

The effect of pyridine treatment on phase Q: Orgueil and Allende

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Abstract—Marrocchi et al. (2005) reported that low-temperature fractions of heavy noble gases were largely removed upon pyridine treatment of the Orgueil CI meteorite. As pyridine is known to induce the swelling of the macromolecular network of organic matter, they concluded that the low-temperature phase Q is macromolecular organic carbon. However, Busemann et al. (2008) showed that pyridine had no significant effect on the noble gas contents for other very primitive meteorites, such as CM and CR. Therefore, we prepared an HF–HCl residue and the pyridine-treated residue of Orgueil, and re-examined the results of Marrocchi et al. (2005) by analyzing all noble gases. We confirmed that heavy noble gases are surely removed by the pyridine treatment, but the degree of the loss of heavy noble gases is generally small, and is even smaller for the lighter noble gases. Furthermore, we could not observe the evidence of Xe isotopic ratios by removing only phase Q after the pyridine treatment. We further prepared the HF–HCl residue and the pyridine-treated residue of the Allende CV3 meteorite and performed noble gas analyses. For Allende, there is no significant change in the elemental abundances after the pyridine treatment. These results suggest that only Orgueil is special, and it is likely that the gas loss of the Orgueil residue is due to the loss of some kind of organic matter that was formed and that adsorbed the fractionated Q and HL gases during the aqueous alteration within the parent body of Orgueil.

INTRODUCTION

Noble gases, especially primordial heavy noble gases, are not uniformly contained in a meteorite, but are trapped in a very small portion of the meteorite called phase Q (e.g., Lewis et al. 1975). It is very puzzling that chemically inert noble gases are only contained in such a small portion of a meteorite. Phase Q is contained in the HF–HCl residue, which is only 0.2–3% of the meteorite in primitive undifferentiated classes (Huss and Lewis 1995; Huss et al. 2003), and is dissolved out by using an oxidant such as HNO₃, Na₂Cr₂O₇ and H₂O₂, etc. In the case of Allende, phase Q is only 0.02–0.04% of the bulk meteorite (Lewis et al. 1975).

The noble gas in phase Q is elementally enriched in heavier noble gases with “isotopically normal”

composition, and is called Q-gas or P1 (Huss and Lewis 1994). “Isotopically normal” means that isotopic compositions are not too different from solar (Wieler et al. 2006). It is now known that phase Q is a carbonaceous phase (Reynolds et al. 1978; Ott et al. 1981), but the specific type of carbonaceous material has not yet been established. Phase Q should be a very minor carbon phase that is different from the major carbon phase, as Verchovsky et al. (2002) reported that the release temperature of major carbon is different from that of noble gases. Phase Q is present in carbonaceous chondrites (Alaerts et al. 1979b; Matsuda et al. 1980), ordinary chondrites (Alaerts et al. 1979a; Moniot 1980), and even in a graphite nodule in Canyon Diablo iron meteorite (Matsuda et al. 2005), suggesting that phase Q was very abundant in the early solar system.

Matsuda et al. (1999) found that a material similar to the HF–HCl residue containing phase Q was also obtained as a material floating on the surface of water during the freeze-thaw disaggregation. They found that this floating fraction has elemental and isotopic abundances of noble gases similar to those in the HF–HCl residue. Only the $^{129}\text{Xe}/^{132}\text{Xe}$ ratio in the HF–HCl residue was much higher than that in the floating fraction, which was considered to be due to the readsorption of ^{129}Xe from iodine minerals in the bulk during the chemical treatment. Amari et al. (2003) further applied a density separation to this floating fraction, and found that the fraction with the density of $1.65 \pm 0.04 \text{ g cm}^{-3}$ had the highest noble gas concentrations, and that half of the Xe-Q in the original floating fraction was contained in this fraction. Matsuda et al. (2009) examined this fraction by Raman spectroscopy and found that this highest Q-rich fraction has the lowest intensity ratios for the D band and G band (I_D/I_G). The carbon material in this Q-rich fraction of Allende was also very sensitive to the laser power of Raman spectroscopy. Recently, Matsuda et al. (2010) showed that phase Q is enriched in amorphous carbon and that the release of Q-gases is due to the rearrangement of the carbon structure because the Raman parameters of carbon in the HF–HCl residue changed noticeably after the oxidation that is supposed to destroy phase Q.

Gros and Anders (1977) proposed that there were two subtypes (Q1 and Q2) for phase Q. Q1 contains most of the heavy noble gases and is readily soluble in cold diluted HNO_3 , while Q2 is slowly dissolved in hot concentrated HNO_3 and contains much less gas than Q1. Busemann et al. (2000), also proposed two carbonaceous phases with slightly distinct chemical properties for phase Q, but it is not clear whether their subphases are the same as those proposed by Gros and Anders (1977).

Marrocchi et al. (2005) reported that heavy noble gases in the HF–HCl residue from the Orgueil meteorite were largely lost, especially at the low-temperature fractions, upon pyridine treatment at room temperature. As pyridine is known to induce swelling of the macromolecular network, they concluded that the low-temperature phase Q is macromolecular organic carbon. However, Busemann et al. (2008) reported that pyridine treatment had no significant effect on the elemental and isotopic noble gas compositions of the HF–HCl residue of Bells (CM2), EET 92042 (CR2), GRO 95577 (CR1), and Murchison (CM2) meteorites.

Therefore, we prepared the HF–HCl residue of Orgueil and its pyridine-treated sample, and re-examined the results of Marrocchi et al. (2005). We measured the elemental abundances and isotopic

compositions of all noble gases by a stepwise-heating method with five temperature steps, although Marrocchi et al. (2005) only measured the concentrations of ^{36}Ar , ^{84}Kr and ^{132}Xe and the isotopic composition of Xe. After the experiment on Orgueil, we also prepared the HF–HCl residue of Allende and its pyridine-treated sample, and examined the elemental abundances and isotopic compositions of Ar and Xe by a stepwise-heating method.

SAMPLE PREPARATION

A 1.2602 g aliquot of Orgueil was dissolved with HF–HCl. The original HF–HCl residue obtained was 43.4 mg. The residue yield of 3.6% for Orgueil was the same as that reported by Huss and Lewis (1995). The original HF–HCl residue was further treated with fresh pyridine for 2 days at room temperature. The pyridine was removed by evaporation at 60–90 °C for 2 days. There was no measurable mass loss during the pyridine treatment. For Allende, a fragment weighing 4.9154 g was dissolved with HF–HCl and another treatment using 0.6 M H_3BO_3 –6 M HCl and 6 M HCl–2 M HF, and we obtained an HF–HCl residue. The residue yield was 1.5%, which is a little bit higher than that obtained by Lewis et al. (1975). The original HF–HCl residue of Allende was treated with pyridine for 3 days at room temperature, and then dried at 100–110 °C for 2 days.

EXPERIMENT

Noble Gases

Noble gas measurements were carried out at Osaka University with a gas extraction at 600, 800, 1000, 1200, and 1600 °C in a Mo crucible with a Ta heater using a sector-type mass spectrometer VG5400 (VG Isotech, UK). The gas purification and the details of the noble gas measurements are given in our previous works (Matsuda et al. 2005; Nishimura et al. 2008). We measured the elemental abundances and the isotopic compositions of all noble gases for the Orgueil samples, but only the isotopic compositions of Ar and Xe for Allende. All the sample data were blank-corrected based on hot blanks measured prior to the sample analysis. We measured the procedural hot blanks at 1000 and 1600 °C, and applied the former to 600, 800, 1000 °C measurements and the latter to the 1200 and 1600 °C measurements of Orgueil, but applied the 1600 °C blank for all the temperature data for Allende. For example, the measured typical hot blanks at 1600 °C were as follows: $^4\text{He} = 7.9 \times 10^{-10}$, $^{22}\text{Ne} = 5.8 \times 10^{-13}$, $^{36}\text{Ar} = 8.4 \times 10^{-12}$, $^{84}\text{Kr} = 1.2 \times 10^{-12}$, $^{132}\text{Xe} = 1.1 \times 10^{-13} \text{ cm}^3 \text{ STP}$. The blank corrections were almost

negligible for all the data. The errors of the noble gas concentrations are on the order of 10%, including the error of the line volume.

Raman Spectroscopy

We carried out Raman spectroscopic studies for the Orgueil HF–HCl residue and its pyridine-treated sample by using a Raman microscope (Kaiser HoloLab 5000; Kaiser Optical Systems, Inc.) equipped with a 532 nm YAG laser, holographic transmission grating, and a charge-coupled device detector. We used a laser power of 0.5 mW at the sample surface. We obtained the Raman spectrum using 10 accumulations of 30 s each. The excitation laser spot size was approximately 2 mm in diameter. A typical Raman spectrum of disordered graphitic carbon (G band of about 1580 cm^{-1} and D band of about 1350 cm^{-1}) was obtained for both samples. The spectra of carbon were corrected from the fluorescence background by subtracting a linear baseline at $1000\text{--}2000\text{ cm}^{-1}$ range, assuming two Lorentzian profile curves. The peak positions (ω_G and ω_D), intensities (I_G and I_D) and the FWHM (full-width at half-maximum; FWHM_G and FWHM_D) of the G and D bands were obtained from these curve fittings to define the spectral parameters used to characterize various forms of carbon.

RESULTS AND DISCUSSION

Orgueil

Tables 1 to 3 show the results of noble gas concentrations and isotopic ratios of the HF–HCl residue of Orgueil and its pyridine-treated sample. We have no Xe data of the $600\text{ }^\circ\text{C}$ fraction of the Orgueil HF–HCl residue because we had an accident which pumped out this gas fraction before measurement. Figure 1 compares the total noble gas concentrations in the HF–HCl residue and its pyridine-treated sample in our study with those reported by Marrocchi et al. (2005) and those of the HF–HCl residue reported by Huss et al. (1996). Marrocchi et al. (2005) and Huss et al. (1996) show nearly identical ^{36}Ar , ^{84}Kr , and ^{132}Xe concentrations, and our elemental noble gas concentrations of the original HF–HCl residue are also almost identical, except for slightly lower ^{36}Ar and ^4He concentrations compared to those of the former studies. The total elemental abundances of noble gases of our pyridine-treated residue were higher than those of Marrocchi et al. (2005), but confirmed that pyridine treatment surely decreased the noble gas concentrations in the original HF–HCl residue. Figure 2 shows the proportion of noble gas contents in each temperature

fraction to the total of the HF–HCl residue of Orgueil. For ^{132}Xe , the proportions are to the total of the HF–HCl residue without the $600\text{ }^\circ\text{C}$ fraction. The very large decrease to about 20% at the $1000\text{ }^\circ\text{C}$ fraction of ^{132}Xe is remarkable. The percentage losses of the total noble gas abundances in the original HF–HCl residue of Orgueil were 21% (^4He), 26% (^{22}Ne), 27% (^{36}Ar), 40% (^{84}Kr), and 45% (^{132}Xe : comparison without $600\text{ }^\circ\text{C}$ fractions). For ^{132}Xe , the percentage loss would be 34% if we assume that the ^{132}Xe concentration in the HF–HCl residue is the same as that in the pyridine residue. If pyridine treatment decreases the ^{132}Xe concentration, this 34% would be the lower limit. The percentage losses of noble gases after the pyridine treatment in Marrocchi et al. (2005) were 58% (^{36}Ar), 55% (^{84}Kr), and 61% (^{132}Xe). Thus, our loss fractions are lower than those of Marrocchi et al. (2005). In addition, the loss fractions in our samples are smaller for the lighter noble gas, suggesting that the dissolved noble gases are fractionated more than those in the original HF–HCl residue. This is very different from the result of Marrocchi et al. (2005) where the percentage decreases were nearly constant (about 60%) for all heavy noble gases.

There is no significant difference in the He, Ar, and Kr isotopic ratios for the HF–HCl residue of Orgueil and its pyridine-treated samples (Tables 1–3). Figure 3 is a Ne three-isotope plot. We also plot the total data of the HF–HCl residue of Orgueil obtained by Huss et al. (1996). All our data are plotted at the lower left side of Ne-Q and Ne-HL, suggesting the presence of Ne-E, as indicated by previous authors (Eberhardt 1974; Huss et al. 1996). The data of $1600\text{ }^\circ\text{C}$ fractions of our HCl–HF residue and its pyridine-treated sample show very low $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{21}\text{Ne}/^{22}\text{Ne}$ ratios, indicating the presence of Ne-E(H) (high temperature Ne-E) whose host phase is SiC. Our total $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{21}\text{Ne}/^{22}\text{Ne}$ ratios are slightly higher than those of Huss et al. (1996). It appears that the $^{20}\text{Ne}/^{22}\text{Ne}$ ratios of the pyridine-treated samples are systematically lower than those of the original HF–HCl residue although the differences are not so large, indicating that the pyridine treatment did not affect SiC (host phase of Ne-E(H)) but dissolved out some phase containing a primordial (HL + Q + air?) component.

Figure 4 shows a $^{134}\text{Xe}/^{132}\text{Xe}$ versus $^{136}\text{Xe}/^{132}\text{Xe}$ diagram of the HF–HCl residue of Orgueil and its pyridine-treated sample. The total Xe data point of the HF–HCl residue by Marrocchi et al. (2005) is nearly identical to that by Huss et al. (1996). The data point of the pyridine-treated sample of Orgueil in Marrocchi et al. (2005) is located at the upper right side and on the Q and HL mixing line, indicating that pyridine treatment surely decreased the Q-gas. Our data points

Table 1. Concentration and isotopic ratio of He, Ne, and Ar for Orgueil.

Sample	Temp. (°C)	[⁴ He]	³ He/ ⁴ He	[²² Ne]	²⁰ Ne/ ²² Ne	²¹ Ne/ ²² Ne	[³⁶ Ar]	³⁸ Ar/ ³⁶ Ar	⁴⁰ Ar/ ³⁶ Ar
		10 ⁻⁶ cm ³ STP g ⁻¹	10 ⁻⁴	10 ⁻⁸ cm ³ STP g ⁻¹	10 ⁻⁸ cm ³ STP g ⁻¹	10 ⁻⁸ cm ³ STP g ⁻¹	10 ⁻⁸ cm ³ STP g ⁻¹	10 ⁻⁸ cm ³ STP g ⁻¹	
HF-HCl residue (1.09 mg)	600	350	2.15 ± 0.02	20	8.944 ± 0.054	0.0292 ± 0.0009	850	0.18835 ± 0.00088	7.81 ± 0.18
	800	770	1.41 ± 0.02	11	8.718 ± 0.072	0.0303 ± 0.0012	210	0.18859 ± 0.00043	0.1119 ± 0.0077
	1000	510	1.53 ± 0.01	25	8.256 ± 0.053	0.0339 ± 0.0008	560	0.18970 ± 0.00045	<0.074
	1200	200	1.54 ± 0.01	16	7.506 ± 0.052	0.0299 ± 0.0011	340	0.18931 ± 0.00042	<0.13
	1600	49	2.25 ± 0.03	8.7	5.068 ± 0.066	0.0188 ± 0.0014	230	0.18894 ± 0.00042	0.212 ± 0.014
Total	1900		1.62 ± 0.01	81	7.997 ± 0.026	0.0298 ± 0.0005	2200	0.18893 ± 0.00037	—
Pyridine residue (1.09 mg)	600	260	2.11 ± 0.02	11	7.169 ± 0.055	0.0268 ± 0.0013	600	0.18689 ± 0.00041	1.4082 ± 0.0064
	800	590	1.50 ± 0.02	9.7	8.436 ± 0.074	0.0324 ± 0.0010	150	0.18885 ± 0.00043	<0.22
	1000	450	1.54 ± 0.02	20	7.979 ± 0.054	0.0321 ± 0.0008	370	0.18945 ± 0.00042	<0.080
	1200	160	1.54 ± 0.02	14	7.172 ± 0.053	0.0303 ± 0.0012	310	0.18899 ± 0.00042	<0.14
	1600	30	2.17 ± 0.03	5.3	5.140 ± 0.081	0.0177 ± 0.0021	170	0.18842 ± 0.00050	<1.2
Total	1500		1.64 ± 0.01	60	7.475 ± 0.028	0.0295 ± 0.0005	1600	0.18823 ± 0.00021	—
Q ^a			1.23–1.59		10.05–10.70	0.0291–0.0321		0.18727	
HL ^b			1.70		8.5	0.036		0.2270	
Air			0.01399		9.80	0.029		0.188	295.5

^aBusemann et al. (2000).^bHuss and Lewis (1994). This HL component of Ne (Ne-HL) is actually Ne-A2 (Ne-HL+P3) (Huss et al. 1996).

Table 2. Concentrations and isotopic ratios of Kr for Orgueil.

Sample	Temp. (°C)	[⁸⁴ Kr]	⁷⁸ Kr/ ⁸⁴ Kr	⁸⁰ Kr/ ⁸⁴ Kr	⁸² Kr/ ⁸⁴ Kr	⁸³ Kr/ ⁸⁴ Kr	⁸⁶ Kr/ ⁸⁴ Kr
		10 ⁻¹⁰ cm ³ STP g ⁻¹	10 ⁻¹⁰ cm ³ STP g ⁻¹	10 ⁻¹⁰ cm ³ STP g ⁻¹	10 ⁻¹⁰ cm ³ STP g ⁻¹	10 ⁻¹⁰ cm ³ STP g ⁻¹	10 ⁻¹⁰ cm ³ STP g ⁻¹
HF-HCl residue (1.09 mg)	600	1200	0.0098 ± 0.0016	0.0445 ± 0.0036	0.2030 ± 0.0186	0.1926 ± 0.0154	0.2906 ± 0.0160
	800	310	0.0060 ± 0.0004	0.0378 ± 0.0005	0.2068 ± 0.0026	0.2082 ± 0.0022	0.3085 ± 0.0031
	1000	1000	0.0061 ± 0.0002	0.0390 ± 0.0004	0.2007 ± 0.0011	0.2053 ± 0.0015	0.3113 ± 0.0010
	1200	590	0.0055 ± 0.0002	0.0366 ± 0.0007	0.2013 ± 0.0015	0.1983 ± 0.0019	0.3099 ± 0.0022
	1600	390	0.0065 ± 0.0003	0.0401 ± 0.0007	0.2102 ± 0.0018	0.2053 ± 0.0018	0.3129 ± 0.0017
Total	3500		0.0073 ± 0.0006	0.0405 ± 0.0013	0.2034 ± 0.0065	0.1999 ± 0.0054	0.3038 ± 0.0056
Pyridine residue (1.09 mg)	600	630	0.0060 ± 0.0003	0.0391 ± 0.0005	0.2043 ± 0.0012	0.2033 ± 0.0014	0.3052 ± 0.0012
	800	210	0.0066 ± 0.0003	0.0374 ± 0.0007	0.2020 ± 0.0025	0.1966 ± 0.0017	0.3084 ± 0.0030
	1000	620	0.0062 ± 0.0002	0.0378 ± 0.0004	0.2064 ± 0.0014	0.2034 ± 0.0023	0.3104 ± 0.0021
	1200	380	0.0055 ± 0.0003	0.0371 ± 0.0008	0.2019 ± 0.0022	0.1971 ± 0.0027	0.3143 ± 0.0032
	1600	270	0.0064 ± 0.0005	0.0392 ± 0.0007	0.2006 ± 0.0021	0.2046 ± 0.0022	0.3256 ± 0.0033
Total	2100		0.0061 ± 0.0001	0.0382 ± 0.0003	0.2038 ± 0.0008	0.2017 ± 0.0010	0.3113 ± 0.0011
Q ^a			0.00603	0.03937	0.2018	0.2018	0.3095
HL ^b			0.0043	0.0308	0.1600	0.1993	0.3603
Air			0.006087	0.03960	0.20217	0.20136	0.30524

^aBusemann et al. (2000).^bHuss and Lewis (1994).

Table 3. Concentrations and isotopic ratios of Xe for Orgueil.

Sample	Temp. (°C)	[¹³² Xe] 10 ⁻¹⁰ cm ³ STP g ⁻¹	¹²⁴ Xe/ ¹³² Xe	¹²⁶ Xe/ ¹³² Xe	¹²⁸ Xe/ ¹³² Xe	¹²⁹ Xe/ ¹³² Xe	¹³⁰ Xe/ ¹³² Xe	¹³¹ Xe/ ¹³² Xe	¹³⁴ Xe/ ¹³² Xe	¹³⁶ Xe/ ¹³² Xe
			—	—	—	—	—	—	—	—
HF-HCl residue (1.09 mg)	600	—	—	—	—	—	—	—	—	—
	800	360	0.0041 ± 0.0002	0.0040 ± 0.0002	0.0801 ± 0.0009	1.036 ± 0.010	0.1694 ± 0.0013	0.8223 ± 0.0048	0.3826 ± 0.0048	0.3296 ± 0.0043
	1000	1400	0.0047 ± 0.0001	0.0043 ± 0.0002	0.0837 ± 0.0010	1.040 ± 0.009	0.1653 ± 0.0013	0.8195 ± 0.0036	0.3849 ± 0.0042	0.3303 ± 0.0039
	1200	740	0.0046 ± 0.0001	0.0041 ± 0.0002	0.0830 ± 0.0011	1.029 ± 0.010	0.1681 ± 0.0013	0.8127 ± 0.0033	0.3909 ± 0.0043	0.3369 ± 0.0042
	1600	430	0.0047 ± 0.0003	0.0040 ± 0.0002	0.0804 ± 0.0011	1.023 ± 0.010	0.1660 ± 0.0015	0.8153 ± 0.0055	0.3798 ± 0.0052	0.3292 ± 0.0042
Pyridine residue (1.09 mg)	Total ^a	2900	0.0046 ± 0.0001	0.0042 ± 0.0001	0.0826 ± 0.0006	1.034 ± 0.005	0.1666 ± 0.0008	0.8175 ± 0.0021	0.3854 ± 0.0025	0.3317 ± 0.0023
	600	920	0.0046 ± 0.0002	0.0040 ± 0.0002	0.0813 ± 0.0011	1.046 ± 0.009	0.1655 ± 0.0013	0.8217 ± 0.0042	0.3830 ± 0.0043	0.3202 ± 0.0038
	800	280	0.0044 ± 0.0002	0.0041 ± 0.0003	0.0823 ± 0.0012	1.023 ± 0.009	0.1666 ± 0.0021	0.8158 ± 0.0039	0.3822 ± 0.0057	0.3281 ± 0.0051
	1000	300	0.0050 ± 0.0003	0.0034 ± 0.0003	0.0857 ± 0.0012	1.038 ± 0.010	0.1655 ± 0.0017	0.8257 ± 0.0062	0.3852 ± 0.0051	0.3193 ± 0.0040
	1200	640	0.0043 ± 0.0002	0.0043 ± 0.0002	0.0828 ± 0.0010	1.037 ± 0.010	0.1655 ± 0.0015	0.8291 ± 0.0039	0.3880 ± 0.0046	0.3319 ± 0.0040
Total	1600	360	0.0048 ± 0.0002	0.0037 ± 0.0002	0.0819 ± 0.0011	1.018 ± 0.011	0.1641 ± 0.0017	0.8202 ± 0.0044	0.3864 ± 0.0052	0.3231 ± 0.0040
	2500	—	0.0046 ± 0.0001	0.0040 ± 0.0001	0.0824 ± 0.0005	1.036 ± 0.005	0.1654 ± 0.0007	0.8232 ± 0.0021	0.3849 ± 0.0023	0.3244 ± 0.0020
	1600	—	0.0046 ± 0.0001	0.0040 ± 0.0001	0.0830 ± 0.0006	1.030 ± 0.005	0.1653 ± 0.0009	0.8241 ± 0.0023	0.3860 ± 0.0026	0.3268 ± 0.0022
	Q ^b	—	0.00455	0.004057	0.0822	1.042	0.1619	0.8185	0.3780	0.3164
	HL ^c	—	0.00842	0.00569	0.0905	1.056	0.1544	0.8442	0.6361	0.7000
Air	—	0.003537	0.003300	0.07136	0.9832	0.1514	0.7890	0.3879	0.3294	

^aThe total without the data of 600 °C fraction. In the case of HF-HCl residue, the gas fraction of 600 °C fraction was accidentally lost.

^bBusemann et al. (2000).

^cHuss and Lewis (1994).

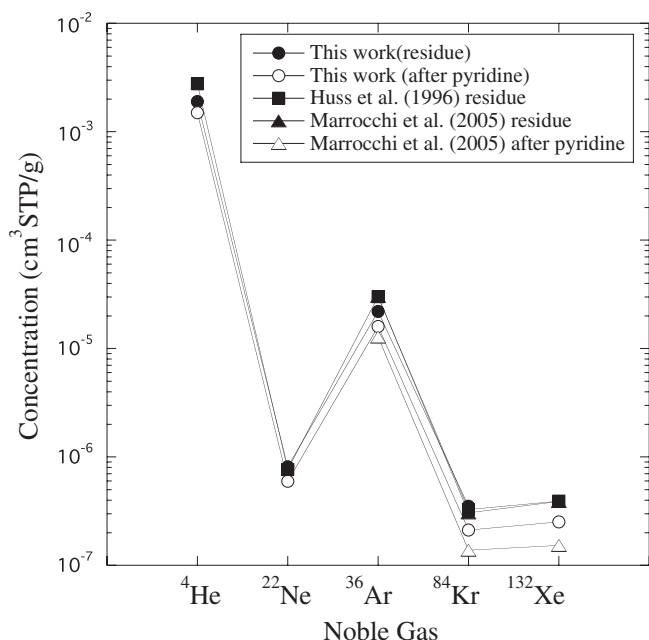


Fig. 1. Comparison of the total noble gas concentrations in the HF–HCl residue of Orgueil and its pyridine-treated sample with those in similar samples reported by Marrocchi et al. (2005) and Huss et al. (1996). The total ^{132}Xe concentration in the original HF–HCl residue of Orgueil in this study is not given because we lost the 600 °C fraction.

of the total shown in Fig. 4 are without 600 °C fractions for both the original and the pyridine-treated samples. The data points of the pyridine-treated sample are systematically located at the left side of our HF–HCl residue. Thus, it is difficult to say that only Q-gases are removed by the pyridine treatment because the data points are on the opposite side from the trend by removing phase Q. The possibility to shift the data point to the left side of this diagram is due to the loss of another component similar to (or with a $^{136}\text{Xe}/^{132}\text{Xe}$ ratio slightly higher than) that in the HF–HCl residue. The removal of HL + Q + air(?) is compatible with the trend seen in the Ne isotope diagram (Fig. 3). Figure 5 is the $^{131}\text{Xe}/^{132}\text{Xe}$ versus $^{136}\text{Xe}/^{132}\text{Xe}$ diagram where the data point of air is not on the mixing line of Q and HL and we can easily detect the contribution of air. From this diagram, it is known that contribution of air is negligible and the lost fraction is a mixture of Q and HL. The mass balance calculation of the totals (without 600 °C fraction) shows that the $^{136}\text{Xe}/^{132}\text{Xe}$ ratio in the loss fraction would be 0.3377 ± 0.0058 . As this ratio is not that of the pure HL component ($^{136}\text{Xe}/^{132}\text{Xe}$ ratio is 0.7000), it is concluded that a mixture of HL and Q component is removed by pyridine. The estimated $^{132}\text{Xe}_Q/^{132}\text{Xe}_{HL}$ ratio ($^{132}\text{Xe}_Q$ and $^{132}\text{Xe}_{HL}$ are the amount of ^{132}Xe of Q and HL components,

respectively) in the loss fraction is 17 ± 5 , which is similar to the $^{132}\text{Xe}_Q/^{132}\text{Xe}_{HL}$ ratio of the original HF–HCl residue (24 ± 4).

An interesting feature is shown in the $^{130}\text{Xe}/^{132}\text{Xe}$ versus $^{136}\text{Xe}/^{132}\text{Xe}$ diagram (Fig. 6). Our data points of both the HF–HCl residue and its pyridine-treated sample are situated above the mixing line of Q and HL. The data points of Marrocchi et al. (2005) and Huss et al. (1996) are also located at positions slightly higher than the mixing line of Q and HL. This supposed to be due to the presence of Xe–S, whose host phase is SiC. SiC is also the carrier of Ne–E(H). Thus, this deviation from the mixing line is not unexpected and is consistent with the presence of Ne–E(H) for these samples. However, our obtained $^{130}\text{Xe}\text{--S}/^{22}\text{Ne}\text{--E}$ ratio is on the order of 10^{-2} , which is about an order of magnitude higher than that reported by Huss et al. (2003). This $^{130}\text{Xe}\text{--S}/^{22}\text{Ne}\text{--E}$ ratio is surely too high and the high $^{130}\text{Xe}/^{132}\text{Xe}$ ratios are in all the temperature fractions. Our obtained $^{130}\text{Xe}/^{132}\text{Xe}$ ratios seem to be about 2–3% higher than the expected values. To reduce the discrimination factor by about 2–3% only for $^{130}\text{Xe}/^{132}\text{Xe}$ ratio is impossible. It may be due to an experimental artifact like the effect of ^{129}XeH during the measurement with a large amount of hydrocarbon, but we could not find a clear explanation for our high $^{130}\text{Xe}/^{132}\text{Xe}$ ratios. The $^{130}\text{Xe}/^{132}\text{Xe}$ ratios in Allende are normal as seen in the later section.

Several combinations of the Raman parameters of carbon from the HF–HCl residue of Orgueil and its pyridine-treated sample are shown in Fig. 7. The G band is assigned to the fundamental E_{2g2} vibration mode of the aromatic plane of graphite. The D band is related to structural defects (D for defect). The D band is not observed in pure graphite, but is observed in general graphitic carbon, including activated charcoal, carbon black and vitreous carbon, etc. Morishita et al., unpublished data, showed that the power of the laser at the Raman spectroscopy had a great effect on the Raman parameters for the carbon material in the Allende meteorite. Busemann et al. (2007) reported a Raman study of many primitive chondrite and also measured the chemical residue of Orgueil. They obtained mean ω_G , ω_D , FWHM_G , FWHM_D , and I_D/I_G ratio as 1580.5 ± 0.3 , 1353.2 ± 0.3 , 97.5 ± 0.1 , 306.0 ± 0.2 , and $1.028 \pm 0.040 \text{ cm}^{-1}$, respectively. Our data have slightly higher ω_G and ω_D , lower FWHM_G and FWHM_D , and similar I_D/I_G ratios with wider variation. However, the variations are small compared to those of the whole primitive chondrites, and our data on Orgueil indicate the very primitive carbon feature with high FWHM_D and low I_D/I_G ratio (fig. 6 in Busemann et al. 2007).

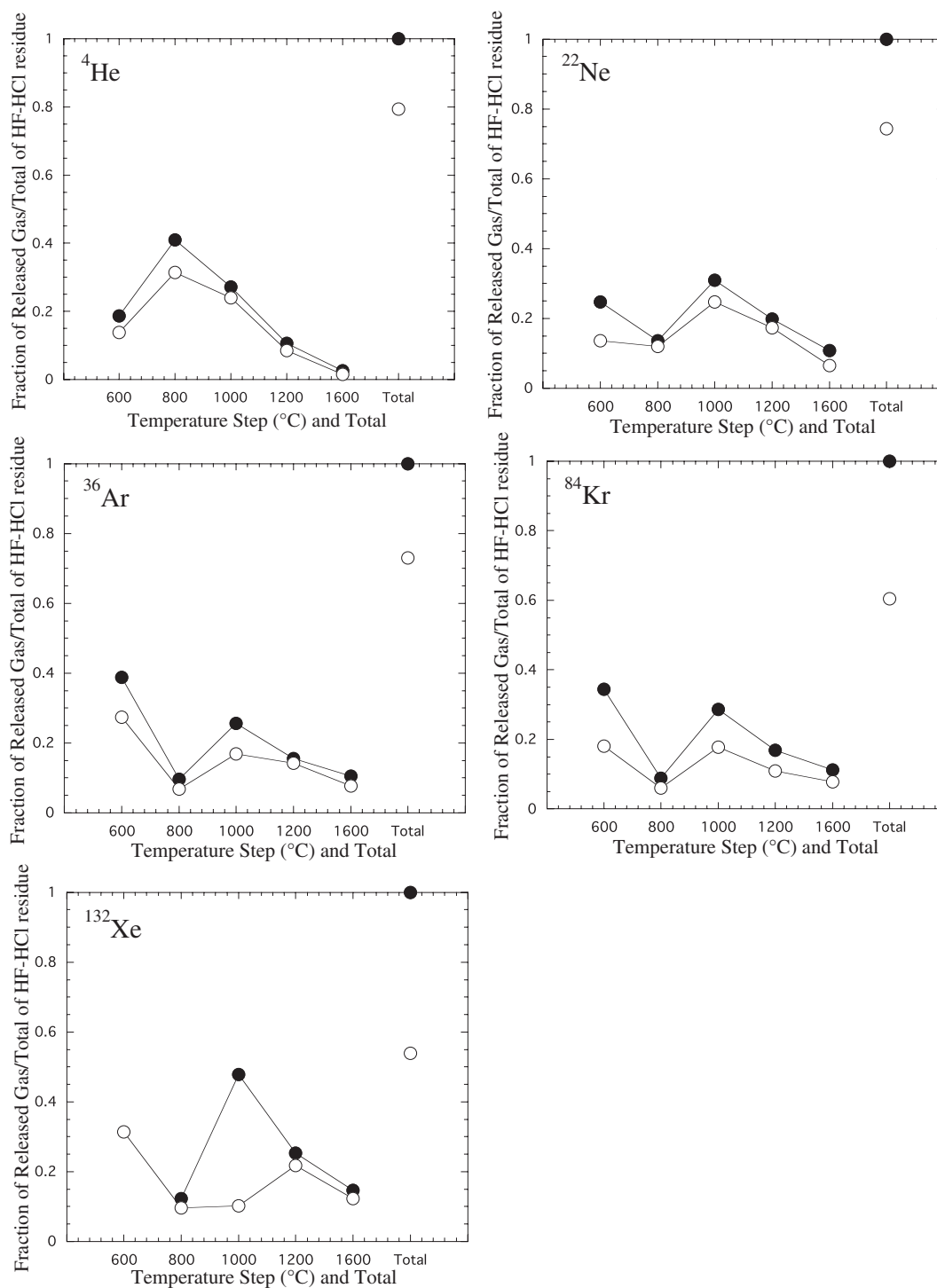


Fig. 2. The fraction of noble gas contents in the pyridine-treated sample relative to those in the HF-HCl residue of Orgueil in each temperature fraction and the total for ^4He , ^{22}Ne , ^{36}Ar , ^{84}Kr , and ^{132}Xe . All fractions are normalized by the total amount of the HF-HCl residue. The normalization of each ^{132}Xe concentration is to the total of the HF-HCl residue without the 600 °C fraction because we lost 600 °C fraction during processing (see text). The comparison of the total amount of the pyridine-treated sample is made without the 600 °C fraction.

There is no significant difference in the Raman parameters between the HF-HCl residue and its pyridine-treated sample although ω_G and FWHM_G of

the pyridine-treated sample are very slightly lower and higher, respectively, than those of the original HF-HCl residue (Fig. 7a). The lower shift of ω_G and the increase

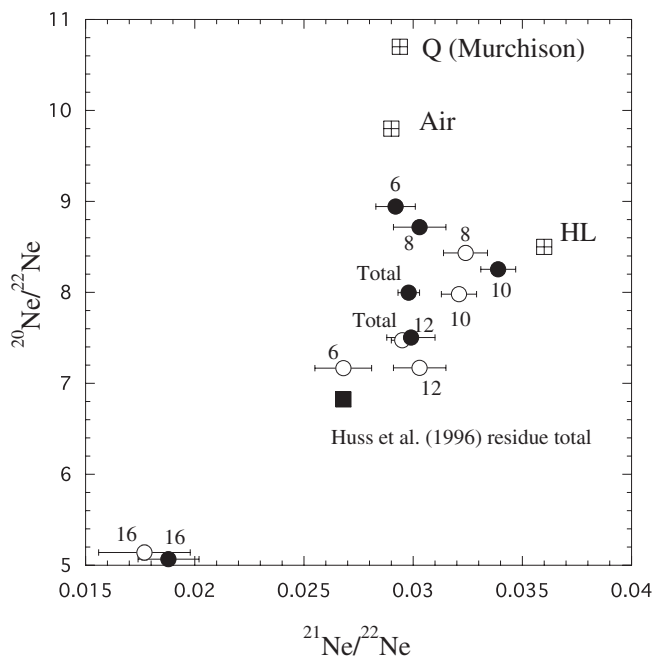


Fig. 3. Neon three-isotope plot for the original HF–HCl residues of Orgueil (closed circle) and its pyridine-treated sample (open circle). The numerical values show the release temperatures ($\times 100$ °C). The data points of Murchison Q and HL are from Wieler et al. (1992) and Huss and Lewis (1994), respectively.

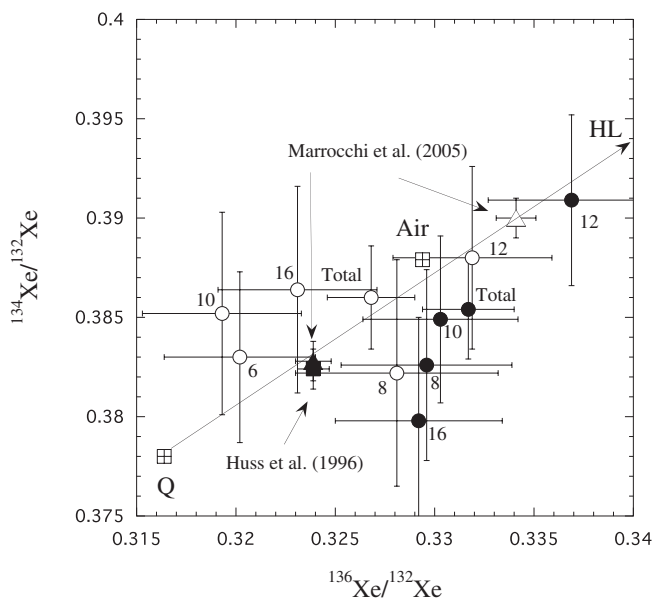


Fig. 4. A $^{134}\text{Xe}/^{132}\text{Xe}$ versus $^{136}\text{Xe}/^{132}\text{Xe}$ diagram of the HF–HCl residue of Orgueil (closed symbol) and its pyridine-treated sample (open symbol). Circles are our data and the numerical values are the release temperatures ($\times 100$ °C). To make the relevant comparison, we show the total without the 600 °C fraction for both the original and the pyridine-treated samples, because we lost the 600 °C fraction of the original HF–HCl residue. The data source of Q is from Busemann et al. (2000) and HL from Huss and Lewis (1994).

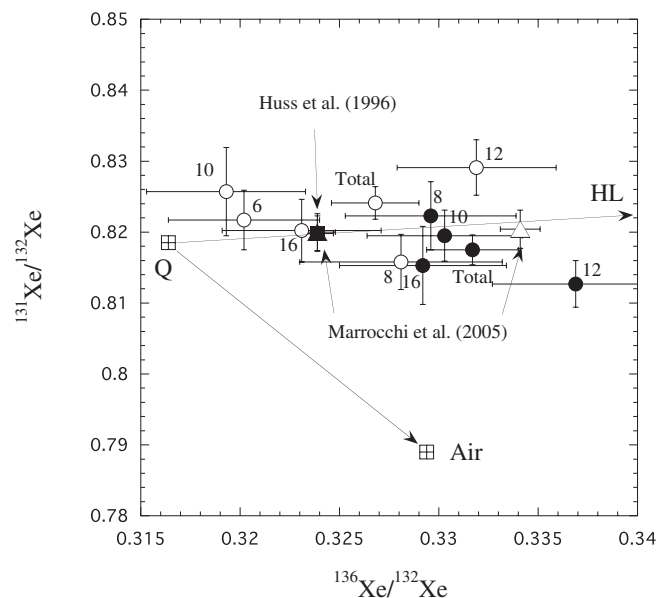


Fig. 5. A $^{131}\text{Xe}/^{132}\text{Xe}$ versus $^{136}\text{Xe}/^{132}\text{Xe}$ diagram. The symbols, numerical values, data points of the total, and other data sources are the same as those in Fig. 4.

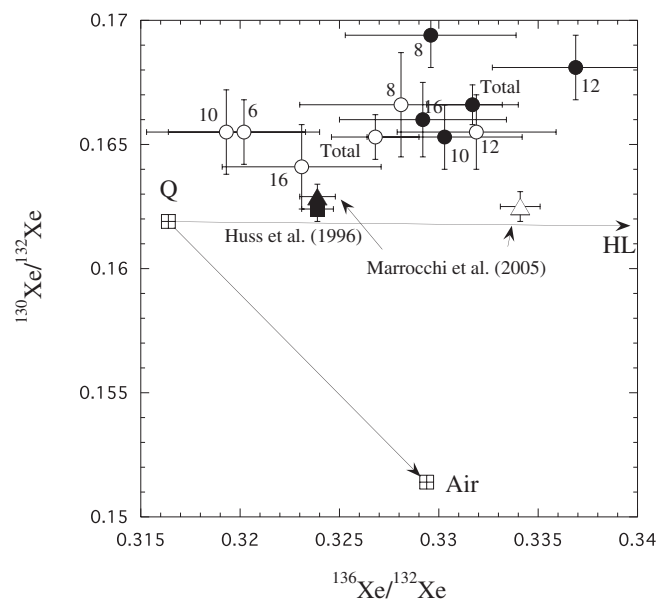


Fig. 6. A $^{130}\text{Xe}/^{132}\text{Xe}$ versus $^{136}\text{Xe}/^{132}\text{Xe}$ diagram. The symbols, numerical values, data points of the total, and other and the data sources are the same as those in Fig. 4.

of FWHM_G are probably due to the swelling of the macromolecular network caused by pyridine, but there is no clear effect on the D band and I_D/I_G ratio (Figs. 7b and 7c). Thus, pyridine treatment did not have a large effect on the carbon structure of the HF–HCl residue. This is significantly different from the

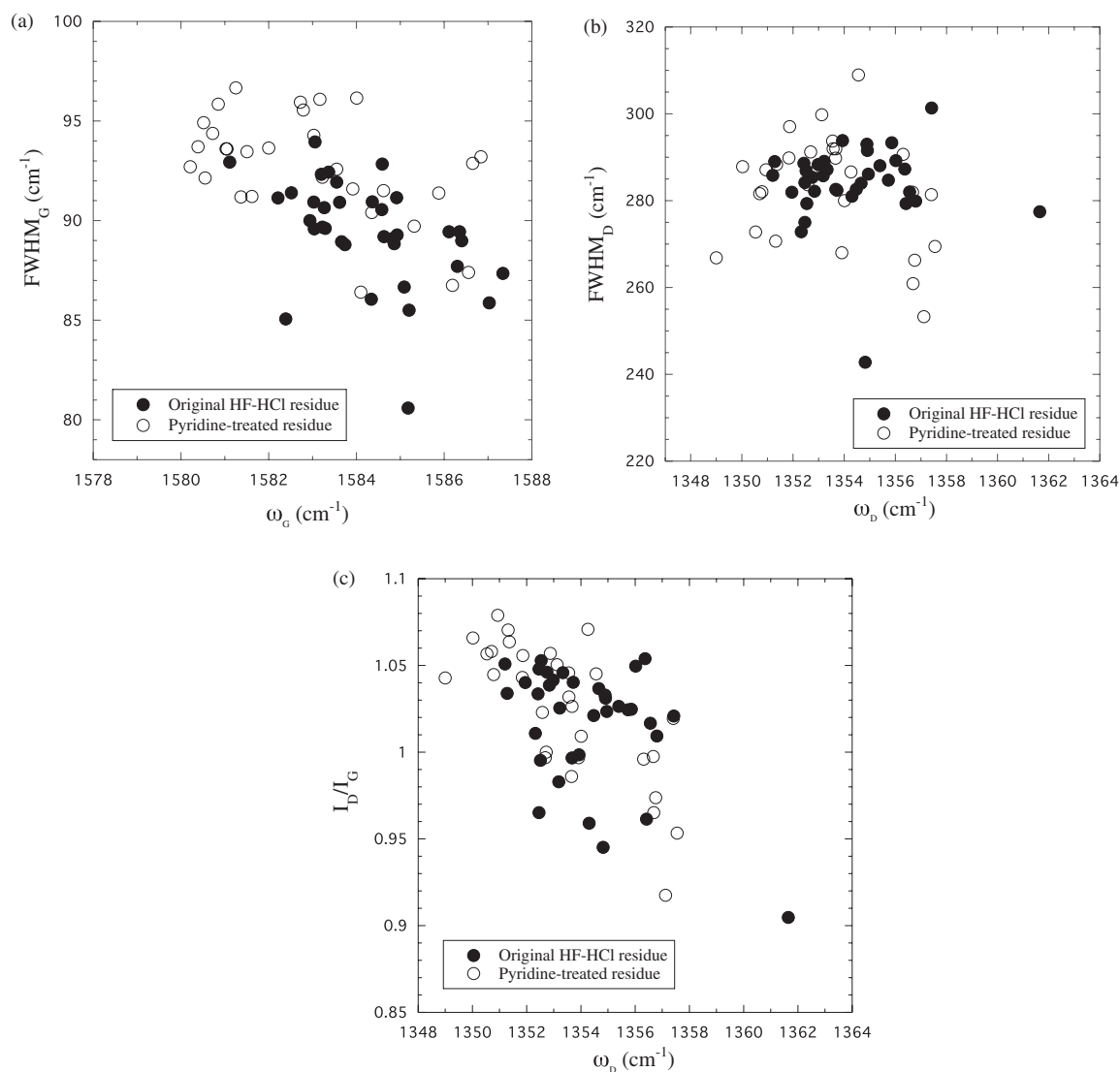


Fig. 7. Comparisons of Raman spectroscopic parameters for samples prepared from the Orgueil meteorite. a) FWHM_G (full-width at half-maximum of G band) against ω_G (peak position of G band). b) FWHM_D (full-width at half-maximum of D band) against ω_D (peak position of D band). c) I_D/I_G (peak intensity ratio of D and G bands) against ω_G for the original HF-HCl residues of Orgueil (closed circle) and its pyridine-treated sample (open circle).

observation that the Raman parameters changed drastically after the oxidation to destroy phase Q (Matsuda et al. 2010). Thus, it is likely that the release of noble gases during the pyridine treatment is different from the general chemical process by which phase Q is removed by oxidation.

Allende

The pyridine treatment surely removed the noble gases of the HF-HCl residue of Orgueil, but Busemann et al. (2008) reported that there was no effect on the chemical residues of other primitive meteorites such as

CM and CR. Thus, we applied the similar pyridine treatment to the Allende CV3 meteorite, which is well studied for phase Q. Tables 4 and 5 show the noble gas concentrations and isotopic ratios of Ar and Xe of the HF-HCl residue of Allende and its pyridine-treated sample.

Figure 8 compares the total noble gas concentrations in the HF-HCl residue and its pyridine-treated sample of our study with those reported by other authors (Lewis et al. 1975; Srinivasan et al. 1978; Wieler et al. 1991; Matsuda et al. 2010). The elemental abundances of noble gases in our HF-HCl residue are low compared to those of 3C1 (Lewis et al. 1975) and

Table 4. Concentrations of He, Ne, Ar and Kr and the isotopic ratios of Ar for Allende.

Sample	Temp. (°C)	[⁴ He] 10 ⁻⁶ cm ³ STP g ⁻¹	[²² Ne] 10 ⁻⁸ cm ³ STP g ⁻¹	[³⁶ Ar] 10 ⁻⁸ cm ³ STP g ⁻¹	³⁸ Ar/ ³⁶ Ar	⁴⁰ Ar/ ³⁶ Ar	[⁸⁴ Kr] 10 ⁻¹⁰ cm ³ STP g ⁻¹
HF-HCl residue (1.09 mg)	600	150	2.7	69	0.18798 ± 0.00075	57.1 ± 2.6	120
	800	230	9.2	64	0.18616 ± 0.00073	< 3.6	38
	1000	210	14	240	0.18653 ± 0.00071	< 0.54	190
	1200	95	9.9	300	0.18855 ± 0.00071	< 0.37	250
	1600	6.4	1.1	56	0.18844 ± 0.00073	< 11	46
Total		690	37	730	0.18760 ± 0.00039	—	650
Pyridine residue (0.93 mg)	600	120	2.6	67	0.19055 ± 0.00183	72.4 ± 3.4	120
	800	230	12	71	0.18797 ± 0.00082	< 4.5	46
	1000	230	14	170	0.18613 ± 0.00071	< 1.4	78
	1200	66	7.5	350	0.18868 ± 0.00073	< 0.43	300
	1600	3.4	0.48	41	0.19023 ± 0.00078	< 18	33
Total		640	37	690	0.18823 ± 0.00021	—	580
Q ^a					0.18727		
HL ^b					0.2270		
Air					0.188	295.5	

^aBusemann et al. (2000).

^bHuss and Lewis (1994). This HL component of Ne (Ne-HL) is actually Ne-A2 (Ne-HL + P3) (Huss et al. 1996).

BA (Wieler et al. 1991), but are similar to those of AMD1 (Matsuda et al. 2010) and ICS (Srinivasan et al. 1978). AMD1 is the sample that was prepared at the same time as our HF-HCl residue in this study (Matsuda et al. 2010). Thus, the prepared HF-HCl residue is a typical chemical residue, including phase Q. The total elemental noble gas abundances of our pyridine-treated residue are almost identical to those of the original HF-HCl residue, indicating that pyridine treatment did not affect phase Q in Allende. Figure 9 shows the proportion of noble gas abundances in the pyridine-treated sample to those in the HF-HCl residue of Allende in each temperature fraction and for the total. There seems no systematic decrease trend for each temperature fraction. The loss fractions of the total noble gas abundances in the original HF-HCl residue of Allende were 7% (⁴He), -1% (²²Ne), 5% (³⁶Ar), 11% (⁸⁴Kr), and 5% (¹³²Xe). Considering the error margins of the elemental abundances (10%), these lost fractions are within the error margins and can be supposed to be identical to zero, which is significantly different from the result of Orgueil, where significant losses of noble gases are observed after the pyridine treatment.

There is no significant difference in the Ar and Xe isotopic ratios for the HF-HCl residue and its pyridine-treated samples of Allende. Figure 10 shows the ¹³⁴Xe/¹³²Xe versus ¹³⁶Xe/¹³²Xe diagram of the HF-HCl residue and its pyridine-treated sample of Allende. The data point of the total in our HF-HCl residue is very close to those obtained by other authors (Lewis et al. 1975; Srinivasan et al. 1978;

Wieler et al. 1991; Matsuda et al. 2010). The data point of the pyridine-treated sample of Allende is also located at a similar position to the original HF-HCl residue, again indicating that pyridine treatment did not affect phase Q in Allende. In contrast to Orgueil, there is no excess of ¹³⁰Xe because SiC, the carrier of Xe-S, is not abundant in Allende.

Thus, the elemental abundance and the isotopic compositions of the HF-HCl of Allende and its pyridine-treated sample do not show any effect of the pyridine treatment on phase Q.

On the Pyridine Treatment

Thus, pyridine treatment surely removed part of the noble gases in the Orgueil HF-HCl residue, but not for Allende. In our experiment, the noble gases dissolved by pyridine were fractionated being enriched in heavy noble gases, whereas those in Marrocchi et al. (2005) were not fractionated. The Xe isotopes of the gas lost in our experiment are similar to those in the original HF-HCl residue, which is also different from the results of Marrocchi et al. (2005) where the Q-gases seem to be removed. So, there are some clear differences in our experiment and theirs. We need to explain how these differences occur.

The HF-HCl residue of type 1 and 2 carbonaceous chondrites generally includes much hydrocarbons, which is a serious problem with noble gas measurements, especially at low-temperature fractions. In our experiments in this study, we had to reduce the amount of gas from the 600 °C fraction of the HF-HCl residue

Table 5. Concentrations and isotopic ratios of Xe for Allende.

Sample	Temp. (°C)	$10^{-10} \text{ cm}^3 \text{ STP g}^{-1}$	^{132}Xe	$^{124}\text{Xe}/^{132}\text{Xe}$	$^{126}\text{Xe}/^{132}\text{Xe}$	$^{128}\text{Xe}/^{132}\text{Xe}$	$^{129}\text{Xe}/^{132}\text{Xe}$	$^{130}\text{Xe}/^{132}\text{Xe}$	$^{131}\text{Xe}/^{132}\text{Xe}$	$^{134}\text{Xe}/^{132}\text{Xe}$	$^{136}\text{Xe}/^{132}\text{Xe}$
HF-HCl residue (1.09 mg)	600	83	0.0045 ± 0.0006	0.0042 ± 0.0004	0.0042 ± 0.0004	0.0817 ± 0.0017	1.778 ± 0.024	0.1589 ± 0.0033	0.8064 ± 0.0149	0.3824 ± 0.0055	0.3262 ± 0.0052
	800	91	0.0050 ± 0.0005	0.0042 ± 0.0005	0.0042 ± 0.0005	0.0790 ± 0.0028	1.141 ± 0.013	0.1622 ± 0.0022	0.8163 ± 0.0093	0.4152 ± 0.0061	0.3541 ± 0.0050
	1000	210	0.0049 ± 0.0004	0.0045 ± 0.0004	0.0045 ± 0.0004	0.0852 ± 0.0019	1.043 ± 0.010	0.1645 ± 0.0019	0.8334 ± 0.0134	0.3933 ± 0.0069	0.3382 ± 0.0066
	1200	280	0.0050 ± 0.0003	0.0042 ± 0.0003	0.0042 ± 0.0003	0.0849 ± 0.0017	1.025 ± 0.008	0.1628 ± 0.0021	0.8364 ± 0.0069	0.4024 ± 0.0039	0.3416 ± 0.0032
	1600	89	0.0039 ± 0.0006	0.0041 ± 0.0006	0.0041 ± 0.0006	0.0762 ± 0.0025	0.992 ± 0.011	0.1585 ± 0.0040	0.7900 ± 0.0135	0.3820 ± 0.0052	0.3300 ± 0.0040
Total	750		0.0048 ± 0.0002	0.0043 ± 0.0002	0.0043 ± 0.0002	0.0829 ± 0.0010	1.122 ± 0.005	0.1623 ± 0.0011	0.8243 ± 0.0052	0.3968 ± 0.0026	0.3391 ± 0.0024
Pyridine residue (0.93 mg)	600	71	0.0034 ± 0.0012	0.0054 ± 0.0011	0.0054 ± 0.0011	0.0811 ± 0.0035	2.014 ± 0.047	0.1572 ± 0.0045	0.8019 ± 0.0261	0.3825 ± 0.0190	0.3178 ± 0.0092
	800	62	0.0038 ± 0.0008	0.0043 ± 0.0012	0.0043 ± 0.0012	0.0923 ± 0.0072	1.275 ± 0.046	0.1659 ± 0.0083	0.8094 ± 0.0247	0.4182 ± 0.0127	0.3848 ± 0.0166
	1000	210	0.0049 ± 0.0005	0.0043 ± 0.0003	0.0043 ± 0.0003	0.0784 ± 0.0016	1.027 ± 0.011	0.1638 ± 0.0018	0.8149 ± 0.0081	0.3851 ± 0.0040	0.3412 ± 0.0040
	1200	330	0.0039 ± 0.0003	0.0039 ± 0.0003	0.0039 ± 0.0003	0.0840 ± 0.0015	1.022 ± 0.009	0.1621 ± 0.0022	0.8182 ± 0.0077	0.3839 ± 0.0052	0.3291 ± 0.0039
	1600	35	0.0054 ± 0.0010	0.0042 ± 0.0008	0.0042 ± 0.0008	0.0820 ± 0.0045	1.001 ± 0.022	0.1579 ± 0.0054	0.7927 ± 0.0182	0.3893 ± 0.0139	0.3151 ± 0.0105
Total	710		0.0042 ± 0.0002	0.0042 ± 0.0002	0.0042 ± 0.0002	0.0827 ± 0.0011	1.144 ± 0.008	0.1622 ± 0.0014	0.8136 ± 0.0056	0.3874 ± 0.0036	0.3357 ± 0.0028
Q ^a			0.00455	0.004057	0.004057	0.0822	1.042	0.1619	0.8185	0.3780	0.3164
HL ^b			0.00842	0.00569	0.00569	0.0905	1.056	0.1544	0.8442	0.6361	0.7000
Air			0.003537	0.003300	0.003300	0.07136	0.9832	0.1514	0.7890	0.3879	0.3294

^aBusemann et al. (2000).^bHuss and Lewis (1994).

of Orgueil when we put the gas into the mass spectrometer from the purification line. Thus, the errors of the isotopic ratios in this fraction are large compared to the other fractions despite the fact that this fraction has large amounts of noble gases. This is probably because there were a lot of hydrocarbon gases at this temperature. However, the gas released from the pyridine-treated residue of Orgueil at 600 °C was rather clean compared to that of the original HF–HCl residue in our experiment, and we did not need to reduce the gas amount before inputting the gas into the mass spectrometer. Thus, it seems that the pyridine not only induced swelling of the macromolecular network of the organic matter but also destroyed some kind of organic matter in the sample.

It is known that pyridine not only induces swelling of the macromolecular network of the organic matter but also plays the role of oxidant (especially when pyridine is not a brand new one). Thus, the following hypothesis may explain the differences between this study and Marrocchi et al. (2005). Some oxidation occurred in our experiment that decomposed organic matter. It is likely that the oxidation was very weak in our experiment, and simply dissolved some kind of organic matter, but not phase Q. Meanwhile, the oxidation by pyridine worked very strongly in Marrocchi et al. (2005) to dissolve out even the phase Q. Here, one may argue that there is no evidence for this hypothesis because neither the total carbon content nor Raman data have been changed. However, it is estimated that the decomposed mass of the organic matter is very small. The line volume of our purification line is about 1000 cm³ (including the crucible) and the vacuum before the inlet of gas to the mass spectrometer is generally set at 10^{-7} Torr at the room temperature (300 K). Thus, it is estimated that the 5×10^{-12} mol of the organic matter has a large effect if it decomposes in the line. Our Ti–Zr getter has good ability to adsorb more than several orders of magnitude of this gas amount, but even 1 µg of the organic matter (8×10^{-8} mol in pure carbon) would give large effect in the vacuum of the purification line. Meanwhile, it is difficult to detect such a small weight difference of the sample after the pyridine treatment. The Raman parameters of G and D bands are due to disordered graphite, and the removal of such a small amount of organic matters does not largely affect the Raman parameters (Fig. 7).

It has been experimentally shown that hydrous alteration affects phase Q and HL components (Nakasyo et al. 2000). The abundance of noble gases decreased by 24% (⁴He), 27% (²²Ne), 38% (³⁶Ar), 23% (⁸⁴Kr), and 34% (¹³²Xe) after the Allende meteorite was sealed with liquid water in a pressurized vessel at 200 °C

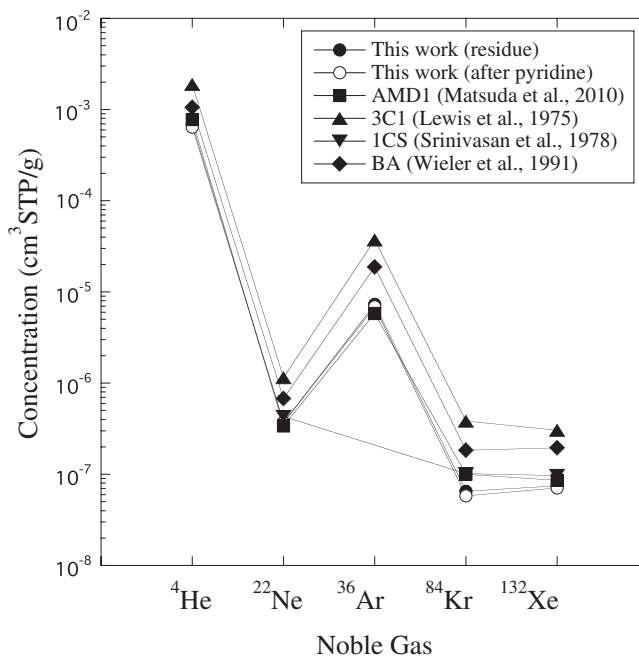


Fig. 8. The comparison of the total noble gas concentrations in the HF–HCl residue and its pyridine-treated sample of Allende with those in similar samples reported by other authors (Lewis et al. 1975; Srinivasan et al. 1978; Wieler et al. 1991; Matsuda et al. 2010). There are only ²²Ne, ⁸⁴Kr, and ¹³²Xe concentrations for 1CS (Srinivasan et al. 1978).

for a week. They concluded that both Q and HL gases were lost by aqueous alteration. This experiment shows that it is likely that some parts of the phase Q and HL could be dissolved out during the aqueous alteration on the Orgueil parent body and the dissolved gases were retrapped in the organic material inside the Orgueil chondrite during the formation of such organic matter. Retrapping of dissolved noble gases has also reported in the case of radiogenic ¹²⁹Xe from sodalite through chemical leaching (Srinivasan et al. 1978). The mechanism of retrapping noble gases seems to be due to their adsorption on the forming organic matter. These adsorbed gases should be fractionated, being enriched in heavy noble gases and heavy isotopes (but not much in isotopes). It is very plausible that the pyridine treatment only attacked such organic matter adsorbing the fractionated noble gases in our experiment. Thus, the fraction enriched in heavy noble gases and the isotopes similar to or slightly heavier than those in the original residue were dissolved out.

Therefore, we suggest that the organic matter that trapped noble gases from Q and HL gases during aqueous alteration was destroyed by the pyridine treatment. In the case of Marrocchi et al. (2005), the oxidation of pyridine worked very strongly and destroyed the phase Q, too. This hypothesis would well

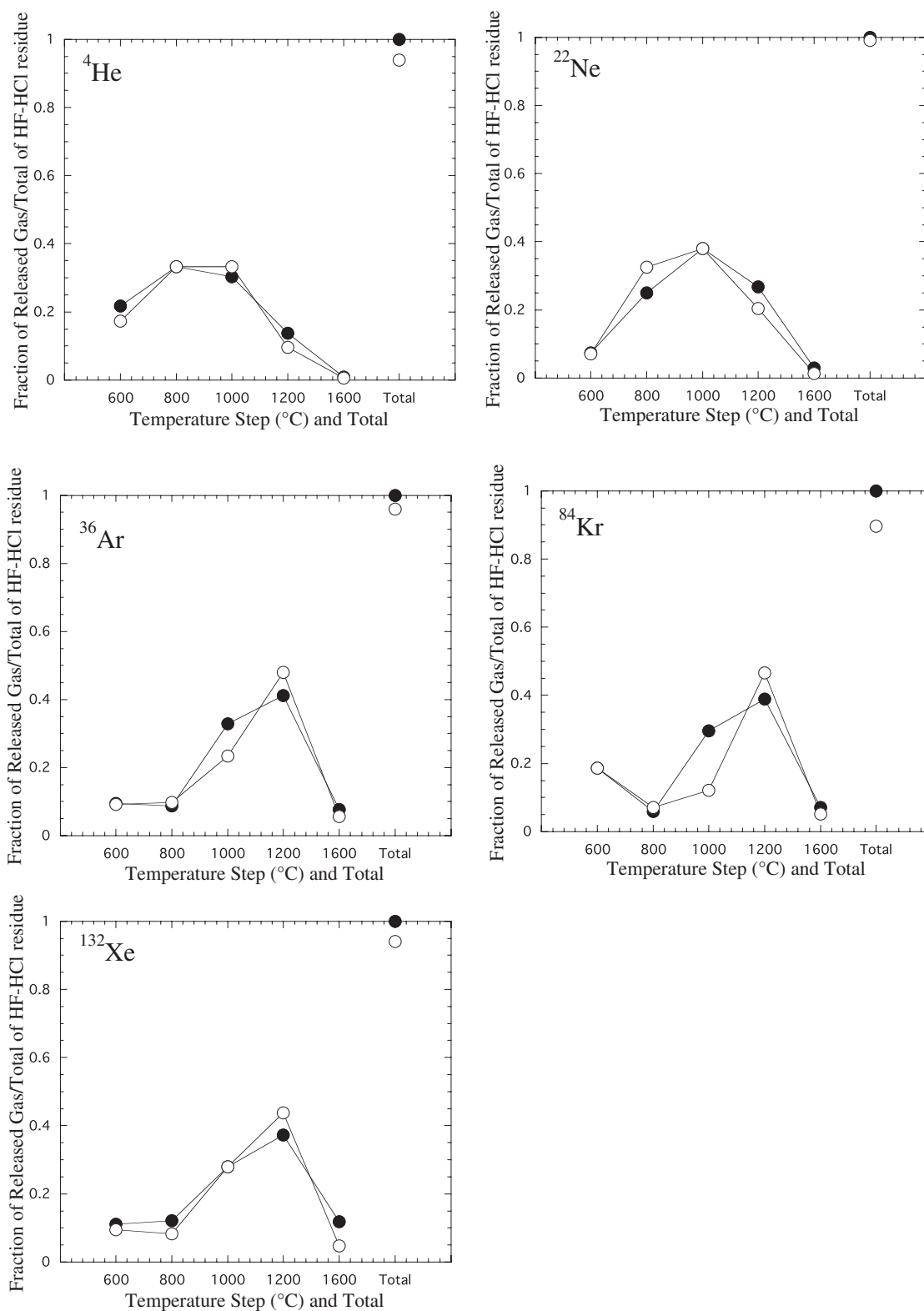


Fig. 9. The fraction of noble gas contents in the pyridine-treated sample to those in the HF-HCl residue of Allende in each temperature fraction and the total for ^4He , ^{22}Ne , ^{36}Ar , ^{84}Kr , and ^{132}Xe . All fractions are normalized by the total amount of the HF-HCl residue.

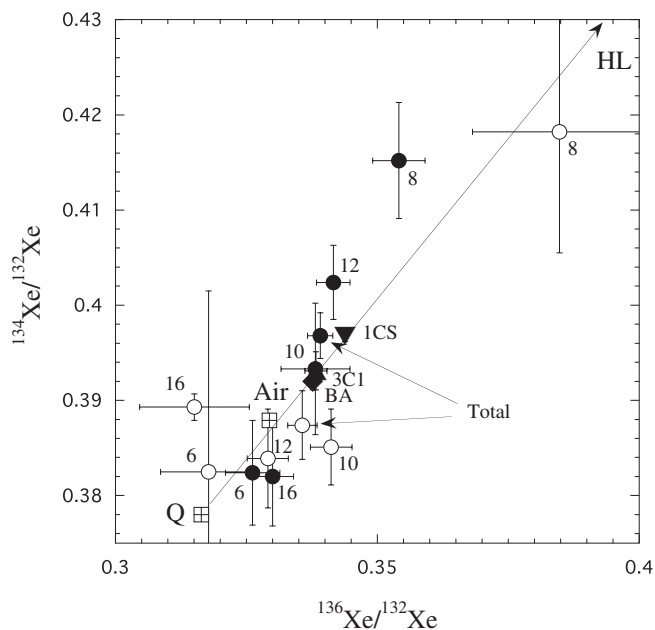


Fig. 10. A $^{134}\text{Xe}/^{132}\text{Xe}$ versus $^{136}\text{Xe}/^{132}\text{Xe}$ diagram of the HF–HCl residue (close symbol) and its pyridine-treated sample (open symbol) of Allende. Circles are our data and the numerical values are the released temperature ($\times 100$ °C). The data source of Q is from Busemann et al. (2000) and HL from Huss and Lewis (1994). The data of total of other HF–HCl residues are also plotted. The data sources are 3C1 (Lewis et al. 1975), ICS (Srinivasan et al. 1978), and BA (Wieler et al. 1991).

explain the differences between the results of our experiment and theirs.

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