Fe^{2+}-Mg order–disorder study in orthopyroxenes from São João Nepomuceno (IVA) iron meteorite

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Abstract São João Nepomuceno (SJN) is an iron meteorite belonging to IVA chemical group. It consists of Fe-Ni metal matrix and silicate inclusions made of a coarse-grained mixture of tridymite, orthopyroxene and clinopyroxene. In spite of the extensive work performed on the IVA group there is still no consensus about their origin and its thermal history is subject of ongoing debates. In this work, we report preliminary results on Fe^{2+} distribution in the non-equivalent octahedral sites in orthopyroxene crystals extracted from São João Nepomuceno in order to infer on the thermal history of this meteorite and therefore acquire more information related to the origin of the IVA iron meteorite group.

Keywords Meteorite · São João Nepomuceno · Orthopyroxene · Fe^{2+}-Mg order–disorder · ^{57}Fe Mössbauer spectroscopy

1 Introduction

São João Nepomuceno (SJN) is an iron meteorite belonging to the IVA chemical group. It consists of Fe-Ni metal matrix and silicate inclusions made of a coarse-grained mixture of tridymite, orthopyroxene and clinopyroxene. In spite of the extensive work performed on the IVA irons there is still no consensus about their origin and thermal history. Their particular chemistry and range in metallographic

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cooling rate are difficult to explain under conventional models [1]. The IVA irons are extremely depleted in volatile elements (e.g., Ga, Ge) with respect to other meteorite groups. Their large spread of metallographic cooling rates—too large for an asteroidal core enclosed by silicate mantle—argues against an origin in a mantled asteroidal core. If this would be the case, uniform cooling rates should to be expected. Nonetheless, metal-silicate mixing of the IVA group remains a complex issue.

Depending on the temperature and pressure history of the host rock, Fe^{2+} and Mg in orthopyroxene crystals fractionate between two nonequivalent octahedral sites, M1 and M2. In slowly cooled crystals, the Fe^{2+} ions populate essentially the M2 position while Mg ions occupy, predominantly, the M1 position. However, in crystals that have been rapidly cooled, a more disorder Mg, Fe distribution over M1 and M2 sites is observed [2]. Hence, the intracrystalline Fe^{2+}-Mg distribution determination is very useful in tracing the thermal history of the host rock. To accomplish this task, ^{57}Fe Mössbauer spectroscopy has played a major role in obtaining site populations in orthopyroxenes through the relative areas of the Fe^{2+} doublets in M1 and M2 sites [2].

In this work, we report preliminary results on Fe^{2+} distribution in the non-equivalent octahedral sites in orthopyroxene crystals extracted from SJN in order to infer on the thermal history of the coarse-grained silicate fraction of the host meteorite and, as a consequence, acquire more information related to the origin of IVA iron meteorite group.

2 Materials and methods

All samples used in this study belong to the Museu Nacional/UFRJ in Rio de Janeiro.

The separation of silicate inclusions of the SJN meteorite from its metallic matrix was done in several thin slides. The cutting process was performed by means of a diamond saw using alcohol as lubricant, to avoid oxidation and contamination. Under a binocular microscope, orthopyroxene crystals were subsequently separated from silicate inclusions. The separate grains were inspected under an electron microscope (Jeol JSM 6490 LV, CBPF, Brazil) to verify their chemical composition. This material was used for preparing the Mössbauer powder absorber with a thickness of 1.8 mg Fe/cm^2. The thickness effect, i.e. the saturation of absorption peaks, is a well-known feature in Mössbauer spectroscopy [3]. As was already shown, such effect in orthopyroxene results in an underestimate of the ordering degree. For instance, an absorber thickness of 5 mg Fe/cm^2 causes an overestimation of Fe at M1 site by 2 % [4]. Thus, a thin Mössbauer absorber is fundamental for an accurate site occupancy determination. In general, absorber thicknesses of 2–5 mg Fe/cm^2 are assumed as thin absorbers. It is worth mention that in our previous work involving clinopyroxene, an absorber thickness of 3 mg Fe/cm^2 yielded Mössbauer results compatible with single-crystal X-ray diffraction experiment, suggesting negligible thickness effect [5]. In this study, the Mössbauer powder absorber thickness (1.8 mg Fe/cm^2) is even thinner than those assumed as thin absorbers in previous works; therefore, we expect negligible thickness effect.

^{57}Fe Mössbauer spectroscopy, in standard transmission geometry using a 25 mCi $^{57}Co/Rh$ radioactive source in sinusoidal mode, was performed at different temperatures as follow: room temperature (RT), 80 K and 4.2 K, with uncertainties of ± 1 K.

Spectra were recorded for 24 h in a 512 channels spectrometer and the calibration was taken at RT with α-Fe foil. The error in source velocity is less than 1 %. The NORMOS code [6] was used for the analyses of the Mössbauer spectra. The isomer shifts are given relative to α-Fe.

Two polished thick sections from São João Nepomuceno were prepared for chemical analysis. Objects were selected using an optical microscope and the major element chemical compositions were obtained using an ARL-SEMQ (WDS) electron microprobe (Icate, Argentina). Electron microprobe analysis were performed at 15 kV acceleration potential, 20 nA sample current and peak and background count times of: 20 s; and 10 s, respectively. Estimated precision for major and minor elements is better than 3 % and for Na about 10 %. Natural and synthetic standards were used for calibration and an online ZAF correction was applied to the data.

3 Results

The orthopyroxene (opx) average chemical composition (mean of 39 individual analyses) is listed in Table 1. In terms of the end-members of pyroxene solid-solution (En: enstatite), (Fs: ferrosilite) and (Wo: wollastonite) opx corresponds to: $En_{85}Fs_{14}Wo_1$. The derived opx unit formula calculated on the basis of six oxygen atoms is given by: $(Fe^{2+}_{0.273}Mg_{1.678}Mn_{0.016}Ca_{0.021}Ti_{0.001}Cr_{0.018})(Si_{1.982},Al_{0.012})O_6$ (Table 1).

The RT ^{57}Fe Mössbauer spectrum of opx from SJN (Fig. 1a) is characterized by an asymmetry that arises from two overlapping doublets attributed to Fe^{2+} at two nonequivalent sites. The first doublet, identified as $Fe^{2+}(M1)$, corresponds to Fe^{2+} ions in the less distorted site M1 (isomer shift (IS) = 1.24 mm/s, quadrupole splitting (QS) = 2.26 mm/s) while the second one, $Fe^{2+}(M2)$, is attributed to Fe^{2+} in the more distorted site M2 (IS = 1.14 mm/s, QS = 2.10 mm/s) (hyperfine parameters are shown in Table 2). The absence of any Fe^{3+} doublets and magnetic components assigned to Fe oxides indicate that terrestrial weathering did not take place in these samples [7], thus Fe site occupancies determination will not be hampered by secondary phases. Previous works [8, 9] on natural opx show that RT splitting of $Fe^{2+}(M1)$ and $Fe^{2+}(M2)$ doublets approach a similar value for low iron content (<23.1 mol%) and the hyperfine parameters measured in these samples, especially the relative areas, become less precise. However, for samples with iron concentration close to 86 mol%, the doublets are well resolvable even at RT. Hence, our RT results suggest low iron content for opx samples from SJN meteorite, in accordance with chemical composition results for these crystals.

At a given iron concentration, as a result of the differential dependence of the quadrupole splitting on temperature, the resolution of the $Fe^{2+}(M1)$ and $Fe^{2+}(M2)$ doublets increase with decreasing temperature [10]. Aiming to improve the accuracy of the measured hyperfine parameters, especially the relative areas that play important role in Fe site occupancy determination, low velocity ^{57}Fe Mössbauer spectroscopy at 80 K was carried out in our opx samples (Fig. 1b). This spectrum was fitted with the same components as RT spectrum and indicates that Fe^{2+} mainly populate M2 site ($A = 86$ %) (see hyperfine parameters in Table 2).

The normalized Mössbauer relative areas at 80 K (Table 2) show that Fe^{2+} fractions at M1 and M2 sites are 0.14 and 0.86, respectively. The occupancies

Table 1 Electron microprobe average chemical composition (wt%) and unit formula (*apfu*) for orthopyroxenes from São João Nepomuceno (IVA) meteorite

SiO_2	56.45	Si	1.982
TiO_2	0.05	^{IV}Al	0.012
Al_2O_3	0.30	Σ	1.994
Cr_2O_3	0.64		
FeO	9.29	Ti	0.001
MnO	0.53	Cr	0.018
MgO	32.07	Fe^{2+}	0.273
CaO	0.57	Mn	0.016
Total	99.90	Mg	1.678
		Ca	0.021
		Σ	2.007

apfu atoms per formula unit

Fig. 1 ^{57}Fe Mössbauer spectra of the orthopyroxene samples from São João Nepomuceno (IVA) meteorite recorded at: **a** room temperature (300 K), **b** 80 K and **c** 4.2 K
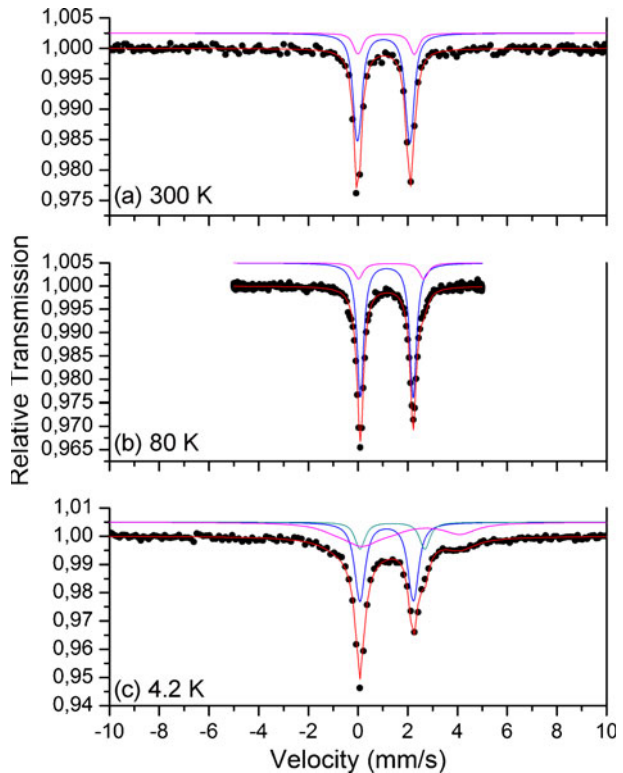
of Fe^{2+} at M1 and M2 sites, $X_{Fe^{2+}(M1)}$ and $X_{Fe^{2+}(M2)}$, respectively, are obtained by multiplying the above mentioned Fe^{2+} fractions by the total amount of Fe^{2+} given by electron microprobe results. Thus, $X_{Fe^{2+}(M1)} = 0.14*0.273 = 0.038$ and $X_{Fe^{2+}(M2)} = 0.86*0.273 = 0.235$. Assuming complete order of Cr and Ti atoms at M1 site and Mn and Ca atoms at M2 site, Mg distribution over M1 and M2 sites can be calculated as follow: $X_{Mg(M1)} = 1 - (X_{Fe^{2+}(M1)} + N_{Cr} + N_{Ti}) = 0.943$ and $X_{Mg(M2)} = N_{Mg} - X_{Mg(M1)} = 0.735$, where N_{Cr}, N_{Ti}, N_{Mg} are the numbers of Cr, Ti and Mg atoms per formula unit (Table 1). The Fe^{2+}-Mg order–disorder reaction in opx can be described by means of the distribution coefficient (K_D) between

Table 2 Mössbauer hyperfine parameters of the orthopyroxenes from São João Nepomuceno (IVA) meteorite obtained at room temperature (300 K), 80 K and 4.2 K

Temperature ($\pm$1 K)	Sites	IS ($\pm$0.03 mm/s)	QS ($\pm$0.03 mm/s)	W ($\pm$0.02 mm/s)	A ($\pm$2 %)	ω (MHz)	B$_{hf}$ ($\pm$1 T)
300 K	Fe^{2+} (M1)	1.24	2.26	0.36	18	–	–
	Fe^{2+} (M2)	1.14	2.10	0.33	82	–	–
80 K	Fe^{2+} (M1)	1.44	2.62	0.43	14	–	–
	Fe^{2+} (M2)	1.26	2.13	0.31	86	–	–
4.2 K	Fe^{2+} (M1)	1.49	2.61	0.42	15	–	–
	Fe^{2+} (M2)	1.26	2.15	0.42	45	–	–
	Fe^{2+} (M2)—magnetic	1.29	1.88	1.10	40	2.6	12.3

IS isomer shift relative to alpha iron, *QS* quadrupole splitting, *A* relative area, ω relaxation rate, B$_{hf}$ hyperfine field

M1 and M2 sites defined as: $K_D = [X_{Fe}{}^{2+}{}_{(M1)}X_{Mg(M2)}]/[X_{Fe}{}^{2+}{}_{(M2)}X_{Mg(M1)}]$. In this work we obtain a $K_D \sim 0.126 \sim 0.13$. To estimate the equilibrium temperature (or closure temperature) of the intracrystalline distribution of Fe^{2+} and Mg between M1 and M2 sites, we can use the geothermometric equation of Wang et al. (2005) [11]. In that equation, the distribution coefficients K_D taken from Mössbauer data are independent of opx composition and they can be related to the equilibrium temperature by: $T = -2205/[\ln K_D - 0.391]$, where T is temperature in K. According to our data, we found T $\sim$ 634 °C.

Measurement at 4.2 K clearly exhibits relaxation effects (Fig. 1c). This feature was previously observed in natural opx and it has been attributed to spin-spin relaxation of Fe^{2+} ions [10]. The 4.2 K spectrum was fitted with the doublets identified at RT and to take into account relaxation effects it was included a component assigned as Fe^{2+}(M2)-magnetic. The decreasing in the relative area of Fe^{2+}(M2) doublet at 4.2 K indicates that Fe^{2+} ions at M2 site mainly contributes for magnetic ordering (probably Fe^{2+} at M1 sites order at lower temperatures). These results are in agreement with previous works where low temperature Mössbauer measurements were carried out in natural and synthetic low iron opx samples with Fe^{2+} ions primarily populating M2 sites [10, 12]. It is important to highlight that even at 4.2 K it was not detected any magnetic component due to terrestrial weathering processes.

4 Discussion

These preliminary results show that, in the studied samples, we have not identified secondary phases related to oxidation processes (e.g., presence of Fe^{3+}). Consequently, the minerals in SJN represent a non-altered assemblage, at least from the latest thermal event that could have affected this meteorite. The resolution of the doublets at RT suggest that theses crystals have low iron content and that Fe^{2+} mainly populate M2 site (high order degree). Both 80 K and 4.2 K measurements argue in favor of high order degree for these samples. Mössbauer spectrum at 4.2 K indicates that magnetic interaction is mainly provided by Fe^{2+} at M2 site, in accordance with Mössbauer measurements carried out in natural and synthetic low iron opx samples with Fe^{2+} ions primarily populating M2 sites [10, 12].

Variable temperature Mössbauer and single-crystal diffractions experiments are in progress to evaluate the accuracy of the site populations and to obtain additional information regarding the thermal/pressure history of these samples.

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