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***IN SITU* SPECIATION OF NICKEL IN HYDROUS MELTS EXPOSED TO EXTREME CONDITIONS**

M. Muñoz^{1*}, H. Bureau², V. Malavergne¹, B. Ménez³, M. Wilke⁴, C. Schmidt⁵, A. Simionovici^{6,7}, A. Somogyi⁶ and F. Farges^{1,8}

¹ Laboratoire des Géomatériaux, CNRS FRE 2455, Université de Marne-La-Vallée, France

² Laboratoire Pierre-Süe, CEA, Saclay, France

³ Laboratoire de Géosciences Marines, IPG, Paris, France

⁴ Institut fuer Geowissenschaften, Potsdam Universitaet, Germany

⁵ GeoForschungsZentrum Potsdam, Germany

⁶ ESRF, Grenoble, France

⁷ Laboratoire des Sciences de la Terre, ENS, Lyon, France

⁸ Department of Geological and Environmental Sciences, Stanford University, USA

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Abstract

In situ high-temperature and high-pressure XAFS experiments were performed at the Ni *K*-edge, at the ID22 μ -beamline of the ESRF (Grenoble, France). The experimental setup consists of an externally heated “Bassett-modified” hydrothermal diamond-anvil cell. The sample chamber is loaded with a water-saturated haplorhyolitic glass: $(\text{NaAlSi}_3\text{O}_8)_{47}(\text{KAlSi}_3\text{O}_8)_{21}(\text{SiO}_2)_{32}$, together with an aqueous NiCl_2 -solution (0.35 mol/L) and an air bubble. The experiment is carried out to a temperature (*T*) of 780 °C, and the corresponding hydrostatic pressure (*P*) is calculated to be around 520 MPa, based on the equation of state of water. μ -XANES spectra are then collected *in situ* in the silicate melt and in the aqueous phase. Spectroscopic data are first interpreted in terms of speciation. At the experimental *P-T* conditions, nickel is essentially four-coordinated in the hydrous melt, whereas its coordination is 5 in the glass. Moreover, based on the theoretical description of the absorption edge, the XANES spectra are used to derive the “fluid/melt” partitioning coefficient for nickel (0.22 ± 0.05), as well as the density of the hydrated melt ($0.9 \pm 0.5 \text{ g/cm}^3$).

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* e-mail: munoz@oreka.com

1. Introduction

Structural and thermodynamical properties of hydrous silicate melts are of major interest for understanding fundamental geological processes related to explosive volcanic eruptions. Particularly, information concerning trace element speciation, and “fluid/melt” partitioning behavior, is required for understanding the transport properties as well as the geochemical processes controlling the formation of deep Earth magmas. Also, information concerning the density of hydrous silicate melts is required to better understand the dynamic properties related to the ascension of “highly-hydrated” magmas. One way to obtain such information is to perform *in situ* experiments using a hydrothermal diamond-anvil cell. That method is particularly adapted for the study of hydrous silicate melts [1], and can typically reach temperatures to 1000 °C and pressures to 1-2 GPa.

2. Experimental

In situ high-temperature and high-pressure experiments are performed using a “Bassett-modified” hydrothermal diamond-anvil cell (HDAC). The sample chamber is loaded with a water-saturated glass of haplorhyolitic chemical composition: $(\text{NaAlSi}_3\text{O}_8)_{47}(\text{KAlSi}_3\text{O}_8)_{21}(\text{SiO}_2)_{32}$. Then, an aqueous NiCl_2 -solution (0.35 mol/L) is added with an air bubble in the sample chamber (see Fig. 1, left). The H_2O “liquid/vapor” homogenization temperature, measured before and after the heating run, is 295 ± 10 °C. Consequently, at the experimental temperature (i.e., 780 °C), the pressure is calculated to be around 520 MPa, based on the equation of state of water [2]. At the melt state, the silicate phase forms hydrated, and nearly-spherical “globules” in equilibrium with the aqueous phase [1, 3] (see Fig. 1, right).

During the experiment, μ -XANES spectra are collected at the Ni *K*-edge in fluorescence mode (ID22 beamline, ESRF, France); an optical monitoring of the sample being systematically performed before and after data acquisition. We used Si(111) double crystals monochromator, and Kirkpatrick-Baez focusing mirrors, so that the spatial resolution of the incident X-ray beam

was $3 \times 5 \mu\text{m}$. Also, XANES spectra were collected using 0.1 eV steps in the pre-edge region and 0.5 eV steps in the main edge crest region.

3. Results and Discussion

The normalized Ni *K*-edge XANES spectra collected for the hydrated melt and the quenched glass are first interpreted in terms of nickel speciation. *Ab initio* calculations were performed using the FEFF 8.28 package assuming the crystal structure of NiO (6-coordinated Ni) and NiCr₂O₄ (4-coordinated Ni); the XANES spectra being calculated using Hedin-Lundqvist potentials and default values for all options.

Based on experimental [4] and theoretical approaches, the absorption edge XANES spectra as well as the position of the first “EXAFS” oscillation (gray line), traduce essentially the presence of NiO₄ moieties in the hydrous silicate melt (see Fig. 2). This important result shows that quenched glasses are not appropriate images of their corresponding melts. Also, the coordination numbers of nickel in hydrous melts as well as in anhydrous melts [5] are similar, suggesting that water does not highly affect the local structural environment of nickel under *in situ* conditions.

The sample density (ρ) as well as the mass fraction of nickel (x_{Ni}) are then extracted from the μ -XANES spectra (edge jumps uncorrected) using the following equation [6]:

$$\alpha \cdot \Delta\mu = \rho \cdot x_{\text{Ni}} \cdot \Delta(\mu/\rho)_{\text{Ni}} \quad (1)$$

in which $\Delta(\mu/\rho)_{\text{Ni}}$ is the variation of the mass absorption coefficient before and after the edge, $\Delta\mu$ is the experimental edge jump at the Ni *K*-edge (modeled using an arctangent; see Fig. 3), and α is an “attenuation factor” due to the experimental setup. More precisely, this attenuation factor traduces the constant thickness of the sample, but also the non-linearity of the absorption coefficient due to the absorption of the X-ray beam by the diamonds, as well as the fluorescence detection at the rear of the HDAC.

In order to determine x_{Ni} and ρ under *in situ* conditions for the aqueous phase and the silicate phase, respectively, the attenuation factors are previously determined, based on the edge jumps of the different XANES spectra collected under ambient conditions:

- Concerning the aqueous phase, the nickel content and the density are well known before the experiment.
- Concerning the silicate phase, the density of the hydrous quenched glass can be estimated around 2.2 g/cm^3 (see [7]). Also, the nickel content is determined after the experiment, using μ -PIXE (Particule Induced X-ray Emission) mapping (see [3]). Analyses were performed using the nuclear microprobe facility of LPS (CEA, Saclay, France).

Consequently, the “fluid/melt” partitioning coefficient obtained for nickel is 0.22 ± 0.05 . Despite their important compatible character (i.e., crystal vs. melt; e.g., [8]), this result suggests a non-negligible mobilization of nickel by the aqueous fluid during the ascension of magmas, beyond the exsolution levels.

Also, the density of the hydrous haplorhyolitic melt at $780 \text{ }^\circ\text{C}$ and 520 MPa is estimated to be $0.9 \pm 0.5 \text{ g/cm}^3$, suggesting a particularly important proportion of water in the melt structure. This study represents the first attempt to measure a hydrous melt density well above the glass transition temperature, involving a major contribution to a better understanding of the structural and macroscopic properties of highly-hydrated magmas in conditions prior to explosive eruptions.

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FIGURE CAPTIONS

Fig. 1. Haplorhyolitic melt in an aqueous NiCl₂-solution (0.35 mol/L), exposed to high temperature and high pressure.

Fig. 2. Comparison between the Ni *K*-edge theoretical XANES spectra for NiO₄ and NiO₆ clusters, and the experimental spectra collected *in situ* for the hydrated silicate melt and for the quenched glass.

Fig. 3. μ -XANES spectra collected at the Ni *K*-edge for the aqueous NiCl₂-solution (up), and the haplorhyolitic phase (down), exposed to *in situ* (high-temperature/high-pressure) and ambient conditions.

FIGURE 1

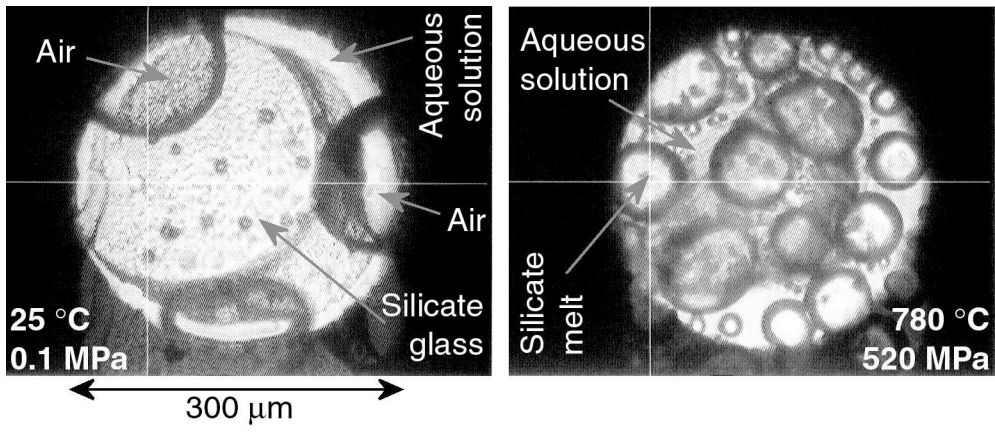


FIGURE 2

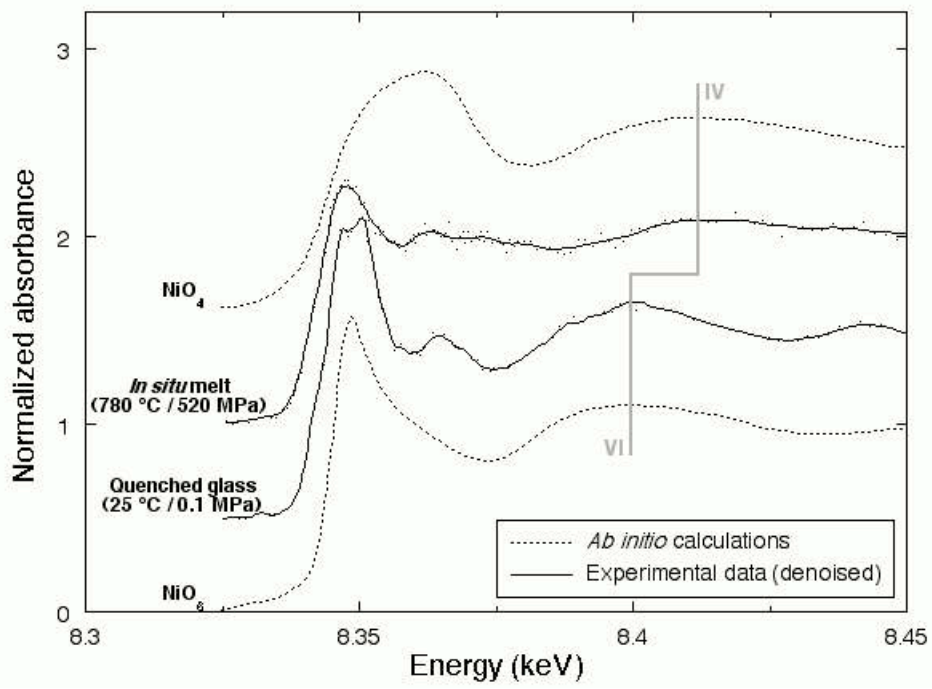


FIGURE 3

