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NOBLE GAS ISOTOPE GEOCHEMISTRY OF VOLCANIC GASES FROM THE AEGEAN ISLAND ARC

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ABSTRACT

Volcanic gas samples from three volcanic centres of the Aegean island arc were analysed for He, Ne, Ar, Kr and Xe isotopes. The gas samples from Milos and Santorini show high $^3He/^4He$ ratios indicating a large contribution of mantle-derived helium, while the low $^3He/^4He$ ratio of the Susaki sample indicates crustal helium, enriched in radiogenic ^4He. Combining the above ratios with the $^4He/^{20}Ne$ ratios it is demonstrated that the samples from Milos and Santorini lie on a common mixing line between atmospheric and mantle-derived helium suggesting common origin. The $^3He/^4He$ ratio defined by that line can be considered as a characteristic feature of this volcanic area. Elemental abundance patterns of the analysed gas samples indicate that Ne, Ar, Kr and Xe are recycled atmospheric noble gases dissolved into ground water.

ΣΥΝΟΨΗ

Δείγματα ηφαιστειακών αερίων από τρία ηφαιστειακά κέντρα του τόξου του Αιγαίου αναλύθηκαν γιά ισότοπα των στοιχείων He, Ne, Ar, Kr και Xe. Τα δείγματα από τη Μήλο και τη Σαντορίνη παρουσιάζουν υψηλούς λόγους $^3He/^4He$ που δείχνουν μία μεγάλη συμμετοχή He από τον μανδύα ενώ ο χαμηλός λόγος $^3He/^4He$ του δείγματος από το Σουσάκι δείχνει συμμετοχή He από τον φλοιό, εμπλουτισμένο σε ραδιογενές ^4He. Συνδυασμός των παραπάνω λόγων με τους λόγους $^4He/^{20}Ne$ δείχνει ότι τα δείγματα από τη Μήλο και τη Σαντορίνη τοποθετούνται πάνω σε μία κοινή γραμμή μεταξύ του ατμοσφαιρικού και του μανδυακού He, που επιτρέπει την υπόθεση της κοινής

K. NAGAO, I. KITA, J. MATSUDA και Π. ΜΗΤΡΟΠΟΥΛΟΣ. Γεωχημεία ισοτόπων ευγενών αερίων σε ηφαιστειακά αέρια από το τόξο του Αιγαίου.

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προέλευσης. Ο λόγος $^3He/^4He$ που ορίζεται από την γραμμή αυτή μπορεί να θεωρηθεί σαν χαρακτηριστικό γνώρισμα αυτής της ηφαιστειακής περιοχής. Από τα διαγράμματα των περιεκτικοτήτων των στοιχείων φαίνεται ότι τα ισότοπα των Ne, Ar, Kr και Xe αποτελούν ανακυκλούμενα ατμοσφαιρικά ευγενή αέρια που έχουν διαλυθεί στα υπόγεια νερά.

INTRODUCTION

Helium has two stable isotopes of mass numbers 3 and 4. Isotopic ratios of $^3He/^4He$ in terrestrial samples vary from over $5x10^{-5}$ (KANEOKA and TAKAOKA 1978) to less than $1x10^{-9}$ (SHOKOLYUKOV, 1970). A portion of ^3He in terrestrial samples is primordial He which was trapped in the solid Earth at the time of accretion (CLARKE et al., 1969). Another portion of ^3He as well as ^4He are produced by nuclear reactions in the solid Earth. It has been established that He isotope ratios show a close relation to the geotectonic features of the region where the samples are collected. In divergent type of plate boundaries such us Mid-Ocean Ridges (MOR), $^3He/^4He$ ratios are about ten times higher than the ratio in the atmosphere. These (MOR type) ratios are extremely uniform with a value of $(1.3\pm0.2)x10^{-5}$, irrespective of differences in sampling sites (LUPTON and CRAIG, 1975; CRAIG and LUPTON, 1976; LUPTON et al., 1977; OZIMA and ZASHU, 1983). In convergent type of plate boundaries (subduction type), the $^3He/^4He$ ratios of hot springs and volcanic fumaroles vary from $7.0x10^{-6}$ to $1.1x10^{-5}$ and show greater variations than the MOR type (NAGAO et al., 1981; TORGERSEN et al., 1982 ; LUPTON, 1983).

The Aegean island arc shows particular tectonic and geochemical characteristics (MAKRIS, 1977; MAKROPOULOS and BURTON, 1984; KONTOPOULOU et al., 1985 MITROPOULOS et al., 1987; MITROPOULOS and MAGGANAS, 1988a, 1988b) giving to it a world-wide importance. The hydrothermal fields of Milos and Santorini are also of great importance and they have been examined in considerable detail by many geologists (FYTIKAS, 1977; LIAKOPOULOS, 1987; VARNAVAS, 1989; VARNAVAS et al., 1989; BOSTROM et al., 1989). As a contribution to the more detailed study of the Aegean island arc a collaboration program on the isotope geochemistry is in progress. The first results on the noble gas isotope geochemistry of the Aegean island arc, are presented in this paper.

SAMPLING AND ANALYTICAL PROCEDURE

Gas samples were collected from three volcanic centres of the Aegean island arc, i.e. Susaki, Milos and Santorini (Fig. 1). Sample GSU1 from Susaki, as well as samples GMI5 and GMI7 from Milos were collected from geothermal pros-

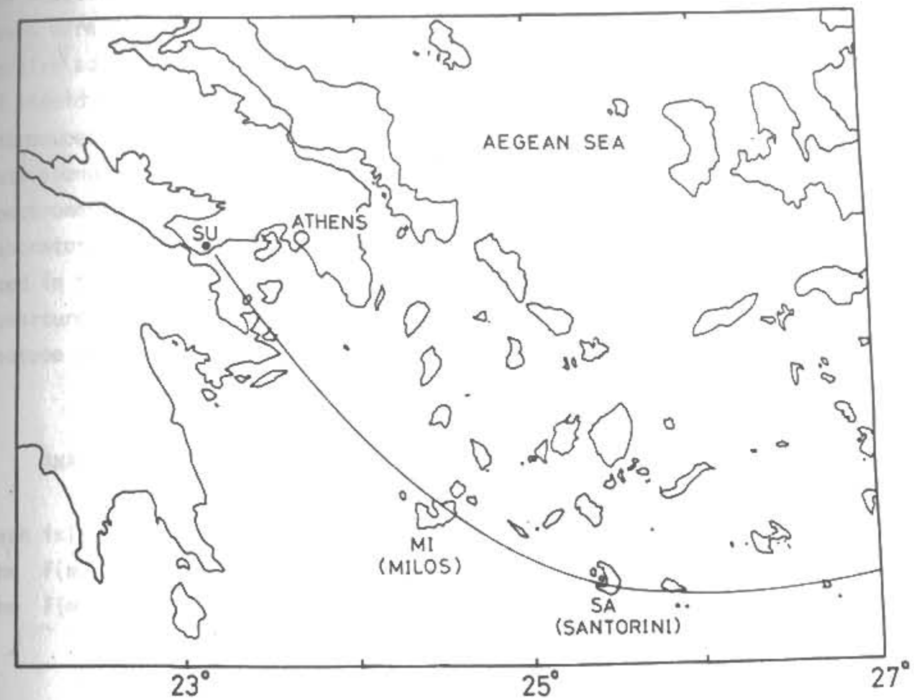

Fig. 1. Location of the volcanic centres of Susaki, Milos and Santorini in the Aegean island arc.
Σχ. 1. Θέσεις των ηφαιστειακών κέντρων του Σουσακίου, της Μήλου και της Σαντορίνης στο τόξο του Αιγαίου.

pecting wells. Samples GMI1 from Milos and GSA2 from Santorini were collected from the undersea bubbling hot springs located at Adamas and Palaea Kameni respectively. Sample GSA1 from Santorini was collected from the fumaroles of Nea Kameni (Figs. 2a & 2b). Each gas sample was transferred in the field into an evacuated lead-glass container with a vacuum-stop valve. Several water samples have also been collected from the above three volcanic centres which are already under isotope analysis.

Before noble gas measurment, each gas sample was divided into several ampoules with breakable seals which were made of glass of low He permeation. The ampoules were attached to the purification system connected to the mass spectrometer. The system was baked out to get an ultra-high vacuum of about 10^{-9} Torr before noble gas analysis. The sample gas was introduced into the purification line by breaking the breakable seal of the ampoule and was purified by removing

Fig. 2. Sampling places at Milos (A) and Santorini (B).
Σχ. 2. Θέσεις δειγματοληψίας στη Μήλο (A) και τη Σαντορίνη (B);

the reactive geses with Ti-Zr getter heated at about 750^{0} C. The purified noble gases were separated into three fractions of He-Ne, Ar and Kr-Xe by means of selective adsorption and desorption on activated charcoal trap at the temperatures of liquid nitrogen and -55^{0} C, respectively. Each fraction of noble gases was introduced into the mass spectrometer and analysed for isotope ratios and absolute abundances. The sensitivities and mass discrimination effects of the mass spectrometer were determined by measuring the standard sample prepared in the laboratory by the same procedure applied to sample gases. The mass spectrometer used in this study is a single focusing 90^{0} sector type with 30 cm radius of ion cuvarture. The resolving power was adjusted to about 1000 to separate noble gas isotope peaks not only from H, D and H_3 peaks but also from hydrocarbon peaks.

ANALYTICAL RESULTS

The absolute abundances of ^{4}He of the analysed gas samples from the Aegean island arc along with the $^{3}He/^{4}He$ and $^{4}He/^{20}Ne$ ratios are given in Table 1. The F(m) values for ^{4}He, ^{20}Ne, ^{36}Ar, ^{84}Kr and ^{132}Xe are also given in Table 1. The F(m) values are calculated by the equation:

$$F(m) = (^{m}M/^{36}Ar)_{sample}/(^{m}M/^{36}Ar)_{air}$$

These F(m) values are used for the construction of the elemental abundance patterns shown in Fig. 4.

DISCUSSION AND CONCLUSIONS

On the basis of their He isotopic ratios, the analysed gas samples from the Aegean island arc can be divided into two groups. Samples from Milos and Santorini belong to the first group while the sample from Susaki belongs to the second. $^{3}He/^{4}He$ ratios in the samples of the former group are higher than the atmospheric $^{3}He/^{4}He$ ratio of $1.4x10^{-6}$. Sample GMI5 shows the highest ratio ($5.55x10^{-6}$), indicating a large contribution of mantle-derived helium into the discharging gases. In contrast to the former group, the $^{3}He/^{4}He$ ratio of the sample GSU1 from Susaki is as low as $0.56x10^{-6}$, which indicates crustal helium, enriched in radiogenic ^{4}He.

The samples from Milos and Santorini lie on a mixing line between atmospheric and mantle-derived helium with a $^{3}He/^{4}He$ ratio of $5x10^{-6}$ and He Ne in the plot $^{3}He/^{4}He$ vs. $^{4}He/^{20}Ne$ (Fig. 3). This suggests that the Milos and Santorini samples have helium of common origin. Although $^{3}He/^{4}He$ ratios of Milos and

Table 1. Absolute abundances, ratios and F(m) values of noble gas isotopes of the analysed volcanic gas samples.

Πίνακας 1. Απόλυτες περιεκτικότητες, λόγοι και τιμές F(m) ισοτόπων ευγενών αερίων των δειγμάτων που αναλύθηκαν.

Sample	Temp. (°C)	$^3He/^4He$ ($x10^{-6}$)	$^4He/^{20}Ne$	$C(^4He)$ (ppm)	F(m) ^4He	^{20}Ne	^{36}Ar	^{84}Kr	^{132}Xe
GSU1	<25	0.56±0.05	21	1.9	29	0.44	=1	1.7	3.7
GSA1	89	3.29±0.03	0.5	6.5	1.9	1.11	=1	1.0	1.0
GSA2	31	4.79±0.14	15	1.8	16	0.34	=1	2.1	4.1
GMI1	36	4.83±0.15	72	14	94	0.42	=1	1.8	2.8
GMI5		5.55±0.10	373	21	552	0.47	=1	1.5	2.8
GMI7		4.87±0.05	174	9.6	289	0.53	=1	1.6	2.6

$F(m) = (^mM / ^{36}Ar)_{sample} / (^mM / ^{36}Ar)_{air}$

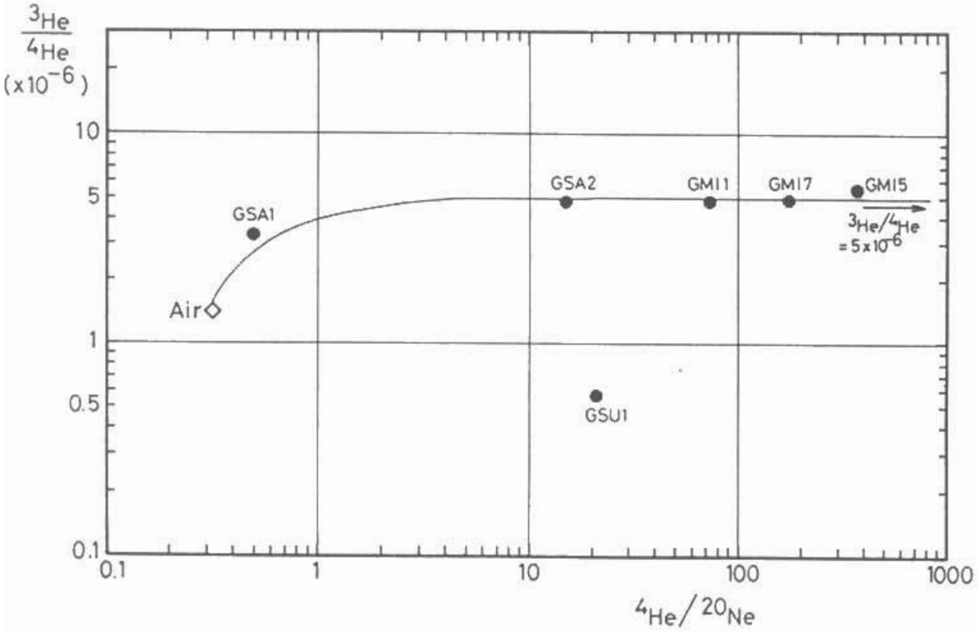

Fig. 3. $^3He/^4He$ vs. $^4He/^{20}Ne$ plot for the analysed volcanic gas samples from the Aegean island arc.

Σχ. 3. Προβολή των λόγων $^3He/^4He$ προς $^4He/^{20}Ne$ των δειγμάτων που αναλύθηκαν από το τόξο του Αιγαίου.

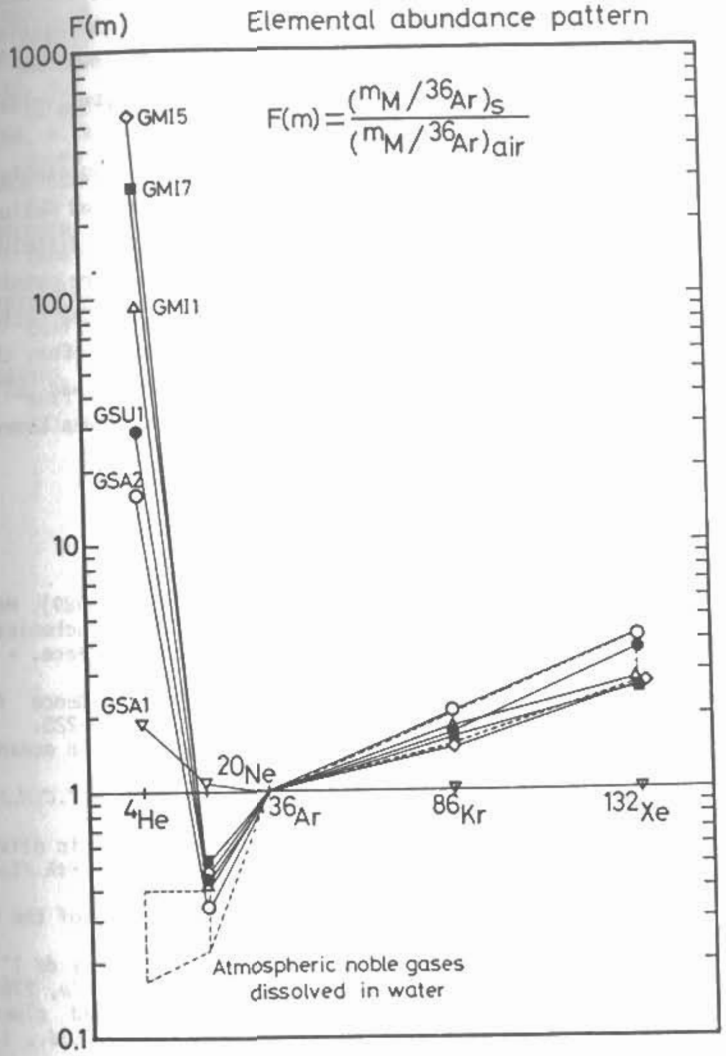

Fig. 4. Elemental abundance patterns of the analysed volcanic gas samples from the Aegean island arc.

Σχ. 4. Διαγράμματα περιεκτικοτήτων των στοιχείων των δειγμάτων από το τόξο του Αιγαίου, που αναλύθηκαν.

Santorini are high, these ratios are about one half of typical ratios of mantle helium found in volcanic gases and rocks from oceanic ridjes and island arcs. The common helium ratios of Milos and Santorini may be produced by contamination with radiogenic ^4He and by regional homogenization on the way from the mantle to the surface. Although the mechanism is not clear, the relatively low $^3He/^4He$ ratio can be considered as a characteristic feature of this, arc type, volcanic area.

Elemental abundance patterns (Fig. 4) of the analysed gas samples, showing high enrichment of He due to the contribution of mantle-derived helium, indicate that Ne, Ar, Kr and Xe are recycled atmospheric noble gases dissolved into ground water. These patterns for the above four elements are very similar to the pattern of the noble gases of water saturated atmospheric air.The pattern of the sample GSA1 is close to that of the atmospheric noble gases. For that sample large contamination from the atmospere was expected because it was collected at the very faint fumarole on the wall of one of the craters of Nea Kameni. However, magmatic helium was also found in that sample.

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