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Distribution and evolution of carbon and nitrogen in Earth

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ABSTRACT

In this paper we discuss the distribution, geochemical cycle, and evolution of CO₂ and N₂ in Earth's degassed mantle, and atmosphere plus continental crust. We estimate the present distribution of CO₂ and N₂ in Earth's degassed mantle based on amounts of He and Ar in the degassed mantle and observed outgassing ratios of CO₂/He and N₂/Ar at mid-ocean ridges. Estimated CO₂ in present degassed mantle is $(1.8^{+9}_{-6}) \times 10^{22}$ mol, representing $(72 \pm 10)\%$ of total degassable CO₂, an amount far higher than fractions previously inferred for noble gases. This strongly suggests that most CO₂ has been recycled from Earth's surface into the degassed mantle through subduction, which is consistent with many recent discussions. For N₂, the estimated amount in the present mantle is $\sim 2.5 \times 10^{19}$ mol, representing $\sim 12\%$ of total degassable N₂. Recycling of N₂ back to the mantle is also inferred, but on a much smaller scale.

A simple model for the outgassing and recycling of CO₂ and N₂ in Earth is presented. Outgassing is assumed to be via melt–vapor partitioning of volatiles. Recycling back into the mantle via subduction is assumed to be proportional to the mass of the volatile component in the crust. This simple model is consistent with all currently available constraints. Difficulties arise from the dependence of the recycling constant on time. Hence, no single evolution history can be obtained for CO₂ based on the available data. Model results tentatively point to a higher CO₂ content on Earth's surface in the Archean and Proterozoic than at present. Important future constraints may come from records in sedimentary rocks, improved understanding of carbonate production, and better modeling of the recycling process.

1. Introduction

The distribution of volatiles among various reservoirs in Earth is an important problem with relevance to the origin and evolution of the atmosphere, oceans and sedimentary carbonates. Noble gases, as a group of volatiles with radiogenic isotopes, provide the basis for much of our present understanding of this problem [e.g., 1–10]. However, assumptions regarding relationships between noble and major gases must be made in order to infer the evolution of major gases in the atmosphere from noble gas evolution models because noble gases comprise only a small fraction of Earth's atmosphere (including volatiles stored in oceans and continental crust). Some authors

assume, either implicitly or explicitly, that all the noble gases in the atmosphere evolved similarly (except, of course, for He which escapes to outer space) [e.g., 2–7]. These models can be termed bulk degassing models and would be easy to extend to major gases. Observed noble gas isotopic ratios (especially He vs. Ar and Xe) in different reservoirs are, however, difficult to reconcile with such assumptions [6–10], especially the not-so-high ⁴He/³He ratios and the high ³He in MORB compared with other noble gases (Fig. 1). The impact degassing model [e.g., 11] is also a bulk degassing model and hence has the same problems. Several models assume that there is a He flux from the undegassed mantle to the degassed mantle. One such model, developed in order to reconcile the less degassed nature of He, proposes an *ad hoc* He flux from the undegassed mantle to the degassed mantle without fluxes of other gases [7]. This He flux unaccompanied by

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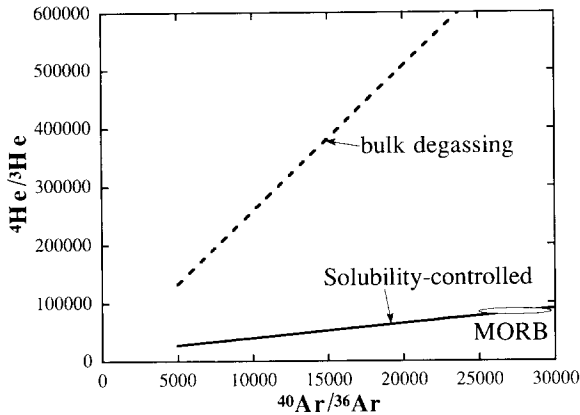


Fig. 1. Present-day ${}^4\text{He}/{}^3\text{He}$ vs. ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ in DM predicted using a bulk degassing model and solubility-controlled outgassing model. ${}^4\text{He}/{}^3\text{He}$ and ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ in DM are correlated because the parents of ${}^4\text{He}$ and ${}^{40}\text{Ar}$ behave coherently and the depletion of ${}^3\text{He}$ and ${}^{36}\text{Ar}$ are related by the same degassing function (bulk degassing model) or the solubilities of He and Ar (solubility-controlled degassing model). The dashed line is the correlation predicted by bulk degassing models (including impact degassing models), and the solid line is the correlation predicted by our solubility-controlled degassing model [9]. ${}^4\text{He}/{}^3\text{He}$ and ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ in MORB lies on the line predicted by solubility-controlled outgassing model. The error on the slope of each curve is $\sim 50\%$. Initial conditions: $({}^4\text{He}/{}^3\text{He})_0 = 7000$, $({}^{40}\text{Ar}/{}^{36}\text{Ar})_0 = 0$. At present, $K_{\text{UM}} = 260$ ppm, $(\text{K}/\text{U})_{\text{UM}} = 12700$, $(\text{Th}/\text{U})_{\text{UM}} = 3.9$. See [9] for details.

other gases is unlikely. Another such model assumes that the plume transports He from the lower mantle to the upper mantle and that He in the degassed mantle is in a steady state [12]. This model is again a bulk degassing model and has the same problems as other bulk degassing models. In contrast, models which assume that outgassing of the mantle is controlled by melt–vapor partitioning can account for observed He/Ar ratios in MORB and in Loihi volcanics [8–10], He, Ar and Xe isotopic ratios in MORB mantle, undegassed mantle and the atmosphere [9] (Fig. 1), and the present degassing rates of He and Ar [9,10]. Both bulk and solubility-controlled de-

gassing models have difficulty in explaining the Ne isotopes in the atmosphere and MORB [13,14], and this must be left to future work.

The solubilities of noble gases in magmas vary widely from one gas to another (Table 1). For example, the solubility of He is $\sim 30\times$ greater than that of Xe, and the solubility of water at $p_{\text{H}_2\text{O}} = 1$ kbar is $\sim 100\times$ greater than that of CO_2 and $\sim 2000\times$ greater than that of Xe [e.g., 15–19]. A solubility-controlled outgassing model asserts that gases with different solubilities have different degassing histories [8–10] due to fractionations between the gaseous species during degassing [8–10,20]. If this is correct, it is impossible to characterize the evolution of major gases in the atmosphere using noble gases alone. We must therefore consider (i) the speciation of volatiles during outgassing and the partition coefficients of those species between solid and melt and between melt and vapor, in addition to (ii) the assumed variation of degassing intensity, (iii) whether or not recycling of the volatile component back to the mantle was important, and (iv) how to characterize the recycling process.

In this paper we discuss the distribution and evolution of CO_2 and N_2 in Earth's various reservoirs. CO_2 and N_2 , together with water, are the three major volatile components of the atmosphere, crust and oceans. Recent work suggests that significant amounts of CO_2 have been recycled back into the mantle [e.g., 21–26]. We first summarize data on fluxes of CO_2 and N_2 from the mantle to the surface and estimate the present distribution of CO_2 and N_2 in various reservoirs of Earth. We then present a simple model for the outgassing and recycling history of CO_2 and N_2 .

Although water is a major volatile component in Earth, we are forced to disregard it in this study due to complexities associated with the role of H_2 . If H_2 were an important outgassing species for water, as it may well be [e.g., pp. 40–58 in 27],

TABLE 1

Solubilities of volatile species ($\text{mol g}^{-1} \text{bar}^{-1}$) in basaltic magma at 1 kbar partial vapor pressure and 1200°C

Species	H_2O	CO_2	N_2	He	Ar
Solubility	1.8×10^{-6}	1.8×10^{-8}	$\sim 3.6 \times 10^{-9}$	2.5×10^{-8}	2.6×10^{-9}

Sources of data: H_2O [15]; CO_2 [18,19]; N_2 [63, and M. Javoy, pers. commun.]; He and Ar [16,17]. Cross-solubility effects are ignored.

the following difficulties arise: (1) The solubility of H_2 is believed to be much lower than that of H_2O but its value is not known; (2) variations in the H_2/H_2O ratio through Earth's history may be sizable but they are not known either; and (3) at present, H_2 escapes from the atmosphere into outer space over a relatively short time interval ($\sim 10^6$ yrs at present by comparison with He [28,29]), making it difficult to estimate what proportion of outgassed H_2 becomes oxidized into H_2O . On the other hand, if the major outgassing species were H_2O and if there were no recycling of water back to the degassed mantle (DM), the outgassing history for the ocean water of Earth would be relatively simple. Using these assumptions and ignoring the pressure dependence of water solubility in silicate melt, it has been shown [9] that ocean water has a mean age of 2.7 Ga in the context of a solubility-controlled outgassing model. Such a simple model predicts that the present outgassing rate of water is 7×10^{12} mol/yr, surprisingly consistent with a recent estimate of 1×10^{13} mol/yr [30]. However, in the absence of data on H_2 solubility, variation in H_2/H_2O ratios, rate of escape and oxidation of H_2 in early atmosphere and recycling of water back into DM, it is difficult to present a more comprehensive model for the evolution of the oceans.

Some definitions are summarized, as follows (mostly following [9]): AC refers to the atmosphere plus continental crust plus oceans; DM refers to the degassed mantle; UM refers to the undegassed mantle. The DM reservoir is a hypothetical end-member reservoir characterized by extreme noble gas isotope ratios and does not necessarily correspond to any actual reservoir (see [9] for more details). We emphasize that estimated inventories of volatile components in DM reflect those in the extremely outgassed end-member DM and should be regarded as a minimum. Degree of outgassing refers to that from the hypothetical DM unless otherwise stated. Impact-generated outgassing is ignored because it is unimportant on Earth, at least for Ar [9], because it cannot explain many noble gas isotopic features that are explained by solubility-controlled degassing models (e.g., Fig. 1), and because we do not fully understand the formation and possible loss of such an atmosphere. Throughout this pa-

per, CO_2 , C and carbon all refer to total carbon in terms of moles of CO_2 ; N_2 , N and nitrogen all refer to total nitrogen in terms of moles of N_2 . Solubility is taken to mean the partition coefficient between vapor and melt in $\text{mol g}^{-1} \text{bar}^{-1}$. Uncertainties are given at the 1σ level, unless otherwise specified. All errors are propagated statistically, except initial error assignments which are somewhat arbitrary. When such a propagation is not straightforward no error is given and the number is preceded by a tilde (\sim).

2. Present outgassing fluxes and inventories of CO_2 and N_2 in Earth

2.1 CO_2

Total CO_2 in AC is estimated to be $(7 \pm 1) \times 10^{21}$ mol [23,29–32]. The present outgassing ratio of $C/{}^3\text{He}$ at mid-ocean ridges is $(2 \pm 0.5) \times 10^9$ [22–26,33]. By comparison with the present-day ${}^3\text{He}$ flux (1140 ± 150 mol/yr [34]), the present outgassing flux of CO_2 is $(2.3 \pm 0.6) \times 10^{12}$ mol/yr [22,33,35]. At the present outgassing rate, CO_2 in AC would accumulate in ~ 3 b.y., less than Earth's age, suggesting recycling of CO_2 back into the mantle, especially when a higher degassing rate in ancient times is taken into account [1–10]. This conclusion has been reached before by Javoy et al. [21,22] and Des Marais [24,26], although Marty and Jambon [33] preferred slow and continuous degassing of CO_2 without recycling.

Total ${}^3\text{He}$ in the initial DM (compositionally identical to the initial UM) is approximately $(3.4 \pm 0.6) \times 10^{14}$ mol, based on a primordial ${}^3\text{He}/{}^{36}\text{Ar}$ ratio of 0.062 ± 0.01 [9] and a total ${}^{36}\text{Ar}$ of 5.56×10^{15} mol in the initial DM (essentially the same as in the present atmosphere [3]). Total ${}^3\text{He}$ in the present DM is estimated to be $(9_{-5}^{+3}) \times 10^{12}$ mol based on the initial ${}^3\text{He}$ and $(97.4_{-1.3}^{+0.7})\%$ degassing (Run 4 in table 3 of [9]). We assume that the present outgassing ratio of $C/{}^3\text{He}$ from the mid-ocean ridges reflects the ratio in the present DM both because experimentally determined solubilities for CO_2 and He are similar (Table 1) (hence outgassing is not expected to strongly affect the ratio), and because observations show that outgassing does indeed not significantly change the ratio [36]. From the $C/{}^3\text{He}$

outgassing ratio and total ^3He in the present DM, the total amount of degassable CO_2 in the present DM is $(1.8_{-0.6}^{+0.9}) \times 10^{22}$ mol and the total amount of CO_2 in the initial DM (present DM + AC) is thus $(2.5_{-0.6}^{+0.9}) \times 10^{22}$ mol. By mass balance, the proportion of CO_2 that remains in the DM is $(72 \pm 10)\%$ of the total degassable CO_2 and the degree of depletion for CO_2 is only $(28 \pm 10)\%$. This contrasts sharply with the high degrees of depletion ($> 95\%$) inferred for the noble gases [5–9]. Based on the above values, the primordial ratio of $\text{C}/^3\text{He}$ in the initial mantle is estimated to be $(7_{-2}^{+3}) \times 10^7$.

The large amount of degassable CO_2 that we calculate to be in the present DM is not an artifact of the outgassing model used. The present-day $\text{C}/^3\text{He}$ ratio in MORB is fairly constant (ratios range from 1×10^9 to 8×10^9) based on estimates made by three independent groups: Des Marais [24], Javoy et al. [22], and Marty and Jambon [33]. The estimate of total ^3He in the present DM of $(9_{-3}^{+5}) \times 10^{12}$ mol is based on Zhang and Zindler [9] and yields a concentration of $\sim 7 \times 10^{-11}$ cm^3 STP/g in the DM, which is not too different from an independent estimate of $\sim 1.7 \times 10^{-10}$ cm^3 STP/g based on measurement of samples [37]. That our estimate is not far off can be checked as follows: Assuming that DM consists of $(70 \pm 10)\%$ of the total mantle [9] with a mass of $(2.9 \pm 0.4) \times 10^{24}$ kg, the estimated total ^3He in the present DM yields a ^3He concentration of $(7_{-3}^{+4}) \times 10^{-11}$ cm^3 STP/g. Taking the degree of melting to be 8–20% [e.g., 38] and assuming that all ^3He partitions into the melt during partial melting, the average ^3He concentration in undegassed MORB is expected to be $(5_{-3}^{+5}) \times 10^{-10}$ cm^3 STP/g, consistent with ^3He contents in the most He-rich MORBs (6 to 10×10^{-10} cm^3 STP/g in popping rocks which may represent non-degassed MORB magma [13,37,39]). The total ^3He brought up by MORB (20 km^3/yr) is therefore (1300_{-650}^{+1300}) mol/yr, which compares favorably with the estimated ^3He outgassing flux from the mantle, (1140 ± 150) mol/yr.

The estimated CO_2 concentration in the DM is also consistent with the estimated CO_2 outgassing flux at mid-ocean ridges. The estimated average CO_2 concentration is 380_{-110}^{+170} ppm by weight in the initial DM and 270_{-100}^{+160} ppm in the present DM. Again, taking the degree of melting

to be 8–20% and assuming that all CO_2 partitions into the melt, the CO_2 concentration in undegassed MORB is expected to be 1900_{-1000}^{+1900} ppm [22,23]. The total CO_2 brought up by MORB (20 km^3/yr) is thus $(2.5_{-1.3}^{+2.5}) \times 10^{12}$ mol/yr. This is similar to the estimated CO_2 outgassing flux of $(2.3 \pm 0.6) \times 10^{12}$ mol/yr and demonstrates an internal consistency for the gas budgets constructed here. This further supports the validity of the high CO_2 contents estimated for the present DM.

Our estimates of the CO_2 content and the $\text{C}/^3\text{He}$ ratio (7×10^7) of Earth's primordial mantle are much lower than those proposed by Marty and Jambon [33], who assumed a chondritic $\text{C}/^3\text{He}$ ratio (2×10^9) for primordial Earth. Allegre et al. [7] have argued that it is difficult to justify an initial gas composition for the Earth based on any meteorite type. Javoy et al. [35] have argued against an initial ratio of 2×10^9 . The $\text{C}/^3\text{He}$ estimate of Marty and Jambon [33] is problematic because the present outgassing ratio (or the ratio in MORB) is also roughly 2×10^9 . If the primordial ratio and the present outgassing ratio were similar, the DM would have been depleted to a similar degree in both ^3He and CO_2 since the degree of outgassing for ^3He is very high, and the outgassed $\text{C}/^3\text{He}^*$ ratio (where the asterisk (*) signifies the inclusion of ^3He lost to outer space) would also be 2×10^9 . However, Marty and Jambon [33], among others, have shown that the outgassed $\text{C}/^3\text{He}^*$ ratio is $\sim 10^7$, much lower than the chondritic ratio of 2×10^9 . Hence, the estimates in Marty and Jambon [33] are not internally consistent.

2.2 N_2

There are 1.38×10^{20} mol of N_2 in Earth's atmosphere [3], $(0.22 \pm 0.10) \times 10^{20}$ mol in sedimentary rocks, and $(0.20 \pm 0.10) \times 10^{20}$ mol in crustal igneous rocks [40,41] (an error of 50% is arbitrarily assigned to the latter two estimates). The total N_2 in the AC is the sum of the above three reservoirs, $(1.8 \pm 0.1) \times 10^{20}$ mol. The outgassing ratio of N_2/Ar at the mid-ocean ridges is ~ 54 [22,23]. Seeing as the ^{36}Ar outgassing rate is presently at 2100_{-1050}^{+2100} mol/yr [9], the outgassing rate for N_2 is $(3.2_{-1.6}^{+3.2}) \times 10^9$ mol/yr using $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{DM}} = 28000 \pm 5000$ [37,42] and assuming that

the above N_2/Ar outgassing ratio is representative of global outgassing. This estimate is similar to that of Javoy et al. [22]. At the current outgassing rate, the total N_2 in the AC would be outgassed in ~ 56 b.y., an order of magnitude longer than the age of Earth.

The total ^{40}Ar production in AC + DM over Earth history is $(2.7 \pm 0.7) \times 10^{18}$ mol [9] assuming that the DM represents $(70 \pm 10)\%$ of the whole mantle and that the K content of the bulk silicate Earth is 260 ppm [43]. ^{40}Ar in the present DM is estimated to be $(4.6 \pm 1.6) \times 10^{17}$ mol, based on the total ^{40}Ar production and $(83 \pm 4)\%$ outgassing (Run 4 in table 3 of [9]). If we further assume, based on similar solubilities of N_2 and Ar (Table 1), that the present outgassing ratio of N_2/Ar at mid-ocean ridges reflects the current ratio in the DM, the amount of N_2 in the present DM is $\sim 2.5 \times 10^{19}$ mol (or ~ 0.24 ppm). Total N_2 in the initial DM was thus $(2.0 \pm 0.2) \times 10^{20}$ mol and N_2 concentration in the initial DM was 1.9 ± 0.2 ppm. N_2 in the present DM is $\sim 12\%$ of the total degassable N_2 , and the depletion of N_2 in DM is therefore $\sim 88\%$, significantly less than the depletion of ^{36}Ar (99.7%, [9]), even though the solubilities of N_2 and Ar are similar.

The above results are summarized in Table 2, which lists our estimates of bulk Earth (excluding the core) volatile contents and their present distributions. These estimates are the first to be

internally consistent and satisfy all currently available constraints based on radiogenic noble gas isotopes and measured outgassing fluxes. Estimated CO_2 and N_2 contents for the DM provide constraints on the volatile evolution of Earth. If Earth's core does not contain a significant fraction of CO_2 and N_2 , our results suggest that Earth is depleted by a factor of ~ 650 in carbon and ~ 3000 in nitrogen, relative to Si, when compared to CI chondrites [44].

2.3 CO_2 and N_2 in the DM and the need for recycling

The present degree of depletion of CO_2 in the DM is only $(28 \pm 10)\%$ based on the above analysis, much lower than the $(97.4^{+0.7}_{-1.3})\%$ calculated for 3He [9]. Hence, the depletion histories of CO_2 and 3He in the DM were different, despite the similar solubilities. The same is true for N_2 and ^{36}Ar , although to a smaller extent. In the context of the solubility-based degassing model, there are two possibilities for these differences. One is that CO_2 has been recycled back into the mantle via subduction [21–26] (hereafter called the recycling model). Alternatively, CO_2 in the DM originally existed primarily in a reduced form that could not be degassed, but was then slowly oxidized to CO_2 , which could then be degassed [33] (hereafter called the slow oxidation and degassing model).

TABLE 2

Volatile Fluxes and Inventories in Earth

	CO_2	N_2	3He	^{36}Ar
Inventories (in mol):				
present AC	$(7 \pm 1) \times 10^{21}$	$(1.8 \pm 0.1) \times 10^{20}$	$(3.3 \pm 0.6) \times 10^{14}$ ^a	5.6×10^{15}
present DM	$(1.8^{+0.9}_{-0.6}) \times 10^{22}$	$\sim 2.5 \times 10^{19}$	$(0.09^{+0.045}_{-0.03}) \times 10^{14}$	$(0.17 \pm 0.06) \times 10^{14}$
Initial DM	$(2.5^{+0.9}_{-0.6}) \times 10^{22}$	$(2.0 \pm 0.2) \times 10^{20}$	$(3.4 \pm 0.6) \times 10^{14}$	5.6×10^{15}
Concentrations ^b (in wt ppm for CO_2 and N_2 , and STP $cm^3 g^{-1}$ for 3He and ^{36}Ar):				
present DM	270^{+160}_{-100}	~ 0.24	$(7^{+4}_{-3}) \times 10^{-11}$	$(1.3 \pm 0.5) \times 10^{-10}$
Initial DM	380^{+170}_{-110}	1.9 ± 0.2	$(2.7 \pm 0.8) \times 10^{-9}$	$(4.3 \pm 1.0) \times 10^{-8}$
Present outgassing flux (in mol/yr):				
	$(2.3 \pm 0.6) \times 10^{12}$	$\sim 3.2 \times 10^9$	1140 ± 150	~ 2100

Errors are at 1σ level. See text for data sources.

^a Corrected for 3He lost to outer space.

^b Concentrations are calculated assuming that the mass fraction of DM is 70% of the total mantle [9].

Marty and Jambon [33] presented the slow oxidation and degassing model primarily because of difficulties with their assumed constant and high $C/{}^3\text{He}$ outgassing ratio throughout Earth history. In the context of their assumption the amount of recycling would be too large. However, as shown above, the $C/{}^3\text{He}$ outgassing ratio increases with time (from $\sim 7 \times 10^7$ initially to $\sim 2 \times 10^9$ today), as recycled CO_2 increases the $C/{}^3\text{He}$ ratio in the DM. The predicted recycling rate poses no difficulty to a recycling model given the amount of CO_2 that is currently brought into subduction zones by sediments and altered oceanic crust [45–47] (and see later discussion). A potential problem for the slow oxidation and outgassing model is that it predicts the presence of very small amounts of CO_2 at Earth's surface during the Early Archean (5–20% of the present amount, depending on the version of the model discussed in [33]). This is difficult to reconcile with intense carbonation during weathering at 3.7 b.y. ago, and the presence of both calcite-rich and dolomite-rich carbonates [27].

Recycling of CO_2 is also supported by other recent observations. Staudigel et al. [46] showed that carbonate veins deposited in altered MORB presently deliver $\sim 4 \times 10^{12}$ mol CO_2/yr to subduction zones. If the altered MORB is recycled back to the mantle without losing the CO_2 , the recycling rate of CO_2 must be greater than the present outgassing rate. If sediments brought to subduction zones are included, the recycling rate of CO_2 can potentially be much higher. At present, $\sim 3 \text{ km}^3$ of sediments, containing $\sim 2.3 \times 10^{13}$ mol/yr CO_2 , are brought to subduction zones each year [47,48], part of which may be accreted to trench slopes via offscraping. Marty et al. [49] estimated CO_2 fluxes due to island arc volcanism at subduction zones to be only $(1\text{--}5) \times 10^{11}$ mol/yr, much less than that delivered to subduction zones. Hence the present CO_2 budget certainly permits the recycling of CO_2 back to the mantle and it is likely that this process was also feasible over much of the course of Earth history.

In view of the evidence discussed above, we prefer the recycling model over the slow oxidation and degassing model. We note that CO_2 is a good tracer for the recycling of Earth's crust into the mantle, for the following four reasons:

(1) CO_2 is primarily stored in carbonate sedi-

ments [e.g., 29,31,32] and pelagic sediments [47,48] which are more likely to be subducted and recycled than the igneous and metamorphic material of the continental crust; hence CO_2 is strongly affected by recycling (in contrast, noble gases and N_2 are not so strongly affected by recycling because they are primarily stored in the air).

(2) CO_2 abundances in the atmosphere and continental crust can be more accurately estimated than those of many other incompatible components because CO_2 is (or is assumed to be) concentrated in the surficial layers of the continental crust, and is therefore not strongly affected by uncertainties in lower crustal composition.

(3) The pathways for CO_2 from mantle to crust and atmosphere are primarily via outgassing, so the CO_2 flux from the mantle can be estimated with better precision [22–26,33,50] than can fluxes of other non-volatile incompatible elements (mantle–crust pathways for components such as K_2O involve ridge and island arc magmatism and underplating processes, and are inherently more convoluted).

(4) We can now estimate the amount of CO_2 in the degassed mantle reasonably well by extending arguments based on noble gas isotope systematics.

The major unknown in constraining the terrestrial evolution of CO_2 is estimating the recycling flux, because we do not know what fraction of CO_2 brought to subduction zones actually descends into the mantle.

3. A model for terrestrial CO_2 and N_2 evolution

In this section, we describe a simple model for the evolution of CO_2 and N_2 on Earth. Earth is assumed to be a closed system for CO_2 and N_2 . Initially there was neither AC nor an impact-generated atmosphere. Hence, AC grew at the expense of DM (see [9] for more discussion of this assumption). Outgassing is assumed to be controlled by solubility, and is modeled in a fashion similar to that developed in [9]. Recycling of CO_2 and N_2 via subduction is assumed to be proportional to the amount of the volatile component in AC. This proportionality (expressed as a recycling coefficient, α) may depend on time. The recycling process is constrained by present distributions of

CO₂ and N₂ in the AC and DM of Earth. Recycling is the least constrained facet of the model and is responsible for most of the uncertainty. The amount of total degassable CO₂ and N₂ in DM plus AC is assumed to be constant. We do not consider the slow oxidation and degassing of CO₂ [33].

3.1 Formulation of the model

Following the notation of [9], the degassing and recycling history of CO₂ and N₂ are described by the differential equations

$$\frac{dC_{DM}^t}{dt} = -\beta B_C C_{DM}^t \frac{e^{-\beta t}}{1 + B_C(1 - e^{-\beta t})} + \alpha_C (C_{DM}^0 - C_{DM}^t) \quad (1)$$

and

$$\frac{dN_{DM}^t}{dt} = -\beta B_N N_{DM}^t \frac{e^{-\beta t}}{1 + B_N(1 - e^{-\beta t})} + \alpha_N (N_{DM}^0 - N_{DM}^t) \quad (2)$$

where C refers to degassable carbon in terms of CO₂ (note that C refers to *carbon*, while *c* in eq. 4 and elsewhere refers to *concentration*) and N refers to nitrogen in terms of N₂. β is the time constant for outgassing, taken to be $(0.19 \pm_{0.09}^{0.17}) \times 10^9 \text{ yr}^{-1}$ from the noble gas modeling (Run 4 of table 3 in [9]). C_{DM}^t is the total amount of degassable CO₂ in the DM at time t , where $t = T$ (4.5 b.y.) refers to the present, and $t = 0$ refers to 4.5 b.y. ago. $C_{DM}^0 - C_{DM}^t$ is the total amount of CO₂ in AC (i.e., C_{AC}^t) at time t . B_C and B_N are inversely proportional to solubility and can be found from

$$B_i = B_{Ar} K_{Ar} / K_i \quad (3)$$

where K_i is solubility of gas i and B_{Ar} is given in [9] as 586_{-176}^{+252} . Using the solubilities in Table 1, $B_C = 85_{-28}^{+43}$ if we assume CO₂ and CO are the degassing species for carbon [p. 50 in 27] and ignore the small difference between the solubilities of CO₂ and CO [51,52]. $B_N \sim 356$ if N₂ is assumed to be the degassing species. The uncertainty in N₂ solubility does not strongly affect our later discussion as long as its solubility is low.

The first term on the right-hand side of eqs. (1) and (2) accounts for outgassing and is proportional to C_{DM}^t (the proportionality decreases with

time due to a decrease in degassing or magmatic intensity). The second term accounts for recycling via subduction. The recycling term for CO₂ can also be expressed as

$$\alpha_C C_{AC}^t = c_C^t Q_{\text{recycle}}^t \quad (4)$$

where c_C^t is the concentration of CO₂ in the recycled material and Q_{recycle} is the total recycled mass per unit time. If CO₂ and N₂ are not fractionated during subduction, α_C and α_N are related by

$$\frac{\alpha_C}{\alpha_N} = \frac{c_C^t / C_{AC}^t}{c_N^t / N_{AC}^t} \quad (5)$$

α_C should be greater than α_N because of the relatively higher proportion of CO₂ expected in subducted material. If average sediments are recycled, c_C^t / c_C^0 is approximately the ratio of total CO₂ (7×10^{21} mol) to total N₂ (2.2×10^{19} mol) in sedimentary rocks, or about 320. C_{AC}^T / N_{AC}^T is ~ 39 (see Table 2), and thus α_C / α_N is ~ 8 for subduction of average sediments. c_C^t / c_N^t in present-day pelagic sediments is ~ 540 [53], and leads to $\alpha_C / \alpha_N = 14$ if pelagic sediments are recycled.

Equations (1) and (2) can be solved numerically given β , B_C , B_N , α_C and α_N . If α_C and α_N were constant through time, they are constrained by C_{DM}^T / C_{DM}^0 and N_{DM}^T / N_{DM}^0 . If, however, they changed with time, additional constraints must be invoked. Since errors in B_C and B_N are correlated with that in βT , it is difficult to do a full error analysis and hence we have not attempted to do so.

3.2 How did α_C vary with time?

It is generally believed that higher temperatures in Earth's mantle during the Archean resulted in a more vigorous convective regime and more rapid production and destruction of surface plates than at present. The occurrence of komatiitic volcanism in the Archean and the paucity of preserved Early Archean crust support this contention. If most of the CO₂ that is recycled into the mantle resided as carbonate vein material in altered oceanic crust, the recycling rate of CO₂ may have been greater early in Earth history due simply to the higher rates of crustal recycling. Were this the only relevant factor, we would

expect α_C to decrease with time (or increase with age).

Other factors, however, suggest the opposite effect. The increase in continental mass and in the average age of oceanic crust with time will both contribute to greater accumulations of sediment on subducting lithosphere. Furthermore, the thermal model of Abbott and Lyle [54; see also 24] suggests that the likelihood of CO_2 passing through the subduction zone into the mantle increases with increasing age of the plate and that CO_2 is returned to the mantle only if the thickly sedimented plate is older than 25 m.y. These considerations will contribute to an increase in α_C with time.

Most present-day ocean floor carbonates are biogenic and it has been suggested that pelagic carbonate accumulation began only in Mesozoic time [55]. If so, α_C may have increased dramatically since Mesozoic time (the last 200 m.y.) due to biogenic fixation of CO_2 . We therefore examine the maximum impact of a recent rapid recycling event by subtracting the maximum possible amount of CO_2 that could have been recycled from AC into DM in the last 200 m.y., as follows. The average production rate (and the rate at which sediments are brought to subduction zones) of sediments in the last 200 m.y. can be found from the mass-age curve to be $\sim 8 \times 10^{12}$ kg/yr [48]. Therefore, total CO_2 brought to subduction zones by sediments is 2.3×10^{13} mol/yr taking CO_2 contents of 12.9% in recent ocean floor sediments [48]. Adding the 4×10^{12} mol/yr of CO_2 carried by altered igneous oceanic crust [46], the maximum recycling rate over the last 200 m.y. is 2.7×10^{13} mol/yr if all CO_2 brought to subduction zones is recycled back to the mantle. Therefore, the maximum amount of CO_2 recycled back into the mantle over the last 200 m.y. is 5.4×10^{21} mol, or about 80% of the total CO_2 present in sedimentary rocks today. The minimum amount of CO_2 in DM at 200 Ma is therefore $(1.3_{-0.6}^{+0.9}) \times 10^{22}$ mol, which represents a $(50 \pm 15)\%$ depletion from initial total CO_2 in the DM. Compared to the degree of depletion for ^3He (97%), it remains necessary to recycle a major fraction of the total CO_2 back into the mantle before the Mesozoic. We will examine cases that satisfy this condition ($C_{\text{DM}}^t/C_{\text{DM}}^0|_{t=4.3 \text{ b.y.}} = 0.5$).

It is clear from the foregoing discussion that variations of α_C with time are presently not well constrained. α_C could have increased, decreased or stayed the same with time, and we consider all three possibilities in our discussion below. Our preference, however, is that α_C has increased with time.

3.3 Model results

3.3.1 Constant α_C and α_N

If α_C and α_N are constant, then, given estimates of β , B_C and B_N , eq. (1) has a unique solution for each specified $C_{\text{DM}}^t/C_{\text{DM}}^0$, and so does eq. (2) for each $N_{\text{DM}}^t/N_{\text{DM}}^0$. The solution in terms of the dimensionless parameter $\alpha_C T$ is $2.73_{-0.80}^{+1.46}$ (excluding error in β and B_C). The evolution of $C_{\text{AC}}^t/C_{\text{DM}}^0$, and the CO_2 outgassing and recycling rates, are shown in Fig. 2, and summarized in Table 3. A prominent feature of this model is that the amount of CO_2 in AC increased rapidly before the Archean, reached a maximum of $2.7_{-0.6}^{+1.3} \times$ the present amount at 4.1 ± 0.1 Ga, and then decreased gradually because the rate of recycling exceeds that of outgassing. The maximum is a consequence of both rapid early outgassing inferred from noble gas isotopic systematics, and constant α_C , which dictates a not-so-rapid early recycling. The outgassing rate for CO_2 changed by only a factor of 3 since 3.8 Ga, and by only a factor of 2 since 2.5 Ga, due to the buffering effect of recycling.

Taking $C_{\text{DM}}^t/C_{\text{DM}}^0|_{t=4.3 \text{ b.y.}} = 0.5$, to account for increased recycling during the Mesozoic, does not substantially affect the predictions of the model (see model B in Table 3).

The solution for $\alpha_N T$ is $0.22_{-0.11}^{+0.22}$. α_C/α_N is 12_{-7}^{+14} , which agrees with our estimate of 8–14 based on CO_2 and N_2 contents in sedimentary rocks. This agreement lends support to the model. The evolution of $N_{\text{AC}}^t/N_{\text{DM}}^0$, and the N_2 outgassing and recycling rates, are plotted in Fig. 3. The basic features for N_2 evolution are similar to those for CO_2 , but the magnitude of the effect is much smaller, with the maximum N_2 amount in AC only about 10% greater than the present amount. The calculated present N_2 outgassing rate is $\sim 3.6 \times 10^9$ mol/yr, which is consistent with our estimate of $(3.2_{-1.6}^{+3.2}) \times 10^9$ mol/yr.

3.3.2 Time-dependent α_C

Model results, taking α_C to be proportional to time ($\alpha_C T = b_C t/T$, where b_C is dimensionless), are shown as curve 'b' in Fig. 4 and as model C in Table 3. Note that the CO_2 outgassing rate has been almost constant since 3.5 Ga. There is no significant difference in the evolution history of N_2 compared to the case with constant α_N .

The effect of taking $C'_{\text{DM}}/C^0_{\text{DM}}|_{t=4.3 \text{ b.y.}}$ as 0.5 is shown in Table 3 as model D, and is not substantial.

If α_C increased exponentially with time, so that $\alpha_C T = a e^{t/\tau}$, where τ is a time constant, a and τ cannot be simultaneously determined from $C'_{\text{DM}}/C^0_{\text{DM}}$. At least one of them has to be specified. We explored the results for various values of τ (> 0). Given τ , the initial recycling coefficient is determined from the present-day distribution of carbon. Two representative examples are shown in Fig. 4 (curves 'c' and 'd'). In all cases, the maximum for CO_2 in AC is greater than obtained for constant α_C , while total recycled CO_2 lies between 1.8 and 3.2×10^{22} mol (1.8×10^{22} mol is total CO_2 in the present DM, and 3.2×10^{22} mol is total recycling for a constant α_C).

In all cases in which α_C increases with time, the maximum for CO_2 in AC is greater than that for a constant α_C . This is a consequence of the fact that if α_C increases with time, then α_C was smaller during ancient times, so that the recycling rate was low and the amount of CO_2 in AC tends to reach a level determined by outgassing. If α_C did indeed increase with time, there is no way of avoiding a profound maximum for the total

amount of CO_2 in AC that is more than $2.7^{+1.3}_{-0.6} \times$ the present amount.

Finally, for comparison, we examine the consequences of an exponential decrease of α_C with time (curves 'e', 'f' and 'g' in Fig. 4). The expression for α_C becomes $\alpha_C T = a^* e^{-t/\tau^*}$. In this case, depending on τ^* (> 0), the total amount of CO_2 in AC during the Archean might or might not have been higher than at present. For $\tau^* > 3$ b.y., there is a maximum; for $\tau^* \leq 1$ b.y., the amount of CO_2 in AC would have increased steadily from the Archean to the present. Total recycled CO_2 ranges from 3.5 to 9×10^{22} mol for $\tau^* > 0.5$ b.y. Only if α_C decreased exponentially with time (i.e., increased with age) and if τ^* is small (≤ 1 b.y.) is it possible for the total amount of CO_2 in AC to increase monotonically with time since the Early Archean. Otherwise there is always a maximum in the total amount of CO_2 in AC.

3.3.3 Recycling fluxes

The predicted recycling flux for CO_2 at present is smaller than 12×10^{12} mol/yr and maximum recycling rates in the past are in the range (6 to 17) $\times 10^{12}$ mol/yr for constant α_C or α_C increasing with time (Fig. 4). If α_C decreased with time, the maximum recycling rates for CO_2 could have been as high as the initial outgassing rate of 150×10^{12} mol/yr. These recycling fluxes can be compared to the total CO_2 flux brought to subduction zones by sediments and altered oceanic crust. At present, this flux is 27×10^{12} mol/yr. Therefore, there is no difficulty in accounting for current recycling fluxes. As men-

TABLE 3

Variations in CO_2 outgassing and recycling parameters for several different recycling models

Model	$C'_{\text{DM}}/C^0_{\text{DM}}$	$\alpha_C T$	b_C	Max. CO_2 in AC (relative to present AC)	Age _{max} (CO_2 in AC) (Ga)	Present Outgassing Rate (in 10^{12} mol/yr)	Present Recycling Rate (in 10^{12} mol/yr)	Maximum Recycling Rate (in 10^{12} mol/yr)	Age _{max} (Recycling rate) (Ga)	Total Material Recycled (in 10^{22} mol)
A ^a	0.72 ± 0.10	$2.73^{+1.46}_{-0.80}$	N/A	2.7 ± 1.3	4.1 ± 0.1	2.5 ± 0.4	4.3 ± 0.2	13 ± 4	4.1 ± 0.1	$3.5^{+0.8}_{-0.6}$
B	0.5^b	1.37	N/A	2.9	3.9			6.3	3.9	2.8 ^c
C ^d	0.72 ± 0.10	$b_C t/T$	3.9 ± 1.7	3.2 ± 1.6	3.7 ± 0.1	2.5 ± 0.3	6.0 ± 0.2	8 ± 1	1.7 ± 0.5	2.6 ± 0.5
D	0.5^b	$b_C t/T$	2.1	3.2	3.6			5.8	0.77	2.3 ^c

^a Case shown in Fig. 4 as curve a.

^b $C'_{\text{DM}}/C^0_{\text{DM}} = 0.5$ at $t = 4.3 \times 10^9$ yr, with maximum recycling over the past 200 m.y.

^c Including recycling over the past 200 m.y.

^d Case shown in Fig. 4 as curve b.

tioned above, the CO₂ contents of ocean floor sediments may have been lower in the past than they are now [48]. We can obtain a lower limit on

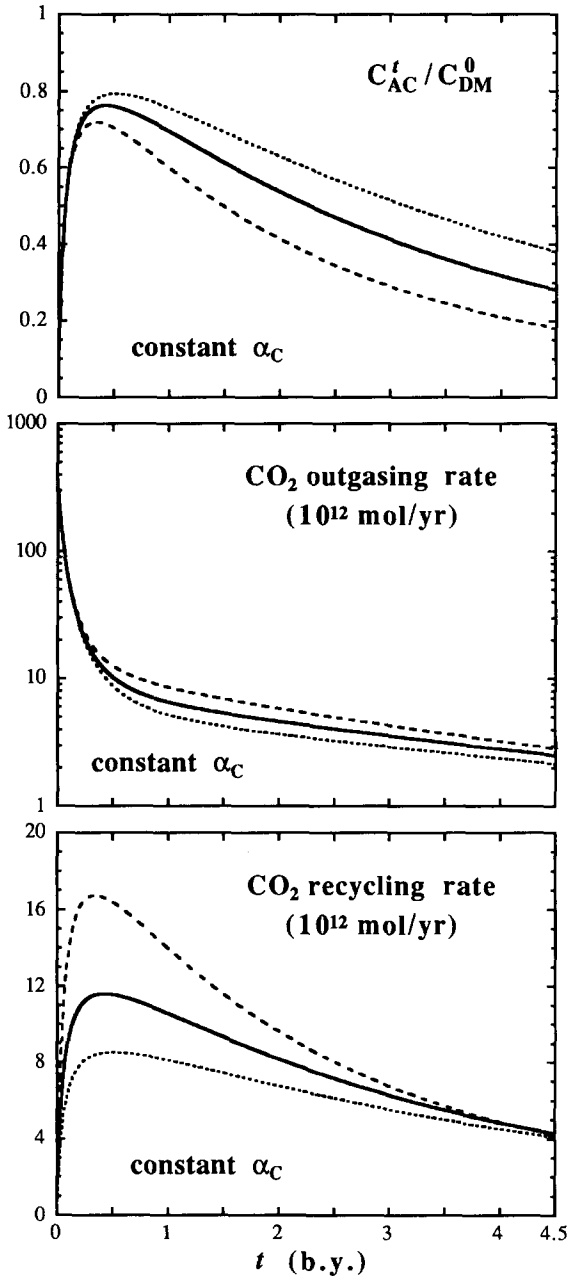


Fig. 2. Evolution of the fraction of degassable CO₂ in AC, and outgassing and recycling rates of CO₂, assuming constant α_C . The heavy line represents $\alpha_C T = 2.73$, corresponding to $C_{DM}^T / C_{DM}^0 = 0.72$. The dashed lines on either side of the heavy line correspond to the upper and lower allowed C_{DM}^T / C_{DM}^0 in a 1σ range. Note that the outgassing rate is plotted on a log scale.

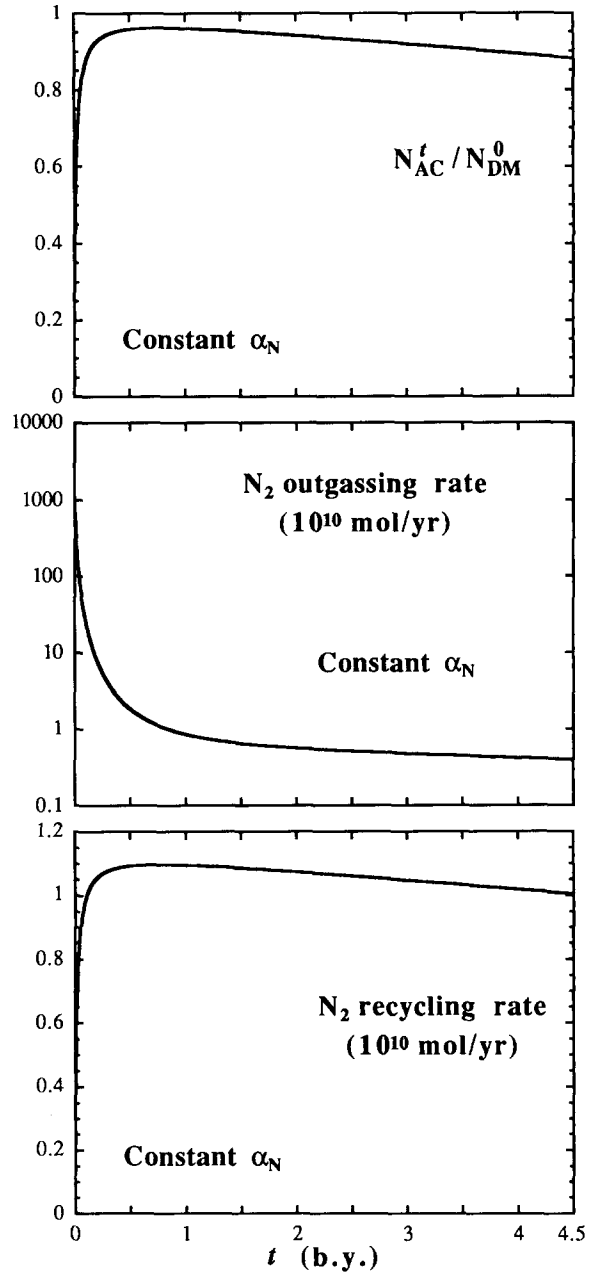


Fig. 3. Evolution of the fraction of N₂ in AC, and outgassing and recycling rates of N₂, assuming constant $\alpha_N T = 0.22$, corresponding to $N_{DM}^T / N_{DM}^0 = 0.12$.

the CO₂ content to be $\sim 4\%$ because preserved ancient sediments contain this much CO₂ [48] and carbonates were preferentially destroyed by weathering. Using this low CO₂ concentration, 3 km³/yr of sediment still brings 7×10^{12} mol/yr of CO₂ to the subduction zones. When combined

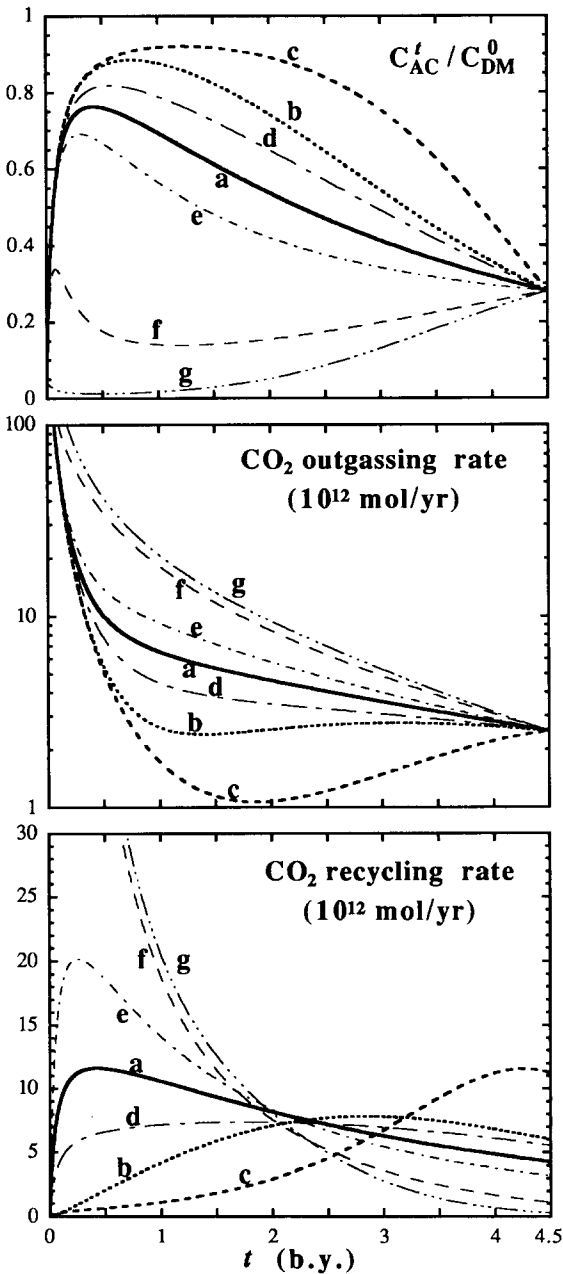


Fig. 4. Comparison of evolution curves for CO₂ in AC for different time dependence of α_C . All curves satisfy the condition $C'_{DM}/C^0_{DM} = 0.72$. Curve 'a': constant α_C (heavy solid line). Curve 'b': α_C proportional to time. Curve 'c': α_C increased with time exponentially with $\tau = 1$ b.y. Curve 'd': α_C increased with time exponentially with $\tau = 4.5$ b.y. Curve 'e': α_C decreased with time exponentially with $\tau^* = 4.5$ b.y. Curve 'f': α_C decreased with time exponentially with $\tau^* = 1$ b.y. Curve 'g': α_C decreased with time exponentially with $\tau^* = 0.5$ b.y.

with CO₂ carried by igneous oceanic crust, it is still possible to account for the maximum recycling fluxes within errors, unless α_C decreased with time. (The large amount of recycling required for decreasing α_C suggests that α_C either is constant or increases with time.) The magnitudes of predicted CO₂ recycling fluxes are large, but not prohibitively so, contrary to a previous assertion by Marty and Jambon [33].

3.4 Comparison with sedimentary records and CO₂ in AC in ancient times

Most model results shown above suggest that the total amount of CO₂ in AC hit a maximum in the Early Archean and has decreased ever since. If substantiated, there are important implications for the global carbon cycle. We now examine records in sedimentary rocks for evidence to test our model results.

Determining the proportion of carbonate in sedimentary rocks is not a simple problem, and a thorough treatment is beyond the scope of this paper. Seeing as the preserved relative proportions of carbonates vs. silicates through time are not robust due to preferential destruction of carbonates [56,57], we use the following approach. We assume that most CO₂ in AC was always stored in the carbonates. At present, only 20% of total CO₂ is in the form of elemental carbon (and only a minute fraction of CO₂ is in the atmosphere and oceans) and can be ignored for present purposes. We further assume that the non-volatile composition of the average sediment and the total mass of sedimentary rocks are constant (some kind of steady state). At present, more than half (54%) of the CaO + MgO in sedimentary rocks is stored in carbonates, which comprise only 10% of the sedimentary mass [40,58]. Therefore, the variation of CaO + MgO in silicate portions of sedimentary rocks should be an indicator of the proportion of carbonates. For example, if the fraction of carbonates in total sedimentary rocks increased by a factor of 2, then CaO + MgO concentration in the silicate portion would be almost zero, compared to the present ~ 3.8 wt.% [40]. If the proportion of carbonate decreased by a factor of 2, CaO + MgO in silicates would increase by 50% (to ~ 5.7%). These variations should be noticeable. Garrels and Mackenzie [40]

have shown that CaO and MgO in shales decrease, relative to Al_2O_3 , with increasing age, and that shales in the Precambrian contained little CaO + MgO (about half the present amount). This suggests that the carbonate/silicate ratio, and hence the total amount of CO_2 in AC, increases with increasing age, consistent with models where α_C either is constant or increases with time.

Dolomite/limestone ratios in carbonates provide another clue as to the total amount of CO_2 in the continental crust. Many authors have concluded that the dolomite/limestone ratios of carbonates increase with age, at least up to the Proterozoic [e.g., 27,40,59,60] (but see [61] for a challenge to this seemingly firmly established observation). If such an increase is true, it can be explained by an increase in CO_2 in the sedimentary mass if we assume that formation of dolomite is controlled by the availability of calcium and CO_2 . When relatively high amounts of CO_2 were present in the continental crust and atmosphere during the Archean, a high proportion of carbonates formed as dolomite because the available calcium could not neutralize all of the available CO_2 . This assertion is supported by the low CaO contents in Precambrian shales mentioned earlier [40]. As carbonates recycle in the continental crust, and as the outgassing rate of CO_2 decreases, more recent carbonates have lower Mg/Ca ratios. In this way a gradual decrease of the Mg/Ca ratio in carbonates with time can be rationalized.

Evidence from the sedimentary record supports the idea that the total amount of CO_2 in AC decreased with time (i.e., increased with age) since the Archean. This is consistent with models in which α_C is constant or increases with time. This result may have important implications for the global CO_2 cycle and climatic conditions during ancient times.

3.5 Implications for recycling of other components in the continental crust

The bulk composition of recycled material will determine the extent to which other elemental and isotopic budgets are affected by the recycling process. To satisfy the CO_2 budget, modern, bulk, average ocean-floor sediment containing 13%

CO_2 [48] would have to be subducted at an average rate of 0.14–1.6 km^3/yr over all of Earth history (or about one third less if the last 200 m.y. is treated as a separate rapid recycling period). If ancient sedimentary rocks, containing only about 4% CO_2 , are more typical of recycled materials, sediment subduction rates of 0.44–5.2 km^3/yr are required. Maximum predicted recycling rates during the Archean would range from 2 to 6 km^3 of sediment per year, depending on the composition. These values, which lead to subduction of continental-crust-like volumes over 4.5 Ga, are in general accord with other independent estimates of subduction rates (see [47] for a review).

Since the average ancient sediment composition is similar to the average upper crustal composition, recycling will not affect the bulk composition of the continental crust, but it will strongly affect the chemical and isotopic systematics of Sr, Nd, Pb, etc. in the DM, especially when crustal materials with long crustal residence times are recycled. In this case, then, recycling can dramatically influence the evolution of the Rb-Sr, Sm-Nd and U-Th-Pb isotopic systems, depending on the time scale for mixing into the DM.

At the other extreme, we can consider the effects of subducting only carbonates, with all terrigenous sediments returning to the surface by island-arc volcanism or underplating. The differentiation of carbonate and terrigenous sediment can occur by virtue of the fact that igneous oceanic crust contains large amounts of CO_2 bound in carbonate veins; this crust (together with the vein CO_2) might subduct more easily than the overlying sediment. In this case, $(2-6) \times 10^{22}$ mol of CO_2 recycled into the DM brings with it $(2-6) \times 10^{22}$ mol of CaO + MgO. This is more than the total CaO + MgO in the present AC, and about (5–15)% of the total continental mass, and, hence provides a way to reduce CaO + MgO and increase SiO_2 in continental crust by 3–10% (i.e., to partially ‘acidify’ the continental crust). The recycling of $(2-6) \times 10^{22}$ mol of CO_2 also brings $(0.4 \text{ to } 1.2) \times 10^{22}$ g of Sr and $(1.8 \text{ to } 5.4) \times 10^{19}$ g of Pb into the DM (using 2000 ppm Sr and 9 ppm Pb as average contents in carbonates [62]). This amounts to 1.4–4 ppm Sr and 6–19 ppb Pb in the DM, or 10–30% of the Sr and Pb budgets in the depleted MORB source mantle [43]. This comparison assumes, however, that the *degassed man-*

tle is the same as the *depleted mantle*, which may not be true [7,9]). The recycling of Sr and Pb without Rb, U and Th may show up as 'unsupported' Sr or Pb in terms of isotopic ratios. Beyond noting the potential importance of recycling for other chemical and isotopic parameters, a detailed examination of possible effects, which may rule out the possibility of recycling *average* sediments or constrain the amount of carbonate that can be subducted, is beyond the scope of this paper.

3.6 Tentative conclusions on CO₂ and N₂ evolution in Earth

Our simple model of volatile evolution suggests that evolution of N₂ in AC was relatively simple. The amount of N₂ increased steadily to the present level over the first 200 m.y., and then stayed almost constant. Although the model does predict a small maximum in the total amount of N₂ in AC during the Archean, the maximum was less than 10% above the present amount and would not have produced any observable effects. The evolution of CO₂ is more complicated. The amount of CO₂ in AC increased initially, probably reached a maximum sometime during the Archean or Proterozoic, and declined gradually to the present. The maximum was 2–3 × the current amount. The inferred recycling of CO₂ may have significantly affected the compositional evolution of the continental crust and the isotopic evolution of both AC and DM. We reiterate that these results are not definitive, due to the lack of adequate data. Important future constraints will be derived from a systematic examination of sedimentary records, a better understanding of carbonate production in ancient times, and a better understanding of the recycling process at arcs.

4. Conclusions

Based on the total amounts of ³He and Ar in Earth's degassed mantle and the present outgassing ratios of CO₂/³He and N₂/Ar in mid-ocean ridge basalts, total degassable CO₂ and N₂ in the present degassed mantle is estimated. Most of the total degassable CO₂ is still in Earth's degassable mantle, in sharp contrast to the estimated extreme depletion of ³He from the de-

gassed mantle even though He and CO₂ solubilities in magma are similar. The inferred high content of CO₂ in the degassed mantle strongly supports the idea that CO₂ has been recycled back into the mantle through subduction of sediments. On the other hand, recycling has a relatively minor effect on atmospheric N₂. This is consistent with the fact that sediments concentrate CO₂ much more efficiently than N₂ and hence recycling of sediments affects the CO₂ budget more than it does N₂.

A simple outgassing and recycling model was constructed based on solubility constraints and the amount of total CO₂ and N₂ in the present degassed mantle. The model results appear to suggest that total CO₂ in sediments was higher in the Archean and Proterozoic than at present. If substantiated, this may have significant ramifications for the evolution of the atmosphere and sedimentary rocks.

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