Quantitative measurement of short compositional profiles using analytical transmission electron microscopy

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Abstract

Analytical transmission electron microscopy (ATEM) was used to quantitatively measure sub-micrometer compositional profiles produced experimentally by Fe-Mg interdiffusion experiments in olivine. Although analysis of minerals by ATEM is common, compositional profiles suitable for quantitative modeling of diffusion are not generally measured in minerals with ATEM. To demonstrate the suitability of ATEM for diffusion studies in minerals, we have investigated Fe-Mg interdiffusion in experimentally annealed olivine. Because the compositional gradients were induced under well-controlled laboratory conditions, the accuracy of the measurements could be tested by comparing compositional profiles measured by both ATEM and EMPA as well as by retrieving diffusion coefficients from both TEM and EMPA data. The agreement in diffusion coefficients shows that point defect equilibration in the interfacial region of the diffusion couple occurs extremely rapidly at 1200 °C. The ability to obtain diffusion data from such short anneals enables various experiments that were not previously possible—for example, to study diffusion rates at high pressures where long furnace anneals are not generally feasible. ATEM profile measurement is compared with other techniques such as SIMS and RBS and some limitations and applications of ATEM profile measurements are also discussed.

INTRODUCTION

Measurements of compositional gradients over short distances (a few nanometers to one micrometer) have been the goal of many mineralogical and petrologic investigations dealing with natural and experimental samples. Such measurements may be applied to the elucidation of short-lived or low-temperature thermal events from compositional zoning in natural mineral samples combined with various geothermometers or geospeedometers (e.g., Lasaga 1983; Ozawa 1984). Examples include transport of xenoliths in melts, sub-amphibolite facies metamorphism and thermal metamorphism of meteorites. Measurements of short compositional gradients can also be used to determine diffusion coefficients from experiments at low temperatures (e.g., Jaoul et al. 1995; Chakraborty and Rubie 1996). The ability to measure short compositional profiles may allow determination of diffusion coefficients in minerals where diffusion rates are slow, e.g., zircons and clinopyroxenes.

A fundamental problem in diffusion studies arises from the fact that elements zoned in minerals, i.e., those which diffuse slowly over geological time scales, are the ones that are capable of providing the most useful information. Measurement of diffusion rates of such species in the laboratory typically requires temperatures much higher than those in most geologic settings to induce observable concentration gradients within reasonable experimental time scales. Measured data must then be extrapolated to geologically relevant temperatures for interpretation of natural zoning profiles, but such extrapolations would be inappropriate if the diffusion mechanisms change over the extrapolated temperature range. An alternative approach is to directly measure diffusion rates at geologically relevant conditions (P, T, etc.) by using a method to measure and quantify much shorter diffusion profiles than those typically measured by electron microprobe analysis (EMPA). The ability to measure such short profiles greatly decreases the time required for diffusion experiments.

Analytical TEM is a technique that has been available for over 25 years. Quantitative microanalysis of nanometer-to-micrometer size objects has been the goal of ATEM studies since the early applications in the 1970s (Lorimer et al. 1973; Cliff and Lorimer 1975). Since that time there have been more applications of ATEM than can be listed here, but examples include investigations of exsolution lamellae in pyroxenes (Champness and Lorimer 1973), feldspars (Cliff et al. 1976), and amphiboles (Gittos et al. 1974, 1976; Smelik and Veblen 1989, 1991, 1993; Klein et al. 1997). The compositions of interstratified phyllosilicates have been also investigated in altered micas and diagenetic clays (Yau et al. 1984; Lee et al. 1984; Ahn and Peacor 1985, 1987; Livi and Veblen 1987;