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## Modelling atmospheric CO<sub>2</sub> changes at geological time scales.

### [Modélisation des variations du CO<sub>2</sub> atmosphérique à l'échelle des temps géologiques]

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#### Introduction

By trapping infrared radiation, atmospheric CO<sub>2</sub> contributes significantly to the greenhouse warming of the planetary surface. Hence, it is thought to have played a key role in the evolution of the Earth's climate over geological time. The history of atmospheric CO<sub>2</sub> is available only for the last few hundred thousand years from the analysis of the air trapped in cores of ice. Therefore, data regarding Pre-Pleistocene atmospheric CO<sub>2</sub> must be derived from proxies. These provide indirect estimates of atmospheric CO<sub>2</sub> and are much less reliable than ice-core data. The main proxies used to reconstruct atmospheric CO<sub>2</sub> are: the <sup>13</sup>C isotopic fractionation of marine organisms, the paleo-pH recorded in the boron isotopic composition of ancient carbonates, the stomatal density of fossil leaves and the <sup>13</sup>C isotopic composition of paleosols. For Paleozoic times paleosols have been the main source of data but these are generally rather imprecise. Consequently, for this period geochemical models are useful to make first order estimates of atmospheric CO<sub>2</sub> levels, as well as to help explain its temporal variation. Such models describe the geochemical cycles of several elements - the core being the carbon cycle - by writing budget equations for these elements in the framework of box models. They are often constrained by isotopic data. In the following

we first summarize the basic principles of these models and then illustrate two applications: (1) changes in Paleozoic atmospheric CO<sub>2</sub> and (2) changes in the carbon cycle across the Permo-Triassic boundary.

#### Basic principles of carbon cycle modelling at geological time scales

All geochemical models designed to calculate changes in atmospheric CO<sub>2</sub> at geological time scales are based on the pioneer work of WALKER *et alii* (1981) who postulated that, at time scales longer than ~1 Myr, atmospheric CO<sub>2</sub> is regulated by the balance between its input from volcanism ( $F_{vol}$ ) and its net consumption by silicate weathering followed by carbonate deposition on the seafloor ( $F_{sw}$ ). At these lengthy time scales weathering of carbonates is unimportant because it is followed by carbonate deposition on the seafloor, so the net carbon budget of the ocean-atmosphere is zero. The global silicate weathering flux  $F_{sw}$  (mol yr<sup>-1</sup>) can be written as the product of the silicate rock outcrop area  $A$  (m<sup>2</sup>), the mean water runoff  $R$  (mm yr<sup>-1</sup>; *i.e.*, liters m<sup>-2</sup> yr<sup>-1</sup>) and the mean concentration  $c$  (mol liter<sup>-1</sup>) of divalent cations (Ca<sup>2+</sup> and Mg<sup>2+</sup>) formed from the weathering of silicates that then enter the rivers draining the outcrop area. Because paleolithological maps are generally not available, the silicate outcrop area 'A' is usually assumed to be in proportion to the continental area, which can be reconstructed

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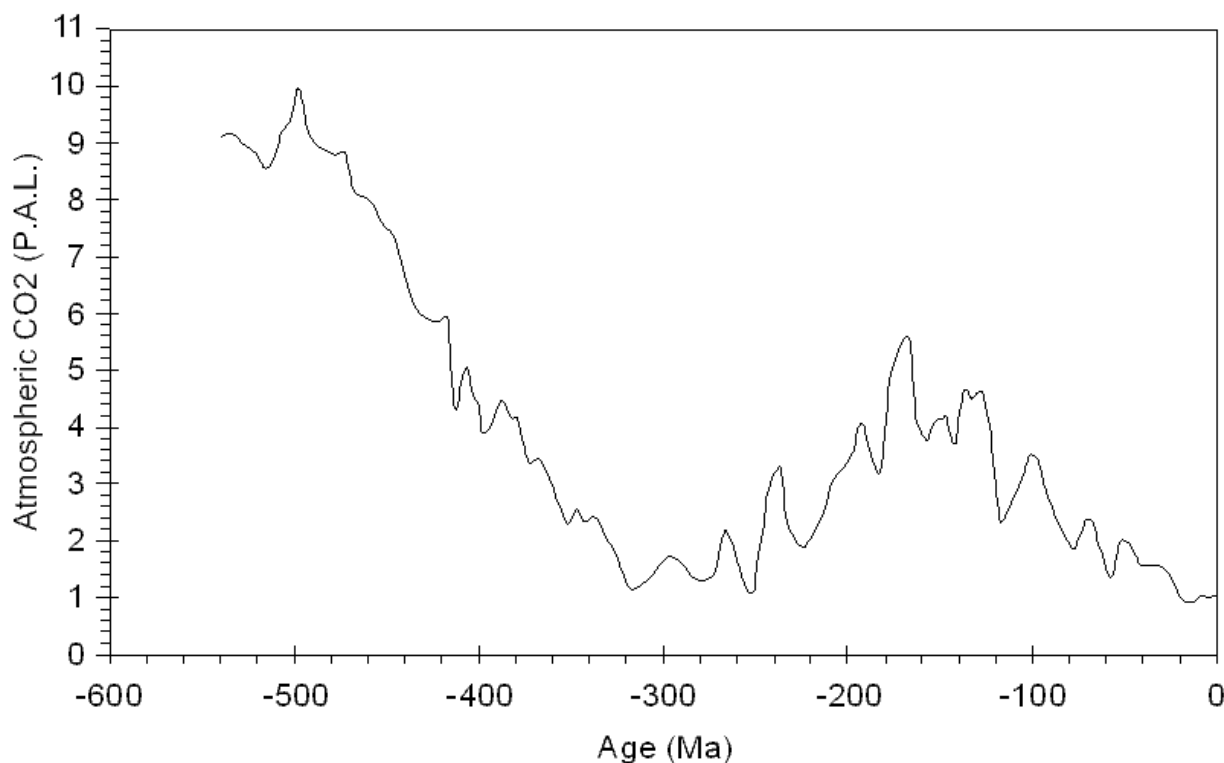
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over geological ages. The runoff 'R' is a function of the climate (temperature, precipitation), itself in turn dependent on atmospheric CO<sub>2</sub> pressure pCO<sub>2</sub>, continental configuration, solar luminosity, etc. Kinetic laws of weathering derived empirically allow 'c' to be expressed as a function of climate (surface temperature), soil pCO<sub>2</sub>, orography, vegetation cover, lithology (*i.e.*, kinds of silicate rocks), etc. Using these data for each time 't' of the geological past, the surface atmospheric CO<sub>2</sub> pressure can be obtained by solving with respect to pCO<sub>2</sub> the following (non linear) equation:

$$F_{\text{vol}}(t) = A(t) \cdot R(\text{climate}) \cdot c(\text{climate}, p\text{CO}_2, \text{orography}, \text{vegetation}, \text{lithology}, \dots)$$

provided that the relationship between climate and pCO<sub>2</sub> is known. This relationship can be represented by a parametric expression or obtained from a climate model. The kinetic relationship adopted to describe the concentration c is central in geochemical modelling. WALKER *et alii* (1981) assumed an exponential dependence on surface

temperature. In their view, silicate weathering is high in warm and humid climates; the effects of orography are ignored in the weathering law. Consequently, the evolution of atmospheric CO<sub>2</sub> and climate is the direct result of changes in global volcanic activity and the area of continents. Periods of high levels of atmospheric CO<sub>2</sub> and warm climates correspond to times of high volcanic activity and/or small continents. But, using the strontium isotopic record as a basis, RAYMO *et alii* (1988) proposed that low CO<sub>2</sub> and cold climates correspond to periods of orogeny. The rate of silicate weathering is high in mountainous areas because rapid uplift and erosion guarantee the existence of abundant fresh exposures to weather and runoff is usually higher in mountains. According to RAYMO *et alii* (1988), orogeny had a more profound impact on the history of atmospheric CO<sub>2</sub> and climate than volcanism or changes in the size of continents. More recent studies have emphasized the roles of vegetation (BERNER, 1991) and lithological (DESSERT *et alii*, 2001) changes on the evolution of atmospheric CO<sub>2</sub>.



**Figure 1:** Model of the evolution of atmospheric CO<sub>2</sub> over Phanerozoic times. CO<sub>2</sub> levels are expressed as multiples of the Pre-industrial Atmospheric Level (P.A.L. = 280 ppm). It is a time-dependent multi-box model of the carbon cycle, containing one reservoir for the ocean-atmosphere and three reservoirs for the crust (organic carbon, shelf carbonates and pelagic carbonates). All major carbon fluxes between these reservoirs are described by the model, as well as the input/output of carbon from/to the mantle associated with seafloor accretion/subduction. The rate of deposition of organic carbon is calculated from the inversion of the δ<sup>13</sup>C evolution recorded in ocean carbonates (see text), which involves a calculation of the isotopic composition of all four model reservoirs. At each time step, the main model calls up an equilibrium sub-model, which subdivides the atmosphere-ocean reservoir into three sub-reservoirs (atmosphere, ocean surface and deep ocean). This sub-model describes the cycles of carbon, alkalinity and phosphorus within the ocean-atmosphere system. It calculates the atmospheric CO<sub>2</sub> pressure, carbonate speciation in the ocean, aragonite and calcite compensation depths (used to evaluate shelf and pelagic carbonate depositional fluxes) and all major <sup>13</sup>C fractionation processes in the system. Global surface temperature is evaluated from the atmospheric CO<sub>2</sub> pressure using a simple parametric relationship and is employed in the calculation of the carbonate and silicate weathering rates in the main model. Silicates are sub-divided into basalts and other silicates, each of them with discrete weathering laws (DESSERT *et alii*, 2001).

## Modelling the Paleozoic carbon cycle and climate

Over periods as long as the Paleozoic carbon cycle modelling is generally more complex than expressing the balance between volcanic CO<sub>2</sub> release and silicate weathering. Other carbon fluxes are important in the determination of the carbon budget: transfer of organic carbon (C<sub>org</sub>) to or from the crust (LASAGA *et alii*, 1985; BERNER, 1991) and the weathering of seafloor basalts (FRANÇOIS & WALKER, 1992). The net transfer of C<sub>org</sub> into the ocean-atmosphere – *i.e.*, the difference between old C<sub>org</sub> ('kerogen') weathering/oxidation F<sub>ow</sub> on the continents (source of C) and C<sub>org</sub> deposition F<sub>od</sub> on the seafloor (sink of C) – is often evaluated from an inversion of the δ<sup>13</sup>C history of ancient seawater recorded in marine limestones. For instance, Fig. 1 shows the evolution of atmospheric CO<sub>2</sub> over Phanerozoic times calculated from the inversion of the oceanic δ<sup>13</sup>C history obtained from a moving average of the data gathered in the Ottawa-Bochum database (VEIZER *et alii*, 1999). This inversion is based on a multi-box model describing the exchanges of carbon between the atmosphere, the ocean and the crust. It assumes that after the emergence of land plants, 50% of the organic carbon deposited on the seafloor (mostly on the shelf) originated from the land biosphere and 50% from the marine biota. A pCO<sub>2</sub>- dependent <sup>13</sup>C fractionation (FREEMAN & HAYES, 1992) is adopted for marine photosynthesis. On land, photosynthetic <sup>13</sup>C fractionation is assumed to be constant before the emergence of C4 plants at about 8 Ma. It is then modified as a result of the progressive evolution of C4 plants, assuming that the C4 contribution to organic carbon deposition from land increases from 0 to 20% between 8 and 6 Ma and remains constant after 6 Ma.

High δ<sup>13</sup>C values recorded during the Carboniferous suggest rapid rates of deposition for C<sub>org</sub> (which removed <sup>12</sup>C preferentially over <sup>13</sup>C, as a result of photosynthetic fractionation) at that time. This large sink of carbon caused a low atmospheric CO<sub>2</sub> and a cold climate during the Carboniferous, which is consistent with the glacial deposits laid down during this period. Another important event in the Paleozoic is the emergence of land plants, which enhanced weathering through the production of soil CO<sub>2</sub> and organic acids. Land plants are not explicitly represented in long-term carbon cycle models. In any case the efficiency of continental weathering is assumed to have been altered by land plants (BERNER & KOTHAVALA, 2001), increasing when the type of vegetation changed from lichens/mosses to gymnosperms (at about 380 Ma) and from gymnosperms to angiosperms (at about 130 Ma). Combined with a relatively small land area, this factor caused

very high levels of atmospheric CO<sub>2</sub> in the early Paleozoic, prior to the existence of land plants (Fig. 1). Such postulated high levels of CO<sub>2</sub> are difficult to reconcile with the observed glacial episodes during the Late Ordovician (VEIZER *et alii*, 2000). Other factors considered in the CO<sub>2</sub> reconstruction of Fig. 1 are the evolution of volcanic-metamorphic fluxes derived from the seafloor accretion rate (GAFFIN, 1987; ENTGEBRETSON *et alii*, 1992), as well as the change of physical erosion through time and its impact on chemical weathering, for which proxy records are provided by the Phanerozoic history of clastic sedimentation (WOLD & HAY, 1990).

It is clear that the calculated evolution of atmospheric CO<sub>2</sub> during the Phanerozoic using an inverse model of this type is strongly dependent not only on the quality of the <sup>13</sup>C data, but also on the various fractionation processes involved, for which large uncertainties remain today. Moreover, the <sup>13</sup>C signal may be contaminated by the release of methane, as might have happened at the Eocene-Paleocene boundary (ZACHOS *et alii*, 2005). However, such methane bursts should have relatively short-term effects (a few 100 kyr) on the ocean-atmosphere carbon cycle. Since the <sup>13</sup>C data are usually smoothed before being used in long-term carbon cycle models, the effect of such short-term events on the <sup>13</sup>C inversion should be rather limited. They are more relevant to the transient models discussed in the next section.

### Carbon cycle modelling at shorter time scales: the Permo-Triassic boundary

At short time scales (*i.e.*, time scales comparable to or shorter than the residence time of carbon in the ocean-atmosphere system) non-equilibrium carbon cycle models must be used. These models must include explicit modelling of ocean biogeochemistry, including nutrients (e.g. phosphorus) limitation of ocean productivity and aragonite/calcite lysocline dynamics. Important examples are the modelling of transitions between geological periods, during which mass extinctions have been observed to occur. Huge and rapid fluctuations of marine δ<sup>13</sup>C are common during such events, but are difficult to explain with carbon cycle models. As previously discussed, many authors (e.g., ZACHOS *et alii*, 2005, and references therein) invoke methane bursts to explain such rapid and high amplitude fluctuations of the oceanic δ<sup>13</sup>C value.

GRARD *et alii* (2005) have compared the impacts on the carbon cycle of two concurrent events that occurred during the Permo-Triassic transition: the emplacement of the Siberian traps and a mass extinction. Starting with a Late Permian atmospheric CO<sub>2</sub> level of ~3000

ppm, the effect of the emplacement of the basaltic trap was, during the first million years, a rise in CO<sub>2</sub> of more than 1000 ppm accompanied by a significant warming. This was followed by a drop in CO<sub>2</sub> and a progressive cooling. After a few million years, the system reached a new steady state at which CO<sub>2</sub> decreased by ~750 ppm and the global mean surface temperature cooled by 1.07°C, when compared to the pre-perturbation situation. The cooling is linked to the CO<sub>2</sub> consumption associated with the weathering of the Siberian basalts, which are much more easily weathered than the average silicate crust on the continents (DESSERT *et alii*, 2001). Combining the calculated effects of the emplacement of the trap and the extinction of a major part of the biota yields a model of oceanic δ<sup>13</sup>C changes with an amplitude of 2-3‰ that is comparable to the data. About 1‰ of this change resulted from the injection of mantle carbon (-5‰) associated with the emplacement of the traps. The rest was caused by a slowing down in the burial of organic carbon as a result of the mass extinction. The model does not elucidate the precise mechanisms leading to the extinction, but it shows that, for this Permo-Triassic transition, the observed δ<sup>13</sup>C change can be accounted for without invoking a release of methane.

### Conclusion

Long-term carbon cycle models are still in their infancy. The major areas for improvement in these models are: (1) a better understanding of the processes governing silicate weathering, (2) a more precise and more realistic description of the organic sub-cycle, (3) a coupling of geochemical and climate models, and (4) exploitation of all available isotopic data by the inclusion of the biogeochemical cycles of many different elements and their isotopes.

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