

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 f_{O_2} buffered 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;

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Sharp et al. 1990; Jiang et al. 1990). Quantitative ATEM has been also used in characterizing high-pressure minerals in shocked chondrites (Langenhorst et al. 1995; Chen et al. 1996; Sharp et al. 1997). High-pressure samples recovered from experiments (Dupas et al. 1994; Martinez et al. 1997) and meteorite samples (Langenhorst et al. 1995; Leroux et al. 1996) have been analyzed with high precision using the parameterless correction method of Van Cappellen (1990) and the method for absorption correction in stoichiometric oxides and silicates of Van Cappellen and Doukhan (1994).

Despite numerous characterizations of minerals using ATEM in the past 25 years, its applications to compositional profiles and diffusion have been limited. Compositional profiles have been measured in minerals to investigate the distribution of solutes between precipitates and exsolution lamellae (Lorimer and Champness 1973; Klein et al. 1997) and to investigate micro-zoning in minerals (Müller et al. 1995; Eisenhouer et al. 1993; Wirth 1996). In a recent study by Ganguly et al. (1996), a 350 nm compositional profile across a grain boundary between an almandine and a grossular-spessartine garnet were used to constrain the duration of Acadian metamorphism to 40–50 Ma. This study highlighted both the potential and shortcomings of the ATEM technique. In the absence of well-defined slopes, Ganguly et al. (1996) were forced to use the overall length of the diffusion zone as a measure of the extent of diffusion. This parameter was used to arrive at the estimate of time scale of metamorphism quoted above. This study clearly demonstrated, however, that quantitative measurement of short, sub-micrometer compositional profiles may substantially improve the understanding of petrologic history of diverse rock types. ATEM has been used to determine low-temperature diffusion coefficients in an Al-Zn alloy (Nicholls and Jones 1983) by measuring compositional zoning near Zn-rich precipitates. More recently, interdiffusion rates in Ni-Ge alloys (Komai et al. 1995) have been measured and Si-Ge quantum wells have been characterized (Bangert et al. 1996) through quantitative profile measurements using ATEM, and similar applications are becoming common in other metallic and alloy systems. Although similar studies of minerals are possible, ATEM has not yet been successfully applied to the acquisition of quantitative diffusion data from minerals either because of difficult sample preparation or because of the common perception that ATEM is not sufficiently accurate for quantitative diffusion profile measurements.

The present study demonstrates that ATEM can be used to measure quantitative profiles in minerals on a sub-micrometer scale. These profiles are adequate for diffusion modeling in natural samples to investigate thermal histories of minerals and in experimental samples to retrieve small diffusion coefficients. Attaining these goals requires (1) preserving diffusion interfaces during preparation of an electron transparent film and (2) obtaining analytical precision sufficient to quantitatively determine diffusion coefficients. The accuracy of these measurements was

tested by retrieving diffusion coefficients from profiles induced during interdiffusion experiments with olivine under controlled conditions and comparing these with data obtained from electron microprobe analysis (EMPA) on the same samples. Potential applications of ATEM-profile measurements in mineralogy and petrology are discussed in the concluding section along with the implications of the diffusion coefficients obtained from the ATEM profiles.

DIFFUSION EXPERIMENTS AND SAMPLE PREPARATION

Diffusion experiments were performed using diffusion couples made from single crystals of synthetic forsterite and an Fe-bearing olivine (Fo_{82}) from San Carlos, Arizona. X-ray diffraction was used to orient the crystals such that the [001] zone-axis directions are aligned. Polished (001) faces of two cubes were held together, in a specially designed sample holder that provides a slight compressive force. The diffusion couples were annealed at high temperature to induce $\text{Mg}^{2+} \leftrightarrow \text{Fe}^{2+}$ interdiffusion and compositional profiles along the [001] direction, which is the fastest diffusion direction in olivine (e.g., Buening and Buseck 1973). All diffusion anneals were carried out at 1 atmosphere and a controlled oxygen fugacity ($f_{\text{O}_2} = 10^{-12}$ bar), obtained using a flowing gas mixture of CO-CO₂. Anneals were run at temperatures of 980, 1050, and 1200 °C for times ranging from 24 min to 336 h. Descriptions of the starting material, methods of temperature and f_{O_2} control and other experimental details are reported in Chakraborty (1997).

After annealing, samples were cut perpendicular to the interface with one half prepared for profile measurement by electron microprobe analysis (details may be found in Chakraborty 1997) and the second half prepared as a polished thin section (thickness $\leq 30 \mu\text{m}$) with [001] within the plane of the section. Thin sections were mounted on 3 mm copper mesh and hole grids, with the mesh grid providing extra support for the interface. The samples were mechanically thinned to 10 μm with a dimple grinder and then ion milled with 5 kV Ar ions at an angle of 12° using a Gatan Duomill system equipped with a sector speed-control device. As interfaces tend to thin preferentially, we controlled the rotation of the sample during milling such that most of the thinning occurred when the beam was approximately perpendicular to the interface. Samples were cleaned under low voltage (1.5 kV) to remove the amorphous surface layer that is generally produced during milling. Although samples may be heated to temperatures up to 250 °C during ion milling (which would be the breakdown temperature of the epoxy used to mount the samples on the grid), interdiffusion occurring at this temperature in the several hour time scale of sample preparation is negligible. Following this procedure it is possible to preserve the interface and adjacent areas as a thin electron-transparent film. Annealed interfaces are clearly visible in TEM images, showing both crystals in direct contact (Fig. 1).

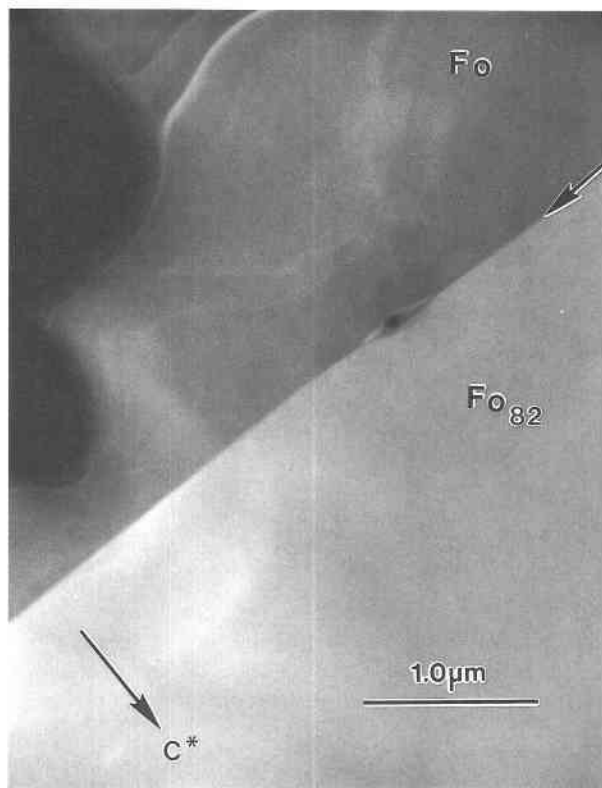


FIGURE 1. TEM Bright-field image (random orientation) showing a tight interface (unlabeled arrow) of a pre-oriented diffusion couple. The c^* axis is indicated by a second arrow.

ATEM MEASUREMENTS

ATEM measurements were made using a Philips CM-20 FEG STEM operated at 200 kV in the STEM mode. This instrument is equipped with a field emission gun (FEG) that makes it possible to obtain an intense electron beam of ≈ 1 nm diameter, resulting in excellent spatial resolution for quantitative EDS analysis. The high current densities produced by the FEG make it possible to excite sufficient X-rays from major elements in a silicate matrix to obtain good counting statistics with reasonable counting times while using a nanometer-sized beam. For beam sensitive samples, irradiation damage can be minimized by scanning rectangular boxes rather than making point analyses. To minimize the time that the beam spends on a reference area outside the scanned area, we used relatively slow scan rates (2.5–5 lines/s) and few lines (144–576) when scanning boxes. An alternative method to avoid beam damage is to defocus the beam in conventional TEM mode. However, scanned boxes can be easily varied in size, aspect ratio, and orientation relative to features of interest, and thus they offer important advantages. The analytical equipment consists of a Noran Voyager EDS system with a Ge detector and a Novar detector window that allows the detection of elements as light as C. For EDS measurements, the sample was inclined toward the detector by an angle of approximately 15° . To

avoid mixing of information from both crystals in the interface region, the sample was oriented in the sample holder such that the interface was nearly parallel to the plane defined by the optical-axis and detector-axis of the microscope.

EDS analyses were quantified using the ratio technique of Cliff and Lorimer (1975). The k factors k_{FeSi} , k_{MgSi} , and k_{Osi} were determined experimentally by applying the parameterless correction method of Van Cappellen (1990). From a series of spectra collected over a range of sample thicknesses, uncorrected elemental concentrations ($k_{\text{AB}^*} = 1$) were calculated and plotted vs. an internal measure of thickness (total X-ray counts)/(total counting time) that monotonically tends to zero with vanishing specimen thickness (Van Cappellen 1990). The uncorrected concentrations, extrapolated to zero thickness, are used to calculate k factors that are free of absorption effects. Standard materials used to determine the k factors were forsterite and fayalite (details given in Chakraborty 1997).

It is possible to neglect small absorption and fluorescence effects as long as the sample is thin enough to fulfill the thin-film criterion (Cliff and Lorimer 1975). To minimize absorption effects, we measured our profiles along the thin edge of the sample following contours of constant thickness. Because the geometry of TEM foils is often complex, it was not always possible to fulfill the thin-film criterion. For thicker samples, an absorption correction was necessary, which requires a knowledge of the mass absorption coefficients and absorption path length (related to sample thickness and sample-detector geometry). We used the absorption correction method of Van Cappellen and Doukhan (1994), which uses absorption of the $\text{O-K}\alpha$ line in stoichiometric oxides to determine a fictive thickness for absorption correction. Because the array of measured spots is generally irregular, the diffusion distance, perpendicular to the interface, must be measured from the array of C contamination spots seen in TEM images recorded after profile measurements. For each sample, three to five profiles were measured and the mean values of diffusion coefficients are compared with EMPA data.

Caution was taken to avoid artifacts that can reduce the accuracy of quantitative EDS results. The loss of volatile elements such as Mg during analysis of olivines may be especially problematic when using a very sharply focused beam with high current density (Champness and Devenish 1992; Peacor 1993). Champness and Devenish (1990) have shown that although olivine is relatively resistant to element loss compared with other silicates, a current density of 10^8 A/m² is sufficient to cause Mg loss. Although the current density used in our point analyses ($9 \cdot 10^7$ A/m², for a spot diameter of 3 nm) was nearly as high as the threshold value of Champness and Devenish (1990), we did not see any deviation in olivine stoichiometry ($[\text{Fe}+\text{Mg}]/\text{Si} = 2$) in our point measurements. Had there been significant Mg loss, the Si and Fe contents would be anomalously high resulting in incorrect olivine

stoichiometry. To be certain that there was no Mg loss, we made a profile measurement using large scanned rectangles (300×300 nm) to reduce the effective current density ($6 \cdot 10^3$ A/m²). Concentration profiles from both types of measurements yielded the same diffusion coefficient. In addition, the unchanged compositions at the ends of the diffusion profiles were used as internal standards and both spot and scanned-rectangle measurements yielded the correct composition. A second artifact that can produce anomalous stoichiometry is electron channeling (Buseck and Self 1993). Because olivine is known to show strong electron channeling effects (Smyth and Taftø 1982; Taftø and Spence 1982), we avoided crystal orientations where strong diffraction was occurring, either in two-beam (Bragg) conditions or in zone-axis orientations (Ottens and Buseck 1987).

DIFFUSION PROFILES

Concentration profiles of iron and magnesium were measured on four diffusion-couple samples with profile lengths ranging from <1 μm to ≈ 30 μm . Normalized element concentrations $[\text{Fe}/(\text{Fe} + \text{Mg})]$ were plotted as a function of the distance perpendicular to the interface. A relatively long diffusion profile of ≈ 30 μm , produced by annealing a Fo-Fo₈₂ couple at 1200 °C and $f_{\text{O}_2} = 10^{-11.95}$ bar for 254 h, was measured by both EMPA and ATEM (Fig. 2a). The EMPA and ATEM profiles have almost identical slopes and forms, showing that both methods can be used to measure diffusion profiles accurately. A much shorter diffusion profile (≈ 7 μm) was produced by annealing at 980 °C and $f_{\text{O}_2} = 10^{-11.95}$ bar for 336 h (Fig. 2b). In this case, the diffusion profile is close to the limit of spatial resolution of EMPA due to the convolution effect caused by the relatively large excitation volume during EMPA analyses (Ganguly et al. 1988). As the ATEM profile is free of convolution effects, the parameter ϵ (the error standard deviation of the X-ray intensity distribution in a sample, resulting from excitation by an electron beam) can be deduced from the difference of the diffusion coefficients obtained using profiles from EMPA and ATEM. Using $\epsilon_{\text{EMPA}} = [2t(D_{\text{EMPA}} - D_{\text{ATEM}})]^{1/2}$ (Ganguly et al. 1988) we obtain $\epsilon_{\text{EMPA}} = 0.57$ μm , which indicates that the diameter of the excited volume for the EMPA analysis is ≈ 2 μm . Ganguly et al. (1988) give a comparable value of $\epsilon_{\text{EMPA}} = 0.53$ μm obtained from a garnet-aluminum pair. It is clear from this example that the ATEM method is better suited for resolving the shapes of profiles that are 7 μm or shorter in length. As a further test of the ATEM profile measurements, we conducted a short duration (24 min) experiment at 1200 °C to produce a compositional profile of about 1 μm in length (Fig 2c). Three separate profile measurements from this sample show that the ATEM data are reproducible. Although such profiles are beyond the resolution of EMPA, diffusion coefficients from such short profiles can be compared with those obtained from EMPA data.

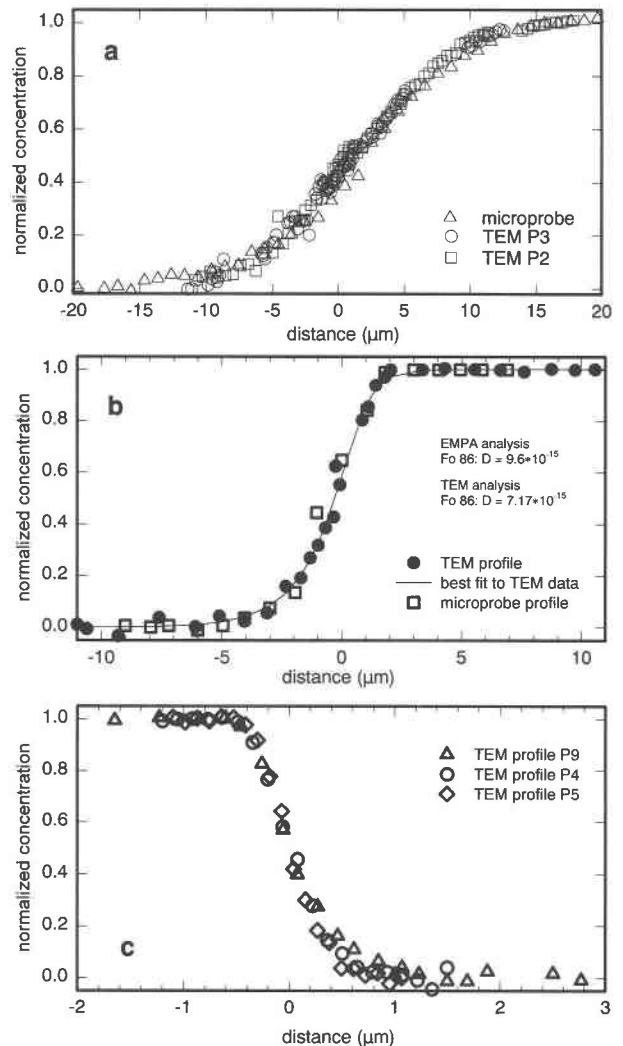


FIGURE 2. Normalized concentration profiles ($[\text{Mg}]/[\text{Mg} + \text{Fe}]$) of Mg-Fe interdiffusion along $[001]$ in Fo-Fo₈₂ diffusion couples. (a) Experimental conditions: $T = 1200$ °C, 254 h at $f_{\text{O}_2} = 10^{-11.95}$ bar. Comparison of ATEM (circles and squares) and EMPA (triangles) data showing that the results of the two techniques are in good agreement. For this long (≈ 30 μm) profile only the region with strong diffusion gradients was measured using ATEM. (b) Experimental conditions: $T = 980$ °C, 336 h at $f_{\text{O}_2} = 10^{-11.95}$ bar. Concentration profiles approaching the convolution limit of the EMPA. The comparison of ATEM (solid symbols) and EMPA data (open symbols) show that the shape of this profile (≈ 7 μm) is better resolved by the ATEM technique. (c) Experimental conditions: $T = 1200$ °C, 24 min at $f_{\text{O}_2} = 10^{-11.98}$ bar. Measurement of short (≈ 1 μm) profile using ATEM. Such profiles are too short to be measured with EMPA. Note the reproducibility of the data as seen from the overlap of multiple measurement profiles.

DIFFUSION COEFFICIENTS AND THEIR IMPLICATIONS

The asymmetry of the profiles, arising from a compositional dependence of diffusion coefficients, necessitated application of Boltzman-Matano analysis to obtain dif-

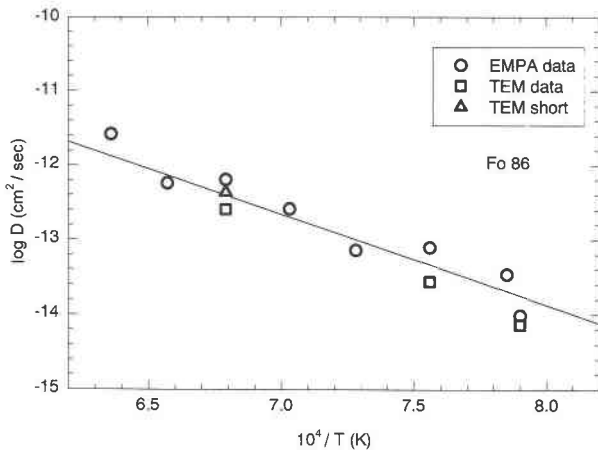


FIGURE 3. Arrhenius plot of the calculated diffusion coefficients from ATEM (squares and triangle) and EMPA (circles) data. Note the agreement of the diffusion coefficient obtained from the short duration (24 min) anneal at 1200 °C (triangle) with results from conventional longer anneals.

fusion coefficients. Diffusion coefficients calculated using conventional numerical Boltzman-Matano analysis (see Chakraborty 1997 for basic details) from both EMPA and ATEM profiles for a mean composition of Fo₈₆ are plotted in an Arrhenius diagram (Fig. 3) for quantitative comparison. The diffusion coefficients from both methods are comparable within experimental error, further demonstrating the utility of ATEM for yielding quantitative diffusion data. The data from the 24 min anneal illustrate that it is possible to obtain diffusion data from experiments of short duration, which considerably reduces the complexity of diffusion studies. The fact that we obtain the same diffusion coefficients from the 24 min anneal as from the longer duration anneals illustrates that point defect equilibrium is attained in the interfacial region of these olivines on a time scale much shorter than half an hour. Thus, for conventional long diffusion anneals at high temperatures designed to measure cation diffusion (in contrast to fast diffusion species such as H⁺), preannealing samples to equilibrate defect concentrations, as often recommended, may be an added complication to diffusion experiments that promises little return. The ability to determine diffusion coefficients from short-duration experiments opens the possibility of studying various aspects of diffusion in minerals. For example, point defect concentrations and diffusion rates in Fe-bearing silicates are a function of oxygen fugacity, and diffusion measurements in such silicates should always be carried out under controlled oxygen fugacity. But because conventional oxygen fugacity buffers have a relatively short lifetime (compared with typical diffusion anneals) in high-pressure cells at high temperatures, it has often not been possible to properly characterize diffusion coefficients measured at high pressures. A particularly important example of this is garnet, where proper application of diffusion data to geospeedometry calculations requires accounting

for the effect of oxygen fugacity on diffusion. But so far it has only been possible to suggest theoretical relationships between oxygen fugacity and diffusion rates, which could be only indirectly verified (e.g., see Chakraborty and Ganguly 1992; Chakraborty and Rubie 1996 for extended discussion). The ability to obtain diffusion coefficients from short experiments makes it possible to directly measure diffusion rates at different oxygen fugacities under high pressure and study the point defect chemistry of minerals such as garnets.

COMPARISON TO OTHER AVAILABLE METHODS AND POTENTIAL APPLICATIONS

Small diffusion coefficients for minerals, comparable to those that may be measured with the ATEM, have been obtained using the ion microprobe with a SIMS attachment (e.g., Giletti et al. 1978; Cygan and Lasaga 1985; Chakraborty and Rubie 1996) and Rutherford backscattering spectroscopy (RBS) or nuclear reaction analysis (e.g., see Jaoul et al. 1991 for a review). However, the ATEM method offers several advantages over the other two techniques. Both the SIMS and the RBS methods rely on the measurement of specific isotopes for observing diffusion. Although these methods are ideally suited for measurement of tracer- or self-diffusion coefficients, it is necessary to improvise to measure interdiffusion coefficients. As both SIMS and RBS are depth-profiling techniques, the source of the diffusant has to be supplied in the form of a non-reactive thin-film, and in the ideal case this film should be removable without disrupting the shallow diffusion zone after the anneal. This poses a considerable and often insurmountable experimental challenge when dealing with complex, natural silicate compositions. As seen in the example studied here, these problems may be avoided by using simple diffusion couples and the ATEM method. Furthermore, while both RBS and SIMS offer excellent resolution in the measurement of depth profiles they lack this resolution in the other dimensions, i.e., any composition along a profile is the average over a large surface area (typically on the order of hundreds of microns in diameter). Thus, both RBS and SIMS impose stringent demands on surface preparation and are useless for measuring small concentration gradients in natural samples where depth profiling is not generally possible. RBS and SIMS are also incapable of distinguishing the effects of small localized disruptions such as cracks, dislocations, and exsolved phases. ATEM, on the other hand, is used on thin foils and offers very high spatial resolution in all three dimensions. Therefore, ATEM is ideally suited for the measurement of short composition profiles in local regions, making it uniquely suitable for the study of natural samples. This applicability to natural samples allows the study of many low-temperature or short-lived thermal events (e.g., rapid cooling or uplift, episodic fluid flow) through the signatures left in zoning profiles near the rims of crystals (e.g., see Eissenhour et al. 1993; Ganguly et al. 1996).

A unique feature of ATEM is the capacity to structur-

ally characterize the sample in the same location where the concentration gradients are measured, allowing one to characterize defect microstructures and determine the orientation of the crystals. By carrying out comparative measurements with samples containing variable dislocation geometries and concentrations, it may be possible to determine to what extent these affect diffusion rates. Second, a major concern in many diffusion studies is whether the sample is stable during the anneal or whether incipient decomposition reactions affect diffusion rates (e.g., see Chakraborty and Rubie 1996). ATEM offers the most direct method for observing reaction products in the annealed samples. Finally, a main reason for the paucity of diffusion data in geological materials is the lack of single crystals suitable for diffusion measurements for many minerals of interest. This problem is particularly acute for high-pressure phases where it is generally impossible to grow large single crystals. The ATEM method, with its highly localized analytical capabilities combined with electron diffraction, allows the measurement of diffusion profiles in various samples using small crystals or even polycrystals. The ATEM method is inherently more accurate because it allows the direction along the diffusion profile to be measured after the anneal, simultaneously with the measurement of the profile. A tantalizing possibility is the measurement of diffusion coefficients along several crystallographic directions from a single polycrystalline sample.

A disadvantage of the ATEM method is that EDS is not well suited for the analysis of trace elements. The SIMS and the RBS methods continue to be superior in the area of measurement of diffusion coefficients of dilute constituents. A second disadvantage concerns the instability of many phases under the intense electron beam used in ATEM (e.g., MgSiO_3 perovskite, several hydrous phases, and glasses) and the likelihood that their compositions can change during the measurement. The problem of elemental loss during ATEM analysis can be quite severe for volatile elements in many structures if the current density used in the measurement exceeds a critical value (Champness and Devenish 1990, 1992; Devenish and Champness 1992). One solution to this problem is to reduce the effective current density by scanning over an area rather than measuring a single point. Although some spatial resolution is lost by scanning larger areas, the aspect ratio and orientation of the areas scanned can be adjusted to minimize the resolution loss in the direction of the profile. The applicability of ATEM to the measurement of diffusion profiles therefore depends on the composition and stability of the samples of interest. For diffusion problems involving major elements in samples that are stable under the electron beam (for example olivine, garnets, pyroxenes), ATEM can be applied to many petrologic processes that produce fine-scale chemical zoning.

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