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The carbon cycle: implications on tectonics and climate changes

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ABSTRACT. — Nowadays a general concern "*flies*" over the human community regarding the increase of carbon dioxide concentration in the atmosphere. Although there are authors that suggest anthropogenic influence of such increase after the discovery of agriculture (about 8,000 years ago; e.g., Ruddiman, 2003), it is evident that the industrial revolution the 19th century in central Europe, when wood and coal were burned extensively to refine iron, definitely influenced the natural trend of CO_2 variation. Only in the last thirty years has the input rate of CO_2 become really fast, and will grow faster and faster in the near future, when developing countries like India and China will reach the standard of life of the western countries, requiring an increasing demand of per capita daily energy need.

The greenhouse effect of carbon dioxide is a well-known phenomenon since the beginning of the 20th century when the Swedish chemist Arrhenius discovered this property by studying the transmission of heat in fluid materials. What is not commonly known is that rapid changes in the concentration of carbon dioxide in the atmosphere are natural events and that, in the past, even in a very recent past, large variations of climatic conditions have been related to sudden carbon dioxide variations in the atmosphere (Petit *et al*., 1999). It is very likely that mass extinction of dinosaurs and other animal species at the end of the Cretaceous may have been caused by such rapid variations.

Causes of temperature variation of the atmosphere have been envisaged in both terrestrial and solar (*Milankovitch Cycles* in Hays *et al*., 1976) systems, but the quantification of the different natural sources of carbon dioxide, as the main cause of climate changes, is still quite poor. It is however well known that the weathering of silicate minerals (and about 99% of the terrestrial crust is made up of silicates) affects the consumption of CO_2 from the atmosphere. Actually, without the discharge of terrestrial carbon dioxide into the atmosphere, plant and animal life would disappear in less than 300,000 years, and the temperature of the atmosphere would drop rapidly to values below 0 °C.

Where is the deep "engine" that provides the continuous re-generation of carbon dioxide and allows its concentration in the atmosphere to be maintained more or less steady (varying roughly from 0.01 to 0.1% by volume)? This engine is not shallow and is located in the Earth's mantle, whose dynamo drives the continental drift as well as the melting of crustal material: volcanic activity continuously supplies carbon dioxide into the atmosphere.

Carbon dioxide, in spite of being a minor component, in both the crust and the atmosphere, really plays a role of paramount importance for both life and climate (through the greenhouse effect). However, our knowledge of the different sources (magmatic, metamorphic, and so forth) is still matter of debate. Experience in Italy has shown that non-magmatic carbon dioxide discharging from hydrothermal systems is an important reservoir of deep-seated carbon dioxide. Nevertheless, inside the carbon cycle the ratio between: *i)* bicarbonates generated by organic acids in silicate weathering of soils and discharged by rivers into the oceans and *ii)* the production of volcanic and non volcanic carbon

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dioxide, remains largely unbalanced, i.e. some deep carbon dioxide is still missing. Where is this carbon dioxide from? Is the increase of carbon dioxide concentration in the atmosphere something that human beings should really care about? The answer cannot be given, yet. The problem could probably be solved in the future, at least when the natural cycle of carbon dioxide and its feedback with solar cycles will be clearer than at present.

KEY WORDS: *carbon cycle, CO_2 budget, Milankovitch Cycles, greenhyouse effect of carbon dioxide*.

RIASSUNTO. — Da qualche anno c'è una grande preoccupazione nella comunità umana in merito all'aumento della concentrazione dell'anidride carbonica nell'atmosfera a causa delle attività antropiche. Anche se alcuni autori ritengono che l'influenza dell'uomo sull'aumento artificiale della CO_2 in atmosfera sia cominciata con l'agricoltura (più o meno 8,000 anni fa; e.g., Ruddiman, 2003), è col XIX secolo, e cioè con la rivoluzione industriale in Europa, quando si è cominciato a produrre ferro in grande quantità, che tale aumento ha cominciato ad essere importante. In realtà, solo negli ultimi 30 anni quest'aumento è diventato parossistico, e lo diventerà sempre più quando paesi come India e Cina, in termini di energia giornaliera pro-capite consumata, raggiungeranno gli standard di vita dei paesi occidentali.

L'effetto serra che l'anidride carbonica genera nell'atmosfera è un fenomeno conosciuto fin dagli inizi del 20° secolo, quando il chimico svedese Arrhenius scoprì questa proprietà della CO_2 studiando la trasmissione del calore in sostanze fluide. Quello che invece è meno conosciuto è che rapidi cambiamenti della concentrazione della CO_2 in atmosfera sono soprattutto dovuti a cause naturali, e che nel passato, anche recente, grandi variazioni climatiche vengono imputate a repentini cambiamenti della concentrazione della CO_2 nell'atmosfera (Petit *et al.*, 1999). È verosimile che in uno di questi periodi di rapide variazioni della CO_2 si siano estinti i dinosauri e molte altre specie animali, contribuendo a far finire il periodo Cretaceo.

La causa principale della variazione in temperatura dell'atmosfera è da ricercarsi nella variazione dell'orbita terrestre (*Cicli di Milankovitch*; Hays *et al.*, 1976) nel moto della Terra intorno al sole dovuta a cause astronomiche, mentre la quantificazione della variazione di concentrazione di CO_2 per cause naturali è ancora poco conosciuta. È comunque ben noto che l'alterazione dei silicati (e più del 99% della crosta è fatta di silicati) incide fortemente sulla concentrazione di CO_2 nell'atmosfera. In effetti, senza la naturale "ricarica" in CO_2 dell'atmosfera operata dalle eruzioni vulcaniche, le piante e la vita animale scomparirebbero in circa 300,000 anni e la temperatura dell'atmosfera scenderebbe rapidamente a 0 gradi.

Qual è il motore che fa sì che ci sia continuamente rigenerazione di CO_2 in atmosfera, in modo tale che vari in volume solo dallo 0,01 allo 0,1% e che non vada a zero mai? Il motore non è superficiale ma è situato nel mantello terrestre, la cui dinamica guida la deriva dei continenti, la fusione della crosta nelle aree di subduzione e quindi il vulcanismo che ricicla la CO_2 dei carbonati subdotti, di nuovo verso l'atmosfera.

L'anidride carbonica quindi, pur essendo un componente minore, sia della crosta terrestre sia dell'atmosfera, gioca un ruolo capitale: sia per la vita sulla terra, sia sul clima, attraverso l'effetto serra. Purtroppo la conoscenza dei diversi rapporti tra le sorgenti (magmatica, metamorfica, organica, etc.) è ancora incerta. Le ricerche condotte in Italia in questo campo, hanno di fatti dimostrato che la CO_2 re-immessa in atmosfera dall'attività idrotermale è una grande quantità di anidride carbonica stoccata nei carbonati. Malgrado questa recente scoperta, ancora poco quantificata, il rapporto tra ioni bicarbonato generati dagli acidi organici nell'alterazione dei silicati del suolo, e trasportati in mare dai fiumi, e la CO_2 riciclata in atmosfera dai processi nelle aree in subduzione, è ancora largamente deficitario (il rapporto) a favore della CO_2 dei primi; il che vuol dire che della CO_2 profonda manca per chiudere il ciclo. Da dove può venire questa CO_2? E comunque, dobbiamo preoccuparci per l'aumento di CO_2 antropica? Al momento una risposta a queste domande non può essere formulata con certezza. Il problema si risolverà nel futuro, almeno quando i rapporti tra il ciclo naturale della CO_2 in funzione dei cicli climatici causati da motivi astronomici saranno più chiari.

INTRODUCTION

From a geochemical point of view, carbon is an incompatible element and can be found, as lonely element, in graphite or diamond. In the shallow crust it is prevalently stocked in coal or oil and it tends to form compounds that are generally volatile, e.g. CO_2, CH_4, CO and many other hydrocarbons. Together with several other elements, such as: nitrogen, boron, mercury, noble gases… etc., it is prevalently concentrated in the shallow crust and/or the atmosphere. This is the result of very long-term differentiation processes, starting at the beginning of the Earth's formation, when volatile elements, being not compatible with the main lattice structure of "*core*" and "*mantle*" minerals, were "*expelled*" towards shallower crustal sectors.

Primordial atmosphere of the Earth was likely very different in chemical composition from the present one, and CO_2, together with H_2O (as vapour), sulphur species (as S, H_2S and SO_2), CH_4 and other hydrocarbons, noble gases (prevalently He), N_2 and H_2, was one of the main gas components (Javoy, 1998).

When the temperature of the lower atmosphere dropped down to the value of condensation of water for the pressure existing on the Earth's surface at that time (likely much more than the present 0.1 MPa), those elements and compounds whose solubility in water is relatively high (among those CO_2) started to dissolve in the newly formed paleo-ocean. The solution of CO_2 in water caused the formation of H_2CO_3 (carbonic acid), bicarbonate ions (HCO_3^-) and carbonate ions (CO_3^{--}), in a complex multiple equilibrium largely depending on local *p*H of solutions.

Carbonic acid, although being a weak acid, is able to alter the silicate lattice of most silicate minerals present in the shallow crust, according to reactions similar to the very simple one reported below:

$$CaSiO_{3(s)} + 2H_2CO_{3(aq)} = Ca^{++}_{(aq)} + 2HCO_{3\,(aq)}^{-} + H_2O_{(aq)} + SiO_{2(aq)} \qquad (1)$$

These kinds of reactions are very common during the weathering of terrestrial crust, being the latter made for more than 99% by silicate minerals.

Primordial rivers formed after the condensation of water used to carry to the primordial ocean(s) very acidic solutions, not only because of acidic carbon, but mainly by the presence of stronger acidic components such as: hydrochloric acid (HCl), sulphuric acid (H_2SO_4)… etc., originated by the volcanic activity. Such acidity gradually decreased in time because the more general and common but slow alteration process of silicates (hydrolysis) is a basic process, leaching into solution metal ions according to reactions similar to the one reported below:

$$CaSiO_{3(s)} + H_2O_{(aq)} = Ca^{++}_{(aq)} + 2OH^{-}_{(aq)} + SiO_{2(aq)} \qquad (2)$$

The continuous flowing of Ca and HCO_3 ions into the ocean provoked the increase of their concentrations in the oceans themselves, eventually turning to $CaCO_3$ over-saturation and precipitation (calcite being a low solubility salt). This step signed the beginning of the formation of limestone.

Suddenly life appeared on the Earth, possibly from bacteria living thermal springs (and preserved in the mineral sinter; Farmer, 2000) and oxygen started to form and spread into the atmosphere. This initiated a long-term change in the atmospheric composition, from a very hot and reducing one to the present temperate and oxygen-and-nitrogen-dominated system.

CO_2 AND LIFE PRESERVATION

It is well known that life depends upon water, temperature, oxygen and carbon dioxide concentration in the atmosphere (Berner *et al.*, 1983). In particular, plants continuously sequester CO_2 from the atmosphere for their nutrition, eventually returning it into soil solutions, through the formation of soil organic acids (formic acid, oxalic acid, etc.) or simply as CO_2 after root respiration. So, a new CO_2 sinking appeared on Earth other than the chemical weathering of silicates, leading to the increase of CO_2 sequestration from the atmosphere: *vegetal life*.

It has been calculated that, without processes generating new carbon dioxide, life would disappear in about 300,000 years (Berner and Lasaga, 1989). Fortunately this does not happen because new CO_2 is continuously released from the "*mother*" Earth into the atmosphere through volcanic eruptions, as well as through the emission of what is called "*non-volcanic CO_2*" (Kerrick, 2001 and references therein) i.e., from CO_2-rich thermal and cold springs ("*soda springs*") and CO_2-rich gas vents ("*mophettes*"). All these thermal emissions could be both associated to the periphery of active volcanic areas and/or to non-volcanic regional deep hydrothermal (i.e.: cooling granite) systems and related geothermal systems (Minissale, 2004 and references therein).

It is well known that the following processes: *i)* volcanic eruptions *ii)* formation of relatively shallow hydrothermal systems and *iii)* CO_2 escape from the crust, are all indirectly driven by the dynamics of the "*lithosphere*" (the top ~100 km of the Earth). The lithosphere is very shallow in the mid-ocean ridges, where mantle basalts are carried to the ocean seafloor. Although not shallow (from 20 to more than 70 km) it is very active at plate boundaries (such as the circum-Pacific "*ring of fire*"), where its subduction below the light continents causes, locally, the melting and rising of mantle material into the crust.

Among others, consequences of this rising and intrusion of mantle magma into the crust are: *i)* the possible digestion of crustal material, among which carbonate material, *ii)* the formation of granite (orogenic granite), *iii)* the settling in of permanent thermal anomalies around granites and, where the pressure of underground fluids equals the lithostatic pressure, *iv)* volcanic eruptions. Any volcanic eruption is actually driven by fluids, both crustal (recycled) and juvenile (from the lower mantle), mainly composed by: *i)* water that above the critical point (373 °C) behaves as a gas and *ii)* CO_2 (Barnes et al., 1988), other than *iii)* sulphur species, i.e. SO_2 and H_2S.

How can CO_2 be produced in subduction areas? Subduction of the lithosphere at continental margins allows the transfer to depth of portions of limestone carried on top and previously precipitated in the ocean. Following reactions opposite to the one described for the alteration of silicates at the surface and leading to the formation of newly deep formed hydrothermal silicates, such as:

$$CaCO_{3(s)} + SiO_{2(aq)} = CaSiO_{3(s)} + CO_{2(g)} \qquad (3)$$

CO_2 is steadily produced by the metamorphism of limestone at plate boundaries and becomes part of the engine of volcanic eruptions (Barnes *et al.*, 1988). This kind of metamorphic-hydrothermal reaction starts going on at about 150 °C. At higher temperatures (~800 °C) the thermal breakdown of calcite (and dolomite; $Ca(Mg)CO_3$):

$$CaCO_{3(s)} = CaO_{(s)} + CO_{2(g)} \qquad (4)$$

may significantly contribute to the formation of CO_2, ready to come back into the atmosphere with explosive volcanic eruptions. This is the end of the cycle of carbon dioxide, whose cycling period can hardly last several hundreds of million years.

Permanent, or long-living hydrothermal systems associated with cooling granite, whose thermal energy can be exploited through the drilling of geothermal wells, can further generate large quantities of metamorphic CO_2 with similar reactions reported in (3), or through gas-gas reactions, such as, for example, the Fisher-Tropsch reaction:

$$CH_{4(g)} + 2H_2O_{(v)} = 4H_{2(g)} + CO_{2(g)} \qquad (5)$$

A conceptual section (redrawn after Minissale, 1991) of the Larderello geothermal field in central Italy, the oldest and one of the most famous hydrothermal systems in the world, is reported in Figure 1. The Larderello thermal anomaly has a granite-related deep origin that has been dated at about 3.5 Ma. The figure shows how the produced CO_2 gets out from the system together with steam into the atmosphere at a rate of about 3000 tons/day (see Table 1, after Minissale 1991), and/or through CO_2-rich gas vents. This type of CO_2 discharges typically occurs at the peripheries (steam condensation zones) of most active hydrothermal systems, where the gas phase splits from steam, whether associated with active volcanoes or not. As shown in the right side of Fig. 1, CO_2 typically moves into much cooler convective aquifers (at boiling temperature) bordering the geothermal field (both laterally and above the vapour zone), dissolving in them and eventually lowering the *p*H of the final water solutions.

Estimates of the released CO_2 into the atmosphere (in tons/day, after Rogie *et al.*, 2000) are reported In Table 1 for both the Larderello geothermal field and relevant CO_2-rich gas emission areas in Italy (Minissale, 2004), some of which are located at the peripheries of other active volcanic (Neapolitan area in Fig. 2) or geothermal systems. This type of CO_2 is referred to in the literature as non-volcanic CO_2 and, as suggested by Berner and Lasaga (1989) in their model of the global carbon cycle,

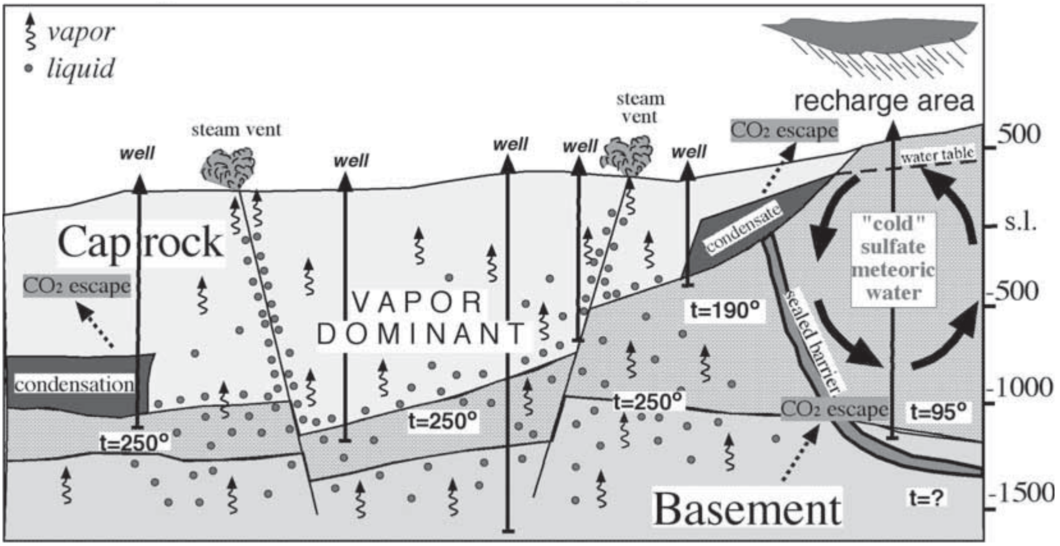


Fig. 1 – Conceptual section of the Larderello geothermal field (after Minissale, 1991).

it is largely underestimated in the global budget of CO_2.

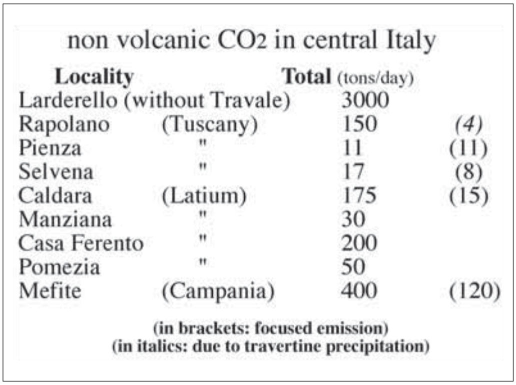
THE PROBLEM OF THE CO_2 BUDGET

In the Berner *at al.* (1983) model related to the Earth degassing and paleo-degassing of CO_2, it is assumed that CO_2 fluxes into the atmosphere correlate with the rate of the lithosphere subduction and with the spreading rates of mid-ocean ridges. It has also been estimated the quantity of CO_2 carried by the rivers as HCO_3 ions into the oceans, as well as the quantity of CO_2 discharged into the atmosphere by volcanoes from their central vents and relative flanks (Kerrick, 2001). The first quantity (the rivers HCO_3), as already reported in the previous paragraph, is much more than the volcanic input and, for this reason, we have to suppose that, what is called non-volcanic CO_2 must play a relevant, although underestimated, role in the global CO_2 budget (Kerrick *et al.*, 1994).

Among the non-volcanic CO_2 sources are worth mentioning the spring waters from which the continental carbonates are precipitated. The continental deposits of $CaCO_3$ (*travertine*, *calcareous tufa* and *speleotems*) precipitate from cold or warm waters, particularly concentrated in Ca, Na, and HCO_3 ions (generally referred to as *soda springs*). Such spring waters are oversaturated with respect to calcite or aragonite (a *polymorphic* phase of calcite) that precipitate at, or near the orifice, according to the reaction:

$$Ca^{++}_{(aq)} + 2HCO^{-}_{3\,(aq)} = CaCO_{3(s)} + H_2CO_{3(aq)} \qquad (6)$$

Table 1 – *Measured flux of carbon dioxide emission (in tons/day) for the Larderello geothermal field in Tuscany (Fig. 1) and some relevant CO_2 emission from natural vents in central Italy*


non volcanic CO2 in central Italy

Locality		**Total** (tons/day)	
Larderello (without Travale)		3000	
Rapolano	(Tuscany)	150	*(4)*
Pienza	"	11	(11)
Selvena	"	17	(8)
Caldara	(Latium)	175	(15)
Manziana	"	30	
Casa Ferento	"	200	
Pomezia	"	50	
Mefite	(Campania)	400	(120)

(in brackets: focused emission)
(in italics: due to travertine precipitation)

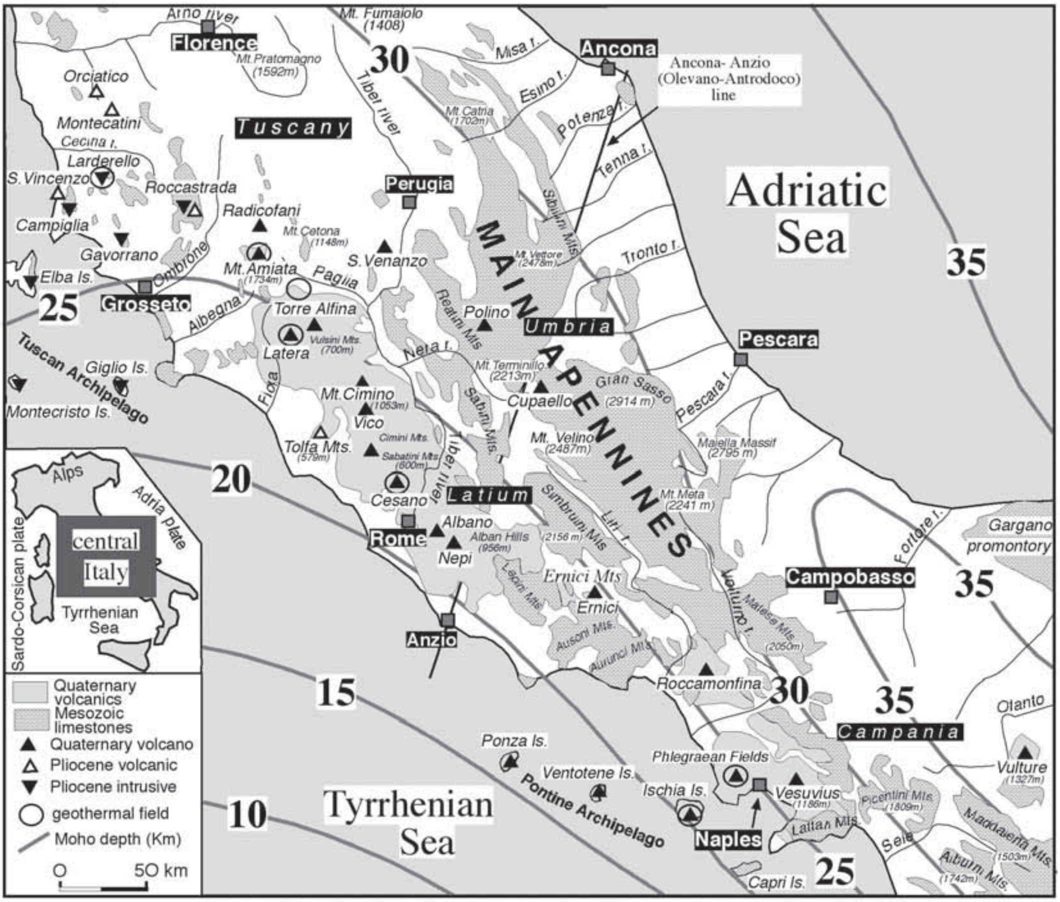


Fig. 2 – Schematic map in central Italy (after Minissale, 2004).

Where H_2CO_3 is in equilibrium with CO_2 according to the reaction:

$$H_2CO_{3(aq)} = H_2O_{(aq)} + CO_{2(g)} \tag{7}$$

The deposition of carbonate sinter represents a shorter cycle of CO_2 inside the more general CO_2 cycle, and it has not been considered in the past in any global carbon cycle modelling. In any case, being related to anomalous CO_2 fluxes, travertine deposits and parent thermal springs, are prevalently concentrated in active tectonic areas (mainly at plate boundaries) together with volcanoes and other geothermal features (Barnes *et al.*, 1978).

Travertines have been extensively investigated in central Italy, where both hydrothermal systems and large outcrops of massive Mesozoic limestone are present (Fig. 2, after Minissale, 2004). CO_2 deriving from volcanic-hydrothermal systems has an isotopic signature (the $^{13}C/^{12}C$ ratio of carbon) much higher than CO_2 deriving from organic activity, the latter generally entering the limestone hydrologic circuit (karstic circuits), together with rainfalls, from soil root respiration and organic acid dissolution. In terms of $\delta^{13}C‰$ referred to a standard PDB, it varies from –3.0 to +2.0‰ when CO_2 is hydrothermal or metamorphic, whereas it is lower than –20.0‰ when deriving from soil organic acids and/or bacteria activity. It is, on the contrary, about –6.0‰ if it is mantle-derived (the primordial $^{13}C/^{12}C$ ratio) or the atmosphere. Whatever the source of CO_2, the isotopic signature of travertine will retain the isotopic signature of the source of CO_2 (Panichi and Tongiorgi, 1976). At the same time the $^{18}O/^{16}O$ ratio of oxygen of the CO_3 ion of travertine (as well as speleotems and calcareous tufa) will be related to the $^{18}O/^{16}O$ of rainfalls during the formation period of the travertine deposit. As a consequence, travertine and calcareous tufa can be used as a further proxy (after polar ice cap, lake lime sediments, marine foraminifera, etc.), to study the isotopic composition of its "*mother*" rainfalls.

In fact, in order to have massive precipitation of karst-derived limestone, such as in central Italy, a large flow of CO_2 is needed; it is also evident that water (rainfall) is needed as well. So, the precipitation rate of travertine is a function of the rainfall rate and its isotopic composition, in turn being related to the evaporation rate of the ocean. If the evaporation rate of the ocean is higher, related to the temperature of the atmosphere, the oxygen-18 will be more abundant in rainfall. Finally, through the analysis of travertine and karst-derived deposits, in terms of precipitation rates and isotopic composition, a relation can be established between the oxygen-18 of carbonates and the oxygen-18 of precipitation and, as a consequence, with the paleo-climate (Cilla *et al.*, 1994).

ALTERNATION BETWEEN WARMING AND COOLING PERIODS

Among others, the quantity and quality of vegetation on Earth is a function of the concentration of CO_2 in the atmosphere, CO_2 being the main green-house gas in the atmosphere, highly variable in time (Petit *et al.*, 1999). Excessive emission of CO_2 into the atmosphere, because of relevant volcanic activity may cause warm periods, whereas reduced emission of CO_2 may bring ice ages. This CO_2 outcome overlaps the effects of the well-known Milankovitch cycles theory (in Hays *et al.*, 1976). This theory states that as the Earth travels through space around the sun, variations in the Earth's orbital plane occur. In particular, changes: *i)* in the shape of the orbit (*eccentricity*) around the sun (every 100,000 years), *ii)* in the angle that Earth's axis makes with the plane (*obliquity*) of Earth's orbit (every 40,000 years) and *iii)* changes deriving by the shifting of the direction of the Earth's rotation axis (*precession;* every 22,000 years) which causes differences in the solar radiation received by the Earth (Martinson *et al.*, 1987).

During one of the warmest periods recorded in the past, such as the Cretaceous, dinosaurs disappeared. It is likely to suppose that the tremendous high temperature of the atmosphere in that period (McLean, 1978), was caused by one or more of the following, almost contemporary processes:

i) high CO_2 concentration caused by the extrusion of the Deccan Basalt Trap (India) during the riding of India above the mantle hot spot located in the Reunion Islands in the Indian ocean (Napier and Cube, 1979; McLean, 1985),
ii) subduction of the lithosphere and massive limestone and related hydro-metamorphism during the formation of Himalaya (Kerrick and Caldera, 1999) with CO_2 production and discharge into the atmosphere,
iii) a particularly strong meteorite impact on Earth (Alvarez *et al.*, 1980),
iv) positive *Milankovitch cycles* feedback.

Coincidence of large extrusion of magmas at the surface and warming periods of the atmosphere is very likely and seriously to be considered as the real engine of climate changes, at least at a macro-scale. The alteration of silicate minerals and rocks, well enhanced during warm periods, is the main process to buffer back to a lower CO_2 concentration in the atmosphere and take the Earth again to cooler periods.

ANTHROPOGENC CO_2 EMISSION INTO THE ATMOSPHERE: A REASON FOR CONCERN?

Figure 3 shows how the CO_2 concentration in the atmosphere has steadily increased in the period 1958-1994 at the Hawaiian Meteorological Observatory (Keeling and Whorf, 1991). Higher summer sequestration of CO_2 by vegetation activity causes the seasonal oscillation shown by the figure. It has been reported that such

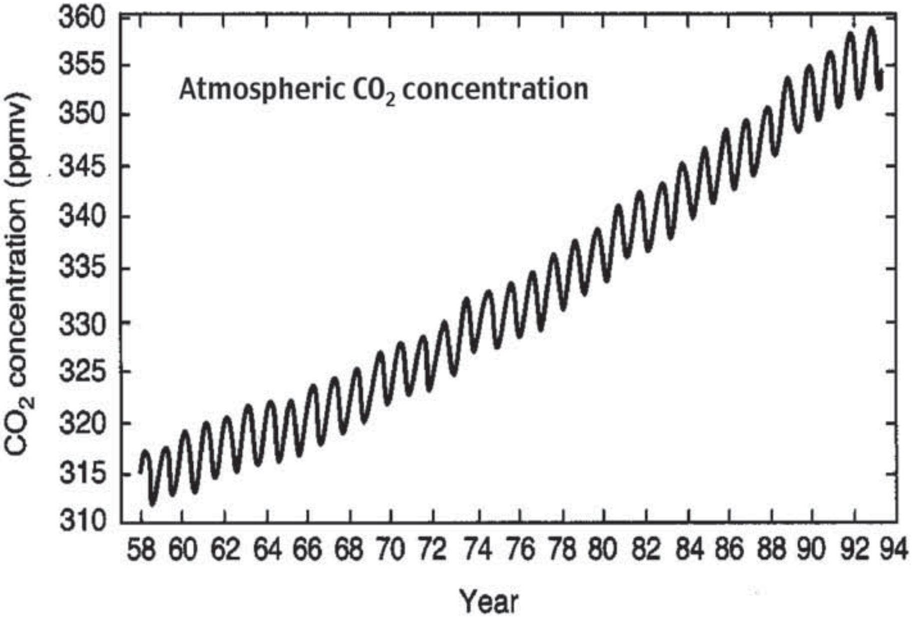


Fig. 3 – Registered increase of CO_2 concentration in the atmosphere from 1958 to 1994 at the Hawaiian Meteorological Observatory (Keeling and Whorf, 1991).

increase of CO_2 concentration in the atmosphere is an ongoing process since the beginning of the industrial revolution in Europe at the beginning of the 19th century (Fig. 4). That period coincides with the beginning of high coal and wood burning to produce steel tools and steel structures for the new heavy industry, including railroad tracks, steel boats, steam engines, etc.

The present extrapolated anthropogenic degassing flux of CO_2 into the atmosphere has been estimated to be about 10^{11} T/y (Berner, 1991), more or less one order of magnitude higher than what is known, at present, to be released by natural biologic, volcanic or metamorphic systems (Kerrick, 2001). Nevertheless, the natural CO_2 emission into the atmosphere is less than the total estimated CO_2 consumed by chemical weathering of silicates and carried back to the oceans by rivers in the form of HCO_3 ions in solution (Kerrick *et al.*, 1994). This unbalance can be partly overcome if we consider the contribution of CO_2 into the

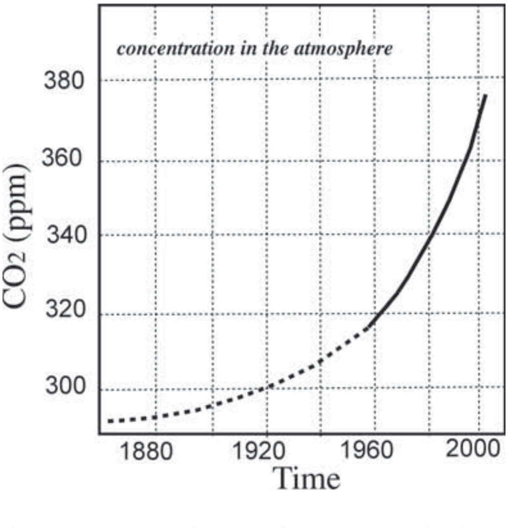


Fig. 4 – Extrapolated increase of CO_2 concentration in the atmosphere from the beginning of industrialisation in central Europe in 19th century.

atmosphere from other sources (Chiodini *et al.*, 1999; 2000) and in short term carbon cycles, such as the one represented by the calcite precipitation in carbonate deposits in continental areas. Such contributions are really unknown and, to some extent, difficult to be evaluated both on a local scale as well as on a global scale. In one active depositing travertine area in central Italy near Rapolano Terme, Minissale *et al.* (2002) have calculated a contribution of 4 T/day of CO_2 into the atmosphere due to the precipitation of travertine from thermal springs. In any case travertine can be considered a further evidence of the presence of active hydrothermal systems at relatively shallow depth, and the relative CO_2-related transfer to the atmosphere might actually play an important role in the global CO_2 budget. Travertine deposition in the CO_2 budget problem might be parallel to the role played by small-scale hydrological systems (such as lakes) in the global water budget of the hydrological cycle.

According to what happened during the Cretaceous and/or similar periods, the present increase of the atmospheric temperature might be due to a synergistic multiple effects causing the CO_2 increasing concentration in the atmosphere:

i) not well known and not well assessed "*natural*" high emission of volcanic, non volcanic and metamorphic CO_2,
ii) reduced CO_2 sequestration capability of vegetation due to massive deforestation, to be added to the anthropogenic CO_2 emission.

Natural CO_2 emission, essentially driven by tectonics, is a quantity really not well known, and difficult to quantify because of un-foreseeable events (volcanic eruptions, earthquakes, etc.). Moreover, knowledge of what has been defined non-volcanic CO_2, probably an important part of the carbon cycle, is still in its primordial stage of assessment. In this uncertainty, paradoxically, anthropogenic CO_2 emission could have a beneficial effect to the buffering the CO_2 concentration in the atmosphere, in period of low natural CO_2 emission. To this generalised uncertainty we have to consider the non CO_2-related causes of temperature variation of the atmosphere related to extraterrestrial factors (Milankovitch Cycles), whose feedback on the terrestrial sources could be either positive or negative. Many CO_2 processes leading to consumption of CO_2 (silicate alteration) or enhanced CO_2 production (e.g., continental carbonate precipitation) on Earth are actually probably driven by temperature variations of the atmosphere because of extraterrestrial causes.

CONCLUSIONS

Our knowledge of the carbon cycle, at least for the part referring to carbon dioxide, is still quite poor. In spite of this, it is evident that CO_2 plays a relevant role for life, at least in terms of quality. The fact that scientists do not agree on the fate of the atmosphere's temperature in the near future is largely related to the described poor knowledge of the carbon cycle, and the impossibility to produce reliable models of variation in time. If short-term variations of temperature of the atmosphere are likely related to cosmic factors, long term variations are on the contrary likely related to the tectonics of the lithosphere. If Milankovitch cycles are regularly spaced in time the tectonic-related CO_2 variations are, on the contrary, likely fast and scattered changes. The resulting equilibrium from these two different causes is the real engine of the temperature changes of the atmosphere. If anthropogenic CO_2 emission is able to affect this natural equilibrium is still very far from being understood because modelling and quantifying the global carbon cycle is still at an early stage.

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