

A NEGATIVE FEEDBACK MECHANISM FOR THE LONG-TERM
STABILIZATION OF EARTH'S SURFACE TEMPERATURE

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Abstract. We suggest that the partial pressure of carbon dioxide in the atmosphere is buffered, over geological time scales, by a negative feedback mechanism in which the rate of weathering of silicate minerals (followed by deposition of carbonate minerals) depends on surface temperature, and surface temperature, in turn, depends on carbon dioxide partial pressure through the greenhouse effect. Although the quantitative details of this mechanism are speculative, it appears able partially to stabilize earth's surface temperature against the steady increase of solar luminosity believed to have occurred since the origin of the solar system.

Introduction

Speculation concerning the evolution of the terrestrial atmosphere is constrained by the problem of the cool sun. As pointed out by Sagan and Mullen [1972], there is a conflict between our understanding of stellar evolution, which implies that the luminosity of the sun has increased by possibly 25 percent over the age of the solar system [Newman and Rood, 1977], and the geological record of waterborne processes of sediment deposition that extends all the way back to 3.8×10^9 years before the present [Lowe, 1980]. Earth would have been too cold to sustain liquid water on its surface unless the greenhouse effect, the absorption and return to the surface of outgoing terrestrial radiation by infrared-absorbing molecules in the atmosphere, were larger in the Archean than it is today. Sagan and Mullen argued that atmospheric water vapor alone could not have provided the necessary greenhouse effect, because of the escape of radiation through windows in the absorption spectrum, and suggested ammonia as a candidate for the additional absorber. Ammonia is unattractive because of its photochemical instability and the absence of any obvious abiotic sources [Kuhn and Atreya, 1979]; the much more plausible alternative of carbon dioxide has recently been put forward by Owen et al. [1979]. With allowance for hot bands at 9, 10, 12, and 18 μ , these authors have shown that the greenhouse effect of carbon dioxide and water together is great enough to solve the cool sun problem provided the partial pressure of carbon dioxide in the past was up to 1000 times larger than it is today. High carbon dioxide partial pressures on a young and tectonically active earth seem entirely reasonable, but we are led to wonder whether it is simply chance

that has caused atmospheric carbon dioxide to decline while solar luminosity has been increasing at just such a rate as to maintain equable temperatures at the surface of the earth. In this paper we describe a negative feedback between surface temperature and carbon dioxide partial pressure that may have helped to maintain this fortunate balance.

Carbon dioxide is released by volcanoes and metamorphism from the solid earth to the atmosphere and ocean at a rate estimated by Holland [1978] to be $(3.3 \pm 1.1) \times 10^{14}$ gm yr⁻¹ CO₂, large enough to double the amount of carbon in the ocean and atmosphere in only 400,000 years. Over geologically significant periods of time carbon dioxide must be returned to the solid earth at an equal rate. The mechanism of this return is well known [Siever, 1968; Broecker, 1971; Garrels and Mackenzie, 1971; Walker, 1977; Holland, 1978]. It is the weathering of silicate minerals followed by the deposition of carbonate minerals in sedimentary rocks. The overall process can be represented as the reaction of a silicate mineral with carbon dioxide and water to yield a carbonate mineral and silica. In more detail, silicate weathering supplies cations (Ca⁺⁺ and Mg⁺⁺) in solution to the ocean where they react with carbonate ions (CO₃⁻) to precipitate as carbonate minerals. The rate of supply of cations by weathering of silicate minerals has a controlling influence on the budget of carbon in the combined atmosphere-ocean system (fluid carbon).

The Rate of Weathering of Silicate Minerals

As part of a study of the rate of supply of dissolved constituents to the ocean, Meybeck [1979] has assembled data that cast light on the factors that control the rate of silicate weathering. He has classified the rivers of the world on the basis of the runoff of water and the average temperature of the watershed, with some allowance for relief, and has then determined the average concentrations and rates of transport of a number of dissolved constituents as a function of morphoclimatic classification. The cations of greatest interest in connection with the carbon budget are Ca⁺⁺ and Mg⁺⁺, but their concentrations in river water are not indicative of silicate weathering because they are derived overwhelmingly from the dissolution of carbonate minerals [Meybeck, 1979]. The redeposition in carbonate sediments of cations released originally by carbonate weathering does not impact the budget of fluid carbon. Volcanic and metamorphic carbon is restored to the solid phase in combination with Ca⁺⁺ and Mg⁺⁺ ions that were released by silicate weathering. In

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what follows we use dissolved silica as an indication of the rate at which silicate weathering releases cations to solution [Meybeck, 1979; Garrels and Mackenzie, 1971; Holland, 1978].

Table 1 shows Meybeck's morphoclimatic classification as well as the rates of transport in solution of SiO_2 , expressed in $10^6 \text{ gm km}^{-2} \text{ yr}^{-1}$. These data show that the rate of silicate weathering increases markedly with increase in either runoff or temperature. Such behavior is entirely in accord with intuitive expectations, but it is worth noting that there may be a third influence at work. The partial pressure of carbon dioxide in the pore space of soils today is enhanced by more than an order of magnitude over the atmospheric value by root respiration and the decay of organic matter [Holland, 1978]. This enhanced pressure may promote dissolution of silicate minerals. Weathering reactions may be further promoted by organic acids. So it is possible that the temperature and runoff dependence in the rate of silicate weathering apparent in Meybeck's data is contaminated, to greater or lesser extent, by corresponding variations in plant productivity.

This complication notwithstanding, suppose that the earth were to grow markedly cooler as a result, for example, of a decrease in solar luminosity. The high-temperature high-weathering rate morphoclimatic zones would be restricted in areal extent or possibly eliminated altogether. There would probably be a decrease in global runoff also because the lower absolute humidity of a colder atmosphere would permit less transport of water vapor from oceans to continents. Both factors would contribute to a decrease in the globally averaged rate of silicate weathering.

This decrease would cause imbalance in the

budget of fluid carbon, unless there had been a parallel decrease in the rate of release of CO_2 by volcanoes and metamorphism. This imbalance would cause accumulation of carbon in the ocean and atmosphere. On a geological time scale the equilibration of the atmospheric partial pressure of carbon dioxide with the oceanic concentration of bicarbonate ions is effectively instantaneous. The partitioning of carbon between gaseous and liquid phases depends on temperature and on oceanic pH, but these factors are not of prime concern in the present connection. The almost inescapable result of a decrease in the rate of silicate weathering below the rate of volcanic and metamorphic release of carbon dioxide is an increase in the carbon content of atmosphere and ocean combined and a consequent increase in the partial pressure of carbon dioxide.

But carbon dioxide is a greenhouse gas, and an increase in its partial pressure must cause an increase in global average temperature, counteracting the assumed original decrease. This is the negative feedback mechanism that we suggest may have maintained equable surface temperatures in the face of a steady increase in solar luminosity. Over geological spans of time, we suggest, the partial pressure of carbon dioxide has adjusted to maintain surface temperatures that balance the flow of carbon through the ocean and atmosphere.

In what follows we present an estimate of the efficacy of this feedback mechanism. We must first develop a tentative functional relationship linking global average weathering rate to temperature and carbon dioxide partial pressure. We must next approximate the dependence of global average surface temperature on solar luminosity and carbon dioxide partial pressure. Then we can see whether the feedback mechanism we propose could plausibly have buffered global climate

TABLE 1. Morphoclimatic Classification and Silicate Weathering Rates [Meybeck, 1979]

Temperature, °C	Runoff, mm yr ⁻¹				
	<30	30-120	120-280	280-630	>630
<4			tundra and taiga, (0.75)	wet taiga, 1.6	very wet taiga (high relief), 5.75
4-15		semi-arid temperate, (0.8)	temperate, 1.4	wet temperate, 2.35	very wet temperate (high relief), (10)
15-25	arid, 0.25				
>20		mixed tropical, 2.35	mixed tropical, 2.35	wet tropical, 4.15	very wet tropical (plains), 11.4 very wet tropical (mountains), 16.4

Weathering rates are expressed in $10^6 \text{ gm km}^{-2} \text{ yr}^{-1}$ of dissolved SiO_2 . Parentheses signify poorly determined values.

against a secular change in solar luminosity. This examination of the feedback mechanism is most conveniently presented as a prediction of what would have happened to average temperature and partial pressure if solar luminosity had been the only relevant external parameter to have changed with time. The result should not be construed as a proposed history of atmospheric carbon dioxide and climate. Too many other factors may also have changed. These factors include the rate of volcanic and metamorphic release of carbon dioxide, paleogeography, including the area of land exposed to weathering, planetary albedo, and the possible influence of land plants on weathering rates. We are not yet in a position to deal with the consequences of possible changes in these other factors external to the feedback system we are considering. We note, however, that many of these factors may have evolved in such a way as to have sustained temperatures and carbon dioxide partial pressures early in earth history higher than the ones we shall calculate, thereby easing still further the problem of the cool sun.

Kinetics of Feldspar Dissolution

A number of experimental studies of the kinetics and mechanisms of silicate weathering reactions have been published [Wollast, 1967; Luce et al., 1972; Paces, 1973; Busenberg and Clemency, 1976; Holdren and Berner, 1979; Berner and Holdren, 1979; Lagache, 1965, 1976]. Of these, the most direct information on the temperature and CO_2 pressure dependence of the dissolution rate is provided by the work of Lagache.

Lagache exposed ground samples of simple feldspar minerals of known total surface area to attack by a known volume of water at constant temperature and constant CO_2 pressure and measured the increase of cation concentration in solution as a function of time. The results from experiment to experiment were quite reproducible and revealed that cation concentration at given temperature and pressure increases in proportion to the square root of surface area multiplied by time. The implication is that the specific dissolution rate (per unit surface area) is inversely proportional to the cation concentration. The hydrogen ion concentration (pH) may be involved; under the conditions of the experiments, H^+ concentration is inversely proportional to cation concentration.

For present purposes it is not necessary to explore kinetic details. Lagache's experiments may provide a reasonable representation of the weathering process in nature. We assume that rain water, in equilibrium with atmospheric or soil carbon dioxide, is exposed to silicate minerals for a limited period of time while it percolates through soil and porous rocks.

If chemical weathering occurs mainly during this limited period of intimate contact between water and minerals, then the overall weathering rate is simply proportional to the cation concentration at the end of this time. Thus, we need to know how this concentration varies with temperature and CO_2 pressure after a fixed period of interaction. Lagache's experiments provide this information directly, admittedly at temperatures and pressures much higher than

those encountered in nature, 100° to 200°C and 2 to 20 bars. We shall assume that the temperature and pressure dependences measured by Lagache apply also under the conditions of weathering at the earth's surface. The extrapolation to lower temperature can be verified by reference to Meybeck's field data, as shown below. We have not devised a method to verify the extrapolation to low CO_2 partial pressure.

Lagache's data on the dissolution of both albite ($\text{Na Al Si}_3 \text{O}_8$) and adularia ($\text{K}_{0.84} \text{Na}_{0.16} \text{Al Si}_3 \text{O}_8$) show cation concentrations after a fixed period of reaction at three temperatures (100° , 150° , and 200°C) that can be represented by an Arrhenius temperature dependence of $\exp(-4600/T)$ where T is absolute temperature. Over a restricted temperature range near 285°K , this dependence can be approximated by $\exp\{(T-285)/17.7\}$. The work of Busenberg and Clemency [1976] shows that calcium-bearing silicate minerals, the ones of interest with respect to the carbon cycle, exhibit the same dissolution kinetics as sodium and potassium silicates as a function of time, but whether the similarity extends to the temperature dependence of the dissolution rate is not known.

Figure 1a plots Meybeck's data on the concentration of dissolved silica in river water against runoff at various temperatures. The concentrations show no obvious dependence on runoff, lending support to our hypothesis that the average time during which a given sample of water can react with silicate minerals is not highly variable.

Figure 1b plots the average concentration of dissolved silica against average temperature. The dashed line shows the slope of the temperature dependence deduced above from Lagache's laboratory data on dissolution of feldspars. The laboratory and field data are reasonably consistent. We shall, therefore, use this expression to represent the direct dependence of weathering rate on temperature.

For the pressure dependence of the cation concentration after a fixed period of reaction Lagache's data for both albite and adularia at $P=2, 6, \text{ and } 20$ bar can be represented as proportional to $P^{0.3}$, where P is the partial pressure of carbon dioxide. We shall assume, for purposes of illustration, that this same expression holds at the much lower partial pressures encountered in natural weathering. The effectiveness of the proposed temperature buffer depends strongly on the pressure dependence of the weathering rate. A weaker pressure dependence would provide stronger feedback.

The average rate of release of cations by the chemical weathering of silicate in a given drainage basin (in units of mass per unit area per unit time) is the product of cation concentration (in mass per unit volume) in river water and runoff expressed in volume per unit area per unit time. We have shown that the concentrations are approximately independent of runoff but depend on temperature and possibly also on CO_2 partial pressure. The weathering rate is $W \propto RP^{0.3} \exp\{(T-285)/17.7\}$ where R is the runoff.

Intuitively we might suppose that R is also an increasing function of temperature because warm air can carry more moisture from ocean to continent than cold air. Indeed, zonally aver-

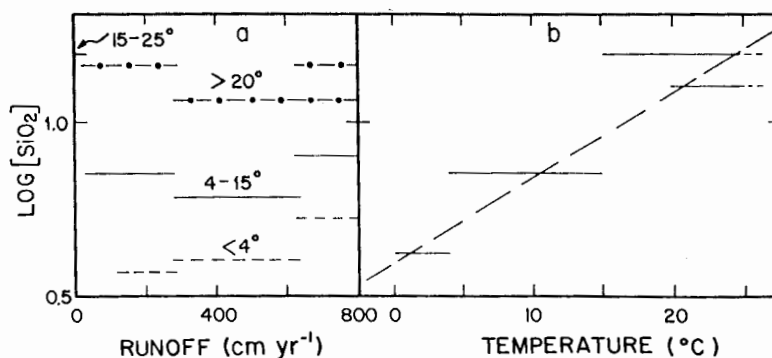


Fig. 1. The logarithm of the concentration of dissolved silica (mg l^{-1}) in river water [Meybeck, 1979]: (a) as a function of runoff at various annual average temperatures ($^{\circ}\text{C}$); (b) as a function of annual average temperature. The dashed line shows the slope of the temperature dependence deduced from the laboratory data of Lagache [1965].

aged annual precipitation [Sellers, 1965] is approximately proportional to the saturated vapor pressure of water at the zonally averaged annual mean temperature, a dependence of precipitation $\propto \exp\{(T-285)/14.1\}$. Climatological models of Manabe and Stouffer [1980], Wetherald and Manabe [1975], and Manabe and Wetherald [1980] show a much weaker dependence of globally averaged runoff on the average global temperature, however, approximately $R \propto \exp\{(T-285)/60\}$. We shall adopt the conservative estimate, noting that a stronger dependence of runoff on temperature would provide a more effective temperature buffer.

Then, combining the direct temperature dependence of the weathering rate deduced from the data of Lagache and Meybeck with the weak temperature dependence of runoff implied by the work of Manabe and colleagues and the pressure dependence deduced from the laboratory experiments of Lagache we obtain for the global rate of silicate weathering

$$W/W_0 = (P/P_0)^{0.3} \exp\left(\frac{\Delta T}{13.7}\right) \quad (1)$$

where ΔT is the departure of global average temperature from its present day value of 285°K [Sellers, 1965], W_0 is the present day rate of silicate weathering, and P_0 is the current partial pressure of CO_2 .

To maintain a balanced flow of carbon through the ocean-atmosphere system, the average rate of silicate weathering must always have been very nearly proportional to the rate of release of CO_2 by volcanoes and metamorphism, which we designate V . Changes in the mass of fluid carbon corresponding, for example, to changes in the bicarbonate ion concentration in sea water become negligible when converted into rates of throughput by dividing by geological spans of time.

Equating W/W_0 to V/V_0 and rearranging (1) we obtain an expression for CO_2 partial pressure

$$P/P_0 = \left(\frac{V}{V_0}\right)^{10/3} \exp\left(\frac{-\Delta T}{4.11}\right) \quad (2)$$

Dependence of Global Average Temperature on Carbon Dioxide Partial Pressure

We estimate average surface temperature, T_s , under varying conditions by separating the greenhouse effect due to water vapor and carbon dioxide

$$T_s = T_e + T_g(\text{H}_2\text{O}) + T_g(\text{CO}_2) \quad (3)$$

an expression that ignores the effect of overlap in the absorption bands of the two species. In this expression, T_e is the effective temperature, dependence on incident solar flux, planetary albedo, and the flux factor [Goody and Walker, 1972; Henderson-Sellers and Meadows, 1976], while T_g refers to the increment in surface temperature resulting from the atmospheric greenhouse.

For the greenhouse effect of water vapor we have used the results of Rodgers and Walshaw [1966] as quoted by Henderson-Sellers and Meadows [1976], together with the assumption that the surface pressure of water vapor is one-quarter of the saturated vapor pressure at the average surface temperature. For surface temperatures not too different from the present average of 285°K the results are closely reproduced by the expression

$$T_g(\text{H}_2\text{O}) = 29.7 + 0.5 (T_s - 285)^{\circ}\text{K} \quad (4)$$

Although vapor pressure increases exponentially with increasing temperature, the greenhouse effect increases logarithmically with vapor pressure, due to saturation of the absorption bands, so a linear dependence of greenhouse effect on surface temperature results.

To estimate the greenhouse effect due to carbon dioxide we have used the results of Owen et al. [1979]. By subtracting from their quoted surface temperatures both T_e and $T_g(\text{H}_2\text{O})$ we find

$$T_g(\text{CO}_2) = 2.3 \left(\frac{P}{P_0}\right)^{.364} \quad (5)$$

This expression agrees quite well with values for the greenhouse effect for a pure CO_2 atmo-

sphere given by Henderson-Sellers [1976]. Our simple expressions ignore the dependence of infrared opacity on total atmospheric pressure and on temperature.

Combining these expressions and writing the results in terms of departures from the present global average surface temperature of 285°K and the present effective temperature of 253°K [Goody and Walker, 1972], we obtain

$$\Delta T = 2\Delta T_e + 4.6 \left(\frac{P}{P_0}\right)^{.364} - 4.6 \quad (6)$$

where $\Delta T = T_s - 285^\circ\text{K}$ and $\Delta T_e = T_e - 253^\circ\text{K}$. This expression reproduces the results of Owen et al., from which it was derived. It yields a temperature increase of 1.3°K in response to a doubling of the carbon dioxide pressure, which can be compared with a typical value of 2°K obtained in detailed studies [Henderson-Sellers and Meadows, 1979; Hoyt, 1979; Manabe and Stouffer, 1979, 1980; Wetherald and Manabe, 1981]. A more detailed parameterization of the dependence of temperature on carbon dioxide partial pressure would result in a more strongly buffered temperature, particularly at low partial pressures.

Response of the Climate-Carbon Dioxide System to External Perturbations

In this highly simplified representation, the feedback system that couples carbon dioxide partial pressure and average surface temperature is described by two equations. Equation (2) expresses the dependence of carbon dioxide pressure P on surface temperature T ($\Delta T = T_s - 285^\circ\text{K}$) and rate of release of CO_2 by volcanoes and metamorphism. Equation (6) expresses the dependence of surface temperature on effective temperature T_e (a function of solar luminosity and albedo) and CO_2 pressure. The controlling factors external to the system are T_e and V . Specification of these two factors uniquely determines surface temperature and carbon dioxide partial pressure.

Figure 2 shows how surface temperature and CO_2 partial pressure vary with effective temperature for various values of the volcanic and metamorphic source of CO_2 . The broken line shows the surface temperature variation for a situation of no negative feedback (constant P). The feedback mechanism we have postulated reduces surface temperature change by about a half for $V/V_0=1$ (the present CO_2 release rate). Larger CO_2 release rates yield more CO_2 and stronger feedback. The curvature of the temperature plots reflects weaker feedback at the lower CO_2 partial pressures that correspond to higher effective temperatures. Our parameterization of the CO_2 greenhouse effect probably underestimates the feedback at low partial pressures.

Effective temperature varies as the fourth root of solar luminosity, other factors being equal, so a reduction of solar luminosity by 25% early in earth history corresponds to $\Delta T_e = 18^\circ$, which yields $\Delta T = 18^\circ$ for $V/V_0=1$, or $T = 265^\circ\text{K}$. With the parameters we have presented, our proposed feedback mechanism cannot solve

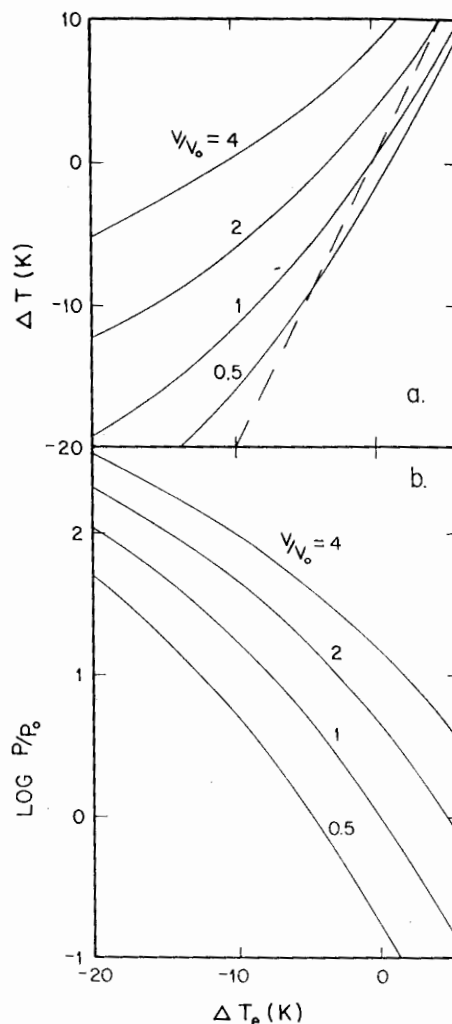


Fig. 2. Change in surface temperature ($\Delta T = T_s - 285^\circ\text{K}$) and carbon dioxide partial pressure (P) as functions of change in effective temperature ($\Delta T_e = T_e - 253^\circ\text{K}$) for several values of the volcanic and metamorphic source of CO_2 . Present day values are designated P_0 and V_0 . The broken line shows the surface temperature variation for constant CO_2 pressure.

the cool sun problem all by itself, although it reduces the magnitude of the problem considerably. Factors that may have yielded higher CO_2 partial pressures and, therefore, a warmer surface early in earth history include more rapid release of CO_2 by volcanoes and metamorphism, less land area exposed to weathering, and less terrestrial vegetation yielding less corrosive groundwater. The possible impact of the first of these factors is illustrated by the curves for different values of V/V_0 in Figure 2. The same curves illustrate the impact of land area since reduced land area is equivalent to increased release rate at the present level of approximation.

Conclusion

We have attempted a quantitative evaluation of our proposed feedback mechanism in the full

realization that our simple parameterization of the problem may be grossly in error. Existing computational schemes should permit immediate improvement in the greenhouse calculation, but more study is needed of the temperature and partial pressure dependences of the weathering rate. A model that incorporated latitudinal variation in temperature, runoff, and exposed land area could be particularly interesting.

Regardless of inadequacies in our quantitative model, we think that the concept of a buffering mechanism involving the greenhouse effect of carbon dioxide and the temperature dependence of silicate weathering is very likely to be correct. In particular, the weathering rate must fall to very low values at temperatures below the freezing point of water due to the cessation of normal processes of precipitation, erosion, and runoff. The corresponding decrease in the rate of consumption of carbon dioxide might well be sufficient to avert the so-called 'ice catastrophe,' which afflicts models of global energy balance in the presence of ice albedo feedback [Budyko, 1977; Sellers, 1969; North, 1975; Warren and Schneider, 1979]. If global glaciation were to occur, the rate of silicate weathering should fall very nearly to zero, and carbon dioxide should accumulate in the atmosphere at whatever rate it is released from volcanoes. Even the present rate of release would yield 1 bar of carbon dioxide in only 20 million years. The resultant large greenhouse effect should melt the ice cover in a geologically short period of time.

The mechanism we have proposed, in which carbon dioxide pressure and consequently carbon dioxide greenhouse effect are buffered by the temperature dependence of the rate of consumption of carbon dioxide in the weathering of silicate minerals, may impact our understanding of the evolution of the atmospheres of Venus and Mars. Such impact remains to be explored. It is worth noting that the mechanism may lose its force when the carbon dioxide pressure falls much below modern terrestrial values, as a result of increasing solar luminosity or decreasing rate of volcanic release of carbon dioxide, and the greenhouse effect of carbon dioxide becomes negligible compared with that of water. The terrestrial biota may, over the long term, have to adjust to the steady disappearance of carbon dioxide as well as the steady increase of average surface temperature.

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