Determination of the Fe oxidation state of the Chassigny kaersutite: A microXANES spectroscopic study

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Abstract—In order to elucidate the formation of low-H kaersutites in Martian meteorites, the Fe$^{3+}/\Sigma$Fe ratio of Chassigny kaersutites in magmatic inclusions was directly determined by the synchrotron microXANES analysis. XANES analysis for standard kaersutites with known Fe$^{3+}/\Sigma$Fe ratios shows a linear relationship between centroid energy positions of XANES pre-edge spectra and the Fe$^{3+}/\Sigma$Fe ratio. Based on the linear relationship, the Fe$^{3+}/\Sigma$Fe ratio of Chassigny kaersutites is estimated to be about 0.05. The low Fe$^{3+}/\Sigma$Fe ratio clearly suggests that low-H kaersutites in Chassigny are not likely to be formed by the oxidation-dehydrogenation reactions. The low-H content of the Chassigny kaersutites is mainly due to the presence of a Ti oxy-component.

INTRODUCTION

The presence of hydrous minerals such as kaersutite amphibole in magmatic inclusions of Martian meteorites has been considered to indicate significant quantities of water in the pre-eruptive magmas because such minerals are considered to have crystallized during the Martian magmatic process (e.g., McSween and Harvey 1993). However, the H$_2$O content of kaersutite in the Chassigny Martian meteorite was about 0.1–0.2 wt% (Watson et al. 1994), and it is doubtful whether the presence of kaersutite in Martian meteorites is direct evidence for the existence of H$_2$O in parent magmas. Several previous studies elucidated this particular low-H kaersutite in the Chassigny Martian meteorite by introducing the oxidation-dehydrogenation reaction so that the Fe$^{2+}$ component in the kaersutite structure is oxidized as a result of thermal dehydrogenation (Popp et al. 1995b; King et al. 1999). This model requires a rather higher Fe$^{3+}/\Sigma$Fe ratios in the micro-area can be analyzed either by electron energy loss spectroscopy (EELS) (Garvie and Buseck 1998), electron microprobe analysis (Höfer et al. 1994; Fialin et al. 2001), X-ray photoelectron spectroscopy (XPS) (Raeburn et al. 1997a; 1997b), or micro-X-ray absorption near edge structure (XANES) (Bajt et al. 1994). The authors employed the nondestructive analysis of XANES spectra using synchrotron radiation X-ray source because the microfocused X-ray beam with high brilliance has been successfully employed in order to obtain the Fe$^{3+}/\Sigma$Fe ratios of micrometer-size minerals on the provided thin sections (e.g., Iida 1997; Nakai et al. 1998). It should be added that electron microprobe analysis is another common nondestructive technique to determine the Fe$^{3+}/\Sigma$Fe ratio as a function of the intensity ratio of FeKβ/FeKα. However, it is often suggested that this method is not very usable for Ti-rich minerals such as kaersutite because Ti indicates a large mass absorption coefficient for FeKα (Fialin et al. 2001).

EXPERIMENTAL

Sample Description

The Martian meteorite Chassigny is a dunite containing magmatic inclusions with low-H kaersutite (Floran et al. 1978; Watson et al. 1994). The two polished thin sections of
Chassigny were supplied by the University of Hawai‘i at Manoa (UH106; ~4 × 6 mm) and the Natural History Museum of Berlin (~3 × 4 mm). Observations with an optical microscope and a scanning electron microscope equipped with a field emission gun (FEG-SEM, Hitachi S-4500) readily revealed several olivine grains in the Chassigny meteorite with magmatic inclusions partially filled by kaersutite crystals. Figures 1a and 1b show typical electron backscattering images of magmatic inclusions in Chassigny. The chemical compositions of kaersutites as well as other constituent phases were analyzed by an electron microprobe analysis (EPMA, JEOL JXA 8900L). Quantitative analyses were carried out at 15 kV accelerating voltage with a beam current of 12 nA and the standard samples used for EPMA are: wollastonite for Si and Ca, albite for Na, sanidine for K, Al₂O₃ for Al, Fe₂O₃ for Fe, TiO₂ for Ti, Cr₂O₃ for Cr, MnO for Mn, and MgO for Mg. It may be added that Watson et al. (1994) measured the H content of kaersutite found in the thin section of UH106.

Wet Chemical Analysis

Three standard kaersutite samples with a variety of Fe³⁺/ΣFe ratios were used to draw a calibration line for the present Fe-XANES analysis. Chemical compositions of the kaersutites from Kaersut (now Quarsut), Umanq District, Greenland (KST), Boulder Dam, Arizona, USA (ARZ), and Iki Island, Nagasaki Prefecture, Japan (IKI) were analyzed by EPMA and the results are summarized in Table 1. The Fe³⁺/ΣFe ratios of these kaersutite samples were determined by wet chemical analysis. The flowchart (Fig. 2) illustrates the analytical procedure we used to determine the Fe³⁺/ΣFe ratio of three standard samples. In order to ensure that the samples were free of absorbed water prior to weighing, the sample was dried at 110 °C for at least 12 h, removed from the oven, and allowed to cool in a desiccator. The weighted samples (10–30 mg) were transferred to Teflon bottles. Five ml of 50% H₂SO₄ and 0.25 ml of 48% HF were added to each bottle and heated at 240 °C on a hot plate for 10–15 min. The contents of each bottle were immediately put into 200 ml beakers with 5 ml of 5% boric acid solution and diluted with distilled water in order to obtain the required concentration for the experiment. The colorimetric assay method with o-phenanthroline was applied for the analysis of the Fe²⁺ content in the prepared solution (Shapiro 1960). Two ml of a specimen solution was mixed with 4 ml of 0.1% o-phenanthroline and 10 ml of acetic acid sodium acetate buffer solution of pH 4.6, and the absorbance at 510 nm was measured. The Fe²⁺ content was determined by using an analytical curve prepared by working solutions of ammonium ferrous sulfate. On the other hand, the content of total Fe was analyzed by using similar colorimetric method after reducing Fe³⁺ in the specimen solution. One gram of ascorbic acid was used as a reducer agent for 2 ml of a specimen solution in the present case. The obtained values of Fe³⁺/ΣFe ratios are also listed in Table 1.

MicroXANES Analysis

XANES spectra at the Fe K-absorption edge were measured by using a synchrotron radiation source and a Si(Li)-solid state detector (SSD) at BL-4A, Photon Factory (PF), Institute of Material Structure Science (IMSS), High Energy Accelerator Research Organization, Tsukuba, Japan. The SR X-ray was monochromatized with a Si (111) double-crystal monochromator. The microfocusing Kirkpatrick-Baez mirrors were used so as to focus the incident X-ray beam less than about 10 µm in diameter at the specimen position (Iida 1997). It may be added that this microfocusing system is also applicable so as to remove the high-energy harmonics for the selected X-ray energy. An ionization chamber was used to monitor the X-ray incidence irradiating a single crystal specimen and SSD was mounted at about 90 degrees to the incident beam within the photon polarization plane. The XANES spectra at the Fe K-absorption edge were obtained in the fluorescence mode by scanning the incident X-ray energy from 7103 to 7153 eV at an interval of 0.13 eV. The incident X-ray energy was calibrated by setting the first inflection point of the Fe K-edge of a metallic Fe foil at 7111.08 eV (Wilke et al. 2001).

The pre-edge peak, which is located about 15–20 eV below the main K-absorption edges, is sensitive to Fe valence states. Such pre-edge signal is related to the metal electronic transition from 1s to 3d and/or from 1s to 4p. This pre-edge position shifts toward higher energy side with increasing Fe³⁺/ΣFe ratios of minerals by indicating a linear relationship as a function of the Fe³⁺/ΣFe ratio (Bajt et al. 1994). A number of research groups employed the XANES techniques and demonstrated its availability for studying the valence state of Fe of terrestrial minerals (Delaney et al. 1998; Dyar et al. 2001, 2002; Wilke et al. 2001). In particular, Wilke et al. (2001) reported a XANES study of a series of Fe²⁺- and Fe³⁺-bearing minerals with a wide range of coordination environments and concluded that the Fe³⁺ contents can be determined with an accuracy of ±10 mol% when the coordination environment is given. Therefore, the present study prepared single crystalline standard samples (KST, ARZ, and IKI), with similar kaersutite structure. The obtained pre-edge centroid positions with the known Fe³⁺/ΣFe ratio were compared with that for two Chassigny kaersutites in MI-A and MI-B.

RESULTS

Mineralogy of Chassigny

Chassigny shows a typical cumulate texture with modal abundances of ~90% olivine, ~5% pyroxene, ~2% feldspar,
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and ~1.4% chromite together with minor phases such as iron sulfides, FeTi oxides, and chlorapatite. The polygonal aggregate of olivine with the average size of 1.5 mm indicates the solid-state grain-boundary adjustment with an anhedral to subhedral texture, occasionally forming 120° triple junctions. Olivine is compositionally homogeneous in Fe-Mg contents (Fo69). It should be noted that olivine grains usually show planar shock features, irregular fractures, and undulatory extinction under a polarized microscope. Some grains include euhedral chromite grains and rounded magmatic inclusions as large as 200 µm in diameter. The magmatic inclusions have been extensively studied by Floran et al. (1978), Johnson et al. (1991), Delaney and Dyar (2001), and Varela et al. (2000). Three types of magmatic inclusions are present in Chassigny olivines: multi-crystalline inclusions, mono-crystalline inclusions and glassy inclusions without any crystals (Varela et al. 2000). The multi-crystalline inclusions are mainly composed of high-Ca pyroxene (Al-Ti rich augite)
Table 1. Chemical compositions of standard kaersutites.

<table>
<thead>
<tr>
<th>Location</th>
<th>KST (USA)</th>
<th>ARZ (USA)</th>
<th>IKI (Japan)</th>
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<tr>
<td>SiO₂</td>
<td>39.16</td>
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<td>0.00</td>
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<td>3.13</td>
<td>12.08</td>
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<td>0.08</td>
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<td>0.03</td>
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<tr>
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<td>0.01</td>
<td>0.02</td>
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<tr>
<td>Total</td>
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<td>100.99</td>
<td>97.44</td>
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<td>1.13</td>
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The Pre-Edge Peak Position as a Function of Fe³⁺/ΣFe Ratio

The chemical composition listed in Table 1 indicates that KST (Fe³⁺/ΣFe = 0.01) does not contain any Fe³⁺-oxy-component. In contrast, IKI (Fe³⁺/ΣFe = 0.93) is considered as typical “Fe³⁺-oxy-kaersutite,” as expected from its reddish brown color. The Fe³⁺/ΣFe ratio of ARZ is 0.36, which is intermediate between the two. The XANES spectra at the Fe K-absorption edge for these terrestrial kaersutite samples are shown in Fig. 3. Since the Fe-XANES spectra for Chassigny kaersutites in MI-A and MI-B closely resemble each other, the spectrum of kaersutite in MI-A is shown in Fig. 3 as an example. The fundamental features in the lower energy side of the main absorption-edge agreed well with those obtained by Dyar et al. (1992). The main-edge and pre-edge positions for three standard samples shift toward high energy with increase of Fe³⁺/ΣFe ratio. In particular, Fig. 4 shows the enlarged illustration of the pre-edge region after the baseline subtraction. The obtained pre-edge peaks were deconvoluted into two or three Gaussian components. The centroid positions of the pre-edge peaks were defined by the intensity-weighted average of the resultant Gaussian components and indicated by the arrows in Fig. 4. The centroid positions and integrated intensities of the pre-edges are summarized in Table 4. The pre-edge centroid of KST (Fe³⁺/ΣFe = 0.01) is located at about 2.5 eV lower energy than that of IKI (Fe³⁺/ΣFe = 0.93) and the centroid of ARZ is located in the middle of those of KST and IKI. This clearly suggests that the pre-edge centroid of kaersutite shifts to higher energy with increasing Fe³⁺/ΣFe ratio. Figure 5 shows a calibration curve indicating the pre-edge centroids of kaersutites as a function of Fe³⁺/ΣFe ratio and the Fe³⁺/ΣFe ratio of Chassigny kaersutites was estimated to be less than ~0.05. It may be added that the obtained calibration curve agrees well with that reported by Bajt et al. (1994), although fayalite, magnetite, and hematite were employed for their standard samples.

The XANES pre-edge position of a single crystalline mineral is known to shift slightly by the effect of X-ray anisotropy (Dyar et al. 2002). This anisotropic phenomena appears to produce a limited accuracy in the determination of the Fe³⁺/ΣFe ratio of Chassigny kaersutite, because it is practically difficult to measure an spectra of Chassigny kaersutite with the X-ray beam polarized along the crystalline orientation similar to standard samples. Therefore, the anisotropic variation of pre-edge positions was analyzed by using the oriented KST samples and the possible inaccuracy in determining the centroid of the pre-edge peak was estimated in the present study. Figure 6 shows the variation of pre-edge peaks measured from KST kaersutites. A and C spectra were measured on the a-c plane, with the X-ray beam polarized along the a- and c-axis, respectively. B spectrum was measured on the b- c* plane, and the b-axis was set in parallel to the polarized direction. Although the pre-edge centroids of A and C spectra located at the lower energy side in comparison with that of B spectrum, the variation of pre-edge centroids is less than about 0.5 eV. This consideration readily indicates that the Fe³⁺/ΣFe ratio of a single crystalline kaersutite can be determined with an uncertainty of ±10% at most, even when the effect of X-ray anisotropy is not taken into account.
Comparison with Previous Studies for XANES Measurement

Wilke et al. (2001) and Giuli et al. (2003) reported that the local coordination environment of Fe atoms together with its oxidation state can be obtained by the high-resolution Fe K-edge XANES spectra. It will therefore be interesting to investigate local coordination environment of Fe in Chassigny kaersutite employed in the present study. The quantitative information obtained from the pre-edge spectra of Chassigny and standard kaersutites was illustrated in Fig. 7 together with those of previous studies reported by Wilke.
Fig. 3. Fe-XANES spectra of standard kaersutites (KST, ARZ, and IKI) and Chassigny kaersutites (MI-A).

Fig. 4. Pre-edge peaks of standard and Chassigny kaersutites: KST: Fe$^{3+}$/ΣFe = 0.01, ARZ: Fe$^{3+}$/ΣFe = 0.36, and IKI: Fe$^{3+}$/ΣFe = 0.93. The spectrum of KST(C) was collected by the condition that crystallographic axes were set in parallel to the polarized direction of X-ray beam, which is common to C in Fig. 5.

Fig. 5. A calibration line on the basis of XANES pre-edge centroids in spectra of standard kaersutites. The errors are estimated by the variation of centroids measured in Fig. 6.

Fig. 6. Pre-edge peaks of standard kaersutites (Fe$^{3+}$/ΣFe ratio = 0) measured at the three different crystallographic orientations. A, B, and C spectra with the X-ray polarized along the a-, b-, and c-axis, respectively.
et al. (2001). The pre-edge parameters of Chassigny and terrestrial kaersutites are located close to the end member area between $[6]\text{Fe}^{2+}$ and $[6]\text{Fe}^{3+}$, suggesting the fundamental structural image of Fe atoms in the octahedral coordination. This information allows us to discuss the $\text{Fe}^{2+}$ distribution of Chassigny kaersutite in a way similar to the ordinary terrestrial amphibole.

**Calculation of the $\text{Fe}^{3+}/\Sigma \text{Fe}$ Ratios of Chassigny Kaersutite in Previous Studies**

Watson et al. (1994) reported that H contents of kaersutites from both Chassigny and Zagami Martian meteorites were 0.1–0.2 atomic formula units (afu) and much lower than that of common hydrous amphibole (~2 afu). The low H content of Martian kaersutite implies the significant amount of oxy-amphibole component. This component is frequently discussed as a consequence of the coupled substitution of:

$$\text{Fe}^{2+} + \text{OH}^- = \text{Fe}^{3+} + \text{O}^{2-} + \frac{1}{2} \text{H}_2 \quad (1)$$

and/or

$$[6]\text{Al}^{3+} + \text{OH}^- = \text{Ti}^{4+} + \text{O}^{2-} + \frac{1}{2} \text{H}_2 \quad (2)$$

In this context, Popp and his colleagues (1992, 1995a, 1995b) performed systematic chemical analysis of natural pargasite, kaersutite together with experimentally equilibrated samples, and proposed an applicable crystal chemical relationships by assuming that $\text{Fe}^{3+}$ and Ti constituents are responsible for the oxy component. The $\text{Fe}^{3+}/\Sigma \text{Fe}$ ratios of Chassigny kaersutites were estimated from 0.58 to 0.65 by utilizing their chemical relationship (Popp et al. 1995b). Another chemical relationship between the content of OH and that of $[6]\text{Al} + \text{Ti} + \text{Fe}^{3+}$ was proposed by King et al. (1999) and the $\text{Fe}^{3+}/\Sigma \text{Fe}$ ratio in Chassigny kaersutites was determined to be from 0.7 to 0.8. These $\text{Fe}^{3+}/\Sigma \text{Fe}$ values show that Chassigny kaersutite has a significant amount of $\text{Fe}^{3+}$ in the structure; nevertheless, this is quite different from those determined by the present microXANES analysis.

This inconsistency can be removed to introduce another substitution mechanism discussed by Oberti et al. (1992) and Hawthorne et al. (1998):

$$(\text{Fe, Mg})^{2+} + 2(\text{OH})^- \Rightarrow \text{Ti}^{4+} + 2\text{O}^{2-} + \text{H}_2 \quad (3)$$

The oxy-component produced by Ti in the Equation 3 is two times that in the Equation 2, leading to the low $\text{Fe}^{3+}/\Sigma \text{Fe}$ ratio for the low-H kaersutite sample. It is quite natural to consider that Equations 1, 2, and 3 each operate effectively in order to increase the oxy-component in the structure of amphibole and that natural process should be a harmony of these substitution. Nevertheless, the present microXANES result strongly stresses that the low-H content of the kaersutite is mainly due to Ti oxy-component represented by Equations 2 and 3. As a consequence, the oxidation of $\text{Fe}^{2+}$ together with dehydrogenation during eruption or an impact event can be readily excluded from the possible history of the Chassigny Martian meteorite. This conclusion indicates that the low-H contents of the Chassigny kaersutites are due to the concentration of Ti at the time of its crystallization.

| Table 3. Chemical compositions of constituent minerals in the multi-crystalline magmatic inclusion (MI-B) with kaersutite in Chassigny olivine. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | MI-B             |                 |                 |                 |
|                 | High-Ca py       | Low-Ca py       | Kaersutite       | Ca-Na glass     |
| SiO$_2$         | 50.94            | 54.06           | 42.52           | 76.10           |
| TiO$_2$         | 1.39             | 0.40            | 6.72            | 0.32            |
| Al$_2$O$_3$     | 4.55             | 1.76            | 12.45           | 15.80           |
| Cr$_2$O$_3$     | 0.74             | 0.00            | 0.98            | –               |
| FeO            | 7.13             | 16.70           | 8.97            | 0.34            |
| MnO            | 0.27             | 0.55            | 0.16            | –               |
| MgO            | 14.17            | 24.79           | 12.08           | –               |
| CaO            | 20.68            | 1.78            | 11.35           | 0.10            |
| Na$_2$O         | 0.51             | 0.00            | 3.41            | 1.78            |
| K$_2$O         | 0.02             | 0.00            | 0.32            | 5.13            |
| Total          | 100.40           | 100.04          | 98.96           | 99.57           |
| $\text{Fe}^{3+}/\Sigma \text{Fe}$ | 0.04$^b$ |                    |                |

$^a$Total iron given as FeO.

$^b$Fe$^{3+}/\Sigma \text{Fe}$ ratio was determined by XANES analysis.

$^c$Fe$^{3+}/\Sigma \text{Fe}$ ratio of chromite was calculated from the stoichiometry constraints.

| Table 4. Integrated intensities and centroid position of XANES pre-edges peaks. |
|-----------------|-----------------|-----------------|
|                 | Integrated intensity | Centroid position |
| Sample          |                  | (eV)            |
| Chassigny       | 0.06113          | 7112.01         |
| KST             | 0.0656           | 7111.9          |
| ARZ             | 0.05781          | 7112.57         |
| IKI             | 0.0712           | 7113.7          |
The Presence of Fe$^{3+}$-Poor Chromite in the Kaersutite-Bearing Inclusion

The present study shows that the Fe$^{3+}$/ΣFe ratio of Chassigny kaersutites is very low. This is also supported by the presence of Fe$^{3+}$-poor chromite in the magmatic inclusion with kaersutite in MI-B. Table 3 shows chemical composition and the Fe$^{3+}$/ΣFe ratio of chromite in the Chassigny magmatic inclusion. The Fe$^{3+}$/ΣFe ratio calculated from the stoichiometry is very low (Fe$^{3+}$/ΣFe = 0.07) and is not dissimilar to that of the kaersutite. The presence of low Fe$^{3+}$ chromite in inclusions strongly suggests that the formation of low-H Chassigny kaersutites is independent of oxidation-dehydrogenation reaction.

The low-Fe$^{3+}$ minerals are expected to crystallize under a reduced condition. The condition is significantly different from the formation condition of the Chassigny parent magma. Since chromites are contained in olivine, and magmatic inclusions in olivine, pyroxene, and intestinal glasses (Floran et al. 1978; Johnson et al. 1991), chromites are an important indicator for the formation process due to their crystallization at all formation stages. The Fe$^{3+}$/ΣFe ratios are significantly high compared to that in MI-B, implying that the parent magma was formed under a relatively oxidized condition. This difference may be because the inclusion was crystallized at the different stage from the parent magma. Since Martian mantle is believed to have been under reducing condition (e.g., Herd et al. 2003), these magmatic inclusions may record such a redox condition. Alternatively, the secondary heating process after crystallization of the parent magma (e.g., contact with other magma, shock event) may have been involved.

CONCLUSIONS

1. Multi-crystalline inclusions in Chassigny olivines are composed of low-Ca and high-Ca pyroxenes, kaersutite, chromite and Si-rich and feldspathic glasses.
2. MicroXANES analysis is a powerful method for determining the Fe$^{3+}$/ΣFe ratios of small sized Martian kaersutites due to its spatial resolution of about 10 µm. The Fe$^{3+}$/ΣFe ratios of Chassigny kaersutites was directly obtained by comparing centroid positions of a pre-edge peak in XANES spectra with those of terrestrial kaersutites with known Fe$^{3+}$/ΣFe ratios.
3. MicroXANES analysis revealed that Chassigny kaersutites have a significantly low Fe$^{3+}$/ΣFe ratio (Fe$^{3+}$/ΣFe = 0.05). This is much lower than that estimated by previous studies, suggesting that the kaersutites are not Fe-oxy kaersutites formed by oxidation-dehydrogenation reaction. The octahedral coordination of Fe (Fe$^{2+}$) in Chassigny kaersutite was also confirmed by the analysis of normalized intensity plot of pre-edge centroids.
4. The low-H content of the Chassigny kaersutites is mainly due to a Ti oxy-component rather than an Fe oxy-component. This conclusion was also supported by the presence of low-Fe$^{3+}$ chromite in inclusions.
Acknowledgments—We thank Prof. A. Iida of Photon Factory of IMSS and Prof. I. Nakai of Tokyo University of Science for providing technical assistance of Fe-XANES spectra measurements. This work has been performed under the approval of the Photon Factory Program Advisory Committee (Proposal No. 04G089). Dr. T. Ishii’s helpful advice and technical support on the chemical analysis at the Ocean Research Institute of University of Tokyo are greatly appreciated. We also thank Dr. A. Greshake of the Natural History Museum of Berlin and the University of Hawai’i, Manoa for Chassigny samples. This manuscript was greatly improved by constructive reviews by Dr. Treiman, Dr. Giuli, and Dr. McCanta.

Editorial Handling—Dr. Allan Treiman

REFERENCES


