Meteoritics & Planetary Science 35, 155–159 (2000)
© Meteoritical Society, 2000. Printed in USA.

Micro Raman spectroscopy of amphiboles and pyroxenes in the martian meteorites Zagami and Lewis Cliff 88516

TAKASHI MIKOUCHI[1,2]* AND MASAMICHI MIYAMOTO[1]

[1]Mineralogical Institute, Graduate School of Science, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
[2]Mail Code SN2, Planetary Science Branch, NASA Johnson Space Center, Houston, Texas 77058, USA
*Correspondence author's e-mail address: TMikochi@ems.jsc.nasa.gov

(Received 1999 June 30; accepted in revised from 1999 October 5)

Abstract–We studied micro Raman spectroscopy of amphiboles and pyroxenes in the martian meteorites Zagami and Lewis Cliff (LEW) 88516. The obtained Raman spectra of the amphiboles are similar to those of kaersutite, reconfirming the previous studies that they are kaersutitic amphiboles enriched in Ca, Al, and Ti. Even though actinolite belongs to the same amphibole group (calcic amphibole) as kaersutite, the Raman spectra of terrestrial actinolite are distinct from those of kaersutite, probably reflecting complex amphibole crystal structures. The Al-Ti-rich pyroxene observed in the magmatic inclusions within LEW 88516 olivine is compositionally similar to kaersutite but shows Raman spectra nearly identical to the regular pyroxene rather than amphibole. In contrast to amphibole, this will be due to relatively simple crystal structures of pyroxene. Thus, the Raman spectra of Al-Ti-rich phases in the martian meteorites are distinct between kaersutite and Al-Ti-rich pyroxene, and this study demonstrates that micro Raman spectroscopy is one of the best tools to perform mineralogical characterization of mineral phases in martian meteorites.

INTRODUCTION

So far, martian meteorites are believed to be the only available samples that give us direct clues to martian igneous processes (*e.g.*, McSween, 1994; Meyer, 1998, and references therein). Although major constituent minerals of martian meteorites are olivine, pyroxene, and plagioclase that are same as the other igneous meteorites (asteroidal achondrites), martian meteorites contain hydrous minerals that are completely absent in asteroidal achondrites. Hydrous minerals in martian meteorites are divided into two types—primary or secondary. Primary hydrous minerals are amphibole and biotite that are found in some martian meteorites (*e.g.*, Meyer, 1998). These two mineral species directly crystallized from the martian magmas. Secondary hydrous minerals are mainly clays, including iddingsite, smectite, illite, ferrihydrite, and FeO(OH), that are most abundantly seen in the nakhlite group (*e.g.*, Meyer, 1998). These phases are also considered as martian aqueous alteration products (*e.g.*, Treiman *et al.*, 1993). In this paper, we pay attention to amphiboles in martian meteorites that are very important phases for understanding martian igneous processes involving water contents of magmas and atmospheric evolution of the red planet. Amphibole has been reported from a few groups of martian meteorites—basaltic, lherzolitic, and dunitic groups (Floran *et al.*, 1978; Johnson *et al.*, 1991; McCoy *et al.*, 1992; McSween and Harvey, 1993; Mikouchi and Miyamoto, 1999; Treiman, 1985, 1997, 1998; Watson *et al.*, 1994). They are always present within magmatic inclusions trapped in pyroxene or olivine in spite of the large difference of the host petrography and mineralogy. Their mineral compositions are almost identical to one another, except for the variable Fe/Mg ratios, and they are close to kaersutitic amphibole, enriched in Ca, Al, and Ti. So far, only observations by optical microscopy and analyses by electron and ion microprobes have been performed on these interesting and important phases (Floran *et al.*, 1978; Johnson *et al.*, 1991; Treiman, 1985, 1998; Watson *et al.*, 1994). Here we present the first results of the micro Raman spectroscopy on amphiboles in martian meteorites, Zagami and Lewis Cliff (LEW) 88516 as a continuing study of our preliminary analysis in order to reconfirm their mineral species (Mikouchi and Miyamoto, 1999).

Terrestrial amphiboles (kaersutite from Oki, Tottori, Japan and actinolite from Iratsu, Ehime, Japan) were analyzed for comparison. Because Al-Ti-rich pyroxene in the magmatic inclusion of martian meteorites has a broadly similar composition to amphiboles in Zagami and LEW 88516 (*e.g.*, Harvey *et al.*, 1993), we also analyzed these Al-Ti-rich pyroxenes to see the difference between kaersutitic amphibole and Al-Ti-rich pyroxene in the Raman spectra. Fassaitic pyroxene (up to 4 wt% TiO_2 and 8 wt% Al_2O_3) in the Asuka 881371 angrite was analyzed for comparison as well. The host pyroxene (pigeonite) of Zagami was analyzed for the standard of typical pyroxene.

SAMPLES AND ANALYTICAL METHODS

We studied amphiboles in the thin sections of martian meteorites Zagami (PTS #1, Mineralogical Institute, University of Tokyo) and LEW 88516 (LEW 88516,24). The LEW 88516 thin section was provided by The Meteorite Working Group, NASA Johnson Space Center. The reference samples are terrestrial amphiboles (kaersutite and actinolite), Al-Ti-rich pyroxene in LEW 88516, pigeonite in Zagami, and fassaite in angrite Asuka 881371 as above. All of these phases are within the regular thin sections and were analyzed by the same methods. Especially, we used the same thin sections of Zagami and LEW 88516 for analyzing both amphibole and pyroxene. The thin section of Asuka 881371 was supplied by National Institute of Polar Research (NIPR), Tokyo.

First, we looked for amphiboles by optical microscopy using the description of Treiman (1985, 1998) and analyzed them by electron microprobe. Then, Raman spectra were measured by a JASCO micro Raman spectrometer (with a triple monochromator of 3 × 60 cm) with a method similar to Miyamoto and Ohsumi (1995). The 488 nm line of an Ar laser was focused to an area of ~1 μm on the sample surface through a microscope (backscattering (180°) geometry). The laser power was ~10 mW on the surface of the sample. The spectra were accumulated for 4–5 min to enhance the signal-to-noise ratio by using a multichannel detector (photodiode array). The wavenumber position and the full width at half maximum (FWHM) of the Raman peak were determined by carrying out a Lorentzian fitting of the spectrum. The wavenumber position of the Raman peak was calibrated by using the 611 cm^{-1} emission lines in Raman shift of a Ne lamp. Spectral slit width was ~3 cm^{-1} and the variation in room temperature was within ±0.5 °C. More detailed analytical methods are described in Miyamoto and Ohsumi (1995).

RESULTS

Mineral Compositions

We could find one amphibole grain in each martian meteorite that was large enough for the analyses (Fig. 1). They are up to a few tens of micrometers across and show pleochroism from brownish orange to bright brown as reported by Treiman (1985, 1998). As Treiman (1997, 1998) described that amphiboles are euhedral to subhedral, this study also shows similar occurrence of amphibole (Fig. 1). Microprobe analysis of amphiboles in both meteorites gave chemical compositions enriched in Al and Ti, similar to the reported values (Floran *et al.*, 1978; Johnson *et al.*, 1991; Treiman, 1985; 1998; Watson *et al.*, 1994), and they were close to the kaersutite in stoichiometry (Table 1). Amphibole in Zagami gives the total sum of only 96.3 wt% and it is close to the reported value of 96.6 wt% (Treiman, 1985). The abundance of each element is also nearly identical to that of Treiman (1985). The reason of the low total sum is unclear but may be due to the presence of significant amounts of Fe^{3+} in amphibole as Delaney *et al.* (1998) reported that ~35% of Fe is present as Fe^{3+} in pyroxene. This high Fe^{3+} abundance is consistent with that of Popp *et al.* (1995) who estimated the $Fe^{3+}/(Fe^{3+} + Fe^{2+})$ ratio of 0.32–0.37 for the Zagami amphibole. Amphibole in LEW 88516 is a few tens of micrometers in size, and microprobe analysis gave a total sum of nearly 100 wt%. This total amount is consistent with the report by Treiman (1998), although our analysis gives an amount poorer in Si and richer in Ti than that by Treiman (1998). It is also uncertain why amphibole in LEW 88516 gives a good total sum, though Zagami amphibole does not. Furthermore, even within the same thin section, Treiman (1997) reported variable total sums by electron microprobe analysis ranging from 96 to 99.4 wt%. Treiman (1998) pointed out that some amphiboles in EETA79001 and LEW 88516 contain insufficient alkalis to qualify as kaersutite *sensu strict*, and they are titano-alumino-ferro-tschermakite (*e.g.*, Leak *et al.*, 1997). However, amphiboles analyzed in this study satisfy the stoichiometric definition of kaersutite rather than titano-alumino-ferro-tschermakite.

TABLE 1. Mineral composition of amphibole in Zagami and LEW 88516.

	LEW 88516*		Zagami†	
SiO_2	37.11		35.58	
Al_2O_3	15.55		14.68	
TiO_2	10.08		9.40	
FeO	14.09		18.05	
MnO	0.32		0.27	
MgO	9.08		5.43	
CaO	10.34		10.23	
Na_2O	1.35		1.68	
K_2O	0.71		0.09	
Cr_2O_3	0.38		0.16	
V_2O_3	0.07		0.09	
NiO	0.04		0.08	
P_2O_5	0.69		0.58	
Total	99.80		96.31	
Si	*5.42*	*8.00*	*5.50*	*8.00*
Al	*2.58*		*2.50*	
Al	*0.10*	*4.95*	*0.17*	*4.88*
Ti	*1.11*		*1.09*	
Fe	*1.72*		*2.33*	
Mg	*1.98*		*1.25*	
Mn	*0.04*		*0.04*	
Ca	*1.62*	*2.13*	*1.69*	*2.21*
Na	*0.38*		*0.50*	
K	*0.13*		*0.02*	

Number of ions based on 23 O. All Fe is assumed to be Fe^{2+}.
*Lewis Cliff 88516 amphibole contains ~0.8 wt% F but no detectable Cl.
†Zagami amphibole does not contain detectable F and Cl.

The Al-Ti-rich pyroxenes were included in many magmatic inclusions within olivine of LEW 88516 (*e.g.*, Harvey *et al.*, 1993). They show variable textural occurrence but are often present as free-floating euhedral crystals or surrounding the olivine walls (Fig. 2). These pyroxenes are noted to have high Al_2O_3 contents of

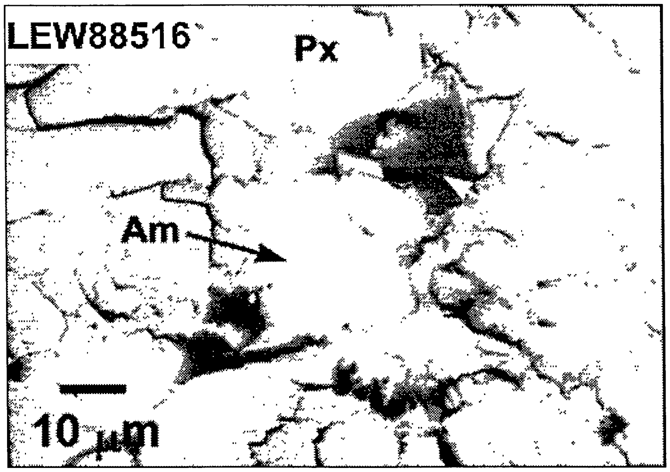

FIG. 1. Backscattered electron image of the amphibole-bearing magmatic inclusion in LEW 88516 pyroxene. Am = amphibole, Fd = feldspathic glass, Px = host pyroxene.

FIG. 2. Backscattered electron image of the magmatic inclusions containing Al-Ti-rich pyroxene within LEW 88516 olivine. Al-Ti-Px = Al-Ti-rich pyroxene, Si gl = Si-rich glass, Fe sul = iron sulfide, Ol = host olivine.

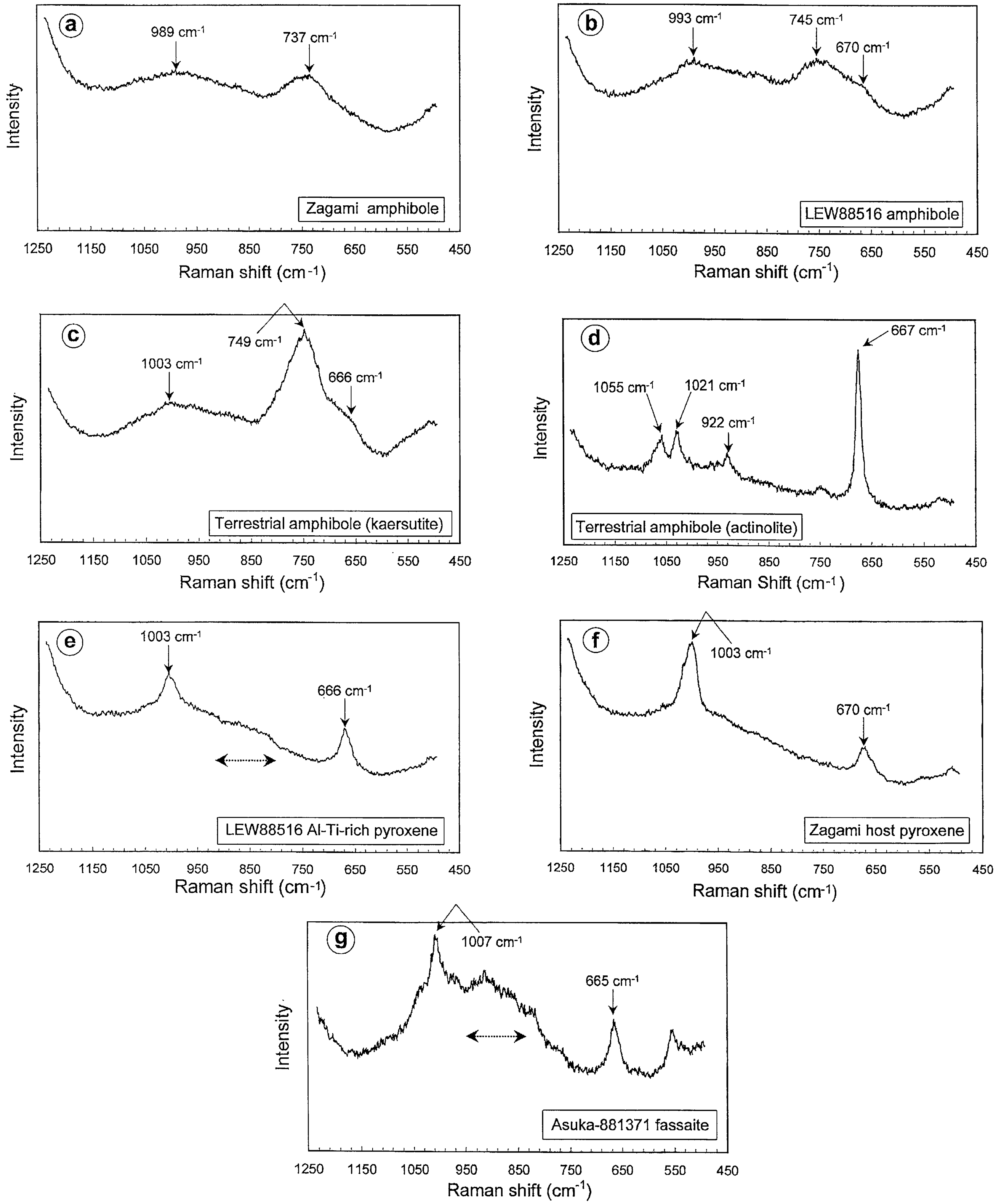

FIG. 3. Micro Raman spectra of the analyzed phases. (a) Amphibole in the Zagami martian meteorite. (b) Amphibole in the LEW 88516 martian meteorite. (c) Kaersutite amphibole from Oki, Tottori, Japan. (d) Actinolite amphibole from Iratsu, Ehime, Japan. (e) Al-Ti-rich pyroxene in the LEW 88516 martian meteorite. (f) Host pyroxene (pigeonite) in Zagami (only ~100 μm from amphibole of (a)). (g) Fassaitic clinopyroxene in angrite Asuka 881371.

TABLE 2. Mineral composition of analyzed reference phases.

	Terrestrial kaersutite*		Terrestrial actinolite		Zagami host pyroxene	Lewis Cliff 88516 A-Ti-rich pyroxene	Asuka-881371 fassaite
SiO_2	39.78		57.13		52.44	50.38	41.24
Al_2O_3	14.13		1.37		0.90	11.06	8.14
TiO_2	7.00		0.01		0.24	2.99	4.03
Fe_2O_3	4.61		n.a.		n.a.	n.a.	n.a.
FeO	7.31		4.90		21.01	5.99	24.00
MnO	0.12		0.28		0.72	0.16	0.20
MgO	12.01		21.10		19.17	9.02	0.55
CaO	10.75		12.28		5.42	18.12	21.73
Na_2O	2.57		0.62		0.07	0.51	0.02
K_2O	1.58		0.04		0.00	0.38	0.01
Cr_2O_3	n.a.		0.44		0.39	0.49	0.00
V_2O_3	n.a.		0.02		0.10	0.30	0.00
NiO	n.a.		0.11		0.00	0.00	0.02
P_2O_5	n.a.		n.a.		0.06	0.00	0.03
Total	99.86		98.30		100.52	99.40	99.97
Si	*5.80*		*7.87*				
		8.00		*8.00*			
Al	*2.20*		*0.13*				
Al	*0.23*		*0.09*				
Ti	*0.77*		*0.00*				
Fe	*1.40*	*5.02*	*0.56*	*5.01*			
Mg	*2.61*		*4.33*				
Mn	*0.01*		*0.03*				
Ca	*1.68*		*1.81*				
Na	*0.73*	*2.70*	*0.17*	*1.99*			
K	*0.29*		*0.01*				

Number of ions in amphiboles based on 23 O. All Fe is assumed to be Fe^{2+} in calculation.
*Data from Wilkinson (1961). Also includes 0.37 wt% H_2O^+ and 0.22 wt% H_2O^-.
n.a. = not analyzed.

8–15 wt% (Table 2). However, they are distinct from amphibole, especially in Si and Ti (45 wt% SiO_2 and up to 4 wt% TiO_2) contents. These Al-Ti-rich pyroxenes also differ in optical property from amphiboles, and they are colorless.

Micro Raman Spectra

Micro Raman spectra of amphiboles in Zagami and LEW 88516 are similar to each other, having Raman peaks near 990 and 740 cm^{-1} (Fig. 3a,b). The LEW 88516 amphibole shows a weak peak at 670 cm^{-1}, near the right shoulder of the 745 cm^{-1} peak (Fig. 3b). This weak peak is obscure in the Zagami amphibole spectra (Fig. 3a). These two amphiboles show broadly similar spectra to those of terrestrial kaersutite (Fig. 2c). Especially, amphibole in LEW 88516 shows a better agreement with terrestrial kaersutite. Both of them show a very broad peak at 990–1000 cm^{-1} and the strongest peak near 745–750 cm^{-1}. The shoulder at the right side of the strong 745–750 cm^{-1} is also observed. In contrast, terrestrial actinolitic amphibole has quite different Raman spectra from kaersutite (Fig. 2d), although these two amphiboles have the same space group and nearly identical cell parameters (space group: $C2/m$; cell parameters: $a \approx 9.85$ Å, $b \approx 18.0$–18.1 Å, $c \approx 5.3$ Å, $\beta \approx 105°$). Terrestrial actinolite has the strongest peak at 667 cm^{-1} (Fig. 2d), which only appears as a very weak peak in kaersutite (Fig. 2b,c). Instead, the strong peak near 750 cm^{-1} in kaersutite is very weak in actinolite. Furthermore, the presence of three peaks between the 920 and 1055 cm^{-1} region in actinolite is distinct from kaersutite (Fig. 2d). The broad peak near 1000 cm^{-1} in kaersutite was not observed in actinolite. Thus, it is evident that amphiboles in martian meteorites show the Raman spectra identical to kaersutite rather than the other phases of amphibole.

The Raman spectra of Al-Ti-rich pyroxene in LEW 88516 are marked by the presence of two dominant peaks near 1000 and 670 cm^{-1}. The presence of the Raman peak near 1000 cm^{-1} is similar to kaersutite (Fig. 2c), but the absence of the peak near 750 cm^{-1} distinguishes it from kaersutite. Rather, the Al-Ti-rich pyroxene spectra are like those of pigeonite and fassaite (Fig. 2f,g). The presence of broad or possibly many weak peaks around 850–900 cm^{-1} is only seen in the fassaite and Al-Ti-rich pyroxene (indicated by the dashed arrows in Fig. 2e,g) and is absent in the regular Al-Ti-poor pigeonite. Therefore, these peaks are probably related to the high Al and Ti contents in the pyroxene structures.

DISCUSSIONS AND CONCLUSIONS

The Raman spectra of amphiboles in the martian meteorites Zagami and LEW 88516 show good agreements with those of terrestrial kaersutite as well as their compositional matches. These matches reconfirm without doubt that they are kaersutites as previous studies suggested from the characteristic chemical compositions and strong pleochroism (Floran *et al.*, 1978; Johnson *et al.*, 1991; Treiman, 1985, 1997, 1998; Watson *et al.*, 1994). The Raman spectra of martian amphiboles are slightly obscured compared with those of terrestrial kaersutite. Probably, heavy shock events experienced by these martian meteorites (*e.g.*, McSween, 1994) affected the crystal structure of kaersutite, causing peak broadening in the spectra. Similar line broadening is reported for olivines in shocked L6 chondrites (Miyamoto and Ohsumi, 1995). However, it is unclear why the peak broadening of Al-Ti-rich pyroxene in the same meteorites is much less than that of kaersutite. Nevertheless, general agreement of the spectra with kaersutite denies the phase transition of amphibole into high pressure polymorphs.

It is surprising that the Raman spectra between kaersutite and actinolite are quite distinct from each other in spite of the same mineral group. Both kaersutite and actinolite belong to a calcic amphibole group. Generally, amphibole formula may be written as $A_{0-1}B_2C_5T_8O_{22}(OH,F)_2$ (*e.g.*, Leake *et al.*, 1997). In structural terms, the *A*, *B*, *C*, and T atoms are in *A* sites, *M*4, *M*1 + *M*2 + *M*3, and T (tetrahedra), respectively (*e.g.*, Leake *et al.*, 1997). In the case of kaersutite, the formula is given as $(Na)(Ca_2)(Mg_4Ti)(Si_6Al_2)(O_{22})(OH,F)_2$. The formula of actinolite (ferro-actinolite) is $\square(Ca_2)(Fe^{2+}{}_5)(Si_8)(O_{22})(OH,F)_2$. Therefore, the difference in the Raman spectra between kaersutite and actinolite is possibly due to the difference of chemical compositions. Probably, the presence of the empty *A* site, Ti incorporation into *M*1 + *M*2 + *M*3 sites, and Al incorporation into the T site produce different Raman spectra of kaersutite from actinolite.

It is also interesting that Al-Ti-rich pyroxenes have clearly different Raman spectra from those of amphiboles, although their mineral compositions are generally similar to each other, especially in high Al and Ti abundances. This is obviously due to different crystal structures between pyroxene (single-chain) and amphibole (double-chain), although they are closely related. However, unlike the calcic amphibole case discussed above, Raman spectra of Al-Ti-rich pyroxene are broadly similar to those of regular Al-Ti-poor pyroxene. This can be explained by the simpler crystal structure of pyroxene comparing with amphibole.

Thus, as this study demonstrates, micro Raman spectroscopy is one of the best analytical methods to mineralogically characterize amphiboles in martian meteorites. In fact, several attempts have been recently conducted to characterize martian meteorite by Raman spectroscopy (*e.g.*, Wang *et al.*, 1999; McHone *et al.*, 1999). Especially, combination analyses using both micro Raman spectroscopy and electron microprobe analysis are essential to fully characterize mineral grains in meteorites.

Acknowledgements–We thank M. W. G. for the LEW 88516 thin section and NIPR for the Asuka 881371 thin section. The kaersutite sample was kindly supplied by The Geological Museum, Geological Survey of Japan by courtesy of Dr. M. Bunno. We acknowledge Mr. K. Kaneda who provided the reference about the chemical compositions of terrestrial kaersutite and also analyzed the terrestrial actinolite by electron microprobe. We are also indebted to Mr. O. Tachikawa and Mr. H. Yoshida for technical assistance during electron beam analyses. The electron microscopy was performed in the Electron Microbeam Analysis Facility of the Mineralogical Institute, University of Tokyo. This work was supported in part by Society for Promotion of Space Science, the Grant-in-Aid for Encouragement of Young Scientists by the Japanese Ministry of Education, Science and Culture (No. 09740391), and the National Academy of Sciences through an NRC associateship at NASA Johnson Space Center (all to T. Mikouchi). We also thank Drs. D. Heymann and L. Haskin for their constructive review of the manuscript.

Editorial handling: P. H. Warren

REFERENCES

DELANEY J. S., SUTTON S. R. AND DYAR M. D. (1998) Variable oxidation states of iron in Martian meteorites (abstract). *Lunar Planet. Sci.* **29,** #1241, Lunar and Planetary Institute, Houston, Texas, USA (CD-ROM).

FLORAN R. J., PRINZ M., HLAVA P. F., KEIL K., NEHRU C. E. AND HINTHORNE J. R. (1978) The Chassigny meteorite: A cumulate dunite with hydrous amphibole-bearing melt inclusions. *Geochim. Cosmochim. Acta* **42,** 1213–1229.

HARVEY R. P., WADHWA M., MCSWEEN H. Y., JR. AND CROZAZ G. (1993) Petrography, mineral chemistry and petrogenesis of Antarctic shergottite LEW88516. *Geochim. Cosmochim. Acta* **57,** 4769–4783.

JOHNSON M. C., RUTHERFORD M. J. AND HESS P. C. (1991) Chassigny petrogenesis: Melt compositions, intensive parameters, and water contents of martian(?) magmas. *Geochim. Cosmochim. Acta* **55,** 349–366.

LEAKE ET AL.. (1997) Nomenclature of amphiboles: Report of the Subcommittee on Amphiboles of the International Mineralogical Association, Commission on New Minerals and New Mineral Names. *Am. Mineral.* **82,** 1019–1037.

MCCOY T. J., TAYLOR G. J. AND KEIL K. (1992) Zagami: Product of a two-stage magmatic history. *Geochim. Cosmochim. Acta* **56,** 3571–3582.

MCHONE J. F., KUDRYAVTSEV A. B., AGRESTI D. G., WDOWIAK T. J. AND KILLGORE M. (1999) Raman Imagery of Martian Meteorites (abstract). *Lunar Planet. Sci.* **30,** #1896, Lunar and Planetary Institute, Houston, Texas, USA (CD-ROM).

MCSWEEN H. Y., JR. (1994) What we have learned about Mars from SNC meteorites. *Meteoritics* **29,** 757–779.

MCSWEEN H. Y., JR. AND HARVEY R. P. (1993) Outgassed water on Mars—Constraints from melt inclusions in SNC meteorites. *Science* **259,** 1890–1892.

MEYER C. (1998) *Mars Meteorite Compendium—1998.* NASA Johnson Space Center, Houston, Texas, USA. 237 pp.

MIKOUCHI T. AND MIYAMOTO M. (1999) Micro Raman Spectroscopy of Amphiboles and Al-Ti-rich Pyroxenes in the Martian Meteorites Zagami and LEW88516 (abstract). *Lunar Planet. Sci.* **30,** #1559, Lunar and Planetary Institute, Houston, Texas, USA (CD-ROM).

MIYAMOTO M. AND OHSUMI K. (1995) Micro Raman spectroscopy of olivines in L6 chondrites: Evaluation of the degree of shock. *Geophys. Res. Lett.* **22,** 437–440.

POPP R. K., VIRGO D. AND PHILLIPS M. W. (1995) H deficiency in kaersutitic amphiboles: Experimental verification. *Am. Mineral.* **80,** 1347–1350.

TREIMAN A. H. (1985) Amphibole and hercynite spinel in Shergotty and Zagami: Magmatic water, depth of crystallization, and metasomatism. *Meteoritics* **20,** 229–243.

TREIMAN A. H. (1997) Amphiboles in Martian meteorite Elephant Moraine 79001 (abstract). *Meteorit. Planet. Sci.* **33 (Suppl.),** A129–A130.

TREIMAN A. H. (1998) Amphiboles in more Martian meteorites: Elephant Moraine 79001B, Elephant Moraine 79001X, and Lewis Cliff 88516 (abstract). *Meteorit. Planet. Sci.* **33 (Suppl.),** A156.

TREIMAN A. H., BARRETT R. A. AND GOODING J. L. (1993) Preterrestrial aqueous alteration of the Lafayette (SNC) meteorite. *Meteoritics* **28,** 86–97.

WANG A., JOLIFF A. L. AND HASKIN L. A. (1999) Raman spectroscopic characterization of a Martian SNC meteorite: Zagami. *J. Geophys. Res.* **104,** 8509–8520.

WATSON L. L., HUTCHEON I. D. EPSTEIN S. AND STOLPER E. M. (1994) Water on Mars—Clues from deutrium/hydrogen and water contents of hydrous phases in SNC meteorites. *Science* **265,** 86–90.

WILKINSON J. F. G. (1961) Some aspects of the calciferous amphiboles, oxyhornblende, kaersutite and barkevikite. *Am. Mineral.* **46,** 340–354.