

Carbon isotope cycle and mantle structure

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[1] Despite that no change is observed in the $\delta^{13}\text{C}$ of sediments and upper mantle rocks over the Earth's history, the carbon isotope cycle is probably not at steady state. The $\delta^{13}\text{C}$ of -5% of the upper mantle is different from that of the subducted carbon, which is close to -1% . Indeed, most of the subducted carbon is made of carbonates: 85% of subducted sedimentary carbon plus carbonates formed by low temperature hydrothermal alteration of oceanic crust. Since no long term evolution is observed for the mantle and sedimentary rocks, the net subduction flux of heavy carbon requires to be compensated by a deep mantle process. End-member models for the carbon isotope cycle at the Gyr scale suggest that it could be a flux from a deep primitive reservoir or the segregation of subducted oceanic crust at the core-mantle boundary. *INDEX TERMS:* 4806 Oceanography: Biological and Chemical: Carbon cycling; 4842 Oceanography: Biological and Chemical: Modeling; 8120 Tectonophysics: Dynamics of lithosphere and mantle—general; 8124 Tectonophysics: Earth's interior—composition and state (1212); 8125 Tectonophysics: Evolution of the Earth. **Citation:** Coltice, N., L. Simon, and C. Lécuyer (2004), Carbon isotope cycle and mantle structure, *Geophys. Res. Lett.*, *31*, L05603, doi:10.1029/2003GL018873.

1. Introduction

[2] If the short term evolution of the carbon cycle has been extensively studied, especially because of its fundamental importance in climate evolution, the geodynamic carbon cycle that operates at the billion year scale is still a very open problem.

[3] The long term carbon cycle can be described by exchanges between surficial reservoirs and the mantle [Javoy *et al.*, 1982]. The mantle provides CO_2 to the surface through degassing and magmatism whereas carbon from sediments and altered oceanic crust can be recycled into the mantle through subduction. The competition between degassing and burial by subduction is the basis of the geodynamic carbon cycle.

[4] The direct measurement of degassing fluxes at mid-ocean ridges, hot spots and convergent margins is almost impossible because CO_2 is already overabundant in the atmosphere and the ocean. Thereafter, the estimates of carbon fluxes from the solid Earth are scaled to the

measured fluxes of ^3He , taking advantage of the similar solubilities of CO_2 and He [Marty and Jambon, 1987]. The oceanic ridge flux can be evaluated and rounds $2.4 \times 10^{10} \text{ kg yr}^{-1}$ [Marty and Jambon, 1987]. Carbon degassing associated with arc volcanism represents a flux of $2.0 \pm 1.7 \times 10^{10} \text{ kg yr}^{-1}$ [Varekamp *et al.*, 1992; Sano and Williams, 1996], and derives partly from slab decarbonation. The hot spot carbon flux is difficult to estimate because accurate ^3He flux measurements are lacking, but is probably at most of the same order as the ridge flux.

[5] In the last ten years, ocean drilling projects combined with kinematic studies permitted the evaluation of accurate mass fluxes of sedimentary carbon back to the mantle [Planck and Langmuir, 1998]. Subduction of sediments occurs at a rate of $0.5 \text{ km}^3 \text{ yr}^{-1}$ with a present-day carbon content of 8200 ppm corresponding to an average flux of $1.2 \times 10^{10} \text{ kg yr}^{-1}$ of C. The biogenic contribution is evaluated at 15% of this sedimentary flux. Another component of the subducting flux comes from the fact that the subducting oceanic crust carries $3 \times 10^{10} \text{ kg yr}^{-1}$ of C as carbonate veins formed during low temperature sea-floor alteration [Staudigel *et al.*, 1989; Alt and Teagle, 1999]. The global rate of subducted carbon therefore rounds $4.2 \times 10^{10} \text{ kg yr}^{-1}$, with a biogenic contribution limited to only 5%.

[6] As pointed out by Javoy *et al.* [1982], the elemental carbon cycle is probably close to steady state. However, considering that carbon isotopes are fractionated among carbonates and organic carbon, the isotope cycle cannot be steady state and is controlled by the composition of surficial carbon subducted into the mantle.

[7] The goal of the present paper is to propose end-member models of the geodynamic carbon isotope cycle and to show whether or not the carbon cycle could constrain mantle structure.

2. Isotopic Carbon Cycle

2.1. Reservoirs

[8] The global inventory of carbon is dominated by the mantle and sedimentary reservoirs. A carbon content in the shallow mantle between 30 and 60 ppm is estimated from carbon fluxes or from the chemistry of mid-ocean ridge basalts (MORBs) according to Jambon [1994] and Saal *et al.* [2002]. The $\delta^{13}\text{C}$ of the shallow mantle lies between -6 and -3.5% [Cartigny *et al.*, 2001]. Depending on the shallow mantle extent (660 km to the core-mantle boundary), the present-day mass of carbon stored in the mantle lies between $3 \times 10^{19} \text{ kg}$ and $2.4 \times 10^{20} \text{ kg}$.

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Carbonates ($\delta^{13}\text{C} \sim 0\text{‰}$) and organic carbon ($\delta^{13}\text{C} \sim -25\text{‰}$) [Schidlowski, 1987] are in a proportion 4:1 and represent a total mass of surficial carbon ranging from 5.4×10^{19} kg to 8.7×10^{19} kg [Bernier, 1998].

2.2. Net Carbonate Subduction

[9] As described above, the rate of carbon outgassed from the mantle is similar to the rate of recycling by subduction. The present-day degassing carbon flux is partitioned between 20% organic reduced carbon and 80% of carbonates along with a fractionation of -25‰ of biological origin [Schidlowski, 1987].

[10] At subduction zones, the present-day sedimentary flux is composed of 15% of biogenic components [Planck and Langmuir, 1998]. As a consequence, the subducted sedimentary carbon has a $\delta^{13}\text{C}$ close to -4‰ . In addition, there is a significant flux of carbon represented by carbonate veins fixed at low temperatures during alteration of the oceanic crust. These carbonates represent an uptake of carbon from the seawater as witnessed by their $\delta^{13}\text{C}$ of 0‰ [Alt and Teagle, 2003]. Hence the total subducted carbon is composed of 95% of carbonates having a $\delta^{13}\text{C}$ of 0‰ . Isotopic studies of arc volcanics suggest that the ratio of carbonate/organic carbon does not decrease upon dehydration and decarbonation of the descending slab [Nishio *et al.*, 1998]. Moreover, magnesite, the most common phase of carbonates in slabs, remains thermodynamically stable even deep in the mantle [Martinez *et al.*, 1998].

[11] The organic reservoir receives 20% of the carbon provided by the mantle, but only recycles 5%, implying that the organic reservoir must grow with time. Heavy carbon being dominantly recycled to the mantle, the carbon isotope cycle is not at steady state. Budyko *et al.* [1987] proposed that the organic reservoir grew since Archean. A growth rate of 3×10^9 kg yr $^{-1}$ is implied by a steady state flux of 2×10^{10} kg yr $^{-1}$ and an imbalance of organic carbon of 15%. This growth rate accounts for the mass of surface organic carbon, 1.2×10^{19} kg, in 4 Gyrs.

2.3. Constancy of the Isotope Record

[12] A remarkable observation is that the carbon isotope composition of carbonates, ($\delta^{13}\text{C} -2$ to 2‰), and kerogen ($\delta^{13}\text{C} -35$ to -20‰) has only slightly varied over geological time without any particular trend [Schidlowski, 1987]. Moreover, the variability observed in the sedimentary carbon over 3.8 Gyrs is as large as the scatter among present-day samples. The isotopic record at the billion year scale has been filtered from rapid $\delta^{13}\text{C}$ variations (time scales shorter than 10 Myrs). These rapid fluctuations documented during catastrophic events like “snowball Earth” [Hoffman and Schrag, 2002] have no impact in the frame of this study.

[13] Mantle-derived samples mostly come from carbonates and peridotitic diamonds older than 1 Gyr. The mode of their $\delta^{13}\text{C}$ distribution is centered around -5 – -4‰ [Cartigny *et al.*, 1998] which is similar to the $\delta^{13}\text{C}$ of the present-day shallow mantle. Within an uncertainty of 1.5‰ , the $\delta^{13}\text{C}$ mantle seems also to have remained constant through most of the Earth’s history.

[14] A paradox emerges: if the isotope cycle is not at steady state, how can the remarkable constancy of the

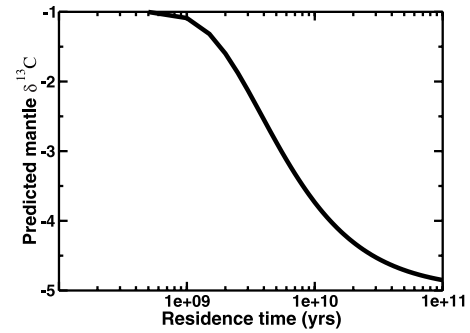


Figure 1. Predicted mantle $\delta^{13}\text{C}$ as a function of residence time after 3.8 Gyrs of carbon recycling back into a homogeneous mantle.

isotope record in sedimentary and mantle rocks over time be explained?

3. Implications for Mantle Structure

3.1. How to Keep a Constant $\delta^{13}\text{C}$ for the System

[15] The observation that the shallow mantle and surficial reservoirs keep approximately constant $\delta^{13}\text{C}$ through time implies that subduction of carbonates has no impact on the evolution of mantle carbon. To explain this paradox, we propose three end-member models: (1) the mantle is so rich in carbon that subduction plays a negligible role, (2) the subducted heavy carbon is not mixed back into the mantle because the oceanic crust segregates in a boundary layer, (3) there is an additional deep mantle source of carbon.

[16] To test these models we use simple mass balance equations, similar to “box models”, keeping their limitations in mind [Coltice *et al.*, 2000]. The isotope evolution of mantle carbon is computed under the constraint that the subducted carbon has a constant $\delta^{13}\text{C}$ of -1‰ (95% inorganic +5% organic). Carbonate production of biological origin varied through time (e.g., Mesozoic radiation of foraminifera), however most biogenic carbonates are finally dissolved below the calcite compensation depth. The inorganic carbon budget is in fact largely dominated by the carbonate hydrothermal veins.

[17] Models are validated using a test of consistency: setting a constant $\delta^{13}\text{C}$ of -1‰ for the subducted carbon over 3.8 Gyrs should not change the $\delta^{13}\text{C}$ of the mantle more than the uncertainty of 1.5‰ .

3.2. Model 1: Carbon-Rich Mantle Buffer

[18] This model represents the $\delta^{13}\text{C}$ evolution of the shallow mantle considering carbon degassing from the mantle and heavy carbon burial at subduction zones. Assuming that the rates of elemental carbon degassing and recycling are equal, we have

$$\frac{d}{dt}\delta^{13}\text{C}_{\text{mantle}} = \frac{1}{\tau}(\delta^{13}\text{C}_{\text{subducted}} - \delta^{13}\text{C}_{\text{mantle}}) \quad (1)$$

where the residence time of carbon in the mantle, τ , is defined as $\tau = M/\Phi$ with M the mass of mantle carbon and Φ the degassing rate.

[19] According to Figure 1, for short residence times (<1 Gyr) the mantle is saturated by subducted carbon. For

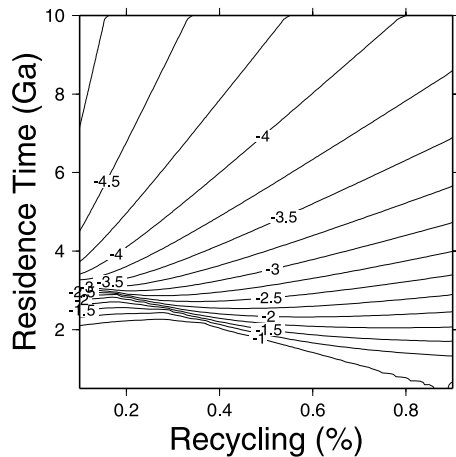


Figure 2. Predicted mantle $\delta^{13}\text{C}$ as a function of residence time and fraction of recycling, considering segregation of the oceanic crust at the core-mantle boundary.

very long residence times (>10 Gyrs) the contribution of subducted carbon is negligible and the $\delta^{13}\text{C}_{\text{mantle}}$ does not change.

[20] Our consistency test requires a residence time larger than 10^{10} yrs; This means that either the degassing rate is low or the mass of carbon is larger than 4×10^{20} kg considering the present-day rate of mid-oceanic ridge degassing for reference. If the shallow mantle extends down to the core-mantle boundary, the carbon concentration would be larger than 100 ppm, and even greater in the case of a layered mantle.

[21] This carbon content of 100 ppm is at least twice the estimates proposed for the shallow mantle concentration [Jambon, 1994; Saal et al., 2002], and matches the suggested content of the undegassed mantle [Jambon, 1994]. It seems that the shallow mantle cannot accommodate the recycling of heavy carbon without changing drastically its $\delta^{13}\text{C}$.

3.3. Model 2: Segregation of Subducted Oceanic Crust

[22] The segregation of the oceanic crust in the deep mantle would prevent the oceanic crust to mix back in the mantle and would maintain the $\delta^{13}\text{C}_{\text{mantle}}$ constant.

[23] High-pressure experiments showed that the basaltic component of the descending lithosphere is slightly denser than the surrounding mantle down to great depth [Kesson et al., 1994]. Many numerical models of mantle convection taking that effect into account predict a layer of dense crust at the core-mantle boundary [Christensen and Hofmann, 1994].

[24] The corresponding box-model equation describes a system where the carbon mantle mass can decrease because of the subtraction of the subducted crust that accumulates at the core-mantle boundary to form a thin layer:

$$\frac{d}{dt}\delta^{13}\text{C}_{\text{mantle}} = \frac{X(\delta^{13}\text{C}_{\text{subducted}} - \delta^{13}\text{C}_{\text{mantle}})}{\tau + (X - 1)t} \quad (2)$$

where X , the recycling fraction, is the proportion of the descending crust that ends up mixing with the mantle.

[25] By analogy with model 1, high residence times favor constancy of $\delta^{13}\text{C}_{\text{mantle}}$ as well as low recycling fractions X (Figure 2). At low recycling fractions X , residence times as low as 3.5 Gyrs can however accommodate the constancy of the isotope records. Assuming a carbon concentration of 40 ppm for the shallow mantle and a degassing flux of 4×10^{10} kg yr $^{-1}$, the recycling fraction should be lower than 40%.

[26] The segregation of 60% of the oceanic crust at the present rate of crustal formation generates a volume comparable to that of D'' in 3.5 Gyrs. Such a model where the oceanic crust segregates at the bottom of the mantle would explain the seismic origin of D'' and more generally most of the geophysical and geochemical observations [Coltice and Ricard, 1999].

3.4. Model 3: Deep Carbon-Rich Reservoir

[27] This model involves a reservoir feeding the shallow mantle with primitive carbon ($\delta^{13}\text{C} = -5\%$) that compensates the input of subducted surficial carbon. This kind of model has been set as a standard model in geochemistry to explain shallow mantle depletion in incompatible elements and noble gases of hotspots [Allègre et al., 1983]. The primitive reservoir was supposed to be the lower mantle before high resolution tomographic images showed deep slab penetration [Grand et al., 1997]. Recently, some authors suggested that a primitive reservoir of half the mantle in size would explain the seismic velocity anomalies and geochemical observations [Kellogg et al., 1999].

[28] Assuming again steady-state for the mantle carbon, the rate of degassing must equal the subduction rate plus the flux of carbon coming from the primitive reservoir:

$$\Phi_{\text{degassed}} = \Phi_{\text{subducted}} + \Phi_{\text{primitive}} \quad (3)$$

In this model, the mass of sedimentary carbon M_{surface} must entirely come from the carbon flux of the deep reservoir. A constant flux of 2×10^{10} kg yr $^{-1}$ is required to account for the observed mass of sedimentary carbon. The degassing rate at oceanic ridges being higher, partial slab decarbonation is likely.

[29] The equation describing the evolution of the carbon isotope composition in the shallow mantle is

$$\frac{d}{dt}\delta^{13}\text{C}_{\text{mantle}} = \frac{1}{\tau}(\delta^{13}\text{C}_{\text{subducted}} + X\delta^{13}\text{C}_{\text{primitive}} - (1 - X)\delta^{13}\text{C}_{\text{mantle}}) \quad (4)$$

where X is the fraction of carbon coming from the deep mantle reservoir.

[30] As shown in Figure 3, large residence times imply a constant $\delta^{13}\text{C}_{\text{mantle}}$ as well as large carbon fluxes from the deep reservoir. Residence times lower than 2×10^9 yrs are obtained for deep carbon fluxes larger than 60% of the degassing flux. Assuming 40 ppm of carbon in the shallow mantle (having a volume half of the whole mantle), and a flux of 4×10^{10} kg yr $^{-1}$, the deep carbon flux exceeds 35% of the subducted carbon flux.

[31] Geochemical studies based on the abyssal layer mantle model suggest that no more than 10% of the plume mass come from a deep undegassed mantle [Coltice and Ricard, 2002]. Geodynamical modeling reveals that the flux

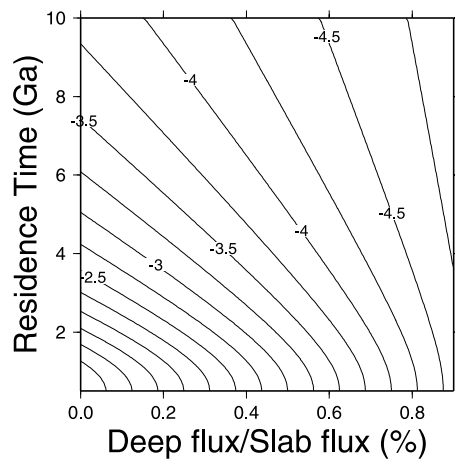


Figure 3. Predicted mantle $\delta^{13}\text{C}$ as a function of residence time and ratio of the deep carbon flux/slab carbon flux, considering entrainment of a deep undegassed reservoir in mantle plumes.

of plumes cannot exceed 20% of the slab flux [Sleep, 1990]. It is noteworthy that the carbon flux coming from this deep layer would be carried by a mass flux less than 2% of the lithospheric subduction flux. Considering that the undegassed mantle contains 100 ppm of carbon, a slab must carry less than 7 ppm of carbon. This composition appears unrealistic as carbonate veins in the altered oceanic crust already account for 50 ppm of carbon in a 70 km thick slab.

[32] Following Javoy [1995] who proposed that the undegassed mantle has a lower $\delta^{13}\text{C}$ of -15% , the composition of the deep mantle reservoir could accommodate the heavy carbon flux carried by slabs. In this case, the deep flux would be reduced by a factor of 3. However a factor of 10, as shown above, is required to explain the carbon concentration in slabs. A satisfactory model for the carbon isotope cycle could also be obtained by combining this model with a crustal segregation above the deep layer instead of the core-mantle boundary.

4. Conclusions

[33] Despite that no change is observed in the $\delta^{13}\text{C}$ of sediments and mantle rocks over the Earth's history, the carbon isotope cycle is probably not at steady state. The mantle constitutes a net sink of ^{13}C whose source is inorganic carbon mainly derived from hydrothermal veins trapped in the oceanic crust. However the mantle $\delta^{13}\text{C}$ does not evolve and this paradox could be solved by considering that the sedimentary organic carbon reservoir is growing with time, and that the excess ^{13}C could be stored in the D'' layer as segregated oceanic crust. Another source of carbon that could help maintain the mantle $\delta^{13}\text{C}$ would be the presence of a deep primitive mantle reservoir.

[34] The ideas presented here applies if the present-day composition of subducted carbon was similar in the past, i.e., if hydrothermal carbonates were present in recycled oceanic crust. This is expected since hydrothermal alteration has been a major process through Earth history. The paradox presented in this paper is similar to that already proposed for ferric iron: the redox state of the shallow mantle remained the same for at

least 3 Gyrs though $\text{Fe}^{2+}/\text{Fe}^{3+}$ differs greatly between extracted basalts and subducted oceanic crust [Lécuyer and Ricard, 1999]. Similarly, it has been proposed that accumulation of altered oceanic crust in the deep mantle would explain this iron paradox.

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