

THE VALENCE OF IRON IN CM CHONDRITE SERPENTINE AS MEASURED BY SYNCHROTRON XANES. T. Mikouchi¹, M. Zolensky², W. Satake¹, L. Le³, ¹Dept. of Earth and Planetary Science, University of Tokyo, Hongo, Tokyo 113-0033, Japan (mikouchi@eps.s.u-tokyo.ac.jp), ²Astromaterials Research and Exploration Science, KT, NASA Johnson Space Center, Houston, TX 77058, USA, ³Jacobs ESCG, Houston, TX 77058, USA.

Introduction: Fe-bearing phyllosilicates are the dominant product of aqueous alteration in carbonaceous chondrites, and serpentine is the most abundant phyllosilicate in CM2 chondrites that are the most abundant carbonaceous chondrite [e.g., 1,2]. Browning et al. [3] predicted that $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of serpentine in CM chondrites should change with progressive alteration. They proposed that progressive CM alteration is best monitored by evaluating the progress of Si and Fe^{3+} substitutions that necessarily attend the transition from end-member cronstedtite to serpentine. Their proposed *Mineralogic Alteration Index*, $2-(\text{Fe}^{3+}/(2-\text{Si}))$, was intended to highlight and utilize the relevant exchange information in the stoichiometric phyllosilicate formulas based upon the coupled substitution of $2(\text{Fe}^{3+}, \text{Al}) = \text{Si} + (\text{Mg}, \text{Fe}^{2+}, \dots)$ in serpentine. The value of this ratio increases as alteration proceeds.

The presence of Fe^{3+} in phyllosilicates is also important for the presence of 0.6-0.7 μm absorption band in reflectance spectroscopy of C-type asteroids that are targets of JAXA Hayabusa 2 and NASA OSIRIS-REx sample return missions [4]. Especially, the Hayabusa 2 target asteroid (1993 JU3) exhibits heterogeneous spectral features (0.7 μm absorption band disappears by rotation) [5] that may be related to the different degree of aqueous alteration.

We always wanted to directly test Browning's prediction through actual measurements of the Fe^{3+} content of serpentine at the micron scale appropriate to EPMA analyses (Zega et al. [6] have measured it at much finer scale), and this test can now be made using Synchrotron Radiation X-ray Absorption Near-Edge Structure (SR-XANES). Thus, we have recently begun investigation with CMs that span a large portion of the range of observed aqueous alteration, and we first analyzed Murray, Nogoya, and ALH 84029 by SR-XANES [7]. However, we did not find clear correlation between $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of serpentine and their alteration degrees [7]. Then, we additionally analyzed serpentine in three more CMs and here report their $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios in comparison with our previous results.

Samples and Methods: In order to analyze more variable CM samples in terms of alteration degrees, this time we selected Murchison (minimum alteration), Cold Bokkeveld (heavy alteration), and a clast of CM1 lithology within Tagish Lake thin section KN1 (complete alteration). We located typical serpentine crystals

in each sample using optical microscope and electron microprobe, and selected multiple crystals with different Fe/Mg compositions in each sample (Fig. 1).

We then performed SR-XANES analyses to obtain $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of each of these serpentines at BL-4A of Photon Factory (PF), KEK in Tsukuba, Japan. The beam size was about $6 \times 5 \mu\text{m}$. We used kaersutite amphiboles for the Fe^{2+} and Fe^{3+} standards whose $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios were well determined by wet chemistry [8]. The XANES analyses for standard kaersutites with known $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios shows a linear relationship between centroid energy position of XANES pre-edge spectra and the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio. Based on this linear relationship, we estimated the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of samples studied. The XANES result is most affected by crystal orientations. However, serpentine in CM chondrites is fine-grained, and we can ignore this effect. Nevertheless, the XANES analysis employed in this study still bears $\pm 10\%$ error mainly because of the orientation effect of the standard samples.

Results: In our previous study, we did not observe clear difference between $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios and alteration degrees [7]. Although we analyzed three additional CM samples showing even wider degrees of aqueous alteration, we still see limited ranges of $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of serpentine (Table 1).

The XANES spectra of Murchison serpentine suggest that 81-84% of the iron is present as Fe^{3+} (Fig. 2a). Similarly, serpentines in Cold Bokkeveld have $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of 0.80-0.84 (Fig. 2b) although we analyzed three serpentine grains with different Fe/Mg ratios. Serpentine in Tagish Lake KN1 shows nearly identical $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios (0.78-0.82) to those of Murchison and Cold Bokkeveld (Fig. 2c). It should be noted that $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios are similar even in the same sample although we analyzed multiple grains with different Fe/Mg ratios. This is similar to what we observed in our previous study [7].

Discussion and Conclusion: The obtained $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of serpentine in Murchison, Cold Bokkeveld, and Tagish Lake are surprisingly all ~ 0.8 in spite of their distinct degrees of aqueous alteration [3]. Murchison and Cold Bokkeveld are two extreme examples in the *Alteration Index* (Murchison: 0.43, Cold Bokkeveld: 1.03) [3], and CM1 lithology of Tagish Lake shows even more extensive aqueous alteration [9].

The intensity of pre-edge peaks are also similar among three samples (Fig. 2), and are not so high, suggesting only small amounts of tetra-coordinated Fe [10]. These results are basically similar to our previous study analyzing Murray, Nogoya and ALH 84029 [7], although Beck et al. [11] reported a trend related to both $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio and pre-edge peak intensity among seven CMs they studied by using a similar XANES technique. Among the six samples we analyzed so far, Fe-rich serpentine in ALH 84029 is the only example suggesting clear enrichment of Fe^{2+} [7].

There will be two explanations for the observed similar high $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of six CM chondrites. One is that the analyzed serpentine contains submicron grains of Fe^{3+} -bearing phases and the SR-XANES beam size was not small enough to exclude them. This may be related to terrestrial weathering. Even if the original serpentine compositions were heterogeneous, terrestrial oxidation has made much of the Fe^{2+} into Fe^{3+} , and the now excess iron forms nano-phase ferrihydrite [2]. The other explanation is that the oxidation state of iron does not vary with alteration degrees against our expectation. At present it is hard to say which is more likely.

The electron microprobe analyses of serpentine suggest that the iron in serpentine is dominantly present as Fe^{2+} in all CM samples [3] although our XANES analysis suggests that most Fe is present as Fe^{3+} . Preparation of appropriate serpentine standards may reduce this discrepancy by the better calibration of the analyses. However, their identical pre-edge positions (Fig. 2) show that they have identical relative $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios although the absolute $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio may be varied by the standards. It will be also necessary to analyze many more CMs (e.g., CM1 lithology in Kaidun and the minimally altered CM Kivesvaara) to see whether the trend is really absent or not.

References: [1] McSween H. (1987) *GCA*, 51, 2469-2477. [2] Zolensky M. et al. (1993) *GCA*, 57, 3123-3148. [3] Browning L. et al. (1996) *GCA*, 60, 2621-2633. [4] Vilas F. and Gaffey M. J. (1989) *Science*, 246, 790-792. [5] Vilas F. (2008) *Astron. J.*, 135, 1101-1105. [6] Zega T. et al. (2003) *American Mineral.*, 88, 1169-1172. [7] Zolensky M. et al. (2010) *Meteoritics & Planet. Sci.*, 45, A226. [8] Monkawa A. et al. (2006) *Meteoritics & Planet. Sci.*, 41, 1321-1329. [9] Zolensky M. et al. (2002) *Meteoritics & Planet. Sci.*, 37, 737-761. [10] Wilke M. et al. (2001) *American Mineral.*, 86, 714-730. [11] Beck P. et al. (2010) *Meteoritics & Planet. Sci.*, 45, A12.

Table 1. The estimated $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios of serpentine in CM chondrites using SR-XANES.

	Mg-rich	Intermediate	Fe-rich
Murchison	0.82-0.84		0.81
Murray ^[7]	0.87-0.88		0.76-0.88
Nogoya ^[7]	0.82-0.84	0.85-0.90	0.75-0.79
Cold Bokkeveld	0.80	0.83	0.84
ALH84029 ^[7]	0.87-0.94		0.18-0.73
Tagish Lake KN1	0.80-0.82		0.78

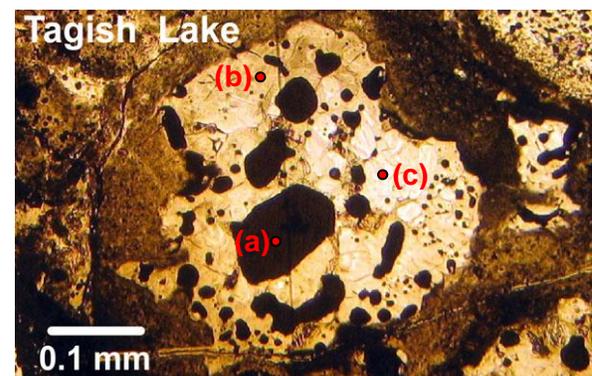


Fig. 1. Optical photomicrograph of Tagish Lake KN1 showing a clast of CM1 lithology. (a) is Fe-rich serpentine, while (b) and (c) are Mg-rich serpentines.

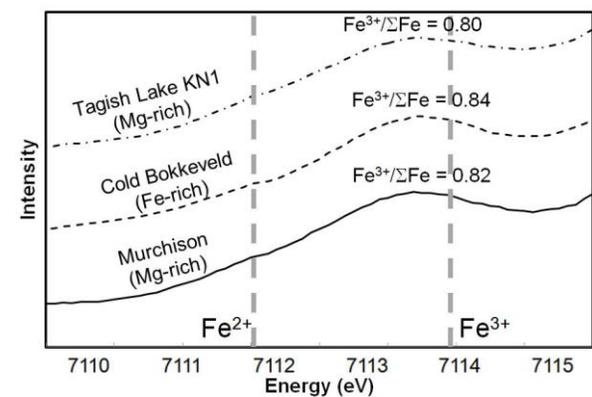


Fig. 2. Representative XANES spectra of serpentines in three CM chondrites near their pre-edge peaks of Fe K edge. Note that they show nearly identical $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios.