

Preferential occupation of pyroxene sites by iron in diogenite meteorites

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Abstract Three diogenite meteorites ALHA77256-121, Tatahounie and Bilanga are studied using Mössbauer spectroscopy to look at the iron occupancy in the two inequivalent pyroxene sites. Though the three meteorites belong to three different conditions, one is an Antarctica find, one is 75 years old fall and one is a recent fall, the iron occupancy in pyroxene sites is very similar. Fe^{2+} occupies only the less distorted site and hence a single sharp doublet is observed in the Mössbauer spectra of all these samples. In contrast eucrites show a distribution of iron ions in the two sites of pyroxenes.

Keywords Mössbauer spectroscopy · Diogenites · Eucrites · Pyroxene

1 Introduction

Howardite, eucrite and diogenite meteorites, collectively known as HED meteorites account for only 6% of the total meteoritic fall on the earth [1]. However, even this smaller class of meteorites has assumed great significance because of the excitement of almost identifying their parent body. Strong similarity between the absorption features in the reflectance spectra from the laboratory studied Eucrite and Howardite

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meteorites, and those from the Vesta asteroid surface studied through various telescopic experiments including Hubble space telescope led to the widespread belief that these meteorites have all originated from the same parent body that is four Vesta asteroid [2, 3]. More recently about 20 smaller asteroids, termed as vestoids, were identified between Vesta and the 3:1 orbit-orbit resonance with Jupiter, which appear to have come to existence due to some collisional event on Vesta [4]. These too show the similar reflectance spectra and are being investigated as the immediate source of HED meteorites [5]. Recent measurements of four Vesta and vestoids reflectance spectra showed an absorption feature near 505 nm corresponding to Fe^{2+} in six-fold coordination that is attributed to Ca in pyroxene [6, 7]. This absorption feature is also seen in the spectra of eucrite and howardite but not in glassy diogenite [8]. Thus although pyroxene is the main mineral constituent of all three classes (howardite, eucrite and diogenite) of meteorites, there are minor differences in the finer structure of pyroxene in these. The pyroxene in the eucrite is mostly pigeonite, which has a monoclinic crystal structure (clinopyroxene), whereas in the diogenites it is mainly Mg rich orthopyroxene that has an orthorhombic structure. In all these, there are two inequivalent sites, generally called M1 and M2 sites, for the cationic occupancy. The occupancy of M1 and M2 sites by Fe is likely to change with the cooling history of the parent object.

Of the many physical and chemical tools that are available to investigate minerals, Mössbauer spectroscopy is one, which is site specific and can give information about the immediate atomic environment of the probe ion. Even in a sample where there are several environments present around iron ions, the spectra can reveal each of them separately with a good quantitative estimate. As iron is an essential constituent of all meteorites, ^{57}Fe Mössbauer spectroscopy has a potential to contribute a lot in the understanding of meteoritic compositions and many researchers have employed it to gain information about iron mineralogy in meteorites [9–12]. The two environments around the M1 and M2 sites in pyroxene give quadrupole doublets of different splittings and hence we expect a characteristic difference in the Mössbauer spectra of eucrites and diogenites. In this article we report Mössbauer spectroscopic studies of three diogenites ALH A77256, Tatahounie and Bilanga. The results are compared with the well-studied eucrite meteorite Piplia-Kalan [10], Ibitira [13] and Stannern [14], howardite meteorite Kapoeta [15] for which Mossbauer studies have been previously reported.

2 Description of meteorites

ALHA77256 was originally obtained from Allen hills of Antarctica during a field trip programme in 1977. As reported in the literature the sample was rounded with the fusion crust randomly distributed over approximately 15% of the surface. Petrographically this meteorite consists almost entirely (~97%) of coarse (grains up to 6 mm) orthopyroxene clasts, with comminuted grain boundaries. On the basis of these studies it was classified a typical hypersthene achondrite (diogenite) [16].

Tatahounie meteorite is a 1931 fall which broke into thousands of small pieces and fallen over half a kilometer of radius in a small village Tatahouine in Tunisia, Africa [17]. About 12 kg of material was collected mostly in minute fragment form. It is well studied for petrology, orthopyroxene crystallography, natural thermoluminescence,

isotopic composition, noble gas and exposure history, reflectance spectroscopy, etc. [18–20]. It is a well-established diogenite monomict.

Bilanga is a relatively newer fall, 27th October 1999, again in Africa. Mineralogical analysis has established it to be a highly brecciated diogenite having orthopyroxene, chromite, plagioclase, silica and very minor Fe, Ni [21]. The composition of the minor phases such as chromite, troilite, diopside, plagioclase and silica in Bilanga meteorite has been studied in detail. Based on concentration and isotopic composition of He, Ne and Ar, the exposure age of Bilanga is calculated to be around 40–50 Ma [22]. Both Tatahouine and Bilanga are procured for the present study from the meteorite collector M/s Schoolers.

3 Experimental

For Mössbauer analysis about 500 mg of the meteorite fragments were ground to fine powder and properly mixed to remove any homogeneity. About 70 mg of this powder was sandwiched between two transparent tapes to make a Mössbauer absorber of diameter 12 mm. Mössbauer spectra were recorded using a conventional constant acceleration Mössbauer spectrometer with ^{57}Co in Rh matrix as the gamma ray source. Spectra were computer fitted using a least squares routine and assuming each spectrum to be a sum of Lorentzian functions. During the curve fitting, the width and the intensity of the two halves of a quadrupole doublet were constrained to be equal. The quality of fit was judged from the value of χ^2 which was close to 1.0 per degree of freedom. The isomer shift (IS) is reported with respect to alpha-iron. The reported values of IS and quadrupole splitting (QS) have an accuracy of about 0.01 mm/s.

4 Results and discussion

Figure 1 shows the Mössbauer spectra of the three diogenite meteorites ALHA77256, Bilanga and Tatahouine. The Mössbauer parameters obtained are given in Table 1. For the sake of comparison, we also provide Mössbauer parameters already available for eucrites and howardites. It can be seen from Table 1 that all the diogenites exhibit similar Mössbauer pattern where only one intense Fe^{2+} doublet is present. Though the two lines of the doublet have slightly different amplitudes in all three diogenite spectra, each line of a doublet in itself is quite symmetric and sharp and possibility of superposition of another doublet of comparable splitting is remote. This means, out of the two sites M1 and M2 available in pyroxene, Fe^{2+} occupies only one site. As Fe^{2+} is known to have a preference for M2 site in pyroxene we assign this site to be M2 [23]. Thus the mineral is highly ordered. On the other hand if we look at the Mössbauer spectrum of the eucrite Piplia Kalan (Fig. 2), there are clear two doublets as seen qualitatively from the asymmetry in the lineshape and revealed quantitatively by the least squares fittings (Table 1). Similar is the case with other eucrites and howardites.

Mössbauer spectra of ALHA77256 were also measured by Viera and Knudsen [24] and they too got Fe^{2+} only in M2 site of the orthopyroxene. On the other hand the spectrum of Stannern (Eucrite), studied in the same work, showed well distributed Fe^{2+} in M1 and M2 sites.

Fig. 1 Mössbauer spectra of the three diogenite samples at 300 K, velocity resolution = 0.01 mm/s

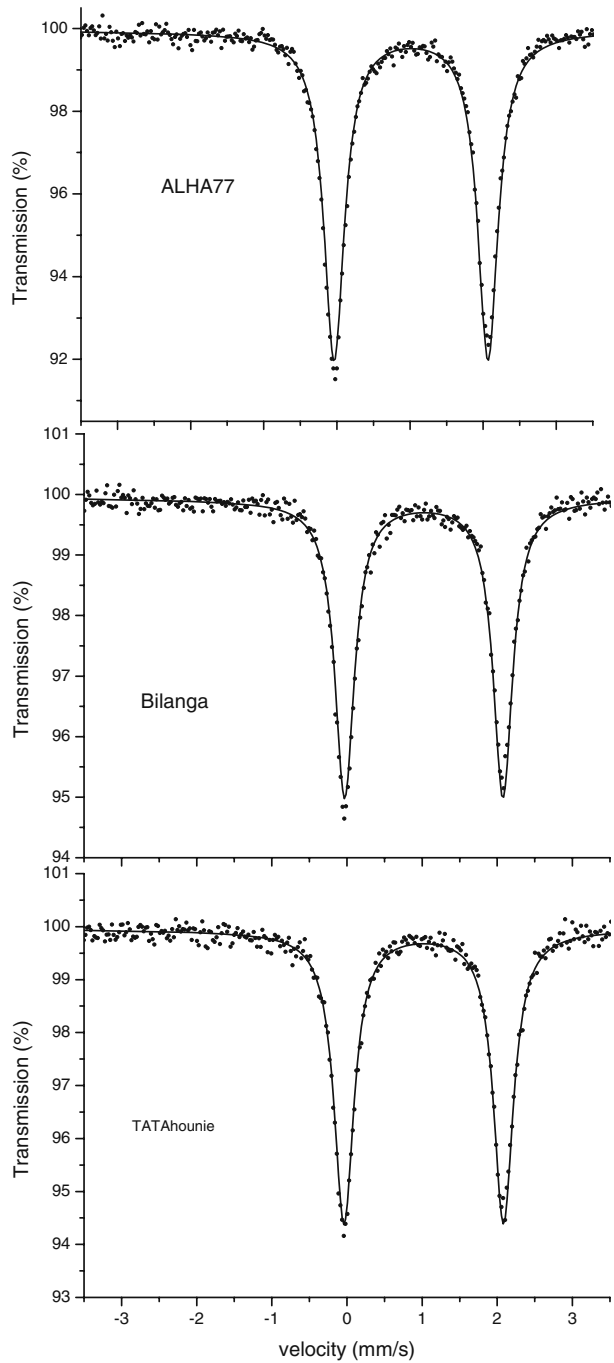
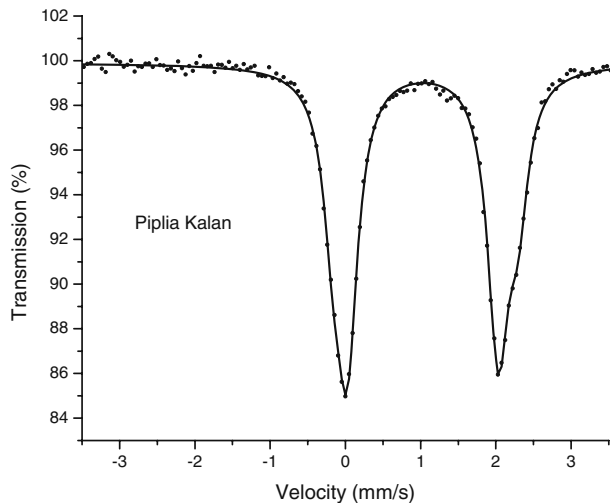


Table 1 Mossbauer parameters for HED meteorites at room temperature

Meteorite	Doublet	IS (mm/s)	QS (mm/s)	Area (%)	Reference
ALH77256 (diogenite)	I	1.10	2.10	100	Present study
Tatahouine (diogenite)	I	1.11	2.12	100	Present study
Bilanga (diogenite)	I	1.11	2.11	100	Present study
Piplia Kalan (eucrite)	I	1.08	1.94	73	Our group [10]
	II	1.13	2.40	22	
	III	0.26	0.93	5	
Ibitira (eucrite)	I	1.15	2.52	–	[13]
	II	1.17	1.94	–	
	III	1.12	0.90	–	
Stannern (eucrite)	I	1.16	2.46	–	[14]
	II	1.13	1.99	–	
Kapoeta (howardite)	I	1.13	1.95	59	[15]
	II	1.14	2.26	41	
Lohawat (howardite)	I	1.18	2.03	73	Our group [10]
	II	1.22	2.52	27	

Fig. 2 Mössbauer spectra of Piplia Kalan (eucrite) at 300 K, velocity resolution = 0.02 mm/s

The three diogenites studied in this work correspond to three different physical situations. Bilanga is a recent fall, Tatahouine is about 75 years old fall and ALHA77256 is recovered from Allen Hills at Antarctica. They must have suffered different terrestrial conditions but the Fe occupancy in the pyroxene sites does not seem to have altered. We thus propose that occupancy of Fe in only one site in pyroxene structure in an HED meteorite should be taken as a serious indicator of diogenite even if all the diogenites do not have such strong ordering.

Our results are in contrast to the single crystal XRD investigation by Zema et al. [25] where they have studied a number of systems including diogenites. Though they found a strong preference of Fe²⁺ for M2 sites, nevertheless it was also present in measurable amount in M1 sites. However all the Mössbauer studies so far indicate only one site for iron in diogenite indicating a much slower cooling in preterrestrial history. A larger volume of data on HED meteorites is needed to resolve the issue.

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