

NITROGEN SOLUBILITY IN AUBRITE AND E CHONDRITE MELTS. Robert A. Fogel, Dept. of Mineral Sciences., American Museum of Natural History, New York, NY

Introduction: Enstatite chondrites and aubrites are nitrogen-rich meteorite groups that contain the N-bearing phases TiN (osbornite; aubrites) and Si₂N₂O (sinoite; E chondrites). An important feature that distinguishes the enstatite meteorites from the other meteorite groups is that *they are extremely reduced* (1,2). The reducing character of the enstatite meteorites is intimately linked to the stabilization of nitrides and N-bearing silicates.

Aubrites are basaltic achondrites derived from the melting of E chondrite-like reducing source material (3). E chondrites contain chondrule melts that formed in reducing parts of the solar nebula. Although the role of volatiles in silicate melts under oxidizing has been studied extensively, their role under reducing conditions is poorly understood. Melting and phase equilibria data from the material sciences suggest that the properties of silicate melts under reducing conditions are different from those under more oxidizing conditions (>IW). Under oxidizing conditions N acts as a trace element dissolving in ppm quantities; however, under reducing conditions, N can dissolve in minor element to major element amounts (>1 wt%)(4). I have been studying the solubility of N in geologically relevant silicate melts under reducing conditions in order to understand the importance of N in reducing igneous activity.

Experimental: A basaltic composition (NMIX-3) approximating an FeO-, K₂O-, Na₂O-, TiO₂-free 1921 Kilauea basalt was formulated from component oxides. NMIX-3, thus, approximates a 1921 Kilauea basalt composition if it were melted under reducing conditions diagnostic of the enstatite meteorites (IW -4-6), since the FeO would be removed and partitioned into a separate Fe-Si phase. This assumption was verified by reducing experiments (similar to those described here) on the 1921 Kilauea basalt itself. Melts were equilibrated in graphite capsules under flow mixtures of pure CO gas and a 98%N₂-2%H₂ gas mixture. Flow rates were monitored by flow meters and rigorously determined by timing experiments of the movement of bubbles through a 50 ml graduated burette under the respective gas flows. All experiments were conducted at similar N₂/CO fugacity ratios (≈ 22) at T's between 1500°C and 1600°C. Glass compositions were determined by electron microprobe with nitrogen and oxygen contents determined using a W-Si multilayer crystal.

Results and Discussion: Run products were clear light pink glasses. SEM examination showed that submicron spheres of an Fe-Si alloy were present and often concentrated near the graphite-silicate melt contact. Since the starting NMIX-3 contained FeO contents below probe detectability, spheres represent the reduction of trace quantities of FeO in NMIX-3 enhanced by the reduction of Si from the silicate melt. EDS analyses of the largest of these spheres (2 μm) show them to contain minor elements: Ti, Cr, Mn and Ni, which are strongly partitioning into the Fe-Si melt which scavenges the silicate melt for these trace elements under reducing conditions.

Glass major element contents show the loss of SiO₂ and the gain of MgO and CaO and are functions of T, time and amount of starting material. Relative to SiO₂, however, MgO and CaO display clear linear trends (e.g., Fig. 1: MgO vs SiO₂). On a molar basis, the gain in MgO as a function of SiO₂ loss is ≈ 3× that of the gain in CaO as a function of SiO₂ loss. Molar SiO₂ contents fell from 59.35% in NMIX-3 to 49.19% due to the high fugacity of SiO; MgO rose from 17.63% (NMIX-3) to 24.65%; CaO rose from 13.85% (NMIX-3) to 16.50%. Al₂O₃ contents did not vary appreciably from the starting composition (9.17%). Additionally, in two of the experiments that lost the most weight, TiO₂ contents rose from trace amounts in the starting material to 0.16 and 0.23 mole %. These trends are important indicators of relative cation volatility determined *experimentally*. In this silicate melt composition and under the experimental conditions investigated, volatility was thus: Si>Al>Ca>Mg>Ti. Interesting differences in this volatility scheme exist from those under more oxidizing conditions where,

Nitrogen Solubility in Aubrite and E Chondrite Melts, Robert A. Fogel

for example, Al is highly refractory instead of volatile. This reversal is consistent with the condensation calculations of (5) who show this difference as a function of nebular C/O ratio.

Nitrogen-solubility as a function of temperature is shown in Fig. 2 where it appears to be linearly correlated with $1/T$; lower T favoring increasing N content. N contents are as high as a 0.5 wt % or 2 mole % at 1500°C , showing that it plays a role far more important than a trace element at these T 's. The large *relative error* in two of the 1600°C runs is probably due to the lack of attainment of equilibrium (run times for these two were 1 hr.) as well as analytical uncertainties due to their low N-contents.

N is thought to speciate in very basic melts as a substitution for O (6). N incorporation by this method causes bridging O bonded to 2 Si to be replaced by N bonded to 3 Si (side panel).

Si-O-Si

"

Si

Si-N-Si

This has a stabilizing effect on the melt and is correlated to increased glass transition T , liquidus depression and many other thermophysical properties (4). Previous experiments on very basic melts (25-38 wt% SiO_2) showed a positive T dependence of N solubility, contrary to that determined here. One explanation is the dependence of N solubility on SiO_2 activity which was previously shown to be positive(6). Since the melts here have SiO_2 contents

in the 50-59 wt% range, it is possible that the nature of N speciation is different in the current melts. Alternatively, since the SiO_2 activity of the melts was variable in the run products due to high SiO fugacities, it is not yet possible to separate out this factor for the current experiments.

These experiments show that the role of N in the petrogenesis of silicate melts of cosmological importance under reducing condition is of a proportion much greater than that of trace element. When viewed on a molar basis N plays the role of a major element dissolving over 2 mole %. The incorporation of N in silicate melts to such high concentrations will effect phase stability, liquidus depression and other parameters pertinent to igneous and plutonic activity under reducing conditions. Experiments are underway to elucidate these effects. The current experiments can also explain existing problems such as the stability of osbornite in aubrite meteorites. Retention of N in silicate melts generated by the melting of E chondrite-like precursor material containing sinoite, may help explain the appearance of osbornite on the aubrite liquidus. An understanding of E chondrite and aubrite melting events awaits a better understanding of silicate melt phase equilibria under reducing igneous conditions.

References & Acknowledgments: [1] Keil (1968) JGR 73, 6945-6976; [2] Watters & Prinz (1979) PLPSC X, 1073-1093; [3] Keil (1989) Meteoritics 24, 195-208; [4] Hampshire et al. (1985) Phys. Chem. Glas. 26, 182-186; [5] Larimer & Bartholomay (1979) GCA 43, 1455-1466; [6] Davies & Meherali (1971) Met. Trans 2, 2729-2733. Support of NASA: Origins grant # NAGW-2873 is gratefully acknowledged.

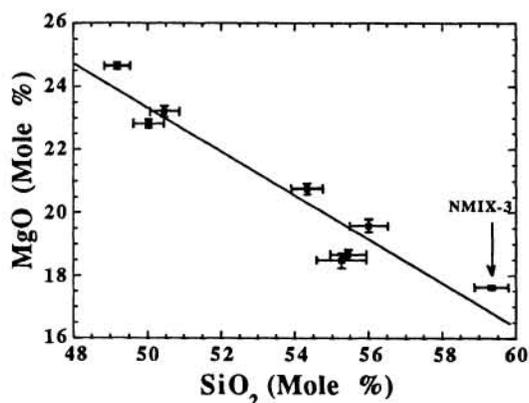


Fig. 1. MgO gain as a function of SiO_2 loss. Errors are 1σ and represent homogeneity of sample.

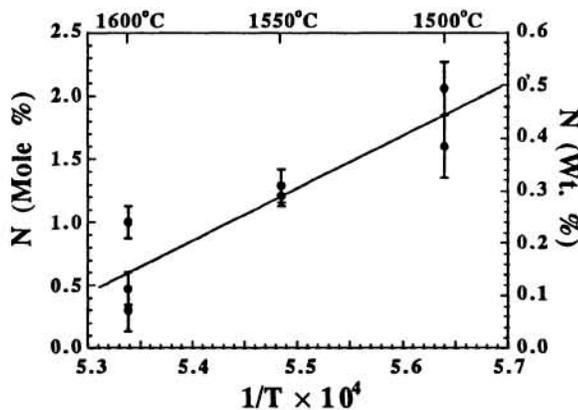


Fig. 2. Silicate melt nitrogen content as a function of $1/T$. Errors are 1σ and represent homogeneity of sample.