Petrographic and Micro-Raman Study of Thermal and Shock Metamorphism in Mezőmadaras, Knyahinya and Mócs L-Chondrites

I . Gyollai[a], Sz. Nagy[a] , J. Fürj[a], Sz. Bérczi[a], A. Gucsik[b], M. Veres[c]

[a]*Eötvös University, Faculty of Science, Institute of Physics, Dept. Material Physics, H-1117 Budapest, Pázmány P. s. 1/a, Hungary*
[b]*Max Planck Institute for Chemistry, Dept. of Geochemistry, Joh.-J. Becherweg 27, D-55128, Mainz, Germany*
[c]*Institute for Solid State Physics and Optics H-1121 Budapest Konkoly-Thege M. út 29-33., Hungary*

Abstract. We investigated three Hungarian L-chondrites: Mezőmadaras, Knyahinya, and Mócs sample. In Knyahinya chondrite, two phenomena were observed as follows: the weak mosaicism (S4) and mechanical twins in pyroxene. The Mócs sample is characterized by strong shock metamorphic effects such as high density of fractures and abundant shock-veins. Planar Deformation Features (PDFs) were identified in two olivine grains, and an olivine grain shows well-developed Planar Fractures (PFs). In Mezőmadaras sample, there are irregular fractures (S1), and PFs (S3), and mechanical twins in pyroxene. We have reinvestigated of these meteorite samples using Raman spectroscopy for the identification of shock-metamorphic effects, which occurred in the structure changes of olivine and pyroxene grains. The olivine doublet peak position is shifted to higher wavenumbers, due to partly disordered olivine structure. We observed that minerals with mechanical twins exhibit less interference color, compared to the non-shocked minerals, especially pyroxene. It is important to note that, the mechanical twins were complicated to describe, only the direction of the deformation was determined. On the basis of the measured FWHM, the following structural disordering degree of the selected samples can be determined as a (growing rate): Castle Rock, Mezőmadaras, Shergotty and Mócs. The result reveals that amorphization rate is the highest in Mócs and Shergotty pyroxene grains.

Keywords: L-chondrite, thermal metamorphism, shock metamorphism, Raman spectroscopy.
PACS: 91.65.Sn, 95.75.De , 95.75.Fg, 96.12.Bc, 96.25.Pq , 96.30.Za

INTRODUCTION

We investigated two phenomena in a series of the Hungarian L- chondrites: shock and thermal metamorphism. Thermal metamorphism transforms the textures into the relatively small chondritic planetary body. Shock metamorphism is caused by an impact processes transforming texture and mineral structure mainly in the outermost layers of the chondritic planetary body [1]. Thermal metamorphic effects were studied in optical microscope, shock metamorphic effects were investigated using optical microscope and Raman spectroscopy.

CP1163, *Micro-Raman Spectroscopy and Luminescence Studies in the Earth and Planetary Sciences*, edited by A. Gucsik

The Mócs and Mezőmadaras meteorites felt in 1882 and 1852, respectively. The Mócs meteorite is a L5 and Mezőmadaras is an L3-type chondrite. The chemical composition of these samples was determined by an Electron Microprobe Analyses [2]. The shock-metamorphic properties of Mócs and Mezőmadaras meteorites were classified as S3-S5 for Mócs, and S2-S3 for Mezőmadaras by Optical Microscope (OM) (based on shock stage classification given by [3]).

We have reinvestigated of these samples using Raman spectroscopy for the identification of the shock-metamorphic effects occurred in the structure changes of olivine and pyroxene grains.

EXPERIMENTAL PROCEDURE

The mineral assemblages and textures were characterized with a Nikon Eclipse LV100POL optical microscope. Knyahinya and Mócs sample were prepared with 35-μm in thickness. Mineral assemblages and textures were characterized by a Renishaw-1000 Raman spectrometer, the laser wavelength was 785 nm, with focused energy of 8 mW. The maximal focus was driven to 1μm spot in diameter. The thin sections were mounted in epoxy material, and the sample thickness is 30 μm.

RESULTS

Optical Microscopy Investigations

Thermal Metamorphism

The detailed OM analyses show mechanical twins in pyroxenes (Fig.1), planar fractures (PF's), and planar deformation features (PDF's) (Fig.2). Furthermore, shock-mosaicism in olivine grains is also discernible (Fig. 3). The Raman spectroscopical investigation revealed β-(Mg, Fe) SiO_4 olivine structure (wadsleyite) in a PDF's enriched and highly deformed olivine grain.

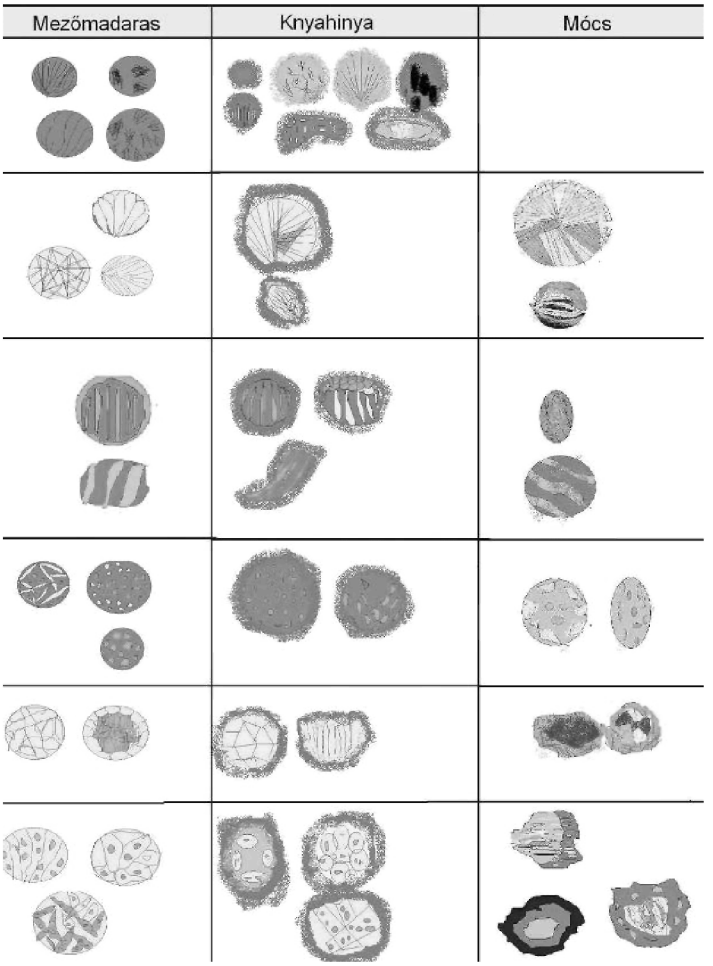
In (L3,7) Mezőmadaras sample, there are a lot of microchondrules, and the boundary of chondrules are in a sharp contrast, but in Knyahinya (L5) sample the margin of chondrules is blurry. Mezőmadaras and Mócs samples contain relatively small number of chondrules, which show the recrystallized texture (Table 2). The grains were grown in the course of thermal metamorphism. The matrix of the Mezőmadaras (L3) sample was kryptocrystalline, in Knyahinya greater crystals appeared in the matrix, while in the Mócs sample (L6) the matrix became microgranular. Compared to the spherical shape of chondrules in Mezőmadaras to those of Knyahinya sample, the Knyahinya chondrules were greater in size, but they were more deformed in shape, and containing more chondrule-fragments in Knyahinya (Table 2). We described the chondrules of three Hungarian L-chondrites as follows (Table 1):

TABLE (1). chondrumtypes in Hungarian L-chondrites
New chondrumtype :
*: symplectitic chondrule (Photo 1) (3 chondrules)
**: beltic chondrules: accreted from little chondrules

Samples	Texture of chondrules					
	Glassy	Excent-roradial	Porphyric	Barred	Granular	Poicilitic
Mezőmadaras*	9	8	20	5	11	10
Knyahinya	7	4	21	6	6	5
Mócs*	0	7	1	1	7	1

TABLE 2: Alteration of chondrules by thermal metamorphism

Rows: texture of chondrules: (1) glassy, (2) excentroradial, (3) barred, (4) porphyric, (5) granular, (6) poicilitic (last row by Mócs: beltic codrules



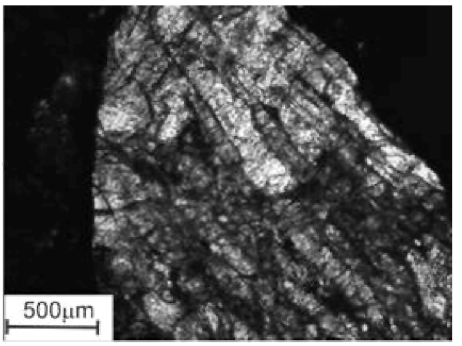


FIGURE 1. Simplectic chondrule in Mezőmadaras chondrite: olivine worm growth with pyroxene.

Shock metamorphism

The shock metamorphism in our sample is a local phenomena, which is not abundant in the whole rock. Based on Stöffler et al. [3], we classified the shocked minerals into the following shock stages (Table 3). In Mezőmadaras sample, there are irregular fractures (S1), and PFs (S3), and mechanical twins in pyroxene.

TABLE 3: Shock stages after Stöffler [3].

Shock stage	**Effects resulting from general shock pressure**	**Effects from local P-T excursions**	**Shock Pressure (GPa)**
S1 unshocked	Sharp optical extinction as seen in microscope. Small number of irregular fractures (cracks)	None	<5
S2 very weakly shocked	Undulatory /wavy/ extinction, irregular fractures	None	5-10
S1 unshocked	Sharp optical extinction as seen in microscope. Small number of irregular fractures (cracks)	None	<5
S3 weakly shocked	Olivine: Planar fractures, undulatory extinction, irregular fractures. Plagioclase: undulatory extinction	Opaque shock veins, melt pockets, sometimes interconnected	15-20
S4 moderately shocked	Olivine: weak mosaicism, planar fractures Plagioclase: undulatory extinction, isotropic in places, planar deformation features	Melt pockets, interconnected melt veins, opaque shock veins	30-35
S5 strongly shocked	Olivine: strong mosaicism, planar fractures and planar deformation features. Plagioclase: maskelynite (isotropic feldspar	Pervasive occurrence of melt pockets and veins, opaque shock veins	45-55
S6 very strongly shocked	Olivine: solid state recrystallization and staining, presence of ringwoodite, local melting. Plagioclase: shock melted	Same as in Stage 5	75-90

We observed that minerals with mechanical twins exhibit less interference color, compared to the non-shocked minerals, especially pyroxene (Fig. 2). It is important to note that, the mechanical twins were difficult to describe, only the direction of the deformation was determined. In Knyahinya chondrite, two phenomena were observed as follows: the weak mosaicism (S4) (Fig. 3) and mechanical twins in pyroxene. The Mócs sample is characterized by strong shock metamorphic effects such as, high density of fractures and abundant shock-veins. Planar Deformation Features (PDFs) were identified in one olivine grain, and an olivine grain shows well-developed PFs (Figs. 4,5).

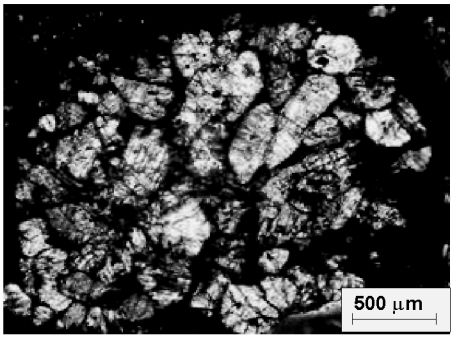


FIGURE 2. : Mechanical twins in pyroxenes in poicilitic chondrule. (Mezőmadaras sample, OM photo, crossed polars – ELTE, Hungary)

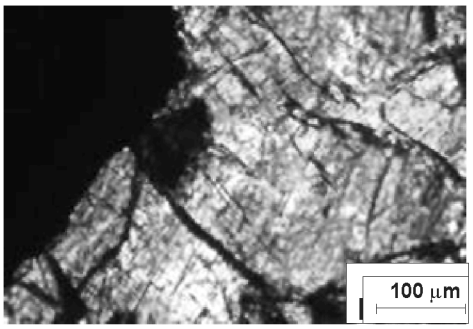


FIGURE 3. Weak mosaicism in olivine (Knyahinya sample, OM photo, crossed polars – ELTE, Hungary)

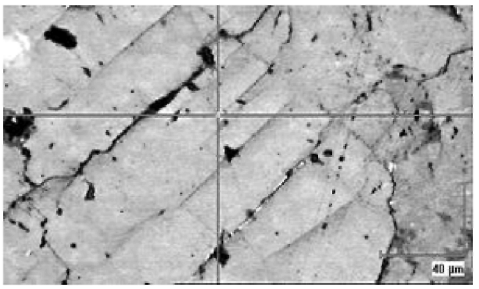


FIGURE 4. Planar fractures in olivine (Mócs sample, reflected light micrograph – KFKI, Hungary)

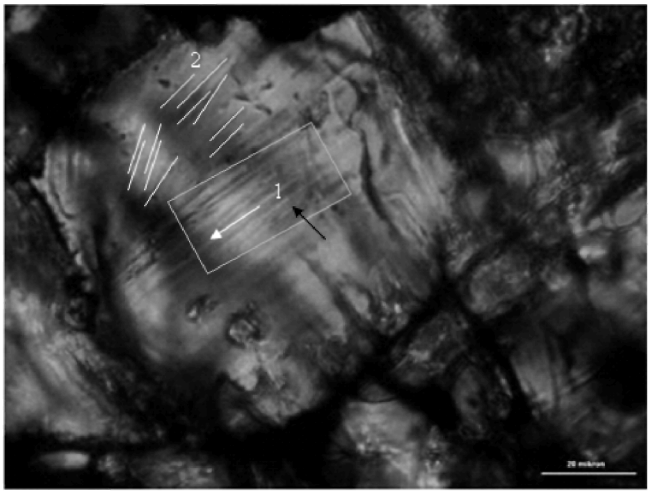


FIGURE 5. Deformation microstructures in olivine (Mócs sample) show strong mosaicism. (OM photo in crossed polars) (Photomicrograph was taken at Department of Petrology and Geochemistry, Eötvös University, Hungary) (1): Kinkband-lamellae in olivine forming after large pressure. The olivine show strongly decreased interference color near the PDFs.

Raman spectroscopy

Mócs Meteorite

The relatively highly deformed olivine grain was selected for the Raman investigations representing two analyzing points, as follows. The first point (Mócs I) was placed on the PDF's lamellae, the other points (Mócs II) was in between PDF's (Fig. 6). The characteristic Raman peaks of Mócs I are: 630 (strong-s), 706 (medium-m), 722 (very weak-vw), 751 (weak-w), 852 (very strong-vs), 883 (very strong-vs), and 987 (strong-s) cm^{-1}. The Mócs II-spectrum contains the following peaks: 421 (s), 577 (m), 642 (w), 822 (vs), 854 (vs), 920 (m), and 958 (m) cm^{-1}. Table 4 used as a reference material from the Trudy's mine olivine to the comparison with the vibrational changes of our spectra (Figs. 7,8). Note that the spectrum was derived from CALTECH Raman database (Table 4, Figs. 7,8.).

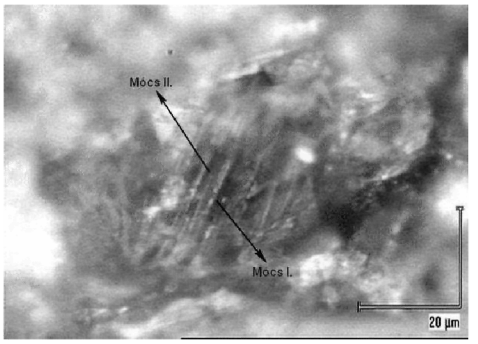


FIGURE 6. Places of two points for Raman spectroscopical analysis in deformation microstructure of an olivine grain from Mócs meteorite. Reflected light micrograph.

TABLE 4: Raman peaks and their vibration types of PDF-rich olivine grain in Mócs chondrite. The intensity of peaks: (vw) very weak, (w) weak, (m) middle, (s) strong, (vs) very strong

Trudy's mine Arizona	**Mócs II.**	**Mócs 1.**	**vibrational oscilation type belonging to top positions**
430(m)	-	-	Olivine SiO_4 tetrahedrals defectioning and symmetrical deformation vibration
496 (s)	496 (s)	496 (s)	Olivine MgO6 octahedras vibration
543(m)	-	-	Olivine SiO_4 tetrahedrals and asymmetrical deformation vibration
598(m)	600	-	Olivine SiO_4 tetrahedrals and asymmetrical deformation vibration
-	674	+	Si-O-Si dimer bands
-	712	+	Forbidden vibrations , polymerizations of SiO4 tetrahedras (based on [4,5]) Si-O-Si dimer bands Forbidden vibrations , polymerizations of SiO4 tetrahedras (based on [4,5])
823(vs)	821(vs)	821 (vs)	Olivine SiO_6 symmetric (60%) and asymmetric (40%) stretching vibration
Trudy's mine Arizona	**Mócs II.**	**Mócs 1.**	**vibrational oscilation type belonging to top positions**
	852 (vs)	852(vs)	Olivine SiO_6 symmetric (60%) and asymmetric (40%) stretching vibration
854 (vs)			Olivine SiO_6 symmetric (60%) and asymmetric (40%) stretching vibration
920(m)	916(m)	-	Olivine SiO_6 asymmetrical vibration
960(s)	956(w)	957(w)	Olivine SiO_6 assymmetrical vibration

The SiO4-related stretching vibrational modes such as peaks between 821 and 852 cm^{-1} shifted to the higher lower wawenumber region in the Mócs sample, which suggests that there is no coordination change of Si. This also indicates that there is no presence of wadsleyte and ringwoodite. The broad peak at 640-720 cm^{-1} might be associated with polymerisation of SiO4 tetrahedra [4-6].

According to McMillan et. al. [7] in every wadsleyite spectra are ringwoodite peaks and in every ringwoodite spectra are wadsleyte peaks. By earlier measurement identified wadsleyte peak by 722 cm^{-1} Raman shift affected by imprecision measuring a peak at 496 cm^{-1} is due to vibration of MgO_6 octahedra. The partly polimerisation of SiO_4 tetrahedra was caused by high stage shock metamorphism.

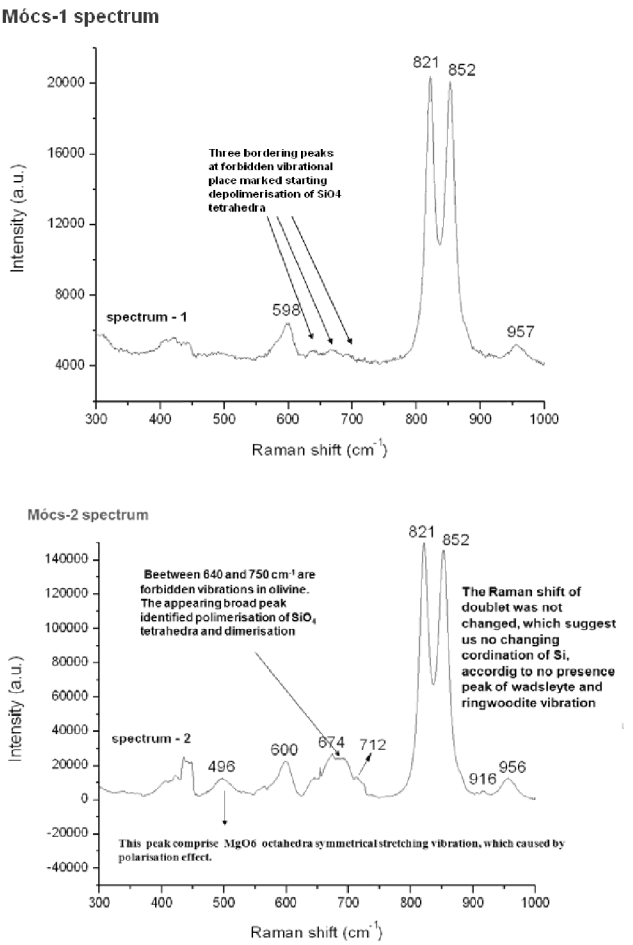


FIGURE 7-8. Raman spectra of olivine from different sources.

Mezőmadaras Meteorite

Mezőmadaras sample contains poikilitic pyroxene chondrules, which show elongated shape. Within these condrules, the pyroxenes have mechanical twins. Within the most common (Mg-Fe-Ca) pyroxenes, we can distinguish more than ten Raman active vibrational modes [8]. The four spectra (Fig. 9) show different chemical composition between the Castle Rock (as a reference spectrum) and three meteorites sample. The Mócs spectrum exhibits the following peaks: 368 (vs), 426 (s), 475 (m), 693 (vs), 710 (vs), 1040 (vs) cm^{-1}. The Mezőmadaras spectrum contains peaks: 372 (s), 475 (w), 694 (vs), 716 (vs), and 1041 (vs) cm^{-1}. The characteristic peaks of Shergotty pyroxenes are: 359 (vs), 426 (vs), 567 (vw), 590 (vw), 698 (vs), and 1043 (vs) cm^{-1}. The Castle Rock pyroxene exhibits the following peaks: 340 (vs), 402 (s), 439 (s), 538 (m), 661 (vs), 682 (vs), 860 (m), 936 (w), and 1009(vs) cm^{-1} (Table 5, Fig. 9).

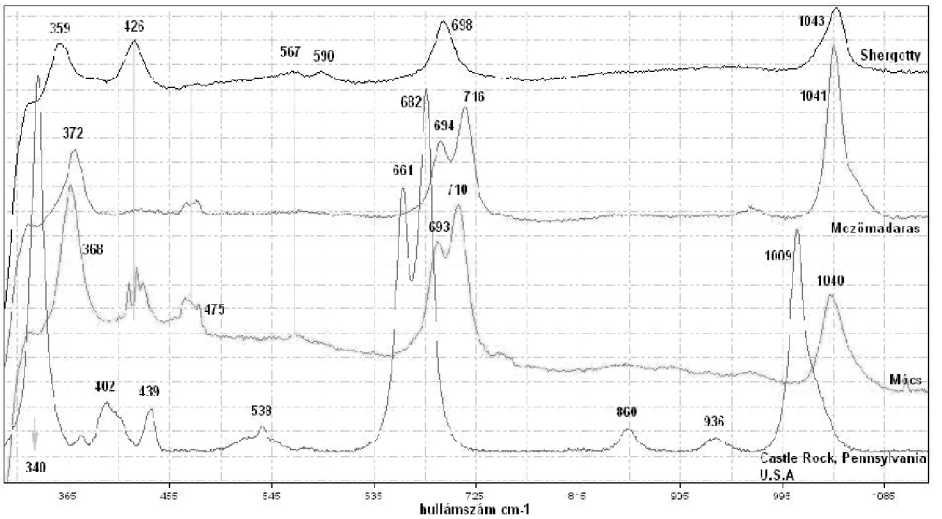


FIGURE 9. Raman spectra of pyroxenes from different meteorite and rock samples (x-axis is wavenumber in cm^{-1}, y-axis is intensity of Raman peaks).

TABLE 5: Vibration types of pyroxenes after Huang et al [8]. The boldfaced intensities were used by FHWM counting.

Castle Rock	Mócs	Mezőmadaras	Shergotty	Vibration types of Raman peaks
340	-	-	-	M-O band stretching vibration
-	-	-	359	Ca-O band stretching vibration
-	368	372	-	Mg-O band stretching vibration
402	-	-	-	Ca-O bandstretching vibration
-	426	-	426	Mg-O band stretching vibration
439	-	-	-	Mg-O band stretching vibration
-	475?	475?	-	Alteration phase?
538	-	-	-	O-Si-O band bend vibration
-	-	-	567?	Alteration phase?
-	-	-	590?	Alteration phase?
661-682	693-710	694-716	698	Si-O-Si band bend vibration
860	-	-	-	Si-O bridge stretching vibration
936	-	-	-	Si-O bridge bend vibration
1009	-	-	-	Si-O bridge bend vibration
-	1040	1041	1043	Si-O bridge bend vibration

On the basis of the measured FWHM, the following structural disordering degree of the selected samples can be determined as a (growing rate): Castle Rock, Mezőmadaras, Shergotty and Mócs. The result reveals that amorphisation rate is the highest in Mócs and Shergotty pyroxene grains (Table 6).

TABLE 6: FHWM in pyroxene

FWHM values of pyroxenes	Under 500 cm-1	500 – 760 cm-1	800 cm-1 above
Castle Rock, PA,. USA	11	32	15
Mezőmadaras	15	34	18
Shergotty	15	33	21

CONCLUSION

Consequently, this study also demonstrates that the micro-Raman spectroscopy is a useful and potential tool for the characterization and determination of the degree of thermal and shock metamorphism of meteorites. The results of Raman spectroscopy suggest the deformation microstructure system (including kink-band lamellae, PFs, PDFs), in a highly deformed olivine grains, which is an evidence for the localized high stage shock-metamorphism in Mócs (L5) as a Hungarian meteorite. The changes in FHWM value are also significant in meteoritical pyroxenes. This indicates structural disordering in Si-O stretching vibrational modes and SiO4 tetrahedra rotational vibrations, which are considerable due to shock-metamorphism. The FHWM represents growing "amorphisation" rate in our investigated meteoritical pyroxenes.

ACKNOWLEDGMENTS

We are grateful to Professors I. Kubovics, Z. Ditrói-Puskás and Cs. Szabó for advices by petrography, and to LRG (Eötvös University) and KFKI for assistance with the analytical instrument.

REFERENCES

1. Sz. Bérczi, S . Józsa, Zs. Kovács, B. Lukács, Gy. Szakmány, *Acta Mineral.-Petrograph.*, **45/2** 55-60 (2004).
2. I. Kubovics, B. Lukács, Sz. Bérczi, K. Gál-Sólymos, A. Kiss, G. Albert, B. Gellért, Cs. Detre, *NIPR Symposium*, Tokyo pp. 13-14 (1997).
3. D. Stöffler, K. Keil, S. Edward, *Geochim. Cosmochim. Acta* **55,** 3845-3867 (1991).
4. D. J. Durben, P.F. McMillan, G.H. Wolf. *American Mineralogist*, **8**, 1141-1148 (1993).
5. P. Gillet, J. A. Barrat, P. B. Beck, Marty, B., R.C.Greenwood, I.A.Franchi, M. Bohn, J.Cotten: *Meteorit. Planet. Sci.* **40**, 1175-1184 (2005).
6. B. van de Moortele , B. Reynard ,P.F. McMillan , M. Wilson , P. Beck , P.Gillet , S. Jahn, *Earth Planet. Sci. Lett.* **261,** 469-475 (2007).
7. P.F. McMillan and A. Akaogi, *Am. Mineral.* **72**, 361–364. (1987).
8. E. Huang, C.H. Chen, T Huang, E.H. Lin, and Ji-an Xu, *Amer. Miner.*, **85**, 473-479 (2000).