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He, Ne and Ar isotopic composition of Fe-Mn crusts from the western and central Pacific Ocean and implications for their genesis

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The noble gas nuclide abundances and isotopic ratios of the upmost layer of Fe-Mn crusts from the western and central Pacific Ocean have been determined. The results indicate that the He and Ar nuclide abundances and isotopic ratios can be classified into two types: low $^{3}He/^{4}He$ type and high $^{3}He/^{4}He$ type. The low $^{3}He/^{4}He$ type is characterized by high ^{4}He abundances of 191×10^{-9} $cm^{3}\cdot STP\cdot g^{-1}$ on average, with variable ^{4}He, ^{20}Ne and ^{40}Ar abundances in the range (42.8—421)$\times10^{-9}$ $cm^{3}\cdot STP\cdot g^{-1}$, (5.40—141)$\times10^{-9}$ $cm^{3}\cdot STP\cdot g^{-1}$, and (773—10976)$\times10^{-9}$ $cm^{3}\cdot STP\cdot g^{-1}$, respectively. The high $^{3}He/^{4}He$ samples are characterized by low ^{4}He abundances of 11.7×10^{-9} $cm^{3}\cdot STP\cdot g^{-1}$ on average, with ^{4}He, ^{20}Ne and ^{40}Ar abundances in the range of (7.57—17.4)$\times10^{-9}$ $cm^{3}\cdot STP\cdot g^{-1}$, (10.4—25.5)$\times10^{-9}$ $cm^{3}\cdot STP\cdot g^{-1}$ and (5354—9050)$\times10^{-9}$ $cm^{3}\cdot STP\cdot g^{-1}$, respectively. The low $^{3}He/^{4}He$ samples have $^{3}He/^{4}He$ ratios (with R/R_A ratios of 2.04—2.92) which are lower than those of MORB (R/R_A=8±1) and $^{40}Ar/^{36}Ar$ ratios (447—543) which are higher than those of air (295.5). The high $^{3}He/^{4}He$ samples have $^{3}He/^{4}He$ ratios (with R/R_A ratios of 10.4—12.0) slightly higher than those of MORB (R/R_A=8±1) and $^{40}Ar/^{36}Ar$ ratios (293—299) very similar to those of air (295.5). The Ne isotopic ratios ($^{20}Ne/^{22}Ne$ and $^{21}Ne/^{22}Ne$ ratios of 10.3—10.9 and 0.02774—0.03039, respectively) and the $^{38}Ar/^{36}Ar$ ratios (0.1886—0.1963) have narrow ranges which are very similar to those of air (the $^{20}Ne/^{22}Ne$, $^{21}Ne/^{22}Ne$, $^{38}Ar/^{36}Ar$ ratios of 9.80, 0.029 and 0.187, respectively), and cannot be differentiated into different groups. The noble gas nuclide abundances and isotopic ratios, together with their regional variability, suggest that the noble gases in the Fe-Mn crusts originate primarily from the lower mantle. The low $^{3}He/^{4}He$ type and high $^{3}He/^{4}He$ type samples have noble gas characteristics similar to those of HIMU (High U/Pb Mantle)- and EM (Enriched Mantle)-type mantle material, respectively. The low $^{3}He/^{4}He$ type samples with HIMU-type noble gas isotopic ratios occur in the Magellan Seamounts, Marcus-Wake Seamounts, Marshall Island Chain and the Mid-Pacific Seamounts whereas the high $^{3}He/^{4}He$ type samples with EM-type noble gas isotopic ratios occur in the Line Island Chain. This difference in noble gas characteristics of these crust types implies that the Magellan Seamounts, Marcus-Wake Seamounts, Marshall Island Chain, and the Mid-Pacific Seamounts originated from HIMU-type lower mantle material whereas the Line Island Chain originated from EM-type lower mantle material. This finding is consistent with variations in the Pb-isotope and trace element signatures in the seamount lavas. Differences in the mantle

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source may therefore be responsible for variations in the noble gas abundances and isotopic ratios in the Fe-Mn crusts. Mantle degassing appears to be the principal factor controlling noble gas isotopic abundances in Fe-Mn crusts. Decay of radioactive isotopes has a negligible influence on the nuclide abundances and isotopic ratios of noble gases in these crusts on the timescale of their formation.

Fe-Mn crusts, noble gases, isotope geochemistry, mantle heterogeneity, Pacific Ocean

Marine ferromanganese deposits include deep-sea manganese nodules, Fe-Mn crusts and hydrothermal Fe-Mn deposits. Fe-Mn crusts (also called Co-rich ferromanganese crusts or Co-rich crusts) are enriched in Co, Ni, Fe, Mn, PGE (Platinum group elements), and REE and are a potentially important resource of strategic minerals in the oceans.

Hydrogenous Fe-Mn crusts occur on the surface of bare rocks exposed on elevated sea floor throughout the oceans [1] where the basement rocks consist primarily of Ocean Island Basalts (OIB) formed at hot spot. According to Morgan[2], hot spot volcanism is related to mantle plumes originating from the lower mantle. These plumes are important pathways for the transfer for material and energy from the lower mantle to the Earth's surface. The formation and distribution of Fe-Mn crusts and their relationship to mantle heterogeneity are therefore key issues in studying the origin of Fe-Mn crusts.

The isotopic composition of noble gases can provide useful information about the formation of Fe-Mn crusts. However, only limited work has been carried out on this topic. Sano et al.[3] have previously reported on the He isotopic composition of manganese nodules from the Izu-Ogasawara and Mariana Arcs. These authors observed that the $^3He/^4He$ ratios of these nodules are extraordinarily high with variations in the range $1.5\times10^{-6}-59.2\times10^{-6}$ and interpreted these ratios as being due to the inclusion of extraterrestrial matter in the nodule samples. However, they were not able to explain the wide range of $^3He/^4He$ ratios in these nodules. Li et al.[4] subsequently reported that both deep-sea nodules and Fe-Mn crusts contain abundant He and also showed that the nodules are characterized by extremely high and variable $^3He/^4He$ ratios of $17\times10^{-6}-133\times10^{-6}$ whereas the crusts are characterized by low and more variable $^3He/^4He$ ratios of $60.5\times10^{-9}-80.8\times10^{-6}$. They attributed the anomalous $^3He/^4He$ ratios of deep-sea nodules and Fe-Mn crusts to the incorporation of extraterrestrial matter and suggested that the difference of $^3He/^4He$ ratios between the deep-sea nodules and Fe-Mn crusts was a result of their differences in both composition and microstructure in the deposits. These authors also interpreted the large variations in the $^3He/^4He$ ratios and ^3He abundances of the crusts as being due to the heterogeneous distribution of cosmic dust within the samples. More recently, Ye et al. [5] have concluded that the noble gases in Fe-Mn crusts originate from mantle plumes.

Here, we aim to focus our study on the composition and variability of the noble gases in Fe-Mn crusts from the western and central Pacific Ocean in order to test the validity of these conclusions.

1 Samples and methods

The Fe-Mn crusts studied here were obtained from 7 seamounts in the Magellan Seamounts (sample MD53), Marcus-Wake Seamounts (Sample CL01), Marshall Island Chain (sample MH68), the Mid-Pacific Seamounts (CX07) and the Line Island Chain (sample MP2-09, MP3-20 and MP5-17) (Figure 1). Samples CL01, CX07, and MD53 were dredged by *R.V.* "Dayangyihao" in 2001 and the other four samples by *R.V.* "Haiyangsihao" in 2002.

All the Fe-Mn crusts studied here were layered and occurred on substrates of tuff, basalt and volcanic breccias. The samples were dense to quite dense, lustrous black to brown black with microbotryoidal to botryoidal surface texture. Descriptions of the crusts are presented in Table 1. In this study, samples were obtained by scratching the uppermost layer of the crusts (to a depth of 9—28 mm) in order to eliminate differences of the noble gas ratios of the crusts with time.

Analysis of the noble gas nuclide abundances and isotopic ratios was carried out by the Geochemical Testing Division of the Analytical Center of the Lanzhou Branch of the Chinese Academy of Sciences using a Micromass MM5400 mass spectrograph. The scratched samples were treated and analyzed as follows: (1) grinding the scratched samples, selecting grains with

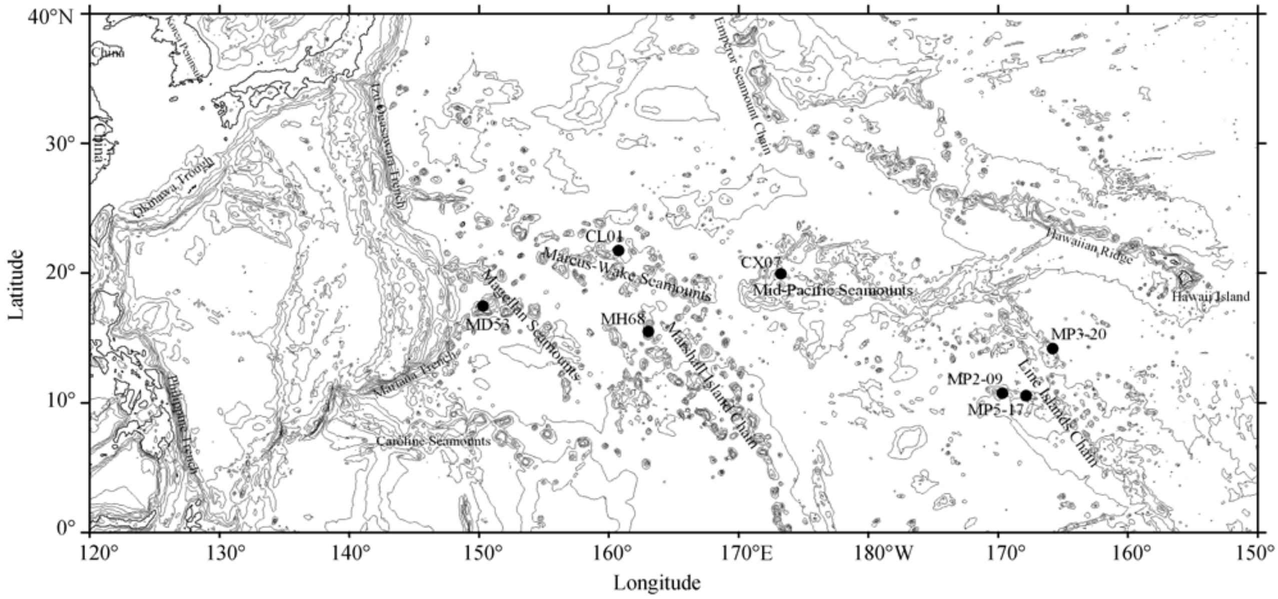

Figure 1 Schematic map showing sampling locations. The base map was downloaded from http://www.noaa.gov/index.html.

Table 1 Sampling discriptions

Type	Sample No.	Sampling depth (m)	Substrate	Surface	Surface texture	Texture	Color	Scratching depth (mm)	Co (%)	Growth rate (mm/Ma)[a)]	Initiation of growth (Ma)
Low $^3He/^4He$	CL01	2109	basalt	smooth	microbotryoidal to botryoidal	dense	lustrous black	22	0.75	2.51	8.8
	CX07	2649	basalt	quite smooth	microbotryoidal	dense	brown black	9	0.76	2.46	3.7
	MD53	2600	tuff	smooth	microbotryoidal	quite dense	brown black	22	0.62	3.37	6.5
	MH68	2016	volcanic Breccia	quite smooth	microbotryoidal	quite dense	lustrous black	24	0.93	1.86	12.9
High $^3He/^4He$	MP2-09	2258	tuff	quite smooth	botryoidal	quite dense	lustrous black	20	1.18	1.36	14.7
	MP3-20	2570	basalt	smooth	microbotryoidal	dense	lustrous black	28	0.52	4.57	6.1
	MP5-17	2676	volcanic breccia	quite smooth	microbotryoidal to botryoidal	dense	lustrous black	22	0.59	3.66	6.0

a) Calculated after the empirical formula derived from ref. [6].

20—60 net mash and washing them with distilled water for 3—5 times; (2) dunking the samples in 4M HCl for 6 hours to remove carbonate and metamorphic components and then washing them with distilled water for 3—5 times and with acetone for 3—5 times; (3) drying the samples and letting them cool down to room temperature, weighing 500 mg of each sample and packing them in aluminum foil; (4) putting the sample packages on the sample stage which was then kept under vacuum at about 130℃ for more than 24 hours in order to eliminate gases adsorbed on the sample surface; (5) heating the sample package up to 1600℃, keeping it at constant temperature for 5 minutes and extracting the noble gases by the high temperature bulk melting method; and (6) purifying the noble gases, separating them into the He+Ne, Ar+Kr, and Xe fractions and introducing each fraction into the MM5400 static state vacuum mass spectrograph to determine its nuclide abundances and isotopic ratios. Ye et al.[7] have described the analytical procedure in detail.

The thermal background isotopic composition of each element at 1600℃ are $^4He=1.10\times10^{-14}$ mol, $^{20}Ne = 1.82\times10^{-14}$ mol, $^{40}Ar=6.21\times10^{-13}$ mol, $^{84}Kr=1.37\times10^{-16}$ mol and $^{132}Xe=1.37\times10^{-16}$ mol. The determination was performed under the following conditions: emission current It4=800 μA, It40=200 μA, with high voltage of 9.000 kV, vacuum of 6×10^{-7} Pa, electron energy of 68 eV, mass resolution of 550 and electrical current of the trap of 0.800 mA.

All analytical results were adjusted to make allowance for their thermal backgrounds. The Ne abundances and isotopic ratios were adjusted for contributions from divalent Ne ion with mass numbers of 40 and 44. The analytical procedure was controlled by the reference to the standard air sample (AIRLZ2003) taken from the top of Gaolan Mountain in Lanzhou, China, which has standard values of $^3He/^4He$=1.134±0.006, $^{20}Ne/^{22}Ne$ = 9.893 ±0.022, $^{21}Ne/^{22}Ne$=0.02906±0.00057, $^{38}Ar/^{36}Ar$= 0.1910 ±0.0012 and $^{40}Ar/^{36}Ar$=297.86±0.55[7]. The analytical precision of nuclide abundance determinations was less than 10%. The analytical precision of isotopic ratio determinations is listed in Table 2.

2 Results

He, Ne, Ar nuclide abundances ($cm^3\cdot STP\cdot g^{-1}$) and isotopic ratios of Fe-Mn crusts are listed in Table 2.

2.1 He, Ne and Ar nuclide abundances

He, Ne and Ar nuclide abundances in the Fe-Mn crust samples display variations of more than 2 orders of magnitude in the abundances of ^4He, ^{20}Ne and ^{40}Ar which are in the range 7.57×10^{-9} — 421×10^{-9} $cm^3\cdot STP\cdot g^{-1}$, 5.40×10^{-9} — 141×10^{-9} $cm^3\cdot STP\cdot g^{-1}$, and 773×10^{-9}—10976×10^{-9} $cm^3\cdot STP\cdot g^{-1}$, respectively (Table 2).

Based on the relationship between the He isotope ratios of samples and that of MORB ($^3He/^4He$=8±1 R_A, where R_A is the air ratio of 1.4×10^{-6})[12−14], the samples can be classified into two types: the low $^3He/^4He$ type and the high $^3He/^4He$ type (Table 2; Figure 2(a)—(j)). The low $^3He/^4He$ type have higher ^4He abundances of 191×10^{-9} $cm^3\cdot STP\cdot g^{-1}$ on average with a greater range of variations of ^4He, ^{20}Ne, and ^{40}Ar of 42.8×10^{-9} — 421×10^{-9} $cm^3\cdot STP\cdot g^{-1}$, 5.51×10^{-9}—141×10^{-9} $cm^3\cdot STP\cdot g^{-1}$, and 773×10^{-9}—10976×10^{-9} $cm^3\cdot STP\cdot g^{-1}$, respectively; while the high $^3He/^4He$ type have lower ^4He abundances of 11.7×10^{-9} $cm^3\cdot STP\cdot g^{-1}$ on average with a relatively narrow range of variations of ^4He, ^{20}Ne, and ^{40}Ar of 7.57×10^{-9}—17.4×10^{-9} $cm^3\cdot STP\cdot g^{-1}$, 10.4×10^{-9}—25.5×10^{-9} $cm^3\cdot STP\cdot g^{-1}$ and 5354×10^{-9} — 9050×10^{-9} $cm^3\cdot STP\cdot g^{-1}$, respectively.

2.2 He, Ne and Ar isotopic ratios

The $^3He/^4He$ and $^{40}Ar/^{36}Ar$ ratios of the low $^3He/^4He$ type and the high $^3He/^4He$ type are quite different (Table 2; Figure 3). The low $^3He/^4He$ type samples have lower $^3He/^4He$ ratios of $2.85\pm0.26\times10^{-6}$—$4.09\pm0.11\times10^{-6}$ with R/R_A values in the range of 2.04±0.19 — 2.92±0.08 which is significantly lower than that of MORB (R/R_A=8±1)[12−14] and $^{40}Ar/^{36}Ar$ ratios in the range of 447±2.5—543±1.5 which are higher than that of air (295.5)[10,11] but lower than that of MORB ($^{40}Ar/^{36}Ar$ >40000)[15]. By contrast, the high $^3He/^4He$ type has higher $^3He/^4He$ ratios in the range of $14.5\pm0.45\times10^{-6}$—$16.8\pm0.66\times10^{-6}$ with R/R_A values in the range of 10.3±0.32—12.0±0.47 and higher than that of MORB (with R/R_A=8±1)[12−14]. The $^{40}Ar/^{36}Ar$ ratios of the high $^3He/^4He$ type are in the range of 293±1.3—299±2.7 and are rather low compared with those of the low $^3He/^4He$ type (447±2.5 — 543±1.5) but similar to that of air (295.5)[10,11]. The $^{38}Ar/^{36}Ar$, $^{20}Ne/^{22}Ne$ and $^{21}Ne/^{22}Ne$ ratios of all samples have narrow ranges with ratios in the ranges of 0.1877±0.0070—0.1963±0.0026, 10.3± 0.52 — 10.9±0.18, and 0.02774±0.00027 — 0.03039± 0.00031, respectively. The ratios are quite similar to those of air ($^{38}Ar/^{36}Ar$, $^{20}Ne/^{22}Ne$ and $^{21}Ne/^{22}Ne$ ratios of 0.187, 9.80 and 0.029, respectively)[9], and cannot be separated into different groups.

Table 2 Noble gas nuclide abundances ($cm^3\cdot STP\cdot g^{-1}$) and isotopic ratios of Fe-Mn crusts

Type	Sample	^4He ($\times10^{-9}$)	^{20}Ne ($\times10^{-9}$)	^{40}Ar ($\times10^{-9}$)	$^3He/^4He$ ($\times10^{-6}$)	$^{20}Ne/^{22}Ne$	$^{21}Ne/^{22}Ne$	$^{38}Ar/^{36}Ar$	$^{40}Ar/^{36}Ar$	$^3He/^4He$ (R/R_A)a)
Low $^3He/^4He$	CL01	421	141	10976	3.14±0.10b)	10.7±0.16	0.03033±0.00042	0.1890±0.0027	457±1.2	2.25±0.07
	CX07	42.8	5.51	773	4.09±0.11	10.9±0.18	0.03014±0.00028	0.1921±0.0011	543±1.5	2.92±0.08
	MD53	216	11.4	6966	3.90±0.38	10.3±0.52	0.02837±0.00013	0.1909±0.0030	447±2.5	2.79±0.27
	MH68	84.5	5.40	1595	2.85±0.26	10.6±0.34	0.03007±0.00072	0.1963±0.0026	481±3.0	2.04±0.19
High $^3He/^4He$	MP2-09	10.2	10.4	5779	14.5 ±0.45	10.7±0.07	0.02774±0.00027	0.1914±0.0022	298±1.1	10.3 ±0.32
	MP3-20	7.57	10.4	5354	16.8 ±0.66	10.6±0.10	0.03039±0.00031	0.1886±0.0040	293±1.3	12.0 ±0.47
	MP5-17	17.4	25.5	9050	14.6 ±0.44	10.5±0.09	0.02856±0.00027	0.1877±0.0070	299±2.7	10.4 ±0.31
	Air c)				1.4	9.80	0.0290	0.187	295.5	1

a) $R_A=1.4\times10^{-6}$. b) The numbers after the symbol "±" are analytical errors of isotopic ratios. c) $^3He/^4He$ ratio of air after [8]; $^{20}Ne/^{22}Ne$, $^{21}Ne/^{22}Ne$, $^{38}Ar/^{36}Ar$ ratios after [9]; $^{40}Ar/^{36}Ar$ ratio after [10, 11].

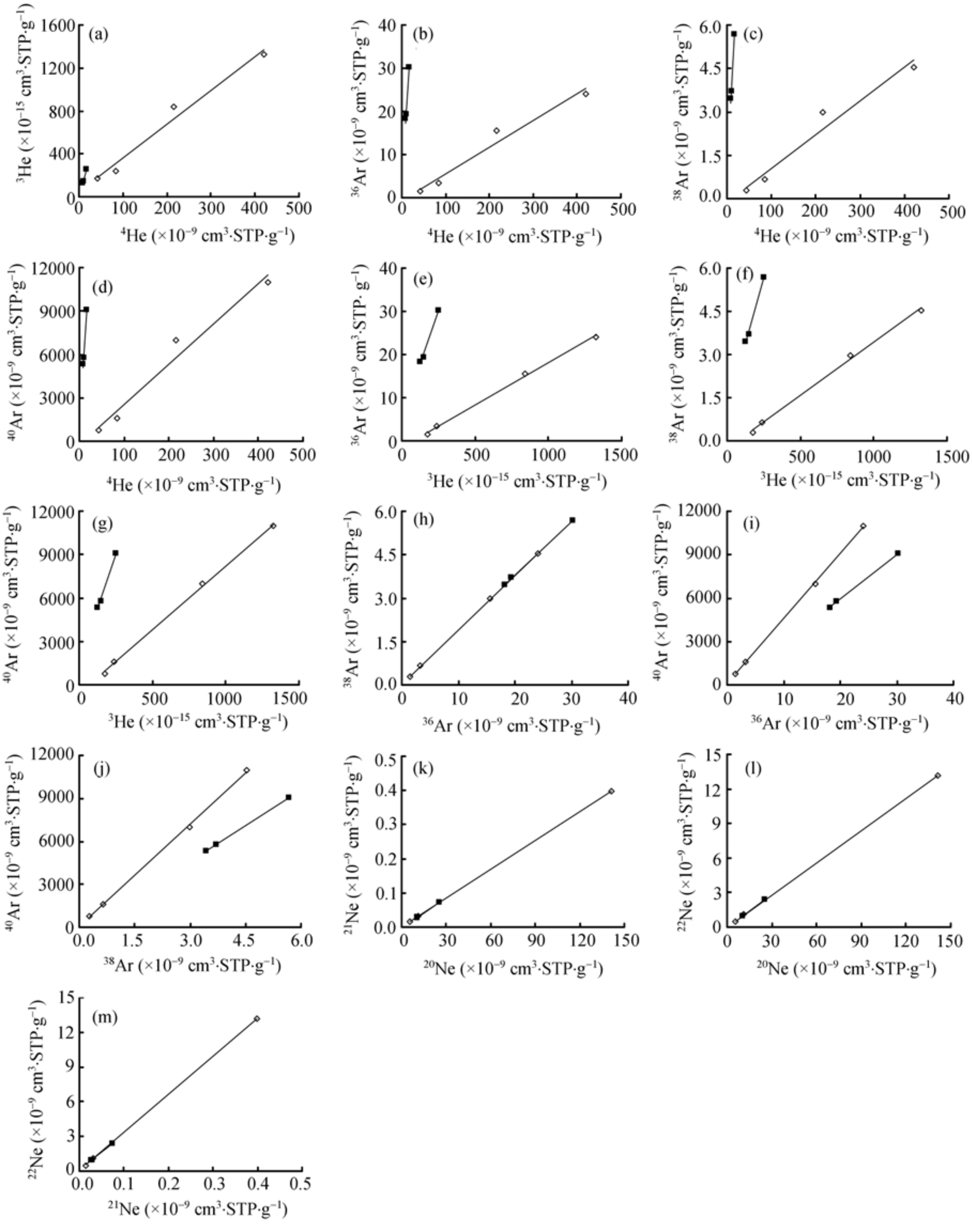

Figure 2 Correlation diagrams of He, Ne and Ar nuclide abundances. ◇, Low $^{3}He/^{4}He$ type; ■, high $^{3}He/^{4}He$ type.

3 Discussion

3.1 The origin of He, Ne and Ar in Fe-Mn crusts

Noble gases in oceanic settings may originate from the Earth's mantle, the Earth's crust and extraterrestrial matter. The high $^{3}He/^{4}He$ ratios and ^{4}He abundances of deep-sea sediments[16,17] as well as deep-sea nodules and Fe-Mn crusts[3,4] have been interpreted as being due to

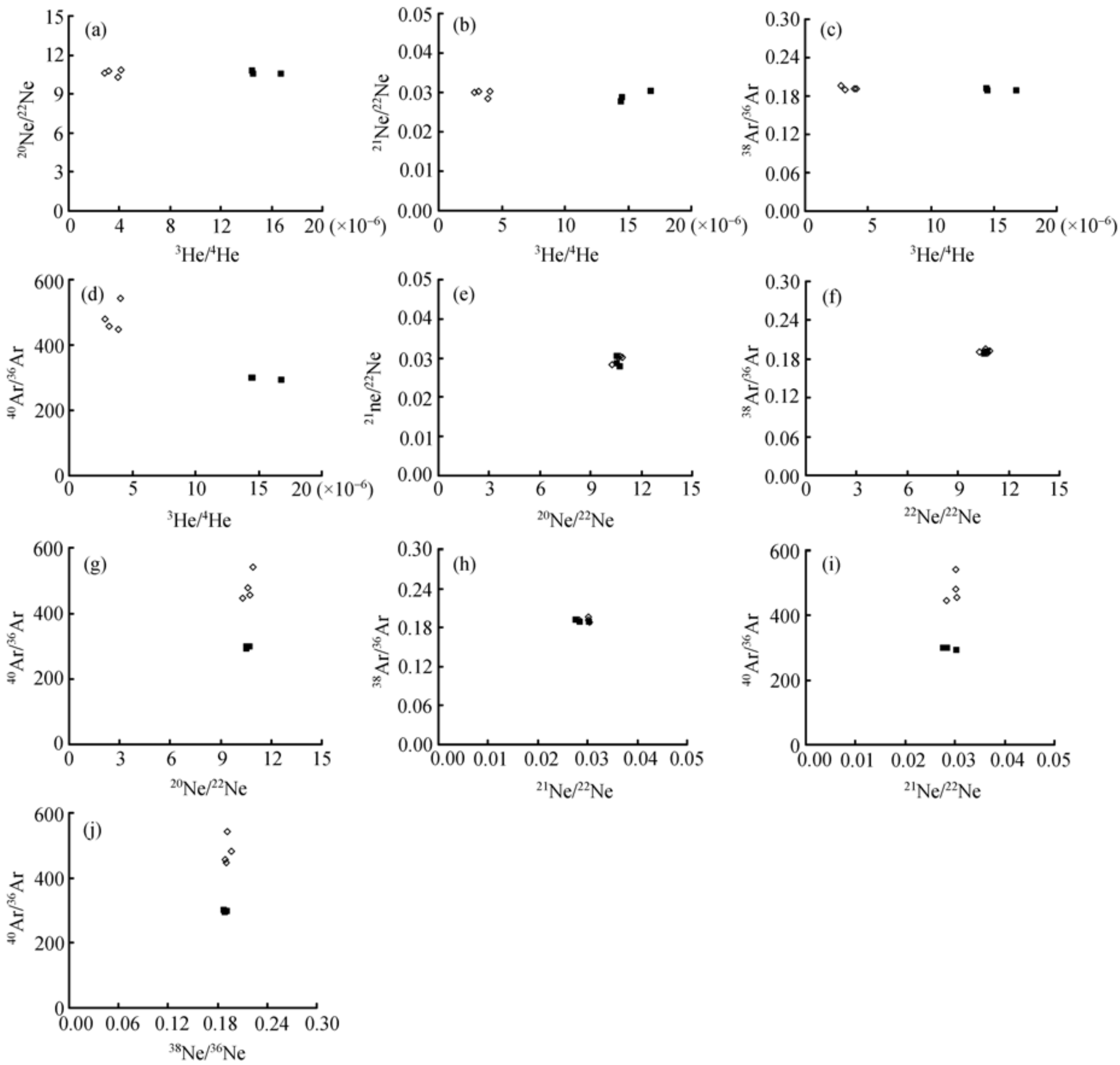

Figure 3 Correlation diagrams of He, Ne and Ar isotopic ratios. ◇, Low $^3He/^4He$ type; ■, high $^3He/^4He$ type.

the influence of cosmic dust. However, the $^3He/^4He$ ratios of deep-sea sediments are about $n\times10^{-4}$ and their ^4He abundances as high as $n\times10^{-5}cm^3\cdot STP\cdot g^{-1}$[16,17] which are 1—2 orders of magnitude higher than the $^3He/^4He$ ratios and ^4He abundances of Fe-Mn crusts and deep-sea nodules[3,4]. The sedimentation rate of deep-sea sediments is about 1000 times higher than those of Fe-Mn crusts and deep-sea nodules[18]. If the high He abundances and high $^3He/^4He$ ratios of Fe-Mn crusts, deep-sea nodules and deep-sea sediments were both caused by the addition of extraterrestrial matter, the ^4He abundances in deep-sea sediments would be about 1000 times lower than those of Fe-Mn crusts and deep-sea nodules and the $^3He/^4He$ ratios of deep-sea sediments would be lower than those of Fe-Mn crusts and deep-sea nodules as a result of dilution by material with the composition of the Earth's crust which is characterized by low $^3He/^4He$ ratios[19]. However, the $^3He/^4He$ ratios and ^4He abundances of deep-sea sediments are actually higher than those of Fe-Mn crusts and deep-sea nodules.

The $^3He/^4He$ ratios of Fe-Mn crusts are higher than those of the air (1 R_A)[8] and the Earth's crust (0.01—0.05 R_A)[19] indicating that He in the Fe-Mn crusts originated primarily from either the Earth's mantle or extraterrestrial matter. Based on the relative values of the He isotopic ratios of Fe-Mn crusts and MORB ($^3He/^4He$=8±1 R_A)[12−14], Fe-Mn crust samples can be classified as low $^3He/^4He$ and high $^3He/^4He$ types (Table

2; Figures 2, 3). Differences in the He and Ar nuclide abundances and isotopic ratios between the two types are so regular that they cannot be explained in the terms of the addition of extraterrestrial matter, although extraterrestrial matter is the most important source of He in deep-sea sediments[20]. OIB originates in the lower mantle and is one of the important sources of He of mantle origin[21]. This suggests that He of mantle origin may be the dominant source of He in Fe-Mn crusts which formed on a substrate of OIB and that the noble gas characteristics of Fe-Mn crusts may be the result of mixing of noble gases of mantle origin with air.

There are two possible types of origin of the noble gases from the mantle: a low mantle plume (OIB)-type origin and an upper mantle MORB-type origin[22]. He isotopic ratios of MORB are uniform with $^{3}He/^{4}He$ ratios of about 8±1 R_A[12−14] and the He is dominantly radio- genic (>90%) in origin[23], with $^{40}Ar/^{36}Ar$ ratios (>40000)[15] higher than that of air ($^{40}Ar/^{36}Ar$= 295.5)[10,11]. However, the He isotopic ratios of OIB are variable with $^{3}He/^{4}He$ ratios of 4－37 R_A[24,25] and $^{40}Ar/^{36}Ar$ ratios of 3000－6000[13] which are more similar to that of air (295.5)[10,11] than MORB (>40000)[15]. The He and Ar isotopic ratios of Fe-Mn crusts from the western and central Pacific Ocean (with $^{3}He/^{4}He$=2.04 － 12.0 R_A and $^{40}Ar/^{36}Ar$=293－543) (Table 2; Figures 2, 3) are therefore more similar to those of OIB (with $^{3}He/^{4}He$=4－37 R_A and $^{40}Ar/^{36}Ar$=3000－6000)[12−14] than MORB, which suggests that the noble gases in Fe-Mn crusts originated primarily from the lower mantle and are con- taminated by the atmosphere. This is consistent with the fact that Fe-Mn crusts occur on the flanks and summits of seamounts derived from lower mantle-derived OIB.

The high $^{21}Ne/^{22}Ne$ ratio of the mantle was caused by the addition of solar component[26−28]. The similarity of mantle Ne isotopic composition to those of solar component is the consequence of the solar nebula being incorporated directly into the Earth's magma ocean during the early evolution of the Earth[29] rather than being derived from captured meteoritic components with solar character[30]. In Figure 4, plots of $^{20}Ne/^{22}Ne$ vs $^{21}Ne/^{22}Ne$ show that the Fe-Mn crust samples lie near the value of air ($^{21}Ne/^{22}Ne$=9.80 and $^{20}Ne/^{22}Ne$=0.029)[9] located between the plot of air and that of solar component ($^{20}Ne/^{22}Ne$=13.5－14.0 and $^{21}Ne/^{22}Ne$=0.0305－0.034)[31] but closer to the plot of air (Figure 4). This suggests that the Ne in the Fe-Mn crusts is related to recycling of the Earth's crust that captured Ne from air and was the result of mixing of Ne in recycled air and captured solar Ne in the early stage of the evolution of the Earth. At this early stage of its evolution, the Earth captured solar air by trapping solar nebula[32,33] or solar wind[34,35]. The mantle therefore displays noble gas characteristics of solar character[26−28,36,37].

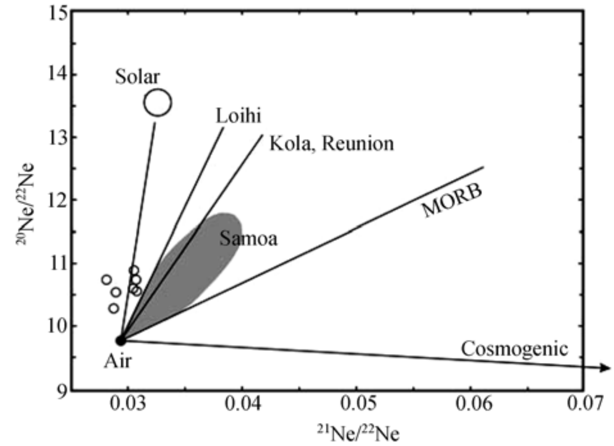

Figure 4 Plots of $^{20}Ne/^{22}Ne$ vs $^{21}Ne/^{22}Ne$ for various types of samples. ○, Fe-Mn crusts. The plots of samples are close to that of air, located between the plot of air ($^{21}Ne/^{22}Ne$=9.80, $^{20}Ne/^{22}Ne$=0.029)[9] and that of solar component ($^{20}Ne/^{22}Ne$=13.5 － 14.0, $^{21}Ne/^{22}Ne$=0.0305 － 0.034)[31] but much close to the plot of air. In this diagram, the trend lines of MORB[38], Kola Peninsula[39], Reunion Island[35,40], Loihi Seamount[34], Cosmogenic material[41], and Samoa[42] have been plotted for comparison.

Differences in the isotopic composition of mantle-derived OIB and MORB are the result of mantle heterogeneity[43−46]. OIB is derived from the lower mantle and provides information about the deep mantle domain. Geochemical studies of OIB have revealed that the deep mantle is more heterogeneous than the upper mantle[47]. Based on Sr, Nd and Pb isotope studies, at least four end member components have been proposed for the source of OIB and MORB[48]: DMM (depleted MORB mantle), EM1 (enriched mantle 1) and EM2 (enriched mantle 2), HIMU (high ^{238}U, high μ, $\mu=^{238}U/^{204}Pb$). On this basis, DMM is equivalent to the MORB component and EM1, EM2 and HIMU are end members of OIB[49].

HIMU and EM have quite different $^{3}He/^{4}He$ ratios. The $^{3}He/^{4}He$ ratios of HIMU samples are quite uniform[47] and slightly lower than those of MORB (R/R_A=8±1)[12−14] with an average of 6.8±0.9R_A[50−52] whereas EM samples are more variable and display higher $^{3}He/^{4}He$ ratios than MORB[50,53]. The $^{3}He/^{4}He$

ratios of the low $^3He/^4He$ type Fe-Mn crusts (2.04±0.19－2.92±0.08 R_A) are lower than those of MORB (R/R_A=8±1)[12−14] and more similar to those of HIMU-type enriched mantle (R/R_A=6.8±0.9)[50−52] while the $^3He/^4He$ ratios of the high $^3He/^4He$ type Fe-Mn crusts (10.3±0.32－12.0±0.47 R_A) are somewhat higher than those of MORB (R/R_A=8±1)[12−14] and quite similar to those of EM-type enriched mantle[50,53]. We therefore presume that the noble gases of the low $^3He/^4He$ type Fe-Mn crusts originate from the HIMU-type enriched lower mantle whereas the noble gases of the high $^3He/^4He$ type Fe-Mn crusts originate from EM-type enriched lower mantle.

3.2 The significance of noble gases in Fe-Mn crusts to regional heterogeneity of the lower mantle

Regionally, the low $^3He/^4He$ type of Fe-Mn crusts occurs on the Magellan Seamounts, Marcus-Wake Seamounts, Marshall Island Chain and the Mid-Pacific Seamounts while the high $^3He/^4He$ type of Fe-Mn crusts occurs on the Line Island Chain. The difference of noble gas isotopic composition of Fe-Mn crusts from the Line Island Chain and those from the other seamounts may indicate that the lower mantle is heterogeneous in the western and central Pacific Ocean.

Fe-Mn crusts from Line Island Chain have noble gas isotopic composition typical of the EM-type lower mantle whereas those from the other seamounts have noble gas isotopic compositions typical of the HIMU-type lower mantle. This suggests that the Line Island Chain may originate from EM-type enriched mantle whereas the other seamounts originate from HIMU-type enriched mantle. This is consistent with the fact that lavas with HIMU-like Pb-isotopes and trace element signatures have been reported from seamounts in the Marshall Island Chain and the Magellan Seamounts[54] and from Resolution Seamount in the Mid-Pacific Seamounts[55] while lavas with EM1 and EM2 signatures have been reported from several other seamount chains[54,56].

3.3 Characteristics of the source regions of noble gases in Fe-Mn crusts and their evolution

The He and Ar nuclide abundances and isotopic ratios of Fe-Mn crusts from the western and central Pacific Ocean can be classified into two groups (Table 2; Figure 2(a)－(g), (i)－(j); Figure 3(a)－(d), (g), (i), (j)). Each group displays regular variations in He and Ar nuclide abundances and isotopic ratios (Figure 2(a)－(g), (i)－(j)). The factors that can cause these variations are the isotopic composition of the mantle source, mantle degassing and accumulation of the radiogenic nuclides over time.

(i) Isotopic composition of mantle source. In the *N*-*N* correlation diagram (Figure 2(a)－(g), (i), (j)), the grouping of He, Ar nuclide abundances and isotopic ratios of Fe-Mn crusts is the result of differences in their mantle sources. Because of their stable behavior, noble gases record the isotopic composition of their source areas. Most noble gases degassed from OIB into seawater were dissipated into air but part was trapped in Fe-Mn crusts. As a result, the Fe-Mn crusts record the isotopic composition and degree of degassing of the mantle sources. Because the low $^3He/^4He$ type and the high $^3He/^4He$ type of Fe-Mn crusts display noble gas isotopic signatures of HIMU-type and EM-type lower mantles, respectively, the seamounts with the low $^3He/^4He$ type of Fe-Mn crusts originate from the HIMU-type of lower mantle, while those with the high $^3He/^4He$ type of Fe-Mn crusts originate from EM-type of lower mantle.

In correlation diagrams of ^{38}Ar-^{36}Ar and Ne-Ne (Figure 2(h), (k)－(m)), both the low $^3He/^4He$ type and the high $^3He/^4He$ type of Fe-Mn crusts are plotted on the same trend line, implying that there is no difference of the Ne isotopic ratios and $^{38}Ar/^{36}Ar$ ratios between the HIMU-type of lower mantle source and EM-type of lower mantle source[47]. The Ne isotopic ratios and $^{38}Ar/^{36}Ar$ ratios of both the low $^3He/^4He$ type and the high $^3He/^4He$ type samples are similar to those of air ($^{40}Ar/^{36}Ar$=0.187, $^{20}Ne/^{22}Ne$=9.80, $^{21}Ne/^{22}Ne$=0.029)[9]. This indicates that the mantle sources of both the HIMU-type and the EM-type mantle sources have mixed with recycled noble gases in air [47] or that the noble gases in the Fe-Mn crusts were a mixture of gases of mantle origin and air.

(ii) Mantle degassing. Since its formation, the earth has degassed in two stages: early fast degassing and continuous slow later degassing[57]. Mantle degassing can cause a decrease in He, Ne and Ar abundances[28,58−60]. High $^3He/^4He$ ratios in the mantle plume may result from the incomplete degassing of the lower mantle[61]. In the *N*-*N* correlation diagram (Figure 2), the nuclide abundances of both the low $^3He/^4He$ type of Fe-Mn crusts which originated in the HIMU-type enriched lower mantle and the high $^3He/^4He$ type of Fe-Mn crusts which originated in the EM-type enriched lower mantle are plotted on separate lines with the trends pointing to the origin of the coordinates (the intercepts of trend lines on y axis approach 0).

This indicates that the noble gases in each type of Fe-Mn crusts are derived from mantle sources with the same noble gas isotopic composition (with the same isotopic ratios and therefore plotted in the same trend line in the *N*-*N* correlation diagram) and suggests that the degree of degassing for mantle sources with the same noble gas isotopic composition is variable (plotted in the same trend line but with different distances from the origin). The abundance of noble gas nuclides in the low $^3He/^4He$ type of Fe-Mn crusts decreases in the order of CL01, MD53, MH68, and CX07, suggesting that the Mid-Pacific Seamounts (CX07) have the most intensively degassed HIMU-type enriched mantle, followed by the Marshall Island Chain (MH68), the Magellan Seamounts (MD53) and the Marcus-Wake Seamounts (CL01) in that order. The high $^3He/^4He$ type of Fe-Mn crusts from the Line Island Chain has decreasing noble gas nuclide abundances going from southwest to northeast along the chain, suggesting that degassing of the lower mantle increases from southwest to northeast along this seamount chain.

Because of differences in the degree of degassing, the noble gas nuclide abundances of the same type of samples vary synchronously (Figure 2). In the *N*-*N* correlation diagram, the closer the plots of the samples to the origin of the coordinate (Figure 5), the more intensive the degree of mantle degassing.

(iii) Accumulation of radiogenic nuclides with time. As a result of the decay of their parent isotopes, the isotopic ratios of He and Ar change with time. Fe-Mn crusts grow slowly with growth rates typically of the order of 1—6 mm/Ma[62]. In this study, we scratched the last generation of the crust (the uppermost crust) of the specimens which had a thickness of 9—28 mm. Based on the growth rate calculations of [6], this layer started growing between 3.7—14.7 Ma (Table 1). As the decay products of long lived radioactive parent isotopes (the half lives for the decay of ^{238}U, ^{235}U and ^{232}Th to ^{206}Pb, ^{207}Pb and ^{208}Pb are 4468 Ma, 703.8 Ma and 14010 Ma, respectively[63] and the half life for the decay of ^{40}K to ^{40}Ar is 1250 Ma[64]), the accumulation rates of radiogenic ^4He and ^{40}Ar are very small and cannot cause detectable changes in the isotopic ratios of the noble gases. As a result, the noble gases in Fe-Mn crusts inherited their isotopic composition from their mantle sources.

Mantle heterogeneity is therefore responsible for the grouping of noble gas nuclide abundances and isotopic ratios of Fe-Mn crusts. Noble gases originating from regions with different mantle sources are plotted on different evolutionary trend lines in the *N*-*N* correlation diagram (Figure 5). Mantle degassing therefore plays an important role in causing differences in the noble gas nuclide abundances in Fe-Mn crusts: the closer the plots of samples to the origin of the coordinate on the noble gas evolution trend lines, the more intensive the degree of degassing of the mantle region. Accumulation of the radiogenic nuclides with time is very small and has almost no influence on noble gas abundance and isotopic composition in the Fe-Mn crusts.

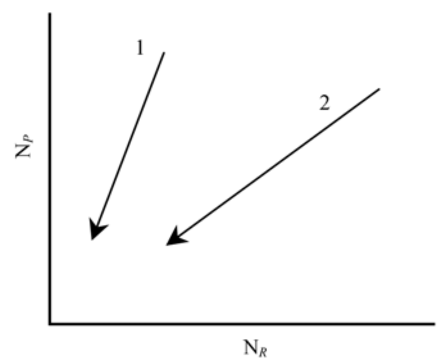

Figure 5 Proposed evolutionary model to explain the nuclide abundances of the noble gases in Fe-Mn crusts from their various sources. N_P is the primary nuclide and N_R is radiogenic nuclide. Line 1 and 2 are evolution trends of noble gases from different types of mantle sources. The differences in slope of trend lines 1 and 2 reflect differences of noble gas isotopic ratios of the two types of samples, the lager the slope of the trend line, the more enrichment of the primary nuclide (N_P) for the underlying mantle. The directions of the arrows show the trend of mantle degassing. Because of degassing, the abundances of the radiogenic nuclide (N_R) and primary nuclide (N_P) vary synchronously.

4 Conclusions

(1) According to the relative values of $^3He/^4He$ ratios between the Fe-Mn crusts and MORB, Fe-Mn crusts from the western and central Pacific Ocean can be classified into two types: a low $^3He/^4He$ type and a high $^3He/^4He$ type. The low $^3He/^4He$ type has higher ^4He abundances and a greater range of ^4He, ^{20}Ne and ^{40}Ar abundance. It is also characterized by lower $^3He/^4He$ ratios than MORB and higher $^{40}Ar/^{36}Ar$ ratios than that

of air. By contrast, the high $^3He/^4He$ type has lower ^4He abundances and a narrow range of ^4He, ^{20}Ne and ^{40}Ar abundances. It is also characterized by higher $^3He/^4He$ ratios than MORB and $^{40}Ar/^{36}Ar$ ratios similar to those of air.

(2) The noble gases in Fe-Mn crusts originated predominantly from the lower mantle. The difference of noble gas nuclide abundances and isotopic ratios between the low $^3He/^4He$ type and the high $^3He/^4He$ type of Fe-Mn crusts are a consequence of the regional heterogeneity in the lower mantle. The low $^3He/^4He$ type originated from HIMU-type enriched mantle and the high $^3He/^4He$ type from EM-type enriched mantle. Mantle heterogeneity is the basic reason for differences in the noble gas isotopic composition between the two types of Fe-Mn crusts while air contamination has some effect on noble gas composition of the crusts, particularly for Ne and Ar.

(3) Fe-Mn crusts from the Magellan Seamounts, Marcus-Wake Seamounts, Marshall Island Chain and the Mid-Pacific Seamounts have a noble gas composition characteristic of the HIMU-type lower mantle whereas Fe-Mn crusts from the Line Island Chain have a noble gas composition characteristic of the EM-type lower mantle. This shows that the Magellan Seamounts, Marcus-Wake Seamounts, Marshall Island Chain and the Mid-Pacific Seamounts originated from the HIMU-type of lower mantle whereas the Line Island Chain originated from the EM-type of lower mantle. This conclusion is consistent with the results of isotope studies of OIB.

(4) Variations in the noble gas isotopic abundances of Fe-Mn crusts appear to be caused by mantle degassing. For samples of the same type, the lower noble gas nuclide abundances may indicate a higher degree of degassing from the mantle and *vice versa*. On the time scale of formation of the Fe-Mn crusts, there is no significant change with time either in the nuclide abundances and isotopic ratios of the noble gases, or in the covariant trend of nuclide abundances caused by mantle degassing.

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