The Effect of Water on Noble Gas Signatures of Volcanic Materials

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Abstract. Noble gas signatures of volcanic materials are often affected by secondary components during the ascent of a magma to the surface from a magma source. Among them, the effect of water is significant and should be evaluated properly in order to infer the original signatures of magmatic components. Through a survey of Ar isotope studies for recent volcanic materials in Japan, the effect of the groundwater on a magma is inferred to be rather common on the basis of systematic mass fractionation of the atmospheric Ar enriched in lighter isotopes.

Similar effects are also observed in phenocrysts of OIB and MORB, where variable $^{40}\text{Ar}/^{36}\text{Ar}$ ratios with relatively uniform $^{3}\text{He}/^{4}\text{He}$ ratios are observed due to possible incorporation of the atmospheric noble gases through the water. Thus, noble gas signatures of volcanic materials are controlled by the environmental conditions of the volcanic conduit and the sites to be extruded.

1. Introduction

Noble gas signatures observed in volcanic materials reflect the characteristics of both the source materials and secondary ones caused mostly by tectonic environments.

Among many factors which control the noble gas signatures, the effect of water is one of the most significant ones, because it exists ubiquitously on the surface of the Earth and contains significant amounts of noble gases. It might also be carried into the Earth's interior with subducted slabs (e.g., STAUDACHER and ALLEGRE, 1988), though it is not clear how deep it would be carried down with subducted slabs. A few cases are shown schematically in Fig. 1, where the groundwater or seawater affect the magmatic noble gases during the ascent of a magma. In this figure, however, the effect of water on magma sources is not indicated, since it needs speculation on more global scale including the identification of characteristics of recycled materials.

Water can dissolve noble gases with selective enrichment in heavier noble gases in comparison with the atmospheric components, though no clear isotopic difference has been observed between the atmosphere and the water (e.g., OZIMA and PODOSEK, 1983). Since the amounts of dissolved gases in water are relatively large compared with those dissolved in a magma, the introduction of water into a magma easily alters
the original noble gas signatures. Typical example has been demonstrated for submarine pillow glasses. The outer pillow glasses show very high $^{40}\text{Ar}/^{36}\text{Ar}$ ratios with large enrichment of He and Ne than those of the atmosphere compared to heavier noble gases, while the inner holocrystalline parts show a sign of reequilibration of noble gases with water as has been identified by the atmospheric Ar isotopic ratios and noble gas abundance patterns of the seawater (e.g., DYMOND and HOGAN, 1973).

In this paper, I want to show the effect of water on noble gas signatures in volcanic rocks which might occur during the process of magma transportation to the surface. However, I do not extend the discussion to those on the characteristics of magma sources here. Because it requires proper evaluation of the data to separate the primary signatures from the secondary ones and that of the retention of water in recycled materials, which needs additional detailed discussions and it is better to be treated in a separate paper.

2. Mass Fractionation of Atmospheric Ar in Recent Volcanic Materials from the Japanese Islands and the Effect of Water-Derived Ar

It has been known that volcanic materials often contain isotopically mass fractionated noble gases from the atmospheric components (e.g., KANEOKA, 1980;
KRUMMENACHER, 1970). Such mass fractionation has been observed both in natural gases and rock samples.

Ar isotope data for recent volcanic materials including gases and rock samples from the Japanese Islands are shown in Fig. 2. As seen in this figure, many gas samples indicate the addition of radiogenic $^{40}\text{Ar}$ to the atmospheric Ar with no significant mass fractionation from the reported value of the atmospheric Ar. This might reflect the mixing of unfractionated atmospheric components with either

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\delta(38/36) / \text{o/oo} \quad \delta(40/36) / \text{o/oo} \quad 40\text{Ar} / 36\text{Ar}
\]

Fig. 2. $^{40}\text{Ar} / 36\text{Ar}$ vs. $^{38}\text{Ar} / 36\text{Ar}$ diagram. $\delta(40/36)$ and $\delta(38/36)$ are defined from the deviation of the atmospheric $^{40}\text{Ar} / 36\text{Ar}$ and $^{38}\text{Ar} / 36\text{Ar}$ ratios in permil, respectively. “Rock” indicates a bulk rock sample and “gas” indicates a natural or volcanic gas sample. Data sources: KANEOKA and TAKAOKA (unpublished data), MATSUMOTO (1990) and NAGAO (1979).
magmatic components and/or addition of radiogenic $^{40}\text{Ar}$ incorporated during the ascent of volcanic gases through old basement rocks. Some gas sample data scatter along the mass fractionation line of the atmospheric Ar. Although a few data of gas samples indicate a slight enrichment in the heavier isotopes, the other gas samples show lower $^{40}\text{Ar}/^{36}\text{Ar}$ and $^{38}\text{Ar}/^{36}\text{Ar}$ ratios than those of the atmospheric Ar along the mass fractionation line.

On the other hand, it is noteworthy that all rock samples show Ar isotope data which are deviated from the atmospheric Ar value with enrichment of lighter isotopes or close to the atmospheric Ar values on the mass fractionation line. Such systematic trend cannot be attributed to the characteristics of rock sample itself. Because rock samples from areas other than the Japanese Islands often show Ar isotopic ratios which indicate the enrichment of heavier Ar isotopes compared to the lighter ones (e.g., KANEOKA, 1980; KRUMMENACHER, 1970). Phenocryst samples in recent volcanic rocks from the Japanese Islands, however, show systematically higher $^{40}\text{Ar}/^{36}\text{Ar}$ ratios than the atmospheric value, being independent of the value of the $^{38}\text{Ar}/^{36}\text{Ar}$ ratio (e.g., HANYU and KANEOKA, 1994; TAKAOKA, 1989). This is considered to reflect the characteristics of magmatic components. Hence, the above mentioned trend for volcanic rocks seems to be characteristic to whole rock samples from the Japanese Islands, which might be related to environmental conditions of the Japanese Islands.

In order to clarify the cause of the phenomena, the outline of mass fractionation process is briefly described here. It is conjectured that the mass fractionation of noble gas isotopes is expected to occur under a condition where the movement of each isotope is so fast and the mutual collision of isotopes to mix them is not sufficient enough to equilibrate them. The existence of a gas phase is not a sufficient condition to cause mass fractionation, but rapid movement of each isotope and the lack of homogenization process would be required. Hence, such processes as the phase change to a gas phase and/or transportation of gases through a narrow conduit would be probable cases. In this study, we need to get a rough idea about the trend of mass fractionation. Hence, only a schematic case is considered that a part of gas is lost from the original gas reservoir in a circumstance where mass fractionation occurs and the diffusive gas is kept in another phase. Since an isotope with a lighter mass would move faster than that with heavier ones, the phase which keeps diffusive gas would be enriched in lighter isotopes compared to the original gas reservoir and the residual gas is enriched in lighter isotopes. Such case is schematically shown in Fig. 3. In this model, it is assumed that the original gas contains two isotopes, $M_1$ and $M_2$, where atomic mass of $M_2 (=m_2)$ is greater than that of $M_1 (=m_1)$. As mentioned above, the diffusive gas will be enriched in the lighter isotope. The volume of a gas is designated by $V$. The original gas, the residual gas and the diffusive gas are indicated by suffixes, o, r, d, respectively. The enrichment factor for the isotopic ratio $R = (m_2/m_1)_o/(m_2/m_1)_d$ in the residual gas can be expressed as follows (ASTON, 1933),

$$R = F^{-(m_2-m_1)/(m_2+m_1)},$$
where $F$ is defined as $V_r/V_o$. The depletion factor of the isotopic ratio $R' = (m_2/m_1)_d/ (m_2/m_1)_o$ in the diffusive gas can be deduced from the above equation and expressed in the following way.

$$R' = \frac{1 - RF}{1 - F}.$$

Although this is a very simple case, it will give us a rough idea about the general characteristics of mass fractionation. If the original gas contains the unfractonated atmospheric Ar, the diffusive gas is expected to have the $^{40}\text{Ar}/^{36}\text{Ar}$ and $^{38}\text{Ar}/^{36}\text{Ar}$ ratios of about 280 and 0.182, respectively, as the lower limits in the case of a single stage mass fractionation (Fig. 4). If multistage mass fractionation occurs, however, lower Ar ratios than the above mentioned values could be observed.

As shown in Fig. 2, many Japanese rocks seem to contain mass fractionated atmospheric Ar, which corresponds to the diffusive gas phase. Two typical circumstances are considered to cause such mass fractionated Ar as possibilities. One is a case that the atmospheric Ar is introduced into a magma when it extrudes to the surface. The other one is that some diffusive gas is introduced into a magma while it still remains at a depth. In the former case, the candidate for the source of diffusive gas is the atmosphere itself, which was not yet equilibrated with the extruded magma. Judging from the amounts of $^{36}\text{Ar}$ in pillow lavas and olivine phenocrysts, the amounts of magmatic $^{36}\text{Ar}$ are much lower than those observed in most volcanic rocks which are considered to be equilibrated with the Ar in the atmosphere (e.g., OZIMA and PODOSEK, 1983). If the extruded lava is not equilibrated with the atmospheric Ar, the amount of $^{36}\text{Ar}$ is expected to be lower than what is anticipated.
from the solubility data of Ar in a silicate melt under the atmospheric pressure. Under one atmospheric pressure, basaltic melt can dissolve $^{36}$Ar with the amount of about $1 \times 10^{-9}$ cm$^3$STP/g (e.g., Hayatsu and Waboso, 1985). However, it is often observed that basaltic samples with a higher amount of $^{36}$Ar than the solubility data contains mass fractionated Ar with the diffusive gas characteristics (e.g., Kaneoka, 1980). Furthermore, if the mass fractionation occurs during the magma extrusion on the surface, it should have no connection with the site and environments. Hence, the former possibility is not likely to explain the trend observed in Fig. 2.

In the latter case, the diffusive gas phase might be produced through the groundwater or seawater when a magma contacts with it at a relatively shallow place during its ascent to the surface. Due to the high temperature of the magma, the water is evaporated with the dissolved noble gases. At the time of evaporation of water, dissolved noble gases might be easily fractionated and dissolved into the magma. Since such process occurs underground, the solubility of noble gases in the magma
is larger than that on the surface due to higher pressures (e.g., HAYATSU and WABOSO, 1985). In this case, the phase change of water through vaporization plays an important role to cause the mass fractionation of Ar as observed in Fig. 2. Above the critical point of water (221 bars, 374.15°C), water exists in the form of supercritical fluid. As long as noble gases remain in such a phase, we cannot find any positive factors which might cause the mass fractionation of noble gas isotopes. Generally, high temperatures and high pressures would only affect to reduce the mass fractionation. Further, as far as available data are concerned, we have no evidence that significant mass fractionation of noble gases might have occurred under such circumstances. Thus, in order to explain the characteristics of the mass fractionation observed for volcanic rocks from the Japanese Islands, the introduction of atmospheric Ar into a magma through the water at a relatively shallow place is most likely.

Fig. 5. Distribution of rock and gas samples which show mass fractionated Ar from the atmospheric Ar or excess 40Ar in Fig. 2. VF indicates a volcanic front.
This inference would be supported by a geographical distribution of the observed mass fractionated Ar in the Japanese Islands as shown in Fig. 5. Samples containing severely mass fractionated Ar are mostly distributed at a site close to the seashore or island except for a few cases. This would possibly reflect the occurrence of water sources at a shallow depth in these areas. Thus, the mass fractionated Ar with the diffusive gas character would be observed in rock samples collected at a site where such an underground water system might have developed. Since gas samples are expected to reflect the diffusive gas phase, it is natural that they show lower $^{40}\text{Ar}/^{36}\text{Ar}$ ratios compared to the atmospheric value, if mass fractionation occurs during degassing from a magma source. Natural gas samples would mostly represent the mixtures of the unfractionated and mass fractionated components of the atmospheric gases.

Thus, the mass fractionated Ar from the atmospheric value with the diffusive gas character observed in volcanic rocks might be regarded as an indicator for the incorporation of water into a magma at a shallow depth. Similar trend is expected for Ne isotopes, where higher $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{21}\text{Ne}/^{22}\text{Ne}$ ratios than the atmospheric values would be observed in the diffusive gas phase. Some Japanese samples show such a trend together with Ar ratios (e.g., NAGAO, 1979). Such information suggests that volcanic rocks of the Japanese Islands reflect an environment where the noble gases in the water might easily affect a magma at a relatively shallow depth.

3. Incorporation of Water-Derived Noble Gases into a Magma as Revealed from Noble Gas Isotopes of Pillow Glasses and Phenocrysts of Volcanic Rocks

Phenocrysts of volcanic rocks are formed in a magma at a depth whose conditions control the kind and size of phenocrysts. Hence, if such phenocrysts are formed at a depth where magmatic gases are still remained, noble gas isotopes in phenocrysts are considered to represent magmatic components (e.g., KANEOKA and TAKAOKA, 1978). Based on such inference, noble gas state in the Earth’s interior has been discussed by using the noble gas isotope data for olivine and/or clinopyroxene phenocrysts of OIB together with submarine pillow glasses (e.g., ALLÈGRE et al., 1983; KANEOKA, 1983). Through such studies, it has been revealed that MORB glasses show relatively uniform $^3\text{He}/^4\text{He}$ ratios with high and variable $^{40}\text{Ar}/^{36}\text{Ar}$ ratios. Since the He/Ar ratio in the atmosphere and the air-saturated seawater are only $5.6 \times 10^{-4}$ and $1.0 \times 10^{-4}$, respectively, the observed large variation in the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio has been ascribed to the mixing effect of the atmospheric Ar to the magmatic component. Since pillow glasses contact directly with the seawater during their formation, the occurrence of such effect is quite likely. The degree of mixing is controlled by the exchange rate of magmatic gas components with the atmospheric components through the seawater, which would be dependent on the temperature of a magma, the size and chemical composition of the extruded magma, the water depth and so on. Hence, there is a possibility that the degree of the mixing between the atmospheric component and magmatic one might be different among different portion of the pillow glass whose distance is different from the surface. If it is, even from the same block of a sample, variable $^{40}\text{Ar}/^{36}\text{Ar}$ ratios might be observed. Since
no detailed examination has been made so far in this respect, this point should be
examined further in order to infer the noble gas signatures as a genuine magmatic
component for a MORB.

Even for OIB samples, there are some examples which show uniform $^{3}$He/$^{4}$He
and variable $^{40}$Ar/$^{36}$Ar ratios from the same island or site. An example is shown for
samples from Réunion Island in Fig. 6. It has been known that the samples from this
island show uniform $^{3}$He/$^{4}$He ratios (e.g., GRAHAM et al., 1990; KANEOKA et al.,
1986; STAUDACHER et al., 1990), while its $^{40}$Ar/$^{36}$Ar ratios are variable among dif-
ferent samples (KANEOKA et al., 1986; STAUDACHER et al., 1990). Such ratios also
seem to reflect the effect of atmospheric components into a magma. Since olivine
phenocrysts with the grain of mm sizes were analysed in these cases, it is difficult
to imagine that the atmospheric components were directly incorporated into a
magma from the atmosphere. Instead, if some water was incorporated into a magma
during its ascent and the olivine phenocrysts were also formed during the ascent of
the magma, olivine phenocrysts would contain noble gas components with different
degree of mixing between the magmatic and atmospheric components through
water. Such situation might differ due to the condition of the conduit for magmas and
would not have occurred at a depth of the magma reservoir. If it occurred at a depth
of the magma reservoir, it may also show systematic time variation, but no clear
systematics has been observed in the case of the Réunion Island.

In addition, even ultramafic nodules show similar trend (e.g., STAUDACHER et

![Figure 6](image.png)

**Fig. 6.** $^{3}$He/$^{4}$He vs. $^{40}$Ar/$^{36}$Ar diagram for recent samples from some hot spot areas (KANEOKA and
TAKAOKA, 1991). “P” and “M” represent the assumed sources for plume-type (P) and MORB-type
(M) materials, respectively. “A” indicates the atmospheric value.
Hence, the incorporation of the atmospheric noble gas components would probably occur through the water layer(s) which might exist around the region of the magma conduit in the Réunion Island. In the case of ultramafic nodules, the incorporation of atmospheric components through water might have occurred after the formation of nodules. As demonstrated by Farley et al. (1994), quite variable $^{40}$Ar/$^{36}$Ar ratios were observed even in a single ultramafic nodule from Western Samoa based on the laser analyses. This implies that the secondary incorporation of atmospheric Ar would have probably occurred through water.

The incorporation of atmospheric noble gas components through water during the ascent of a magma may be more common than what we have conjectured. In the case of Mt. Unzen Volcano, located in the western part of Japan, it started to erupt dacitic magmas since 1992 until now and the rocks contain relatively large phenocrysts of plagioclase, biotite and hornblende with the grain sizes of more than a few mm. Among these phenocrysts, plagioclase phenocrysts show $^{40}$Ar/$^{36}$Ar ratios ranging 310–367, while biotite and hornblende phenocrysts indicate the ratios ranging 293–312 (Hanayu and Kaneoka, 1994). Since plagioclase phenocrysts are considered to have formed earlier than biotite and hornblende phenocrysts, the difference in the observed $^{40}$Ar/$^{36}$Ar ratios among these phenocrysts are interpreted to reflect different environments when they were formed. Plagioclase phenocrysts of smaller sizes show lower $^{40}$Ar/$^{36}$Ar ratios than those of larger sizes. This is also interpreted that plagioclases with smaller sizes were formed later than the larger ones. These observations indicate that at least some atmospheric components would have been added to the environment where biotite, hornblende and plagioclase of smaller sizes were formed. Since these phenocrysts were of mm sizes and considered to have formed at a depth, the incorporation of the atmospheric Ar into a magma would have occurred through the water. Since the phenocrysts of lavas which erupted about 200 years ago show a similar trend, such effect would not be a temporal one, but rather reflect its environment. Thus, the groundwater system in a tectonic environment may become an important factor to control the noble gas signatures observed in the geologic materials. Even if we cannot observe any significant sign of secondary effect from a water in the chemical composition data, noble gas data might be altered to some extent, since noble gas isotopes are quite sensitive to such an effect.

Thus, noble gas signatures often reflect the addition of secondary components through a water system under the ground, which is also controlled by geologic environments. For samples collected at such sites where an underground water system is developed, we should properly evaluate the secondary effects by the incorporation of atmospheric noble gases in order to evaluate the genuine magmatic signatures from them.

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