

NITROGEN SOLUBILITY IN BASALTIC MELT. EFFECTS OF OXYGEN FUGACITY, MELT COMPOSITION AND GAS SPECIATION. G. Libourel^{1,2}, B. Marty^{1,2}, F. Humbert³ and E. Gayer¹. ¹ CRPG, CNRS-EPR2300, BP20, 54501 Vandoeuvre-les-Nancy, France. ² ENSG-INPL, BP40, 54501 Vandoeuvre-les-Nancy, France. ³ CFC-DAUM, 54112 Vannes le Chatel, France libou@crpg.cnrs-nancy.fr

Introduction: Nitrogen is a major forming element of the Earth's atmosphere and one of the key elements of the biological evolution. Knowledge of its (elemental or isotopic) behavior is therefore of prime importance to understand and quantify processes which might have controlled the exchange of nitrogen between the mantle and the atmosphere through time. However in contrast to rare gases, mechanisms governing the incorporation of nitrogen in basaltic melts are not well documented.

Experimental: In order to provide much needed constraints, we have developed a combined experimental and analytical approach to measure nitrogen solubility in silicate melts. Equilibration were performed at one atmosphere and at 1425°C over a large range of oxygen fugacity controlled by mixtures of gases belonging to either [C-N-O] or [C-N-O-H] vapor systems. Nitrogen contents in equilibrated samples were measured using a technique based on CO₂ laser extraction in high vacuum line and static vacuum mass spectrometry and N speciation by FTIR measurements on selected N-bearing glass samples.

Oxygen fugacity: Over a redox range of 18 oxygen fugacity log units, the incorporation of nitrogen in silicate melts equilibrated with the [C-N-O] vapor systems follows two different behaviors. For log fO₂ values between -0.7 and -10.7 (the latter corresponding to IW-1.3), nitrogen dissolves as a N₂ molecule into cavities of the silicate network (physical solubility). Nitrogen presents a constant solubility (Henry's) coefficient of $2.21 \pm 0.53 \times 10^{-9} \text{ mol.g}^{-1} \text{ atm}^{-1}$ at 1425 °C, identical within uncertainties to the solubility of argon. Further decrease in the oxygen fugacity (log fO₂ between -10.7 and -18 corresponding to the range from IW-1.3 to IW-8.3) results in a drastic increase of the solubility of nitrogen by up to 5 orders of magnitude as nitrogen becomes chemically bounded with atoms of the silicate melt network (chemical solubility). The present results strongly suggest that under reducing conditions nitrogen dissolves in silicate melts as N³⁻ species rather than as CN⁻ cyanide radicals.

Melt composition: We also show that the effect of melt composition on nitrogen solubility depends on oxygen fugacity. Between air and IW-1, we found that nitrogen solubility is low and increases with the bulk polymerization of the melt, as rare gases do, in agree-

ment with a dissolution mechanism controlled by the steric effect of the N₂ molecule, filling holes of interstitial location of the silicate melt network. This contrast with results obtained in more reducing conditions (<IW-1), in which high N solubility is anticorrelated with the bulk polymerization of the melt due to the substitution of non-bridging oxygen for nitrogen in the melt silicate network, very likely by forming Si(O₃N)⁵⁻ structural groups where nitrogen is three-fold coordinated to silicon.

Gas speciation: If equilibration under H₂-bearing gaseous environments don't alter the physical solubility of nitrogen between air and IW-1, we found that N solubility drops by ~33% by comparison with equilibration in H₂-free vapors, due to the more complex speciation of nitrogen in these conditions, i.e., (NH₂⁻), (NH⁻) and (N³⁻) species.

All these results have important implications for the mechanisms of nitrogen dissolution in basaltic melts in both terrestrial and extra-terrestrial environments and complement our knowledge on nitrogen outgassing.

References: [1] Mulfing H. O. (1966) *J. Am. Ceram. Soc.* 49, 462-467. [2] Libourel G., Marty B., Humbert F. (2003) *GCA*, 67, 4123-4135.