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Laser Ablation MC-ICP-MS and its Application to Diffusion in Silicate Glasses and Melts

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Laser ablation coupled with multi collector inductively coupled plasma mass spectrometry (MC-ICP-MS) has been established as a powerful tool to study elemental and isotopic fractionation in condensed systems on the micrometer scale [1,2]. In recent time an increasing effort was made to use this technique in diffusion studies, *i.e.*, for measurement of diffusion profiles in glasses and minerals.

The method involves ablation of material induced by short UV laser pulses, transport of the formed aerosol with a helium carrier gas into a mass spectrometer and subsequent analyses of isotopes using a multi collector inductively couple plasma mass spectrometer. The in-house built laser ablation system is based on a 100 femtosecond (fs) Ti-sapphire regenerative amplifier system (Hurricane I, Spectra Physics, USA) operating at a fundamental wavelength of 785 nm in the infrared spectra (IR). Subsequent harmonic generations produce the wavelengths 393 nm in the second, 262 nm in the third and 196 nm in the fourth stage. After the fourth harmonic generation stage, the 196 nm beam is steered by four dichroic mirrors into a 8× objective (OFR, USA) and focussed onto the sample. Spot size can be adjusted by means of a variable and motorized iris mounted at a distance of 2 m from the objective. At this distance, a demagnification ratio of 100 is reached resulting in a maximum achievable spot diameter of 35 µm. Within this spot, an energy density of 1.5 J/cm^2 can be maintained, sufficient to ablate silicates. Compared to traditional ablation systems using nanosecond pulses, the use of femtosecond pulses considerably reduces instrumental fractionation of isotopes during the ablation process. Additionally the spatial resolution is improved since deposition of ablated material on the sample is depressed.

In diffusion studies laser ablation MC-ICP-MS can be used to measure diffusion profiles of elements and isotopes by line scanning. Polished samples were mounted on stage which was moved with constant velocity (1 – 10 µm/s) so that the effectively distance probed by the beam was ~30µm for each measurement point. For isotope analyses a Neptune MC-ICP-MS of ThermoFinnigan was used. The simultaneous measurement of different isotopes allows determining isotope ratios with very high precision (Figs. 1, 2). This makes the technique particularly useful to study self diffusion of elements in homogeneous materials. However, due to the spatial resolution of the system a profile length of several hundred micrometers has to be adjusted in the experiment. Thus very slow diffusion processes (*i.e.*, silicon self diffusion in silicate) cannot be analyzed. Two examples of application of the tech-

nique are presented: (i) Analysis of self diffusion of iron in rhyolitic melts after quenching to glass and (ii) simultaneous measurements of electrical conductivity and lithium self diffusion in $LiAlSi_2O_6$ glass.

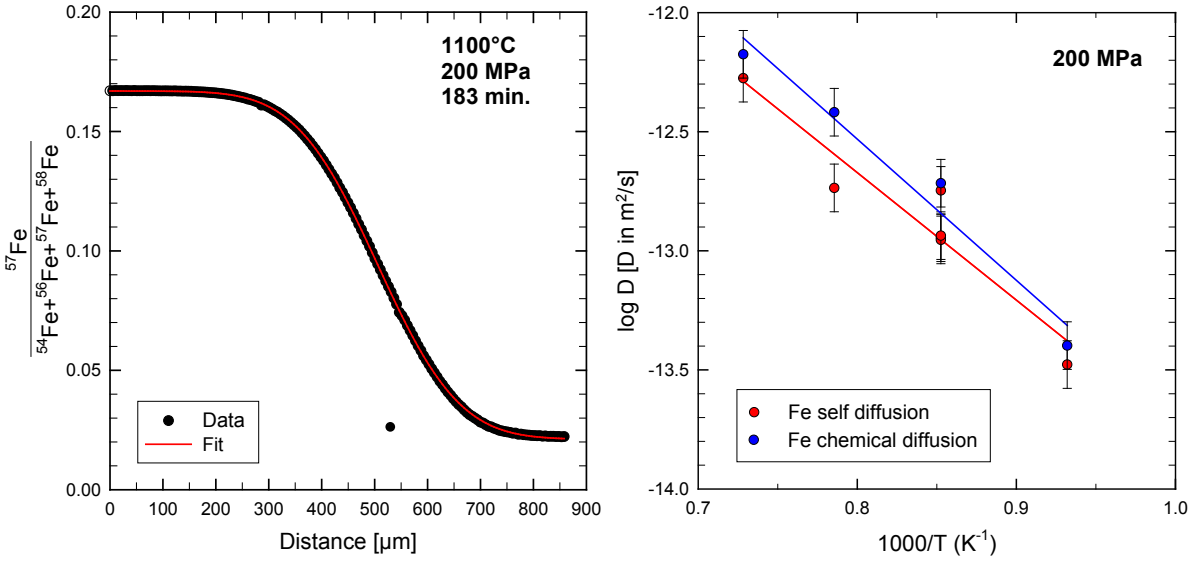

Fig. 1 (left) Profile of the fraction of ^{57}Fe in a rhyolitic glass after a diffusion couple experiment. (right) Comparison of self diffusion and chemical diffusion of iron in a ryholitic melt.

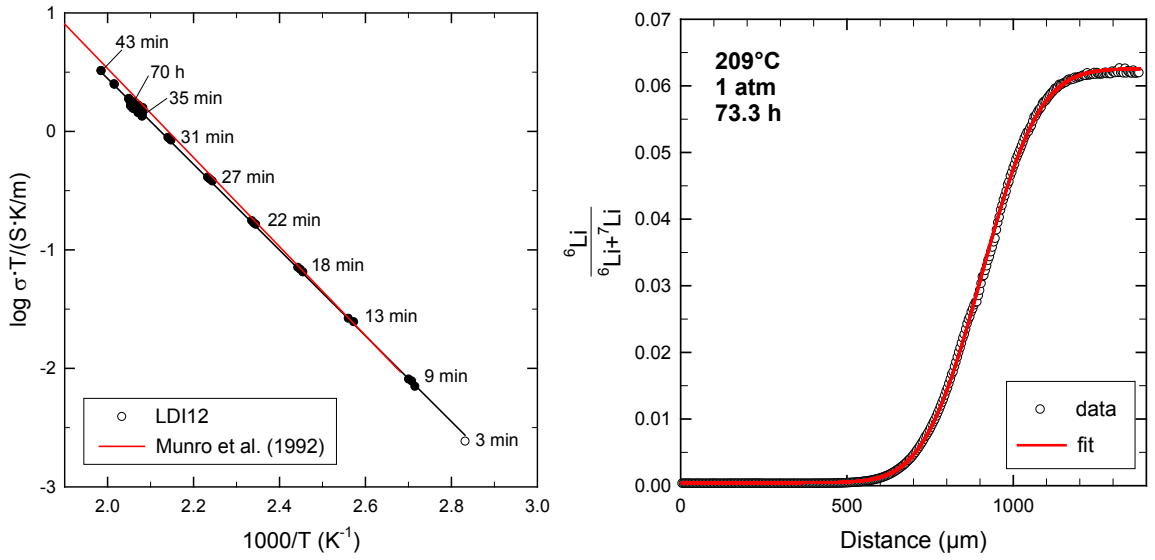

Fig. 2 (left) dc conductivity of $LiAlSi_2O_6$ glass measured during an Li isotope exchange experiment compared to results from impedance measurements by Munro et al. [3]. (right) Diffusion profile of lithium isotopes in the same sample measured after experiment.

Diffusion couple experiments with rhyolitic glasses were performed at 200 MPa and temperatures between 800 and 1100 °C (Fig. 1). In chemical diffusion runs an iron-free and an iron-bearing glass (~3 wt% FeO_{total}) were contacted and profiles were measured by electron microprobe. In iron self diffusion experiments both halves of the couple differ only in iron isotopes (one half enriched in ^{57}Fe) and profiles were measured by LA-MC-ICP-MS. Iron self diffusion was found to be systematically slower than chemical diffusivity by ~30%.

A sandwich assembly was used to measure in a single experiment impedance spectra and isotopic diffusion in $LiAlSi_2O_6$ glass. This allows determining very precisely the Haven ratio

for Li diffusion in the glasses. For the example shown in Fig. 2 we derived a Haven ratio of 0.31 which indicates that ionic conductivity is controlled by cooperative processes.

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