

SCANNING ELECTRON MICROSCOPY, X-RAY DIFFRACTION, MAGNETIZATION MEASUREMENTS AND MÖSSBAUER SPECTROSCOPY OF SARIÇİÇEK HOWARDITE

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Howardites, eucrites and diogenites (HED) is a group of stony meteorites (achondrites). Asteroid (4) Vesta is considered as parent body of HED meteorites [Mittlefehldt, 2015; Burbine et al., 2018]. Howardites are achondrites which consist of orthopyroxene (Fe, Mg)SiO₃, Ca-rich and Ca-poor clinopyroxenes (Fe, Mg, Ca)SiO₃ as well as small amount of troilite FeS, chromite FeCr₂O₄ and other minerals [Mittlefehldt, 2015]. The HED parent body was early differentiated with possibly very rapid solidification and cooling [McSween Jr. et al., 2013]. Therefore, the study of this type of meteorites by means of various physical techniques is of interest. A bright bolide was seen in Turkey (Bingol province) on September 2, 2015, at 20:10:30 UTC. A lot of meteorite fragments were found at the village Sariçiçek. Further, this meteorite was named Sariçiçek and classified as achondrite howardite (*Meteoritical Bulletin*, 105, 2016). The first studies of this howardite were performed in [Unsalan et al., 2019; Maksimova et al., 2020]. In the present work the results of iron-bearing minerals in Sariçiçek howardite and its fusion crust investigation using optical microscopy, scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), magnetization measurements and Mössbauer spectroscopy with a high velocity resolution are presented and compared with data for similar minerals in some other meteorites.

Optical microscopy analysis of the bulk interior of Sariçiçek showed the presence of the silicate matrix with metal grains located either separately or in association with troilite inclusions. Troilite and chromite were also found as separate inclusions in the matrix. It should be noted that one xenolith clast with a large amount of metal grains was observed. A spherical chondrule xenolith with small metal grains was also found in the matrix. Scanning electron microscopy demonstrated the presence of metal grains as well as troilite, chromite and ilmenite FeTiO₃ inclusions. EDS showed the presence of α -Fe(Ni, Co), α_2 -Fe(Ni, Co) and γ -Fe(Ni, Co) phases. EDS analysis of chromite inclusions showed the presence of Al in the range ~3–5 at.% that may indicate the possible presence of hercynite FeAl₂O₄. The fusion crust of Sariçiçek represents

a glass-like re-melted silicate matrix with cavities in the glass [Unsalan et al., 2019]. SEM with EDS analyses of the Sariçiçek fusion crust showed several chromite grains as well as the presence of ~3.5–4.5 at.% of Al, suggesting the presence of hercynite in FeCr₂O₄.

XRD analysis of the bulk interior of Sariçiçek fragment showed the following minerals: anorthite CaAl₂Si₂O₈ (22.9 wt.%), orthopyroxene (37.6 wt.%), Ca-rich clinopyroxene (12.3 wt.%) and Ca-poor clinopyroxene (23.9 wt.%), ilmenite (1.0 wt.%), troilite (0.6 wt.%), chromite (1.1 wt.%), hercynite (0.4 wt.%) and α -Fe(Ni, Co) phase (0.2 wt.%). Rietveld full profile analysis of XRD pattern of the Sariçiçek bulk interior allowed calculating the unit cell parameters for orthopyroxene and clinopyroxene. XRD pattern of the Sariçiçek fusion crust demonstrated a glass-like shape with weak orthopyroxene reflexes.

Magnetization measurements of the Sariçiçek howardite bulk interior and its fusion crust (M(T) and M(H) curves) indicated that both materials consisted of two fractions: paramagnetic and magnetic. However, the quantity of these fractions in the bulk interior and fusion crust is slightly differing. The M(T) zero-field-cooling (ZFC) and field-cooling (FC) plots for the bulk interior in the range 5 and 300 K under 250 Oe exhibit a paramagnetic behavior. The ZFC branch of the fusion crust shows a well-defined peak at 41 K that may be related to the ferrimagnetic-paramagnetic phase transition in chromite [Gattacceca et al., 2011]. At 5 K the saturation moment M_s is 12.7 emu/g for the bulk interior, while that for the fusion crust is 3.9 emu/g.

Mössbauer spectrum of the Sariçiçek bulk interior measured at room temperature is shown in Fig. 1a. The result of the best spectrum fit showed the presence of two magnetic sextets, nine quadrupole doublets and one paramagnetic singlet. Magnetic sextets were related to α -Fe(Ni, Co) phase and troilite. Three pairs of quadrupole doublets with the largest values of quadrupole splitting were associated to the ⁵⁷Fe in the M1 and M2 sites in orthopyroxene, Ca-poor and Ca-rich clinopyroxenes. Two quadrupole doublets were related to Fe²⁺ and Fe³⁺ in ilmenite because of the inter-valence charge-transition

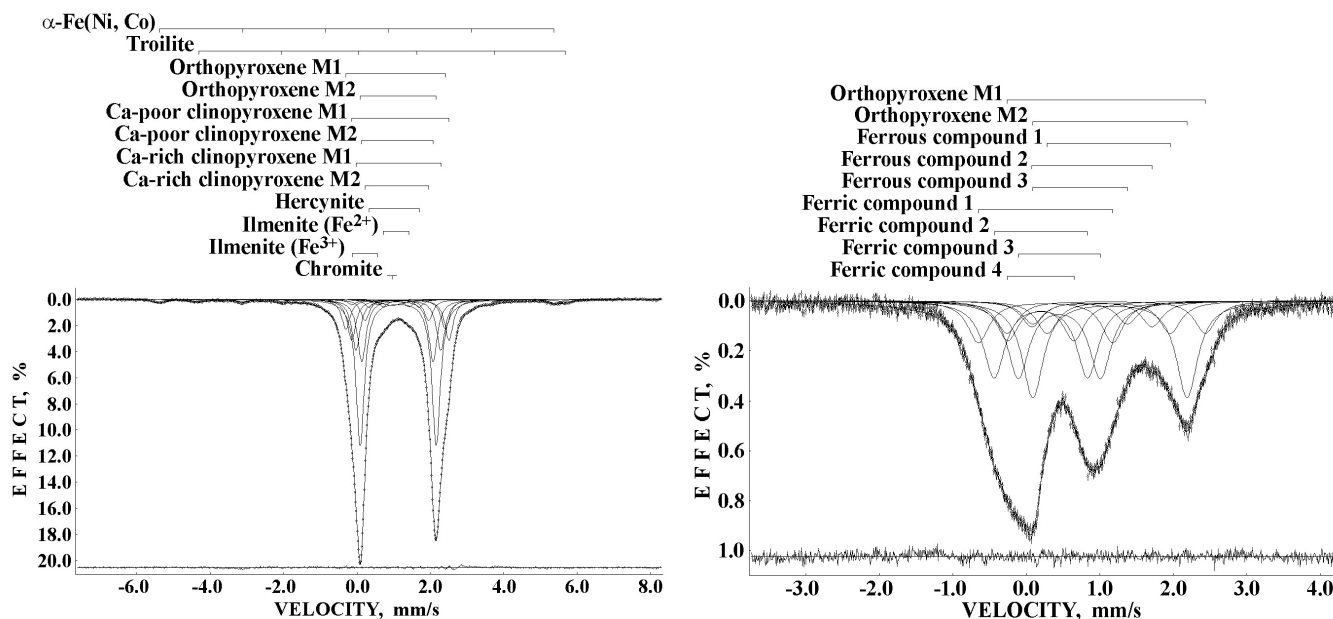


Fig. 1. The Mössbauer spectra of the Sariçiçek bulk interior (a) and the fusion crust (b) measured at 295 K.

Indicated components are the results of the best fit. The differential spectra are shown below

mechanism $\text{Fe}^{2+} \text{Ti}^{4+} \rightarrow \text{Fe}^{3+} \text{Ti}^{3+}$ is possible in ilmenite (see [Burns, 1981]). The hyperfine parameters of the remaining doublet appeared to be close to those of hercynite [Osborne et al., 1981]. One singlet was related to chromite (see, e.g. [Maksimova et al., 2018; Oshtrakh et al., 2019] and references therein).

Mössbauer spectrum of the Sariçiçek fusion crust measured at room temperature is shown in Fig. 1b. The hyperfine parameters of two quadrupole doublets corresponded to the ^{57}Fe in the M1 and M2 sites in orthopyroxene. However, these parameters differ slightly from those for the bulk interior. These differences can be a result of thermal effect on orthopyroxene during the fusion crust formation. Remaining seven quadrupole doublets demonstrate hyperfine parameters corresponding to ferrous and ferric compounds. However, it is not possible to identify chemical compounds related to these components.

The Fe^{2+} occupancies of the M1 and M2 sites in orthopyroxene and clinopyroxene of Sariçiçek bulk interior were evaluated similar to those in [Maksimova et al., 2018; Oshtrakh et al., 2019]. The distribution coefficient (K_D) and the temperature of Fe^{2+} and Mg^{2+} cation equilibrium distribution (T_{eq}) in orthopyroxene were estimated using XRD and Mössbauer data: $K_D=0.12$ and $T_{\text{eq}}=886$ K (XRD) and $K_D=0.12$ and $T_{\text{eq}}=878$ K (Mössbauer spectroscopy). These results obtained using two independent techniques appeared to be in agreement. In addition, the closure temperature for the Fe^{2+} redistribution between the M1 and M2 sites in orthopyroxene with the fusion crust rapid cooling was evaluated as 1177 K.

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REFERENCES

1. Burbine T.H., Buchanan P.C., Klima R.L., Binzel R.P. Can Formulas Derived from Pyroxenes and/or HEDs be Used to Determine the Mineralogies of V-type Asteroids? // *J. Geophys. Res.: Planets*. 2018. V. 123. P. 1791–1803.
2. Burns R.G. Intervalence transitions in mixed valence minerals of iron and titanium // *Ann. Rev. Earth Planet. Sci.* 1981. V. 9. P. 345–383.
3. Gattacceca J., Rochette P., Lagroix F., Mathé P.-E., Zanda B. Low temperature magnetic transition of chromite in ordinary chondrites // *Geophys. Res. Lett.* 2011. V. 38. L10203.
4. Maksimova A.A., Oshtrakh M.I., Chukin A.V., Felner I., Yakovlev G.A., Semionkin V.A. Characterization of Northwest Africa 6286 and 7857 ordinary chondrites using X-ray diffraction, magnetization measurements and Mössbauer spectroscopy // *Spectrochim. Acta, Part A: Molec. and Biomolec. Spectroscopy*. 2018. V. 192. P. 275–284.
5. Maksimova A.A., Unsalan O., Chukin A.V., Karabanalov M.S., Jenniskens P., Felner I., Semionkin V.A., Oshtrakh M.I. The interior and the fusion crust in Sariçiçek howardite: Study using X-ray diffraction, magnetization measurements and Mössbauer spectroscopy // *Spectrochim. Acta, Part A: Molec. and Biomolec. Spectroscopy*. 2020. V. 228. P. 117819.

6. McSween H.Y., Jr., Binzel R.P., De Sanctis M.C., Ammannito E., Prettyman T.H., Beck A.W., Reddy V., Le Corre L., Gaffey M.J., McCord T.B., Raymond C.A., Russell C.T. Dawn; the Vesta–HED connection; and the geologic context for eucrites, diogenites, and howardites // *Meteorit. & Planet. Sci.* 2013. V. 48. P. 2090–2104.
7. Mittlefehldt D.W. Asteroid (4) Vesta: I. The howardite-eucrite-diogenite (HED) clan of meteorites? // *Chem. Erde.* 2015. V. 75. P. 155–183.
8. Osborne M.D., Fleet M.E., Bancroft G.M. Fe^{2+} – Fe^{3+} ordering in chromite and Cr-bearing spinels // *Contrib. Mineral. Petrol.* 1981. V. 77. P. 251–255.
9. Oshtrakh M.I., Maksimova A.A., Chukin A.V., Petrova E.V., Jenniskens P., Kuzmann E., Grokhovsky V.I., Homonnay Z., Semionkin V.A. Variability of Chelyabinsk meteoroid stones studied by Mössbauer spectroscopy and X-ray diffraction // *Spectrochim. Acta, Part A: Molec. and Biomolec. Spectroscopy.* 2019. V. 219. P. 206–224.
10. Unsalan O., Jenniskens P., Yin Q.-Z., Kaygisiz E., Albers J., Clark D.L., Granvik M., Demirkol I., Erdogan I.Y., Bengu A.S., Özel M.E., Terzioğlu Z., Gi N., Brown P., Yalcinkaya E., Temel T., Prabhu D.K., Robertson D.K., Boslough M., Ostrowski D.R., Kimberley J., Er S., Rowland D.J., Bryson K.L., Altunayar-Unsalan C., Ranguelov B., Karamanov A., Taztchev D., Kocahan Ö., Oshtrakh M.I., Maksimova A.A., Karabanalov M.S., Verosub K.L., Levin E., Uysal I., Hoffmann V., Hiroi T., Reddy V., Ildiz G.O., Bolukbasi O., Zolensky M.E., Hochleitner R., Kaliwoda M., Öngen S., Fausto R., Nogueira B.A., Chukin A.V., Karashanova D., Semionkin V.A., Yeşiltaş M., Glotch T., Yilmaz A., Friedrich J.M., Sanborn M.E., Huyskens M., Ziegler K., Williams C.D., Schönbächler M., Bauer K., Meier M.M.M., Maden C., Busemann H., Welten K.C., Caffee M.W., Laubenstein M., Zhou Q., Li Q.-L., Li X.-H., Liu Y., Tang G.-Q., Sears D.W.G., Mclain H.L., Dworkin J.P., Elsila J.E., Glavin D.P., Schmitt-Kopplin P., Ruf A., Le Corre L., Schmedemann N. Howardite fall in Turkey: Source crater of HED meteorites on Vesta and impact risk of Vestoids // *Meteorit. & Planet. Sci.* 2019. V. 54. P. 953–1008.