



# Crystal surface integrity and diffusion measurements on Earth and planetary materials



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## ABSTRACT

Characterization of diffusion behavior in minerals is key to providing quantitative constraints on the ages and thermal histories of Earth and planetary materials. Laboratory experiments are a vital source of the needed diffusion measurements, but these can pose challenges because the length scales of diffusion achievable in a laboratory time are commonly less than 1  $\mu\text{m}$ . An effective strategy for dealing with this challenge is to conduct experiments involving inward diffusion of the element of interest from a surface source, followed by quantification of the resulting diffusive-uptake profile using a high-resolution depth-profiling technique such as Rutherford backscattering spectroscopy (RBS), nuclear reaction analysis (NRA), or ion microprobe (SIMS). The value of data from such experiments is crucially dependent on the assumption that diffusion in the near-surface of the sample is representative of diffusion in the bulk material. Historical arguments suggest that the very process of preparing a polished surface for diffusion studies introduces defects—in the form of dislocations and cracks—in the outermost micrometer of the sample that make this region fundamentally different from the bulk crystal in terms of its diffusion properties. Extensive indirect evidence suggests that, in fact, the near-surface region of carefully prepared samples is no different from the bulk crystal in terms of its diffusion properties. A direct confirmation of this conclusion is nevertheless clearly important. Here we use transmission electron microscopy to confirm that the near-surface regions of olivine, quartz and feldspar crystals prepared using careful polishing protocols contain no features that could plausibly affect diffusion. This finding does not preclude damage to the mineral structure from other techniques used in diffusion studies (e.g., ion implantation), but even in this case the role of possible structural damage can be objectively assessed and controlled. While all evidence points to the reliability of diffusivities obtained from in-diffusion experiments, we do not recommend experiments of this type using a powder source as a means of obtaining diffusant solubility or partitioning information for the mineral of interest.

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## 1. Introduction

Knowledge of diffusion rates of atoms in Earth and planetary materials can yield information on sample histories that is obtainable by no other means. Constraints on the temperature dependence of diffusion, in particular, are key to the quantitative reconstruction of thermal histories (cooling and/or heating paths) and to assessment of the reliability of age information acquired by measurement of accumulated radiogenic or cosmogenic isotopes. Given the importance of diffusion in geo-/cosmochemistry and petrology, it is not surprising that the data base of diffusion measurements on

minerals has expanded dramatically in recent decades (see summary in Zhang and Cherniak, 2010). Many of the new data have come from laboratory experiments designed to introduce a diffusant of interest into a sample and measure its migration progress at high temperature over a period of days to months. However, practical constraints on experiment duration lead to significant challenges in the analysis of diffusion experiments. In particular, because the diffusivities of many elements in crystals of geological interest are quite low, the length scales of transport in a laboratory time frame are commensurately small—in many cases considerably less than a micrometer.

In most laboratory protocols, diffusion experiments are set up in such a way that the diffusant of interest is supplied by a source at or near the mineral surface. This source could be in the form of

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a contacting powder (e.g., Cherniak and Watson, 1994; Van Orman et al., 2002; see also Watson and Dohmen, 2010 and references therein), a thin film deposited by pulsed laser deposition (PLD; see Chrisey and Hubler, 1994; Lowndes et al., 1996; Dohmen et al., 2002a, 2007; Marquardt et al., 2010), a contacting aqueous solution (Fortier and Giletti, 1991; Giletti, 1991), a precipitate formed by evaporation of an aqueous solution (e.g., Sneeringer et al., 1984; Chakraborty and Rubie, 1996; Van Orman et al., 1998, 2001), a gaseous atmosphere (e.g., Sharp et al., 1991; Wartho et al., 1999; Thomas et al., 2008) or a near-surface concentration horizon deposited by ion implantation (e.g., Cherniak et al., 1991, 2014; Cherniak and Ryerson, 1993). The combination of a surface source and a sub-micron diffusion length scale raises a vitally important question about the samples used for laboratory experiments: *Is the near-surface region representative of the “deep” crystal structure in terms of its volume diffusion properties?* If the results of a diffusion experiment are to be taken as representative of the bulk crystal and accorded broad geochemical value, the answer to this question must be yes. If the near-surface of the mineral differs from the bulk structure in some way that affects diffusion, the value of the measurement may be compromised. The purpose of the study described here is to evaluate directly the assumption that the near-surface of appropriately prepared samples is representative of the bulk structure.

## 2. Definition of “near-surface”

The adjective “near-surface” is a relative descriptor, so clarification of terms is needed in order for the following discussion to be meaningful. It has been recognized for decades that the *immediate* near-surface (INS) of crystals is structurally and chemically distinct from the deep (bulk) crystal structure even under conditions of chemical and mechanical equilibrium (e.g., Hall, 1953; Kingery, 1984; and reviews by Dowben and Miller, 1990 and Sutton and Balluffi, 1995). Adjustments of bond lengths and bond angles in this region occur as near-surface atoms relax from their regular lattice positions due to the proximity of a free surface or other phase discontinuity. Differences in the local bonding environment between the INS and the bulk crystal lead, in turn, to differences in equilibrium impurity content, commonly referred to as *surface- or interface segregation* in the materials science literature. Importantly, the length scale of this particular type of near-surface structural and chemical anomaly is now understood to be only 1–2 nm, as determined by direct measurements using X-ray reflectivity (e.g., Fenter et al., 2000a, 2000b, 2003; Schlegel et al., 2002; Zhang et al., 2007) and also from molecular dynamics simulations (e.g., Lanzillo et al., 2014). Not surprisingly, the INS is similar in width to grain boundaries (e.g., Hiraga and Kohlstedt, 2007). Because of the distorted atomic structure in the INS relative to the bulk structure, diffusion of atoms within this 1- to 2 nm-wide region may indeed differ from diffusion at depth in the lattice (e.g., Lanzillo et al., 2014); however, no research group of which we are aware is publishing volume diffusion data based upon profiles only 1–2 nm in length. As far as volume diffusion measurements in crystals are concerned, the structurally-relaxed immediate near-surface (i.e., outermost 2–3 polyhedral layers) of a crystal is of no relevance to the present discussion (Note, however, that this region may influence the trace-element or isotopic composition of a crystal that is acquired during growth; Watson, 2004; Lanzillo et al., 2014; Watkins et al., *in press*).

Beyond the INS, the term “near-surface” has also been applied to the region of a crystal subject to structural damage, mainly in the form of cracks and dislocations, as a consequence of the cutting, grinding and polishing steps used to produce the surface intended for diffusion experiments. The introduction of damage to the atomic structure of crystals through aggressive grinding

and polishing was recognized nearly 100 yrs ago (Beilby, 1921). The phenomenon seems to be best documented in metals (see, e.g., French, 1933; Finch et al., 1934), but is widely recognized in oxides and silicates as something to be avoided in samples intended for electron backscatter diffraction (EBSD) measurements, in which the signal comes from the outermost ~2 nm of the crystal (Winkelmann, 2010; Zaefferer, 2007). Reddy and Cooper (1982) also noted an effect of surface-preparation damage on oxygen diffusion in sapphire, and Pinilla et al. (2012) recently presented a TEM image of obvious near-surface damage in a gem-quality olivine crystal subjected to an unspecified grinding and polishing procedure. Because this kind of damage is characterized by extended defects—and because the damaged region can reach hundreds of nanometers into the crystal (see Fig. 1 of Pinilla et al., 2012)—it certainly has the potential to influence the results of experiments in which near-surface diffusion profiles are generated and measured. Like other laboratory groups involved in the study of slow-diffusing elements using depth-profiling techniques (e.g., Farver and Giletti, 1985; Jaoul et al., 1983; Ryerson et al., 1989; Giletti, 1991; Ryerson and McKeegan, 1994; Chakraborty and Rubie, 1996; Van Orman et al., 1998, 2001, 2002; Tirone et al., 2005; Dohmen et al., 2002b, 2007; Sano et al., 2011; Marschall et al., 2013), the RPI research group typically designs experiments to produce diffusion profiles in the ~50- to 500-nm depth region, simply because longer profiles are usually precluded by practical constraints on experiment duration. Our preferred analytical techniques—Rutherford backscattering spectroscopy (RBS) and nuclear reaction analysis (NRA)—are well suited to this depth range. Depth-profiling by ion microprobe (SIMS) works best in the depth range between ~100 nm and 1–2  $\mu\text{m}$  (see, e.g., Van Orman et al., 2001).

In the present study, we use transmission electron microscopy (TEM) to demonstrate that proper sample preparation leaves the near-surface region indistinguishable from the deep interior of the crystal in terms of atomic structure and presence of extended defects. Consequently, a diffusion profile acquired from this region by depth-profiling with RBS, NRA or SIMS should accurately reflect volume diffusion in the bulk crystal. There exist precedents to the present study in which TEM images of the near-surface of a diffusion sample are provided (e.g., Ratteron et al., 1998; Marquardt et al., 2010; Pinilla et al., 2012) but these generally focus upon a single mineral, and evaluation of the near-surface for possible polishing damage is not the primary thrust of the work.

## 3. Materials, preparation and imaging

### 3.1. Cutting and polishing

The materials examined by TEM in this study were San Carlos  $\text{Fe}_{90}$  olivine (SCO), commercial synthetic (hydrothermal) quartz, and Itrongay orthoclase from Madagascar. These minerals were chosen because they represent a range of silicate structures (nesosilicate to tectosilicate) with and without cleavage, and they are all common targets for diffusion studies by ourselves and other research groups. Tabular pieces of SCO and quartz ~1 mm thick and ~4 mm on a side were cut from cm-sized specimens with a low-speed diamond saw (SCO cut  $\perp c$ ; quartz  $\parallel c$ ). Two orthoclase slabs of similar thickness were prepared by manually cleaving the Itrongay material along (010) with a knife; one of these slabs was set aside for TEM work directly on the cleaved surface. The other orthoclase slab and the SCO and quartz slabs were polished on one side following the procedure used at RPI to prepare all of our samples for diffusion studies (see Watson and Cherniak, 2003; Thomas et al., 2008; Cherniak et al., 2014). Briefly, the slabs are attached to a 2.5-cm diameter brass or aluminum disk with Crystal

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