Mantle degassing of major and minor volatile elements during the Earth's history

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Abstract. Total amounts of major and minor volatile elements (H_2O, C, S, N, F, Cl, Br, ^{3}He, ^{36}Ar, ^{40}Ar, and ^{20}Ne) degassed from the mantle throughout the Earth's history are estimated based on the present-day mantle degassing rates and on the results of the ^{40}Ar degassing model coupled with models of thermal evolution of the mantle and magma generation at midocean ridges. Relative contribution of continuous degassing due to volcanism throughout the Earth's history to the abundance of each volatile element in the surface reservoirs at present are obtained. The results suggest that, although both early and continuous degassing processes (and/or a late accretionary veneer) might have influenced all these volatile histories, contribution of each process seems to be very different for each volatile, probably because of differences in solubility into silicate melt, partition coefficient between liquid and solid phases, and efficiency of recycling into the mantle.

Introduction

Studies of geochemical balances have revealed that the large abundances of some elements contained in the atmosphere, the ocean, and sedimentary rocks cannot be explained by continental weathering, and they are called "excess" volatiles [*Rubey*, 1951]. The excess volatiles were considered to have degassed from the mantle by continuous degassing during the history of the Earth [*Rubey*, 1951]. However, studies of isotopic systematics of radiogenic and nonradiogenic rare gases such as ^{40}Ar/^{36}Ar in the atmosphere and the mantle suggest that an early catastrophic degassing event occurred [*Hamano and Ozima*, 1978]. Impact degassing, caused by planetesimal impacts during the accretion of the Earth, is considered to be a probable candidate for the mechanism of the early catastrophic degassing [e.g., *Abe*, 1993], although the early atmosphere might have been lost and a late accretionary veneer of icy planetesimals could have supplied volatiles to the surface during the earliest history of the Earth [*Owen et al.*, 1992]. However, it is not necessary for the degassing history of chemically-reactive volatile elements to be constrained by the studies of inert gases. Relative contribution of continuous degassing to the total supply of various excess volatiles has not been well understood.

In this paper, degassing rates of various volatiles (H_2O, C, S, N, F, Cl, Br, ^{3}He, ^{36}Ar, ^{40}Ar, and ^{20}Ne) are compiled and/or estimated to calculate the total amounts of these

volatiles degassed from the mantle throughout the history of the Earth, based on the results of the ^{40}Ar degassing model coupled with models of the thermal evolution of the mantle and magma generation at midocean ridges by *Tajika and Matsui* [1993]. Relative contribution of continuous degassing throughout the Earth's history to the present surface abundance of each volatile element will be estimated and discussed.

Degassing rates

Degassing rates of volatile elements from the mantle have been estimated by many authors [e.g., *Schilling et al.*, 1978; *Ito et al.*, 1983; *Allégre et al.*, 1986; *Javoy et al.*, 1986; *Marty and Jambon*, 1987; *Marty*, 1995]. These are based mainly on estimates of the global ^{3}He flux and analyses of chemical and isotopic composition of vesicles in the "popping rock", but some of them are based on analyses of volatile abundances in the mid-ocean-ridge basalt (MORB) glasses and estimate of crustal production rate. The estimates of degassing rates for several volatile elements are summarized in Table 1. Most of them are adopted from the previous studies, but some of them are estimated in this study as described bellow.

Degassing rate of ^{36}Ar may be obtained from the molar ratios of ^{4}He/^{3}He$\sim$90000, ^{4}He/^{40}Ar=0.99, and ^{40}Ar/^{36}Ar$>$40000 found in vesicles in popping rock [*Javoy and Pineau*, 1991; *Burnard et al.*, 1997], and also from the degassing rate of ^{3}He [*Lupton*, 1983]. The estimated value of 2.43×10^3 mol/yr should be an upper limit for the ^{36}Ar degassing rate because ^{40}Ar/^{36}Ar in the mantle may be larger than 40000 [*Burnard et al.*, 1997]. However, this estimate is within the ranges of $(1.6-6.1) \times 10^3$ mol/yr obtained by using rare gas degassing models with isotopic constraints [*Zhang and Zindler*, 1989]. Similarly, degassing rate of ^{20}Ne may be estimated to be 6.26×10^2 mol/yr, which is obtained from ^{20}Ne/^{22}Ne=11.69, ^{21}Ne/^{22}Ne$\sim$0.032, ^{4}He/^{21}Ne=5.6$\times 10^7$ in MORB glasses [*Marty*, 1989].

Although there are several estimates of sulfur degassing rate from subaerial volcanoes (hot spot and island arc), there seems to be no established value for the degassing rate of sulfur at the midocean ridges. Because typical MORB glasses contains sulfur of about 850 ppm [*Sakai and Matsuhisa*, 1996], if all this sulfur was released to the atmosphere-ocean system during the formation, alteration, and subduction of oceanic crusts, then the degassing rate of sulfur is about 1.4×10^{12} mol/yr. This value is considered to be an upper estimate. Sakai and Mastuhisa [1996] assumed that alteration of an upper 1 km of oceanic crust and release of 50% sulfur to the ocean, and estimated the degassing rate of sulfur to be 1.44×10^{11} mol/yr. This may be a conservative estimate, but, in this study, I adopt this value as a lower estimate for the sulfur degassing rate.

Table 1. Degassing rates (F_D), present surface abundances (S), present upper mantle abundances (M), and contribution of continuous degassing to the surface abundances (T/S) of various volatiles.

Volatile i	F_D (mol/yr)	S (mol)	M (mol)	T_1/S	T_2/S	T_3/S
^{3}He	$1.1 \times 10^{3~a)}$	$1.2 \times 10^{9~h)}$	$1.1 \times 10^{13~l)}$	4.2×10^3	$(6.3\text{-}9.7) \times 10^3$	$(9.1\text{-}18.1) \times 10^3$
^{20}Ne	$6.3 \times 10^{2~b)}$	$2.9 \times 10^{15~h)}$	$1.4 \times 10^{13~l)}$	9.8×10^{-4}	$(1.5\text{-}2.3) \times 10^{-3}$	$(1.8\text{-}3.1) \times 10^{-3}$
^{36}Ar	$2.4 \times 10^{3~b)}$	$5.6 \times 10^{15~h)}$	$1.7 \times 10^{13~l)}$	2.0×10^{-3}	$(3.0\text{-}4.6) \times 10^{-3}$	$(5.0\text{-}12.0) \times 10^{-3}$
N	$4.4 \times 10^{9~c)}$	$4.3 \times 10^{20~i)}$	$2.0 \times 10^{20~c)}$	4.8×10^{-2}	$(7.1\text{-}11.0) \times 10^{-2}$	$(7.9\text{-}13.0) \times 10^{-2}$
H_2O	$6.1 \times 10^{12~d)}$	$8.2 \times 10^{22~i),k)}$	$5.6 \times 10^{22~m)}$	3.4×10^{-1}	$(5.1\text{-}7.9) \times 10^{-1}$	$(7.9\text{-}16.2) \times 10^{-1}$
C	$2.2 \times 10^{12~e)}$	$7.6 \times 10^{21~j)}$	—	1.2×10^{0}	$(1.8\text{-}2.8) \times 10^{0}$	—
S	$1.4 \times 10^{11~f)}$	$3.4 \times 10^{20~j)}$	—	2.0×10^{0}	$(2.9\text{-}4.5) \times 10^{0}$	—
F	$6.8 \times 10^{11~b)}$	$7.4 \times 10^{19~k)}$	—	4.2×10^{1}	$(6.3\text{-}9.7) \times 10^{1}$	—
Cl	$7.6 \times 10^{10~d)}$	$2.3 \times 10^{21~i)}$	$9.0 \times 10^{20~n)}$	1.5×10^{-1}	$(2.3\text{-}3.5) \times 10^{-1}$	$(3.2\text{-}6.1) \times 10^{-1}$
Br	$8.5 \times 10^{7~g)}$	$1.3 \times 10^{18~g)}$	$8.5 \times 10^{17~o)}$	3.0×10^{-1}	$(4.5\text{-}6.9) \times 10^{-1}$	$(6.7\text{-}13.4) \times 10^{-1}$

a) Lupton [1983], b) This study, c) Marty [1995], d) Ito et al. [1983], e) Javoy et al. [1986], Marty and Jambon [1987], f) Sakai and Matsuhisa [1996], g) Schilling et al. [1978], h) Allégre et al. [1986/87], i) Holland [1978], j) Holser et al. [1988], k) Ronov and Yaroshevsky [1976]. l) Staudacher et al. [1989]. m) Wänke et al. [1984]. n) Stueber et al. [1968]. O) Newsom [1995].

Similarly, although the fluorine degassing rate from subaerial volcanoes has been estimated, there seems to be no estimate for the degassing rate of fluorine at midocean ridges. Analyses of glassy rims of submarine pillow basalt show fluorine concentration of 230 ppm [*Muenow et al.*, 1980]. If this were released to the surface, then an upper estimate for the degassing rate of fluorine is estimated to be 6.78×10^{11} mol/yr.

Contribution of continuous degassing

When we assume an early catastrophic degassing which might have been caused by impact degassing during the accretion of the Earth, there are several methods to estimate T, the total amount of volatiles that has degassed from the mantle to the surface via volcanism throughout the Earth's history after the early catastrophic degassing event.

The simplest way to estimate this value is to multiply the present-day degassing rate by the age of the Earth ($t^* \sim 4.6 \times 10^9$ years), that is,

$$T_1 = F_D^* \times t^* \tag{1}$$

where F_D is the degassing rate and $*$ represents the present-day value. This is defined here as "Method 1".

It is almost certain that the degassing rate must have decreased during the Earth's history owing to the cooling of the Earth. Therefore, Method 1 should underestimate T. It is, however, difficult to estimate the change in the efficiency of mantle degassing during the history of the Earth. *Tajika and Matsui* [1993] constructed an ^{40}Ar degassing model coupled with thermal evolution of the mantle, and constrained the temporal variation of degassing efficiency of volatiles from the mantle. In that model, ^{40}Ar is generated by the decay of ^{40}K and degasses to the atmosphere from the mantle and the continental crust. For the mantle degassing, volatiles in a certain volume of the mantle are assumed to degas to the atmosphere in an unit time when oceanic crusts are formed at the midocean ridges. Assuming a first order rate process, the degassing rate, F_D, of volatile i from the mantle may be expressed as $F_D^i = f^i \cdot \dot{V}_D(t) \cdot M^i(t)/V_M$, where $M^i(t)$ is the amount of volatile, V_M is volume of the mantle (hence M^i/V_M represents the concentration), and $\dot{V}_D(t)$

is the volume of mantle material from which degassing occurs in an unit time. The f^i is the degassing fraction which represents the mass ratio of volatile i partitioning into the gas and melt phases to the total amount originally included in the degassing volume. In this model, the efficiency of mantle degassing is not a constant, but assumed to vary as $\dot{V}_D(t) = Sr(t) \times d_m(t)$ where the seafloor spreading rate, Sr, depends on the mantle heat flow and the melt generation depth in the mantle, d_m, depends on the mantle potential temperature. It is noted that the efficiency of mantle degassing varies with time because the seafloor spreading rate and the melt generation depth should change with the mantle cooling (i.e., decreases with mantle heat flow and mantle potential temperature). Then, temporal variation of $\dot{V}_D(t)$ can be obtained under the constraint that the total amount of ^{40}Ar degassed to the atmosphere is an observational value. The value of $\dot{V}_D$ averaged over 4.6×10^9 years is expressed as $\alpha = (1/t^*) \int_0^{t^*} [\dot{V}_D(t)/\dot{V}_D^*] dt$. According to the results of *Tajika and Matsui* [1993], the value of α is 1.5-2.3 within the possible ranges of initial conditions and mantle potassium abundance (it is noted that α does not mean an average degassing rate, but means an average efficiency of mantle degassing). By using this result, the value of T could be estimated more properly including a decrease in the degassing rate through the Earth's history due to the mantle cooling as, $T = \int_0^{t^*} F_D(t) dt = \int_0^{t^*} F_D^* [\dot{V}_D(t)/\dot{V}_D^*][M(t)/M^*] dt$.

In the case of small change in the abundance of volatile i in the mantle during the history of the Earth (i.e., $M(t) \sim M^*$), which implies small net loss of volatile from the mantle (i.e., amount of volatile degassed by continuous degassing is small, or it is largely offset by rapid recycling), we can approximate T as,

$$T_2 = F_D^* \times \alpha \times t^* \tag{2}$$

This is defined here as "Method 2".

When we assume no volatile recycling into the mantle and $M(t) = M^* + T(t^*) - T(t)$, T can be obtained from the following equation by using a numerical iteration under the boundary conditions of $T(0) = 0$ and $T(t^*) = T_3$.

$$T_3 = \int_0^{t^*} F_D^* \frac{\dot{V}_D(t)}{\dot{V}_D^*} \frac{M^* + T_3 - T(t)}{M^*} dt \tag{3}$$
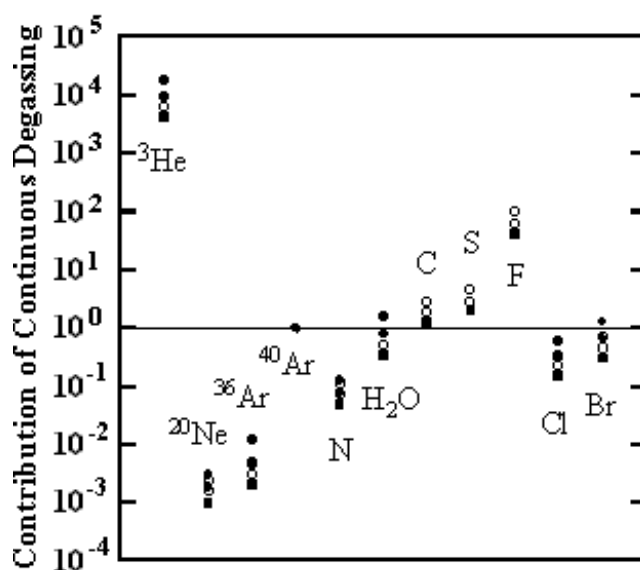
Figure 1. Contribution of continuous degassing to the present surface abundances of various volatile elements estimated by Method 1 (filled square), Method 2 (open circle), and Method 3 (filled circle).

This is defined here as "Method 3'. In this case, volatile abundances in the mantle at present, M^*, must be assumed in order to estimate T. The values of M^* are adopted from studies of chemical analyses of mantle xenoliths and model calculations of mantle degassing (Table 1) [*Stueber et al.*, 1968; *Wänke et al.*, 1984; *Staudacher et al.*, 1989; *Marty*, 1995; *Newsom*, 1995].

In Table 1, the estimates for the present-day abundances of volatiles in the surface reservoirs (the atmosphere, the ocean, and the sedimentary rocks), S, are shown. The ratio of T to S may represent a relative contribution of continuous degassing during the history of the Earth to the surface volatile budget at present. This ratio, T/S, is estimated for various volatiles, and shown in Table 1. It is noted that, in order to obtain an upper estimate for T/S, the upper mantle, rather than the whole mantle, is assumed to be the only source for excess volatiles in Method 3 (Table 1), because large change in volatile contents in that reservoir and large supply of volatiles during the history of the Earth are expected. However, because the "degassed" mantle is estimated to comprise $70\pm18\%$ of the whole mantle (much larger than the upper mantle) [*Zhang and Zindler*, 1989], the most likely estimate might be closer to the whole mantle case. It is noted that Method 3 may not be appropriate for the volatiles of $T/S > 1$, because $T/S > 1$ suggests volatile recycling into the mantle (^{3}He is the only exception because of the effect of its escape to space; note that the amount escaped to space should be also included in T). Hence the results of $T_3/S > 1$ for H_2O and Br obtained in Method 3 should be artificial.

Discussion

Figure 1 shows the estimated values of T/S obtained from Methods 1, 2 and 3. It is noted that the $T/S = 1$ for ^{40}Ar is assumed to estimate T/S for other volatiles in Methods 2 and 3.

Among these, the T/S value for ^{3}He is very large (4200~18000), reflecting an effective escape of ^{3}He from the atmosphere to space. On the other hand, the T/S values of other two nonradiogenic rare gases (^{20}Ne and ^{36}Ar) are very low (<several %). This may reflect quite large contribution of the early catastrophic degassing to the total supply of these elements, which is consistent with the study of argon degassing history constrained by argon isotope data [*Hamano and Ozima*, 1978]. A late accretionary veneer (CI chondrite or icy planetesimal) could have been another possible mechanism to supply volatiles during the earliest history of the Earth [*Owen et al.*, 1992]. However, it may be difficult to explain small T/S for ^{20}Ne by accretion of icy planetesimals, because neon cannot be trapped in amorphous ice except at temperature below 20 K [*Owen et al.*, 1992]. Behavior of nitrogen seems to be similar to these nonradiogenic rare gases although the T/S value of N (~10%) is larger than those of ^{36}Ar and ^{20}Ne. Because solubility of N in silicate melt is similar to that of Ar [*Zhang and Zindler*, 1989], the difference in the T/S values for N and Ar might imply the possibility of preferential recycling of N into the mantle.

The T/S values of H_2O and two halogens (Cl and Br) imply comparable contribution of the early and the continuous degassing processes to the present surface abundances of these volatiles (20-100%). It is noted that a proto-ocean of almost the present ocean mass might have been formed as a consequence of impact degassing [e.g., *Abe*, 1993], while studies of mass budget of H_2O at subduction zones suggest recycling of H_2O (and Cl) into the mantle at present [*Ito et al.*, 1983].

On the other hand, the T/S values are > 1 for C and S. This suggests large contribution of continuous degassing and rapid recycling of C and S into the mantle. Both C and S are reactive elements which form carbonates, organic carbon, sulfates, and sulfides, and subduction of these materials could result in recycling of them into the mantle. Recycling of C into the mantle is suggested by studies of mass budget of C at subduction zones [e.g., *Javoy et al.*, 1982]. It is noted that there might have been an additional ~100 bar (~ 10^{22} mol) of CO_2+CO in the proto-atmosphere formed during the accretion of the Earth [e.g., *Abe*, 1993].

The results for fluorine might be an upper estimate because fluorine is a lithophile element and may not be released preferentially as the other atmophile elements (on the other hand, this result might suggest rapid recycling of fluorine for the same reason). Because there is not enough data for fluorine to discuss the mantle degassing and later release from oceanic crusts due to alteration, the results shown here are tentative.

Differences in the T/S values for various volatiles must be significant even when we consider possible errors in the estimates for F_D, S, M, and $\dot{V}_D(t)$. There may be several factors to cause the differences. The early catastrophic degassing, probably due to impact degassing, would have resulted in degassing of large quantities of all the volatile elements. However, because a proto-steam-atmosphere generated by impact degassing would have resulted in the formation of magma ocean owing to its blanketing effect, volatiles in the proto-atmosphere and the magma ocean might have been in dissolution equilibrium [e.g., *Abe*, 1993]. If it were the case, volatile amounts in the proto-atmosphere would probably depend on solubility of each element into silicate melt and molten metallic iron. Fractionation of volatiles

trapped in amorphous ice which might have accreted as a late veneer [*Owen et al.*, 1992] could have also resulted in differences in the T/S values. The efficiency of the continuous degassing due to volcanism would depend on partition of volatile between solid and liquid phases, and its solubility into the silicate melt. The efficiency of recycling of each volatile into the mantle due to subduction of oceanic crusts and seafloor sediments would depend on its abilities to form chemical precipitates or to alter oceanic crusts, and on their stability under the shallow mantle conditions. The wide range of the T/S value shown in Fig. 1 suggests large differences in these factors for each volatile element.

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