

New insights into the carrier phase(s) of extraterrestrial ^3He in geologically old sediments

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Abstract

To better understand the composition, characteristics of helium diffusion, and size distribution of interplanetary dust particles (IDPs) responsible for the long-term retention of extraterrestrial ^3He , we carried out leaching, stepped heating, and sieving experiments on pelagic clays that varied in age from 0.5 Ma to ~ 90 Myr. The leaching experiments suggest that the host phase(s) of ^3He in geologically old sediments are neither organic matter nor refractory phases, such as diamond, graphite, Al_2O_3 , and SiC , but are consistent with extraterrestrial silicates, Fe–Ni sulfides, and possibly magnetite. Stepped heating experiments demonstrate that the ^3He release profiles from the magnetic and non-magnetic components of the pelagic clays are remarkably similar. Because helium diffusion is likely to be controlled by mineral chemistry and structure, the stepped heating results suggest a single carrier that may be magnetite, or more probably a phase associated with magnetite. Furthermore, the stepped outgassing experiments indicate that about 20% of the ^3He will be lost through diffusion at seafloor temperatures after 50 Myrs, while sedimentary rocks exposed on the Earth's surface for the same amount of time would lose up to 60%. The absolute magnitude of the ^3He loss is, however, likely to depend upon the ^3He concentration profile within the IDPs, which is not well known. Contrary to previous suggestions that micrometeorites in the size range of 50–100 μm in diameter are responsible for the extraterrestrial ^3He in geologically old sediments [Stuart, F.M., Harrop, P.J., Knott, S., Turner, G., 1999. Laser extraction of helium isotopes from Antarctic micrometeorites: source of He and implications for the flux of extraterrestrial ^3He flux to earth. *Geochim. Cosmochim. Acta* **63**, 2653–2665], our sieving experiment demonstrates that at most 20% of the ^3He is carried by particles greater than 50 μm in diameter. The size-distribution of the ^3He -bearing particles implies that extraterrestrial ^3He in sediments record the IDP flux rather than the micrometeorite flux.

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1. Introduction

High $^3\text{He}/^4\text{He}$ ratios in many deep-sea sediments result from accumulation of extraterrestrial material (Merrihue, 1964). From the observation that $^3\text{He}/^4\text{He}$ ratios in sediments are inversely correlated to sedimentation rates, Ozima et al. (1984) concluded that interplanetary dust particles (IDPs) were the carriers of extraterrestrial ^3He ($^3\text{He}_{\text{ET}}$). However, modeling indicates that $^3\text{He}_{\text{ET}}$ is sensitive to the accretion of IDPs less than ~ 35 μm in size because larger particles are intensely heated during

atmospheric entry and lose helium (Farley et al., 1997). ^3He -bearing IDPs in oceanic sediments are preserved for geologically long periods (Farley, 1995) and at least in one instance for 480 Myrs (Patterson et al., 1998). The long-term retention of $^3\text{He}_{\text{ET}}$, therefore, provides an opportunity to characterize the delivery history of IDPs over geologic time. The carrier phase(s) responsible for the long-term retention of ^3He however, remains unclear. In addition, the diffusive loss of ^3He from sediments residing at the bottom of the ocean for millions of years, or during sediment diagenesis, is poorly characterized. For example, extrapolation diffusivities obtained from high-temperature step-heating experiments (e.g., Amari and Ozima, 1985) to temperature corresponding to the bottom of the ocean

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indicates that greater than 99% of the extraterrestrial ^3He is expected to be lost in 50 Myrs. This is clearly at odds with the pelagic clay ^3He record from the Central Pacific (Farley, 1995). Identification of the ^3He carrier phase is also important for understanding He-retentivity as a function of environmental variables such as redox conditions. Furthermore, the size-distribution of $^3\text{He}_{\text{ET}}$ -bearing particles in geologically old sediments is controversial. Stuart et al. (1999) suggested that instead of IDPs, micrometeorites might be responsible for the long-term retention of ^3He , where micrometeorites are defined as dust particles greater than 50 μm in diameter (e.g., Klock and Stadermann, 1994). Knowledge of the size-distribution of ^3He -bearing particles is important for understanding how sedimentary phenomena such as resuspension and transport by ocean bottom currents may redistribute these particles on the seafloor (e.g., Farley and Patterson, 1995; Marcantonio et al., 1996).

Based on magnetic separations and chemical dissolution experiments performed on Quaternary sediments, previous studies have suggested magnetite and an unknown silicate phase as the carriers of $^3\text{He}_{\text{ET}}$ (Fukumoto et al., 1986; Amari and Ozima, 1988; Matsuda et al., 1990). The suggestion of magnetite as one of the carriers is, however, problematic. Magnetite in IDPs is not primary but formed during atmospheric entry heating through oxidation of Fe–Ni sulfides, olivine, pyroxene, and poorly ordered silicates (Fraundorf et al., 1982; Brownlee, 1985; Bradley et al., 1988). Because magnetite formation during entry heating will involve breaking chemical bonds and diffusion of oxygen, pervasive loss of ^3He from the material undergoing the chemical transformation might be expected.

Fukumoto et al. (1986) noted that in Quaternary sediments approximately 50% of the ^3He was in the non-magnetic fraction, probably associated with extraterrestrial

silicates. While extraterrestrial silicates may be responsible for the long-term retention of ^3He , the diffusivity of ^3He in the non-magnetic fraction is not well characterized. Furthermore, olivine and pyroxene, the dominant silicate phases in IDPs would be susceptible to diagenetic alteration on the seafloor. Chemical leaching on recent sediments suggests that refractory phases such as diamond, graphite, SiC, and Al_2O_3 do not account for more than 10% of the $^3\text{He}_{\text{ET}}$. However, no systematic studies have been carried out in geologically old sediments and thus, refractory phases may or may not be the major carriers in older sediments. Therefore, to understand the nature of the phase(s) responsible for the long-term retention of ^3He and the size-distribution of He-bearing particles, we carried out chemical leaching, stepped heating, and sieving experiments on geologically old sediments.

2. Samples and experimental techniques

2.1. Samples

The sediments used in this study are from the LL-44-GPC-3 core (Corliss and Hollister, 1982; Kyte et al., 1993), Deep Sea Drilling Project (DSDP) Site 596B, and the 1.85 Ga Onaping Breccia in the Sudbury impact crater (Becker et al., 1986). The GPC-3 and DSDP 596B samples were selected on the basis of high ^3He concentrations, available mass from the curators, and to cover a wide range in ages. Samples from the GPC-3 core are between 32 and 51 Ma, while the sample from DSDP 596B (1-6 80-83) has an age between 75 and 90 Ma (Montgomery and Johnson, 1983) (Table 1). The Onaping Breccia was selected to confirm the preservation of extraterrestrial ^3He in fullerenes (Becker et al., 1996) in 1.85 Ga old sediment.

Table 1
Helium concentration in bulk and leached pelagic clays from the GPC3 core and DSDP 596B

Sample	Age (Ma)	Procedure	Reside (%)	$^3\text{He}/^4\text{He } R_A$	$[^3\text{He}] 10^{-12}$ cc STP g^{-1}	$[^4\text{He}] 10^{-9}$ cc STP g^{-1}
GPC3 1092–1093	33	Bulk pelagic clay	—	47.7	16.0	240.7
		Pelagic clay leached with				
		(i) 12 M HF–3 M HCl	7.8	44	1.0	15.7
		(ii) 6 M HCl	58	57.9	4.7	56.7
		(iii) 98% HNO_3	67	28.2	2.1	51.0
Dried acid waste		12 M HF–3 M HCl	—	3.8	0.02	3.3
		6 M HCl	—	4	0.04	6.5
		98% HNO_3	—	3.8	0.02	3.2
GPC3 1136–1144	35.14	Bulk pelagic clay	—	176.3	129.7	529.0
		Pelagic clay + 12 M HF–3 M HCl	13	60.3	13.6	160.1
DSDP 596B 1-6 80-83	75–90	Magnetic fraction (MF)	—	60.9	75.2	875.2
		MF leached w/6 M HCl	78	15.7	2.3	106.5
		Non-magnetic (NMF)	—	33.5	29.2	630.1
		NMF leached w/6 M HCl	82	23	3.8	114.4
Onaping Breccia	1850	Bulk rock	—	0.01	0.4	30992.0
		Bulk rock + 12 M HF–3 M HCl	29	0.04	0.00	362.0

The total volume of acids used in all cases were 50 ml. Helium concentrations have been reported per gram of starting material and not to the amount of residue left following the leach. R_A is the $^3\text{He}/^4\text{He}$ ratio normalized to the air ratio of 1.39×10^{-6} . Age assignments for GPC3 samples are from Kyte et al. (1993). Age for the DSDP sample is from Montgomery and Johnson (1983).

To determine if magnetic and non-magnetic carrier(s) exist, some of the samples were separated into magnetic and non-magnetic fractions. The sediment was suspended in water in a beaker, and a test tube containing a rare earth magnet (Nd-B magnet) was immersed in the beaker. Magnetic particles were found to stick to the walls of the test tube adjacent to the magnet. The test tube was then taken out of the beaker and the particles washed off into a separate beaker (the magnetic fraction). The above step was repeated multiple times until no more particles were found to stick to the test tube when it was immersed in the beaker.

2.2. Chemical leaching

The acid dissolution procedure is shown in Fig. 1. Aliquots of the bulk sediment samples were treated with either 12 M HF–3 M HCl, 6 M HCl, or concentrated HNO_3 solutions for 2 days at room temperature. The leaching time and temperature are similar to those used by previous researchers (e.g., Fukumoto et al., 1986; Matsuda et al., 1990). In addition, magnetic and a non-magnetic fraction of 596B 1-6 80-83 were treated with 6 M HCl solution for 2 days at room temperature. Following the dissolution, samples were rinsed in distilled water and centrifuged to isolate the residue. The residues were transferred onto tin foil and dried in an oven at approximately 60 °C and then loaded into the Caltech Noble Gas Laboratory's automated gas extraction system. Helium was extracted at temperatures of 1400 °C in a radiatively heated double-walled vacuum furnace.

2.3. Stepped heating

Stepped heating experiments were conducted on bulk clay as well as on the magnetic and non-magnetic frac-

tions from the GPC-3 (Kyte et al., 1993) and DSDP 596B samples. Prior to the experiments, samples were dried in an oven for 0.5–1 h at 75 °C and then loaded into copper envelopes. The apparatus used (Fig. 2) for the diffusion experiments is a modification of that described by Farley et al. (1999). In their design, the only heat source is a halogen lamp, whose inside reflector is coated with aluminum to increase the forward transmission of radiation through the sapphire window. Because the thermocouple is directly embedded into the Cu-foil housing the sample, the sample temperature is known accurately (± 3 °C). However, using the lamp as the only heat source, we could not reach temperatures greater than about 550 °C for 150 mg of pelagic clay. To achieve higher temperatures, we added a second heat source in the form of a tungsten filament grid located inside the vacuum chamber about 3–5 mm below the Cu-envelope (Fig. 2). Because we can achieve good temperature control, thermal stability and rapid heating with the lamp, at low-temperatures (<500 °C), heating is accomplished exclusively by the lamp. At higher temperatures, the tungsten filament grid is activated to reach temperatures about 20 °C below the desired set point. The final temperature is reached by heating with the lamp, and temperature set points were reached in less than 4 min and with under 3 °C overshoot. The pill getters (Fig. 2) were used for adsorbing H_2 while activated charcoal at liquid nitrogen temperature was used to freeze down CO_2 and H_2O . The schematic shown in Fig. 2 was used for temperatures ≤ 850 °C, following which samples were transferred to a resistively heated furnace and the temperature was monitored using a dual wavelength optical pyrometer. Estimated temperature accuracy for furnace runs is ± 10 °C. Stepwise heating began as low as 150 °C and step intervals were usually 50–100 °C. The duration of each step was 30–60 min.

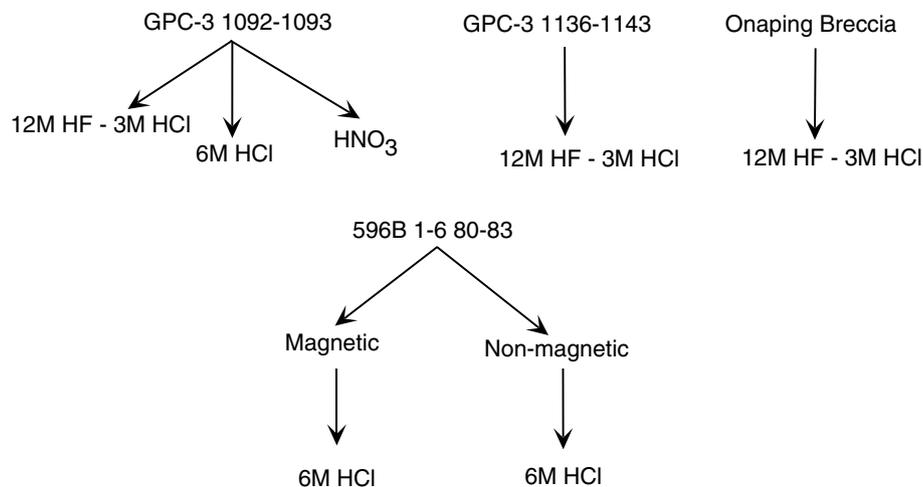


Fig. 1. Chemical dissolution scheme for the different samples used in this study.

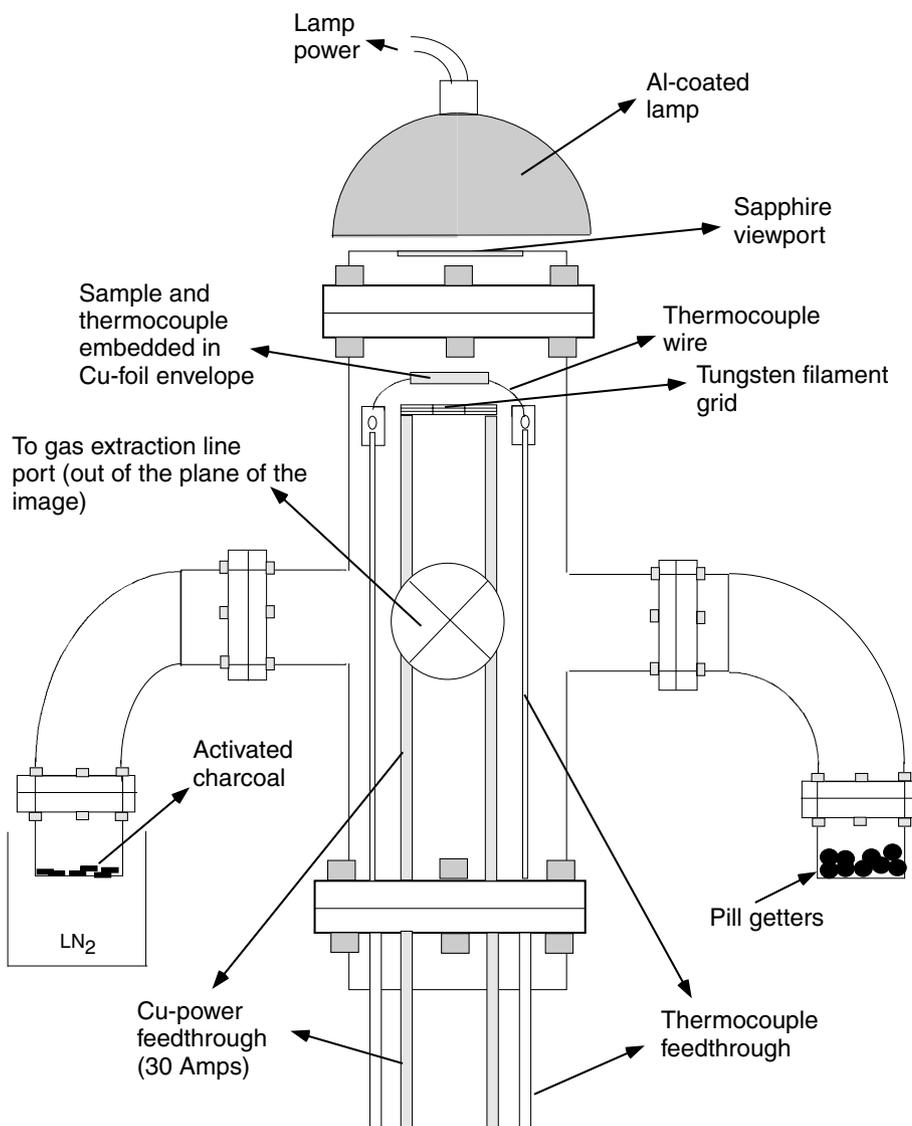


Fig. 2. Schematic diagram of the diffusion cell used in the stepped heating experiments.

2.4. Size distribution

To determine the size distribution of ^3He -bearing IDPs, we studied a 33 Ma old pelagic clay (1092–1093) from the GPC-3 core, selected based on the available mass. The sample was immersed in a beaker of water and swirled with a non-magnetic rod to disaggregate the clay. We then used mesh sizes of 53, 37, and 13 μm to sort the sediment into four size bins of >53 , 37–53, 13–37, and <13 μm . The sample was sieved under ethanol and then dried in an oven for 1 hr at 100 $^\circ\text{C}$ following which it was transferred onto tin foil and loaded into the gas extraction system. Like the other samples, helium was extracted at temperatures of 1400 $^\circ\text{C}$ in a radiatively heated furnace.

2.5. Helium measurements

Gas cleanup and mass spectrometric techniques have been described by Patterson and Farley (1998). Typical

^4He blanks for both the resistance furnace and the diffusion cell were less than 0.1×10^{-9} cc STP, and averaged less than 1% of the ^4He from the samples. ^3He hot blanks were always less than 1×10^{-15} cc STP, in all cases constituting $<1\%$ of the sample. The 1σ variation on standards of similar sizes to the samples analyzed was 0.5% for ^4He and $\sim 3.5\%$ for ^3He .

3. Results and discussion

3.1. Chemical leaching

The results of our acid leaching experiments on the pelagic clays are summarized in Table 1 and Fig. 1. The chemical leaches removed 71–94% of the ^3He . To verify that ^3He -bearing IDPs were not lost during centrifuging and subsequent decanting procedures, the acid waste from some of the leaches were collected, dried, and analyzed for ^3He content. The dried acid waste has negligible amounts

of ^3He (Table 1), and hence, we conclude that ^3He was lost because the acids chemically destroyed the carrier phase(s). Treatment of bulk pelagic clays with a mixture of 12 M HF–3 M HCl removed 90–94% of the ^3He , consistent with previous observations (Fukumoto et al., 1986). Refractory phases found in meteorites, such as chromite, diamond, SiC, graphite, amorphous carbon, Al_2O_3 , and organic material, are chemically resistant to HF–HCl (Huss and Lewis, 1995). If these phases, residing in IDPs on the ocean floor for tens of millions of years, behave chemically in an analogous fashion to those in meteorites, our observations preclude them as the primary carriers of ^3He in geologically old sediments. However, silicates, magnetite, ilmenite, Fe–Ni sulfides, and Fe–Ni metal are dissolved or etched by HF–HCl (Fukumoto et al., 1986; Wieler et al., 1986) and, thus, may be responsible for the long-term retention of $^3\text{He}_{\text{ET}}$.

Leaching bulk pelagic clay with 6 M HCl removes about 70% of the ^3He . Because magnetite is attacked by 6 M HCl (Scott et al., 1981), the HCl step is consistent with magnetite being a carrier of $[\text{}^3\text{He}]_{\text{ET}}$ (Amari and Ozima, 1985; Fukumoto et al., 1986; Matsuda et al., 1990). Matsuda et al. (1990) observed that 75% of the ^3He in the magnetic fraction of the sediments is lost by treatment with 3 M HCl in two days at room temperature. Since the magnetic fraction usually accounts for $\leq 50\%$ of the total ^3He (Fukumoto et al., 1986; Amari and Ozima, 1988), our HCl leaching results suggest that, if other carriers of ^3He exist, they are not resistant to 6 M HCl either. To verify this assertion, we separated the 90 Myr old pelagic clay from DSDP Site 596B into a magnetic and non-magnetic fraction. Approximately 50% of the ^3He was in the magnetic fraction (Table 1). Both magnetic and non-magnetic components were leached with 6 M HCl. While 97% of $[\text{}^3\text{He}]_{\text{ET}}$ was lost from the magnetic fraction, 87% was lost from the non-magnetic fraction (Table 1). The result implies either (1) magnetic and non-magnetic carriers exist and both are strongly attacked by 6 M HCl or (2) the carrier is magnetic, or associated with a magnetic phase, and the magnetic separation only removed 50% of magnetic grains from the sediment. We discuss this possibility later.

Fukumoto et al. (1986) observed that $[\text{}^3\text{He}]_{\text{ET}}$ in the magnetic fraction in Quaternary sediments is resistant to 98% HNO_3 and, therefore, suggested magnetite as a carrier. If so, we argue against magnetite as the dominant carrier of $[\text{}^3\text{He}]_{\text{ET}}$ in geologically old sediments because following our HNO_3 leach on bulk pelagic clay, 87.5% of $[\text{}^3\text{He}]_{\text{ET}}$ is lost (Table 1). However, we cannot rule out the possibility that residence on the ocean floor for tens of millions of years makes magnetite more susceptible to attack by HNO_3 acid.

Becker et al. (1996) suggested that fullerenes are a carrier phase of extraterrestrial ^3He in the 1.85 Ga ejecta layer that is associated with the Onaping Breccia in the Sudbury impact crater. Because fullerenes are resistant to HF and HCl, our leaching experiments do not support fullerenes as the host of ^3He in oceanic sediments. To test for the

presence of extraterrestrial ^3He in the 1.85 Ga sediments associated with the Sudbury impact structure, we analyzed the supposed fullerene-bearing impact breccia. The samples were collected from the same locality (Dowling township) as Becker et al. (1996), although not from the same outcrop (Tom Ahrens, personal communication). To avoid the potentially problematic extraction of fullerene, we simply analyzed the bulk rock. Fusion at 1400 °C yielded a ^3He concentration of 0.4×10^{-12} cc STP g^{-1} (1.08×10^7 atoms/g) comparable with the ^3He concentration of 7.4×10^6 atoms/g measured by Becker et al. (1996). However, the $^3\text{He}/^4\text{He}$ ratio of the bulk rock is 1×10^{-8} , similar to the value expected from the reaction $^6\text{Li}(n, \alpha) \rightarrow ^3\text{H} \xrightarrow{\beta} ^3\text{He}$ (Andrews, 1985) and provides no evidence for an extraterrestrial component. Furthermore, we treated 0.5 g of bulk rock with HF–HCl, which removed more than 99% of the ^3He and ^4He (Table 1 and Fig. 1). While He loss could result from chemical attack by HF–HCl, there is no evidence that HF–HCl treatment destroys the fullerenes in preference to the HF– BF_3 demineralization scheme used by Becker et al. (1996). First, Becker et al. (1994) documented a fullerene content of 6–10 ppm in the Onaping formation using the HF–HCl demineralization technique. In 1996, Becker et al., used HF– BF_3 to demineralize the rock. Although they do not report the fullerene content of the rock, we have calculated an upper limit to the fullerene concentration based on the measured ^3He concentration in the bulk rock, the measured ^3He concentration in the fullerene, and assuming that all the ^3He in the bulk rock is associated with fullerenes. The calculation implies at most 2.5 ppm fullerene in the rock, which is comparable to or slightly lower than the concentration determined by Becker et al. (1994). If fullerenes preferentially get hydroxylated or chlorinated by the HF–HCl treatment, fullerene content in the HF–HCl demineralized residue should have been lower. Second, Robl and Davis (1993) found no relative difference in organic alteration between the HF–HCl and HF– BF_3 techniques using elemental analyses, FTIR, and microscopic examinations. However, the HF–HCl demineralization technique led to higher Cl and F content in the residue. While this may indicate a slightly enhanced organic alteration, formation of insoluble salts is also an explanation (Robl and Davis, 1993). Hence, we believe that the two orders of magnitude decrease in the ^3He content following HF–HCl treatment does not result from destruction of fullerenes and thus, we find no evidence of fullerene-hosted ^3He in the Sudbury impact breccia.

In summary, our chemical leaching experiments are consistent with extraterrestrial silicates, ilmenite, Fe–Ni sulfides and possibly magnetite, but not with organic matter (including fullerenes), SiC, graphite, amorphous carbon, Al_2O_3 , or diamond as the primary phase(s) responsible for the long-term retention of ^3He in the sedimentary record. The dominant silicates in IDPs are olivines and pyroxenes. Layer silicates such as serpentine and smectite may be abundant in a few IDPs (up to 40% modal abundance; Germani et al., 1990). While ter-

restrial layer silicates are stable on the seafloor for millions of years, olivine and pyroxene crystals, such as those found in Mid Ocean Ridge Basalts, undergo alteration within a few million years. Extraterrestrial olivine and pyroxene are likely to behave similarly. For example, in 50 Myr old silicate cosmic spherules recovered from the seafloor, the silicate minerals are completely altered and only magnetite grains are preserved (Brownlee, 1985). In IDPs, olivine and pyroxene grains are often rimmed by magnetite, a few to few tens of nm thick, which forms during atmospheric entry-heating (Bradley et al., 1988; Germani et al., 1990). Because magnetite is stable on the ocean floor for tens of millions of years (Brownlee, 1985), the magnetite rims may protect the silicate phases against chemical alteration and may also explain the association of the ^3He carrier(s) with magnetite. If Fe–Ni sulfides and/or magnetite are the carriers of extraterrestrial ^3He , the long-term retention of ^3He in the sedimentary record may be affected by redox conditions, such as Eh and pH of pore waters in sediments. Compared to magnetite, Fe-sulfides, such as troilite and pyrrhotite, are stable in more reducing environments and over a narrower range of Eh and pH conditions (e.g., Brookins, 1988). Thus, Fe-sulfides may be more susceptible to variations in redox conditions on the seafloor than magnetite. However, it is possible that the mineral transformation reactions are controlled by kinetics, and minerals out of equilibrium with the environment may survive over geologically long periods. More work is required to identify the carrier of ^3He in sediments and understand the stability of the phase(s) to variations in redox conditions.

Finally, we note that following the chemical leaches about 5–30% of the total ^3He remains in the residue, implying either multiple carriers of ^3He , or incomplete dissolution of the carrier phase. We favor the latter interpretation because the HCl step on DSDP 596B, which had a higher acid volume to sample mass ratio compared to the HCl step on GPC3 1092–1093, lost significantly more ^3He .

3.2. Stepped heating

Results of the stepwise degassing experiments are listed in Table 2. Like previous workers (Fukumoto et al., 1986; Matsuda et al., 1990; Hiyagon, 1994), we find that approximately half of the extraterrestrial helium is associated with the magnetic fraction, while the rest is in the non-magnetic fraction. All seven samples display remarkably similar ^3He release patterns, characterized by a small peak between 350–400 °C and a larger but broader peak between 600–750 °C (Figs. 3 and 4). Approximately 15% of the ^3He is released at temperatures between 300 and 400 °C, while between 70% and 80% of the total ^3He is released between 450 and 800 °C. The bimodal release has been previously observed in one sample from DSDP Site 607 (Farley, 2001) although the low temperature peak was associated with a $^3\text{He}/^4\text{He}$ ratio of 0.1 R_A and, thus, attributed to

Table 2

Results of diffusion runs on pelagic clays

Temperature (°C)	^3He 10^{-12} cc STP	$^3\text{He}/^4\text{He}$ R_A	$\text{Log } D/a^2 \text{ s}^{-1}$
<i>Sample: GPC3 115 Non-magnetic fraction; age = 0.54 Ma; mass = 100 mg</i>			
150	0.00	0.0	—
250	0.06	0.4	–8.2
350	0.29	0.5	–6.7
400	0.06	0.2	–7.1
450	0.16	0.5	–6.6
500	0.23	1.0	–6.2
550	0.37	2.4	–5.8
600	0.36	3.3	–5.7
650	0.42	6.7	–5.4
700	0.66	14.4	–5.0
750	0.57	21.5	–4.8
800	0.35	23.9	–4.7
850	0.13	5.7	–5.0
950	0.24	20.1	–4.2
1400	0.03	4.4	—
<i>Sample: GPC3 1092–1093 bulk pelagic clay; age = 33 Ma; mass = 100 mg</i>			
150	0.01	1.0	–11.6
250	0.11	1.8	–9.3
350	1.18	21.9	–7.3
400	0.83	30.5	–7.1
450	0.62	47.0	–7.0
500	1.29	44.4	–6.5
550	1.04	60.2	–6.5
600	1.38	99.5	–6.2
650	2.51	151.1	–5.8
700	3.61	165.3	–5.5
750	5.55	166.8	–5.0
800	3.66	172.1	–4.9
850	3.03	158.2	–4.8
950	3.32	171.2	–4.0
1000	0.13	64.8	–4.2
1400	0.02	11.8	—
<i>DSDP 596B 1-6 80-83 bulk pelagic clay; age = between 75 and 90 Ma; mass = 150 mg</i>			
100	0.00	3.2	–12.8
150	0.01	2.2	–12.0
200	0.02	1.7	–11.0
250	0.17	4.2	–9.2
300	0.62	9.3	–8.0
400	1.16	8.7	–6.8
450	0.35	3.0	–7.2
500	1.11	11.4	–6.6
550	2.21	33.0	–6.2
600	3.68	66.9	–5.8
650	4.34	70.1	–5.5
700	6.64	58.5	–5.1
750	5.65	86.1	–4.9
755	2.19	65.4	–5.1
850	0.95	134.8	–5.4
900	3.04	163.2	–4.6
1400	2.44	162.7	—
<i>Sample: GPC3 1136–1143 magnetic fraction; age = 35.1 Ma; mass = 14 mg</i>			
150	0.00	9.9	—
250	0.06	76.2	–8.5
350	0.89	153.0	–6.1
400	0.31	128.5	–6.2
450	0.23	112.2	–6.2
500	0.21	114.0	–6.1
550	0.26	95.3	–5.9
600	0.38	163.2	–5.7
650	0.64	145.0	–5.5

Table 2 (continued)

Temperature ($^{\circ}\text{C}$)	^3He 10^{-12} cc STP	$^3\text{He}/^4\text{He}$ R_A	$\text{Log } D/a^2 \text{ s}^{-1}$
700	0.85	197.0	-5.2
750	1.00	162.2	-4.4
800	0.34	170.5	-4.4
850	0.04	114.0	-4.8
950	0.05	104.2	-4.3
1400	0.00		

Sample: GPC3 1136–1143 Non-magnetic fraction; age = 35.1 Ma; mass = 82 mg

150	0.00	6.0	-11.5
250	0.05	12.6	-8.7
350	0.29	29.1	-7.1
400	0.41	38.9	-6.4
450	0.38	45.9	-6.2
500	0.30	54.9	-6.1
550	0.41	86.1	-5.9
600	0.52	110.9	-5.6
650	0.83	139.1	-5.2
700	0.79	141.8	-5.0
750	0.69	136.2	-4.8
800	0.53	135.2	-4.6
850	0.19	154.2	-4.8
950	0.19	126.0	-4.3
1400	0.03	122.0	

Sample: GPC3 1506–1514 magnetic fraction; age = 50.6 Ma; mass = 16 mg

150	0.00	1.3	—
250	0.95	27.7	-9.0
350	16.48	121.0	-6.4
400	12.39	110.6	-6.1
450	6.63	88.2	-6.2
500	9.08	122.2	-5.9
550	8.83	98.2	-5.8
600	9.64	105.2	-5.7
650	16.29	138.9	-5.3
700	14.00	167.6	-5.2
750	17.75	207.2	-4.9
800	11.20	222.0	-4.9
850	7.30	44.9	-4.8
950	8.40	239.5	-4.3
1400	1.99	7704.0	

Sample: GPC3 1506–1514 Non-magnetic fraction; age = 50.6 Ma; mass = 130 mg

150	0.00	6.0	-12.3
250	0.17	6.0	-9.0
350	1.31	24.6	-7.2
400	2.02	35.5	-6.5
450	0.83	16.6	-6.6
500	1.10	32.0	-6.4
550	1.65	61.6	-6.1
600	4.07	101.0	-5.5
650	5.46	121.6	-5.1
700	3.72	110.8	-5.0
750	2.93	117.6	-4.9
800	2.00	157.4	-4.8
850	1.11	143.7	-4.8
950	1.37	141.1	-4.3
1400	0.24	160.8	

For all samples duration of each step was 60 min. Age assignments for GPC3 samples are from Kyte et al. (1993). Age for the DSDP sample is from Montgomery and Johnson (1983).

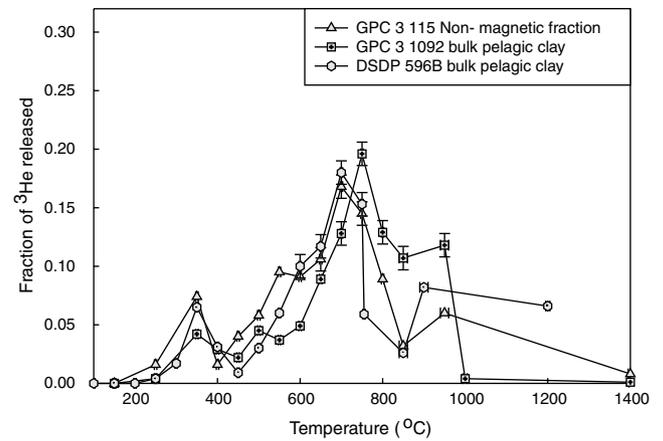


Fig. 3. Fraction of ^3He released from pelagic clays as a function of temperature. Note the small peak at 350 $^{\circ}\text{C}$ and a larger but broader peak between 600 and 750 $^{\circ}\text{C}$. $^3\text{He}/^4\text{He}$ ratios $>20 R_A$ indicate that the low temperature peak is from the release of extraterrestrial ^3He . Sample ages are listed in Table 2. The errors in the fraction of ^3He released are based on the uncertainty in ^3He measurements, which is $\sim 3.5\%$. Uncertainty on temperature measurements is $\pm 3^{\circ}\text{C}$ at steps $<850^{\circ}\text{C}$. At higher temperatures the uncertainty is $\pm 5\text{--}10^{\circ}\text{C}$.

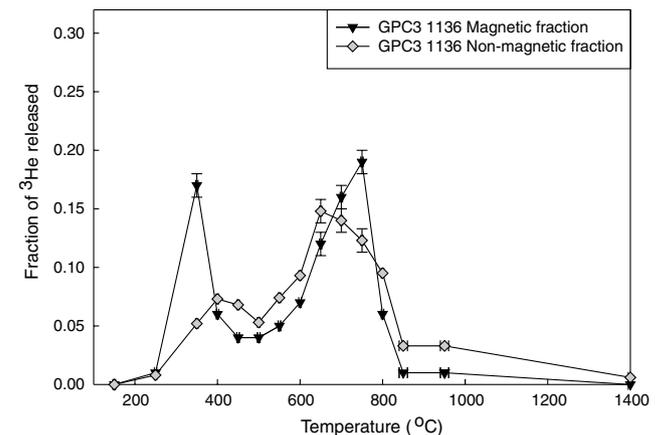
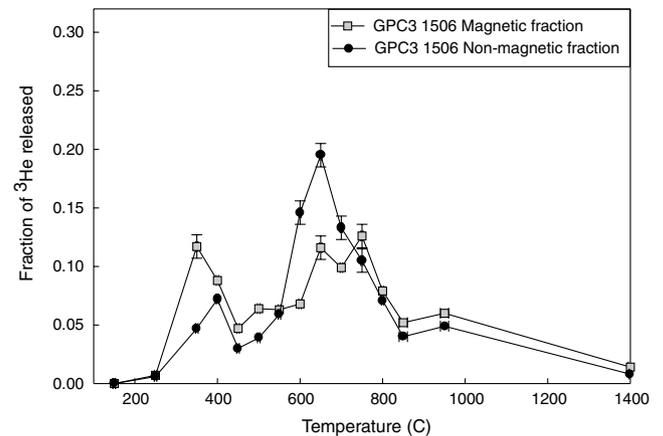


Fig. 4. ^3He release profile as a function of temperature in magnetic and non-magnetic fraction of pelagic clays from the GPC3 core. Sample ages are listed in Table 2. Note the similarity in release profiles in the magnetic and non-magnetic components of the two samples. Symbols have been chosen to be consistent with Fig. 5. Error bars as in Fig. 3.

release of crustal helium. However, $^3\text{He}/^4\text{He}$ ratios in excess of 20 R_A (Table 2) in our experiments strongly suggest that the ^3He released in the lower temperature steps is either extraterrestrial or cosmogenic in origin. If we assume that ^3He released at temperatures $\leq 450^\circ\text{C}$ is cosmogenic helium, exposure ages of ≥ 5 Myrs are required to account for all the ^3He in the samples using the production rate at sea level and high latitude (Cerling and Craig, 1993). Such long exposure ages are improbable, especially since detrital minerals have low ^3He retentivity (Farley, 1995). Hence, we conclude that ^3He released at low temperatures ($< 450^\circ\text{C}$) is extraterrestrial. Previous workers may have failed to identify the low-temperature peak because their experiments started at temperatures in excess of 500°C (e.g., Amari and Ozima, 1985; Amari and Ozima, 1988; Hiyagon, 1994). The high temperature peak observed in our experiments ($600\text{--}750^\circ\text{C}$) is also different from previous studies, occurring at temperatures significantly lower than the peak release temperature of 900°C in seafloor magnetic fines (e.g., Hiyagon, 1994). This difference is probably related to the larger number of steps in our experiments (discussed later).

Our stepped heating experiments provide additional insights into whether the ^3He carrier phase(s) in the magnetic and non-magnetic fraction of the sediments are different. Because helium diffusivities in IDPs must be controlled by mineral structure and chemistry (e.g., Trull et al., 1991; Wolf et al., 1996; Reiners and Farley, 1999), if the ^3He is carried in both a magnetite and a non-magnetic phase, for identical laboratory heating schedules, the ^3He release pattern in the magnetic and non-magnetic components would in general be expected to be distinct. It is clear that the ^3He release profiles, shown in Fig. 4, in the magnetic and non-magnetic separates from two GPC3 samples are remarkably similar, suggesting a single non-magnetic carrier. Alternatively, the carrier is magnetic or associated with a magnetic phase, and the magnetic separation was not effective in removing all the magnetic grains from the sediment. To test this possibility we measured the magnetic properties of a pelagic clay (GPC3 1136–1144) in the Superconducting Rock Magnetometer in the Caltech paleomagnetic lab. The saturation magnetic moment of the pelagic clay obtained during the IRM (isothermal remanent magnetization) acquisition was 2.37×10^{-2} emu, implying ~ 500 ppm by weight of magnetite (Joe Kirschvink personal communication). The pelagic clay was then separated into magnetic and non-magnetic components by procedures described earlier. The non-magnetic component had a saturation magnetic moment of 1.36×10^{-2} emu, suggesting that 57% by weight of the magnetite remained in the non-magnetic component. Thus, although the magnetic separation technique concentrates the magnetic particles in the “magnetic fraction” of the sediment, it removes only $\sim 50\%$ of all the magnetic particles. As a result, we conclude from our step heating results that ^3He is probably carried by a single phase, that is either magnetic (e.g., magnetite, pyrrhotite) or a phase associated with

magnetite. We favor the latter since extensive loss of ^3He might be expected in the material that transforms into magnetite during atmospheric entry heating.

3.2.1. Comparison with seafloor magnetic fines

Stepped heating experiments on seafloor sediments have typically used different step-heat schedules to study the ^3He release profile (e.g., Amari and Ozima, 1985; Amari and Ozima, 1988; Hiyagon, 1994; Farley, 2001). Therefore, we cannot directly compare the ^3He release profiles from the stepped heating experiments. To facilitate the comparison, we computed apparent ^3He diffusivities at each temperature step from the fraction of gas released at that temperature, using the solution to the spherical diffusion equation given by Fechtig and Kalbitzer (1966). We use the term “apparent diffusivity” because implicit in this calculation are the assumptions that volume diffusion through a sphere adequately describes He diffusion in IDPs, the carrier phase does not undergo thermal decomposition or reactions with other minerals present, and the ^3He concentration in the carrier phase(s) prior to the stepped heating experiments was homogeneous. The last two assumptions are difficult to verify and are unlikely to be strictly valid. For example, the implantation depth of solar wind ions, the probable ^3He source, is only about 30 nm. Hence, a near-surface step-function may be a better description of the initial ^3He concentration profile (e.g., Harris-Kuhlman, 1998), but it is not clear how atmospheric entry heating and residence on the seafloor for tens of millions of years perturbs this profile.

The diffusivity profiles from our experiments are shown on an Arrhenius plot in Fig. 5. The diffusion profiles are characterized by linear segments from about 250 to 400°C and above 450°C , and are not consistent with simple volume diffusion from a single diffusion domain (e.g., Lovera et al., 1991; Reiners and Farley, 1999). The shape of the diffusion profile is qualitatively similar to the profile for Ar diffusion through K-feldspar, attributed to a range of diffusion domain sizes (e.g., Lovera et al., 1997).

To better understand the diffusion profile in our stepwise outgassing experiments, we analyzed a separate aliquot of the magnetic fraction of GPC-3 1136–1143. Four steps, each of 30 min duration, were initially performed at 400°C , following which the sample was cooled to a lower temperature (300°C). The outgassing then followed a monotonic schedule with temperature increments of $25\text{--}50^\circ\text{C}$. The results from this cycled experiment are listed in Table 3. The diffusivity of the first step at 400°C is identical to the original outgassing experiment but drops to lower diffusivities in the next few steps (Figs. 6 and 7). Similar profiles have been observed for Ar diffusion through K-feldspar (Lovera et al., 1991) and He diffusion through titanite (Reiners and Farley, 1999). The ^3He diffusion profile can be reasonably attributed to rapid depletion of a weakly bound gas-fraction that is nearly exhausted at 400°C , significantly prior to depletion of a high temperature ^3He reservoir.

The amount of ^3He released in the lower temperature steps (corresponds to the first peak on the step heat profile)

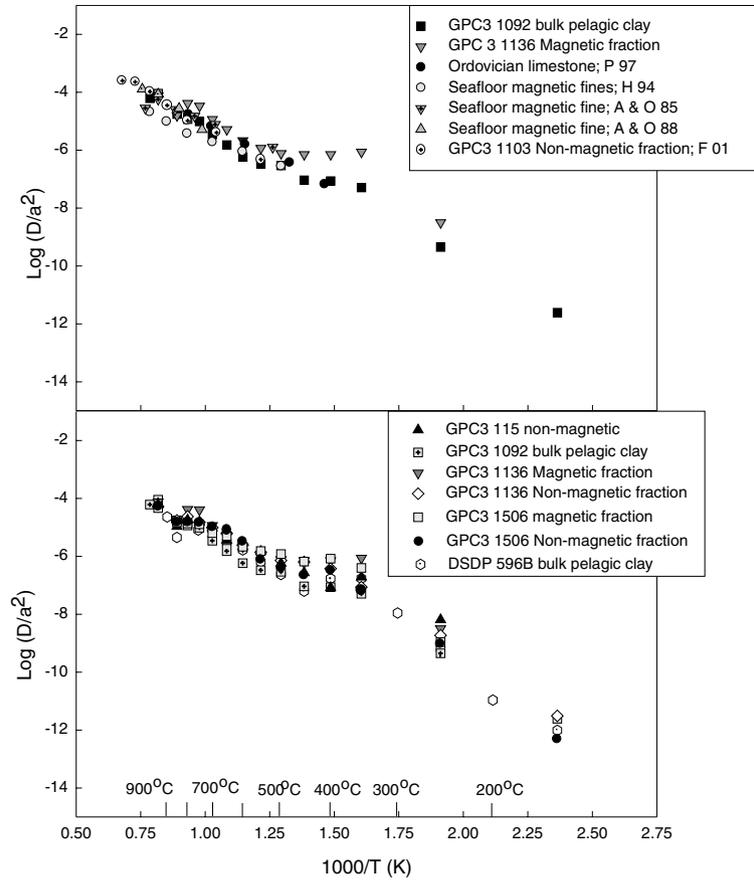


Fig. 5. Arrhenius plot of ^3He diffusion in IDPs. Diffusivity at each step was calculated using the formulation for diffusion through a sphere (Fechtig and Kalbitzer, 1966). The bottom panel is our new experimental data. The top panel is a comparison of two of our samples with previous studies. P 97 is Patterson et al., 1998; H 94 is Hiyagon 94; A and O 85 is Amari and Ozima, 1985; A and O 88 is Amari and Ozima, 1988; F 01 is Farley, 2001.

Table 3
Results of cycled diffusion run on the magnetic fraction of GPC3 1136

Temperature (°C)	Duration (min)	^3He 10^{-12} cc STP	$^3\text{He}/^4\text{He}$ R_A	$\text{Log} D/a^2$ s^{-1}
400	30	2.01	134.8	-6.2
400	30	0.30	161.1	-6.7
400	30	0.17	218.6	-6.8
400	30	0.12	193.0	-7.0
300	30	0.001	5.8	—
325	30	0.002	28.9	—
350	30	0.01	85.8	-8.0
375	30	0.02	138.6	-7.6
410	30	0.12	176.3	-6.9
450	30	0.25	168.8	-6.6
475	30	0.32	178.6	-6.4
500	30	0.32	230.1	-6.4
550	30	0.83	170.2	-5.9
600	30	1.80	195.9	-5.4
625	30	1.73	196.7	-5.2
650	30	1.97	198.5	-5.0
1400	30	7.58	179.4	—

$\text{Log} D/a^2$ was not computed for the 300 and 325 °C steps because of the low gas yields and high associated uncertainties. Mass of sample was 31 mg.

accounts for about 15% of the total ^3He . At least two distinct physical processes may account for the weakly bound ^3He in IDPs. Irradiation of IDPs by solar wind and solar

flare ions may damage the crystal lattice and produce an outer amorphous layer that is on the order of a few to few tens of nm thick (e.g., Ducati et al., 1973; Ziegler et al., 1985). Solar wind implanted He (SW-He) residing in this amorphous layer would be lost by diffusion more readily than SW-He residing deeper in the relatively undamaged crystal lattice at depths of >30 nm (Ducati et al., 1973). Koscheev et al. (2001) have demonstrated that ion implantation of a single energy and isotopic composition into diamonds can produce both low and high-temperature release peaks from the same grains. Although these authors did not give a physical explanation of their results we suggest that creation of an amorphous layer by radiation damage may explain the bimodal release pattern that they observed in diamonds, and that we see in our stepped heating experiments.

Alternatively, 15% of the ^3He released at low temperatures in our stepped heating experiments may be SW-He, with the high temperature gas-fraction representing He from solar energetic particles (SEP). SEPs typically have energies on the order of 100 KeV/amu (Wieler et al., 1986), and the stopping distance for such particles would be a few tenths of a micron to few microns (Ziegler et al., 1985). Thus, compared to SW-He, SEP-He would be implanted significantly deeper into minerals. An

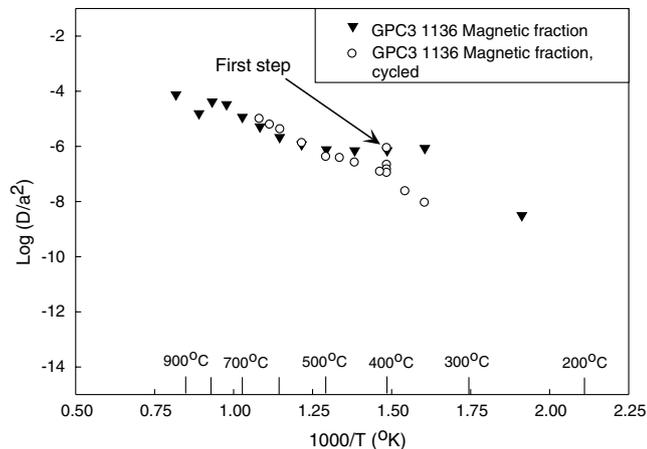


Fig. 6. Arrhenius plot of the thermally cycled run of GPC3 1136–1143. For comparison, data from the monotonic run have been plotted.

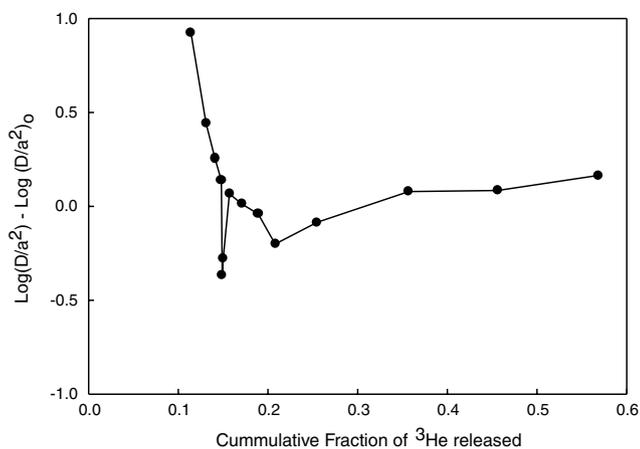


Fig. 7. Extent of deviation from linearity of the diffusion profile vs. cumulative fraction of ^3He released in the cycled diffusion experiment from the magnetic fraction of GPC3 1136–1143. The parameter $\log(D/a^2) - \log(D/a^2)_0$ (Reiners and Farley, 1999), is similar to $\ln(R/R_0)$ of Lovera et al. (1991), and is the extent of deviation from linearity, where the linear segment is defined by the high temperature steps ($>450^\circ\text{C}$). $\log(D/a^2)_0$ is $\log(D/a^2)$ for a perfectly linear correlation. Compared to the high temperature segment ($>450^\circ\text{C}$), diffusivities in the first two steps at 400°C are anomalously high, followed by transient low diffusivities.

implication of this hypothesis is that $>99\%$ of the SW-He has been lost from IDPs now residing on the ocean floor, because the ratio of solar particles with energies of ~ 1 KeV/amu to particles with ~ 100 KeV/amu is about 10,000 (Wieler et al., 1986; Geiss and Bochsler, 1991). The loss of SW-He may result from atmospheric entry heating, or diffusional loss on the seafloor, or both.

The high temperature diffusivities calculated from our experiments are in broad agreement with previous studies (Fig. 6; e.g., Hiyagon, 1994; Farley, 2001). Hence, the shift in peak release temperature from 900°C to between 600 and 750°C in our experiments is a result of the heating schedule we used. To compute the mean activation energy and the frequency factor for our experiments, we use the linear segment of the high temperature profile, from 450

to 800°C , for the seven stepped heating experiments (Table 2) and the cycled experiment on the magnetic fraction of GPC3-1136 (Table 3). The primary reason for selecting this segment of the profile is that in six out of the seven step heating experiments (Table 2) the diffusivity suddenly decreases, or flattens off, at 850°C (Table 2, Fig. 5). The reason for this is not apparent but could be related to a transformation of the ^3He carrier to a more retentive phase, or might indicate an additional diffusional domain. The mean activation energy for the high temperature portion of the profile (450 – 800°C), which accounts for 70 – 80% of the total ^3He released, is 20.3 kcal/mol (range = 14.0 – 25.2 kcal/mol). This estimate is higher than the 17 kcal/mol estimate of Amari and Ozima (1985) but comparable to Hiyagon's (1994) estimate of 19.1 kcal/mol. If we use the entire segment from 450 to 1000°C but neglect the 850°C step, the results are similar with the mean activation energy being 20.1 kcal/mol.

To investigate the ^3He -retentivity at seafloor temperatures, we extrapolated the high temperature part (450 – 800°C) of the diffusion profile, to 2°C . Using the mean activation energy (20.3 kcal/mol) and the measured mean value of the frequency factor ($\log D_0/a^2 = -0.54$), our experiments suggest a diffusivity of $2 \times 10^{-17} \text{ cm}^2\text{s}^{-1}$ at 2°C . This estimate is one to two orders of magnitude lower than previous estimates (Amari and Ozima, 1985; Hiyagon, 1994) and indicates that at ambient temperatures of the ocean floor, 19% of the ^3He would be lost from the IDPs in 50 Myrs, about 25% in 100 Myrs, and 53% in 500 Myrs.

Mukhopadhyay et al. (2001a) noted that although the ^3He flux pattern obtained from Cretaceous and Cenozoic limestones exposed in the Italian Apennines is similar to the pelagic clay core (GPC3), the absolute values at Gubbio are a factor of four lower. Our diffusivity calculations suggest that sediments deposited on the seafloor 50 Myrs ago and exposed on the Earth's surface at 25°C for the past 20 Myrs would lose $\sim 60\%$ of its ^3He , a factor of three higher than sediments that have resided on the seafloor at 2°C for 50 Myrs. This provides a possible explanation for the discrepancy between the Gubbio and GPC3 results.

Assuming a geothermal gradient of $25^\circ\text{C}/\text{km}$, sediments that are buried to depths of 2 km for 1 and 5 Myrs would lose 40% and 75% of their ^3He , respectively (Fig. 8). Because we are extrapolating diffusivities over many orders of magnitude, the retentivity calculations are extremely sensitive to the slope (activation energy) of the diffusion profile and the absolute values should be treated with some caution. Furthermore, the absolute magnitude of the ^3He loss must depend upon the ^3He concentration profile within the IDPs, which we have assumed to be uniform and, thus, unlikely to be strictly valid. Nonetheless, the retentivity computations qualitatively suggest that sedimentary rocks exposed on continents or sediments that have undergone diagenesis to low temperatures (50°C) would have lost significantly more ^3He than sediment cores recovered from the ocean floor. Further, because each sedimentary basin may have different thermal histories and geothermal gradients

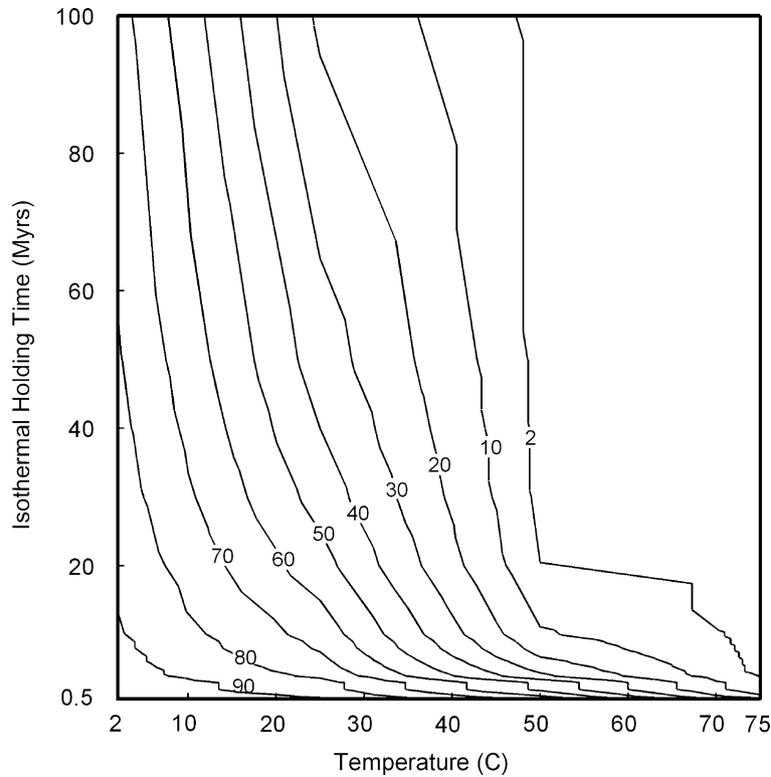


Fig. 8. ^3He retentivity in IDPs contoured as a function of temperature and holding time. The number on the contours is the percent of ^3He still remaining in the IDPs. Because of the discrete number of computations the contours are a little rough.

(Choquette and James, 1987), the magnitude of the ^3He loss in different stratigraphic sections might be distinct. Additional work is required to better characterize He diffusivities, particularly at temperature relevant to sediment diagenesis ($<350^\circ\text{C}$).

3.3. Size distribution

The results from our sieving experiment on the 33 Ma pelagic clay are summarized in Table 4 and Fig. 9. ^3He concentration and $^3\text{He}/^4\text{He}$ ratios increase as the particle size decrease, suggesting that ^3He is preferentially incorporated in the smaller particles. About 60% of the $[\text{}^3\text{He}]_{\text{ET}}$ resides in particles $<37\ \mu\text{m}$ in diameter and only about 20% in particles with diameters greater than $53\ \mu\text{m}$ (if the particles are not spheres then 37 and $53\ \mu\text{m}$ refer to the intermediate axis of the grains). It is important to note that immersing the sample in water and gently stirring it is unlikely to have disaggregated all the particles. Furthermore, sieving is

biased against smaller particles because such particles can stick or ‘clump’ together and, therefore, the 20% must be considered an upper limit to the amount of $[\text{}^3\text{He}]_{\text{ET}}$ in particles $>53\ \mu\text{m}$ in size. We note that the sample (GPC3 1092–1093) may have ^3He -bearing particles from the late Eocene comet shower (Farley, 1995; Farley et al., 1997) and could have a particle size distribution that is distinct from sediments samples where the ^3He flux is dominated by asteroidal particles. The step heating experiments however, do not indicate that the ^3He -bearing particles in GPC3 1092–1093 have significantly different diffusivities compared to ^3He -bearing particles in the other samples (Table 2, Fig. 5). Thus, we do not find evidence that the ^3He -bearing particles in sample GPC3 1092–1093 are biased to a finer grain size, and we conclude that the results from our size distribution experiments are robust. Hence, contrary to the suggestion of Stuart et al. (1999), we demonstrate that ^3He in geological old sediments do not predominantly reside in $50\text{--}100\ \mu\text{m}$ micrometeorites. While

Table 4
 ^3He concentration in pelagic clay as a function of particle size

Size (μm)	Weight (mg)	Fraction of total ^3He	$[\text{}^3\text{He}] 10^{-12}$ cc STP	$^3\text{He}/^4\text{He}$ (R_A)
<i>Sample: GPC3 1092–1093; age 33 Ma</i>				
<13	42	0.29	0.76	47.3
13–37	43	0.28	0.75	47.0
37–53	46	0.22	0.60	34.4
>53	53	0.21	0.55	28.1
Bulk sediment	50		0.8	47.7

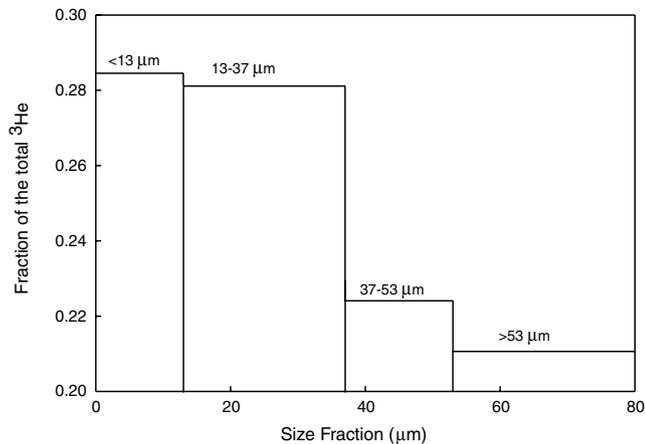


Fig. 9. ³He as a function of particle size in a 33 Ma old pelagic clay from the GPC3 core.

³He-bearing particles >50 μm in diameter do exist (Stuart et al., 1999), such particles are probably rare, having experienced lower than average heating upon atmospheric entry, possibly from unusually low entry velocities or angles (Farley et al., 1997).

The size distribution of ³He-bearing IDPs has implications for the use of ³He as a tracer of extraterrestrial matter. If ³He in seafloor sediments predominantly reflects contribution from micrometeorites, then ³He will document events such as meteor showers, passage of a single short-period comet through the inner solar system, or breakup of a meteorite in the upper atmosphere (Stuart et al., 1999), rather than the time-averaged flux of asteroidal or cometary particles. Recently, Lal and Jull (2005) suggested that rather than IDPs, secondary particles produced by fragmentation of meteoroids during their passage through the atmosphere are the dominant contributor of ³He to marine sediments. According to the model proposed by Lal and Jull (2005), ~44% of the ³He should be carried by secondary particles <50 μm in size while the rest of the ³He are in secondary particles >50 μm in size. These predictions are quite distinct from our observations from the GPC3 sediment sample that ~80% of the ³He are in particles <53 μm in size. We, therefore, do not find evidence for secondary particles produced by fragmentation of meteoroids as the dominant source of ³He to marine sediments (Lal and Jull, 2005), although we cannot rule out the possibility that these particles undergo post-depositional disaggregation on the seafloor. Our observation that at least 60% of the ³He is in particles <37 μm in size is, however, in remarkable agreement with Farley et al.'s (1997) atmospheric entry heating results. Based on a numerical model of frictional heating of cosmic dust particles during atmospheric entry, Farley et al. (1997) concluded that about 70% of the ³He is carried by particles 3–35 μm in size. Hence, we suggest that ³He in seafloor sediments do not reflect the micrometeorite flux but predominantly represents the accretion of IDPs less than 35 μm in diameter.

4. Conclusion

We performed chemical leaching, stepped heating, and sieving experiments to better characterize the ³He carrier(s) responsible for the long-term retention of ³He in sediments. Our data indicate:

- Organic matter, diamond, spinel, SiC, graphite, and amorphous carbon are not the primary carrier phase(s) of ³He although they may account for up to ~10% of the total ³He. Our data, however, are consistent with extraterrestrial silicates, ilmenite, Fe–Ni sulfides, and possibly magnetite as the principal carrier phase(s) of extraterrestrial ³He.
- ³He release profiles as a function of temperature in both the magnetic and non-magnetic fractions in sediments are similar, suggesting a single carrier phase that may be magnetite or more probably a phase associated with magnetite. The association may be in the form of composite grains, inclusions, or few nm thick rims around the grains.
- In contrast to previous suggestions that extraterrestrial ³He would be quantitatively lost from the magnetic fraction in a few million years at seafloor temperatures (e.g., Amari and Ozima, 1985), our stepped heating experiments indicate that 80% of the ³He might be retained after 50 Myrs and about 75% after 100 Myrs, although the absolute values will likely depend upon the ³He concentration profile within the IDPs.
- Contrary to previous suggestions (Stuart et al., 1999), the size distribution of ³He-bearing IDPs in geologically old sediments has not been shifted to larger grain sizes. Greater than 60% of the ³He resides in particles less than 37 μm in diameter in 33 Ma sediments. Hence, ³He in sediments and sedimentary rocks predominantly records the IDP flux and not the micrometeorite flux.

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