Energy-filtered transmission electron microscopy (EFTEM) of intergrown pyroxenes

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ABSTRACT

It is demonstrated that energy-filtered transmission electron microscope (EFTEM) imaging in a conventional TEM (CTEM), equipped with a field-emission gun (FEG) electron source, can be used to characterize the local chemical distribution in exsolved pyroxenes. EFTEM imaging, which can be performed in one to tens of minutes, yields two-dimensional compositional maps that can have nanometer-scale resolution. The combination of electron energy-loss spectroscopy (EELS) and EFTEM imaging with techniques such as bright-field and dark-field imaging, high-resolution TEM (HRTEM) imaging, energy-dispersive X-ray spectroscopy (EDS), and electron diffraction allows for the chemical and structural characterization of any sample able to withstand the electron beam.

EFTEM imaging, HRTEM, and EDS data suggest that the augite → orthopyroxene reaction in the samples examined occurs in two-steps; augite → pigeonite → orthopyroxene. In this two-step process, the chemical and structural components are accomplished separately, suggesting that it is energetically or kinetically favorable to dissociate the two components rather than have them occur simultaneously. This two-step transformation is supported by the pigeonite → orthopyroxene transformation, which appears to be an isothermal martensitic transformation since the pigeonite and orthopyroxene compositions are identical within analytical error.

INTRODUCTION

Application of EFTEM to minerals

Energy-filtered transmission electron microscopy (EFTEM) is fundamentally based on electron energy-loss spectroscopy (EELS), which is a quantitative way of measuring the amount of energy lost by high-energy electrons as they pass through a material. This loss of energy is due to inelastic interactions between the incident beam electrons and the electrons atomically bound within the sample being examined. Electrons that have lost a specific amount of energy can yield quantitative information about local chemical composition by either an EELS spectrum or a two-dimensional elemental image. A two-dimensional valence-state EFTEM image can also be achieved (Wang et al. 2000).

EFTEM is commonly used in both biological and materials sciences, however, it has been rarely employed in the mineralogical sciences. Initially, most EFTEM was performed using a scanning transmission electron microscope (STEM). However, this form of EFTEM has a major drawback. The spatial resolution and image acquisition time are dictated by the number of points sampled by the beam as it rasteres across the specimen. Therefore, the acquisition times for STEM EFTEM images with high spatial resolution are quite long, often hours. Alternatively, EFTEM imaging can be performed using a conventional transmission electron microscope (CTEM), where images are acquired using a stationary beam of electrons. Depending on acquisition conditions, these images can have nanometer (Jäger and Mayer 1995; Mayer et al. 1998) or even sub-nanometer (Freitag and Mader 1999) spatial resolutions and can be acquired in minutes.

Several EELS studies have been published on mineralogical samples. Some of these studies presented data on chemical composition and electronic structure of silicates (McComb et al. 1991; Garvie et al. 1994), borates (Buseck and Garvie 1996), pyrochlore and uraninite (Xu and Wang 1999), and on Ce⁴⁺/Ce³⁺ ratios (Garvie and Buseck 1999). These studies were limited to point analyses because the EELS spectra were formed from the average of scattering from an excited volume. EFTEM imaging offers an increased number of spatial dimensions allowing the creation of two-dimensional composition images. Two-dimensional valence-state EFTEM images can also be achieved (Wang et al. 2000).

Mineralogical applications of EFTEM imaging include Harrison et al. (1999) on ilmenite-hematite solid solutions, and Elbert et al. (1999, 2000) on pyroxenes and carbonates. Czank et al. (1997) used EFTEM imaging with a CTEM to reveal fine-scale hornblende lamellae in cummingtonite using a Zeiss EM 912 TEM equipped with a LaB₆ thermionic source and an omega filter (for descriptions, see Reimer 1995). A spatial resolution of approximately 6 nm, measured as full width at half