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電子エネルギー損失分光法（EELS）による緑泥石中の鉄の二価三価比測定
Ferrous to ferric ratio measurement in chlorite using electron energy-loss spectroscopy (EELS)

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Determination of Fe^{3+}/Fe_{total} ratio in iron-bearing minerals is important and has been conducted using several analytical techniques such as Mosbauer spectroscopy, X-ray absorption near-edge structure (XANES) and X-ray photoelectron spectroscopy. Compared to these techniques, electron energy-loss spectroscopy (EELS) in Transmission electron microscopy (TEM) is capable of giving information of the chemical state of constituting elements in specimens, with a spatial resolution down to the nanometer scale. Detailed analysis of energy-loss near-edge structure (ELNES) of Fe-$L_{2,3}$ core-loss edges provides information about the iron oxidation state, and several methods have been proposed to quantify Fe^{3+}/Fe_{total} from the ELNES of iron (Garvie and Buseck, 1998; van Aken et al., 1998). However, because a number of silicate minerals are electron-beam sensitive, the influence of radiation damage on the quantification of Fe^{3+}/Fe_{total} by EELS should be considered. Moreover, sample preparation processes for TEM such as argon ion-milling and focused-ion-beam (FIB) milling form a damage layer on the specimen surface, which may also affect the quantification. In this study Fe^{3+}/Fe_{total} quantification in chlorite, rather beam-sensitive iron-bearing phyllosilicates, has been performed using EELS equipped to a field-emission gun TEM with a monochromator, considering the influence of radiation damage and sample conditions on the measurement.

Fe^{3+}/Fe_{total} ratios obtained from the same grain of chlorite indicated that the ratio increases significantly with the electron dose to be radiated during TEM observation and EELS acquisition, suggesting that the oxidation of iron proceeds with vitrification of chlorite by radiation. Hence, it was necessary to acquire several Fe^{3+}/Fe_{total} ratios as a function of electron dose (i.e., time) and estimate 'the damage-free ratio' by extrapolation. The surface damage layers with a thickness of several tens of nanometers, which were formed during FIB milling, are likely oxidized and therefore partially associated with the increase in the Fe^{3+}/Fe_{total} ratios.

Keywords: EELS, TEM, Phyllosilicate, Chlorite, Iron valence state, FIB