

# Nitrogen solubility in silicate melts as a function of oxygen fugacity and melt composition

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Nitrogen is the most abundant element of the atmosphere. Nevertheless, the cycle of this element between mantle and atmosphere is poorly understood. First, nitrogen might have been incorporated into the Earth during a primitive magma ocean stage. Presently, nitrogen is outgassed from the solid earth through partial melting and degassing of mantle derived magmas. So, nitrogen solubility in silicate melt and gas phase is a critical parameter. Moreover, at the present time, oxygen fugacity during magma generation is oxidizing, but the possible occurrence of a hydrogen-rich atmosphere during the accretion of the Earth might have imposed much more reducing conditions. Therefore, it is important to determine the nitrogen solubility in silicate melt over a large range of oxygen fugacity. We have developed new experimental and analytical methods based on: (i) high temperature equilibrium of silicate melt under controlled nitrogen and oxygen fugacities, and (ii) laser extraction in high vacuum line, purification of extracted volatiles and static vacuum mass spectrometric measurement of nitrogen. In this paper, we detailed the influence of oxygen fugacity and melt compositions on this nitrogen solubility.

## Methods

Nitrogen solubility experiments were performed on about 300 mg of degassed synthetic glasses of several compositions iron-free. Experiments were carried out in a vertical furnace, at a temperature of 1425°C at 1 atmosphere total pressure under controlled atmosphere. A large range of oxygen fugacity was studied from air to close to silicon/silicon dioxide buffer, covering 17 log units. The oxygen partial pressure was imposed using the following gas mixtures: N<sub>2</sub>-CO/CO<sub>2</sub>, N<sub>2</sub>-CO<sub>2</sub>/H<sub>2</sub> and N<sub>2</sub>-CO, N<sub>2</sub>-CO/H<sub>2</sub>. Depending on imposed oxygen fugacity, platinum in oxidized and graphite in reduced conditions were used to hold the samples. In order to determine the time necessary to attain equilibrium, experiments

were run from hours to several days. Each experiment was terminated by quenching the sample in the imposed atmosphere to preserve equilibrium conditions obtained.

Measurement of nitrogen is difficult for several reasons. First, nitrogen is a major component of the atmosphere and involves some pollution problems. Secondly, carbon species, in particular carbon monoxide which has the same molecular weight as molecular nitrogen, interfere during spectrometry analyses. Thirdly, nitrogen content in many silicates is on the order of about ten ppm, this dynamic spectrometry measurement required too much sample. For these reasons, we have designed a new technique for the extraction and purification of sub-nanomole quantities and stable isotopic analysis of nitrogen on silicates. These analyses are performed with a static vacuum mass spectrometer (VG 5400) because of its very low detection limit.

A few mg of samples, without bubbles, are loaded in the stainless-steel sample chamber under high vacuum and are degassed at 150°C for 12 hours. After cooling, samples are melted with a CO<sub>2</sub> laser for several minutes. Infrared laser radiation is admitted through a ZnSe window. A view window allows to position the laser and check the fusion of the sample on a monitor. Secondly, the extracted gas are purified to remove carbon species which interfere with nitrogen measurement (1). For this purpose, a copper oxide furnace is heated from 450°C to 720°C to release O<sub>2</sub> and to oxidize carbonaceous gases into CO<sub>2</sub>. A cryogenic trap is decreased from room temperature to -183°C to condense CO<sub>2</sub> and copper oxide is reduced to 450°C to resorb excess O<sub>2</sub>. The platinum furnace allows to catalyse oxidation of carbonaceous gases and also reduce NO<sub>x</sub> species into N<sub>2</sub>. Thirdly, an aliquot of purified gas is introduced into the static mass spectrometer for quantitative and isotopic analysis.

This technique allows to obtain a nitrogen blank around  $2 \times 10^{-12}$  mole N<sub>2</sub> and then to analyse

samples containing as little as  $2 \times 10^{-11}$  mole  $N_2$  with a precision of isotopic ratio of 1 to 2‰.

## Results

Concerning the times necessary to obtain equilibrium between gas phase and silicate melt, experiments show that chemical equilibrium is attained close to 48 hours. The isotopic equilibrium required much longer and is attained around of 72 hours.

Analysis of experimental charges shows that nitrogen solubility is a function of oxygen fugacity. In oxidizing conditions, between air and iron/wüstite buffer, nitrogen solubility is low and stable around  $1.3 \pm 0.8 \times 10^{-9}$  mole  $g^{-1}$   $atm^{-1}$   $N_2$ . But in reducing conditions, below iron/wüstite buffer up to C/CO minus 3 log units, nitrogen solubility increases dramatically with decreasing oxygen fugacity. The nitrogen solubility increases from the value under oxidizing conditions to  $2.3 \pm 0.1 \times 10^{-4}$  mole  $g^{-1}$   $atm^{-1}$  N, a variation of over 9 log units. These data are in agreement with few data available in the literature (2, 3, 4, 5).

In order to investigate the influence of nitrogen speciation in the gas phase on solubility, we performed experiments with  $H_2$  and without  $H_2$ . Although, thermodynamic calculations show that the partial pressures of N-bearing species are very different, we do not observe any significant difference in our solubility measurements. So, we conclude that N-bearing species do not significantly control the nitrogen solubility in silicate melts.

Moreover, we carried out experiments on several compositions varying from silica-saturated to under-saturated melts under oxidizing and reducing conditions. The results show that nitrogen solubility varies significantly with the melt composition in reduced conditions, i.e. N solubility increasing with decreasing melt polymerization. However in oxidizing conditions and at present time, such

compositional dependence can not be unambiguously established due to the very low solubility of nitrogen.

## Conclusions

Under oxidizing conditions, the low and stable solubility suggests that nitrogen dissolves as molecular  $N_2$ . In this case  $N_2$  occupies 'holes' in the silicate network which corresponds to a physical solubility. This interpretation is consistent with results of rare gas solubilities which are a function of atomic diameter (4, 6). Under reducing conditions, nitrogen is calculated with nitrogen content divided by square root of nitrogen partial pressure. Solubility increases with decreasing oxygen fugacity. This suggests that nitrogen is dissolved as atomic N. In this case N might replace non bridging oxygen in silicate melt which corresponds to a chemical solubility. Therefore, nitrogen content in silicate melts is a function of nitrogen fugacity, oxygen fugacity and melt composition. The major consequence of this study is that nitrogen could have been incorporated in the early Earth assuming the hypothesis for a magmatic ocean under  $H_2$ -rich atmosphere.

## References

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