Noble gas study of a philippinite with an unusually large bubble

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Abstract—A philippinite with a large bubble (volume ≈ 5 cm³) was crushed in a specifically constructed device under vacuum. The total pressure, the major gas components, and the concentration and the isotopic composition of noble gases in the trapped gas were measured. The total gas pressure was found to be low, ~10⁻⁴ atm. Compared to terrestrial atmosphere, the abundances of He and Ne are considerably more enriched than the concentrations of the heavy noble gases. Unusually high ²⁰Ne/²²Ne and ²¹Ne/²²Ne ratios were measured in the bubble gas. These ratios are higher than values expected for any steady state process and are interpreted to reflect very fast nonsteady state diffusion in the early stages of tektite formation.

INTRODUCTION

Tektites are natural glass that are found in four distinct strewn fields on the Earth (North American, Central European, Ivory Coast, and Australasian). They are commonly up to a few centimeters in size and have chemical and isotopic compositions that are very similar to those of terrestrial upper continental crustal rocks, and they are unlike any intrusive or volcanic rocks. They also have much lower H₂O contents (~0.001–0.005 wt%) than terrestrial volcanic or other natural glasses on Earth. Research on tektites during the last decades has shown that they have formed during hypervelocity impacts on Earth and that they show some similarities to "normal" impact glasses (which occur directly at a source crater). Despite almost general agreement on the origin of tektites, there are still numerous open questions regarding the exact formation process. For detailed discussions on tektites see, for example, Taylor (1973), Stöffler (1984), and Koebler (1996, 1992a,b, 1994), and references therein.

Bubbles are a common feature in tektites and may provide some clues to the formation conditions of tektites. Although they occur in all types of tektites (Muong Nong or layered, splash-form, and aerodynamically ablated tektites on land; microtekites in deep-sea sediments), bubbles are most abundant (and largest) in Muong Nong-type tektites. O'Keefe et al. (1962) studied the gas of a bubble in a bediasite using electrodeless discharge spectroscopy and detected Ne, He, and O as main constituents. They concluded that the Ne and He had probably diffused into the bubble from the atmosphere because of the high permeability of the tektite glass for these gases but also noted that the O may be "atmospheric oxygen incorporated into the tektite during its formation." Matsubara and Matsuda (1991) confirmed that only He and Ne are enriched in tektites compared to the heavy noble gases (Ar, Kr, and Xe). The He/Ar and Ne/Ar ratios in tektites are much higher than those in the terrestrial atmosphere, but heavy noble gas ratios are close to the atmospheric ratios.

The exact composition of the gases in the tektite bubbles remains controversial. While O'Keefe et al. (1962) did not detect Ar, H, or N, Muller and Gentner (1968) used gas chromatography to detect N, CO₂, and O, with the relative ratios of these gases being atmospheric. On the other hand, Suess (1951) found CO₂, CO₂, H₂O, and H in bubbles in Australasian tektites, while Friedman (1963) observed only H₂O and dismissed the finding of other gases by previous authors as contamination.

Jessberger and Gentner (1972) measured the composition of gas in Muong Nong-type tektites from Indochina using mass spectrometry. They found that the N₂:Ar:Kr:Xe ratios, as well as the noble gas isotope ratios, were atmospheric and that the pressures within the bubbles were always <1 atm. This result was confirmed in a study of thaiandites by Hennecke et al. (1975). Some related work in the former Soviet Union by Dolgov and coworkers has been summarized by Bouška (1993). Recently, Matsuda et al. (1993) showed that heavy noble gases dissolved in tektite glass (in contrast to gas in bubbles) indicated that the glass solidified at atmospheric pressures equivalent to ~40 km altitude (in agreement with an earlier experiment on a moldavite bubble by Rost, 1964). All the results mentioned above indicate that tektites are of terrestrial origin and solidify under low pressures at high altitude.

Bubbles in tektites, in general, only a few mm in size, with large bubbles in splash-form tektites being rather rare. Due to the courtesy of D. Heinlein (Germany), we had the chance to examine such a rare tektite with an exceptionally large bubble. The tektite is a philippinite from Anda measuring ~6.0 cm × 4.5 cm and weighing 199.6 g (Fig. 1a). The existence of a large internal bubble was revealed by x-ray photography (Fig. 1b). The volume of the bubble was estimated to be 5.4 cm³, from comparing the density of the sample (2.288 g/cm³) with that of normal philippinite glass (2.438 g/cm³; see also O'Keefe, 1976). For the present study, we crushed the tektite in vacuum and measured the total gas pressure in the bubble, the bulk gas composition, and concentrations and isotopic ratios of noble gases in the bubble gas.

EXPERIMENTAL METHODS

A crushing device was specifically built to crush the present sample under vacuum (at room temperature). The sample chamber of the crushing device is cylindrical, with a diameter of 10 cm and a height of 10 cm. A piston allows gentle crushing of the sample by turning a handle. Various disk spacers can be used to adjust the inner space height to that of the sample. The device was machined from stainless steel to keep a low blank level for the noble gas analysis. The pressure in the device was monitored with a Schulz gauge. The chamber was connected to a purification line (Maruoka and Matsuda, 1995) and a VG 5400 noble gas sector-type mass spectrometer.

For crushing, the tektite sample was wrapped in clean Al foil. A first crushing attempt, using stainless steel disk spacers, failed and resulted only in damage to the stainless steel spacers. The total weight on the sample was estimated at ~1 ton. For the second attempt, disk spacers made from tool steel (Japanese Industrial Standard SKD11), which is harder than stainless steel, were used. This led to a slightly increased ambient pressure in the sample chamber of the crushing device to ~10⁻⁴ Torr. However, the blank levels of the noble gases were negligible. The background pressure was 2 × 10⁻⁴ Torr, which increased to 3 × 10⁻⁴ Torr after crushing. Considering the volume of the crushing device (~3800 cm³) and that of the bubble (~5.4 cm³), the total gas pressure in the bubble was estimated to be 1 × 10⁻⁴ atm (or at least 3 × 10⁻⁴ atm, including the background pressure). Part of the
mixture for H₂, H₂O, and Ne was available. However, as the sensitivities of the mass spectrometer were within a factor of two for the former gases, similar sensitivity values were also applied for the other gases.

In addition, the major element composition of the sample was measured by electron microprobe analysis of a polished section of shards obtained after the crushing using an ARL SEMQ microprobe and standard measurement and data reduction techniques.

BULK GAS ANALYSES

Hydrogen makes up ~90 vol% of the total gas, the rest is mostly H₂O. The measured H pressure was higher after opening the leak valve than before. In addition, small amounts of H₂O, CH₄, Ne, and He were found, but N₂, O₂, and CO₂ were not detected. The amounts of H₂O, Ne and He were only ~2× the blank level at the measurement, with CH₄ being present only in trace amounts. Unfortunately, due to experimental constraints, the bulk composition of the gas in the sample chamber during crushing could not be measured (only the noble gas composition was monitored). Thus, it is very difficult to determine whether some of these gases originated from the Fe spacer. However, as Fe, in general, contains H₂, it is likely that some, or most, or the H (and maybe some CH₄ and H₂O) may have come from the metal.

NOBLE GAS ANALYSES

Our results are listed in Table 1. The amounts of Ar, Kr, and Xe were almost at the blank level, if the variation of the blank is estimated to be ~50%, while those of He and Ne were ~3 to 4 orders of magnitude higher than the blank level. The Ne/Ar ratio in the bubble gas is ~4 orders of magnitude higher than the atmospheric value, which is in agreement with previous observations for tektites (Hennecke et al., 1975; Matsubara and Matsuda, 1991; Matsuda et al., 1993). These effects are due to the high permeability of light noble gases in silicate glasses (Matsuda et al., 1989). As the Ne/Ar concentration is at the blank level, the actual Ne/Ar ratio could be much higher than the above value.

The isotopic ratios of Ar, Kr, and Xe are, within uncertainties, similar to those of the terrestrial atmosphere but are not listed because the Ar, Kr, and Xe concentrations are more or less at the blank level. No radiogenic Ar was found in the bubble gas. Within experimental uncertainties, the Ne/He ratio is identical to the atmospheric value.

However, it is noticeable that the Ne isotopic ratios are significantly different from atmospheric values, which is in contrast to the results reported in previous studies (Matsubara and Matsuda, 1991; Hennecke et al., 1975). Both the Ne/Ar and Ne/Ne ratios are higher than those in the atmosphere. Although Ne could not be produced in the upper atmosphere by reactions such as O⁺ (α, n) Ne or Mg (n, α) Ne, Ne cannot be produced in detectable amounts by nuclear reactions in the atmosphere or inside the Earth (Wetherill, 1954). Experimental error can also be excluded as a source for the high Ne/Ne ratio because the high amount of Ne allowed precise determinations of the isotopic ratios. Double charged Ar (which could be a source for the high Ne/Ne ratio) can also be excluded because of the high Ne/Ar ratio in the sample.

Table 1. Noble gas contents (in cm³ STP) and their isotopic ratios of the phillipinite bubble gas.

<table>
<thead>
<tr>
<th></th>
<th>He</th>
<th>³He/⁴He (×10⁻⁶)</th>
<th>²²Ne</th>
<th>²⁰Ne/²²Ne</th>
<th>²¹Ne/²²Ne</th>
<th>³⁶Ar</th>
<th>⁴⁰Kr</th>
<th>¹³⁰Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>8.01 × 10⁻⁷</td>
<td>8.22 × 10⁻¹²</td>
<td>7.42 × 10⁻¹³</td>
<td>3.32 × 10⁻¹³</td>
<td>0.79 × 10⁻¹⁵</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample</td>
<td>2.98 × 10⁻⁵</td>
<td>1.30 ± 17</td>
<td>10.520 ± 52</td>
<td>0.02993 ± 32</td>
<td>5.01 × 10⁻¹⁵</td>
<td>4.02 × 10⁻¹²</td>
<td>1.29 × 10⁻¹³</td>
<td></td>
</tr>
<tr>
<td>Air</td>
<td>1.40</td>
<td>9.80</td>
<td>0.029</td>
<td>0.029</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Quoted uncertainties refer to the last digits.
DISCUSSION

The major element composition of the sample (Table 2) is similar to data obtained for other phillipinites, although the sample is Si-rich and has slightly lower Ca, Fe, and Mg contents than the phillipinite average reported in the literature (see, e.g., Koeberl, 1986). Despite the unusual Ne isotope ratios, the data plot on the mass fractionation line from the atmosphere in a $^{20}\text{Ne}/^{22}\text{Ne}$ vs. $^{21}\text{Ne}/^{22}\text{Ne}$ three-isotope diagram (Fig. 2), which suggests that Ne diffused in from the atmosphere. However, it is generally believed that the isotopic fractionation during a steady-state process is very small, and the observed Ne values are higher than those calculated from simple mass fractionation. While the lighter isotope is enriched during diffusion, there is a limit in the degree of mass fractionation, assuming a simple first-order process equation. The mean velocity of gas molecules is proportional to the inverse square root of their mass. Therefore, this limit is very close to $(m_2/m_1)^{1/2}$, where $m_2$ and $m_1$ are the masses of each isotope. For the $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{21}\text{Ne}/^{22}\text{Ne}$ ratios, these values are 1.049 and 1.024, respectively. Thus, if only a single-stage mass fractionation process controls the effect, $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{21}\text{Ne}/^{22}\text{Ne}$ ratios should be $<10.3$ and 0.0297, respectively, assuming atmospheric ratios at the beginning (see Table 1 for atmospheric values; 9.8 $\times$ 1.049 = 10.3; 0.029 $\times$ 1.024 = 0.0297). Neon isotope data obtained for volcanic material were less than these values, with samples plotting on the fractionation line (Kaneoka, 1980), implying that steady-state diffusion is predominant on the terrestrial surface. The high Ne found in the present study is likely to be associated with a different gaseous diffusion process and/or with the nonequilibrium conditions prevailing during the impact melting and formation of the tektite.

Marty (1984) discussed two gaseous diffusion mechanisms in nature, namely, mutual diffusion and thermal diffusion. The former process describes the interaction of two or more gas species, but recent diffusion studies of noble gases in silicic glasses suggest that there should be no significant interactions between different dissolved gas atoms in natural melts (Draper and Carroll, 1995). Furthermore, this process produces only very small degrees of fractionation, less than that of free-molecule diffusion considered by Kaneoka (1980).

Thermal diffusion occurs when a gas mixture is in a nonequilibrium thermal state because the lighter noble gases tend to concentrate in the hotter regions. The degree of fractionation in a steady state in thermal diffusion is given by $(T_H/T_L)^a$, where $T_H$ and $T_L$ are the highest and lowest temperature, respectively, and $a$ is the thermal diffusion parameter, which depends on the isotopic pair and the temperature range. Taylor and Weissman (1974) and Taylor (1975) measured the diffusion parameter for Ne isotopes for a wide range of temperatures. When using their values, the degree of fractionation is only 1.008, which is again much less than the value in our study.

However, Rama and Hart (1965) examined Ne isotope fractionation during transient permeation through a membrane consisting of a vycor tube and reported as much as 45% enrichment of $^{20}\text{Ne}$ relative to $^{22}\text{Ne}$. During steady-state permeation, a gas flow attains a constant value, and the ratio of their diffusion coefficients is proportional to the inverse of the square roots of their masses. Therefore, the so-called "Rama and Hart's effect" is a nonsteady-state process, and the observed fractional changes agree with those calculated from diffusion theory, which suggests that such a high fractionation can be achieved very rapidly at the beginning of the permeation process. Therefore, Ne in our tektite should have diffused in from the atmosphere in a very short time at the beginning of the formation of tektite. Even if we assume that all the Ne released by crushing originated from the large bubble, the partial pressure of $^{20}\text{Ne}$ was only $5.2 \times 10^{-8}$ atm, which is much less than that of atmospheric pressure ($1.6 \times 10^{-2}$ atm), indicating that no steady-state diffusion of Ne from the atmosphere has yet taken place after formation of the tektite.

![Fig. 2. Diagram of $^{20}\text{Ne}/^{22}\text{Ne}$ vs. $^{21}\text{Ne}/^{22}\text{Ne}$. The tektite gas composition is indicated by the solid circle. "Ne-A" is planetary Ne, which is characteristic of carbonaceous meteorites (Black and Pepin, 1969). "Ne-B" is solar Ne found in samples with solar elemental pattern (Black, 1972). "Solar wind" indicates direct measurements of the solar wind composition trapped on foil (Geiss et al., 1972). The tektite gas data plot on the mass fractionation line from the terrestrial atmospheric composition.](image-url)

### Table 2. Major element composition of phillipinite sample with large bubble

<table>
<thead>
<tr>
<th></th>
<th>Philiininite with bubble</th>
<th>Philiininite Range</th>
</tr>
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<tbody>
<tr>
<td>SiO₂</td>
<td>72.1 ± 0.45</td>
<td>68.9 – 72.1</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.86 ± 0.02</td>
<td>0.75 – 1.02</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>14.5 ± 0.20</td>
<td>12.33 – 15.23</td>
</tr>
<tr>
<td>FeO</td>
<td>4.50 ± 0.09</td>
<td>4.55 – 5.37</td>
</tr>
<tr>
<td>MnO</td>
<td>0.10 ± 0.03</td>
<td>0.08 – 0.12</td>
</tr>
<tr>
<td>MgO</td>
<td>2.14 ± 0.04</td>
<td>2.22 – 2.93</td>
</tr>
<tr>
<td>CaO</td>
<td>2.38 ± 0.03</td>
<td>2.50 – 3.97</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.36 ± 0.08</td>
<td>1.18 – 1.61</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.55 ± 0.02</td>
<td>2.17 – 2.56</td>
</tr>
<tr>
<td>Total</td>
<td>100.5</td>
<td>99.93 – 100.5</td>
</tr>
</tbody>
</table>

Data in wt%; all Fe as FeO; the data reported for the present sample are an average of 9 analyses, with 2σ standard deviation; the range of phillipinite compositions (excluding the HCa and LCa/HAl groups) is taken from the literature (Schnetzler and Pinson, 1963; Koeberl, 1986).
According to Rama and Hart (1965), the degree of fractionation of $^{20}\text{Ne}$ and $^{22}\text{Ne}$ at time $t$ is given by:

$$F_t = \frac{D_{20}}{D_{22}} \left[ \frac{1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp \left( -\frac{D_{20} \pi^2 \cdot t}{l^2} \right)}{1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp \left( -\frac{D_{22} \pi^2 \cdot t}{l^2} \right)} \right]$$

where $l$ is the thickness of the membrane, $n$ is an integer number, and $D$ is the respective diffusion coefficient.

We assume that the tektite has incorporated the gas from the surrounding atmosphere during the impact melting of the source rocks and/or during the flight (and solidification) in the atmosphere. The diffusion of atmospheric gas could have been achieved in a nonsteady-state process, which can be approximated by the "Rama and Hart effect." Therefore, we used the mathematical model of Rama and Hart (1965) and calculated the change of $^{20}\text{Ne}/^{22}\text{Ne}$ ratio with time $t$. The actual geometry of the bubble suggests that the Rama and Hart model is applicable because the bubble is situated at one side of the bulk sample, and only one side of the bubble was exposed to the atmosphere.

Five different diffusion pair coefficients (Frank et al., 1961; Reynolds, 1960; Frischat and Oel, 1967; Lux, 1987; Matsuda et al., 1989) were used for the model (Fig. 3). Among these diffusion coefficients, only Frank et al. (1961) measured the diffusion coefficient of $^{20}\text{Ne}$ and $^{22}\text{Ne}$, while the others measured only $^{20}\text{Ne}$. However, Frank et al. (1961) confirmed that the ratio of the two diffusion coefficients is the inverse square roots of their respective masses, namely, $D_{20}/D_{22} = (22/20)^{1/2} = 1.049$. Therefore, we assume that $D_{22} = D_{20}/1.049$ for the diffusion data. The data of Lux (1987) are for volcanic glass melt at a temperature of 1350 °C. The data of Frank et al. (1961) are for fused quartz at temperatures between 400 °C and 1000 °C, and those of Reynolds (1960) are for a tektite (australite) at 78 °C to 450 °C. Matsuda et al. (1989) measured the diffusion coefficient of Darwin impact glasses from 300 °C to 700 °C. The data of Frischat and Oel (1967) are for commercial glass at 948 °C to 1196 °C. For these four data sets, we extrapolated the diffusion coefficients to 1350 °C, using the preexponential factor and the activation energy. In the calculations, a thickness of $l = 0.5$ cm was used.

The best fit is obtained when time $t$ is $<16,000$ s ($<4.4$ h) for the various types of melt, except for data of Reynolds (1960), possibly because the diffusion coefficients were measured at very low temperatures and the extrapolation may be too far. A duration of a few hours is, of course, much too long for the tektite formation process. However, a temperature of 1350 °C, as used here, is still much lower than the formation temperature of tektites as estimated from O-fugacity measurements (Brett and Sato, 1984) or relict minerals and mineral melts (e.g., Glass and Barlow, 1979; Koebel, 1994). Increasing the melting temperature causes the Rama and Hart effect to reduce the time $t$ by at least one order of magnitude. Unfortunately, no diffusion coefficients have been measured at such high temperatures, and, therefore, no quantitative calculations are possible. However, it can be concluded that a very high $^{20}\text{Ne}/^{22}\text{Ne}$ ratio was obtained in a very short time (seconds or minutes) during melting and lowered later by slow diffusion from the atmosphere. These results indicate that the fractionation was the consequence of a fast nonsteady-state diffusion process. The preservation of a high fractionated Ne isotope ratio implies that shortly after its formation the tektite itself was sealed airtight. However, the partial pressure of He in the bubble is almost the same as the partial pressure in the atmosphere. Helium has much higher permeability than Ne, which is the reason that the $^3\text{He}^4\text{He}$ ratio in the bubble is identical to that in air.

The low gas pressure measured in the bubble is compatible with values reported previously by Zähringer (1963) and Zähringer and Gentner (1963), who found pressures $<2.5 \times 10^{-3}$ atm in bubbles in phillipinmites. It should be noted that the bubble could not have formed if the bubble pressure was lower than the ambient pressure during the formation of tektite. The bubble gas pressure in tektite would be higher than the measured value ($1 \times 10^{-3}$ atm at room temperature) by only one order of magnitude when taking a formation temperature of tektite as several thousand degrees into account. This indicates that the ambient pressure of the gas in the tektite during formation was $\leq 10^{-3}$ atm, suggesting that the tektite formed at high altitude of the atmosphere (40 km–50 km), which is in agreement with results obtained by Matsuda et al. (1993).

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