

Spectroscopic study of interactions between nitrogen and silicate melts under high pressure and temperature: insights into the evolution of geochemical reservoirs. M. Roskosz¹ and B. O. Mysen¹, Geophysical Laboratory, 5251 Broad Branch Rd., Washington, D.C., USA, m.roskosz@gl.ciw.edu, b.mysen@gl.ciw.edu.

Introduction: The early history of the Earth was a time of profound differentiation. After the main sequence of accretion, it is generally supposed that a transient magma ocean formed. Therefore, the main features of the planet was acquired during the differentiation of a volatile-bearing magma ocean. A number of chemical, physical and structural studies have been dedicated to volatiles in magmas, especially to noble gases and H₂O solubility.

Somewhat surprisingly, the behavior of nitrogen is poorly characterized in spite of its high concentration in the present atmosphere and in some meteoritic materials. Nitrogen elemental and isotopic budgets are also used to model the evolution of atmospheric and deep geochemical reservoirs [1-2]. It is thus essential for such approach to accurately understand its behavior in melts, metals and minerals as a function of compositions, structures and intensive. In this respect, some studies recently addressed this question in silicate melts under ambient pressure and different oxygen fugacity [3-4]. These mainly confirm previous but scarce results reported in material and metallurgical literature. The solubility of nitrogen follows a Henry's law and dissolves in liquids as an inert species, as do noble gases. Under very reducing conditions however, nitrogen is chemically bonded to the silicate network *via* a partial nitridation of the melt as observed in nitride glasses.

Nevertheless, the effect of pressure and melt composition has not been studied extensively. The effect of pressure on speciation, solubility and degassing processes of nitrogen in silicate melts is important to model the evolution of geochemical reservoirs. Pressure is, therefore, an important variable for understanding processes in the early magma ocean. An indication that pressure is important in this respect is that it has been recently demonstrated that the reactivity of molecular nitrogen is strongly affected by the pressure, such that, unknown nitrides (e.g., PtN) may be synthesized under pressures and recovered after quenching to room pressure and temperature [5]. Furthermore, experimental limitations prevent from studying directly relevant compositions of a hypothetical magma ocean. Thus, a structural and chemical characterization of the interactions between silicates and volatiles has to be developed for relevant compositions as a function of attainable pressure and temperature prior to modeling of such properties in ultramafic melts.

Materials and methods: In this respect, we have studied three sodium-bearing silicate melts with different polymerization states (NS8, NS4 and NS2 where N is Na₂O and S is SiO₂). These compositions were selected because they are structurally well known under ambient and high-pressure conditions and have Raman spectra exceptionally well resolved. They also cover a range in degree of polymerization.

Experiments were performed in a piston cylinder apparatus. The nitrogen source is a silver azide, which down to Ag (that forms an alloy with the capsule and thus do not interact with the melt) and molecular N₂ below 300°C. As a consequence an anhydrous, hydrogen- and carbon-free N₂-atmosphere is formed below the melting point of the samples. Ag azide in aqueous solution is first poured in a Pt-capsule and dehydrated at 105°C for several hours. Then, glass powders are added and the capsule is welded under a flow of pure Ar or dry air. Capsules were loaded in 1/2 and 3/4 inch assembly, which allows rapid quenching and the heating of different samples during the same experimental run. With the temperature varying from 1400 to 1700°C and pressure from 10 to 30 kbars, the run duration is typically of one hour to reach the equilibrium. After the quenching, samples are generally crystal-free and some small, scarce and randomly-distributed bubbles indicate that complete saturation of the melt was obtained during the experiments and a negligible quench effect occurred. Glass chips were used for microprobe and Raman spectroscopy analyses. The nitrogen contents were determined with a JEOL 8800 microprobe operating at 10nA and 15 kV. The beam was defocused to analyze a 100 μm² area to avoid sodium and nitrogen volatilization. Raman spectra of glass chips were recorded at room temperature with a Dilor XY microRaman spectrometer and with the 514.5 nm line of a SpectraPhysics Ar⁺ laser.

Results: The solubility of nitrogen is a strong function of melt composition, pressure and possibly temperature. At given P-T conditions, the solubility of nitrogen is higher in polymerized melts, which is qualitatively consistent with an empirical ionic porosity model. Increasing the pressure results in a dramatic increase of the nitrogen solubility (Fig.1). This increase is significantly higher in the most polymerized liquids than in others. Finally, a slight temperature-dependence is observed and an

activation energy may be derived as a function of pressure and melt composition. However, more accurate analyses are required to confirm this temperature-dependence.

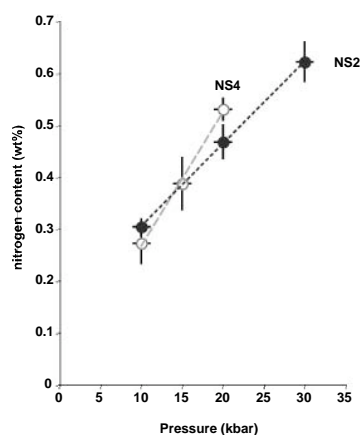


Fig.1: Pressure dependence of nitrogen solubility for NS2 and NS4 glasses synthesized at 1600°C under N₂-atmosphere.

Raman spectroscopy of the quenched glass indicates that nitrogen is not only dissolved as N₂ (Fig.2). Indeed, glasses synthesized in air at ambient and high-pressure only show the typical Raman bands of silicates (200-1200 cm⁻¹) and of the atmospheric, molecular nitrogen (~2330 cm⁻¹). Glasses prepared under pressure and N₂-atmosphere show very different spectra. Additional bands are observed at ~2100 cm⁻¹ and ~2200 cm⁻¹ while the signal at ~2330 cm⁻¹ is clearly composed of at least two different vibrational contributions. The relative intensities of these bands are function of pressure and melt composition. No signature of dissolved water was detected and the additional bands cannot be assigned to NO_x and NH_y compounds, which do not have significant modes in these frequency region. In addition, the broad, Gaussian shape of the additional bands are typical of disordered structures and thus likely represent a bond between the silicate network and nitrogen. Nevertheless, no clear assignment can be proposed yet on the base of Raman spectroscopy.

Conclusion: Though preliminary, our spectroscopic results clearly indicate that part of nitrogen is chemically bonded to the melt at moderate pressures. This behavior is probably more pronounced at higher pressures. As a consequence, nitrogen cannot be considered as a molecular volatile like a noble gas in magmatic processes in the Earth's mantle. The nitridation of silicate melts has been observed at very low oxygen fugacity (well below the iron-wüstite buffer). Nevertheless, it is not regarded

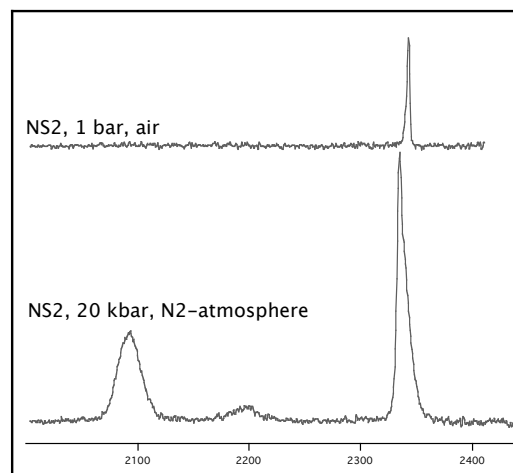
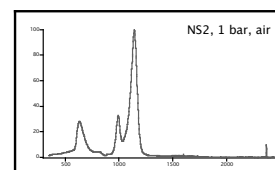


Fig.2: Raman spectra of NS2 glasses at ambient condition and under pressure and N₂-atmosphere

as a common reaction among other planetary processes because such redox conditions are extreme. However, our results indicate that even in a shallow magma ocean or during the partial melting of the mantle, some chemical interactions exist between silicate and nitrogen even under relatively oxidizing conditions. The implications may be dramatic in terms of nitrogen budget of the upper and lower mantle. Moreover, it is also possible that a N/Ar fractionation occurred during degassing, if N is chemically stabilized in the melt while Ar is inert at least up to several GPa. Finally, if chemical interactions and a complex speciation of nitrogen are confirmed, then isotopic fractionations may be expected through partial degassing driven by adiabatic decompression. This fractionation has been studied experimentally in the case of the D/H of water-bearing silicate liquids [6]. Such experiments are beyond the focus of this study.

References: [1] Tolstikhin I. N. and Marty B. (1998) *Chem. Geol.*, 147, 27-52. [2] Javoy M. (1997) *GRL.*, 247, 177-180. [3] Libourel G. et al. (2003) *GCA* 67, 4123-4135. [4] Miyazaki A. et al. (2004) *GCA* 68, 387-401. [5] Gregoryanz E. et al. (2004) *Nature Materials*, 3, 294-297. [6] Pineau et al. (1998) *Chem. Geol.*, 147, 173-184.