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Environment International



journal homepage: www.elsevier.com/locate/envint

Review article Global warming and carbon dioxide through sciences

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A R T I C L E I N F O

Article history: Received 17 March 2008 Accepted 15 July 2008 Available online 28 August 2008

Keywords: Carbon dioxide Global warming Palaeoclimate Greenhouse gas

ABSTRACT

Increased atmospheric CO₂-concentration is widely being considered as the main driving factor that causes the phenomenon of global warming. This paper attempts to shed more light on the role of atmospheric CO_2 in relation to temperature-increase and, more generally, in relation to Earth's life through the geological aeons, based on a review-assessment of existing related studies. It is pointed out that there has been a debate on the accuracy of temperature reconstructions as well as on the exact impact that CO_2 has on global warming. Moreover, using three independent sets of data (collected from ice-cores and chemistry) we perform a specific regression analysis which concludes that forecasts about the correlation between CO₂concentration and temperature rely heavily on the choice of data used, and one cannot be positive that indeed such a correlation exists (for chemistry data) or even, if existing (for ice-cores data), whether it leads to a "severe" or a "gentle" global warming. A very recent development on the greenhouse phenomenon is a validated adiabatic model, based on laws of physics, forecasting a maximum temperature-increase of 0.01-0.03 °C for a value doubling the present concentration of atmospheric CO2. Through a further review of related studies and facts from disciplines like biology and geology, where CO₂-change is viewed from a different perspective, it is suggested that CO₂-change is not necessarily always a negative factor for the environment. In fact it is shown that CO₂-increase has stimulated the growth of plants, while the CO₂-change history has altered the physiology of plants. Moreover, data from palaeoclimatology show that the CO2content in the atmosphere is at a minimum in this geological aeon. Finally it is stressed that the understanding of the functioning of Earth's complex climate system (especially for water, solar radiation and so forth) is still poor and, hence, scientific knowledge is not at a level to give definite and precise answers for the causes of global warming.

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1. Introduction

The climate of the Earth is constantly undergoing changes due to a variety of factors. These factors include, among others, changes in the Earth's orbit, changes in the Sun's intensity, changes in the ocean currents, volcanic emissions and changes in greenhouse-gas concentrations. Global warming during the last decades has been a "hot" phenomenon concerning the scientific, and not only, community. According to the Intergovernmental Panel on Climate Change (IPCC) of the United Nations, it is the phenomenon, experienced in recent decades, where the average temperature of the Earth's near-surface air and oceans increases.

According to IPCC, the observed increase in globally averaged temperatures since the mid-20th century is very likely to have occurred due to the increase in anthropogenic greenhouse-gas concentrations that leads to the warming of the Earth's surface and lower atmosphere (see increase of the greenhouse effect). The greenhouse effect is the phenomenon where water vapour, carbon dioxide (CO_2), methane and other atmospheric gases absorb outgoing infrared radiation resulting in the raising of the temperature. In its turn, CO_2 is essentially blamed to be the main factor causing the greenhouse effect because it is the most important anthropogenic greenhouse gas (IPCC, 2007).

The increase in global temperature has caused concern that other changes, such as the rising of sea level and the amount and pattern of precipitation, may follow, along with increases in the frequency and intensity of extreme weather events, changes in agricultural yields, glacier retreat, species extinctions, increases in the ranges of disease vectors and others.

A good number of engineers consider global warming as an unprecedented event in the geological history of Earth and that for this fact anthropogenic CO_2 emissions are to be blamed. It is probably true that the CO_2 -increase in the atmosphere has contributed to global warming in some extent during the 20th-century, but CO_2 -increase is not only anthropogenic; it is in addition a result of the temperature rise and various natural processes, like ocean changes in CO_2 solubility. It also is worth noting that in various other disciplines, as biology and geology, CO_2 -change is viewed from a different perspective and it is not necessarily always a negative factor for the environment. For instance CO_2 -increase has stimulated the growth of the plants, while the CO_2 -change history has modified the physiology of plants.

Moreover, it is undeniable that phenomena like today's global warming have been experienced throughout Earth's long history and will probably continue to be experienced irrespective of human contribution toward increasing the greenhouse-gas concentrations. It is noteworthy that palaeoclimatological data show that the CO_2 content in the atmosphere is at a minimum in this geological aeon.

The present study concentrates on the effect of CO_2 in climatic, geological and biological changes, relating all these to its palaeohistory. The aim of this paper is to contribute toward the view that this human contribution in global warming may not be so crucial as widely believed, based on the assessment and the analysis of available climate data, as well as on CO_2 's palaeo-history and its effect on Earth's life through the geological aeons using facts that have thus far probably been overlooked.

Finally it must be stressed that the understanding of the functioning of Earth's complex climate system (especially for water and its forms, solar radiation and so forth) is still poor. This fact is not always adequately considered in most available climate models.

The paper is organised as follows. In Section 2 are presented an analysis of the existing data (with emphasis given to findings, not generally mentioned broadly and opposing the view that CO_2 is the main factor causing the greenhouse effect), an assessment of the available studies related to temperature and CO_2 -concentration, and the debate that has been going on recently in the scientific community

about the accuracy of temperature reconstructions as well as the exact impact that CO_2 has on global warming. In Section 3 is performed a regression analysis, based on three different available sets of data (two from ice-cores and one from chemical experiments), studying the correlation between CO_2 -concentration and temperature-increase, concluding that probably no such correlation exists (based on the likely more [or at least as] reliable chemical CO_2 -records). In Section 4 is presented the adiabatic theory which through the use of laws of physics estimates the greenhouse effect. In Section 5 the CO_2 history through the geologic aeons is presented and in Section 6 the important role of CO_2 in geology and biology is assessed. We conclude with Section 7.

2. An analysis of the existing climate data

Meteorological stations record the temperature since 1850. Today there are over 3000 stations taking records of temperatures. For marine regions sea-surface temperature (SST) measurements are taken on board merchant and some naval vessels. To overcome problems resulting from the fact that stations on land are at different elevations, and that different countries estimate average monthly temperatures using different methods and formulae, it has been established that the period 1961–90 is considered as the "zero-base" (on the grounds of available combined data). Hence recorded temperatures are expressed as anomalies from the 0-base. Data analysed with the above method are available to the public by the Climatic Research Unit datasets, developed in conjunction with Hadley Centre of the UK Met Office (Hadley Centre, 2007).

2.1. Temperature-increase during the 20th century

Based on available data (Hadley Centre, 2007), the land-air temperature anomalies for the global, north and south hemisphere, for the period of 1850 to 2007, are drawn in Fig. 1. One can see that from the year 1850 to about 1910 the temperature gradient is essentially 0. Then there is an increase in the temperature gradient for the next 30 years. From about 1940 to 1980 the gradient is again essentially 0. Finally, there is a definite increase of about 0.6 °C in the mean global temperature since 1980.

2.2. Carbon dioxide and temperature

Carbon dioxide is a naturally occurring gas, a by-product of burning fossil fuels and biomass and a result of land-use changes and other industrial processes. It is the principal anthropogenic gas that is thought to affect the Earth's radiative balance (IPCC, 2007). For this reason it is believed that there is a close correlation between CO_2 and the change of the Earth's temperature. The way this relation has been



Fig. 1. Land air temperature anomalies, for global, north hemisphere and south hemisphere for the period of 1850 to 2007. (File: CRUTEM3v-global variance adjusted version of CRUTEM3. Hadley Centre, 2007).

established is largely based on plotting the average temperature anomalies and the amount of CO_2 present in the atmosphere versus time. Such a demonstration is presented in Fig. 2, where are plotted the annual global temperature anomalies (for the period 1850–2005, Hadley Centre, 2007) together with the historical CO_2 record data from (a) the Law Dome in Antarctica (DE08, DE08-2 and DSS ice-cores for the period 1850–1978, Etheridge et al., 1998) and (b) the atmospheric CO_2 -concentrations derived from air samples collected at the South Pole, for the period 1957–2004 (Keeling and Whorf, 2005).

It must be noted that the mixing of the data derived from ice-core measurements together with the actual direct atmospheric measurements as in Fig. 2 (following for example the demonstration of IPCC– Climate Change, 2001) is questionable because of the unreliability of the ice-core measurements, as explained below.

- (a) The sampling and the analytical methods used for the CO₂concentration data in ice-cores, described in detail by Etheridge et al. (1996) can be rejected since they are based on an assumption on ice/gas difference that is not supported by convincing experimental results. In particular, assumption that air from two Law Dome cores is 30 years younger than ice, in which the air was entrapped, was needed for assigning the age of air samples as 1969 and 1978, although they were deposited in 1939 and 1948, respectively. This manipulation enabled a smooth overlapping of the pre-industrial CO₂ ice-core data from Law Dome (ending in 1939 and 1948), with the contemporary direct measurements of CO₂ in the atmosphere at the South Pole, which were started in 1957. The same manipulation had been done earlier by the Schwander group (Schwander and Stauffer, 1984; Schwander et al., 1988, 1993; Schwander, 1989) with the data from Siple (Antarctic) ice-core, was never supported experimentally and was found groundless by Jaworowski et al. (1992) and Jaworowski (1994).
- (b) Moreover, Etheridge et al. (1996) neglect and misuse the information on fractionation of gases, in which one of the factors is formation of solid CO₂ clathrates. Jaworowski et al. (1992) and Jaworowski (1994), insist that CO2-concentration in ice-cores does not represent its original atmospheric composition. Because fractionation of gas components occurs in the air samples and there are chemical reactions, diffusion through micro-cracks and gas-liquid-solid phase changes occurring in the ice-sheet, during drilling and during decompression from several hundred bars down to the atmospheric pressure.
- (c) Leroux (2005) attests too that two laboratories carrying research in palaeoclimatology could not answer affirmatively if measurements taken from ice and from the atmosphere can



Fig. 2. Annual global temperature anomalies (Hadley Centre, 2007) and CO₂ record data from (a) the Law Dome in Antarctica (DE08, DE08-2 and DSS ice-cores, Etheridge et al., 1998) and (b) the atmospheric CO₂-concentrations derived from air samples collected at the South Pole–shaded area, (Keeling and Whorf, 2005). Profiles do not follow the same trend between 1890 and 1950.

really be compared. One of the laboratories added that such a comparison could probably be valid for very recent periods, cross-checking with current measurements (i.e. only at levels near the surface).

More objections regarding the reliability of Fig. 2 can be raised about the estimation of the temperature anomalies as follows:

- (a) A simple statistical average of temperatures from around the globe is not adequate to summarise the climate change. As Essex et al. (2007) effectively declare, mean global temperature is not a single, well-defined physical quantity and statistics cannot stand in as a replacement for the missing physics. Furthermore, the climate is not governed by a single temperature but it is the temperature-differences that drive the processes and create the storms, sea currents, thunders, etc. which make up the climate.
- (b) The temperature measurement sides are not located randomly. The grand majority of the weather stations are on land despite the fact that 70% of the Earth's surface is covered by ocean (http://www.sailwx.info/wxobs/stationpick.phtml). The number of measurement sides varies extensively through time, starting in 1850 at 200 sides and then declining to about 5000 by 2000. The stations providing "mean temperature" in 1850 were about 200, increasing to about 6000 in the 1970s but decreasing to about 2800 nowadays. The stations supplying "max-min" temperatures from non-existent in 1850 increased to about 4100 in the 1970s but decreased to about 1500 nowadays. It may also be noted that the corresponding grid boxes (of $5^{\circ} \times 5^{\circ}$) have fallen to 500 (for "mean temperatures") and to 100 (for "max-min" temperatures) being well under the 2592 boxes required by the models (Peterson and Vose, 1997). All the fluctuations above influence the validity of estimates of the temporal trends of the average global temperature, which seem less reliable than the estimates of the overland trends in the United States.
- (c) Leroux (2005) mentions that the presumed global warming might merely well be an urban phenomenon as is pollution. Because of built-up, paved area, industry, road traffic etc, urban station measurements, which produce most land-based data, reflect climatic evolution on a local scale. In addition, weather stations once situated in rural locations have progressively been covered by the growing towns' heat domes. Keenan (2007) questions the integrity of temperature measurements of stations moved over time in China. These improper estimates, as he mentions, were cited for resolving a major issue in the 2007 assessment report of the IPCC. Recently NASA has been forced to correct calculations for temperatures of the last 120 years taken from ground-based measuring facilities including urban ground, because these measurements were distorted by human activities and cannot accurately represent atmospheric conditions. According to NASA's newly published data the hottest year on record in the USA is 1934, not 1998; three of the five hottest years on record occurred before 1940; and six of the top 10 hottest years occurred before 1960 (http:// data.giss.nasa.gov/gistemp/graphs/Fig.D.lrg.gif).

Even if all of the reasonable objections are completely ignored, one cannot avoid observing (in Fig. 2) that, although for both sets of data (temperature and CO_2 -concentration) a rising trend is obvious for the last decades, there are large time-intervals where the profiles do not follow the same trend (see for example the period from about 1890 to 1950).

Fig. 2 is based on data restricted to a period of 150 years. We believe that a more thorough examination of temperature change behaviour can be achieved by considering a longer period in time. Unfortunately available data as regards CO₂-concentration for the past



Fig. 3. Temperature anomalies presented by various authors.

one thousand years come from the same unreliable source, raising the objections described above (Etheridge et al., 1998). We still find useful to present what is available and we leave a more detailed discussion on CO₂-concentration in the sequel. In Fig. 3, we plot available data of CO₂-records from the Law Dome ice-cores (DE08, DE08-2 and DSS) for a time-period from 1006 A.D. to 1978 A.D (Etheridge et al., 1998). One can see that pre-industrial (before 1850 A.D.) CO₂ mixing ratios were in the range of 275–284 ppm, with a global minimum between 1550 and 1800 A.D. On the other hand one observes a continuous increase in atmospheric CO₂ levels over the industrial period.

In Fig. 3 are also plotted available temperature anomalies reconstructed from instrumental and high-resolution climate "proxy" data sources and climate modelling studies by Jones and Mann (2004) and Mann and Bradley (1999) (as presented in Jones and Mann (2004)). Jones and Mann conclude that natural factors appear to explain relatively well the major surface temperature changes of the past millennium through the 19th century and that the recent anomalous warming in the late 20th century is only explained by anthropogenic forcing of climate.

In addition, in Fig. 3 are presented temperature reconstructions by Moberg et al. (2005) and Huang (2004). Moberg et al. (2005) reconstructed the northern hemisphere temperatures for the past 1800 years by combining low-resolution proxies with tree-ring data, using a wavelet transform technique to achieve timescale-dependent processing of the data. The reconstruction in Moberg et al. (2005) has a larger multi-centennial variability than most previous multi-proxy reconstructions and agrees well with temperatures reconstructed from borehole measurements (Dahl-Jensen et al., 1998) and with temperatures obtained with a general circulation model. One can see that, in this reconstruction, maximum temperatures near the 0-base (similar to those observed in the 20th century) occurred between 1000 and 1100 A.D. whereas minimum temperatures (of about -0.7 K) occurred between 1550 and 1700 A.D. They (Moberg et al., 2005), therefore, argue that this large natural variability of the past suggests an important role of natural multi-centennial variability that is likely to continue.

Huang (2004), integrated the complementary information preserved in the global database of borehole temperatures, the 20th century meteorological records and an annually resolved multi-proxy model for a more complete picture of the northern hemisphere temperature change over the past five centuries. It is clear from Huang's data in Fig. 3 that the 20th century warming is a continuation to a long-term warming that started before the onset of industrialization (since 1650 A.D.). Huang states that the rate of warming appears to be increasing towards the present day and that the analysis of the reconstructed temperature and radiative forcing series offers an independent estimate of the transient climate-forcing response rate of 0.4–0.7 K per Wm² and predicts a temperature-increase of 1.0–1.7 K in 50 years.

2.3. The debate about the temperature reconstructions

The climate reconstructions of Jones and Mann (2004) is in general agreement with the reconstruction of Mann et al. (1999, 1998) which have been adopted by the IPCC as the accepted temperature history of the northern hemisphere. The IPCC has based on this reconstruction the claim that the 1990s has been the warmest decade and 1998 the warmest year of the millennium for the northern hemisphere. The IPCC's view of temperature history has in turn been widely disseminated by governments and used to support major policy decisions (McIntyre and McKitrick, 2003).

The climate reconstruction of Mann et al. (1999, 1998), has received severe criticism by McIntyre and McKitrick (2003), the National Academy of Sciences (NAS) (2006) report, the Wegman (2006) report and others that have independently ascertained that Mann's PC method produces unreal "hockey-stick" shapes.

McIntyre and McKitrick (2003) checked the data sets of proxies of past climate used by Mann and collaborators, and claim that these contain unjustifiable use of data as well as a lot of errors and defects. Using corrected and updated source data they applied the initial methodology and reconstructed the northern hemisphere average temperature index for the 1400–1980 A.D. period (Fig. 4). Their major conclusion is that the values in the early 15th century exceed all values in the 20th century and that the particular "hockey-stick" shape is primarily an artefact.

Based on the uncertainties inherent in temperature reconstructions that are larger for individual years and decades than for longer time-periods, and because not all of the available proxies record temperature information on such short time-scales, the NAS (2006) report states that less confidence can be placed in the original conclusions by Mann et al. (1999) that the 1990s are likely to be the warmest decade and 1998 the warmest year, in at least a millennium. The NAS report states that only for the last four centuries a high level of confidence on Mann et al. (1999) statement about the warmest decade can be correct. Furthermore, it is suggested that it would be helpful to update proxy records that were collected decades ago, improve access to data used in publications and use new analytical methods, or use more carefully existing ones, to help circumvent some of the existing limitations associated with surface temperature reconstructions based on multiple proxies.

In the Wegman (2006) report it is stated that the Chairman of the US Committee on Energy and Commerce as well as the Chairman of the Subcommittee on Oversight and Investigations have been interested in an independent verification of the critiques of Mann et al. (1999, 1998) by McIntyre and McKitrick (2003) as well as the related implications in the assessment. The conclusions from the studies of Mann et al. (1999, 1998), adopted by the IPCC generated a highly polarized debate over the nature of global climate change, and whether or not anthropogenic actions are the source. The committee has reviewed the work of both articles, as well as a network of journal



Fig. 4. Updated reconstruction of McIntyre and McKitrick of recalculated Mann et al. (1998) temperature reconstruction, drawn together with Mann et al. (1998) original reconstruction. (Redrawn from http://www.uoguelph.ca/~rmckitri/research/trc.html).

articles that are related either by authors or subject matter and concluded that Mann et al. (1999, 1998) are somewhat obscure and incomplete and that the criticism of McIntyre and McKitrick (2003) is valid.

The study of Jones and Mann (2004) is also in contrast to the work of Soon and Baliunas (2003), who reviewed the 1000-year climatic and environmental history of the Earth contained in various proxy records. They mention that although as indicators, the proxies represent local climate and cannot be combined into a hemispheric or global quantitative composite, because each is of a different nature, many records across the world, reveal that the 20th century is probably not the warmest nor a uniquely extreme climatic period of the last millennium. The assemblage of these local representations of climate establishes both the Little Ice Age and Medieval Warm Period as climatic anomalies with worldwide imprints. To show this, use is made of a local proxy record in central Greenland based on stable isotope analysis of the GISP2 ice-core data by Alley (2004) and the Oxygen 18/16 variability measured by Grootes and Stuiver (1997). In Fig. 5 the aforementioned data are plotted versus time. It is clearly shown that numerous "warm-periods" (some of which are even wellknown historical periods) have occurred in the past with even higher maxima than the present warm period.

2.4. Dispute about CO₂ being the climate driving factor

During the past thirty years the Soviet Union drilled a number of holes at Vostok Station in Antarctica which showed that ice of the last glacial period was present at a depth of about 400 m. The deepest hole was stopped at a depth of 3623 m because of worries about possible contamination of the Lake Vostok which is presently under the icecap and has been sealed under it for more than 500,000 years. The extracted ice-cores produced a record of past environmental conditions stretching back to 420,000 years and covering four previous glacial periods. Vostok ice-core data for 420,000 years (Petit et al., 2001) are plotted in Fig. 6. It is clearly seen (and this is exactly what researchers have observed) that a repeating pattern concerning correlation exists between CO_2 and temperature through the four glacial–interglacial cycles.

However, there has been objection about the simultaneity of the measurements taken for the two sets of data (for CO_2 and temperature-difference). To overcome this inconvenience, Fischer et al. (1999), examined contemporaneous records of atmospheric CO_2 -concentration and temperature derived from Antarctic ice-cores that extended back in time through the last three glacial-interglacial transitions. Their conclusion was that atmospheric CO_2 -concentrations show a similar increase for all three terminations, connected to a climate-driven net transfer of carbon from the ocean to the atmo-



Fig. 5. Oxygen 18/16 variability and temperature in central Greenland based on the GISP2 ice-core data.



Fig. 6. Vostok ice-core data correlation between CO_2 and temperature through the four glacial-interglacial cycles, for the last 420,000 years. Temperature-difference and CO_2 concentration from Petit et al. (2001).

sphere. The CO₂-concentration rise lags temperature change by 400 to 1000 years during all three glacial–interglacial transitions, hence, indicating that the relationship between temperature and CO₂ appears to be the exact reverse of what is assumed to be in the conventional climate model studies. As is readily evident in natural processes temperature rises first, followed by an increase in atmospheric CO₂.

A similar analysis was performed by Caillon et al. (2003), for air bubbles in the Vostok core during Termination III (240,000 years before present), measuring the isotopic composition of argon. The sequence of events during Termination III suggests that the CO₂increase lagged Antarctic deglacial warming by 600 to 1000 years and preceded the northern hemisphere deglaciation.

The above-mentioned studies imply, therefore, that an initial temperature trigger (as small changes in the Earth's orbit, for instance) results in a release of CO_2 from natural reservoirs, like the ocean, to the atmosphere with a time-lag of several centuries.

2.5. Atmospheric CO₂-concentration

As already mentioned, there has been reasonable opposition in accepting the ice-core data as representative of the atmospheric CO₂-levels of the past (Jaworowski et al., 1992; Jaworowski, 1994; Leroux, 2005).

Recently, Beck (2007) evaluated the historical literature on atmospheric CO₂-levels between 1857 and 1958 when reliable chemical measurements were performed directly in the atmosphere. The standard analytical method for determining atmospheric CO₂-levels usually achieved a very good accuracy (with an error of less than 3%). More than 90,000 individual determinations of CO₂-levels from 138



Fig. 7. Beck's yearly average atmospheric CO₂ curve for the northern hemisphere, based on chemical measurements, opposed to Antarctica ice-core measurements.

sources and locations were evaluated and combined to produce a yearly average atmospheric CO_2 curve for the northern hemisphere (plotted in Fig. 7). It is probably worth mentioning that the determinations were made by skilled investigators and several Nobel Prize winning scientists.

Beck argues that the historical data, although consisting of local measurements, represent a globally meaningful CO₂ curve because there is correspondence between the curve and other global phenomena, including both sunspot cycles, moon phases and average global temperature statistics. Furthermore, that the historical data are reliable in themselves is supported by the credible seasonal, monthly and daily variations that they display, the pattern of which corresponds with modern measurements. Since 1812, the CO₂concentration in northern hemispheric air has fluctuated exhibiting three high-level local maxima in (around) 1825, 1857 and 1942, with the latter reaching more than 400 ppm. Beck also mentions that it is surprising that the quality and accuracy of these historic CO₂ measurements has escaped the attention of other researchers. Modern climatologists have generally ignored the historic determinations of CO₂, despite the techniques being standard textbook procedures in several different disciplines. Chemical methods were discredited as unreliable, with only very few "approved" to fit the assumption of a climate CO₂ connection.

An indirect way of estimating atmospheric CO_2 -concentration is by the stomatal frequency in tree leaves. Stomata are small openings or pores, present on the leaves of plants, which allow CO_2 to enter and oxygen to escape the leaf in order to facilitate photosynthesis. In addition, water is lost through stomata during a process called transpiration (see Section 6.2 for a more detailed discussion).

Wagner et al. (1999), mention that stomatal frequency provides an accurate method for detecting and quantifying century-scale CO₂ fluctuations, and that the frequency fluctuates in an inverse order than the atmospheric CO₂-concentration. Their study concludes that, in contrast to conventional ice-core estimates of 270 to 280 ppmv, the stomatal frequency signal suggests that early Holocene CO₂-concentrations were well above 300 ppmv.

Kouwenberg et al. (2005), developed a well-dated high-resolution history of the atmospheric CO_2 -concentration for the period 800– 2000 A.D., based on measurements of stomatal density made on *Tsuga heterophylla* needles. Their CO_2 reconstruction history reveals three major peaks, one centered on (approximately) 1000 A.D., one in the early 1300s, and one at the end of the record in the latter half of the 20th century.

In Fig. 8 are plotted the CO_2 records from Law Dome that are compared with the CO_2 history as revealed from stomata (redrawn from Kouwenberg, 2004 PhD Thesis). The observations support the conclusion of Kouwenberg that the ice-core data represent general-



Fig. 8. CO₂ records from Law Dome and Mauna Loa compared to the CO₂ history as revealed from stomata (redrawn from Kouwenberg, 2004).



Fig. 9. Temperature-difference versus CO₂-concentration for (A) the Vostok ice-core data, (B) the Law Dome (DE08, DE08-2 and DSS) ice-cores and air samples collected at the South Pole in Antarctica, and (C) chemical CO₂-records.

ised averages and appear not to preserve the decadal–centennial changes in atmospheric CO_2 in the time span of 750 to 2000. It is also pointed out that the absence of centennial-scale fluctuations in the ice-core reconstructions may be explained by varying age distributions of the air in the bubbles related to the enclosure time in the firmice transition zone and/or post depositional physicochemical reactions in the ice that may increase as well as decrease the CO_2 concentration in air bubbles. The above observation by Kouwenberg (2004), affirms the position that the ice-core data are artifacts and do not represent reliably the chemical composition of the ancient atmosphere. This is because the ice is not a closed system, and even the best analytical methods cannot be of help when the matrix of the samples is wrong.

For the time-period between 200 and 750 AD Kouwenberg's (2004) results do not correlate with global temperature changes based on multi-proxy records. (Mann and Jones, 2003). She then argues that her results are unlikely to reflect pronounced changes in the global atmospheric CO_2 regime. However if one compares Kouwenberg's results to the temperature variation in Greenland (Alley, 2004), as also shown in Fig. 8 (shaded part), one may arrive at a different conclusion. In addition, as is apparent in Fig. 8 and for the time-period between 200 and 750 AD, the differences between the CO_2 -concentration form the Taylor Dome ice-cores (assumed to be around 280 ppm-Climate Change, 2001) and from stomata reach up to about 110 ppm.

3. CO₂ and temperature: the assumed correlation

In this section we concentrate on the study of a possible correlation between CO₂-concentration and temperature-difference (Hadley Centre, 2007) making use of three different sets of data, namely the Vostok ice-core (VIC) data (Petit et al., 2001), the Law Dome ice-core together with air samples collected at the South Pole (LDAS) data (Etheridge et al., 1998; Keeling and Whorf, 2005) and the chemical CO₂-records of Beck (2007).

For (a) VIC and (b) LDAS, we plot the CO₂-concentration against the temperature-difference as presented in Fig. 9. As shown, two different relations can be recognised, one for the VIC data and a separate one for the LDAS. The natural processes at work during the Vostok time-period show that the concentration of CO₂ in the atmosphere increases with temperature. A linear regression analysis yields a gradient of about 0.1 and a determination coefficient of 0.75 (see shaded region in Fig. 9). The temperature-difference varies from about -9 to 3 K for a CO₂-concentration from about 180 to 280 ppm. On the other hand, the data from the LDAS clearly show that although the CO₂-concentration reaches values well over 300 ppm the temperature-difference remains very close to the 0-base. In fact a separate linear regression analysis for LDAS yields a gradient of about 0.01 with a determination coefficient of about 0.685. The temperature-difference (Figs. 9 and 10) varies from about -0.6 to 0.6 K (i.e. a total



Fig. 10. A magnification of Fig. 9 for (B) and (C).

increase of 1.2 K) for a CO₂-concentration from about 280 to 380 ppm, with a temperature-difference projection of about 3.8 K when CO₂-concentration reaches 700 ppm (provided that all other natural factors remain the same). Even if one accepts that a certain increase in the temperature of the atmosphere may be due to the CO₂-change one cannot overlook that the projected temperature-increase (for a CO₂-concentration of 700 ppm) based on the VIC data would be in the order of about 39 K. Obviously there is a significant difference between the two forecasts. Now, looking for a unifying model of both sets of data one could possibly view a relation close to a hyperbola of the form: $Y = A - \frac{B}{X-C}$, where "saturation" occurs with temperature not increasing further as CO₂-concentration increases.

Even this speculation may become questionable if one considers the probably more (or at least as) reliable, in our view, chemical CO₂records of Beck (2007). A regression analysis based on Beck's data essentially shows no relation between temperature-difference and CO₂-concentration. The temperature-difference varies from about -0.6to 0.1 K (i.e. a total increase of 0.7 K) for a CO₂-concentration from about 280 to 440 ppm (Figs. 9 and 10), with an essentially zero temperaturedifference projection when CO₂-concentration reaches 700 ppm.

The conclusion derived from the analysis above is that one cannot be positive that indeed a relationship exists between temperaturedifference and CO₂-concentration. But even if this is the case the influence of CO₂-concentration on temperature is very weak. This conclusion is supported by Lindzen (2006) who, through a logarithmic relationship between the addition of CO₂ to the atmosphere and radiative heating, he estimated that the 100 ppm post-industrial increase in CO₂-concentration (from pre-industrial 280 to today's 380 ppm) has already caused about 75% of the anticipated 1 K warming. And all that remains to occur is an additional warming of a few tenths of a degree.

4. The adiabatic theory of the greenhouse effect

As Sorokhtin et al. (2007) mention, until recently a sound theory using laws of physics for the greenhouse effect was lacking and all numerical calculations and predictions were based on intuitive models using numerous poorly defined parameters. In order to investigate the phenomenon they devised a model based on wellestablished relationships among physical fields describing the mass and heat transfer in the atmosphere. This model uses a general approach for obtaining analytical solutions for global problems and can be further refined to incorporate additional parameters and variables for examining local problems.

Their model was based on the observation that in the troposphere (the lower and denser layer of the atmosphere, with pressures greater than 0.2 atm) the heat transfer is mostly by convection and the temperature distribution is close to adiabatic. The reasoning for this is that the air masses expand and cool while rising and compress and heat while descending.

Basic formulae describe among others, the heat transfer in the atmosphere by radiation, the atmospheric pressure and air density change with elevation, the effect of the angle of the Earth's precession and the adiabatic process. For the adiabatic process the formula considers the partial pressures and specific heats of the gases forming the atmosphere, an adiabatic constant and corrective coefficients for the heating caused by water condensation in the wet atmosphere and for the absorption of infrared radiation by the atmosphere. The adiabatic constant and the heat coefficients are estimated using actual experimental data.

This adiabatic model was verified, with a precision of 0.1%, by comparing the results obtained for the temperature distribution in the troposphere of the Earth with the standard model used worldwide for the calibration of the aircraft gauges and which is based on experimental data. The model was additionally verified with a precision of 0.5%–1.0% for elevations up to 40 km, by comparing the results with the measured temperature distribution in the dense troposphere of Venus consisting mainly of CO₂. The above results are shown in Fig. 11.

The main conclusions of this work are:

- (a) Convection accounts for approximately 67% of the total amount of heat transfer from the Earth's surface to the troposphere, the condensation of water vapour for 25% and radiation accounts for only 8%. As the heat transfer in the troposphere occurs mostly by convection, accumulation of CO_2 in the troposphere intensifies the convective processes of heat and mass transfer, because of the intense absorption of infrared radiation, and leads to subsequent cooling and not warming as believed.
- (b) The analysis indicates that the average surface temperature of the Earth is determined by the solar constant, the precession angle of the planet, the mass (pressure) of the atmosphere, and the specific heat of the atmospheric mixture of gases.



Fig. 11. Comparison of the results of the adiabatic model (curves 5 and 3) with the experimental data of Venus (curves 1 and 2) and Earth (curve 4). Source: Sorokhtin et al. (2007).



Fig. 12. A. GEOCARB model results showing the best estimate (solid line) and model results using older climate models (dashed line), redrawn from Berner and Kothavala (2001) in Skelton (2006). B. GEOCARB III model results with range in error shown for comparison with combined atmospheric CO_2 -concentration record as determined from multiple proxies in average values in 10 Ma time-steps, redrawn from Royer et al. (2004). C. Intervals of glacial (dark colour) and cool climates (lighter colour) redrawn from Royer et al. (2004). D. Estimated temperature drawn to time scale (Scotese, 2002). E. Temperature deviations relative to today (solid line—Shaviv and Veizer, 2003) from the "10/50" δ^{18} O compilation presented in Veizer et al. (2000) and temperature deviations corrected for pH (dashed line) reconstructed in Royer et al. (2004) and redrawn from Veizer et al. (2000).

- (c) If the nitrogen-oxygen atmosphere of the Earth would be replaced by a CO_2 atmosphere with the same pressure of 1 atm, then the average near-surface temperature would decrease by approximately 2.5 °C and not increase as commonly assumed.
- (d) The opposite will happen by analogy if the CO₂ atmosphere of Venus would be replaced by a nitrogen–oxygen atmosphere at a pressure of 90.9 atm. The average near-surface temperature would increase from 462 °C to 657 °C. This is explained easily by observing how the results of the derived formulae are affected, considering that the molecular weight of CO₂ is about 1.5 times greater and its specific heat 1.2 times smaller than those of the Earth's air.
- (e) If the CO₂ concentration in the atmosphere increases from 0.035% to its double value of 0.070%, the atmospheric pressure will increase slightly (by 0.00015 atm). Consequently the temperature at sea level will increase by about 0.01 °C and

the increase in temperature at an altitude of 10 km will be less than 0.03 °C. These amounts are negligible compared to the natural temporal fluctuations of the global temperature.

(f) In evaluating the above consequences of the doubling of the CO_2 , one has to consider the dissolution of CO_2 in oceanic water and also that, together with carbon, a part of atmospheric oxygen is also transferred into carbonates. Therefore instead of a slight increase in the atmospheric pressure one should expect a slight decrease with a corresponding insignificant climate cooling.

5. The geologic record

To obtain a more complete understanding of the effect of CO_2 on the Earth's history we attempt an assessment of CO_2 history through the geologic aeons.

Palaeo-climatologists calculated palaeolevels of atmospheric CO_2 using the GEOCARB III model (Berner and Kothavala, 2001). GEOCARB III models the carbon cycle on long time-scales (million years resolution) considering a variety of factors that are thought to affect the CO_2 -levels. The results are in general agreement with independent values calculated from the abundance of terrigenous sediments expressed as a mean value in 10 million year time-steps (Royer et al., 2004).

As shown in Fig. 12A and B, CO₂ levels were very high (about 26 times higher than at present according to Berner and Kothavala, 2001 or 20 times higher according to Royer et al., 2004) during the early Palaeozoic-about 550 million year ago (Ma). Then a large drop occurred during the Devonian (417-354 Ma) and Carboniferous (354-290 Ma), followed by a considerable increase during the early Mesozoic (248–170 Ma). Finally, a gradual decrease occurred during the late Mesozoic (170-65 Ma) and the Cainozoic (65 Ma to present). In Fig. 12C, D and E the range of global temperature through the last 500 million years is reconstructed. Fig. 12C presents the intervals of glacial (dark colour) and cool climates (dashed lines). Fig. 12D shows the estimated temperatures, drawn to time scale, from mapped data that can determine the past climate of the Earth (Scotese, 2002). These data include the distribution of ancient coals, desert deposits, tropical soils, salt deposits, glacial material, as well as the distribution of plants and animals that are sensitive to climate, such as alligators, palm trees and mangrove swamps. Fig. 12E presents the temperature deviations relative to today from δ^{18} O records (solid line) and the temperature deviations corrected for pH (dashed line).

As indicated in Fig. 12A, one of the highest levels of CO₂concentration (about 16 times higher than at present) occurred during a major ice-age about 450 Ma, showing that is not the CO₂concentration in the atmosphere that drives the temperature. The only logical conclusion drawn from Fig. 12 is that when the temperature of the Earth decreases the CO₂-concentration in the atmosphere decreases too because the solubility of CO₂ in the sea water increases. This physical phenomenon is very well-established as shown in Table 1. For example if seawater of salinity 35 is cooled from 20 °C to 10 °C it will absorb about 35.7% more CO₂ (aq).

Table 1

Solubility coefficient of CO_2 in sea water in equilibrium with the pure gas at a pressure of 1 atm for given temperatures

Temperature °C	Solubility coefficient
0	6.465
10	4.507
20	3.322
30	2.572
40	2.082

The solubility coefficient is the concentration of the dissolved gas ($CO_{2 (aq)}$), in moles per litre of seawater of a salinity of 35 (Weiss, 1974 in Skelton, 2006).

6. The CO₂ role in geology and biology

In this section is attempted a demonstration of the role that CO_2 has played on Earth via the biological and geological changes throughout Earth's history.

6.1. Earth's atmosphere and the recorded role of CO₂ in geologic strata

At the beginning of the Earth's history there was a great amount of CO_2 in the atmosphere as has been shown in Fig. 12. Gradually, the biological and natural processes locked a large amount of it in the rocks. Today the atmosphere of the Earth consists primarily of nitrogen (78.08%) and oxygen (20.95%). The rest 0.97% consists of the inert gas argon (0.93%) and components at trace level such as carbon dioxide (0.038%), the inert gases neon, helium and krypton, as well as hydrogen (all well under 0.002%). In addition, natural air always contains a certain amount of water vapour (0–7%). This is often neglected when giving the composition of air, although it is a very important constituent. The analogy of water vapour varies greatly with the air temperature, pressure, and humidity but typically makes up about 1% of the air (National Space Science Data Center (NSSDC), Earth Fact Sheet, 2007), a quantity much larger than CO₂.

The changes that occurred in the atmosphere and the surface of the Earth, related to CO₂, through the geological aeons are described below.

(a) Coal deposits: The geological records show that the great coal deposits of the Earth were laid down mostly in the Carboniferous period (known as the first coal-age) about 300 Ma. Coal formation continued throughout the Permian, Triassic, Jurassic, Cretaceous, and Tertiary Periods (known collectively as the second coal-age).

Coal consists mostly of carbon, which gave the name to the Carboniferous period. Coal is a member of a group of easily combustible organic sedimentary rocks composed mostly of plant remains from ancient forests. As plants and trees died, their remains formed peat deposits in swamps that were buried by sediments from rivers and lakes. With deeper and deeper burial, the heat and pressure transformed the peat to coal. A probable source of all this carbon was the atmosphere, presumably by conversion from gaseous hydrocarbons such as methane or possibly from free CO₂. The massive deposits of high-carbon rocks laid down at the end of the Paleozoic (Fig. 13), therefore suggest a major change in the atmosphere at that time. The World Energy Council, in a Survey of Energy Resources for Coal (including Lignite), gives the recoverable

reserves at the end of 2005 as 847,488 million tonnes (World Energy Council).

- (b) Chalk deposits: Cretaceous at the end of the Mesozoic era (65 Ma) was another period of major change. Cretaceous comes from the Latin world 'creta' (chalk) because of the 'chalky' deposits of that period. Chalk largely consists of minute skeletons of single-celled algae and isolated plates of calcite derived from their breakdown together with the remains of other planktonic organisms. The chalk deposits accumulated at the shallower parts of the ocean floors have thicknesses between 500 and 4000 m (Skelton, 2003).
- (c) Carbonate minerals: The carbonate mineral calcite is a chemical or biochemical calcium carbonate (CaCO₃) and one of the most widely distributed minerals on the Earth's surface, formed during the Cretaceous period. Limestone is a sedimentary rock also formed in the Cretaceous period, composed largely of this mineral. Limestone often contains variable amounts of other material like silica, clay and silt in different forms within the rock. The primary source of the calcite in limestone is usually the shells of marine organisms, especially corals and molluscs. The role of atmospheric partial pressure of carbon dioxide (pCO₂) on marine organisms and ecosystems still remains poorly understood but again, a possible source of the chalk and limestone could possibly be the conversion of the atmospheric CO₂.

The changes described above were enormous and affected the composition of the Earth's atmosphere greatly. The relative amounts of carbon in different forms on Earth are shown in Table 2 (Skelton, 2006). As it is observed the amount of carbon left in the atmosphere is actually extremely small. Almost everything that once was in the atmosphere has since been locked in the rocks.

6.2. Biological changes due to the change of CO_2 in the atmosphere

The change of the concentration of CO_2 in the atmosphere has also affected the plant physiology which evolved to adjust in an environment with a continuously diminishing amount of CO_2 .

There are three types of plants differing in their efficiency of use of CO₂. These are called C3, C4, and CAM plants, depending on the metabolic pathway for carbon fixation in photosynthesis. It is thought that C3 plants are the ancestral form that evolved at a time of elevated CO₂ concentration. Following the Cretaceous period, within the last 30 million years, in response to a period of low atmospheric CO₂-concentration and high O₂-concentration, C4 photosynthesis has evolved (Von Caemmerer et al., 2000). This is a more efficient method



Fig. 13. Map showing the main carboniferous deposits of the world (redrawn from Arduini and Teruzzi, 1994).

Table 2

The major carbon reservoirs of the Earth

Carbon reservoir	Kg×10 ¹⁵
Carbon rocks (limestone, chalk, dolomite)	42,000
Organic-rich rocks (oil, coal etc)	10,500
Methane hydrates (including marine and continental deposits)	~10
Oceans	38
Marine sediments	3
Soil and organic detritus	1.50
Atmosphere	0.76
Biosphere	0.56

of photosynthesis in the lower CO₂ conditions. Modern plants have evolved to be CO₂ 'hungry' and have therefore produced mechanisms to chase after tiny amounts of it in the air. CAM (Crassulacean acid metabolism) plants also have an extremely effective CO₂concentrating mechanism that have adapted in arid environments and in environments in which the water supply is unpredictable. Most plants on Earth are C3, with examples including sugar beet, rice and potatoes. Maize and sugarcane are examples of C4 plants.

Leaves and their stomata constitute one more indication of the changing amount of CO₂ in the atmosphere of the past (recall Section 5). Simple leafless vascular plants first colonized the land in the Late Silurian-Early Devonian period. These plants had few stomata, which served them well in a CO₂-rich atmosphere and helped them from drying out. Forty (40) million years after megaphyll leaves (leaves with a broad lamina-flat blade-like those of ferns and flowering plants) made their widespread appearance with their branched veins and planate form at the close of the Devonian period-at about 360 Ma. Beerling et al. (2001), show that this delay was causally linked with a 90% drop in the atmospheric CO₂-concentration during the Late Palaeozoic era. When planate leaves first appeared in the Late Devonian and subsequently diversified in the Carboniferous period, they possessed substantially higher stomatal densities. This observation is consistent with the effects of the pCO₂ on stomatal development. Therefore, the drawdown in atmospheric pCO₂ in the Late Palaeozoic era and the concurrent observed increase in stomatal density, is a likely ancient example of plant response to lower concentrations of CO₂. Moreover, a 40-million-year delay between the axial form of Late Silurian/Early Devonian land plants and the development of megaphyll planate leaves is consistent with the timescale required to remove CO₂ from the atmospheric reservoir by silicate rock weathering and organic carbon burial.

Summarising, great changes have occurred in the atmosphere of the Earth in the past aeons that affected life on Earth (evolution from C3 to C4-type of plants, change in stomatal density and development of megaphyll planate leaves). When the atmosphere begun to acquire its present form in the Cenozoic aeon (following the death of the dinosaurs) plants, and animals for that matter, relative to the ones we know today started emerging.

6.3. Plant growth and CO₂ enrichment

Carbon dioxide could act as a fertilizer on biomass production because it is essential for plant nutrition and it has a positive effect on photosynthesis. Discovery that the atmospheric CO₂, and not the humus as was then believed, is the only source of carbon in plants, was made more than 135 years ago by Godlewski (1873). Thus, biomass production could be higher following an increase in CO₂-concentration. Forest growth or re-growth after burning could also be stimulated (Tremblay, 2005). Such an experiment with increased concentration of atmospheric CO₂ (by 200 μ lt/lt) in a forest plantation resulted in a 26%-increase, relative to trees under ambient conditions, in the growth rate of the dominant pine trees, as well as in an increase of litterfall and fine-root, after 2 years (DeLucia et al., 1999). The total net primary production increased by 25%. Such an increase in forest net primary production, globally would fix about 50% of the anthropogenic CO_2 projected to be released into the atmosphere in the year 2050. The response of this young, rapidly growing forest to CO_2 may represent the upper limit for forest carbon sequestration (DeLucia et al., 1999).

Numerous other field experiments demonstrate that plants exhibit positive gain (although varying greatly in magnitude) when grown at elevated CO_2 -concentration. Most crop responses range from 30 to 50% increase in yield. Results from long-term experiments with woody species and ecosystems are even more variable. Huge growth responses (100 to nearly 300% increase relative to controls) are reported from several tree experiments and the salt–marsh ecosystem experiment. Other results from experiments with woody species and the tundra ecosystem suggest little or no effect of CO_2 on physiology, growth or productivity (Dahlman, 1993).

In general, the strength of the response of photosynthesis to an increase in CO_2 -concentration depends on the photosynthetic pathway used by the plant. Plants with the C3 photosynthetic pathway (all trees, nearly all plants of cold climates, and most agricultural crops including wheat and rice) generally show an increased rate of photosynthesis in response to increases in CO_2 -concentration above the present level. Plants with the C4 photosynthetic pathway (tropical and many temperate grasses, some desert shrubs, and some crops including maize and sugar cane) already have a mechanism to concentrate CO_2 and therefore show either no direct photosynthetic response, or less response than C3 (IPCC, 2001).

Carbon dioxide enrichment is commonly practiced in the cultivation of greenhouse crops because it increases both yield and profit. The response to this of pot plants, cut flowers, vegetables and forest plants is to increase dry weight, plant height, number of leaves and lateral branches. Also it is reported (Islam et al., 1996) that CO_2 enrichment increased the water-use efficiency by about 30%. Experiments on tomatoes have shown that CO_2 -enrichment enhances fruit growth and colouring, and improves their ascorbic acid content. Furthermore, the elevated CO_2 results in higher sugar concentrations and related enzyme activities than in the control.

6.4. Seasonal variation of CO₂-concentration related to plant life

At the northern hemisphere, there is a pronounced seasonal dip in CO₂-concentration (about 1–4%) below the annual mean. The yearly dip begins towards the end of the northern spring, reaching its low point towards the end of the northern summer in August-September. The peak in CO₂ each year occurs around April–May. Generally, the higher the latitude, the more pronounced the seasonal swing is. In the southern hemisphere the seasonal pattern is less pronounced and is reversed, with the peak occurring in the southern spring. The seasonal CO₂ oscillation, with a summer dip, is probably caused by the greater photosynthetic uptake during the months that are both warmer at high latitudes and wetter in the outer tropics. During spring and summer carbon is stored in leaves, fruits and other seasonal plant parts. During autumn and winter plants stop taking up carbon, fall and rot together with older parts of plants shed in previous years. Plant parts decompose at the base of the soil litter layer and continually release CO₂ through much of the year. When the photosynthetic extraction of CO₂ stops, the CO₂-release by the soil continues and pushes the CO₂concentration up slightly (Adams and Piovesan, 2002).

7. Conclusions

Earth is a dynamic planet with a continuous variation of its climate. The present study has indicated that in their turn the atmosphere, the lithosphere and the biosphere of the Earth change constantly through complex mechanisms affecting the climate. Many of these changes are unpredictable, enormous and sometimes sudden. It is certain that such natural climate-changes—both cooling and warming—will occur again and again in the future. Studying the climate record indicates that the 20th-century changes fall well within frequently seen past natural variations.

It is our view that, there is not yet sufficient let alone rigorous evidence that anthropogenic CO₂-increase is indeed the main factor contributing towards the global warming of the 20th-century. This conclusion is supported by a mere study of the inconsistent related literature, reinforced by our analysis on the (probably more reliable and thus far overlooked) chemical CO₂-records, essentially showing that one cannot be positive for a relationship between temperature-difference and CO₂-concentration. On the contrary the conclusions using the adiabatic theory show that global warming due to atmospheric CO₂-increase is impossible.

Our study also points that even when the presence of CO₂concentration in the atmosphere was at levels much higher than today, the temperature still considerably fluctuated.

Regardless of CO₂'s role on global warming, CO₂ is a key factor for biological activity that has generally benefited because of the increase observed in the last century. The change of CO₂-concentration in the atmosphere through the geological aeons has caused adaptation in plants. At the beginning of their evolution the plants had no leaves, in the next stage they produced leaves and captured CO₂ very effectively producing large deposits of coal, and in a final stage they changed their efficiency in photosynthesis to survive in a deficient environment. Palaeoclimatological data show that the atmospheric content of carbon in this geological epoch is at its minimum value.

Science today still does not really offer an adequate scheme toward understanding the Earth's complex climate system. It is therefore our belief that temperature is significantly affected by natural factors that have not yet been adequately assessed or even identified. For example one could think of water's role, as water predominantly present on land, in the ocean and in the atmosphere, as well as the Sun is the main driving force of climate. Both of these factors are rather poorly understood at present.

Finally, we would support a suggestion that the objective of better understanding the phenomenon of global warming can be realised by a collaboration of specialists from various disciplines and backgrounds, who can give detailed interpretations, explanations and sources of uncertainties for each subject related to this phenomenon.

We are grateful to the comments and suggestions made by the Referees that make the work presented in this paper more complete.

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