Experimental constraints on the diffusion of volatile and redox-sensitive elements in pyroxenes

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'We **experimentally** investigate **diffusion** of volatile (**copper** and **lithium**) and redox-sensitive (**vanadium**) elements in **pyroxene** group minerals (**enstatite** and **diopside**).'

Introduction Modelling diffusion across growth zones of minerals enable us to estimate timescales of geological processes. Advances in **analytical instrumentation and methodology** enables accurate constraints on **diffusion coefficients** [1,2,3]. We are interested in investigating diffusion of trace elements with physical properties relevant to magmatic processes: **lithium and copper** can track **fast and volatile-sensitive processes** e.g. magma **ascent** [4]. **Vanadium** and its multiple oxidation states (V^{3+}, V^{4+}, V^{5+}), may track **redox-sensitive processes** in the magma reservoir.

Pyroxene group minerals e.g. **enstatite ($(Mg, Fe)_2(SiO_3)_2$)** and **diopside ($Ca(Mg,Fe)(SiO_3)_2$)** are excellent candidates for experimental diffusion studies because they are found in various magmatic environments and commonly have growth zones. We chose an **enstatite from Tanzania ('Opx-7', $Mg_{1.795}Fe_{0.184}Ca_{0.005}Al_{0.004}Si_{2.003}O_6$)** used in previous studies [1,5,6] and natural **euhedral diopside from Otter Lake, Canada ('OL-Di', $Mg_{0.659}Fe_{0.314}Ca_{0.935}Al_{0.040}Si_{1.997}O_6$)** as our pyroxene crystals. Due to the distinct behaviours of Li/Cu and V, we developed two setups involving both **thin film diffusion** [1,2] and **powder-source** [7] experiments**.**

Project Questions

1. How fast do lithium, copper, and vanadium diffuse in/out of pyroxenes?
2. What are the factors influencing Li, Cu, and V diffusion in pyroxenes?
3. Why are there differences in diffusion rates between Li, Cu, and V in pyroxenes?

Objectives

1. Determination of diffusion coefficients (D_{Li}, D_{Cu}, and D_V) in enstatite (Opx-7) and diopside (OL-Di).
2. Quantification of the effect of temperature, fO_2 and substitution mechanisms on D_{Li}, D_{Cu}, and D_V.

Experimental Workflow

1. Mineral cube preparation (RUB + ULg)

Crystals were separated by SelFrag (ULg) or hand-picked.

The selected crystals were oriented to expose the c-axis [001], before being polished.

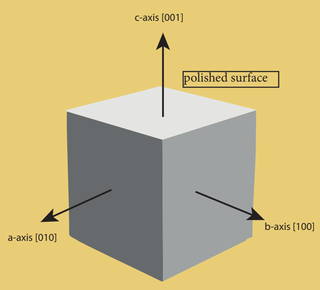

Figure 1: orientation of mineral cubes for experiments

Figure 2: Freshly cut OL-Di diopside cubes with polished [001] surface.

2 x 2 x 2 mm cubes cut by wire saw and cleaned in an ultrasonication bath with distilled water.

2. Diopside powder synthesis (ULg + RUB)

Trace-element grade (99.9% purity) MgO, SiO_2, and $CaSiO_3$ powders in stoichiometric proportion, then mixed in an agate mortar and pestle.

The powder mixture was fused in a Pd crucible using a muffle furnace at 1400°C to form synthetic diopside glass.

The glass was crushed by hand with an agate mortar and pestle in ethanol and dried overnight.

N.B. *RUB = Ruhr-Universität Bochum. ULg = University of Liège.*

3a. Pulsed laser thin film deposition (RUB/ULg)

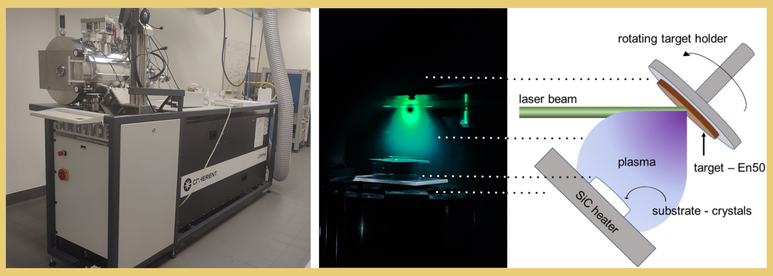

Figure 3 (left - right)**:** The Pulsed Laser Deposition apparatus; thin film deposition process, and an annotated diagram of PLD process [8].

Synthetic diopside powder was mixed with ~1000-1400 ppm V_2O_5 and CuO powder in an agate mixer, pressed into a disc, and then fused in a muffle furnace.

The glass disc was vaporized into plasma and deposited as a thin film onto the mineral cubes' surface using pulsed laser deposition (Fig. 3).

3b. Evacuated silica capsule preparation (ULg + RUB)

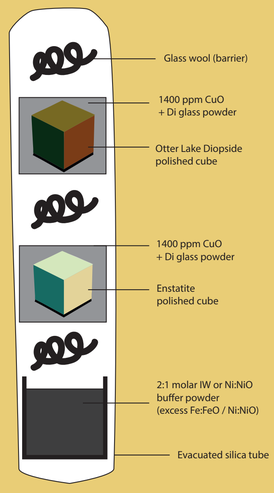

Figure 4 (above): general setup for a typical evacuated silica tube experiments run.

Synthetic diopside powder was mixed with ~1400 ppm CuO powder for the powder-source diffusion experiments (Fig 4).

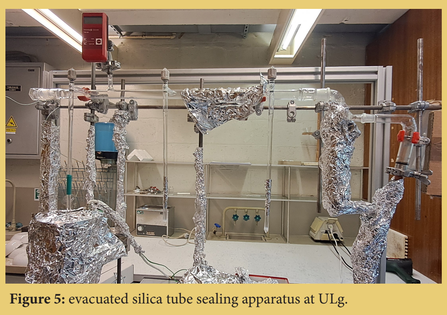

Figure 5: evacuated silica tube sealing apparatus at ULg.

Silica tubes with powder source experiments (Fig. 5) were held at vacuum (< 0.6 mbars) and heated at 115°C for 24-48 hours before sealing.

4. Annealing in 1-atm vertical furnace or muffle furnace (RUB/ULg)

Figure 6: 1 atm vertical furnace (this apparatus is at RUB) at T = 950-1200°C for 20-164 hours. Evacuated silica capsule experiments were annealed in 1-atm muffle furnaces at ULg (not pictured).

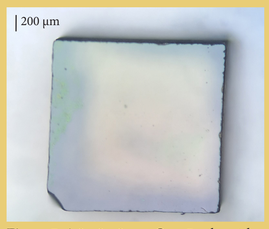

Figure 7: A 2 x 2 x 2 mm Opx-7 cube with a thin film of doped diopside powder before an experimental run.

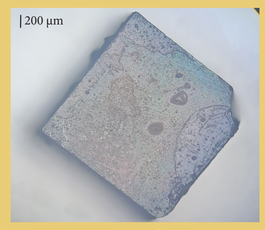

Figure 8: A 2 x 2 x 2 mm Opx-7 cube with a thin film of doped diopside powder after an experimental run.

Experiments were annealed in a 1-atm vertical furnace (RUB) or muffle furnace (ULg) (Fig. 6-8) according to the experimental conditions outlined in Table 1.

Setup	Conditions	Analytical Instrument
Thin film diffusion couple experiments	T = 950-1200°C, P = 1 atm, log fO_2 = -6 to -10 t = 5 - 164 hours n = 14	Time of Flight Secondary Ion Mass Spectrometer (Duisburg-Essen)
Powder source diffusion experiments	T = 950-1080°C, P = 1 atm, fO_2 = IW to NNO buffer t = 5 - 96 hours n = 10	Laser Ablation Inductively Coupled Plasma Mass Spectrometer (RUB)

Table 1: Experimental conditions for Opx-7 and OL-Di.

5. Analyses by TOF-SIMS / LA-ICP-MS (RUB / Duisburg-Essen)

Figure 9: Time-of-Flight Secondary Ion Mass Spectrometer at the U. Duisburg-Essen, Germany

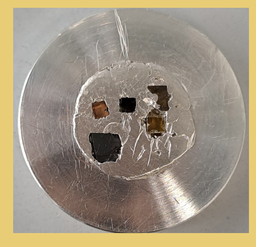

Figure 10 (left): Grain mount set in indium with samples for TOF-SIMS analyses. Clockwise from top left: Opx-7 (ref); OL-Di (ref); 1:1 $CuAl_2O_4$ on Opx-7 (not included); and 1200°C, 1 atm, log fO_2 = -10 for Opx-7 and OL-Di, respectively.

Experimental runs were analyzed on the Time-of-Flight Secondary Ion Mass Spectrometer (TOF-SIMS) at U. Duisburg-Essen (Fig. 9-10) or the laser ablation inductively coupled mass spectrometer (LA-ICP-MS) at RUB.

For TOF-SIMS, crystals were embedded in In grain mounts. Crystal orientation for some runs may be determined using EBSD on the Focused Ion Bean Scanning Electron Microscope at RUB.

Li, Cu, and V diffusion in pyroxene

For **powder-source experiments** we present results of a run at 1050°C, 1 atm, and buffered at ΔNNO (Fig. 11). The chemical gradient induced diffusion of Cu from the powder into the pyroxene cubes, but the sealed silica tube enabled Li to diffuse out of the OL-Di (Li ~ 46 ppm) into the Opx-7 (Li ~ 23 ppm) crystals (Fig. 12-13). The relative diffusion rates are: $D_{Li} > D_{Cu}$.

For **thin film diffusion experiments**, diffusion of V in Opx-7 and OL-Di crystals is slower than Cu/Li in the same crystal by around 3-4 orders of magnitude.

Diffusion of V in Opx-7 is faster than OL-Di crystal. At 1050°C, 1 atm, buffered at $\log_{10} fO_2$ = -10, the relative diffusion rates are ${}^{Opx\text{-}7}D_V$ (${}^{Opx}D_{V\text{-}best\text{-}fit} = 2.45 \times 10^{-19}\ m^2\ s^{-1}$) > ${}^{Cpx\ (OL\text{-}Di)}D_V$ (${}^{Cpx\ (OL\text{-}Di)}D_{V\text{-}best\text{-}fit} = 1.30 \times 10^{-20}\ m^2\ s^{-1}$) (Figs. 14-15).

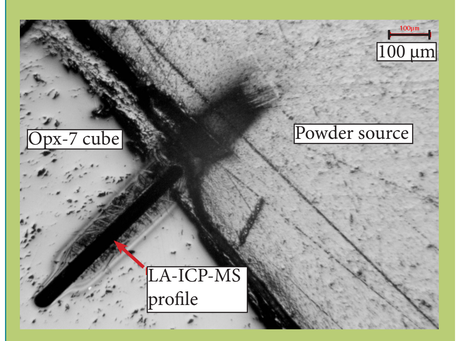

Figure 11: LA-ICP-MS ablation profile from powder to mineral of and Opx-7 crystal.

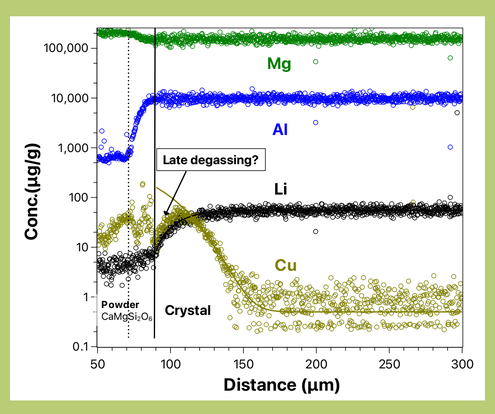

Figure 12: Profile of ^{65}Cu concentrations of the OL-Di crystal, showing diffusion across the powder-cube boundary.

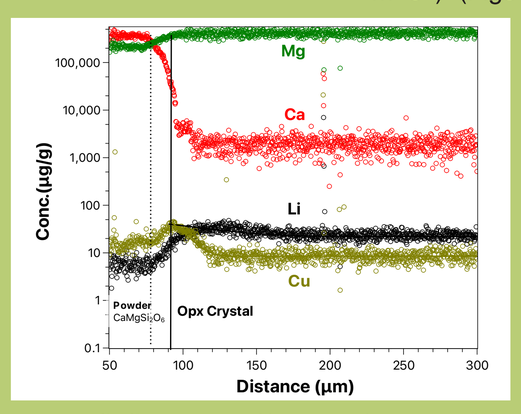

Figure 13: Profile of ^{7}Li concentrations of the OL-Di crystal in Figure 12. Diffusion in Li concentration is induced by Li diffusing out of the OL-Di and into the Opx-7.

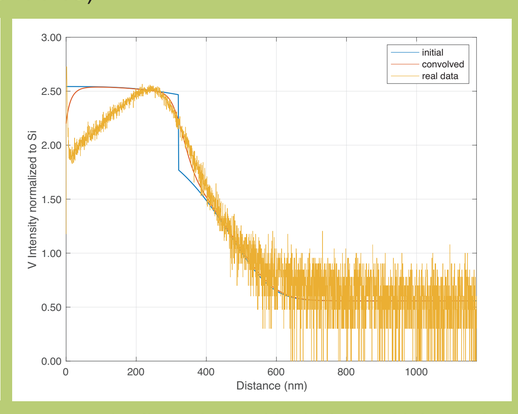

Figure 14: Initial profile, convolution model, and diffusion model of Si-normalized V intensity of OL-Di crystal compared to the analyzed profile.

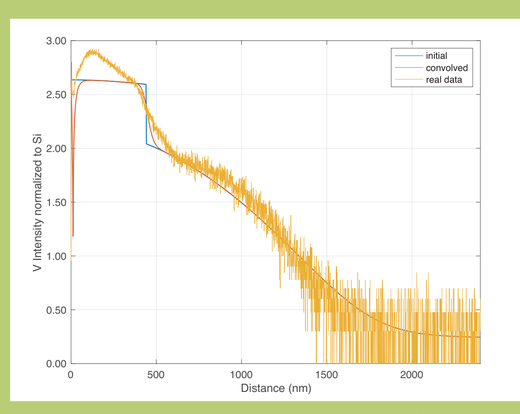

Figure 15: Initial profile, convolution model, and diffusion model of Si-normalized V intensity of Opx-7 crystal compared to the analyzed profile.

Next Steps

All experimental runs were completed and will be analyze on the TOF-SIMS and LA-ICP-MS in 2025/2026.We plan to test the hypothesis that $D_{Li} > D_{Cu} > D_V$ in pyroxenes. Intensive factors that may influence diffusion of Li, Cu, and V in pyroxenes include temperature and oxygen fugacity. Results of our study may benefit a range of fields including crustal and mantle processes, and ore deposits formation.

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Acknowledgements We thank Nils Hartmann (Duisburg-Essen), Niels Jons, Stephan Schuth, Sabine Weisel, Raul Fonseca, Christoph Beyer, Maria Dias, Charlotte Huck, Sumit Chakraborty (RUB), Nicolas Delmelle, Raphael Deville, Mohamed Aatach (ULg). R. Dohmen is funded by Research Unit FOR 2881. Sri Budhi Utami is funded by the F.R.S-FNRS as a Postdoctoral Fellow.

Abstract ID: 29724

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