

Temperature quenching effect on cathodoluminescence of quartz

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Cathodoluminescence (CL) has been extensively used in sandstone diagenetic studies because of the different CL properties of authigenic and detrital quartz. The CL characteristics of quartz, however, are still debated by the reason of complicating features of diverse defect centers and impurity centers. Furthermore, CL intensity of quartz considerably varies with sample temperature. In this study we attempt to estimate the effect of temperature quenching on the CL emission of quartz because of no quantitatively evaluation made so far.

The sample used for CL spectral measurement is colorless quartz occurred in basaltic geode from Poona, India. All measurements were made with a CL scanning electron microscopy (CL-SEM), which comprises a SEM (Jeol: JSM-5410) combined with an integral monochromator (Oxford: Mono CL2). The sample stage can be controlled at various temperatures using liquid nitrogen and embedded heater.

CL spectra with doublet peaks of 450 nm and 500 nm were obtained below 203 K, while no obvious CL emission could be detected above 243 K. Blue luminescence at 450 nm to 500 nm may be assigned to E' center caused by oxygen deficient defect in framework lattice.

The CL emission efficiency (A) was obtained from integrated intensities after a Gaussian peak fitting of the CL spectra converted to energy scale (eV). In this case blue CL spectral curves were deconvoluted into two Gaussian peaks with 450 nm (2.75 eV) and 517 nm (2.4 eV). The CL efficiency of both emissions considerably increased as sample temperature is raised, where the efficiency for both emissions at 81 K was approximately 100 times those at 298 K. Such unusual temperature effect on CL emission is peculiar for quartz.

The plot of the value of $\ln(1/A-1)$ against $1/T$ (T: absolute temperature) exhibits a linear relationship to each other between 81 K to 163 K and 183 K to 223 K for both emissions of 2.4 eV and 2.75 eV, respectively. We obtained activation energy of 0.03 eV from 81 K to 163 K and 0.25 eV from 183 K to 223 K for the emission of 2.4 eV. Almost same activation energy was evaluated for the emission of 2.75 eV. It indicates two processes of temperature quenching responsible for different excitation states. At lower temperature the electron was excited from ground state by a gain of relatively low energy of 0.03 eV. As temperature increases, additional energy in excess of 0.25 eV leads the electron in the trap to the radiationless return to the ground state. It results in abrupt extinction of CL emission at higher temperature.

Evaporation experiments of Li from Li₂O-SiO₂ melt and accompanied isotopic mass fractionation

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Introduction

In order to understand evaporation of moderately volatile elements and accompanied isotopic mass fractionation during chondrule formation, many experimental studies have been made. However, most of them have not distinguished kinetic parameter from thermodynamic one. Shirai et al. [1] obtained apparent evaporation coefficient, α^* , of Na as the kinetic parameter for Na₂O-SiO₂ melt, where the activity coefficient, $\gamma(\text{Na}_2\text{O})$, was known. However, isotopic fractionation of Na cannot be examined. In this study, we examined evaporation of Li from Li₂O-SiO₂ melt with known $\gamma(\text{Li}_2\text{O})$ together with accompanied isotopic fractionation.

Experiments

The experiments were made at 1400°C at 1 atm under controlled $p(\text{O}_2)$ (10^{-8} – 10^{-10} bar) and vacuum. The ⁷Li/⁶Li ratios of evaporation residues were measured with SIMS (Cameca ims 5f at Okayama University).

Results and discussion

The evaporation rate of Li was not affected by $p(\text{O}_2)$ (Fig.1) in contrast to Na, where the evaporation rate is proportional to $p(\text{O}_2)^{-1/4}$, because the vapor pressure of O₂ in equilibrium with the Li₂O-SiO₂ melt is larger than $p(\text{O}_2)$. The evaporation rates showed that $\alpha^* \sim 1$ and 0.6 at 1 atm and vacuum, respectively ($\text{LiO}_{0.5}(\text{liq}) = \text{Li}(\text{g}) + 1/4\text{O}_2(\text{g})$; Fig.1) (c.f., $\alpha^* \sim 0.2$ for Na [1]). The large α^* values may suggest that Li evaporates without recondensation and thus, large isotopic fractionation is expected. However, preliminary results showed that isotopic fractionation was smaller than those expected by Rayleigh fractionation even in vacuum.

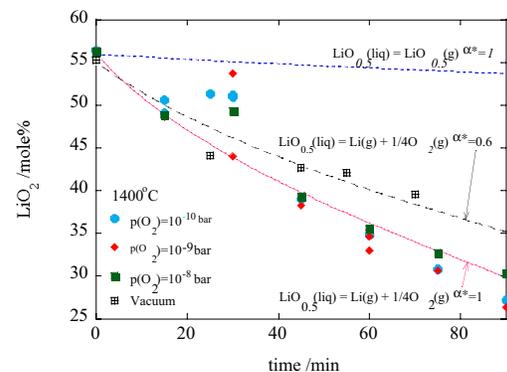


Figure 1. Experimental results and calculated evaporation curves for two evaporation reactions with α^* .

Reference

[1] T. Shirai, S. Tachibana and A. Tsuchiyama (2000) *Lunar Planet. Sci.*, XXXI, CD-ROM#1610.