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W. H. Schwarz · M. Trieloff · R. Altherr

Subduction of solar-type noble gases from extraterrestrial dust: constraints from high-pressure low-temperature metamorphic deep-sea sediments

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Abstract Solar-type helium (He) and neon (Ne) in the Earth's mantle were suggested to be the result of solar-wind loaded extraterrestrial dust that accumulated in deep-sea sediments and was subducted into the Earth's mantle. To obtain additional constraints on this hypothesis, we analysed He, Ne and argon (Ar) in high pressure–low temperature metamorphic rocks representing equivalents of former pelagic clays and cherts from Andros (Cyclades, Greece) and Laytonville (California, USA). While the metasediments contain significant amounts of ^{4}He, ^{21}Ne and ^{40}Ar due to U, Th and K decay, no solar-type primordial noble gases were observed. Most of these were obviously lost during metamorphism preceding 30 km subduction depth. We also analysed magnetic fines from two Pacific ODP drillcore samples, which contain solar-type He and Ne dominated by solar energetic particles (SEP). The existing noble gas isotope data of deep-sea floor magnetic fines and interplanetary dust particles demonstrate that a considerable fraction of the extraterrestrial dust reaching the Earth has lost solar wind (SW) ions implanted at low energies, leading to a preferential occurrence of deeply implanted SEP He and Ne, fractionated He/Ne ratios and measurable traces of spallogenic isotopes. This effect is most probably caused by larger particles, as these suffer more severe atmospheric entry heating and surface ablation. Only sufficiently fine-grained dust may retain the original unfractionated solar composition that is characteristic for the Earth's mantle He and Ne. Hence, in addition to the problem of metamorphic loss of solar noble gases during subduction, the isotopic and elemental fractionation during atmospheric entry heating is a further restriction for possible subduction hypotheses.

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W. H. Schwarz (✉) · M. Trieloff · R. Altherr
Mineralogisches Institut, Universität Heidelberg,
Im Neuenheimer Feld 236,
69120 Heidelberg, Germany
E-mail: winfried.schwarz@urz.uni-hd.de
Tel.: +49-6221-546015
Fax: +49-6221-544805

Introduction

Isotopic compositions of noble gases in the various geochemical reservoirs of the Earth are quite distinct (Ozima and Podosek 2002). Deep mantle plume sources as analysed in ocean island basalts (OIB) contain relatively high amounts of primordial noble gas isotopes (e.g. ^{3}He, $^{20, 22}$Ne and $^{36, 38}$Ar), with He and Ne being of solar origin (Honda et al. 1991; Trieloff et al. 2000, 2002), contrasting the 'planetary' isotopic signature of the terrestrial atmosphere. The shallow upper mantle contains a higher proportion of radiogenic or nucleogenic noble gases sampled through mid-ocean ridge basalts (MORB) or mantle peridotites (e.g. ^{4}He, ^{21}Ne and ^{40}Ar; Allègre et al. 1986/87).

The preferred explanation for the ongoing degassing of solar-type He and Ne from the Earth's mantle (e.g. Craig et al. 1975; Lupton and Craig 1981) is that these gases were trapped and stored since the time of the Earth's accretion in an incompletely degassed reservoir (e.g. Ozima and Podosek 2002; Trieloff et al. 2000, 2002; Allègre et al. 1986/87). Another hypothesis (Sarda et al. 1988; Allègre et al. 1993a, b; Anderson 1993) for the occurrence of solar-type noble gases and their varying distribution in the Earth's mantle suggests their acquisition by subduction of slowly grown sea floor sediments which contain extraterrestrial dust loaded with solar wind (SW) implanted helium (He) and neon (Ne) during space exposure (e.g. Wieler 2002a), before captured by the Earth. A similar model was recently suggested by Tolstikhin and Hofmann (2005) who consider subduction of SW loaded, chondritic (i.e. metal-rich and dense) dust from collisional debris settling onto the early Earth after core formation, and final storage in the lowermost region of the Earth's mantle (D'' layer).

Indeed, numerous studies in the last 4 decades demonstrated the association of SW implanted noble gases and interplanetary dust particles (IDP) that were either enriched by magnetic separation from deep-sea sediments (Merrihue 1964; Ozima et al. 1984; Amari and Ozima 1985, 1988; Fukumoto et al. 1986; Takayanagi and Ozima 1987; Nier et al. 1990; Matsuda et al. 1990; Farley 1995, 2001), recovered as micrometeorites from the antarctic ice sheet (Stuart et al. 1999; Osawa and Nagao 2002) or collected in the Earth's stratosphere (Nier and Schlutter 1992, 1993; Pepin et al. 2000, 2001; Kehm et al. 2002). In magnetic separates from deep-sea sediments, extraterrestrial dust may be enriched because it contains magnetite which is most probably formed during atmospheric entry as a reaction product of metallic iron in chondritic dust and atmospheric oxygen. Stepwise degassing experiments showed that extraterrestrial He and Ne are more retentively bound than radiogenic or atmospheric isotopes (Amari and Ozima 1988; Nier et al. 1990; Hiyagon 1994; Farley 2001) and are also retained over geological time scales in sea floor sediments (Farley 1995, 2001). Even without knowledge of the specific carrier phase(s) of solar noble gases, this circumstance would favour preferential retention of solar isotopes and simultaneous loss of radiogenic or atmospheric isotopes at elevated pressure–temperature (*P*–*T*) conditions, as required by the subduction hypothesis.

However, some studies have raised serious objections against this hypothesis, e.g. based on mass balance considerations (Stuart 1993). Hiyagon (1994) argued that solar He and Ne are unlikely to survive subduction, based on diffusion parameters evaluated by in vacuo stepwise heating experiments of deep-sea magnetic fines. However, in vacuo conditions certainly do not represent the environment during subduction, so further studies are required, e.g. on natural analogues, particularly as further examination of the subduction hypothesis has been recommended (Ozima and Igarashi 2000; Trieloff and Kunz 2005).

Hence, we present this study as a first step towards quantifying the solar noble gas content of high pressure–low temperature (H *P*–L *T*) metasediments that (1) once were deep-sea sediments, i.e. accumulated slowly in order to gain a large fraction of extraterrestrial dust particles and (2) had been subducted subsequently and re-exhumed. If the IDP subduction hypothesis was true, there should be some detectable solar noble gases in these metasediments.

Sample description

As IDP noble gas reference samples, we analysed two ODP deep-sea sediments from a piston core of a pelagic clay from the central North Pacific (LR44-GPC-3, 30°19′N, 157°49.9′W), from two different segments (1,138–1,143 cm and 1,159–1,164 cm depth) which are 66.15 Ma and 66.36 Ma old, respectively (Farley 1995). They are dominated by aeolian and hydrothermal components accumulated at slow sedimentation rates.

Furthermore, we analysed H *P*–L *T* metasediments with thin alternating Mn-, Fe- and Si-rich layers that represent overprinted equivalents of slowly grown pelagic ocean-floor sediments due to their chemical composition and layering (Reinecke 1985; Mottana 1986). As all analysed pelagic sea floor sediments contain measurable amounts of extraterrestrial noble gases (Merrihue 1964; Ozima et al. 1984; Amari and Ozima 1985, 1988; Fukumoto et al. 1986; Takayanagi and Ozima 1987; Nier et al. 1990; Matsuda et al. 1990; Farley 1995, 2001), the subduction hypothesis demands the presence of measurable traces left in these samples.

Sample Lay-3 is from the quarry in Laytonville (CA, USA, 5 miles south of Laytonville, 39°55′0″N, 123°27′3″W). It is a metasediment which belongs to the Franciscan complex and mainly contains zussmanite, riebeckite, quartz, pumpellyite, minnesotaite, glaucophane, stilpnomelane, phengite, albite and garnet. The Franciscan complex is of Upper Jurassic to Cretaceous age as evidenced by fission track dating on zircons as well as K–Ar dating on whole rock and different mineral samples (e.g. Suppe and Armstrong 1972; Tagami and Dumitru 1996). The mineral assemblage (e.g. zussmanite–Laytonville quarry is the only type location) indicates *P*–*T* conditions representing rapid blueschist-facies metamorphism at about 400°C and up to 1.0 GPa (Muir Wood 1979a, b, 1980), and suggests a subduction depth of 30 km.

Metasediments AN-1 and AN-6 are from Andros (Cyclades, Greece, 37°45′N, 24°48′E, AN-1: central Andros, ~1 km west of Strapouris; AN-6: ~1 km southeast of the coast nearby Aghios Ioannis). The mineralogical composition of the Andros metasediments is different. AN-1 is a spessartite-crossite (glaucophane) schist which contains garnet (about 80% spessartine, with 25% Mn), quartz, zoned glaucophane, epidote, apatite, hematite and phengite (~8% K). AN-6 is a piemontite schist and contains piemontite, quartz, apatite, hematite, and phengite (~8% K), but also titanite, K-feldspar (~13.5% K) and todorokite (~8% Mn; H. Marschall, personal communication). The mineralogical (blueschist-facies) compositions of both samples indicate a rapid metamorphic event at about 450°C and up to 1.0 GPa (Reinecke 1986a, b; A. Kalt, personal communication) of the Permian pelagic sediment (Papanikolaou 1978) during the Eocene as dated by comparison with the K–Ar, Rb–Sr and U–Pb age data from the other Cyclade islands (Altherr et al. 1979; Schliestedt et al. 1987; Wijbrans et al. 1990; Tomaschek et al. 2003), corresponding to a similar subduction depth as for the Laytonville rocks (ca. 30 km).

Analytical procedure

The sea floor sediment samples (1.55 g and 1.69 g, respectively) were mixed into a paste with distilled

water and a portion of the magnetic fraction was separated by a permanent magnet covered with a plastic foil. The grain sizes of the separated material were typically 5–20 μm. The weights of the separated magnetic fractions were 1.25 mg and 1.40 mg, respectively, about 0.08% of the initial sample weight. Magnetic fines were re-cleaned with distilled water. Aliquots of each sample weighing 0.8 mg and 0.65 mg were wrapped in Al-foil and loaded into the noble gas extraction line.

The metasediment samples were separated by handpicking and cleaned with distilled water. For the Laytonville sample, three separates were prepared consisting of coarse-grained fragments of individual sedimentary layers. Lay-3 Qtz is quartz with small amounts of garnet, Lay-3 Ri is riebeckite (~0.1% bulk K) and Lay-3 Zu is zussmanite, containing small amounts of stilpnomelane, minnesotaite, quartz, garnet and riebeckite (~0.05% bulk K). From AN-1 we separated a glaucophane/quartz mixture (AN-1 Gln + Qtz, ~0.2% bulk K) and from AN-6 piemontite with quartz and phengite inclusions (AN-6 Pi + Qtz, ~2.0% bulk K).

Fine-grained samples were wrapped in Al-foil, the samples consisting of coarse (> 5 mm) fragments were placed unwrapped in the noble gas extraction line. The samples were not preheated before mass spectrometric analyses, in order to avoid unrecognised loss of loosely bound (both atmospheric or possibly solar implanted) noble gases. Instead, to remove and also analyse this component, the first thermal extraction was conducted at 500°C or 900°C (Table 1). After evacuating the system to $\sim 10^{-13}$ bar, the samples were stepwise heated in an inductively coupled Mo-crucible, and noble gases were extracted in three temperature steps ranging up to 1,600°C (Table 1). The gases were exposed to an SAES-Al-Getter to remove active gases. Subsequently, argon (Ar) was separated using a charcoal cooled with liquid nitrogen, and He and Ne were fixed at a cryogenically cooled second charcoal at ~11 K. Before gas inlet into the mass spectrometer, He and Ne were released at temperatures of 30 K and 60 K, respectively, to avoid simultaneous release of possible residual Ar.

The noble gas isotopic compositions were measured with a Faraday cup or single ion counting using an in-house modified VG3600 mass spectrometer at the Max-Planck-Institut für Kernphysik (Heidelberg). In the case of Ne measurements, isobaric interference corrections for all masses ($^{40}Ar^{++}$, mass 42^{++}, CO_2^{++}, $H_2^{18}O^{+}$) were applied. Repeated measurements of standard gases were used to correct for experimentally-induced mass fractionation and variations of sensitivity. System blanks were $\sim 9\times10^{-9}$ cm^3 STP for ^{4}He, between 0.6×10^{-12} cm^3 and 8×10^{-12} cm^3 STP for ^{20}Ne, and between 2×10^{-12} cm^3 and 6×10^{-12} cm^3 STP for ^{36}Ar for the different extraction temperatures. The isotopic compositions of the blanks were atmospheric within uncertainties. All errors given in the text and Table 1 are 1σ.

Results

ODP core samples

Both magnetic fine samples ('LR44-GPC-3 1,138–1,143 cm' and 'LR44-GPC-3 1,159–1,164 cm') were heated to temperatures of 500°C (releasing the gas which is loosely bound, adsorbed or from less retentive sample impurities), 1,200°C (releasing the main gas fraction from the extraterrestrial particles, see Farley 2001) and 1,400°C (to ensure that all gas was released). Results for He, Ne and Ar are shown in Table 1.

The He content of these samples is 36×10^{-10} cm^3 and 19×10^{-10} cm^3 STP/g ^{3}He and 145×10^{-7} cm^3 and 124×10^{-7} cm^3 STP/g ^{4}He with ^{3}He/^{4}He ratios of $\sim 2.5\times10^{-4}$ and $\sim 1.6\times10^{-4}$, respectively (Fig. 1). Compared to the He measurements by Farley (1995) for the respective bulk samples, the ^{3}He/^{4}He ratios of 1.76×10^{-4} and 1.56×10^{-4} are in the same range for the 1,159–1,164 cm, but lower for the 1,138–1,143 cm core segment, indicating minor contributions of radiogenic ^{4}He in the bulk sediment. The bulk sample ^{3}He concentrations measured by Farley (1995) were 1.30×10^{-10} and 0.97×10^{-10} cm^3 STP/g, i.e. up to 30 times lower than those measured in this study. This is due to the separation method, because Farley (1995) measured the bulk sample and, for the samples measured in this study, parts of the sediments were removed by collecting the magnetic fraction. Hence, an enrichment of the extraterrestrial dust particle concentrations by a factor of 30 and 20, respectively, was achieved. As magnetic fractions yielded 0.08% of the initial sample mass, we conclude that we collected about 2% of all extraterrestrial dust particles of the sediment.

The isotopic composition of Ne in the main release at 1,200°C is close to the solar energetic particle (SEP) composition of $^{20}Ne/^{22}Ne = 11.20 \pm 0.20$, but significantly below the SW (low energy solar particles) value of 13.80 ± 0.10 (e.g. Wieler et al. 1986; Benkert et al. 1993; Wieler 2002b, see Fig. 2). Note that the $^{20}Ne/^{22}Ne$ ratios of 11.21 ± 0.35 and 10.75 ± 0.31 are significantly higher (3σ-error level) than the atmospheric value of 9.80.

Argon isotopic compositions are shown in Fig. 3. The $^{40}Ar/^{36}Ar$ ratio is higher than the atmospheric value, and the $^{38}Ar/^{36}Ar$ ratio is atmospheric within uncertainties. This indicates radiogenic Ar from ^{40}K decay in the terrestrial K-bearing minerals of the ca. 66 Ma old sea floor sediment (potassium was detected by electron microprobe measurements in both magnetic aliquots, but its carrier phases could not be identified), and variable addition of atmospheric Ar. Thus, there is no compelling evidence for a solar-wind implanted Ar component, whether SEP, SW or a mixture of both.

Metasediments

These samples were degassed in three temperature steps: 900°C, 1,250°C and 1,450°C for the Andros samples and

Table 1 Isotopic data for the sea floor and metasediments

Sample	Weight (mg)	Temp (°C)	^{3}He (10^{-10} cm^3/g)	^{4}He (10^{-7} cm^3/g)	$^{3}He/^{4}He$ (10^{-4})	^{22}Ne (10^{-11} cm^3/g)	$^{20}Ne/^{22}Ne$	$^{21}Ne/^{22}Ne$	^{36}Ar (10^{-9} cm^3/g)	$^{38}Ar/^{36}Ar$	$^{40}Ar/^{36}Ar$
LR44-GPC-3 1, 138–1, 143 cm	0.80	500	6.87 ± 0.29	27 ± 12	2.58 ± 0.11	90 ± 7	9.8 ± 0.7	0.026 ± 0.008	55.8 ± 0.8	0.1907 ± 0.0018	472 ± 6
		1,200	28.8 ± 0.5	116 ± 12	2.47 ± 0.04	426 ± 13	11.21 ± 0.35	0.0311 ± 0.0023	13.3 ± 0.5	0.194 ± 0.008	578 ± 16
		1,400	0.48 ± 0.28	2 ± 12	2.2 ± 1.3	285 ± 58	9.2 ± 1.9	0.018 ± 0.008	48.0 ± 1.0	0.1898 ± 0.0034	297 ± 7
LR44-GPC-3 1, 159–1, 164cm	0.65	500	2.22 ± 0.25	15 ± 12	1.52 ± 0.17	37 ± 8	13.4 ± 2.8	0.026 ± 0.024	4.20 ± 0.25	0.199 ± 0.020	451 ± 31
		1,200	15.7 ± 0.4	92 ± 12	1.71 ± 0.05	424 ± 12	10.75 ± 0.31	0.0281 ± 0.0030	37.5 ± 0.6	0.1837 ± 0.0022	379 ± 6
		1,400	1.22 ± 0.31	17 ± 12	0.73 ± 0.18	305 ± 55	9.8 ± 1.8	0.020 ± 0.007	56.2 ± 1.0	0.1877 ± 0.0025	301 ± 5
AN-1 Gln + Qtz	1,555	900	–	12.4 ± 0.2	–	0.713 ± 0.006	9.80 ± 0.08	0.0346 ± 0.0011	0.364 ± 0.006	0.1888 ± 0.0009	1,127 ± 2
		1,250	–	0.370 ± 0.009	–	0.089 ± 0.006	10.0 ± 0.7	0.060 ± 0.009	0.117 ± 0.003	0.1913 ± 0.0022	3,772 ± 7
		1,450	–	0.007 ± 0.005	–	0.227 ± 0.004	10.13 ± 0.19	0.0334 ± 0.0029	0.033 ± 0.002	0.177 ± 0.009	784 ± 17
AN-6 Pi + Qtz	482	900	–	1.449 ± 0.033	–	2.680 ± 0.021	9.73 ± 0.07	0.0343 ± 0.0022	0.116 ± 0.004	0.190 ± 0.005	19,755 ± 51
		1,250	–	0.200 ± 0.019	–	0.613 ± 0.017	9.41 ± 0.26	0.0352 ± 0.0029	0.153 ± 0.006	0.191 ± 0.007	11,256 ± 39
		1,450	–	0.024 ± 0.017	–	0.101 ± 0.038	10.6 ± 3.9	0.046 ± 0.024	0.045 ± 0.010	0.20 ± 0.09	2,856 ± 172
Lay-3 Zu	2,244	500	–	100.2 ± 1.8	–	20.20 ± 0.04	9.82 ± 0.02	0.0304 ± 0.0003	7.54 ± 0.12	0.1859 ± 0.0007	482.6 ± 0.7
		1,200	–	4.87 ± 0.09	–	1.390 ± 0.006	9.46 ± 0.04	0.1003 ± 0.0013	1.139 ± 0.019	0.1883 ± 0.0008	613.8 ± 0.9
		1,400	–	0.006 ± 0.004	–	0.120 ± 0.004	10.23 ± 0.33	0.0552 ± 0.0037	0.468 ± 0.008	0.1889 ± 0.0009	596.7 ± 1.1
Lay-3 Qtz	422	500	–	0.229 ± 0.023	–	10.61 ± 0.06	9.75 ± 0.06	0.0288 ± 0.0006	2.117 ± 0.026	0.1869 ± 0.0005	293 ± 3
		1,200	–	1.415 ± 0.024	–	1.62 ± 0.37	9.84 ± 0.22	0.0304 ± 0.0019	0.629 ± 0.008	0.1883 ± 0.0009	467 ± 5
		1,600	–	0.024 ± 0.023	–	0.5 ± 1.3	9.5 ± 26.4	0.025 ± 0.104	–	–	–
Lay-3 Ri	706	500	–	3.418 ± 0.023	–	1.606 ± 0.016	9.76 ± 0.09	0.0304 ± 0.0010	1.498 ± 0.019	0.1882 ± 0.0005	310 ± 3
		1,200	0.002 ± 0.001	52.45 ± 0.28	0.00032 ± 0.00020	21.19 ± 0.12	9.78 ± 0.05	0.0312 ± 0.0004	3.63 ± 0.05	0.1898 ± 0.0006	465 ± 4
		1,400	–	0.023 ± 0.014	–	0.48 ± 0.05	10.0 ± 1.1	0.031 ± 0.006	0.167 ± 0.002	0.1883 ± 0.0011	442 ± 4

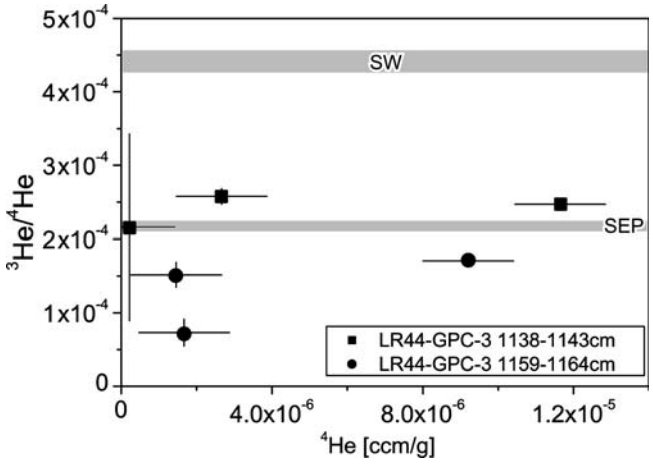

Fig. 1 $^{3}He/^{4}He$ versus ^{4}He concentration diagram of the two stepwise heated sea floor sediments from drillcore LR44-GPC-3. A major contribution of SEP He is indicated

500°C, 1,200°C and 1,400°C for the Laytonville samples, except for Lay-3 Qtz, for which the highest extraction temperature was 1,600°C (see Table 1). The samples have variable He concentrations, between 1.6×10^{-7} cm^3 and 105×10^{-7} cm^3 STP/g ^{4}He. However, no ^{3}He could be detected, maybe except for the 1,200°C extraction of the riebeckite sample Lay-3 Ri. This extraction contained $2.0\pm1.0\times10^{-13}$ cm^3 STP/g ^{3}He and $52.45\pm0.28\times10^{-7}$ cm^3 STP/g ^{4}He yielding a ratio of $^{3}He/^{4}He$ $3.8\pm2.0\times10^{-8}$ (Table 1). A clear systematic relationship of He concentration and specific mineral or location cannot be evaluated from these data.

Neon isotopic compositions and concentrations of the samples from the two different areas (Cyclades and California) are also quite different (Table 1, Fig. 2). For $^{20}Ne/^{22}Ne$ ratios, only slight deviations from atmospheric composition could be observed, e.g. the 1,450°C extraction of the Andros sample 'AN-1 Gln + Qtz' with $^{20}Ne/^{22}Ne = 10.13\pm0.19$ (1σ error). However, within 2σ uncertainties, no value is significantly higher than the atmospheric value. In contrast, almost all samples have $^{21}Ne/^{22}Ne$ ratios higher than the atmospheric value of 0.029, ranging up to 0.100 (Table 1, Fig. 2), indicating the presence of nucleogenic Ne from nuclear reactions related to U, Th decay.

Similar to $^{21}Ne/^{22}Ne$, the $^{40}Ar/^{36}Ar$ ratios are also highly variable (Fig. 3). Maximum values obtained for the Laytonville and Andros separates are 614 and ~20,000, respectively (Table 1, Fig. 3), due to radiogenic Ar from ^{40}K decay, sited in K-rich phases like phengite. The $^{38}Ar/^{36}Ar$ ratios are indistinguishable from the atmospheric value at the 2σ level, with no discernible contributions of SW or SEP Ar.

To summarize, there is no compelling evidence for solar-type light noble gases in these metasediments.

Discussion

Atmospheric entry loss of extraterrestrial He and Ne from IDPs accumulating in ocean-floor sediments

The $^{3}He/^{4}He$ ratios of the magnetic fraction of the sea floor sediments (Fig. 1) are all below the SW ratio of

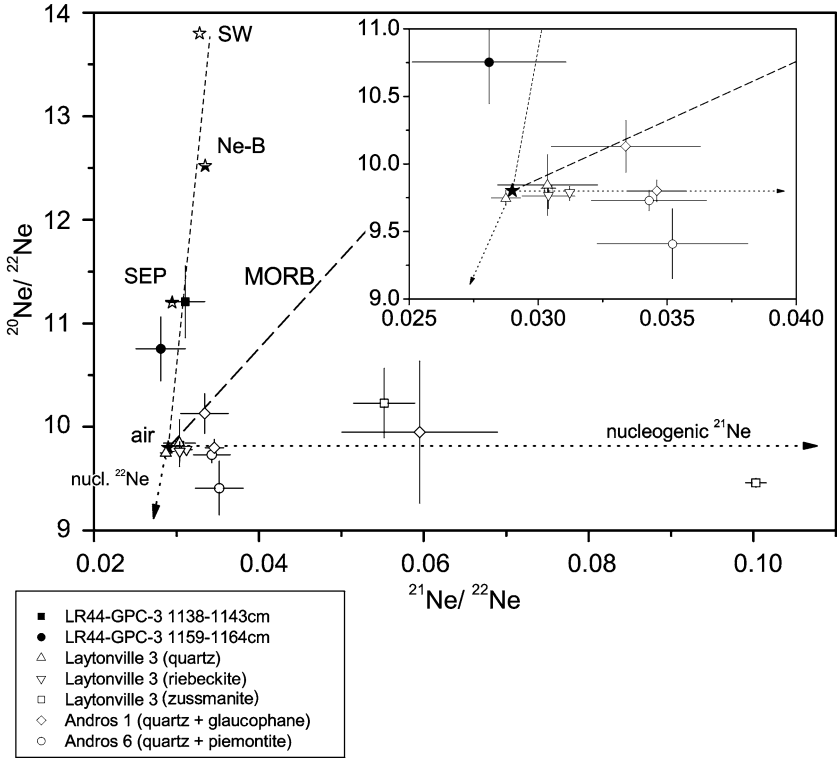

Fig. 2 Neon three isotope plot ($^{20}Ne/^{22}Ne$ vs $^{21}Ne/^{22}Ne$) for all samples measured in this study; for reference, the MORB correlation line and points for air, SW, SEP and Ne–B are included; data points with more than 20% uncertainty are not plotted; *inset* shows the same diagram with expansion of axes

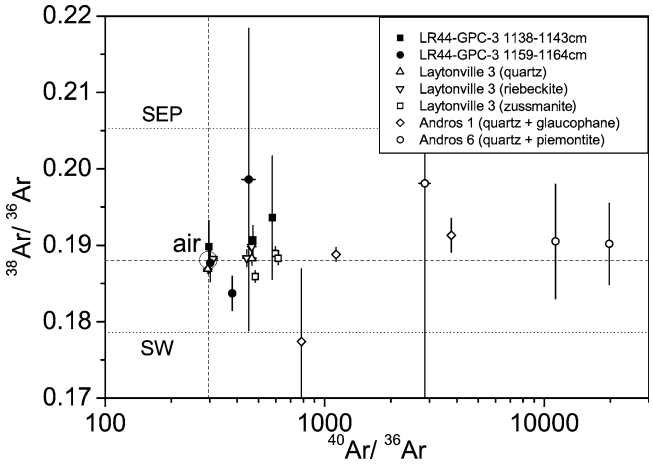

Fig. 3 Isotopic composition of Ar for the sea floor and metasediments in a $^{38}Ar/^{36}Ar$ versus $^{40}Ar/^{36}Ar$ diagram. Argon is composed of a mixture of atmospheric and radiogenic Ar, contributions of solar-type Ar are not discernible

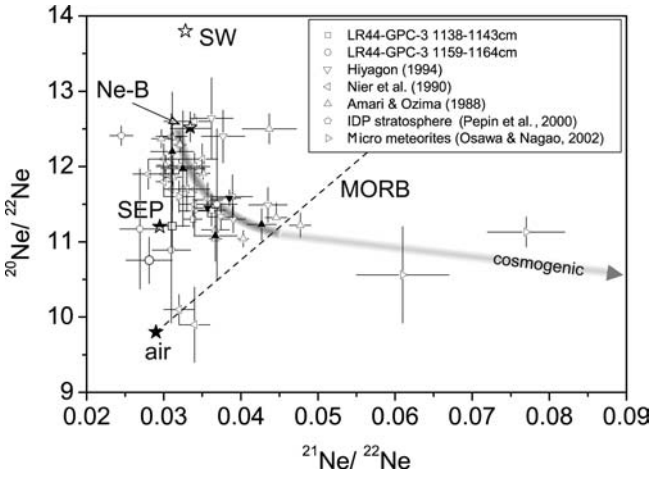

Fig. 4 Three isotope plot displaying Ne data of extraterrestrial particles and sea floor magnetic fines from this and previous studies. Only data with 1σ errors smaller than 10% are plotted. *Filled symbols* are total fusion data from stepwise heating extractions. Most data can be explained by a ternary mixture of SEP, implanted SW composed of a typical mixture of high and low energetic particles ('Ne–B'), and cosmogenic Ne. Data dominated by atmospheric Ne or low energetic SW are not observed; *open symbols* are total fusion samples without stepwise heating or stepwise heating data from *filled symbols*

4.5×10^{-4} (e.g. Benkert et al. 1993; Pepin 1995; Wieler 2002b), but very similar to the SEP ratio of 2.17×10^{-4} (e.g. Benkert et al. 1993; Wieler 2002b). The constancy of SEP-like $^{3}He/^{4}He$ ratios at high and low He concentrations (Fig. 1) suggests that SEP He is indeed the pristine component in these extraterrestrial dust particles, rather than an accidental mixture of SW He and a component rich in ^{4}He, such as radiogenic or atmospheric He. However, other magnetic fines from deep-sea sediments display a larger range of isotopic composition, with values scattering towards the SW composition not being uncommon (Merrihue 1964; Ozima et al. 1984; Amari and Ozima 1985, 1988; Fukumoto et al. 1986; Takayanagi and Ozima 1987; Nier et al. 1990; Matsuda et al. 1990; Farley 1995, 2001).

The isotopic composition of Ne (Figs. 2, 4) of the LR44-GPC-3 samples also plot near the SEP value. Comparing the Ne data with previously published data for magnetic fines (Amari and Ozima 1988; Nier et al. 1990; Matsuda et al. 1990; Hiyagon 1994), IDP (Pepin et al. 2000) and micrometeorites (Osawa and Nagao 2002), it can be verified from Fig. 4 (only data points with 1σ-errors lower than 10% were plotted) that the compositional range is more variable: most values have $^{20}Ne/^{22}Ne$ ratios between the SEP and Ne–B ratio (12.52 ± 0.18; Ne–B is a bulk-rock measurement interpreted as a mixture of SEP and SW isotopic composition, e.g. Black (1972), Benkert et al. (1993)). Some micrometeorite data with non-atmospheric $^{20}Ne/^{22}Ne$ ratios (Osawa and Nagao 2002) plot to the right of the MORB line. Those points must be affected by cosmic ray exposure, producing cosmogenic ^{20}Ne, ^{21}Ne and ^{22}Ne in approximately equal proportions (Ozima and Podosek 2002; Wieler 2002b). This is demonstrated by very high $^{3}He/^{4}He$ ratios (up to 10^{-3}; Osawa and Nagao 2002) due to cosmogenic He in the same extractions.

It is plausible that the larger grain sizes of the micrometeorites (50–250 μm, Stuart et al. 1999; Osawa and Nagao 2002) compared to the extraterrestrial dust particles in magnetic sea floor separates and/or stratospheric IDP particles (typical e.g. <100 μm, Nier et al. 1990; 50–100 μm and <10 μm, Amari and Ozima 1988; <74 μm, Hiyagon 1994; ~15 μm, Kehm et al. 2002) are important to explain the difference. During atmospheric entry, the dust particles are heated and partially degassed. Nier and Schlutter (1992, 1993) calculated from He degassing experiments on SW loaded lunar grains and IDPs a maximum of 600°C for that kind of heating. The extent of heating and degassing strongly depends on the particle grain size (Stuart et al. 1999): while small particles effectively lose heat by radiation, large particles have both a higher kinetic energy converted to heat at their surface layer, and a smaller surface to volume ratio preventing effective heat loss.

For the largest grains surviving atmospheric entry, heating effects induce severe loss of surface sited, SW implanted He and Ne (Amari and Ozima 1988; Stuart et al. 1999). On the other hand, cosmogenic Ne produced by cosmic ray-induced spallation reactions in the rock matrix is hardly lost. These particles plot on a trend towards cosmogenic Ne in Fig. 4. However, the amount of cosmogenic Ne is only very small because the largest particles surviving atmospheric entry are readily penetrated in space by high energy protons that effectively produce spallation nuclides (see e.g. Amari and Ozima 1988). Smaller particles (as contained in magnetic fractions of sea floor sediments) suffer a much

weaker entry heating and weaker loss of solar wind-implanted gases, but effects are occasionally still sufficient to induce loss of the shallow implanted, low energetic SW component from the uppermost grain surface layers, leading to a preferential retention of SEP He and Ne (for e.g. in our 'LR44-GPC-3' separates and other data in Fig. 4). Finally, only the smallest particles—subject to relatively modest atmospheric entry heating—are capable of retaining SW implanted He and Ne almost completely, demonstrated in Fig. 4 by the presence of the original Ne–B signature which is the common mixture of high- and low-energy ions, usually observed in solar-wind irradiated meteorites (note that extraction by acid etching alone can separate the low-energy SW component with $^{20}Ne/^{22}Ne = 13.8$; Wieler 2002a, Benkert et al. 1993). All in all, the curved trend of data extending from Ne–B to SEP and cosmogenic Ne in Fig. 4 can be interpreted as increasing degree of heating-induced loss of surface-sited Ne with a specific isotopic structure.

The above interpretation is also supported by considering the $^{3}He/^{22}Ne$ ratio (Fig. 5). The hatched area marks possible mixtures of SW and atmospheric composition. Most data plot below this mixing line which means that low $^{3}He/^{22}Ne$ ratios are not due to simple admixing of atmospheric He and Ne. Instead, the data indicate a fractionation between He and Ne, most probably caused by preferential He loss during atmospheric entry heating (Nier and Schlutter 1992, 1993). Remarkably, micrometeorites with discernible contributions of cosmogenic Ne and He (Osawa and Nagao 2002) have also the lowest $^{3}He/^{22}Ne$ ratios, suggesting severe loss of surface-sited SW-implanted gases, along with preferential loss of He.

On the other hand, extraterrestrial dust particles from sea floor sediments constitute a broad trend between relatively low $^{3}He/^{22}Ne$ ratios at $^{20}Ne/^{22}Ne = 11.2$ (SEP-Ne) and almost solar-like $^{3}He/^{22}Ne$ ratios at

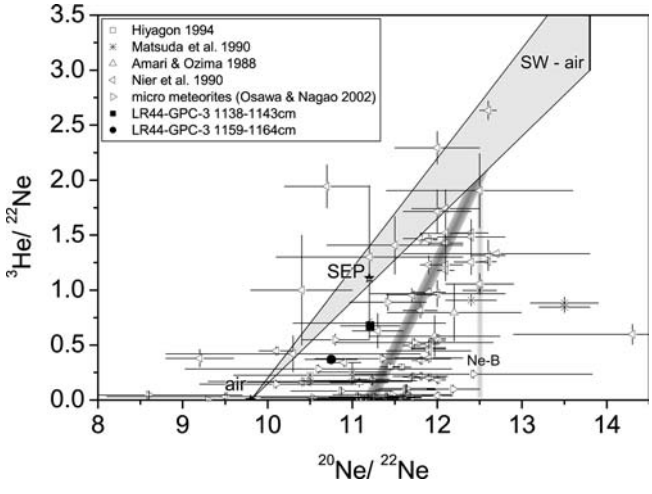

Fig. 5 $^{3}He/^{22}Ne$ versus $^{20}Ne/^{22}Ne$ diagram demonstrating the elemental fractionation between He and Ne in IDP and micrometeorite samples

$^{20}Ne/^{22}Ne = 12.5$ (Ne–B). This trend is also in agreement with variable degassing degrees: partial degassing causes preferential loss of low-energy SW Ne ions and SW He, and only some particles (probably the smallest) can retain SW-implanted noble gases with the full complement of low-energy ions sited in the outermost few hundred angstrom ($1\ \text{Å} = 10^{-10}$ m) thick layers resulting in Ne–B composition and nearly unfractionated solar He/Ne ratios.

The spread of data from magnetic deep-sea separates in Fig. 5, i.e. variable gas loss and variable grain-size, may be either related to the separation technique which may preferentially recover larger or smaller dust particles when using slightly differing separation procedures, or just simply related to the circumstance that sediment layers contain different extraterrestrial dust fluxes that could differ in their size distribution. On the other hand, we should note a possible bias of the present He and Ne data to partially degassed (i.e. relatively large-sized) extraterrestrial dust: most data are from magnetic separates (in bulk sediments, solar Ne can hardly be measured due to high amounts of atmospheric Ne), most probably predominantly magnetite-bearing IDPs are sampled. However, as magnetite is a reaction product of metallic iron in chondritic dust and atmospheric oxygen formed during atmospheric entry heating, probably only large particles that were sufficiently heated to form magnetite were collected and also those which inevitably suffered loss of SW or SEP implanted He and Ne. It is plausible that non-magnetic (i.e. non-magnetite bearing, non-heated) IDPs with the original, unfractionated complement of low-energy SW He and Ne contribute significantly to the extraterrestrial dust component in deep-sea sediments (Farley 2001), but it is not clear if this component can dominate the noble gas inventory. It should be noted that we consider the contribution of atmospheric Ne to most of the data plotted in Fig. 4 as insignificant. Although it could be reasoned that Ne will be a mixture of the locally available He and Ne during heating and magnetite formation in the atmosphere, such a contamination—if significant—would cause much more data points with $^{20}Ne/^{22}Ne$ ratios between SEP and atmospheric composition of 11.2 and 9.8, respectively. Moreover, if atmospheric contamination was the only reason for data with $^{20}Ne/^{22}Ne$ ratios lower than Ne–B (towards SEP) composition, this should result in a straight mixing line with atmospheric composition in Fig. 4, and not in a curved trend bending to cosmogenic Ne composition indicating a three (SW, SEP, cosmogenic) rather than four (incl. atmospheric) Ne-component mixture. Finally, the intimate association of both SEP Ne and SEP He in individual samples also supports a pristine composition largely unaffected by atmospheric contamination.

The case may be different for Ar which could be completely dominated by atmospheric Ar due to the different elemental abundance patterns of solar and atmospheric noble gases (Ozima and Podosek 2002). As

solar gases contain higher abundances of light species, addition of atmospheric gases affects the isotopic pattern of heavy noble gases first. In contrast, some analyses (of the same samples plotted in Fig. 4) with $^{40}Ar/^{36}Ar$ ratios lower than the atmospheric value (indicating a solar origin), and even $^{38}Ar/^{36}Ar$ ratios tending to SEP composition (e.g. Amari and Ozima 1988; Osawa and Nagao 2002) suggest occasional, only marginal atmospheric contamination for Ar.

As mentioned above, in our samples there is no compelling evidence for solar-type Ar in the 'LR44-GPC-3' samples, as the Ar isotopic composition (Fig. 3) may simply be explained by a mixture of radiogenic and atmospheric Ar. However, this does not mean, that there is no solar Ar in the samples, which was demonstrated previously for other IDP containing sediments (e.g. Amari and Ozima 1988). It is probably a very minor component, but its exact contribution is hard to quantify.

Loss of solar-type He and Ne from metasediments

Nearly all of the ^{4}He in the metasediments must be from α-decay of U or Th, because there is no ^{3}He detectable. Only the 1,200°C extraction of the separate Lay-3 Ri shows a small amount of ^{3}He, but the very low $^3He/^4He$ ratio of $(3.8 \pm 2.0) \times 10^{-8}$ confirms the mainly radiogenic source of ^{4}He (Table 1), and most probably also ^{3}He which is produced in the crust by Li via $^6Li(n,\alpha)^3He(\beta^-)^3$He reactions, with a production rate of $^3He/^4He \sim 4\times10^{-8}$ (depending on the U, Th and Li content). Hence, if at all ^{3}He is present in the metasediment (note the high uncertainty), it is most probably due to radiogenic production, and not of extraterrestrial origin. Even assuming an extraterrestrial origin of ^{3}He in this sample, and a similar concentration of ^{3}He in the other minerals of the Laytonville metasediment, the maximum amount of ^{3}He in the whole rock (1σ upper limit) would be 3×10^{-13} cm^3 STP/g. This value is still very low when compared with concentrations between 10^{-11} cm^3 and 10^{-10} cm^3 STP/g ^{3}He measured by Farley (1995) for Cenozoic bulk sea floor sediment samples. The ^{3}He content in the metasediments investigated in this study is lower by at least about two or three orders of magnitude, so it is justifiable to say that none or nearly none ^{3}He survived subduction-related metamorphism.

The metasediment Ne isotopic ratios were affected by nucleogenic ^{21}Ne and ^{22}Ne (Ozima and Podosek 2002) as seen in Fig. 2. These two isotopes were produced by the reactions $^{18}O(\alpha,n)^{21}Ne$ and $^{19}F(\alpha,n)^{22}$ $Na(\beta^+)^{22}Ne$ as a by-product of the radioactive decay (e.g. U or Th) and also ^{4}He, as mentioned above. Only the 1,450°C extraction of the separate AN-1 Gln + Qtz yielded Ne with $^{20}Ne/^{22}Ne = 10.13 \pm 0.19$, higher than the atmospheric value at the 1σ error level. Assuming a $^{20}Ne/^{22}Ne$ upper limit of 10.3, about < 20% could be of solar origin, i.e. $< 0.05\times10^{-10}$ cm^3 STP/g ^{20}Ne, which would also be an upper limit for the bulk metasediment. On the other hand, in our LR44-GPC-3 separates SEP ^{20}Ne was 470×10^{-10} cm^3 STP/g, and using the same enrichment factors (~24) as for solar ^{3}He, we can calculate bulk values of 20×10^{-10} cm^3 STP/g solar ^{20}Ne for our exceptionally gas-rich ODP core sections, or about an order of magnitude lower than concentrations for other Cenozoic sediment sections with lower extraterrestrial dust concentrations. Hence, this comparison suggests that no more than 0.25–2.5% of the solar Ne originally in the Andros metasediments survived during metamorphism. Again, the conclusion is tenable that there is no solar Ne detectable, or at best a very minor fraction, left in metasediments.

Argon is also strongly affected by radiogenic ingrowth, with $^{40}Ar/^{36}Ar$ ratios reaching values as high as ca. 20,000 for the Andros metasediments (Fig. 3), which contain K-rich phengites in several layers. In the Laytonville samples, K-bearing minerals (e.g. phengite, zussmanite) are also present, but radiogenic Ar causes $^{40}Ar/^{36}Ar$ ratios of only up to ca. 600, as atmospheric contamination is an order of magnitude higher than in the Andros samples (see Table 1). $^{38}Ar/^{36}Ar$ ratios are atmospheric within uncertainties which point to no detectable SEP or SW like Ar, due to atmospheric contamination. The Ar concentration in the metasediments is also smaller than in the sea floor sediments, which means that Ar loss occurred during subduction-induced metamorphism of these rocks.

Conclusions

Our results on metasediments from Andros (Greece) and Laytonville (USA) suggest that most solar He and Ne (> 98%) that must be initially present in pelagic sea floor sediments is lost during subduction-induced metamorphism, most probably before reaching *P–T* conditions of 400°C and 1.0 GPa, or ~30 km subduction depth. In the investigated rocks peak-metamorphic mineral assemblages do not show any sign of retrogressive overprint, suggesting rapid exhumation, with no loss of noble gases.

We can infer an additional constraint that restricts possible scenarios explaining solar-type He and Ne in the Earth's mantle by subduction of extraterrestrial dust (Sarda et al. 1988; Allègre et al. 1993a; Anderson 1993). Solar noble gases in IDPs reaching the Earth's atmosphere and the ocean-floor (Amari and Ozima 1988; Nier et al. 1990; Matsuda et al. 1990; Hiyagon 1994; Pepin et al. 2000; Osawa and Nagao 2002) seem to be influenced by atmospheric-entry heating that depends on particle size. Only IDPs sufficiently small to avoid severe entry heating and ablation can retain the full complement of shallowly implanted low energetic SW ions and deeper implanted SEP, and still have unfractionated solar-like He/Ne ratios.

It follows that subduction scenarios—even if they solve the obvious problem of metamorphic loss of solar gases during subduction—can only account for solar He

and Ne in the Earth's mantle, if sufficiently fine-grained material is subducted, as larger particles lose a considerable fraction of the low energy-SW ions due to ablation during atmospheric entry heating. Alternatively, subduction scenarios involving irradiated coarse-grained material could still be considered, if the respective dust or particles enter the terrestrial atmosphere at sufficiently low speed (losing some or none of noble gases due to atmospheric ablation), possibly slowly settling debris orbiting the Earth after a large impact during early solar system history (Tolstikhin and Hofmann 2005).

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