

# Oxygen diffusion and water-related defects in feldspar minerals: information from experimental and modelling studies

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## Introduction

The diffusion of oxygen in a variety of silicate and oxide minerals has been studied under both dry conditions (exchange with a dry gas, frequently oxygen or CO<sub>2</sub>) and hydrothermal conditions ('wet'; exchange with fluid enriched in <sup>18</sup>O at high pressure). An early summary of the data (Freer and Dennis, 1982) showed that oxygen diffusion under dry conditions was associated with slow diffusivities and high activation energies (typically 300–400 kJ mol<sup>-1</sup>) whilst oxygen diffusion under 'wet' conditions was associated with faster diffusion rates and small activation energies (of the order 100–150 kJ mol<sup>-1</sup>). Direct comparison between the types of experiment is difficult since many of the early 'dry' experiments employed powdered specimens whilst most of the hydrothermal, 'wet', experiments were performed on single crystals, with the short (~1 μm) diffusion profiles analysed directly by SIMS or nuclear reaction analysis (Elphick and Graham, 1991).

During the last decade good quality data from experiments performed under wet and dry conditions (using single crystals) has confirmed that the presence of water causes oxygen diffusion rates to be higher and activation energies lower in both anorthite (Elphick and Graham 1988) and quartz (Elphick *et al.*, 1988). It has been postulated that protons somehow mediate in the jump process leading to a lowering of the activation barrier and hence faster diffusion. However, the exact mechanism responsible for this phenomena remains unknown. Oxygen could migrate in 'wet' conditions as either OH groups or as H<sub>2</sub>O molecules. In order to elucidate the effects of water in oxygen diffusion in feldspar at an atomistic level, we have used computer simulation techniques to probe the energetics and geometry of a range of defects and to ascertain migration energies for oxygen and OH groups in Albite. Complementary experimental studies of oxygen diffusion in sanidine have been performed under 'wet' and dry conditions. An assessment is made of

experimental data for oxygen diffusion in various feldspar minerals under wet and dry conditions.

## Experimental diffusion studies

Single crystals of sanidine feldspar from Volkesfeld (Eifel) were cleaved along natural (100) cleavage planes to yield specimens approximately 2–3 mm in size. Samples were pre-annealed at 1050°C for 14 days prior to use. For 'wet' experiments crystals were sealed with water enriched in <sup>18</sup>O in gold capsules and annealed in Bridgman-type autoclaves at 550–850°C and 1 kbar pressure. For dry experiments the crystals were annealed at 900–1100°C with oxygen gas enriched in <sup>18</sup>O, at 1 bar total pressure.

After the experiments, oxygen diffusion profiles in the single crystals were determined by Secondary Ion Mass Spectrometry (SIMS) in terms of <sup>18</sup>O/(<sup>16</sup>O + <sup>18</sup>O) ratios. The data were recast into inverse error function profiles to yield oxygen diffusion coefficients.

## Simulation studies

Atomistic simulation methods have been successfully employed to simulate the structure, thermodynamics, point defect and diffusional properties of a range of materials (see Catlow and Price, 1990 for review). Static lattice simulations, where no account is taken of thermal motions, are based on energy minimisation procedures. Interactions between ions are described by interatomic potential functions whose parameters are derived by empirical fitting to experimental data. Potential parameters for albite were taken from Purton and Catlow (1990). The computer code CASCADE was used to calculate the energy required to form a variety of defect configurations including vacancy, interstitial, substitutional, and the energy required to move oxygen and oxygen-bearing species through the lattice. For such calculations the Mott and Littleton (1938) strategy was adopted,

TABLE 1. Activation energies for oxygen diffusion in feldspar minerals

Phase	Q (kJ mol <sup>-1</sup> )	Single/ Polycrystalline	Wet/Dry
Albite	89	S	Wet
	155	P	Wet
Anorthite	109	S	Wet
	234	S	Dry
	376	P	Dry
	107	S	Wet
Orthoclase	123	P	Wet
	109	S	Wet

where the lattice ions are relaxed around the defect. Full details of the method are given in Catlow and Mackrodt (1982) and Catlow (1986).

### Results and discussion

*Experimental studies* Oxygen diffusion profiles in sanidine were typically 1–2 μm in length. For the hydrothermal studies diffusion coefficients were in the range  $5 \times 10^{-19} \text{ m}^2 \text{ s}^{-1}$  to  $5 \times 10^{-17} \text{ m}^2 \text{ s}^{-1}$ . When plotted in the form of an Arrhenius diagram the data could be described by an equation of the form:

$$D = 3.95 \times 10^{-12} \exp(-109 \text{ kJ mol}^{-1}/RT) \text{ m}^2 \text{ s}^{-1}$$

Preliminary data from the 'dry' experiments suggest an activation energy of 157 kJ mol<sup>-1</sup>.

A summary of experimentally determined activation energies for oxygen diffusion in feldspar minerals is given in Table 1.

In general, oxygen diffusion rates in feldspars are faster and activation energies lower under wet conditions than under dry conditions. Activation energies obtained from powdered, polycrystalline, specimens are higher than those from single crystal specimens.

*Simulation studies* Since diffusion through the bulk lattice takes place via the movement of point defects, an appreciation of the nature of such defects is crucial to our understanding of diffusion processes. In ionic crystals, point defects can be formed intrinsically, where their numbers are governed by the thermodynamics of the system, or extrinsically due to the presence of impurities. Using CASCADE, formation energies of various defects were determined. Defects involving interstitials are predicted to be energetically more favourable than Schottky defects.

In the case of water-related defects, water may

be present in albite as OH groups or molecular water. One of the simplest reactions leading to OH formation is the dissociation of a water molecule into a hydroxyl group and a proton; the OH going into an interstitial site and the H combining with a lattice oxygen to form a second OH group. The energy required to form OH via this route was calculated to be 3.75 eV. Alternatively, water may react with oxygen vacancies, but in view of the large energy needed to form oxygen vacancies, such reactions are unlikely. For water entering the lattice, as an interstitial defect, the energy to form such a defect is low, only 0.9 eV.

The diffusion activation energies and pathways have been calculated for both 'dry' oxygen and for OH. Our initial results predict that oxygen diffusion will take place by an interstitial mechanism. The lowest activation energy is found for movement along the x direction (0.86 eV), with the highest being in the y direction (2.6 eV). In contrast, the shortest vacancy hop has an activation energy of 3.05 eV. OH is also predicted to migrate as an interstitial but with much lower activation energies than in the case oxygen alone.

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