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7 September 1993; accepted 15 December 1993

Retention of Solar Helium and Neon in IDPs in Deep Sea Sediment

Hajime Hiyagon

It was recently proposed that subduction of interplanetary dust particles (IDPs) contained in deep sea sediments could have introduced substantial solar helium and neon to the Earth's mantle. However, it is not certain if IDPs would retain solar noble gases during subduction. A diffusion experiment that examined He and Ne in IDPs in a magnetic separate from Pacific Ocean sediments showed that He and Ne would be lost from IDPs within 3 years at 500°C, and possibly within 10^5 years at 200°C, which suggests that they would be lost from subducting slabs at shallow depths.

An important recent discovery in noble gas geochemistry is the presence of a solar-like Ne component (^{20}Ne/^{22}Ne ~ 13) in mantle-derived samples such as midocean ridge basalts (*1–3*), Loihi and Kilauea basalts (*3, 4*) and gases (*1*), xenoliths (*5*), diamonds (*6*), CO_2-well gases (*7*), and geothermal gases (*8*). The observation of solar-like Ne in such a wide variety of sample types suggests that it is a characteristic noble gas signature of the mantle.

Interplanetary dust particles are rich in solar He and Ne and characterized by high ^{3}He/^{4}He and ^{20}Ne/^{22}Ne ratios of $\sim 10^{-4}$ and 12 to 13, respectively (*9, 10*), and deep sea sediments, especially their magnetic fractions, contain solar He and Ne associated with IDPs (*11–18*). On the basis of these observations, Allègre *et al.* (*19*) attributed solar-like Ne in the mantle, and Anderson (*20*) attributed solar-like Ne and ^{3}He in the mantle, to subduction of sediments carrying IDPs rich in extraterrestrial (ET) noble gases. Because some deep sea sediments subduct into the mantle, He and Ne in IDPs may contribute to the present noble gas signature in the mantle if the fallout rate of IDPs is high enough to account for the present noble gas signature in the mantle and if IDPs can retain solar He and Ne during subduction.

Allègre *et al.* (*19*) and Anderson (*20*) estimated the fluxes of ET noble gases (^{3}He and Ne) to deep sea sediment and compared them with the outgassing fluxes from the mantle. As Anderson discussed (*20*), the ET flux of noble gases to deep sea sediment must be estimated on the basis of noble gas data (*12*) instead of refractory element data (*21*), because noble gases would be lost from large IDP grains ($\gtrsim 50$ μm) by frictional heating on entering the atmosphere (*22, 23*). The flux of ^{3}He to the sea floor that is associated with IDPs is estimated to be 8×10^3 cm^3/year (*12*), whereas the outgassing flux of ^{3}He from the mantle is calculated to be $\sim 3 \times 10^6$ cm^3/year (*20*)—a value two to three orders of magnitude greater. A similar result was obtained for Ne by Allègre *et al.* (*19*), though their preference seems to be for a larger IDP flux and for nearly balanced fluxes of ET Ne in and out of the present mantle. Although it is not necessary to assume a complete balance between the above two fluxes (*19, 20*), the present ET flux is apparently too small to make an important contribution to the present noble gas composition of the mantle (*20*). Hence, the contribution of IDP flux in the past must be considered (*19, 20*). However, it is not certain whether the fallout rate of IDPs in the past was high enough to account for the present Ne (and ^{3}He) in the mantle.

The second question is whether IDPs can retain solar He and Ne during subduction. Amari and Ozima (*16*) conducted a diffusion experiment for He in magnetic separates from deep sea sediments and obtained the activation energy of 17 kcal/mol (71 kJ/mol). Matsuda *et al.* (*18*) also conducted a stepwise heating experiment for He and Ne in a magnetic separate (and its HCl-treated samples) and determined the D/a^2 values (D is the diffusion coefficient and a is the radius of the grains) at 1000°C to be (6 to 8) $\times 10^{-5}$ s^{-1} for ^{4}He and (6 to 7) $\times 10^{-6}$ s^{-1} for ^{20}Ne. Activation energies were not given in their paper, supposedly because of the small number of data points. Allègre *et al.* (*19*) and Anderson (*20*) argue that IDPs are rather retentive of solar noble gases, because some solar noble gases were retained in IDPs even above 1000°C in the stepwise heating experiments (*16, 18*). However, heating time for noble gas extraction in such experiments was only ~1 hour, and the results cannot be directly applied to the geological process at subduction zones.

To measure more precisely the retention of solar He and Ne in IDP grains, I conducted a diffusion experiment. A magnetic fraction was separated from a Pacific Ocean sediment (92SAD01) dredged at 9°30′ to 9°31′N, 174°17′W, and at a depth of 5737 to 5810 m, by the ship *Hakurei-maru No. 2* (Geological Survey of Japan). About 300 g of wet sediment, corresponding to about 85 g of dry sediment, was sieved and grains of <74 μm in size were separated out (*24*). About 200 mg of magnetic material was collected from this fine sediment by use of hand magnets. The collected sample was magnetite with some impurities of silicate grains containing inclusions of magnetic minerals. Two samples, MG1-2 (60.10 mg) and MG1-3 (106.95 mg), were prepared from this magnetic fraction for noble gas analysis. Each sample was wrapped with platinum foil to avoid possible reactions between magnetite and the molybdenum crucible (*25*). Stepwise heating was applied to extract noble gases from the samples; MG1-2 was heated from 600° to 1400°C with 200°C steps and MG1-3 was heated from 500° to 1300°C with 100°C steps. The temperature was maintained for 2 hours at each step. The samples were finally melted at 1600°C to extract the remaining gases. Helium and neon were separated with the use of a cryogenic refrigerator and analyzed separately with a sector-type mass spectrometer (*3*). Hot blanks for ^{4}He and ^{20}Ne were $\sim 5 \times 10^{-9}$ cm^3 [standard temperature and pressure (STP)] and $\sim 7 \times 10^{-11}$ cm^3 (STP), respectively, for the temperatures from 500° to 1600°C, and hot blank corrections (though negligible for most of the temperature fractions) were applied in the calculation of the amounts of gases released from the samples.

The observed concentrations of ^{4}He and ^{20}Ne were $\sim 9 \times 10^{-6}$ cm^3/g and $\sim 8 \times 10^{-8}$ cm^3/g, and the observed ^{3}He/^{4}He and ^{20}Ne/^{22}Ne ratios were (2.3 to 2.6) $\times 10^{-4}$ and 11.2 to 12.6, respectively (Table 1), which are characteristic of noble gas signatures of IDPs (*14, 16–18*). Atmospheric contamination was negligible for He, judging from the high ^{3}He/^{4}He ratios (>100 times the atmospheric ratio of 1.4×10^{-6}) and the high concentration of He. Contamination was minor for Ne, judging from the high ^{20}Ne/^{22}Ne ratios as compared with the atmospheric ratio (9.8). However, to avoid the possible contribution of atmospheric Ne, I used the following definition of excess ^{20}Ne in the diffusion calculation

Department of Earth and Planetary Physics, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan.

$$\text{Excess } {}^{20}\text{Ne} = [{}^{22}\text{Ne}]_{\text{obs}} \times \{({}^{20}\text{Ne}/{}^{22}\text{Ne})_{\text{obs}} - ({}^{20}\text{Ne}/{}^{22}\text{Ne})_{\text{air}}\}$$

where obs refers to the observed concentration or the observed isotopic ratio for the sample run. This correction does not change the result greatly but improves linearity in the Arrhenius diagram (Fig. 1).

From the stepwise heating data, the diffusion coefficients (D) of He and Ne can be calculated based on the assumptions that IDPs are spheres with a single grain radius a and that the initial concentrations of solar He and Ne are uniform in the grains. Because the grain radius of IDPs is not known (only an upper limit of 74 μm is given), I calculated values of D/a^2 instead of D. Because some silicate grains in the sample started to melt at $\gtrsim$1300°C and this might have affected gas release from the sample, I used the data taken below 1200°C in calculating D.

Both ^{4}He and excess ^{20}Ne data in Fig. 1 show good linearity for a temperature range from 800° to 1200°C, which suggests that the observed gas release was controlled by a diffusion process. At lower temperatures (from 500° to 700°C), however, the data show discrepancies from the linear trend toward higher D/a^2 values. This may be explained by a contribution of He and Ne from very fine IDP grains, which would release all the gases they contained at low temperatures (*26*). Because it is assumed in the present calculation that IDP grains have a single radius a, gases released at low temperatures from such fine particles would result in an increase of the apparent D/a^2 values at low temperatures but have a negligible effect on D/a^2 values at higher temperatures. Most gases (more than 80% of excess ^{20}Ne and about 60% of ^{4}He) were released above 800°C. Therefore, in the following discussion, I ignore the contribution of gas release from fine IDP grains and consider only the data from the high-temperature steps (800° to 1200°C).

The linear correlation line in the Arrhenius diagram can be expressed as

$$(D/a^2) = (D_O/a^2)\exp(-E/RT)$$

where E is the activation energy for diffusion, R is the gas constant, T is temperature, and D_O is a pre-exponential factor. The D/a^2 values obtained at 1000° to 1200°C are comparable to those of previous results (*18*). Calculated activation energies are 80 ± 4 kJ/mol and 106 ± 4 kJ/mol for ^{4}He and ^{20}Ne, respectively, and the former is consistent with the previously obtained value [71 kJ/mol (*13*)] and with the value for irradiated magnetite [~70 kJ/mol (*27*)]. This is only about three times that for He-permeable glass [25.3 kJ/mol for fused quartz (*28*)] and is comparable to that for basaltic glass [83.3 kJ/mol (*29*)] but much lower than that for olivine [420 to 500 kJ/mol (*30*)].

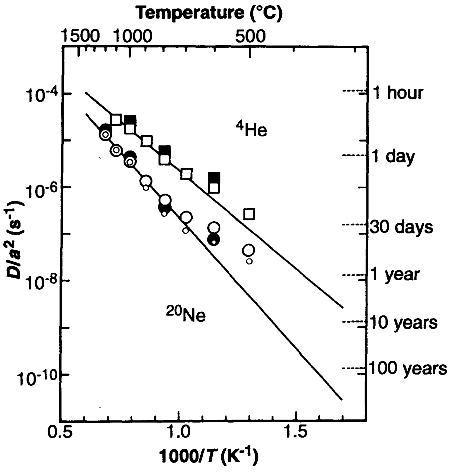

Fig. 1. Arrhenius plots for diffusion of solar ^{4}He and ^{20}Ne in a magnetic separate from Pacific Ocean sediment for the temperature range from 500 to 1200°C. The results of two duplicate samples, MG1-2 (solid symbols) and MG1-3 (open symbols), are shown. In the data for ^{20}Ne in MG1-3, both the data corrected for the atmospheric component (excess ^{20}Ne, large open circles; see text) and the uncorrected data (small open circles) are shown. The corrected data (excess ^{20}Ne) show better linearity in the figure. The linear regression lines are fitted to the data from MG1-3 for a temperature range from 800° to 1200°C for excess ^{20}Ne and from 800° to 1100°C for ^{4}He. The times required for 99% gas release are also shown for corresponding D/a^2 values.

The time (t) required for a gas to diffuse out of spherical grains can be calculated by using D/a^2; for example, 50% of the gas will be released when $Dt/a^2 = 0.03$, and 99% of the gas will be released when $Dt/a^2 = 0.42$. The results shown in Fig. 1 imply that solar He and Ne can be easily released from IDPs; for example, 99% of He and 99% of Ne will be released within 40 days and 3 years, respectively, at 500°C. This suggests that solar He and Ne would be released from IDPs at a depth of less than 40 to 80 km in the subduction system (*31*), where large amounts of water would be released by the decomposition of serpentine and lost from the subducting slab (*32*). Furthermore, if the linear trends are extrapolated to lower temperatures, we may expect that 99% of

Table 1. Helium and neon in a magnetic separate from Pacific Ocean sediment (±1 SD).

Sample mass (g)	Temperature (°C)	^{4}He (10^{-6} cm^3/g)	^{3}He/^{4}He (10^{-4})	^{20}Ne (10^{-9} cm^3/g)	^{20}Ne/^{22}Ne	^{21}Ne/^{22}Ne	Excess ^{20}Ne (10^{-9} cm^3/g)
MG1-2	600	2.89	2.27 ± 0.14	4.15	12.41 ± 0.55	0.0307 ± 0.0059	0.87 ± 0.34
(0.06010)	800	2.59	2.43 ± 0.15	7.09	11.72 ± 0.44	0.0374 ± 0.0033	1.16 ± 0.33
	1000	2.86	2.41 ± 0.14	27.81	11.42 ± 0.21	0.0362 ± 0.0018	3.94 ± 0.49
	1200	0.43	2.41 ± 0.18	29.34	11.30 ± 0.11	0.0338 ± 0.0012	3.89 ± 0.32
	1400	0.03	—	3.24	11.18 ± 0.46	0.0443 ± 0.0059	0.40 ± 0.22
	1600	0.00	—	6.78	11.60 ± 0.29	0.0389 ± 0.0026	1.05 ± 0.27
Total		8.80	2.36 ± 0.13	78.41	11.45 ± 0.12	0.0357 ± 0.0015	11.32 ± 0.83
MG1-3	500	1.25	2.49 ± 0.18	3.79	12.27 ± 0.38	0.0332 ± 0.0047	0.76 ± 0.19
(0.10695)	600	1.31	2.32 ± 0.16	3.37	12.64 ± 0.54	0.0362 ± 0.0028	0.76 ± 0.22
	700	1.33	2.37 ± 0.15	3.47	12.40 ± 0.35	0.0377 ± 0.0028	0.73 ± 0.19
	800	1.54	2.38 ± 0.15	5.33	12.16 ± 0.29	0.0390 ± 0.0041	1.03 ± 0.19
	900	1.77	2.52 ± 0.16	10.43	11.59 ± 0.21	0.0409 ± 0.0030	1.61 ± 0.21
	1000	1.22	2.60 ± 0.19	17.94	11.30 ± 0.18	0.0390 ± 0.0016	2.38 ± 0.28
	1100	0.42	2.33 ± 0.24	15.69	11.33 ± 0.17	0.0374 ± 0.0016	2.12 ± 0.24
	1200	0.07	—	11.83	11.56 ± 0.22	0.0357 ± 0.0020	1.80 ± 0.24
	1300	0.00	—	2.18	11.64 ± 0.39	0.0374 ± 0.0065	0.34 ± 0.15
	1600	0.00	—	9.32	11.49 ± 0.23	0.0435 ± 0.0025	1.37 ± 0.21
	1700	0.00	—	0.19	—	—	—
Total		8.91	2.42 ± 0.13	83.55	11.58 ± 0.11	0.0385 ± 0.0015	12.91 ± 0.67
Air			0.0140		9.80	0.0290	

^{4}He and 99% of Ne will be released from IDPs within 10^5 years, even at 100°C and 200°C, respectively. Because an oceanic plate moves at a speed of 1 to 10 cm/year, or only 1 to 10 km in 10^5 years, the above calculation shows a possibility that solar He and Ne in IDPs would be released at the very beginning of subduction [at a depth of <12 km for 100°C and <24 km for 200°C (*31*)]. At such shallow depths in subduction zones, the solar-type He and Ne released from IDPs would be easily carried away with fluids and lost from the subducting slabs. If this is the case, the solar Ne and ^{3}He observed in the mantle-derived samples is unlikely to be the result of subduction of IDP grains but should be considered as reflecting a primordial noble gas component in the mantle.

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33. I thank K. Yamakoshi for providing the Pacific Ocean sediment; I. Kaneoka and N. Sugiura for valuable discussions; and M. Ozima, J. Matsuda, and D. B. Patterson for valuable comments and suggestions on the manuscript.

30 September 1993; accepted 4 January 1994

Superconducting Mercury-Based Cuprate Films with a Zero-Resistance Transition Temperature of 124 Kelvin

C. C. Tsuei, A. Gupta, G. Trafas, D. Mitzi

The synthesis of high-quality films of the recently discovered mercury-based cuprate films with high transition temperatures has been plagued by problems such as the air sensitivity of the cuprate precursor and the volatility of Hg and HgO. These processing difficulties have been circumvented by a technique of atomic-scale mixing of the HgO and cuprate precursors, use of a protective cap layer, and annealing in an appropriate Hg and O_2 environment. With this procedure, a zero-resistance transition temperature as high as 124 kelvin in *c* axis–oriented epitaxial $HgBa_2CaCu_2O_{6+\delta}$ films has been achieved.

The recent discovery of superconductivity in mercury-based cuprates (*1, 2*) ($HgBa_2Ca_{n-1}Cu_nO_{2n+2+\delta}$) has pushed the superconducting transition temperature (T_c) to values higher than 130 K. More recently, the T_c of Hg-cuprate with $n = 3$ has been reported to increase to 153 K under quasi-hydrostatic pressure (*3*). To put these new materials to effective use in superconducting microelectronic devices—such as in superconducting quantum interference devices (SQUIDs) and microwave applications and in the measurement of their basic intrinsic properties—we must be able to fabricate high-quality thin films. In addition to the experimental complications caused by the severe air sensitivity of the cuprate precursor ($Ba_2Ca_{n-1}Cu_nO_x$), the highly volatile and toxic nature of Hg and HgO makes the synthesis of such films an extremely difficult task.

Recently, Wang *et al.* (*4*) reported the growth of micrometer-thick films of $HgBa_2CaCu_2O_{6+\delta}$ with a magnetically determined T_c of ~120 K. They prepared the films by reacting radio-frequency–sputtered films of $Ba_2CaCu_2O_x$ in a controlled Hg atmosphere. Although a diamagnetic transition was reported, no resistive transition was observed. Clearly, alternative methods for fabricating films with better superconducting characteristics need to be explored.

The difficulties of synthesizing Hg-containing cuprate films mainly stem from the high volatility of Hg and Hg-based compounds. For example, HgO decomposes at ~500°C, whereas the formation of the superconducting phase of Hg-cuprates calls for thermal annealing at 800°C. Similar problems were also encountered in the fabrication of Tl-based cuprate films (*5*), except that Tl_2O_3, the HgO counterpart, is stable up to 800°C. Furthermore, the sticking coefficient of Hg, unlike that of Tl, is vanishingly small unless the substrate temperature during deposition is kept quite low (*6*).

To overcome these experimental difficulties, we developed a technique for the atomic-scale mixing of HgO and the alkaline earth–copper oxide precursor by means of layer-by-layer pulsed laser deposition (PLD). To fabricate films of $HgBa_2CaCu_2O_{6+\delta}$ ($n = 2$) (referred to as Hg-1212), for example, we use the PLD technique to deposit sequential layers of HgO (~5 Å) and $Ba_2CaCu_2O_x$ (~25 Å) from two separate targets. This technique provides a convenient means for controlling the film composition and homogeneity. The films are deposited at room temperature in a vacuum atmosphere (~10^{-6} torr) on (100) $SrTiO_3$ substrates. The film thickness is of the order of 0.5 to 2 μm.

To minimize the detrimental effects of moisture and CO_2 in the air, we deposit

IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, NY 10598–0218, USA.