NITROGEN SOLUBILITY IN MOLTEN METAL AND SILICATE AT HIGH PRESSURE AND TEMPERATURE: A FIRST EXPERIMENTAL APPROACH.

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Introduction: Nitrogen is the dominant gas in the Earth's atmosphere. Its concentration and its isotopic composition are commonly used to constrain nitrogen rise in the atmosphere and the degassing of our planet's interior [1]. Nitrogen is also of interest because its concentration in the system Silicate Earth + atmosphere does not follow the qualitative trend between volatility and atomic mass. It appears to be anomalously depleted compared to carbon and water for instance. Nevertheless, the nitrogen distribution within planetary reservoirs is poorly known. Nitrides might be stable at mantle conditions and stored as osbornite or ammonia-bearing silicates. The formation and the stability of iron nitrides at high pressure and temperature also make the core a reasonable candidate reservoir [2].

Experimental data collected at ambient pressure indicates that nitrogen solubility in metals is 3 to 4 orders of magnitude larger than in silicates [e.g. 3-5]. Consequently, planetary cores could contain a large amount of nitrogen. However, such extrapolation neglects possible pressure effects on nitrogen solubility and redistribution of nitrogen during metal-silicate segregation in a magma ocean during the core formation. The quantification of the entrapment of nitrogen in mantle and core phases and its subsequent degassing depends, therefore, on knowledge of the partitioning behavior of nitrogen between molten silicates and metals over a large range of pressures and temperatures. Such data are currently lacking with solubility data for nitrogen only available for iron-free silicate melts up to 3 GPa [6-8]. Here we performed experiments up to 18 GPa on a mixture of Fe-bearing silicates and Fe-Ni metal alloys in order to study the nitrogen solubility in both phases at the same oxygen fugacity, temperature and pressure.

Experiments: The laser-heated diamond anvil cell (LHDAC) technique was chosen instead of a multi-anvil apparatus to alleviate several experimental difficulties (including the need for sealed capsules sequestering the fluid phase at very high temperature without interactions with the molten silicate and iron alloy). The starting material was a silicate glass of simplified CI composition mixed with iron and nickel metal powders. A gas-loading device was used to trap nitrogen between the anvils. Pressure was determined by fluorescence emission of a ruby grain at the edge of the gasket hole at room temperature before and after heating of each run. The samples were heated with a 100 W air-cooled fiber laser for an average of 10-15 minutes for each heated area. To decrease the temperature gradient across the samples, a relatively broad, defocused beam was used (hot spot size around 20 µm, with central temperature gradients of less than 20 K/µm). The temperatures were determined spectro-radiometrically with a fit to a grey-body Planck function. The temperatures were about 2500-3000 K. Compositions were determined with an electron microprobe (CAMECA SX100 at the University of Lille1, France). Boron (BN) and stoichiometric iron nitrides (Fe_2N and Fe_4N) were used as standard for nitrogen. In addition, glass standards from [3], containing 6100 to less than 200 ppm nitrogen were analyzed using the same analytical protocol to confirm that the quantification limit of the microprobe is lower than 1500 ppm for nitrogen.

Results: Nitrogen concentration in the metal fraction is positively correlated with confining pressure (Fig.1) and negatively correlated with the nickel content of the metal alloy. Therefore, the higher the nickel content, the lower the N content as reported in the metallurgical literature at low pressure [5]

The nitrogen content of the silicate reservoir (mainly glass with some olivine quench crystals) quenched from high pressure and high temperature is systematically lower than in the metallic phase (Fig.1). The N content increases with pressure up to about 3-4 GPa. At higher pressures, it remains constant in the range 4-8 GPa, before a moderate solubility drop at around 8 GPa. In the low pressure domain (up to 3 GPa), our data are comparable to those reported for pure sodium silicate melts synthesized in piston-cylinder apparatus, at comparable oxygen/hydrogen fugacities (close to the iron-wüstite buffer) and analyzed both by electron microprobe and mass spectrometry [6-8]. Our new high-pressure data, together with previous ones, show that some dependence on temperature, compositional and structural properties of the melts exists. However, the most important factors determining nitrogen solubility in silicate melts are pressure and redox conditions.
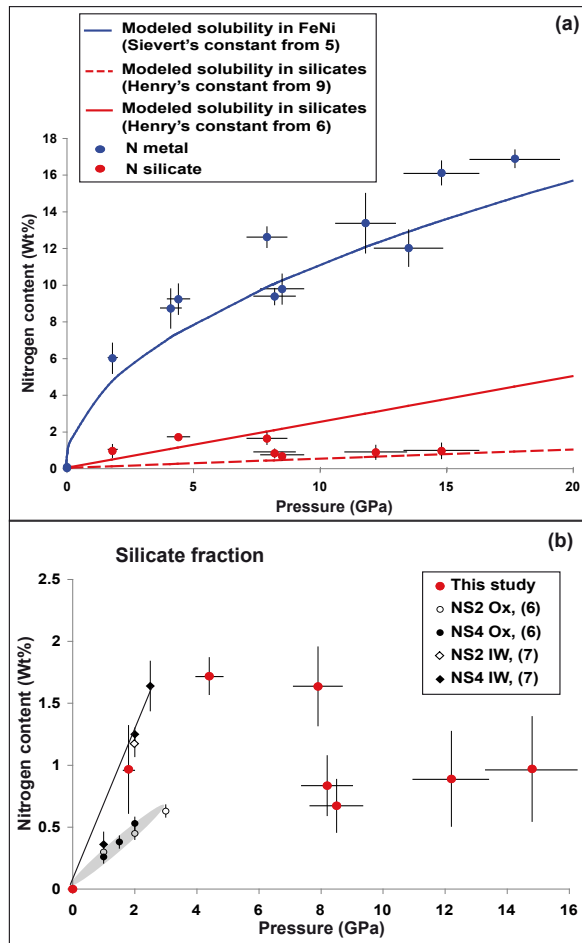
Figure 1: Nitrogen solubility in molten metal and silicate as a function of pressure. (a) General trends defined by metal and silicates. The blue line represents the parameterless Sievert's law, using a constant value derived experimentally at one bar in [4]. The two red lines are Henry's law crude approximation of nitrogen solubility in molten silicates using two different Henry's constants proposed in [4 and 8]. (b) Detailed view of nitrogen contents in silicate melts and comparison with piston-cylinder data collected on simple binary silicate systems in both oxidizing and reducing conditions (close to the hydrogen fugacity of the IW buffer).

Discussion: The Earth and most chondritic meteorite groups have comparable $^{15}N/^{14}N$ and D/H ratios, very different from both solar and cometary values [10]. Hence, it seems likely that the major terrestrial volatiles including water, carbon and nitrogen were supplied from a cosmochemical reservoir akin of chondrites. In this framework, a comparison of the carbon, nitrogen and water contents of the bulk Earth (silicate Earth + atmosphere + hydrosphere) normalized to chondrites should lead to a flat pattern unless some mantle phases still retain some volatiles (and not others) in the mantle and does not release them during partial melting or geodynamical mixing. Such a flat pattern has indeed been found for water and carbon [11]. Conversely, nitrogen content (estimated from the same ^{40}Ar normalization proposed in [12]) appears to break this pattern and is depleted by about an order of magnitude compared to H_2O and C.

Our experimental results provide an interpretation of this depletion as it provides an estimate of the nitrogen dissolved in the core. Based on available experimental data at ambient pressure [3, 5], the partition coefficient of nitrogen between metal and a silicate reservoir (D_{N2}) is ~ 15000-7500 at IW and ~3000-1500 in conditions as reducing as IW-2. As soon as pressure increases to the GPa range, the picture changes dramatically. At 4 GPa, the partitioning coefficient is only ~5 and even after the possible solubility drop, does not exceed 15 at 15 GPa. Our results are consistent with a D_{N2}-value of about 3 recently determined in a piston-cylinder apparatus in comparable redox conditions at 1.5 GPa [13].

This changing behavior has important implications for the nitrogen budget of the Earth because the N depletion reported above is consistent with the storage of the missing nitrogen in the core, with a metal/silicate partition coefficient compatible with the range 5 to 15. It is therefore reasonable to propose that the nitrogen depletion relative to other volatiles is accomplished by a moderately efficient segregation into the core-forming material. Even if the general picture is certainly more complicated, our data provide a first order explanation to the general nitrogen depletion relative to chondritic concentrations.

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