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Raman spectroscopic study of the solubility behavior of H_2 in the system Na_2O-Al_2O_3-SiO_2-H_2

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ABSTRACT

The solubility of hydrogen in liquids quenched at high pressure in the system Na_2O-Al_2O_3-SiO_2-H_2 was studied by Raman spectroscopy. Hydrogen fugacities (f_{H_2}) were controlled with double-capsule techniques with the f_{H_2} buffered by the iron-wüstite (IW) assemblage.

In Raman spectra of H_2-bearing glasses along the joins Na_2O-SiO_2 and $NaAlO_2$-SiO_2, bands assigned to the stretching vibrations of molecular H_2 (at ~4125 cm^{-1}) and of OH groups (at ~3580 cm^{-1}) are present. The low-frequency region of the Raman spectra of the Na_2O-SiO_2 glasses changes only subtly upon dissolution of H_2. The low-frequency region of the spectra of $NaAlO_2$-SiO_2-H_2 glasses, however, is identical to spectra of H_2O-bearing glasses of the same composition that were studied by Mysen and Virgo (1986). There were no bands at ~2250 cm^{-1} attributable to the presence of vibrations from Si–H species, nor at ~1300 cm^{-1} from Na–H vibrations, although the expected intensity of this band would be very low because of the ionic nature of the Na–H bond. A band at ~1635 cm^{-1} attributed to bending vibrations of molecular H_2O is detectable in the aluminosilicate glasses quenched from ≥1400°C.

At the f_{H_2} of the IW buffer, Si from the silicate interacts with the Pt container and H_2 to form a Pt-Si alloy and H_2O. The H_2O thereby formed dissolves in the silicate liquid as molecular H_2O and as OH, causing the bands observed at ~1635 cm^{-1} and at ~3580 cm^{-1}, respectively, in the Raman spectra of the glasses. The formation of Pt-Si alloys at temperatures as low as 1100°C at the f_{H_2} of the IW buffer, as found in this study, indicates that H_2O-free conditions cannot be attained within Pt capsules under such reducing conditions. Consequently, the effects of volatiles such as H_2 or CH_4-H_2 mixtures on phase equilibria determined at reducing conditions must be re-evaluated in light of possible formation of H_2O at the experimental conditions.

INTRODUCTION

The study of the interactions of volatiles with silicate liquids has been an active area of research for many years (e.g., Goranson, 1931; Tuttle and Bowen, 1958; Wasserburg, 1957; Yoder and Tilley, 1962; Luth et al., 1964; Eggler, 1975; Mysen and Boettcher, 1975; Mysen, 1976; Burnham, 1979; Mysen et al., 1980; Stolper, 1982; among many others). This research has concentrated primarily on the effects of H_2O and CO_2 on phase relations in silicate systems and, more recently, on the solution mechanisms of these two volatiles in silicate liquids.

Another volatile, H_2, has been investigated recently for several reasons (Luth and Boettcher, 1986). First, because H_2 is ubiquitous in some high-pressure experimental apparatus, the effects of H_2 on phase equilibria and on the solubility of other volatiles, such as H_2O and CO_2, must be studied to evaluate the significance of the presence of H_2 and the applicability of experimental studies to natural systems. Second, the study of H_2 provides insight into the general problem of the interactions of volatiles with silicate liquids because it has different effects on phase relations (Luth and Boettcher, 1986) and, potentially, different solubility mechanisms in silicate liquids than do H_2O and CO_2. Third, Arculus et al. (1984) and Haggerty (1986), among others, have suggested that some regions of the mantle of the Earth are relatively reduced, corresponding to oxygen fugacities close to the synthetic iron-wüstite (IW) buffer in f_{O_2}-T space. An O-H vapor in equilibrium with the IW buffer would contain a significant proportion of hydrogen (Fig. 1), varying from ~2% at 25 kbar and 700°C to ~34% at 7.5 kbar and 1600°C.

To investigate further the role of H_2 in silicate liquids, the solubility mechanism of H_2 in liquids in the system Na_2O-Al_2O_3-SiO_2-H_2 has been investigated with Raman spectroscopy. If hydrogen dissolves both as molecular H_2 and by reacting with cation–oxygen bonds in the liquid to form hydroxide and hydride species, Raman spectra of H_2-bearing glasses should contain bands from vibrations involving the resulting hydrogen-containing species. In addition, the low-frequency region (200–1400 cm^{-1}) of the Raman spectra will provide information on the effects of the dissolution of hydrogen on the structure of the silicate network.

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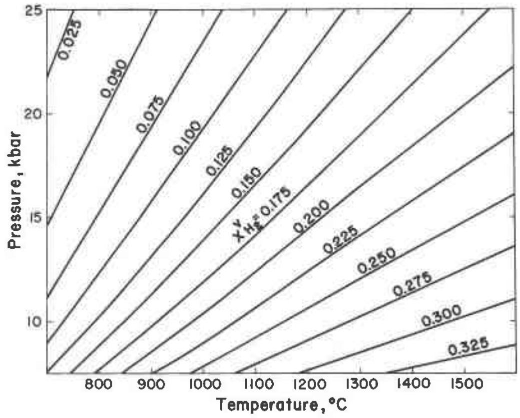

Fig. 1. Composition of O-H vapor in equilibrium with the iron-wüstite buffer assemblage as a function of pressure and temperature. Numbers along the curves are the mole fraction of H_2 in vapor. Vapor composition calculated using modified Redlich-Kwong formulation of Holloway (1977).

Table 1. Compositions of glasses studied

Composition	Na_2O	Al_2O_3	SiO_2
NS2	34.03	0.00	65.97
NS4	20.50	0.00	79.50
NS7	12.84	0.00	87.16
Jd	15.33 (15.16)	25.22 (25.06)	59.45 (59.77)
Ab	11.82 (11.52)	19.44 (19.32)	68.74 (68.95)
A2S	10.60 (10.53)	17.44 (17.65)	71.95 (71.82)

Note: Compositions are given in weight percent. Numbers in parentheses are derived from microprobe analyses; other numbers are nominal compositions.

Experimental methods

Glasses in the system Na_2O-Al_2O_3-SiO_2, synthesized at 1 atm from oxide and carbonate mixes (Table 1), were used as starting materials for experiments in high-pressure, solid-media apparatus (Boyd and England, 1960). Approximately 40 mg of the glass were loaded into an open-ended 3-mm Pt capsule and dried at 400°C for ~16 h. After welding shut, this capsule was sealed into a 5-mm Pt capsule, together with the f_{H_2}-buffer assemblage consisting of iron, wüstite, and H_2O. In some cases, H_2O was replaced with D_2O to obtain further Raman spectral information on hydrogen-bearing species. The double capsule was run vertically in a 19-mm-diameter furnace assembly (Kushiro, 1976), with the temperature monitored by a Pt-$Pt_{90}Rh_{10}$ thermocouple in contact with the top of the capsule. The piston-out technique, with a −7% friction correction, was used. To ascertain if H_2 was diffusing in from the furnace assembly and if H_2O adsorbed on the starting material was an important source of H_2, samples of glass were synthesized in single Pt capsules at the same pressures and temperatures as the double-capsule experiments, but with the f_{H_2} buffered between NNO (Ni + NiO + H_2O) and HM (Fe_2O_3 + Fe_3O_4 + H_2O) by the furnace assembly.

Raman spectra of the quenched glasses were obtained with the automated Raman system described by Mysen et al. (1982) and Seifert et al. (1982). Small, 2–10-mm^3 chips of the glasses were excited by the 488-nm line of a Coherent CR-18 Ar^+ laser operating at 1.5 to 2.5 W. Other details of the data acquisition and storage, the corrections of instrumental background and of temperature- and frequency-dependent scattering are described by Mysen et al. (1982).

Results

The experimental conditions are listed in Table 2. Analysis of the quenched glasses for the concentration of H_2 dissolved in the liquid was not attempted because of problems that previous workers encountered with diffusion of H_2 out of the glass after the quenching of the experiment. For example, Faile and Roy (1971) reported that approximately half of the H_2 dissolved in a high-silica glass diffused out over ~100 days.

The Raman spectra of the high-frequency (3000–4500 cm^{-1}) region of the quenched liquids show a sharp, symmetric band at ~4123 cm^{-1} and a broad, asymmetric band at ~3580 cm^{-1} (Fig. 2). The band at ~3580 cm^{-1} is assigned to the stretching vibrations of OH groups, either in molecular H_2O or in OH groups bonded to cations in the silicate network (Scholze, 1960). The topology of this band is similar to that found for H_2O-bearing glasses in the system Na_2O-Al_2O_3-SiO_2 by McMillan and Remmele (1986) and by Mysen and Virgo (1986). In the spectra of the H_2-bearing glasses on the join $NaAlO_2$-SiO_2, however, there is a small shoulder at ~3313 cm^{-1} associated with the OH-stretching band (arrow, Fig. 2) that is absent in the spectra of the H_2O-bearing glasses. In the Raman spectra of the aluminosilicate glasses quenched from ≥1400°C, a band at 1630 cm^{-1}, attributed to bending vibrations of molecular H_2O (Herzberg, 1945; McMillan et al., 1983), is present.

Raman spectra of the samples of glass synthesized in single Pt capsules, with the f_{H_2} buffered by the furnace assembly, lacked bands in the 3000–4500-cm^{-1} region. This contrast indicates that the OH and H_2 bands observed in the spectra of the IW-buffered glasses were not the result of either adsorbed H_2O or H_2 from the furnace assembly.

The sharp band at ~4123 cm^{-1}, attributed to the stretching vibration of the H_2 molecule, occurs at lower frequency in these glasses than in H_2 vapor at 1 atm (4159.4 cm^{-1}; Nakamoto, 1978), and the frequency increases with increasing pressure, temperature, and silica content on both the Na_2O-SiO_2 and $NaAlO_2$-SiO_2 joins (Fig. 3). Although no bubbles were visible with either the optical or the scanning-electron microscope, it is conceivable that the H_2 is present in submicroscopic bubbles. There is, however, some evidence against this possibility. The Raman spectra of a bubble-rich glass of NS7-H_2O-H_2 composition (Table 2) contains two well-resolved peaks, one at ~4126 cm^{-1} with a full width at half-maximum peak height (FWHM) of ~14 cm^{-1}, and one at ~4154 cm^{-1} with a FWHM of ~8 cm^{-1}. The 4154-cm^{-1} band is interpreted as resulting from vibrations of H_2 molecules contained in the gas bubbles, offset from ~4159 cm^{-1} by interaction of the H_2 with H_2O molecules, whereas it is suggested that the 4126-cm^{-1} band would then result from H_2 dissolved in the silicate glass. The difference between the high-frequency spectrum of this

TABLE 2. Summary of experimental conditions and results

Run no.*	Composition	Pressure (kbar)	Temperature (°C)	Duration (min)
142†	NS2	15	1100	30
81	NS2-H_2	15	1100	30
83	NS2-D_2	15	1100	30
02	NS4	0.001	1150	90
01	NS4-H_2	15	1350	30
143	NS4-H_2	15	1450	20
03	NS4-D_2	15	1350	30
118	HS4-H_2	25	1450	30
S.M.‡	NS7	0.001	1460	120
77§	NS7-H_2	15	1500	10
96†	Ab	15	1400	20
116†	Ab	25	1400	20
89	Ab-H_2	15	1400	20
108	Ab-H_2	20	1400	20
126	Ab-H_2	20	1450	20
109	Ab-H_2	25	1400	20
120	Ab-D_2	15	1400	20
119	Ab-D_2	25	1400	20
124†	Jd	15	1450	20
122	Jd-H_2	15	1450	20
125	Jd-H_2	20	1450	20
123	Jd-H_2	25	1450	20
138†	A2S	20	1500	20
139	A2S-H_2	15	1500	15
141	A2S-H_2	20	1475	15
140	A2S-H_2	20	1500	15

* All high-pressure experiments run with IW buffer except where noted.

† Experiments run under furnace-buffered (f_{H_2} between HM and NNO) conditions.

‡ S.M. = starting material.

§ Inner capsule leaked during experiment; bubble-rich NS7-H_2O-H_2 glass resulted.

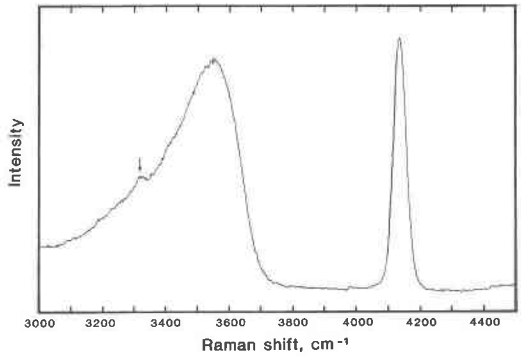

Fig. 2. High-frequency Raman spectrum of Ab-H_2 (run 109). Symmetric band at ~4123 cm^{-1} from H_2 stretching vibration, asymmetric band at ~3580 cm^{-1} from OH stretching and bending modes. Arrow indicates the small band that is present in the spectra of H_2-bearing samples. This band is absent in the spectra of H_2O-bearing samples studied by Mysen and Virgo (1986).

sample and the spectra of the other, apparently bubble-free, H_2-containing glasses indicates that the molecular H_2 in the latter is dissolved in the glass.

If the hydroxide groups that cause the ~3580-cm^{-1} band are generated by the reaction

$$X\text{–}O\text{–}Y + H_2 = X\text{–}O\text{–}H + Y\text{–}H \qquad (1)$$

(X, Y = Na, Al, or Si), then, from charge-balance considerations, hydride groups should be present as well. Van der Steen and van den Boom (1977) attributed a band at ~2250 cm^{-1} in SiO_2 glass fused in a He-H_2 atmosphere at P_{total} = 1 bar to Si–H stretching vibrations. No such band was present in the spectra of the glasses in this study. Another possible hydride is Na–H, which would be characterized by a band at ~1132 cm^{-1} (Nakamoto, 1978), a region that has strong scattering from Si–O vibrations. Because of this overlap, and because the highly ionic nature of the Na–H bond makes this bond a poor Raman scatterer, the presence of a band at ~1132 cm^{-1} could not be confirmed.

Alternatively, the formation of a Pt-Si alloy by interaction between the sample container and the silicate sample at the high temperatures and low f_{O_2} of these experiments would explain the presence of OH in these glasses. Chen and Presnall (1975) found such alloys formed in Pt capsules run at 7 kbar, 1665°C for 4 h under furnace-buffered conditions. We observed a mosaiclike texture of Pt and Pt-Si alloy, similar to that shown in Figure 6 of Chen and Presnall (1975), in the capsule wall from an experiment that was buffered by IW at 15 kbar and 1450°C for 20 min. Furthermore, ~0.03-mm^2 areas of homogenous Pt-Si alloy were observed in the capsule wall of an experiment that was buffered by IW at 15 kbar and 1100°C for 30 min. Analysis of these alloys using energy-dispersive analysis on a JEOL scanning-electron microscope detected only Pt and Si. Formation of this alloy would liberate oxygen that reacts with H_2 diffusing into the capsule from the buffer assemblage to form H_2O. This H_2O could dissolve in the silicate liquid both as molecular H_2O and as OH, resulting in the vibrations that were observed at ~1630 cm^{-1} and ~3580 cm^{-1}, respectively.

The low-frequency (200–1400 cm^{-1}) region of the Na_2O-SiO_2 glasses (Fig. 4a) changes only subtly with the addition of H_2 (and concomitant H_2O), with a possible new band at ~900 cm^{-1}. In contrast, a new band at ~900 cm^{-1} is quite obvious in the spectra of glasses along the $NaAlO_2$-SiO_2 join upon the addition of H_2 and H_2O (Fig. 4b). This band was observed in hydrous albite glass by Mysen et al. (1980) and McMillan et al. (1983) and in hydrous glasses on the $NaAlO_2$-SiO_2 join by Mysen and Virgo (1986). This band is attributed by Mysen et al. (1980) and Mysen and Virgo (1986) to Si–O vibrations involving nonbridging oxygens generated upon the solution of H_2O in the liquid. McMillan et al. (1983), however, argued that this band results from Si–OH and/or Al–OH stretching vibrations. For this interpretation to be correct, a decrease in the frequency of this band should be observed upon the substitution of D_2O for H_2O. Such a change in frequency was not observed by Mysen and Virgo (1986) or in this study.

When D_2 is substituted for H_2 in these glasses, the O–D vibrations result in an asymmetric band at ~2640 cm^{-1}. In addition, a symmetric band is observed at ~2975 cm^{-1} from D–D stretching vibrations, along with a smaller, symmetric band at ~3605 cm^{-1} from H–D vibrations.

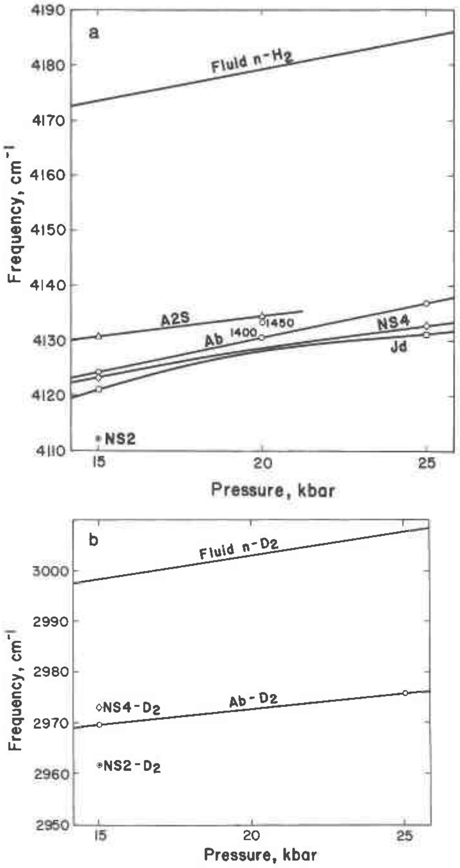

Fig. 3. Dependence of the band from the stretching vibration of H_2 (a) and D_2 (b) on matrix, temperature, and pressure. Data for fluid n-H_2 and n-D_2 from Sharma et al. (1979) and Sharma et al. (1980), respectively.

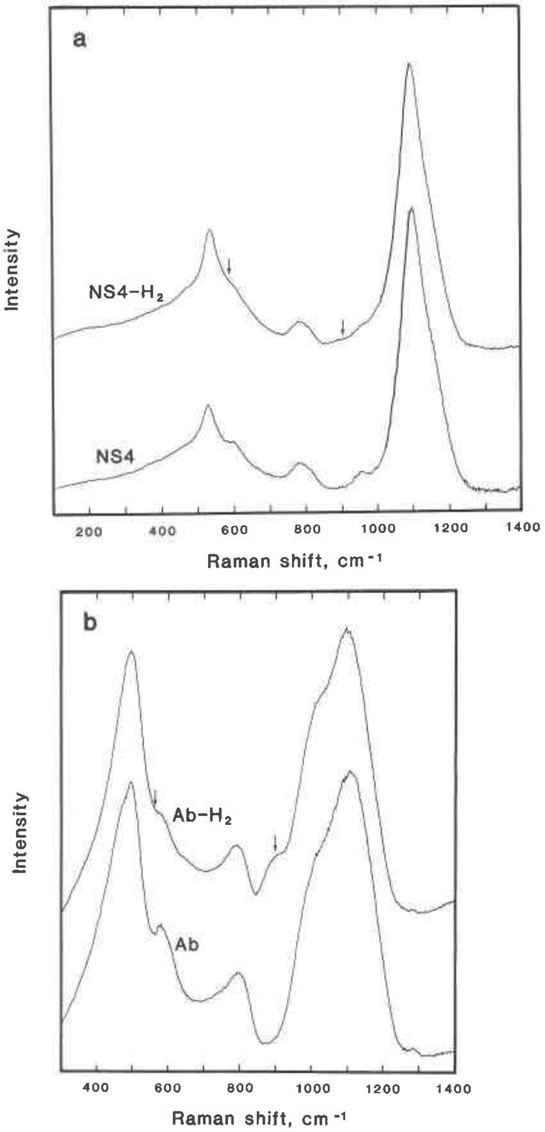

Fig. 4. Temperature- and frequency-corrected Raman spectra. NS4, NS4-H_2, Ab, and Ab-H_2 glasses. Arrows note regions of spectra that change upon the addition of H_2. (a) NS4 (run 02) and NS4-H_2 (run 01). (b) Ab (run 96) and Ab-H_2 (run 109).

The HD molecule is present because the D_2O that was loaded into the buffer capsule contained ~5% H_2O.

The change in frequency of the OH and H_2 bands upon the substitution of D_2 for H_2 may be calculated from

$$\frac{\nu_i}{\nu_j} = \sqrt{\frac{\mu_j}{\mu_i}} \qquad (2)$$

(Herzberg, 1950), where ν = the frequency of the vibration, μ = the reduced mass [= $(m_a m_b)/(m_a + m_b)$, where m_a and m_b are the masses of the two entities involved in the vibration], and subscripts i and j represent DD and HH or OD and OH. Equation 2 assumes that the force constant for the vibration is unaffected by the isotopic substitution. The observed values for ν_{OD}/ν_{OH} of ~0.74 and ν_{D_2}/ν_{H_2} of ~0.72 compare well with the values of 0.73 and 0.71 predicted for ν_{OD}/ν_{OH} and ν_{D_2}/ν_{H_2}, respectively, by Equation 2.

DISCUSSION

Before considering the solution mechanisms of H_2, the variation in the frequency of the band from the H–H stretching vibration with pressure, temperature, and composition (Fig. 3a) should be examined. The frequency of this vibration in the glasses, which is consistently lower by ~50 cm⁻¹ than that in fluid H_2 (Sharma et al., 1979), increases systematically with increasing pressure, temperature, and silica content of the glass on the joins Na_2O-SiO_2 and $NaAlO_2$-SiO_2. Similar effects are observed for D_2 (Fig. 3b). The ν_{D_2}/ν_{H_2} ratios for the different matrix materials are all 0.719 ± 0.001, as mentioned above, indicating that the systematic variation in frequency with pressure, temperature, and composition is not a result of scatter in the data. The lower frequency of the H–H stretching vibration in silicate liquids compared with H_2 fluids results from the interactions between the hydrogen dissolved in the silicate glass and the surrounding atoms of the silicate network (Hartwig, 1976). Stone et al. (1984)

interpreted a similar decrease in the frequency of the stretching vibration of N_2 upon dissolution in silica glass as resulting from the interaction of the N_2 molecules with the silica. The systematic decrease in the frequency with decreasing silica content in glasses on the joins Na_2O-SiO_2 and $NaAlO_2$-SiO_2 (Fig. 3a) would therefore indicate a concomitant increase in the interaction between molecular H_2 and the silicate network with decreasing silica content, perhaps because of greater affinity of molecular H_2 for Al- or Na-containing species in the liquid.

The solution mechanism of H_2 may be expressed by the reaction

$$H_{2(v)} = H_{2(l)}. \quad (3)$$

The evidence for the presence of molecular H_2 in these glasses has been outlined above. Bands caused by vibrations of hydride species, if present, were too weak to be observed. The presence of bands from vibrations of OH and H_2O result from the reaction of H_2 with O_2 liberated by the silicate when a Pt-Si alloy is formed, and they have nothing to do with the solubility mechanism of H_2 per se. Therefore, unlike H_2O and CO_2, H_2 appears to dissolve in silicate liquids only as a molecular entity.

The formation of a Pt-Si alloy at relatively low temperatures (~1100°C) at the high f_{H_2} of the IW buffer and concomitant generation of H_2O requires re-evaluation of previous experimental work at reducing conditions. In systems containing H_2O, such as those studied by Holloway and Jakobsson (1986) and Luth and Boettcher (1986), the formation of this alloy will decrease slightly the amount of SiO_2 in the bulk composition and increase the H_2O present, although the magnitude of this effect cannot be quantified at present. The separation of the Pt capsule from the sample by a graphite capsule possibly inhibited the formation of the Pt-Si alloy in the experiments of Holloway and Jakobsson (1986); in any case, the coexistence of graphite and vapor at given pressure, temperature, and f_{O_2} in their experiments fixes the vapor composition, and the H_2O generated by reduction of Si^{4+} would not affect the composition of the vapor. In the experiments of Luth and Boettcher (1986), where C-bearing phases were not present, the formation of the alloy would make the vapor slightly more H_2O-rich than predicted by the modified Redlich-Kwong equation of state used to calculate vapor compositions. The reduction of Si^{4+} and consequent liberation of oxygen will, however, have very significant effects in H_2O-absent systems. For example, the large effect on phase equilibria attributed to CH_4 by Eggler and Baker (1982) and to H_2 by Luth and Boettcher (1985) may be a result of the formation of this alloy and concomitant contamination of the experiments with H_2O. Because of the formation of the Pt-Si alloy, H_2O-free conditions cannot be achieved in Pt capsules at elevated temperatures at high f_{H_2}.

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