

Occlusion of noble gases (He, Ne, Ar, Kr, Xe) into synthetic magnetite at 500–1300°C

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Abstract

The trapping mechanism of noble gases during growth of magnetite is investigated by oxidizing Fe with water vapor at temperatures ranging from 500 to 1300°C. An apparent negative correlation between the concentration of argon and synthetic temperatures suggests that gases are trapped by adsorption. The fixation of adsorbed gas atoms is probably due to crystal growth. The elemental fractionation pattern of noble gases resembles so-called ‘planetary type’ patterns, with enrichments in heavier noble gases at high trapping temperatures. However, at lower temperatures, significant fractionation is not observed, reflecting a smaller absolute value of the negative heat of adsorption for lighter noble gases.

The amount of argon in chondritic magnetite (Orgueil, CI) can be explained by adsorptive trapping of ambient noble gases at the suggested condensation temperature of magnetite in the solar nebula (~400 K). ‘Solar type’ helium, neon and argon elemental ratios observed for the Orgueil magnetite are also qualitatively consistent with the results of the present experiments. Comparison experiments which synthesize magnetite with aqueous water are necessary for further discussion on the origin of the chondritic magnetite and its noble gases.

Keywords: noble gases; magnetite; condensation; chondrites; meteorites

1. Introduction

Magnetite, Fe₃O₄, in primitive CI chondrites occurs as small (<10 mm diameter), irregular grains and in a variety of forms including framboidal aggregates, plaquettes and spheroidal grains [1–4]. The

apparent ancient age of the magnetite, which is implied by the strikingly high ¹²⁹Xe content of magnetite from the CI chondrite Orgueil [5], suggests an origin in the primitive solar nebula (e.g., [6,7]), either by direct condensation from the nebular gas or by reaction between water vapor and previously condensed, Fe-bearing phases at around 400 K. However, it is difficult to form pure magnetite by condensation in the nebula, because condensation at higher temperature of Fe-rich minerals, such as fayalite (Fe₂SiO₄) and troilite (FeS), would effectively remove Fe before magnetite condensation [4,8]. Hydration of pre-existing anhydrous silicates in the nebula is probably inhibited because water would not

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have condensed until the temperature had dropped to a point where water–ice could have formed [9]. The morphology and chemical composition of magnetites in some CI chondrites is also against the speculated nebular origin for chondritic magnetite, and favours the alternatives of aqueous alteration on planetesimal surfaces [4] or meteoritic parent bodies (e.g., [10–12]).

He/Ar and Ne/Ar ratios of noble gases trapped in chondritic magnetite separated from the Orgueil are similar to cosmic ratios ('solar type' pattern). In addition, these ratios are distinct from those of other CI chondrites (including silicate phases separated from the same chondrite), which show progressive enrichments of heavier noble gases ('planetary type' pattern). A major carrier of this 'planetary type' noble gas is now believed to be some form of carbon ('Q component') (e.g., [13]). Noble gases in the Q component are retentively bound, generally released above 1000°C in vacuum, and are apparently surface-sited, since they are removed by mild oxidation (e.g., [14]). The origin of the 'solar type' noble gases observed in the Orgueil magnetite may be closely related to the origin of magnetite crystals. In order to understand the noble gas composition in the chondritic magnetite, it is important to examine the mechanism by which noble gases have been trapped within magnetite.

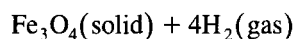
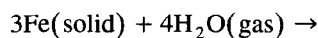
Concerning the 'planetary type' noble gases, adsorption of noble gases with solar compositions on nebular dusts is likely to be an important process for producing the enrichments in heavier noble gases from ambient solar noble gases [15–20]. This process is most efficient for various forms of carbon [18–20], in terms of observed elemental fractionation patterns and strong bonding of the noble gases in the 'Q component'. Wacker and his co-workers [19,20] suggested that the 'Q component' is a set of sheltered adsorption sites in a pore-labyrinth in amorphous carbon, which would prevent the adsorbed gases from being desorbed. However, the combination of adsorption and fixation by intrinsic structural properties of amorphous carbon cannot account for the observed unfractionated noble gases in chondritic magnetite, because adsorption of noble gases would fractionate He–Ne–Ar ratios. Moreover, the structure of magnetite (closed packed crystal) is completely different from porous amorphous carbon.

The aim of the present work is to understand the trapping mechanism of noble gases in magnetite, and to provide useful information on its origin. In addition, we address the general process of noble gas trapping during the formation of solid phases in the presence of gas phases. As an initial attempt, we carried out laboratory experiments to synthesize magnetite in a noble gas atmosphere by oxidizing Fe with water vapor. Magnetite formed as a stable phase across a wide range of temperatures in the Fe–O–H system under 1 atm. pressure. Thus, the temperature dependence of the trapped noble gases may help to identify the physical process involved. For example, larger quantities of noble gas would be trapped at lower temperatures, if adsorption [20] or diffusion to equilibrium [21] is the principle mechanism. As previous laboratory experiments on trapping of noble gases in magnetite have suffered from atmospheric contamination [22], which prevented previous workers from constraining the partial pressure of the noble gases during the experiments, we carried out our synthetic experiment under a rather dense noble gas atmosphere (partial pressures higher than those of the atmosphere) in order to avoid possible contamination of atmospheric noble gases during and/or after the experiments.

2. Experimental methods

2.1. Sample preparation

Synthesis of magnetite (Fe₃O₄) was carried out in a 1 atm. gas-mixing furnace with a mixture of H₂O and noble gases (in most of the runs, only Ar was introduced into the furnace) using the reaction:



About 1 g of Fe powder (a few microns in diameter) settled in an alumina crucible was oxidized by water vapor generated at 130–160°C. The water vapor was carried in a mixture of Ar (or noble gases) and H₂. The temperature of the reaction crucible was measured by thermocouples (Pt40Rh–Pt20Rh) located near the crucible. The flow rate of H₂O was determined by the amount of evaporated water in a

flask. The flow rate of H₂ and Ar was controlled by monitoring a flow meter, in order to obtain magnetite as a stable phase (e.g., $\log(P(\text{H}_2\text{O})/P(\text{H}_2)) = 2 \sim 4.6$; Table 1). The partial pressure of ³⁶Ar during the experiments was typically on the order of 10⁻⁴ atm, which is an order of magnitude higher than that in the atmosphere.

After being allowed to react overnight in the furnace, the samples were quenched to room temperature under a stream of H₂-H₂O-noble gas atmosphere. Run products were observed under a SEM equipped with an electron probe microanalyzer (JEOL733 at Osaka University). The reaction to synthesize magnetite was almost completed for run temperatures above 800°C. In the case of the synthe-

sis at lower temperature, about 20% of the Fe remained unreacted. Wüstite was also observed in the experiments done at 600–800°C. To remove unreacted Fe from magnetite, 10% peroxosulfate was applied. Separation of magnetite and wüstite was not feasible.

A total of 12 samples were prepared in order to examine the Ar trapped in the magnetite during the experiments. In order to examine possible elemental fractionation, syntheses were carried out under a dense noble gas atmosphere at 500 and 1200°C. The standard noble gas mixture used in this study consists of 96% of Ar and 1% each of He, Ne, Kr, Xe by volume (isotopic compositions are atmospheric).

From the SEM observations, the synthesized mag-

Table 1
Experimental conditions and ³⁶Ar abundance in synthetic magnetite

Sample	Time (min.)	Temp. (°C)	log(H ₂ O/H ₂)	P- ³⁶ Ar (10 ⁻⁴ atm)	Products(*) (wt% of Fe)	³⁶ Ar (x10 ⁻⁸ cm ³ STP/g)		
						800°C	1600°C	Total
500-03	363	500	2.0	3.56	Mt+Fe(19)	0.952	20.4	21.4
600-01	270	600	2.0	3.87	Mt+Wu+Fe(15)	0.166	4.01	4.18
600-02	882	600	2.3	4.00	Mt+Wu+Fe(8)	0.352	2.55	2.90
600-03	1274	600	2.1	0.689	Mt+Wu	0.375	2.98	3.36
700-01	333	700	2.3	3.70	Mt+Wu+Fe(17)	0.193	4.76	4.95
800-01	363	800	2.4	3.38	Mt+Wu	0.712	2.25	2.96
800-02	454	800	2.7	2.98	Mt	0.729	2.02	2.75
800-03	1108	800	2.2	4.54	Mt	0.128	1.72	1.85
1000-01	380	1000	4.7	3.61	Mt	0.336	1.12	1.46
1000-02	1277	1000	2.2	4.31	Mt	0.518	1.41	1.93
1200-01	1409	1200	2.5	4.48	Mt	0.160	0.823	0.983
1300-01	1042	1300	2.6	3.86	Mt	0.211	0.783	1.00

^a Mt = Magnetite, Wu = Wüstite.

netite appears to have a structure typical of sinter, which is an aggregate of euhedral crystals with large numbers of pores. The grain size of the run products tended to be larger than the iron powder of the starting material (a few microns), and the grain size shows a clear increase with temperature (from < 10 μm at < 900°C to a few hundred micrometers at 1300°C). The sizes of the pores are variable and typically smaller than approximately 100 μm (Fig. 1).

2.2. Noble gas measurement

Amounts of noble gases were measured by mass spectrometer at Osaka University. The mass spectrometer used is a single focusing instrument with a 15 cm radius, and a 55° angle for both incident and exit paths. The details of sample handling for noble gas analysis (e.g., sample cleaning, baking of samples and vacuum line, purification, blank corrections, etc.) are essentially the same as those used by of Osaka University noble gas group [23], thus will not be described fully. The samples were heated at 150°C for several hours in the high-vacuum line to remove surface adsorbed atmospheric gases. Noble gases trapped in the samples are extracted in two steps, at 800°C (for further removal of adsorbed atmospheric gases) and at 1600°C (for total fusion). Extracted reactive gases were trapped by two-stage Ti–Zr getters at 800°C. He and Ne were separated from the heavier noble gases, which remained on a charcoal trap at liquid nitrogen temperature, and analyzed. Then, desorbed heavier noble gases were admitted to

the mass spectrometer. Blank level was monitored occasionally during sample analysis; typical blank levels during the runs are: 1×10^{-9} cm³ STP for ⁴He; 6×10^{-11} cm³ STP for ²⁰Ne; 2×10^{-11} cm³ STP for ³⁶Ar; 1.5×10^{-12} cm³ STP for ⁸⁴Kr and 6×10^{-13} cm³ STP for ¹³²Xe. Blanks were subtracted from the sample yields (they are negligible in most cases; < 1% of sample). Sensitivities for each noble gas were calibrated by analyzing known amounts of standard gases between the sample runs. Variations in the sensitivities were generally less than 10%.

2.3. Size dependence of noble gas concentration

There are three possible sources of noble gases in the samples:

1. noble gases adsorbed on the surface of the samples;
2. noble gases trapped in the crystal lattice during experiments;
3. noble gases trapped in the pores (Fig. 1).

Our interest is, in this case, the composition of noble gases in the lattice. The effect of (1) and (3) should be removed experimentally. With regard to removing the adsorbed noble gases, both the step-heating technique and prebaking the samples in the vacuum are known to be effective. Gases trapped in pores were removed before the installation of the samples into the high-vacuum line by crushing the samples smaller than the size of the vesicles.

In order to find an appropriate grain size for determining the amount of noble gas trapped in the

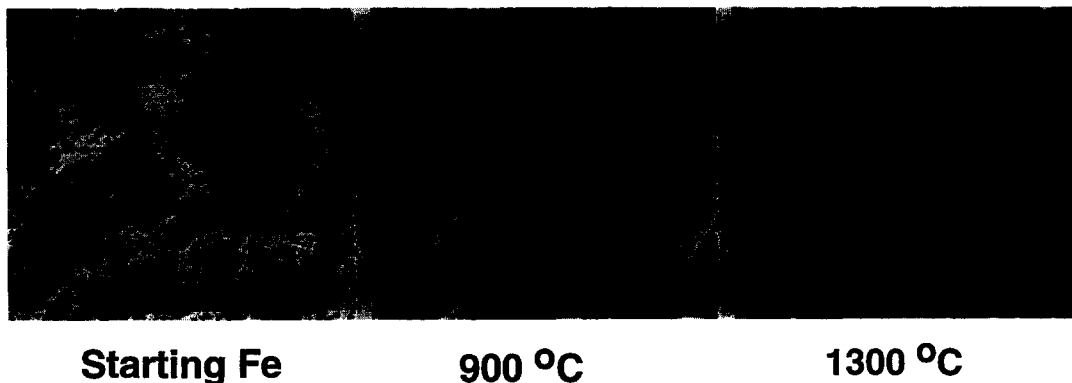


Fig. 1. SEM images of the starting material and products of the experiments. Scale shown is 50 μm .

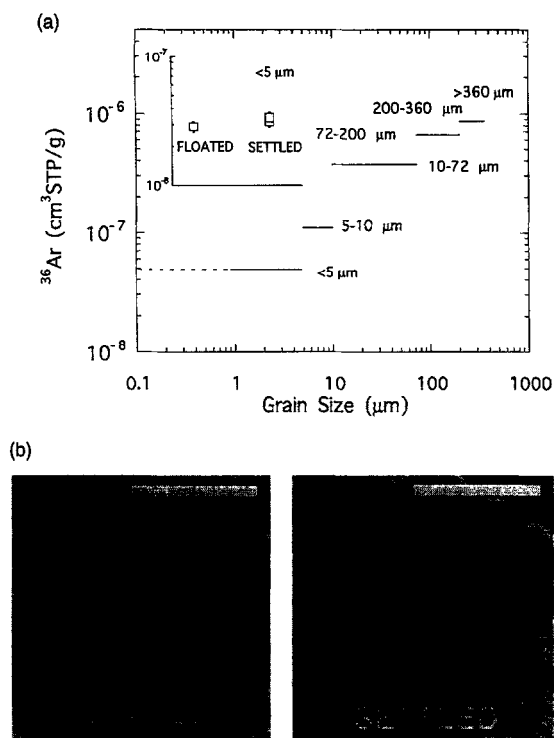


Fig. 2. (a) Argon concentrations in magnetite vs. the grain size of the samples. Separation was made by nylon filters for > 5 mm fractions. The results of < 5 mm grains are superimposed in the upper left-hand side of the diagram. (The sample used for the < 5 mm separation is not the same sample as for the nylon filter separation.) (b) SEM image of the grains separated using liquid flotation.

crystal lattice, we prepared several size fractions of samples by using nylon filters (5–360 mm), and analyzed the argon concentration in each size fraction. Fig. 2a illustrates the size dependence of argon concentration in our sample. The concentration of argon gradually decreases from 10^{-6} cm^3 STP/g in uncrushed sample to 5×10^{-8} cm^3 STP/g in grains filtered by 5 mm mesh. We conclude that argon trapped in pores is released by crushing.

As separation by the nylon filter appeared to be ineffective for grains smaller than the ~ 5 micron range, because of the contamination of relatively larger grains, we used the relation between grain size and settling time in a liquid medium for further separation. The grains passing through the 5 mm mesh were agitated ultrasonically in acetone, then floating particles were scooped and gathered after 90

sec to allow larger grains to settle to the bottom. Floated grains were smaller than 3 mm in diameter, whereas settled grains were up to 10 mm in diameter as, observed by SEM (Fig. 2b). This means of separation appeared to be effective.

As shown in the upper left-hand portion of Fig. 2a, the concentrations of argon in the floated and settled fractions agree within 10% experimental uncertainty. Therefore, the effect of gases trapped in pores can be removed by crushing the bulk sample to less than 5 mm. As the diameter of the starting iron powder used in this study is a few microns, we can conclude that no further crushing is required for removing the gases in the pores. However, we sieved grains through a 1 mm mesh in order to ensure that our measurements reflect noble gas content trapped in the lattice.

3. Results and discussions

The results of measurements of noble gases by two-stage step heating of < 1 mm grains are shown in Table 1 for argon and Table 2 for all noble gases, together with the experimental conditions.

Table 2
Noble gas abundance in synthetic magnetite

	Partial Pressure (10^{-4} atm)	Concentration ($\times 10^{-8}$ cm^3 STP/g)		
		800 °C	1600 °C	Total
500 °C (304 min.)				
^4He	8.28	< 12.6	10.2	< 11.4
^{20}Ne	7.49	0.996	13.0	14.0
^{36}Ar	2.67	7.30	5.89	13.2
^{84}Kr	4.72	1.33	9.95	11.3
^{132}Xe	2.23	0.324	8.98	9.31
1200 °C (373 min.)				
^4He	8.56	< 0.710	0.160	< 1.55
^{20}Ne	7.75	0.0331	0.707	0.740
^{36}Ar	2.76	0.133	1.06	1.19
^{84}Kr	4.88	0.029	1.74	1.77
^{132}Xe	2.30	0.969	2.41	3.38

In most of the runs, the fraction of argon released in the 800°C fraction was at most 30% of the total gas, thus most of the gases trapped during synthesis are held in retentive sites in the magnetite structure. We believe that the gases released at 800°C were the atmospheric component adsorbed on to the grain surface during sample handling, because we observe a weak positive correlation between the amount of argon released at 800°C and the grain size of the samples (surface area per mass is proportionately larger for smaller grains). Given this type of treatment, we consider that only the gas released during the 1600°C steps reflects the trapped noble gas component.

3.1. Pressure dependence

If gas concentrations trapped in synthetic magnetite are due to equilibrium solubility or adsorption, one would expect them to obey Henry's law; gas concentration would be proportional to ambient partial pressures at given temperatures. As we noted above, magnetite synthesis was carried out under relatively high noble gas partial pressures. The ambient partial pressure during the experiments was one or two orders of magnitude higher than that in the atmosphere for He, Ne and Ar, and three to four orders of magnitude higher for Kr and Xe. Lancet and Anders [24] reported that noble gases trapped in magnetite reached saturation levels at pressures above 10^{-5} atm for Ar, Kr and Xe. In our experiments, partial pressures are even higher. Therefore, it would be reasonable to assume that Henry's law is not applicable for the pressure range of our experiments, and that the concentrations of noble gases in the synthetic magnetite in our experiments represents the saturated concentration of noble gases. The observed constant argon concentration over an order of magnitude variation in partial pressure for the three 600°C runs (Table 1) actually suggests that our magnetites are saturated with about 10^{-8} cm³ STP/g of argon. In addition, three runs performed at 800°C also show constant argon concentrations irrespective of the ambient pressure they synthesized.

It is known that silica glasses [21] and some silicates [25] can trap large amounts of noble gases without reaching saturation. Silica glass is the most significant for its noble gas capacity: up to 1 wt% of

argon can be incorporated [21]. However, it is also known that the lunar ilmenite is supposed to be saturated with ⁴⁰Ar at 1×10^{-4} cm³ STP/g [26], which is a much lower concentration than argon in the silica glasses but is comparable to the amount of ⁴⁰Ar in our magnetites. Therefore, noble gas saturation levels are highly dependant on host phases, and it is not surprising that we observed a significantly lower saturation level for argon concentration in our magnetites than that observed in silica glass and silicate minerals. One important factor which affects the saturation level of noble gases would be an openness of the crystal structure. The structure of silica glass is open for noble gases, since it has abundant structural holes of a size large enough for noble gas atoms (the suggested number of structural holes occupied by argon in silica glass is about 4×10^{20} hole/cm³, which is about 5% of total structural holes [21]). In contrast, for closed-packed crystals like magnetite, where structural holes cannot be effective sites [24], noble gas must be occupying either more confined interstitial sites or defects such as cation or anion vacancies.

3.2. Temperature dependence

As there is no apparent pressure dependence of argon concentrations, we will use concentration data themselves to discuss the temperature dependence of the trapped noble gas amounts, instead of presenting distribution coefficients to cancel the pressure effect expected from Henry's law. The concentrations of ³⁶Ar varied over an order of magnitude from 8×10^{-9} cm³ STP/g at 1300°C to 2×10^{-7} cm³ STP/g at 500°C. As shown in Fig. 3, there is a clear negative correlation between temperature and argon concentration. The observed negative temperature dependence of the trapped argon in the magnetite implies that the argon is trapped either by adsorption [20] or diffusion processes [21].

Incorporation by diffusion can be excluded, because of the apparently slow diffusion of noble gases in magnetite. Extrapolating the diffusion data obtained by Futagami et al. [27] for helium implanted into magnetite, we estimated the diffusion coefficient [$\log_{10} D$ (cm²/sec)] of helium in magnetite. The diffusion coefficients vary from -15.0 at 500°C to -12.1 at 1300°C, and corresponding helium diffu-

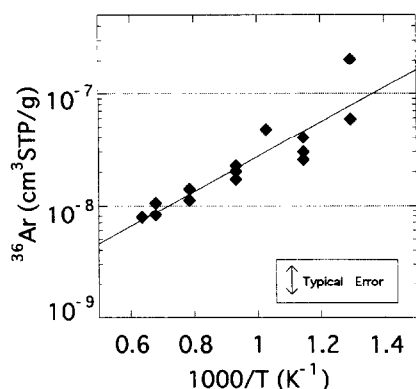


Fig. 3. Arrhenius diagram of argon concentration and synthetic temperature. The solid line represents the least-squares fit for the data ($R = 0.89$).

sion lengths at those temperature ranges in 24 hours are from 0.1 μm to 3 μm . Thus, the estimated diffusion length of helium appears to be insignificant in comparison with the grain sizes of magnetites. In addition, the distances between pores in magnetite grains are also larger than the estimated diffusion length of helium. Taking into account much slower diffusion rates for heavier noble gases, we conclude that trapping by diffusion is not responsible for the noble gas trapped in our experiments. Rather, we conclude that the observed negative temperature dependence of argon concentrations is due to an adsorption process. The slope of the correlation line can be converted to the heat of adsorption (ΔH) using the relation:

$$\Delta H = RT^2 \frac{d(\ln C)}{dT}$$

where R = gas constant; T = absolute temperature; C = concentration of noble gases. The heat of adsorption of argon on magnetite is calculated to be -32 kJ/mol, which is within the range of physisorption, and close to the value (-24 kJ/mol) obtained by Maruoka and Matsuda [28] on a sintered steel filter element. Physical adsorption is not consistent with the high release temperatures for noble gases from our samples. In fact, there is an example of (relatively retentive) chemical adsorption of noble gases, involving a relatively high activation energy ($> \sim 80$ kJ/mol). Xenon is known to be chemisorbed on fresh or thoroughly outgassed sur-

faces (e.g., 'anomalous adsorption of xenon', where a significant amount of atmospheric xenon is chemisorbed on freshly created grain surfaces of lunar gas-rich breccias [29]). However, the apparently low activation energy of adsorption suggests that the adsorption of argon is probably physisorption. We can assume that this is true for lighter noble gases (He, Ne and probably true for Kr). Tight bonding of xenon in our samples might be enhanced by chemisorption, but the majority of xenon would be trapped by physisorption. Yang et al. [24] suggested that a chemisorbed xenon component in their synthetic magnetite was about 10% of total adsorbed xenon. Since the efficiency of chemical adsorption of noble gases is strongly dependent upon sorbent [30], we can assume that the chemisorbed xenon is not a major component in our magnetite samples as well.

3.3. Fixation process (trapping model)

The observation of tightly bonded but adsorbed noble gases in the magnetite implies an involvement of some additional process(es), which is responsible for fixing the adsorbed noble gases retentively in magnetite. According to the SEM observations of our samples (Fig. 1), crystal growth undoubtedly occurred during synthesis, and played an important role in fixing the adsorbed noble gas atoms. The surface of magnetite on which the noble gas atoms are adsorbed keeps growing during the experiment. Through the crystal growth process, adsorbed gases are occluded by the newly created lattice, and fixed (i.e., *occlusion* [30]). This process can explain the temperature dependence of adsorption as well as the tight bonding of noble gases into magnetite.

The most probable mechanism for the observed crystal growth would be oxidation of iron. In addition, as mentioned earlier in this paper, we observed grain growth, which is typical for the sintered material. In the case of synthesis at higher temperatures, grain growth is probably enhanced by a ripening process. Therefore, coarsening of magnetite crystals, or grain growth, is another mechanism for fixing the adsorbed noble gas atoms. However, as we did not observe any correlation between the amount of trapped noble gases released at 1600°C during step heating and experimental time, fixing of the adsorbed noble gases must clearly have occurred by

crystal growth of magnetite during oxidation of the iron.

Some over-saturated gases might be occluded through the oxidation process. They might be sited in the lattice and during experiment become exsolved to form pores on the atomic scale. However, as we observed the clear negative correlation between the amount of trapped gases and synthetic temperature, the amount of occluded over-saturated gases would have only a minor effect on the overall trapping model presented here.

A temperature dependence for trapped argon in magnetite was not observed by Yang et al. [22]. This might be partly because of difficulty in obtaining appropriate distribution coefficients for their experiments (the source of the gases is likely to be a contaminant from atmosphere rather than from the reaction vessel, as the authors themselves indicated). This problem is negligible in our experiment, because the pressures of noble gases are well above the atmospheric level. The model we presented above based on the argon results can be expanded to the other noble gases, as discussed below. The results of experiments carried out under a noble gas atmosphere at 500 and 1200°C are shown in Table 2, and the resultant fractionation of the trapped noble gases (defined as $C_{\text{noble gas}}/C_{\text{Xe}}$; where C denotes concentration) is shown in Fig. 4. Concentrations of trapped noble gases at 500°C are greater than those at 1200°C, suggesting that adsorption is the principal mechanism governing the amount of trapped noble gases in magnetite. Although we cannot calculate heats of

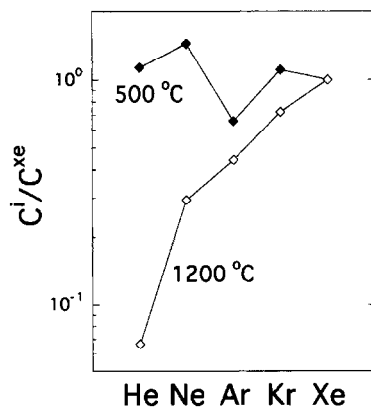


Fig. 4. Fractionation pattern of noble gases in synthesized magnetite at 500 and 1200°C (C^i is the concentration of noble gas i).

adsorption for each noble gas, because of a lack of data points, we can crudely estimate the relative heat of adsorption by obtaining the ratio $C_{500^\circ\text{C}}^i/C_{1200^\circ\text{C}}^i$ (C_T^i = concentration of noble gases i at temperature T). The value of $C_{500^\circ\text{C}}^i/C_{1200^\circ\text{C}}^i$ progressively decreases as the mass of noble gases increases; 63 for helium to 3.7 for xenon, suggesting that the adsorption of lighter gases is dramatically enhanced at lower temperatures, whereas that of heavier gases is less sensitive to temperature variations. This indicates a smaller absolute value for the negative heat of adsorption for lighter noble gases, which is quite a common feature of adsorption of noble gases on solid materials. For example, the heat of adsorption of noble gases on a sintered stainless steel filter element given by Maruoka and Matsuda [28] is a good example of the small absolute value of negative heat of adsorption for the lighter noble gases. Therefore, we can expand the trapping model discussed above to all five noble gases.

The fractionation pattern of noble gases adsorbed onto a solid surface is a function of temperature. This is due to a larger absolute value of negative heat of adsorption for the lighter noble gases, compared with less temperature dependence for the adsorption of heavier noble gases (Kr and Xe). In our experiments, and at low trapping temperatures, the fractionation pattern is relatively flat (He/Xe = 1.1). In contrast, at 1200°C, the elemental pattern shows enrichments of the heavier noble gases (He/Xe = 0.066).

3.4. Implication for noble gases in the chondritic magnetite

Jeffery and Anders [5] studied noble gases in magnetite separates from the CI chondrite Orgueil. If the magnetite in Orgueil had formed through direct condensation from the nebular gas, or by reaction between water vapor and previously condensed Fe-bearing minerals, the trapping process of noble gases should resemble our experiment. The Orgueil magnetite samples contain $(1-3) \times 10^{-7}$ cm³ STP/g of ³⁶Ar. If the correlation line shown in Fig. 3 is extrapolated, the trapping temperature expected from the correlation line would be 400–700 K. This temperature range is consistent with the condensation temperature of magnetite (< 400 K) in primitive

solar nebula, as suggested by the theoretical calculation done by Grossman and Larimer [7]. If we take into account the pressure difference between our experiment and that in the primitive solar nebula, the temperature of noble gas trapping should be lower than 400 K, because the adsorption of noble gas would not be saturated at nebular pressure.

Another interesting aspect of chondritic magnetite is that the elemental ratios of He, Ne and Ar are close to that of the solar composition. The unfractionated light noble gases in the Orgueil magnetite have been interpreted as implanted solar noble gases [5], because adsorption would fractionate noble gas compositions. However, the present magnetite experiment shows that adsorbed noble gases could show seemingly unfractionated noble gas elemental patterns even though noble gases are actually adsorbed on magnetite. We have to admit that the argument is rather qualitative because of the small data set for He, Ne, Kr and Xe, but the point is that the apparently non-selective adsorption is possible, especially at lower temperatures.

There are, however, several lines of evidence to suggest that the chondritic magnetite has been formed by aqueous alteration on planetesimal surfaces or parent bodies of meteorites [4,10,11,31]. Although the observed amount of argon and the elemental pattern is consistent with the formation of magnetite by a reaction between water vapor and Fe (or Fe-bearing minerals) in the primitive solar nebula at low temperature, we cannot discount the aqueous alteration model. Comparison experiments which synthesize magnetite with aqueous water are necessary for further discussion on the origin of the chondritic magnetite and its noble gases.

Finally, the presented results confirm the general importance of adsorption as the principle mechanism for noble gas incorporation into grains formed in the presence of gas phases (e.g., [32]). The fixation of loosely physisorbed gas atoms by grain growth should be applicable for other minerals condensed in the early solar nebula.

4. Conclusions

From the above the following conclusions can be drawn:

(1) The synthesis of magnetite across a wide temperature range and under a noble gas atmosphere has been successful under a noble gas atmosphere. We observed a clear negative temperature dependence for retentively-sited argon. Both the temperature dependence of trapped noble gases and the elemental fractionation pattern suggest that the first step of noble gas trapping in magnetite is (physical) adsorption. As this adsorption and growth by oxidation proceed, adsorbed noble gas atoms can be buried by newly created crystal and be occluded in the magnetite structure.

(2) The elemental fractionation pattern is also temperature dependent, as indicated by smaller absolute values of negative heats of adsorption for lighter noble gases. In this respect, the fractionation pattern of noble gases trapped into solids become less steep as trapping temperature decreases.

(3) The concentration of argon in the chondritic magnetite can be explained by adsorptive trapping of ambient noble gases at the likely condensation temperature of magnetite in the solar nebula. Unfractionated helium, neon and argon compositions in the chondritic magnetite are qualitatively consistent with the results of the present study.

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