters for the corresponding M1 and M2 sites in silicates in studied LL ordinary chondrites indicate similar or slightly varied the ^{57}Fe local microenvironments in these microcrystals in meteorites. The differences in the ^{57}Fe local microenvironment may be a result of different extreme conditions in the space on the meteorite matter resulting in small variations in the crystal structure. Similar comparison of the ^{57}Fe hyperfine parameters (H_{eff} and δ) for α-Fe(Ni, Co), α_2-Fe(Ni, Co) and γ-Fe(Ni, Co) phases in NWA 6286 LL6, NWA 7857 LL6 and Chelyabinsk LL5 fragments is shown in Fig. 4. Some variations in this case may be related to different Ni and Co concentrations.

Small variations in the ^{57}Fe hyperfine parameters (H_{eff} and δ) for troilite in NWA 6286 LL6, NWA 7857 LL6 and Chelyabinsk LL5 fragments are shown in Fig. 5. The observed

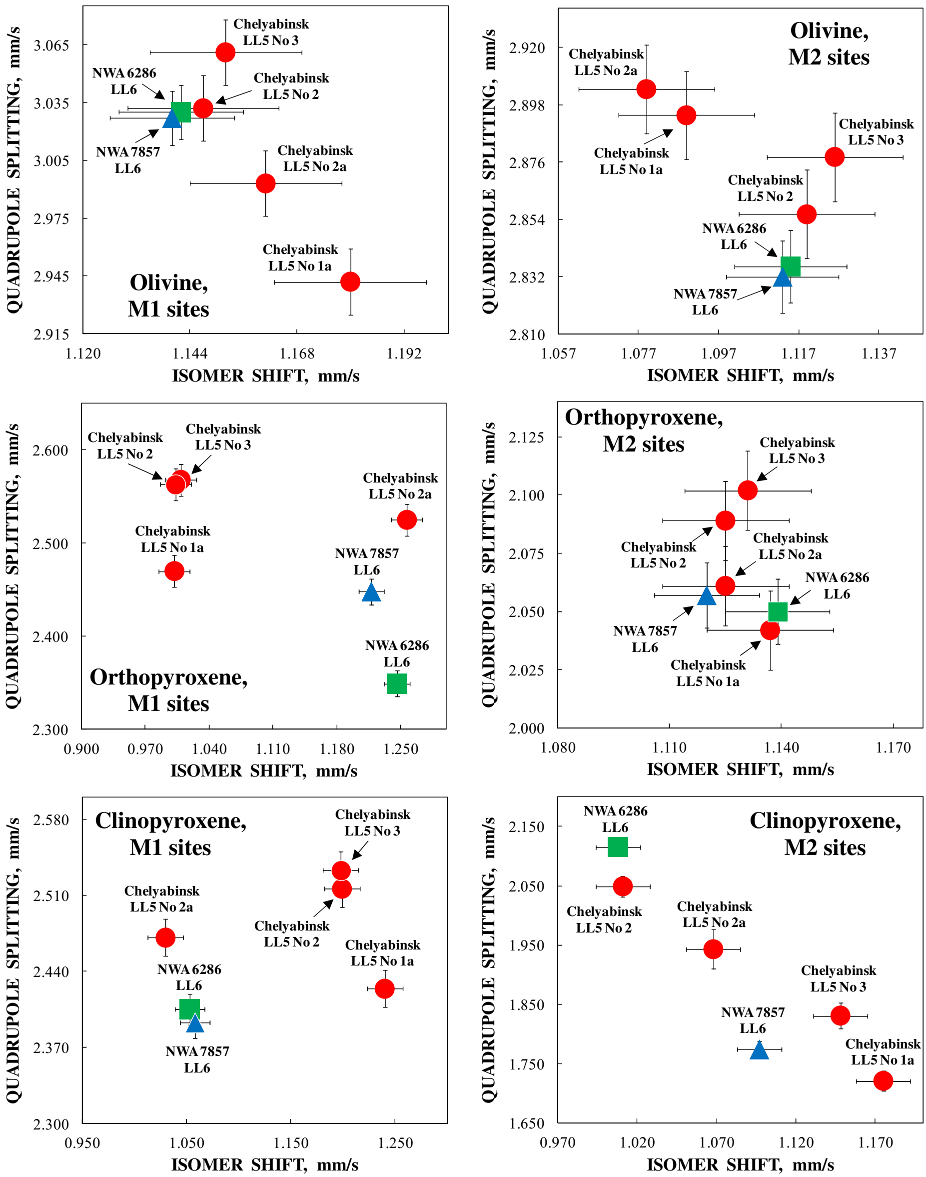


Fig. 3 Comparison of the ^{57}Fe hyperfine parameters for the M1 and M2 sites in olivine, orthopyroxene and clinopyroxene in LL ordinary chondrites: four Chelyabinsk LL5 fragments with different lithology (●), NWA 6286 LL6 (■) and NWA 7857 LL6 (▲)

tiny differences may be a result of small variations in Fe deficiency in troilite, but this deficiency is significantly smaller than that in the case of non-stoichiometric $Fe_{1-x}S$. This Fe deficiency in troilite as well as $Fe_{1-x}S$ formation may be a result of reheating and/or re-melting processes.

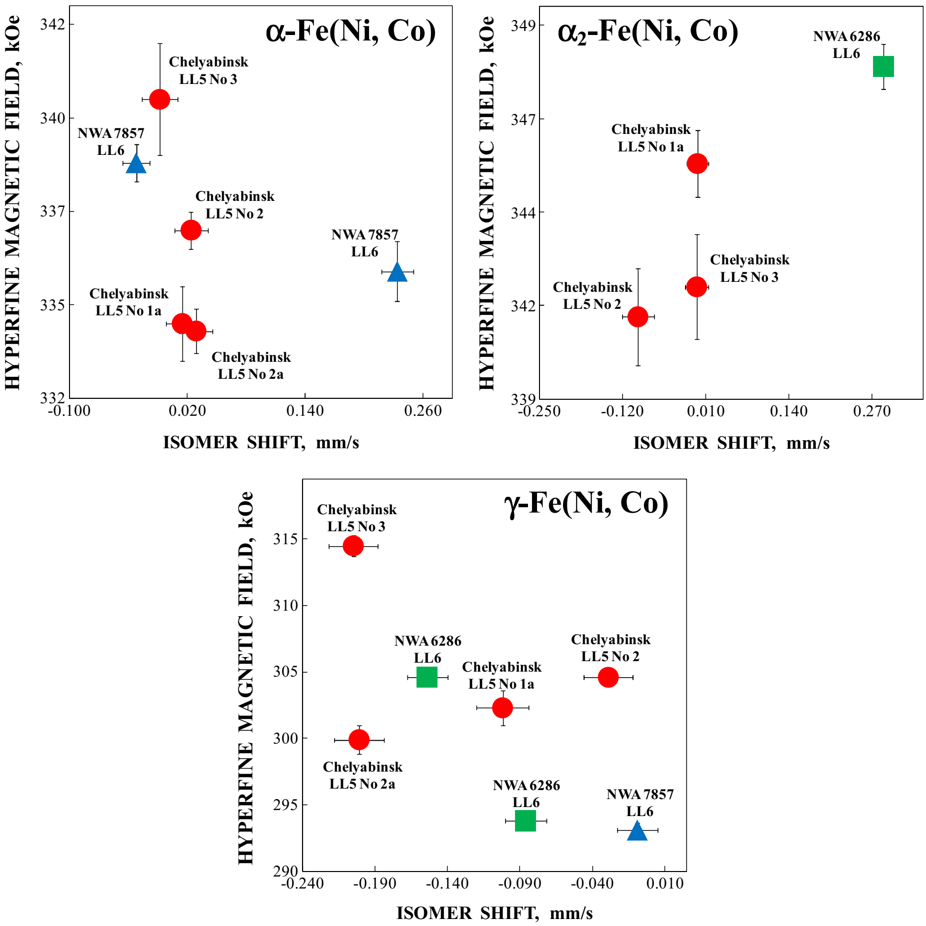
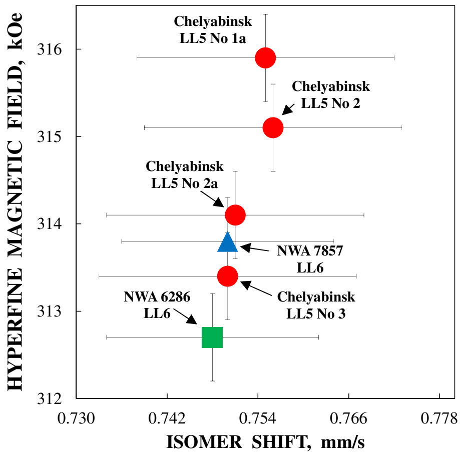


Fig. 4 Comparison of the ^{57}Fe hyperfine parameters for α-Fe(Ni, Co), α_2-Fe(Ni, Co) and γ-Fe(Ni, Co) phases in LL ordinary chondrites: four Chelyabinsk LL5 fragments with different lithology (●), NWA 6286 LL6 (■) and NWA 7857 LL6 (▲)

Fig. 5 Comparison of the ^{57}Fe hyperfine parameters for troilite in LL ordinary chondrites: four Chelyabinsk LL5 fragments with different lithology (●), NWA 6286 LL6 (■) and NWA 7857 LL6 (▲)



4 Conclusion

Study of LL ordinary chondrites NWA 6286 LL6 and NWA 7857 LL6 using SEM with EDS, XRD and Mössbauer spectroscopy with a high velocity resolution in comparison with Chelyabinsk LL5 four fragments with different lithology demonstrated similar phase composition with some variations in the content of various phases. It was possible to reveal the minor iron-bearing phases using three different techniques and compare the ^{57}Fe hyperfine parameters for the same phases in different ordinary chondrites. The differences observed for these parameters may reflect small structural changes in the phases' microcrystals and variations in Ni and Co concentration in metallic phases resulting from the thermal history of studied meteorites in space.

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