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The major volatile elements of the Earth: Their origin, behavior, and fate

M. Javoy

Laboratoire de Géochimie des Isotopes Stables, Université Paris VII et Institut de Physique du Globe de Paris, URA CNRS 1762

Abstract : Stable isotope constraints impose a heterogeneous accretion of the earth's volatiles : the primary, reduced material, 99.8% of the planet, brought 6% of the hydrogen, 48% of the carbon and 70% of the nitrogen of the Upper Earth (upper mantle, crust, ocean-atmosphere). A late veneer (1.4 per mil of the bulk Earth's mass), of CI composition, supplied 94% of the hydrogen, 52% of the carbon and 30% of the nitrogen.

The present distribution of the major volatiles in the Upper Earth corresponds to a negligible supply from the lower mantle. Measured in units of the superficial reservoirs the upper mantle contains: 0.21 ocean masses of water, ~10 atmosphere masses of nitrogen, 5.4 crustal carbon masses of carbon.

This corresponds to a very significant trapping of carbon and nitrogen by the mantle during the Earth's history, whereas water repartition stayed about unchanged and strongly favoured the superficial reservoir. There is, however, a very significant difference between carbon and nitrogen, the present outgassing and subducting fluxes of carbon being equilibrated both in masses and isotopically, whereas there is still a gross isotopic disequilibrium for nitrogen, the large, isotopically heavy, subducted flux, still outweighing the small, isotopically light, outgassed flux.

This is due to the fact that, while carbon and water are essentially incompatible components, nitrogen is a compatible element because of the presence of very stable mantle nitrides (probably osbornite).

That description is based on simple ideas :

the first idea, that the Earth accretion history is composed essentially of two parts, one hot and one cold, is, in fact, the simple stylisation of most models which consider first a reduced then an oxidized component [eg *Wänke,* 1981]. The reduced component corresponds to the conditions prevailing in the inner part of the early solar system and are operative during most of the Earth's accretion. Several authors have more or less identified that component to enstatite chondrites [*Javoy and Pineau*, 1983, *Javoy et al.*, 1986, *Smith*, 1982, *Hartmann*, 1986, *Javoy*, 1995]. In my model this component prevails for ~ 99.8%. The oxidized component is brought by limited inward incursions of external material when the early solar system cools down in the very late stage of the planet's accretion. It has a CI composition.

the second idea is to link those steps to well established stable isotope characteristics, which are among the only signals able to survive up to the surface of a differenciating planet : in the multispace of elemental and stable isotope compositions, there is a very limited number of processing paths from one composition to another. My assumption is that this limited number is one : for example, if one think that the primordial nebular composition is CI, then there has been only one path from that composition to any other present in the solar nebula, like for example the common composition of primary bulk Earth, the Moon an Moon Impactor [*Hartmann*, 1986], and the Enstatite chondrites [*Javoy*, 1995].

Introduction

In a recent paper [*Javoy*, 1995], I have described a Model Earth accreted to more than 99,5% from EH enstatite chondrite material. My choice was based on oxygen isotope constraints, but was influenced also by other stable isotope characteristics, particularly nitrogen .

The model I shall develop for volatile elements is also strongly influenced by stable isotope considerations but the constraints they give are broader, since volatile elements, unlike oxygen, have suffered very strong outgassing,which, for carbon, nitrogen and hydrogen, was probably linked to sizable isotopic fractionations.

However the $\delta^{15}N$ distributions between inner and outer enveloppes of the Earth leave very little room for another model than a heterogeneous accretion of the volatiles.

The veneer corresponding to that heterogeneous accretion is very small (less than 2 per mil of the Earth's mass) but essential nevertheless "volatile-wise".

I have purposedly given the simplest possible description of the accretion mechanism, because I think that the obvious role of models of bulk Earth composition based on extraterrestrial analogues should be to constrain that a priori unknown composition from the external analogues and not the contrary as complex models using many steps, mechanisms and components do most of the time.

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Outline of the model

The critical observation which led us to propose the enstatite chondrite model was made on terrestrial nitrogen isotopes : our study of Mbuji Mayi diamonds had shown distinctly negative $\delta^{15}N$ [*Javoy, et al.*, 1984] . At that time the available data on residual nitrogen in basalts gave strongly positive $\delta^{15}N$ whereas the external nitrogen (atmosphere + sediments + continental crust) was also distinctly positive. How could a source of negative $\delta^{15}N$ be split into a degassing product and a residue both with positive $\delta^{15}N$ (fig 1)? We came to the conclusion that we needed at least two distinct sources, that is, a heterogeneous accretion for nitrogen [*Javoy and Pineau*, 1983, *Javoy et al.*, 1986].

Ten years later, with data accumulating, the description is, quite normally, a little more complicated than at the time of our pioneer study. Nevertheless the situation is basically the same : diamonds with normal mantle $\delta^{13}C$ values (-4±2‰/PDB) have a majority of negative $\delta^{15}N$ and the $\delta^{15}N$ domain now extends down to -25‰/ATM [*Cartigny et al.*, 1996] that is, reaches the limit that we predicted in 1983 for an Enstatite Chondrite Earth.

MORB vesicles have negative $\delta^{15}N$ (average -5‰ [*Javoy and Pineau*, 1991]) which represent the outgassed mantle nitrogen, whereas the residual dissolved nitrogen, extracted upon fusion, has a mean $\delta^{15}N$ of + 6‰ [*Exley et al.*, 1986]. Finally the external nitrogen (atmosphere + sediments + continental crust) can be set between +5 and +12‰.

There is a need for more data on MORB and continental crust but we can already construct a good picture of the "upper earth" (upper mantle +ocean-atmosphere +crust) nitrogen structure :

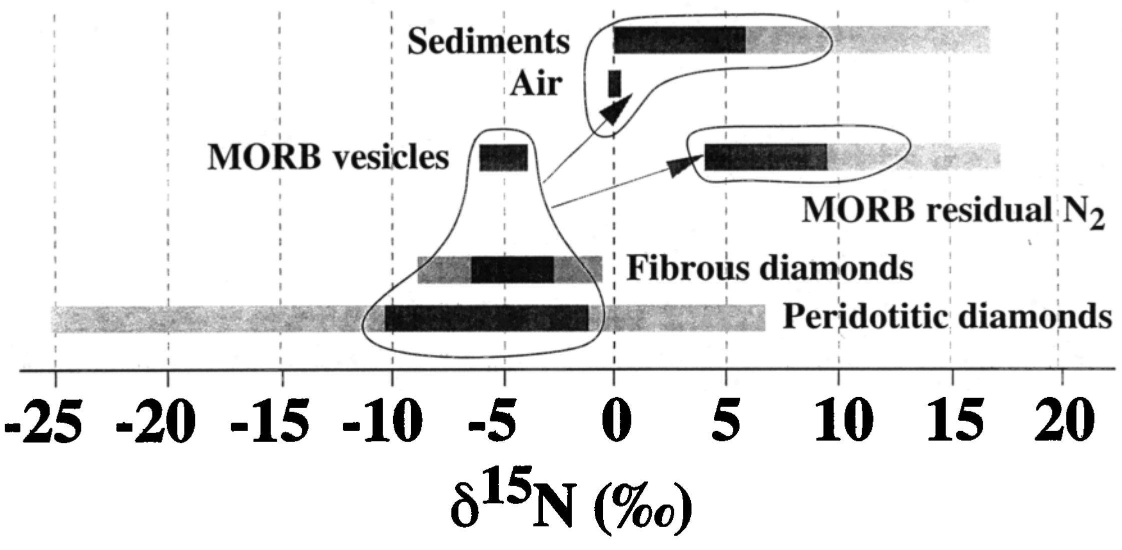

Figure 1. This figure illustrates the isotopic imbalance between mantle and superficial nitrogen. With mantle nitrogen of negative $\delta^{15}N$ it is impossible to make outgassed products (superficial nitrogen)and their complement, the outgassing residue, both with positive $\delta^{15}N$: we need a positive $\delta^{15}N$ veneer.

an oceanic (MORB vesicles [*Javoy and Pineau*, 1991]) as well as subcontinental (fibrous diamond phenocrysts [*Javoy et al.*, 1984]) upper mantle with a $\delta^{15}N$ of -6± 1‰

a deep mantle (lower mantle or transition zone) with $\delta^{15}N$'s around -25‰ [*Cartigny et al.*, 1996]

a crustal(continental crust + sediments) nitrogen with a $\delta^{15}N$ of +8.5 ‰ [*Boyd et al.*, 1993].

an ocean-atmosphere at $\delta^{15}N$ =0

The simplest way of explaining that structure is to call for a two step heterogeneous accretion :

1) first of a negative $\delta^{15}N$-hot material whose best image are the EH chondrites [eg *Javoy and Pineau*, 1983, *Kung and Clayton*, 1978,]

2) then a late, cold veneer, of CI composition, which displays the very positive $\delta^{15}N$ necessary to balance the first component in the elaboration of the mantle nitrogen component at $\delta^{15}N$ =-6‰ [*Kerridge*, 1985, *Kung and Clayton*, 1978]. Arriving on a close-to-full-size planet, this component is supposed to be non-fractionated for all volatile components of molecular mass ≥20.

The deposition scenario of that veneer probably corresponds to a mixture of components 1 and 2 becoming richer and richer in component 2 with time. The extension in time of that episode has to be tested by the analysis of archean crust nitrogen : if the CI input is early and massive we shall start from very positive crustal values, progressively lowered by mantle outgassing of ^{15}N-poor material; if it is extended over a long period of time we shall begin with a thin, ^{15}N-poor, mantle-degassed atmosphere, progressively driven to ^{15}N richer values by input of ^{15}N rich-material. In either case, the present $\delta^{15}N$ value of the upper mantle must be obtained by significant down-cycling of late ^{15}N-rich material into the mantle.

From these parameters and this scenario we can derive the size of the veneer and its initial contributions to the volatiles' budget of the bulk Upper Earth (UE : upper mantle, crust, ocean atmosphere) as well as the size of the nitrogen upper mantle reservoir, which, because of the persisting isotopic disequilibrium between mantle and surface reservoirs, cannot be estimated a priori from mantle results only.

Size of the Upper Earth's water and carbon reservoirs and their isotopic composition

I explain below that a CI veneer fitted to the whole mantle's size would provide too much rare gases compared to the actual size of the atmospheric reservoir. Our model implies, as I did for the solid part [*Javoy*, 1995], that the upper and lower mantle are mostly decoupled with respect to volatiles. The size of carbon and water upper mantle reservoirs are derived from undegassed MORB concentrations [*Javoy and Pineau*, 1991, *Pineau and Javoy*, 1994], obtained by considering that they behave as incompatible components in mantle processes and that the average degree of melting is around 10%. Added respectively to the masses of crustal carbon and superficial water, they give the numbers of Table 1a

The isotopic composition of carbon is about the same for the superficial reservoir and the MORB mantle ($\delta^{13}C$~-4‰, [*Javoy and*

Table 1a :Available pertinent data for the determination of the volatile elements distribution of the Upper Earth. The nitrogen content of the crust plus sediments has been taken equal to 0.45 atmospheres with a $d^{15}N$ of +8.5‰. For the EH material the choice of $d^{15}N$ =-25‰ is derived from the value **observed on diamonds,** supposed to reflect the average effect of the accretion process. dD =-460 is taken from meteorite analysis because the present mantle water has retained no memory of the initial value.

	C1 chondrites	**Upper Mantle**	**Upper Earth**	**EH source**
H_2O %	18	0.025	0.145	0.045
dD	36	-70	-9	-460
Cppm	35000	400	466	4000
$d^{13}C$	-9	-4	-4	-8 to-4
N ppm	1500	?	?	425
$d^{15}N$	+42	-6	?	-20 to -40 (-25)
Mass grams	?	1.07 10^{27}	1.09 10^{27}	1.07 10^{27}

Pineau, 1991]), due to the efficiency of the carbon recycling and of the isotopic reequilibration process of subducted carbon . A $\delta^{13}C$ of -4‰ corresponds to an average 16% of organic carbon in the superficial reservoir.

Mantle water has an average δD of -70‰, corresponding both to the mantle outgassing and residual subducted water flux. With the relative masses given in Table 1a it corresponds to a δD_{UE} of -9‰.

Size of the veneer

It can be derived in at least two ways. In order to explain the high mantle content of siderophile elements, *Morgan et al.*, [1981] postulated the need for a chondritic veneer (0.74% of the mantle). Note that it has to be 0.74% of **the upper mantle only** : 0.74% of the whole mantle would bring ~four times the atmospheric xenon content. This is coherent with the idea developped in [*Javoy*, 1995] that upper and lower mantle are strongly decoupled, hence for volatiles as well, with the possible exception of helium.

We can also derive the veneer size from the consideration of D/H ratios. The existing data need to be precised but they already allow a fair evaluation, from the data of Table 1a.

The most imprecise data are for enstatite chondrites, because they contain little water, and are prone to terrestrial contamination. The data range from 400 to 1500 ppm with corresponding δD's between -600 and -100. The lower values are more likely but they have to be substantiated by more data [*Yang and Epstein*, 1983]. The relative veneer/bulk Upper Earth (UE) contributions can be calculated from the balance equations :

$$(H_2O)_E + (H_2O)_{CI} = (H_2O)_{UE}$$

$$(H_2O)_E/(H_2O)_{CI} = (\delta D_{UE} - \delta D_{CI})/(\delta D_E - \delta D_{UE})$$

We obtain a value of 8.4 10^{24} g for the CI veneer (0.77% of UE), a value very close to that given by the siderophile elements' considerations. It varies very little (of less than 2%) for any value of δD_E lower than -400 ‰, which is the most probable range.

Table 1b Results of the calculations shown in the text. The new results obtained are displayed in bold characters, replacing the question marks of Table 2a. Note that $d^{13}C$ of the primitive mantle is changed relative to the original range of EH, which is normal for a 94% degassing. dD probably changed also but the -460‰ value served only as a check of the mass of veneer calculated from siderophile element data . The mass calculated from dD's changes very slowly for EH values between -400 and -800 ‰.

	C_1 Veneer	Upper Mantle	Upper Earth	primitive mantle
H_2O %	18	0.025	0.145	**0.009**
dD	36	-70	-9	-460
Cppm	35000	400	466	**230**
$d^{13}C$	-9	-4	-4	**+2.4**
N ppm	1500	**36**	**41**	**29**
$d^{15}N$	+42	-6	**-5**	-25
Mass grams	**8.3 10^{24}**	1.07 10^{27}	1.09 10^{27}	1.07 10^{27}

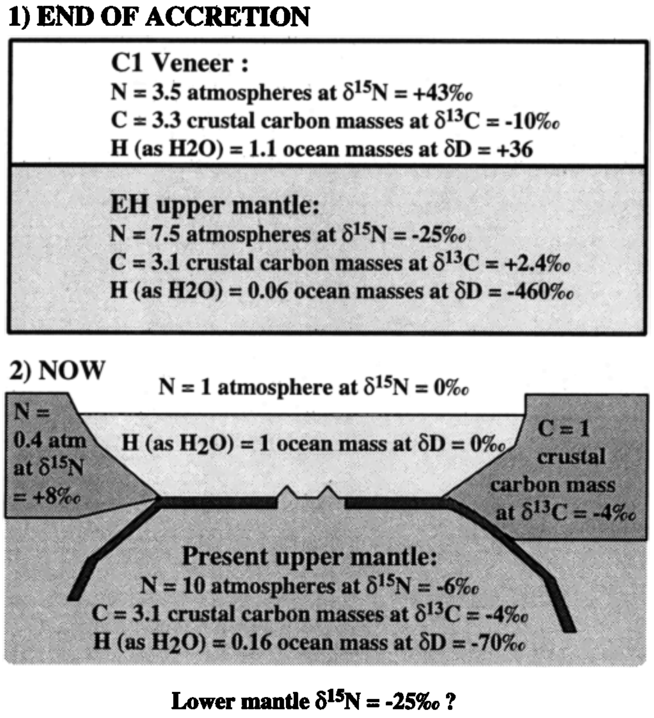

Figure 2. Distribution of H, C and N at the end of the accretion process and now. The contents are expressed in equivalent masses of oceans, crustal carbon and atmosphere, respectively.

The early surface volatiles

Once the veneer size is chosen, the early surface volatile components are determined : the C/N/H ratios are known and the results of the calculation are given in Table 1b and Figure 2.

These masses can be compared to the present surface budget of these elements : surface waters (~oceans), crustal carbon, atmospheric nitrogen. We see that the early Earth's surface bore ~1.1 times its present load of water, 3.3 times its present carbon content and 3.5 potential atmospheres of nitrogen.

The water distribution was thus very similar to the present one but the surface reservoir contained more than three times its present content of carbon and nitrogen. Under what form? It is certainly difficult to answer that question : translating the above numbers into a "venusian" description for carbon (under the form of CO_2 or CH_4) and nitrogen would give a total pressure of ~130 atmospheres, and a partial nitrogen pressure of 3.5 atmospheres.

That comparison is purely formal, since we do not have the slightest indication of the temperature conditions.

More realistically we see that carbon and nitrogen have had to be heavily recycled into the mantle since these early days, while, from a balance point of view, this was not the case for water. This may give some insight into the nature and stability of the recycling forms and mantle storage forms of the three components, more stable for carbon and nitrogen than for water, but we have first to derive the global Upper Earth budget for nitrogen.

Calculation of the nitrogen global content

While it is relatively safe to assume that carbon and water behave presently as incompatible components, allowing the calculation of their mantle budget, no such thing can be said of nitrogen, all the more, as said above, that mantle nitrogen is isotopically heterogeneous. Its present mantle and total content can be calculated, however, assuming that the present well-mixed MORB and subcontinental mantle $\delta^{15}N$ has been obtained by mixing in adequate proportions the recycled veneer nitrogen and the primordial component, whose maximum $\delta^{15}N$ value is given by the lowest $\delta^{15}N$ seen in diamonds (-25‰) [*Cartigny, et al.*, 1996]. Wether that component comes from the lower mantle or, perhaps more realistically, is an infinetely small residue left in the transition zone due to incomplete mixing [*Allegre and Lewin*, 1995] remains to be seen [*Cartigny et al.*, 1996]. Whatever the answer to that question and whatever the real primordial value, the results of the following calculations do not change very much, since the proportion of the upper mantle homogeneized is certainly close to 100% and the calculations, which are very sensitive to variations of the primordial $\delta^{15}N$ down to ~-20‰, are much more stable for variations below that value. The equations giving the masses of mantle (M), and total (T), nitrogen, from the knowledge of the mass of veneer (V), primordial (E), atmospheric (A) and crustal (C) nitrogen and the corresponding $\delta^{15}N$ values (from Table 1a), δM, δV, δE, δA, δC are :

$$V+E = A+M+C=T$$

and

$$V\delta_V + E\,\delta_E = A\delta_A + M\,\delta_M + C\delta_C = T\delta_T$$

They can be solved to give

$$M = V(\delta_V-\delta_E)/(\delta_M-\delta_E) + A\,(\delta_E-\delta_A)/(\delta_M-\delta_E) + C(\delta_E-\delta_C)/\,(\delta_M-\delta_E).$$

Given in atmosphere mass units (A=1) from the use of Table 1 data, the results are :

M =10.4 atmospheres and T = 11.8 atmospheres, which means that ~ 90% of the Upper Earth nitrogen now resides in the mantle, up from ~70% right after the accretion . These numbers may explain why, 4.5 by after , a residual heterogeneity persists in the subcontinental Upper mantle, the overall amount of nitrogen added being only ~ 25%. With such a small proportion of new material it is not unreasonable to think that minute amounts of nitrogen have retained the original isotopic composition, especially in zones protected from the overall convection under old continental blocks. Of course the low ^{15}N values must also represent the lower mantle and possibly part of the transition zone if we accept the stratified model of the upper mantle of *Allegre and Lewin* [1995].

Initial and final concentrations in the upper mantle

The above numbers may be translated in terms of initial concentrations in the upper mantle material at the end of accretion (EH material), before any veneer recycling. These concentrations are : 230 ppm of carbon, 29 ppm of nitrogen and 90 ppm of water (or hydrogen expressed conventionally as water). The average initial concentrations in EH material [*Wasson and Kalleymen*, 1988] are 4000 ppm carbon (range 1500-4200), ~400 ppm nitrogen (range 150-980) [*Kung and Clayton*, 1978] and 450 to 1100 ppm water [*Yang and Epstein*, 1983]. Hence, after the accretion, the reduced material has managed to retain ~6% (range 3-15) of its carbon ~7% (range 3-19) of its nitrogen and about 8 to 20% of its water. The C/N ratio has remained rather constant, from ~12 to 9, suggesting that i) C and N are only moderately volatile in such a material, which agrees with the analytical experience in this type of material and ii) that nitrogen is slightly less volatile than carbon, owing maybe to the great stability of minerals such as sinoite and osbornite.

The present upper mantle concentrations are ~400 ppm carbon, ~35 ppm of nitrogen and ~250 ppm of water. All have increased as a result of partial trapping of the veneer, of a factor ~2 for carbon 1.2 for nitrogen and ~3 for water. These are variations considered from inside.

From outside (the veneer) the order of the relative variations is changed : 70% of the carbon and 60% of the nitrogen, but only 13% of the water, have been absorbed into the mantle.

Recycling fluxes

Water and carbon fluxes from and to the mantle are probably about equal with 1 and 2 10^{14}g/year respectively [*Bebout*, 1995, *Javoy and Pineau*, 1991], leading to a presently steady state. By contrast the nitrogen outgassing flux of ~5 10^{11}g/year [*Javoy and Pineau*, 1991] is about 5 times lower than the subducted flux (2 10^{12}g/year) [*Bebout*, 1995]. This corresponds to very different C/N ratios in the upper mantle (~10) and in volatiles outgassed from MORB (~430) [*Javoy and Pineau*, 1991].

The most likely explanation is that nitrogen, unlike carbon, is a compatible element, the dissociation pressure of nitrogen bearing species in the mantle being about 400 times lower than that of the carbon bearing phase, most likely a carbonate [*Biellman et al*, 1993]

Hence while the mantle carbon cycle has presently reached a quasi-steady state, and carbon is no more accumulating in the mantle, this is still the case for nitrogen. The difference is probably due to the following scenario : while both major subducting species (carbonate for carbon, ammonium ion for nitrogen) have comparable stabilities, the storage forms in the mantle have different stabilities : carbon has probably gone from a reduced form at the beginning of the Earth's history to an oxidized one presently (carbonate), when the oxidized oceanic crust and surface carbon became heavily recycled, while nitrogen has still retained a nitride storage form, most probably osbornite, Ti N, which is the main species compatible both with the concentrations of its building elements, Ti and N, and the stability under the present mantle oxygen fugacities as calculated from Janaf Tables [1985]. Both TiO_2 and TiN may be dissolved in the same major minerals, clinopyroxene for example, or spinel.

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