



ELSEVIER

Palaeogeography, Palaeoclimatology, Palaeoecology 146 (1999) 33–51

PALAEO

On the possible influence of extraterrestrial volatiles on Earth's climate and the origin of the oceans

David Deming*

School of Geology and Geophysics, University of Oklahoma, Norman, OK 73019, USA

Received 16 October 1997; revised version received 17 August 1998; accepted 24 August 1998

Abstract

A consideration of observational and circumstantial evidence suggests that Earth may be subject to high influx rates (10^{11} – 10^{12} kg/yr) of extraterrestrial-sourced volatile elements (carbon, hydrogen, oxygen, nitrogen) derived from comets or other primitive solar-system material. The total extraterrestrial influx rate may be four to five orders of magnitude greater than previously thought, large enough to account for today's total near-surface inventories of water and carbon. The possibility of high rates of extraterrestrial volatile-accretion suggests a new climatic paradigm wherein Earth's surface temperature is influenced by conflicting internal and external processes. A variable influx of volatile elements tends to warm the Earth, while terrestrial processes cool the planet by absorbing these gasses at a more uniform rate. Variations in extraterrestrial influx rates may explain the variation of sea level and mean global temperature over geologic time, as well as some types of climate change, the occurrence of the Pleistocene ice ages, and the asymmetry of the Phanerozoic climate record (sudden warmings, slow coolings). The extraterrestrial influx rate may also act as the pacemaker of terrestrial evolution, at times leading to mass extinctions through climatic shifts induced by changes in accretion rates with concomitant disruptions of the carbon and nitrogen cycles. Life on Earth may be balanced precariously between cosmic processes which deliver an intermittent stream of life-sustaining volatiles from the outer solar system or beyond, and biological and tectonic processes which remove these same volatiles from the atmosphere by sequestering water and carbon in the crust and mantle. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: paleoclimatology; climate; catastrophism; ice ages; mass extinctions; biologic evolution; comets

1. Introduction

Over the past ten to fifteen years, our understanding of Earth's climate has been challenged by new data which cannot easily be explained by existing paradigms. Cores collected as part of the Deep Sea Drilling Program document that a remarkably large and abrupt warming occurred near the Paleocene–

Eocene boundary about 55.5 Myr ago (Kennett and Stott, 1991; Thomas and Shackleton, 1996; Dickens et al., 1997). Simultaneous with this warming, an immense quantity of carbon greatly enriched in ^{12}C was rapidly added to the combined ocean–atmosphere inorganic carbon reservoir. The amount of carbon that was added is much greater than can be obtained from any conventional terrestrial reservoir (Dickens et al., 1997).

Analyses of ice-cores and ocean-floor sediments show that repeatedly during the last ice age

* Tel.: +1-405-325-6304; Fax: +1-405-325-3140; E-mail: ddeming@ou.edu

Earth's climate underwent frequent, large and abrupt changes that were synchronous worldwide (Dansgaard et al., 1993; Grootes et al., 1993; Blanchon and Shaw, 1995; Nicholls et al., 1996, p. 177; Broecker, 1997a,b). The ultimate cause of such abrupt shifts in mean global temperature is unknown. It was previously thought that these rapid changes in climate were confined to the North Atlantic and Arctic, and thus could be explained by changes in Atlantic circulation. However, the discovery that these climatic events were worldwide makes them much more difficult to explain (see discussions by Broecker, 1997a,b).

New results have also cast doubt on whether or not the Milankovitch theory adequately explains the 100,000-yr cycle of Pleistocene glaciations. Precise radioactive-dating of a calcite vein from Devil's Hole, Nevada, shows that about 140,000 yr ago an interglacial period may have already been underway, even though solar insolation was at a minimum (Winograd et al., 1992). Analyses of proxy climate records from cores collected in the western Pacific Ocean have found that the inclination of Earth's orbit may drive the Pleistocene glacial cycles, even though inclination has no significant effect on solar insolation (Muller and MacDonald, 1997a,b).

Over the same time period that new data have challenged existing climatic paradigms, quantitative estimates have shown that volcanic outgassing rates are too low to explain the origin of the oceans and the crustal carbon inventory (Bebout, 1995). Water and carbon are being carried down into the mantle by subduction much faster than they are being released to the surface by outgassing. Simultaneously, mineralogic studies have concluded that subduction may carry vast amounts of water down into the mantle where it can be stored in the form of dense hydrous magnesium silicates (DHMS) (Smyth, 1994; Bose and Navrotsky, 1998).

It is entirely possible that these separate and apparently unrelated phenomena could be attributable to one or more terrestrial mechanisms which are unknown or poorly understood at the present time. However, it is also possible that these unsolved problems could be explained through a new and unifying theory. The purpose of this paper is to suggest as a working hypothesis that Earth's supply of volatile elements may have largely originated from on-

going extraterrestrial accretion. The extraterrestrial volatile-accretion (ETV) hypothesis also postulates that the accretion of volatile elements may have had a significant effect on Earth's climate over geologic time, and thus influenced organic evolution. With the exception of observational evidence for the accretion of small, water-rich comets (Frank and Sigwarth, 1993, 1997a,b, 1997c,d), the evidence for an ETV hypothesis is largely circumstantial and subject to interpretation. Taken by itself, each line of evidence is weak and inconclusive; it is the sum of the evidence that is compelling. Phenomena which are apparently unrelated and difficult to explain with existing theories fall neatly into place when the possibility of a previously unsuspected astronomical mechanism is considered.

In the following sections, I first review in moderate detail two examples of climatic mysteries which suggest that our current understanding of Earth's climate may be incomplete. The absence of suitable hypotheses thus implies the necessity of entertaining a new hypothesis. I then present the ETV hypothesis itself, broadly painted in general terms, with the understanding that what is being proposed is not to be interpreted as dogma, but as working hypothesis subject to being tested and possibly disproven. I review evidence that supports the hypothesis, and finally discuss and speculate on some of the possible consequences.

2. Two climatic mysteries

In this section, I briefly review the existence of two climatic phenomena for which we either have no viable hypothetical explanations, or for which existing hypotheses have large difficulties. The relative importance of some of these difficulties is subject to interpretation and may be extremely controversial. However, there can be no doubt that there exist some terrestrial climatic phenomena for which data may conflict with current theories in some respects.

2.1. *The Pleistocene ice ages*

For the last 60 to 70 million years, the Earth has been cooling, especially at high latitudes (Fig. 1). The culmination of this cooling trend has been the

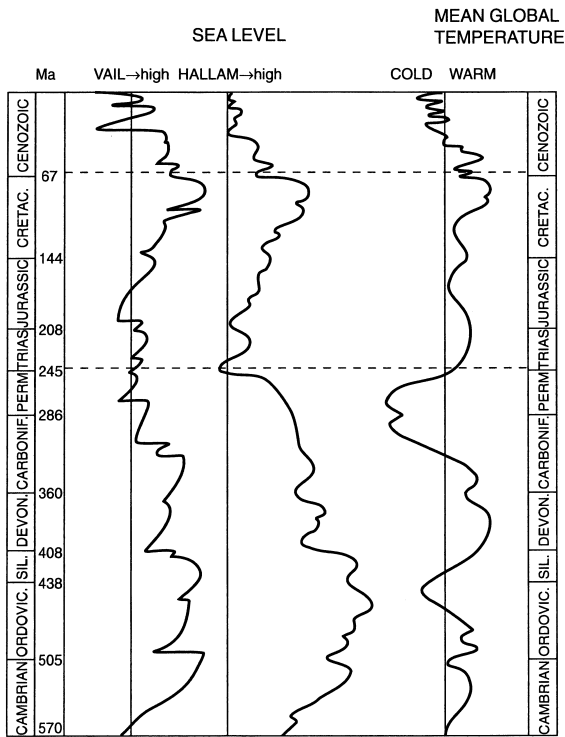


Fig. 1. Estimated mean global temperature and sea level for Phanerozoic times. Sea level curves are from Vail et al. (1977) and Hallam (1992). Note inflections in sea-level curves at both the Permian–Triassic and Cretaceous–Cenozoic boundaries (after Frakes et al., 1992).

occurrence of the Pleistocene ice ages, wherein mean planetary temperatures drop periodically by 5°C or more and large areas at high latitudes are covered by vast ice sheets. For the last 600,000 yr, ice ages have occurred in a 100,000-yr cycle (Frakes et al., 1992, p. 138). The prevailing theory which explains this glacial cycle is the Milankovitch theory of variations in insolation related to changes in Earth's orbital parameters (Milankovitch, 1930; Hays et al., 1976; Imbrie et al., 1992, 1993a,b). As more detailed and precise climatic data have become available, however, certain inadequacies in the Milankovitch theory have become apparent (see Muller and MacDonald, 1995, for a succinct review).

First, the Milankovitch theory does not explain the cooling over geologic time which is the actual cause of the ice ages. The Pleistocene glaciations did not suddenly spring into existence without antecedent. They are the logical culmination of a long-term cool-

ing trend which began about 60 million years ago. The Milankovitch theory only seeks to explain the relative timing of glacial–interglacial episodes. Even in that respect, however, there are difficulties. Although there can be no doubt that variations in solar insolation affect Earth's climate, the 100,000-yr insolation cycle is out of phase with the 100,000-yr climate cycle (Imbrie et al., 1993a). Because Earth's climate system is complex, phase problems are not necessarily a fatal weakness. For example, Imbrie et al. (1993a) have argued that phase lags are a natural consequence of the thermal inertia of the ice sheets. However, there are other problems. Milankovitch theory predicts insolation cycles of 23,000, 41,000, and 100,000 yr. The largest temperature changes have a 100,000-yr periodicity, but the 100,000-yr Milankovitch cycle exhibits the smallest insolation variation. In fact, changes in insolation associated with the 100,000-yr Milankovitch cycle (0.2%) are too small by a factor of ten to explain planetary temperature changes (Frakes et al., 1992, p. 141). The 100,000-yr insolation cycle may be amplified by terrestrial feedbacks. However, we then encounter the logical problem of explaining why the larger 23,000- and 41,000-yr insolation cycles are not similarly amplified by terrestrial processes.

The Milankovitch theory may also suffer from causation problems. Isotopic data from Devil's Hole, Nevada, and the Vostok Ice Core from the Antarctic, show that prior to the penultimate glacial termination about 140,000 yr ago, temperature began to increase when insolation was decreasing. Temperature continued to increase for 10,000 yr while insolation decreased (Fig. 2). If variations in insolation control planetary temperature, as the Milankovitch theory predicts, it is difficult to understand how temperature could have begun rising before solar insolation increased. It is also difficult to avoid this logical contradiction by supposing that the Devil's Hole and Vostok records are not representative of global climatic conditions, but rather record local warming events. The simultaneous initiation of local warming trends, each lasting 10,000 yr, at sites in different hemispheres, would be a profound coincidence. It is more parsimonious to interpret the Devil's Hole and Vostok records as the common reflection of a global trend (Winograd et al., 1992, 1997; Shaffer et al., 1996; Edwards et al., 1997). Another causa-

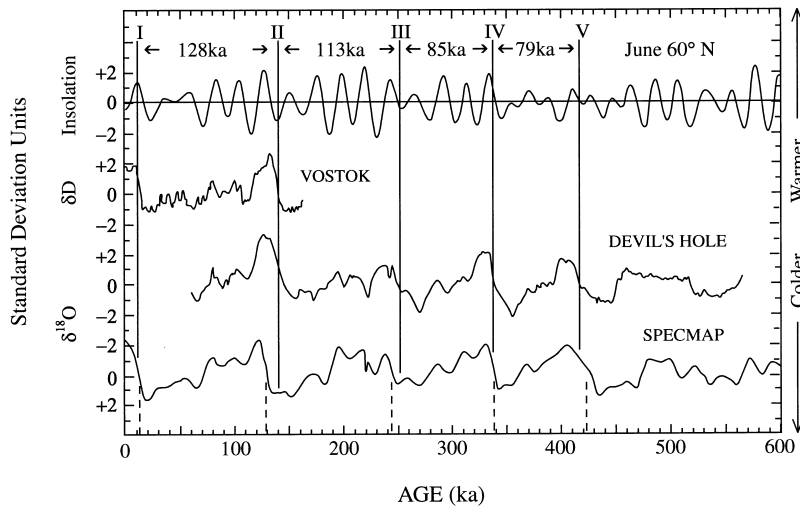


Fig. 2. June insolation at 60°N and isotopic variations from the Vostok Ice Core, Devil's Hole vein calcite (DH-11), and marine cores (SPECMAP). Solid vertical lines represent time of glacial terminations as inferred from Vostok and Devil's Hole records. Dashed vertical lines represent time of terminations as inferred from the SPECMAP record (after Winograd et al., 1992, p. 257).

tion problem is that isotopic data from both Devil's Hole (Winograd et al., 1992, 1997) and SPECMAP (Imbrie et al., 1984) show that a glacial termination (Termination V) occurred about 420,000 yr ago even though there was no significant increase in insolation.

While the 100,000-yr insolation change is out of phase with climate change, concentrations of greenhouse gasses are both correlated with temperature and in phase. Raynaud et al. (1993) described the overall correlation between temperature and CO₂ concentrations inferred from analysis of Antarctic ice cores as 'remarkable'. Most conventional climatic theories explain the correlation of greenhouse-gas concentrations and temperature through feedback mechanisms that amplify Milankovitch insolation variations (e.g., see discussion by Raynaud et al., 1993), reversing the normal cause and effect relationship between temperature and greenhouse-gas concentration. This reversal is an awkward consequence of forcing data to fit theory. Planetary temperatures for the last 600,000 yr have exhibited a 100,000-yr periodicity. If the periodicity is attributed to the effect of greenhouse-gas changes, then there must be a terrestrial mechanism that produces changes in greenhouse-gas concentrations with a 100,000-yr periodicity. However, it is difficult to imagine any terrestrial mechanism which might

modulate a process such as vulcanism into releasing CO₂ at regular intervals. To obtain a rhythmic forcing periodicity, we need to look to an astronomical mechanism. The only known forcing function with a 100,000-yr periodicity is a Milankovitch insolation cycle. Paleoclimatologists are thus led to the awkward conclusion that greenhouse-gas concentrations follow temperatures, reversing the usual thermophysical relationship.

The lack of an alternative hypothesis to explain the correlation between temperature and greenhouse-gas concentrations forces conflicting data to be ignored. For example, although feedback mechanisms undoubtedly operate to some degree, there is some question as to whether or not they can fully explain the high in-phase correlation of CO₂ with temperature changes inferred from oxygen isotopes. If increases in CO₂ concentrations are caused by temperature changes, increases in CO₂ concentrations should lag temperature increases, yet they do not. During the penultimate deglaciation (about 140,000 yr ago), increases in CO₂ concentrations unambiguously preceded local temperature increases (Raynaud et al., 1993). Clearly, these data do not support the idea that greenhouse-gas concentrations follow temperature.

Estimates of paleotemperatures from low-latitude sites in Jamaica and Australia (e.g., Goodfriend

and Mitterer, 1993; Miller et al., 1997) have found that Late Pleistocene land temperatures were 8–9°C colder than during the Holocene. It is thus apparent that the Pleistocene ice ages represented a profound change in the thermal state of the entire Earth; they were not merely changes in the manner in which heat was distributed over the surface of the planet. The ice ages cannot be explained solely through changes in terrestrial mechanisms such as ocean currents or winds which merely redistribute the sun's heat. Planetary-wide changes in temperature imply fundamental changes in either the amount of solar energy reaching Earth or the radiative balance of the planet.

A vexing question to which we have no good answer is this: why do ice ages end? Why did the fundamental thermal balance of the planet in Pleistocene times change abruptly every 100,000 yr? There are positive feedbacks associated with planetary cooling which should have led to further cooling. The growth of ice sheets increases the mean albedo of the planet and reduces the amount of solar radiation absorbed. Greenhouse warming is also reduced by colder temperatures. Cold air contains less water vapor than warm air, and cooler oceans would have retained CO₂ at higher concentrations. It is thus not surprising that the record of the last four glaciations (Fig. 2) is generally one of decreasing temperature over time. What is extraordinary is the sudden end of these ice ages. If, as Winograd et al. (1992) wrote, "orbitally controlled variations in solar insolation were not a major factor in triggering deglaciations", then why did warm interglacial episodes appear suddenly from the coldest extent of the Pleistocene ice ages? The 100,000-yr periodicity of the glacial cycle suggests an astronomical origin, yet the 100,000-yr insolation cycle is both out of phase with the climate cycle and too small to explain planetary temperature changes.

2.2. *The Paleocene–Eocene boundary*

The Paleocene–Eocene boundary (about 57–58 Ma) is marked by a unique climatic and biotic disturbance (Kennett and Stott, 1991; Thomas and Shackleton, 1996; Dickens et al., 1997). Oxygen isotope data indicate that in the Late Paleocene (about 55 Ma), temperatures at high-latitude locations and in the deep ocean increased by 4–6°C in less than

10,000 yr. There was a simultaneous disruption of the planetary carbon-cycle, with the concentration of ¹³C decreasing rapidly. Carbonate and organic matter show a δ¹³C change of about –2.5‰ over 10⁴ yr, followed by an exponential return to initial values over about 2 × 10⁵ yr. The carbon excursion was global in its nature, with isotope anomalies occurring in both deep and surface ocean waters as well as on continents. The remarkable magnitude, timing, and global nature of the δ¹³C excursion imply that an immense quantity of carbon greatly enriched in ¹²C was rapidly added to the combined ocean–atmosphere inorganic carbon reservoir (Kennett and Stott, 1991, p. 225; Dickens et al., 1997, p. 259). The temperature and carbon anomalies were accompanied by a mass extinction of benthic foraminifera; the extinction was unique in its global synchronicity, extent, and rapidity (Thomas and Shackleton, 1996, p. 403).

The Paleocene–Eocene anomaly can not be explained by the addition of CO₂ from volcanic sources, because mantle CO₂ is not sufficiently enriched in ¹²C. The anomaly also can not be explained by a transfer of terrestrial biomass, because the terrestrial biomass is not large enough (Dickens et al., 1997). Dickens et al. (1997) recently proposed that the isotopic anomalies near the Paleocene–Eocene boundary could be explained by the sudden release of methane from hydrates in the upper few hundred meters of the oceanic crust. Although methane release may have been an important factor in the rapid climate change that occurred near the Paleocene–Eocene boundary, there are some problems with this hypothesis as a sole explanation. Heat-conduction theory shows that the rate at which a sudden warming at the sea-floor surface propagates into the subsurface and causes the release of methane decreases exponentially with increasing time (Carslaw and Jaeger, 1959). It may thus be difficult to achieve a methane release sufficiently rapid to satisfy the constraints, depending upon the rate of warming, the distribution of clathrates, and the thermal properties of the oceanic crust. The hypothesis also leaves unanswered the cause of the warming which released the methane. The ocean floor can be warmed by a reversal in the pattern of deep-ocean circulation, but then we are left with the question of what caused the change in oceanic circulation.

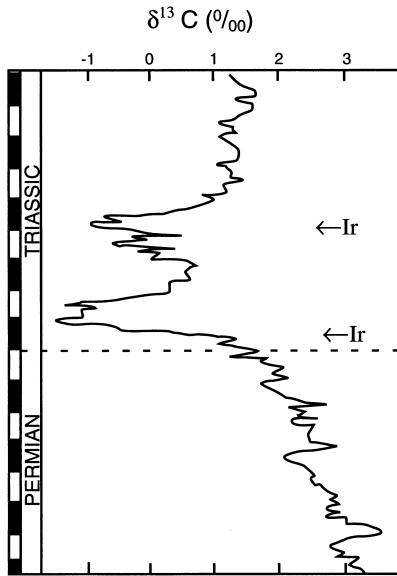


Fig. 3. Carbon-isotope curve for a core from the Carnie Alps, Austria, encompassing the Permian–Triassic boundary. Core covers about 50 m of section; alternating black-and-white bars represent about 110,000 yr of time per bar. Arrows indicate sites of elevated iridium (Ir) concentrations (after Rampino and Haggerty, 1996, p. 16).

The Paleocene–Eocene boundary is unique in that the magnitude and rapid timing of the ^{12}C excursion exclude the possibility that any conventional mechanism in the global carbon-cycle was a primary cause of the carbon-cycle disruption (J. Dickens, pers. commun., 1997). However, the events which occurred at the Paleocene–Eocene boundary were not unique in their character. The geologic record shows a repeated pattern over Phanerozoic times of mass extinctions coinciding with iridium and stable-isotope anomalies (see review by Rampino and Haggerty, 1996). Major biostratigraphic boundaries commonly exhibit an increase in the concentration of iridium with simultaneous or nearly simultaneous carbon and oxygen isotopic anomalies (Fig. 3). The usual interpretation of the oxygen anomalies is a global warming of the order of 1 to 10°C.

3. The ETV hypothesis

As a working hypothesis, I suggest that Earth is subject to ongoing accretion of volatile elements at

rates orders of magnitude higher than previously suspected. Volatile accretion through geologic time has resulted in the accumulation of significant stores of water and carbon near the Earth's surface. Volatile accretion is also postulated to affect the radiative balance of the planet, and thus climate and organic evolution. The extraterrestrial-volatile-accretion (ETV) hypothesis has the following tenets:

(1) Earth accretes substantial amounts of volatile elements (carbon, hydrogen, oxygen, nitrogen) from extraterrestrial sources. These volatiles may enter Earth's atmosphere in the form of compounds such as H_2O , CO_2 , CH_4 , NH_3 , CO , and NO_2 , thought to exist in comets. Other elements may oxidize during atmospheric entry (e.g., carbon to carbon dioxide) or undergo complex chemical reactions. The exact composition and influx rate is unknown; however, the influx rate is high enough to exert a climatic influence, and therefore orders of magnitude higher than previously suspected. The nature of the climatic effect is to increase the mean planetary temperature, this is probably accomplished primarily through the accumulation of CO_2 in the atmosphere.

(2) The influx rate may be modulated by one or more periodicities related to astronomical factors. The influx rate may also be highly variable, as has been observed for more conventional objects such as meteors, whose influx rate at times may be as much as 100,000 times the background rate. Sudden and large influxes of extraterrestrial volatiles may disrupt planetary biological and geochemical cycles and leave isotopic markers in the geologic record.

(3) The prevailing assumption of balanced hydrologic and carbon cycles is false. The rate at which carbon and water are fixed in the solid Earth exceeds the rate at which these elements return to the atmosphere, oceans, and biosphere through processes such as volcanic outgassing. Fixation of carbon through terrestrial processes such as weathering, sedimentation, and subduction, tends to cool the Earth as the concentration of atmospheric CO_2 drops (e.g., Raymo et al., 1988; Berner, 1990; Raymo and Ruddiman, 1992). Terrestrial processes are thus inherently inimical to life, and the Earth's natural state in the absence of ongoing volatile accretion may be an ice-covered planet. The conflict of accretionary and terrestrial processes leads to an asymmetry in the climatic record, as warming accretionary events

tend to be rapid, abrupt, and discontinuous, while cooling terrestrial processes tend to be slower and more uniform in their temporal character.

(4) Unusually high or low volatile-accretion rates may be responsible for high extinction rates and moderate the evolution of life on Earth. Low volatile-accretion rates produce biotic stresses by leading to cold and dry climates. High volatile-accretion rates produce more equable warm and humid climates, during which life may flourish. Catastrophic accretion events such as likely happened at the Cretaceous–Tertiary border may not be isolated events, but extreme end points on a continuum. The extraterrestrial-accretion rate may act as the pace-maker of biologic evolution by both sustaining and destroying life.

(5) When the Earth and solar system were younger, accumulation events were likely larger in magnitude or more frequent, or both. As geologic time has progressed, the extraterrestrial influx has likely lessened as the source reservoir has diminished. However, the chemical (e.g., silicate weathering), mechanical (e.g., subduction), and biological processes (e.g., formation of limestones) which fix carbon and water in Earth's crust and mantle have continued with little abatement. Thus the overall trend over geologic time has been for the surface of the Earth to cool.

(6) The source of accreted volatiles is unspecified and unknown at the present time. The most likely candidates for the extraterrestrial reservoir in which accreted material originates are the classical Oort cloud and the massive inner Oort cloud (Hills, 1981), which may contain up to 100 times as many comets as the classical Oort cloud (Weissman, 1986, p. 219). Sources outside the solar system are also conceivable. The mechanism which delivers volatiles to Earth is similarly unknown and unspecified. Several mechanisms are possible. These include an unseen solar companion (the Nemesis of Davis et al., 1984), a dark planet (Frank, 1990), random passing stars, encounters with giant molecular clouds (Weissman, 1986), and galactic tides (Matese and Whitmire, 1996).

4. Supporting evidence

4.1. The small-comet hypothesis

The small-comet hypothesis (Frank et al., 1986) proposes that Earth is currently accreting water at a rate of $(0.2\text{--}1.0) \times 10^{12}$ kg/yr from an influx of small [mass $(0.2\text{--}1.0) \times 10^5$ kg, diameter about 4–6 m], comet-like objects. Small comets are believed to be composed primarily of water, but a carbon mantle is required to avoid vaporization in interplanetary space. Putative estimates of carbon-mantle density and thickness made by Frank and Sigwarth (1993) imply that small comets are probably about 90% water, 10% carbon. The extent to which these hypothetical bodies may contain minor amounts of other volatile elements is unknown. The current rate of water accretion from small comets is sufficient to increase mean global sea level by 2–10 mm in 3600 yr, and account for the entire mass of Earth's oceans in 1.4–7.0 Ga. The inferred small-comet accretion rate is 4 to 5 orders of magnitude higher than generally accepted for the total accretion rate of all extraterrestrial material (Tuncel and Zoller, 1987; Peucker-Ehrenbrink, 1996).

Evidence for the existence of small comets comes largely from satellite observations of Earth's atmosphere. Data include global images of Earth's ultraviolet dayglow, detection of atomic-oxygen trails and OH emissions from small comets, microwave radiometer observations of transient water-bursts in the atmosphere, and visual sightings from ground-based telescopes (Frank and Sigwarth, 1993, 1997a,b, 1997c,d).

Following its introduction in 1986, the small-comet hypothesis proved extremely controversial. The original publication in *Geophysical Research Letters* (Frank et al., 1986) unleashed a flood of criticism (e.g., see Davis, 1986; Donahue, 1986; Chubb, 1986; Dessler, 1991). Both of the reviewers of the original paper recommended against publication, one of them noting that “if this is correct, we would have to burn half the contents of the libraries in the physical sciences” (Frank, 1990, p. 23).

The small-comet hypothesis has recently received renewed attention due to apparent substantiation from a new generation of satellites (Frank and Sigwarth, 1997a,b, 1997c,d). However, these new data

have been followed by a new generation of criticisms. Parks et al. (1997, 1998) supported Dessler's (1991) hypothesis that the data interpreted by Frank and Sigwarth (1993, 1997a,b, 1997c,d) to be small comets are instrumental artifacts. However, Frank and Sigwarth (1998) have disputed the interpretations of Parks et al. (1997). Grier and McEwen (1997) found no visual evidence for small-comet impacts on the moon, adding to criticisms by earlier workers (Davis, 1986; Nakamura et al., 1986) that small-comet impacts on the moon were undetected by seismometers left by Apollo astronauts. Rizk and Dessler (1997) argued that the collision of small comets with Earth's atmosphere should create intermittent appearances of bright, rapidly moving points of light. Because such events have not been observed, Rizk and Dessler (1997) concluded small comets do not exist. Summers et al. (1997) found what appeared to anomalously high levels of water near altitudes of 65 to 70 km in the atmosphere, suggesting the possibility of an external source. However, Hannegan et al. (1998) concluded that the amount of water in the stratosphere was 100 times less than that consistent with the small-comet hypothesis.

Criticisms of the small-comet hypothesis are abundant, but it is not clear at the present time if the small-comet hypothesis is faulty or if the criticisms instead are based upon faulty assumptions. It seems likely that the small-comet hypothesis shall remain controversial for some time to come.

4.2. *Origin of water and carbon inventories*

In a classic paper on the origin of the oceans, Rubey (1951) pointed out that volatile compounds found near the Earth's surface such as water and carbon dioxide are much too abundant to have formed through the process of rock weathering. Rubey (1951) also concluded that all of the volatile compounds found near the surface today could not have been present early in the Earth's history in the form of a 'dense primitive atmosphere'. High atmospheric concentrations of carbon dioxide, nitrogen, and hydrogen sulfate in contact with sea water would have led to a highly acidic ocean with the concomitant deposition of large quantities of carbonate rocks. However, the percentage of limestone in sediments

of Precambrian age is about the same as that in younger sedimentary rocks.

Rubey (1951) reasoned that carbon has been added to the atmosphere and oceans continuously through geologic time. The amount of carbon tied up in rocks is 600 times the amount of carbon present in today's atmosphere, hydrosphere, and biosphere combined. As carbon is continuously extracted from the atmosphere–ocean system by sedimentation, Rubey (1951) pointed out that if a continuous rate of supply were not present, brucite would replace calcite as a common marine sediment. Yet the geologic record contains no brucite deposits. Rubey (1951) concluded that the geologic record strongly indicated that Earth's oceans and crustal carbon inventory formed as the result of slow accumulation over geologic time from a more-or-less continuous and gradual supply mechanism. The only such mechanism known to Rubey (1951) was volcanic outgassing. Earth scientists have subsequently accepted with little question that the Earth's oceans and its near-surface inventory of volatiles such as carbon have originated from volcanic outgassing.

However, Rubey (1951) never measured the rate at which water and carbon are added to the terrestrial surface environment through volcanic outgassing. Any attempt by Rubey (1951) to make such estimates would have been badly flawed, because he was unaware of the process of subduction. Subduction carries both water and carbon down into the mantle at significant rates, and it is questionable if the water and carbon thus removed from the near-surface environment is fully returned through outgassing.

For the past 15 years or so, quantitative estimates have been made which compare the rate at which water and carbon are released by volcanic outgassing to their uptake by subduction (see review by Bebout, 1995). It turns out that the net rate at which water is added to the hydrosphere by volcanic outgassing is only 5–15% of the rate at which it is carried down into the mantle by subduction. Similarly, the net rate at which carbon is added to the atmosphere by volcanic outgassing is only 10–44% of the rate at which it is lost to the mantle (Table 1). Based upon all existing estimates and studies, volcanic outgassing is a grossly inadequate mechanism to explain the abundant existence of water and carbon at and near the Earth's surface.

Table 1

Rates at which water and carbon are consumed by subduction compared to production from volcanic outgassing (data from Bebout, 1995)

Compound	Consumption rate (10^{10} kg/yr)	Production rate as % consumption
Water	91–194	5–15
Carbon	6–28	10–44

If near-surface supplies of water and carbon did not come from volcanic outgassing, where did they originate? There are at least three possible explanations. First, it is eminently possible that substantial amounts of water and carbon return to the surface through processes other than volcanic outgassing. One possibility is updip transport back up a subducting wedge. Seafloor fluid venting occurs along trenches, and studies of accretionary complexes document updip fluid flow (Fisher, 1996). On the other hand, the estimates of water loss rates cited in Table 1 are very conservative because they only include water which is mineralogically bound. Pore fluids, which account for 90% of subducted water, are not included. It is therefore possible that all accounts of seafloor venting and other evidence for shallow return near subduction zones could be accounted for by the return of pore fluids.

A second possibility is that the rate of volcanic outgassing was higher early in the Earth's history. This is not really an attractive hypothesis, however. High outgassing rates would have resulted in the 'dense primitive atmosphere' which Rubey (1951) showed was geochemically impossible. It is also probable that high levels of volcanic activity on a young and hotter Earth would have been matched by higher subduction rates.

A third possibility is the existence of an external source of supply, perhaps similar to the small comets inferred by Frank et al. (1986). This hypothesis can be put to a test of logical consistency. That is, how does the estimated rate of water and carbon accretion inferred from satellite data compare to the rate implied by geological data as necessary to create and maintain Earth's near-surface inventories of water and carbon? If it is assumed that the Earth formed without water and carbon at the surface, then the supply rate necessary to explain existing

inventories can be estimated as:

Supply Rate =

$$\frac{\text{Present Inventory}}{\text{Age Earth}} + \text{Depletion Rate}$$

where 'depletion rate' refers to the net depletion rate (subduction minus outgassing). Based upon current estimates from several studies (Table 1), net depletion rates for water and carbon are in the range of $(0.8\text{--}1.8) \times 10^{12}$ kg/yr and $(0.3\text{--}2.5) \times 10^{11}$ kg/yr, respectively. Estimating present water and carbon inventories to be 1.37×10^{21} kg and 1.0×10^{20} kg, respectively, and the age of the Earth to be the age of the oldest known rock (4.0×10^9 yr), the water and carbon supply rates necessary to explain current inventories are in the range of $(1\text{--}2) \times 10^{12}$ kg/yr and $(0.6\text{--}3) \times 10^{11}$ kg/yr, respectively. These estimates are not significantly affected by the assumed amount of volatiles present early in the Earth's history, because the calculated supply rate is largely determined by the depletion rate.

Frank and Sigwarth (1993) estimated water was being added to Earth from small comets at a rate of $(0.2\text{--}1.0) \times 10^{12}$ kg/yr. Based upon putative estimates of carbon-mantle density and thickness made by Frank and Sigwarth (1993), small-comet carbon content is probably equivalent to about 10% of the total water mass. Thus small-comet carbon-accretion rates are in the range of $(0.2\text{--}1.0) \times 10^{11}$ kg/yr. In consideration of the uncertainties involved in assuming accretion, subduction, and outgassing rates constant over geologic time, these numbers are very close to those which satisfy the geologic constraints.

If water and carbon are being carried down into the mantle and not returned, there should be substantial amounts of these elements stored in the Earth's interior. Presumably, most storage would take place in the upper mantle, although the degree to which the lower and upper mantle mix is poorly known. Assuming that the rates cited in Table 1 have been constant over geologic time, the net amount of water carried down into the mantle over the last 4.0×10^9 yr should be in the range of $(3\text{--}7) \times 10^{21}$ kg, two to five times the mass of today's oceans (1.37×10^{21} kg). Ten years ago, there was little to no evidence for substantial amounts of water storage in the upper mantle (Ahrens, 1989). However, in the past few years it has become apparent that large amounts of water may be

stored in the upper mantle in the form of dense hydrous magnesium silicates (DHMS). One of the most important minerals in this group is wadsleyite, which may contain up to 3.3% H₂O by weight (Smyth, 1994). Smyth (1994) estimated that if the mantle between the depths of 400 and 525 km were composed of 60% fully hydrated wadsleyite, the amount of water contained therein would be “more than four times the amount of H₂O currently in the Earth’s hydrosphere”. More recently, Bose and Navrotsky (1998) showed “there is no barrier to subducting substantial amounts of water to depths of 400–600 km in colder slabs, since the slab can remain in the stability field of hydrous phases throughout its descent”. Other evidence for the presence of water in the upper mantle is provided by seismic tomography (Nolet and Zielhuis, 1994, p. 15,816), excess helium in groundwater (Torgersen et al., 1995), and deep-focus earthquakes (Meade and Jeanloz, 1991).

4.3. *Correlations between sea level and temperature*

If the ETV hypothesis is correct, geologic periods characterized by high rates of volatile accretion should be times of relative warmth during which sea level rises; while low accretion rates should result in falling sea level and cooling. This correlation is present in the geologic record (Fig. 1). Each of the three eras of Phanerozoic time (~570 Ma–present) show general correlations between temperature and sea level (Frakes et al., 1992, p. 194; Hallam, 1992, p. 158). The correlation is not perfect for at least two reasons. Both climate and sea level are affected by numerous processes and factors in addition to hypothetical changes in the rate of extraterrestrial accretion, and the Phanerozoic record of sea level and temperature is partly qualitative and subject to future revision. For example, correlations between sea level and global temperature exist partly because of glacial storage. However, there were significant changes in sea level over periods of Phanerozoic times when little or no polar ice existed. Sea level dropped significantly from Late Cretaceous times (about 70 Ma) through the Paleocene and Eocene (about 36 Ma), yet there is little evidence for the existence of major ice caps or glacial deposition in ocean sediments until the end of the Eocene (about 36 Ma) (Frakes et al., 1992, p. 102).

4.4. *Correlations between sea-level trends and mass extinctions*

The two largest mass extinctions of Phanerozoic times (Permian–Triassic and Cretaceous–Tertiary) were essentially synchronous with inflections in eustatic sea-level curves (Fig. 1). Dating of melt rock from the Chicxulbu Crater (Swisher et al., 1992) has now established at a high level of probability that the mass extinction which occurred at the Cretaceous–Tertiary boundary was caused by a catastrophic accretion event as suggested by Alvarez et al. (1980). There is also substantial evidence that the Permian–Triassic extinction event was related to extraterrestrial accretion. Although complete sections which encompass the Permian–Triassic boundary are relatively scarce (Bice et al., 1992), iridium anomalies at the Permian–Triassic boundary have been found at 10 different locations (Rampino and Haggerty, 1996, p. 15). Shocked quartz, diagnostic of impact ejecta, has also been found near the Permian–Triassic boundary at a site in northern Tuscany, Italy (Bice et al., 1992).

Temporal correlations between changes in sea level, extraterrestrial accretion, and biologic evolution, suggest the probability that these phenomena are causally related. Conventional theories attribute large eustatic changes in sea level to changes in the volume of the ocean basins that result from changes in the rate of sea-floor spreading. If we are to accept this theory, however, then we have to believe that catastrophic accretion events coincidentally occurred at the very moments in geologic time when sea-floor spreading rates changed. This seems implausible. It may be more parsimonious to postulate that the same gravitational mechanism (e.g. galactic tides) which is responsible for catastrophic meteoritic impacts may simultaneously deflect large amounts of volatiles into Earth-crossing orbits. Rapidly changing terrestrial climates might result from the accretion of these very different materials which have climatic effects over different time scales. The catastrophic impact of one or more solid bodies could result in the atmosphere being loaded with smoke, dust, and sulfate aerosols. The amount of solar insolation reaching the Earth’s surface would drop substantially for a period of time of 1–10 yr, and significant cooling would occur (Toon et al., 1997). However, as light-blocking

aerosols settled out of the atmosphere, the climatic effects of greenhouse gasses with longer residence times might dominate. The residence time of CO_2 is about 50–200 yr, and high CO_2 levels could lead to a substantial greenhouse warming. This type of scenario could explain why oxygen isotope data show that global warmings are commonly synchronous with, or immediately postdate, several mass extinctions, including the important Cretaceous–Tertiary and Permian–Triassic events (Rampino and Hagerty, 1996).

4.5. The inclination cycle

Like orbital eccentricity, the inclination of Earth's orbit about the plane of the solar system has a 100,000-yr periodicity. There is also a strong correlation between the inclination of Earth's orbit and climate over the last 600,000 yr (Fig. 4; Muller and MacDonald, 1995, 1997a,b). Recent analyses of ocean cores have found climate signals related to both eccentricity and inclination (Muller and MacDonald, 1997a,b). However, inclination appears to be much more strongly related to climate. This is surprising, because the inclination of Earth's orbit does not have a significant effect on solar insolation.

Muller and MacDonald (1995) suggested that the inclination of Earth's orbit may drive Pleistocene glacial cycles by modulating the accretion of extraterrestrial materials. Some confirming evidence for a 100,000-yr periodicity in extraterrestrial accretion rates has been found by Farley and Patterson

(1995) in the form of a 100,000-yr periodicity in the flux of extraterrestrial ^3He to the Earth's sea floor. However, Muller and MacDonald (1995, 1997a,b) have never specified the mechanism involved. Neither has anyone else been able to propose a mechanism which could establish a causal link between inclination and climate. One possibility is that meteoric materials may induce glacial episodes through aerosol cooling. However, there are two difficulties with this hypothesis. First, glacial episodes do not require an explanation of this type. The Earth has been cooling at high latitudes for 60 million years, and glaciations are most parsimoniously interpreted as the logical consequence of whatever factors are responsible for this long-term cooling trend. Once they begin, glacial episodes induce positive climatic feedbacks that should result in further cooling. The high albedo of increased ice cover, the higher solubility of CO_2 in colder oceans, and decreased amounts of water vapor in a colder atmosphere should all tend to reduce planetary temperature. As glaciations proceed, ice volume increases. Thus, it is the sudden appearance of interglacial episodes from the coldest extent of the ice ages which is anomalous and requires an explanation in the form of a strong external forcing.

A second difficulty with an aerosol-cooling hypothesis is that the accretion rate necessary to achieve global coolings of the magnitude associated with Pleistocene glaciations (5°C) is likely to be many orders of magnitude greater than the observed accretion rate of meteoric materials. If we assume that accreted material is as efficient in generating a

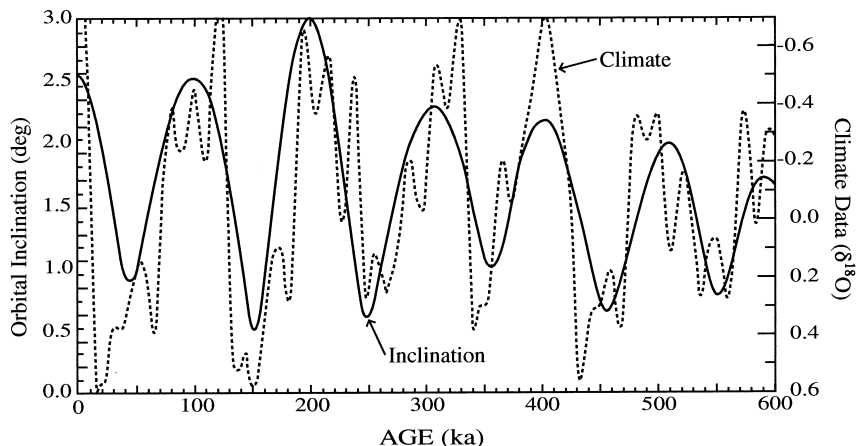


Fig. 4. Orbital inclination (solid line, lagged by 33 ka) and $\delta^{18}\text{O}$ climate proxy (after Muller and MacDonald, 1995).

cooling effect as sulphate aerosols, an order-of-magnitude calculation can be made of the extraterrestrial flux necessary to induce a 5°C global cooling.

The total anthropogenic sulfur-aerosol flux today is 1.4×10^{11} kg/yr, which is estimated to exert a total climatic forcing of -0.4 W/m² with a factor of two uncertainty (Schimel et al., 1995, pp. 104, 113). The relationship between mean global temperature change (ΔT) and radiative forcing (ΔQ) is

$$\Delta T = \lambda \Delta Q \quad (1)$$

where λ is the climate sensitivity parameter (Cubasch and Cess, 1990, p. 77). Taking $\lambda = 0.3$ K m⁻² W⁻¹ (no climate feedbacks), the radiative forcing necessary to induce an ice-age cooling of 5°C is -17 W/m². If a present-day anthropogenic sulfur-aerosol flux of 1.4×10^{11} kg/yr exerts a climatic forcing of -0.4 W/m², then a simple linear extrapolation to the flux required to produce a forcing of -17 W/m² implies a necessary flux of 5.8×10^{12} kg/yr. However, the accretion rate of conventional meteoritic material averaged over tens of millions of years is well constrained to be in the neighborhood of 10^7 – 10^8 kg/yr (Tuncel and Zoller, 1987; Peucker-Ehrenbrink, 1996). Thus the accretion of extraterrestrial material appears to be four to five orders of magnitude too small to exert a significant effect on Earth's climate by direct aerosol cooling. Even if the linear extrapolation is not strictly justified, the mass insufficiency is nevertheless enormous. If glaciations are induced by the accretion of extraterrestrial dust, it would seem to be necessary to invoke a profound amplification by some unknown or exotic process.

Recent calculations by Kortenkamp and Dermott (1998) also indicate that the terrestrial accretion of interplanetary dust particles from the zodiacal cloud, the tenuous cloud of dust which envelops the four terrestrial planets of the solar system, is not controlled by the inclination of Earth's orbit, but rather by its eccentricity. If dust accretion is controlled by eccentricity, and not inclination, it may be difficult to link correlations between inclination and climate with dust accretion.

Orbital inclination does differ in phase by 33 ka (see Fig. 4) from global ice volume as inferred from the SPECMAP data (Imbrie et al., 1984). However, this is not an impediment to the viability of the Muller–MacDonald theory, for two reasons. First, the

orientation of the dust or other material whose accretion may be modulated by orbital inclination is unknown. There is no reason to postulate that the lowest or highest accretion rates should occur during arbitrary values of inclination. Second, global ice volume is itself not in phase with climate change. Winograd et al. (1997) concluded that there are phase offsets of thousands of years between proxies for global ice volume (e.g., SPECMAP) and other climate proxies.

It is possible to reconcile the spectral evidence for the Muller–MacDonald hypothesis with the criticisms listed above if the mechanism which affects climate is not the accretion of interplanetary dust, but rather the accretion of extraterrestrial carbon. In this modified form of the Muller–MacDonald hypothesis, extraterrestrial accretion is modulated by orbital inclination, but the climatic effect is not dust-induced cooling. Rather, the sudden appearance of interglacial episodes is attributed to temporary increases in the carbon influx rate with concomitant increases in atmospheric CO₂ concentration and changes in the planetary radiative balance. As carbon-accretion rates diminish, the planet once again cools as ongoing terrestrial processes such as subduction and sedimentation remove carbon from the surface faster than it is introduced by accretion and outgassing.

4.6. *The temperature–volatiles conundrum*

Standard planetary formation models show that the Earth likely formed without its present day inventories of water, nitrogen, and carbon. At expected temperatures of accretion, volatile temperatures are sufficiently high that water, nitrogen, and carbon remain in the gaseous phase and are not incorporated in planet-forming planetesimals. This problem is termed the “temperature–volatiles conundrum” (Chyba et al., 1994, p. 13). The conundrum is that although our current understanding precludes Earth forming with volatile elements, the elements are here. The standard hypothesis which accounts for the missing volatiles is an Archean late-accretionary bombardment of volatile-rich material (Anders, 1989). However, there appears to be no independent evidence that such an event occurred.

The ETV hypothesis proposes that the volatile influx rate has declined over geologic time, but perhaps by one order of magnitude, instead of three (Chyba

and Sagan, 1992, p. 127). In either case, high rates of volatile accumulation subsequent to Earth's formation are necessary to explain present day volatile inventories. The ETV hypothesis merely suggests that the influx rate has declined gradually instead of precipitously.

4.7. Water in the solar system

The presence of water on Earth's moon (Nozette et al., 1996) and the planet Mercury (Slade et al., 1992) implies the existence of a transport process which delivers water to the inner solar system. Surface features on the planet Mars show evidence of running water (Baker, 1982). Frank (1990) has proposed that the presence of surface water on Mars may be cyclic. Accreted water would be stored in growing polar ice caps until a short-lived period of rapid volatile accretion could warm the planet sufficiently so as to melt the polar ice caps and allow for the presence of increased water vapor in the atmosphere. Further warming would occur from positive feedbacks as water vapor is itself a greenhouse gas. Eventually, much of the water in the atmosphere would be lost to space, and Mars would once again cool and begin to store accreted water at its poles until the cycle was repeated.

4.8. Cooling of the Earth

Oxygen isotope data from cherts (Fig. 5) show that Earth has cooled significantly over geologic time, even though solar luminosity has increased by approximately 30% (Knauth and Lowe, 1978). The temperature decrease is thought to be due to decreases in the concentration of CO₂ and other greenhouse gasses (Rye et al., 1995). The magnitude of the inferred cooling is large. Knauth and Clemens (1995) concluded the data are consistent with a warm (>45°C) early Earth which has progressively cooled to the present day mean planetary air-temperature of 15–16°C. Knauth and Clemens (1995) also concluded that the temperature history of Earth has been highly variable, with both cool periods and major global warming events. The warming episodes lasted about 100 Ma, and were characterized by mean global temperature increases of 10 to 15°C.

The most common objection to the warm early Earth inferred from isotopic studies of cherts is evidence for ice ages as long ago as Early Proterozoic times (2.3–2.5 Ga). However, it is possible that these ice ages did not occur, or were short-lived anomalies that occurred during periods of otherwise high temperatures. The primary evidence for Proterozoic glaciations is the presence of diamictites,

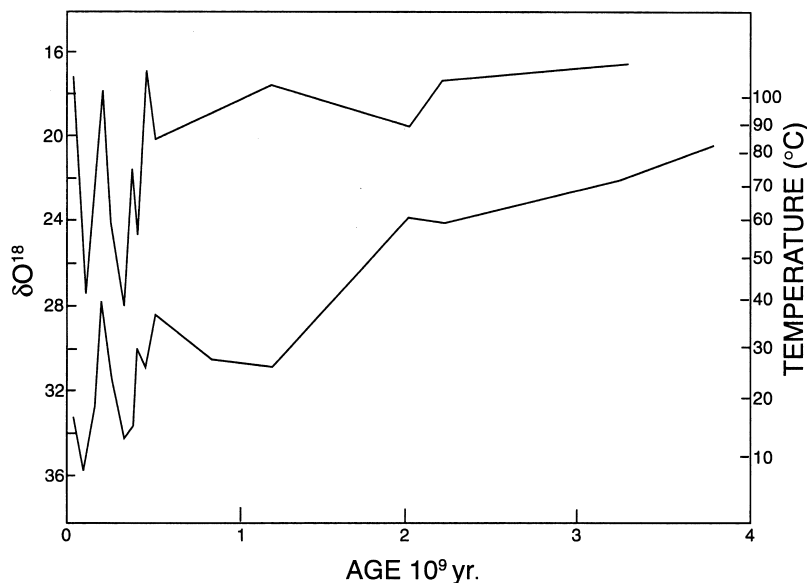


Fig. 5. Range of oxygen isotope data from cherts (after Knauth and Lowe, 1978, p. 218).

poorly sorted sediments which have been interpreted as glacial till. Rampino (1994) argued that most, if not all, diamictites may have originated as the fallout of ballistic ejecta from the impact of large asteroids or comets. If this were true, it would explain the puzzling occurrence of ‘glacial deposits’ at low latitudes in close proximity to indicators of tropical climates such as carbonates, red beds, and evaporites (Evans et al., 1997).

4.9. Abrupt climate change

The occurrence of rapid climate changes unexplainable by any known terrestrial process suggests the possible presence of an unsuspected catastrophic mechanism. Recent analyses of ice core data show that interstadial transitions between warm and cold conditions during the last ice age were rapid, of the order of decades (Grootes et al., 1993). For example, a reconstruction of climate records based on cores from Greenland, Antarctica, and the North Atlantic, reveals what appear to be about twelve rapid climate changes over approximately the last 100,000 yr. The changes are large in magnitude, and their correlation between sites implies that they were global. Most typically, warmings of 5 to 7°C that take place in a few decades are followed by slow coolings (Dansgaard et al., 1993; Grootes et al., 1993; Nicholls et al., 1996, p. 177).

It is not possible to explain such rapid variations by changes in solar insolation related to changes in Earth’s orbit; these occur on a much longer time scale. It is also difficult to attribute rapid temperature changes to changes in terrestrial processes such as ice volume changes or deep-ocean circulation which operate on characteristic time scales of several hundred to several thousand years. Surficial changes in ocean circulation may have important climatic consequences (Broecker et al., 1990); however, we are still left with the question of what triggers these changes.

4.10. Asymmetry of the climate record

There is a striking and unexplained asymmetry to the reconstructed terrestrial temperature record that appears across all time scales. Warming episodes generally occur suddenly, while the onset of cool

modes is gradual (Frakes et al., 1992, p. 195). Examples include the sudden warming at the Paleocene–Eocene boundary (Kennett and Stott, 1991), the Pleistocene ice ages (Fig. 2), and interstadial warmings (Nicholls et al., 1996, p. 177), all discussed earlier. Other than the ETV hypothesis, there is no theory known to the author which even attempts to explain this asymmetry.

4.11. Noctilucent clouds

Some models of mesospheric noctilucent-cloud formation require the accretion of extraterrestrial water at a rate of 10^{11} – 10^{12} kg/yr (Lebedinets and Kurbanmuradov, 1992).

5. Discussion

5.1. Accretion rates

Estimates of volatile accretion rates from the small-comet hypothesis are four to five orders of magnitude greater than generally accepted estimates (10^7 – 10^8 kg/yr) of the total extraterrestrial influx rate (Tuncel and Zoller, 1987; Peucker-Ehrenbrink, 1996). Conventional estimates of influx rates are largely derived by extrapolating minute tracer (e.g., iridium, osmium) concentrations up through several orders of magnitude based on assumed chondritic abundances. However, the volatiles which enter Earth’s atmosphere may be derived from an entirely different class of objects whose composition does not resemble chondrites (Frank et al., 1987). The designation ‘small comet’ does not refer to a comet which is small. Rather, the bodies inferred by Frank et al. (1986) are thought to represent an entirely new class of celestial objects which lack the dust and other constituents of conventional large comets. For example, recent observations of small-comet impacts are inconsistent with the presence of dust (Frank and Sigwarth, 1997d). Therefore, the small-comet influx rate cannot be estimated by assuming chondritic composition. Similarly, there is no reason to believe that methods such as satellite observations, visual sightings, and radio-meteor studies, which are suited to the detection of large bodies composed of rock and/or metal, would ordinarily be capable

of detecting low-density (0.1 g/cm^3) small comets which disintegrate at altitudes greater than 300 km and are thought to be composed almost entirely of water, with small amounts of carbon and perhaps other cometary volatiles.

5.2. *Disruption of the nitrogen cycle*

Terrestrial geochemical cycles are extremely complex, and a complete discussion of the consequences of disrupting them is beyond the scope of this paper. However, it is worth noting that there may be several possible ways in which extraterrestrial accretion could perturb the nitrogen chemistry of Earth's atmosphere, oceans, and biosphere, with possible climatic ramifications. It has been recognized for a long time that catastrophic impacts of the type that apparently happened at the Cretaceous–Tertiary border would create large amounts of nitric oxide by oxidation of nitrogen in the atmosphere (Toon et al., 1997). The amounts of nitric oxide which can be created by this mechanism are very large, and may exceed the mass of the impacting object. For example, Turco et al. (1982) calculated that the mass of nitric oxide added to Earth's atmosphere by the 1908 Tunguska event may have been up to six times the total mass of the impacting object. Environmental effects associated with nitric-oxide formation include acidification of the near-surface terrestrial and ocean environments and depletion of the Earth's protective ozone layer (Hsu and McKenzie, 1985; Toon et al., 1997). Less is known about the complexities of nitrogen-cycle disruptions. Hsu and McKenzie (1985) suggested that acidification due to nitric-oxide formation caused release of CO_2 from the ocean to the atmosphere and led to global warming at the Cretaceous–Tertiary boundary. It is also not clear how a sudden and massive input of nitric oxide would affect the production of nitrous oxide, a powerful and relatively long-lived greenhouse gas, at the other end of the nitrogen cycle. If impacting bodies contain even trace amounts of sulfur, as most comets and asteroids do, the chemistry of nitric oxide formation in the atmosphere by impact-created shock waves and heating may not be straightforward. For example, Muzio and Kramlich (1988) found that the amount of nitrous oxide produced in fossil-fuel combustion increased by two orders of magnitude when the concentration

of SO_2 exceeded a critical threshold of about 1000 ppm.

5.3. *Climate change*

Although the radiative effects of high-altitude water vapor are unknown, it seems unlikely that direct addition of water vapor to Earth's atmosphere is capable of inducing a perceptible greenhouse effect. Even if accretion rates were very high for short periods of time, the residence time of water vapor in the troposphere is so short (11 days) that it would be difficult to maintain an appreciable increase in humidity. It is more probable that the importance of water accretion is in building and replenishing the oceans over long periods of time.

The accretion of carbon in the form of carbon dioxide may be a more efficacious mechanism for effecting climate change. During the last glacial termination (18 to 11 ka), atmospheric CO_2 concentration rose from 200 to 280 ppm. Considering the increased uptake of carbon by ocean surface waters and the biosphere that probably occurred as atmospheric CO_2 concentrations increased, Sundquist (1993) estimated that the total amount of carbon necessary to explain the entire deglacial budget was in the range of $(6.5\text{--}9.5) \times 10^{14}$ kg. Averaged over 7000 yr, this is equivalent to an average flux of $(0.9\text{--}1.4) \times 10^{11}$ kg/yr. The current carbon-accretion rate from small comets is estimated to be $(0.2\text{--}1.0) \times 10^{11}$ kg/yr.

Even if the ends of the Pleistocene ice ages were caused by increases in the influx of extraterrestrial carbon, it remains to be shown that the radiative forcing associated with the concomitant addition of CO_2 to the atmosphere is strong enough to initiate interglacial episodes. The total increase of CO_2 in Earth's atmosphere during the last termination was about 80 ppm (Sundquist, 1993). Assuming a radiative forcing of 1.8×10^{-2} W/m² for each 1 ppm CO_2 increase (Schimel et al., 1995, p. 92), the total radiative forcing due to CO_2 at the last termination was 1.4 W/m². Applying Eq. 1 above, this is approximately strong enough to raise mean planetary temperature by only 0.4°C, too small by a factor of ten to explain an interglacial warming of 5°C. However, the Milankovitch trigger is even smaller. The estimated magnitude of insolation changes associated with changes in orbital

eccentricity is only $\pm 0.5 \text{ W/m}^2$, about one third of the radiative forcing due to the CO_2 increase. In the absence of climatic feedbacks, no mechanism by itself seems energetically sufficient.

5.4. Isotopic anomalies

In theory, it should be possible to test for the presence of volatile accretion and its possible influence on Earth's hydrologic and carbon cycles by looking for correlations between isotopic markers and climatic events. For example, major carbon-isotope anomalies occur precisely at the Cretaceous–Tertiary and Paleocene–Eocene boundaries (Boersma, 1984, p. 269). In practice, however, it is difficult to discriminate between cause and effect because terrestrial climatic processes also lead to changes in oxygen and carbon isotopic ratios. A corollary is that the entire practice of evaluating terrestrial processes from isotopic shifts may need to be reevaluated.

5.5. Life on Earth

If the young Earth was hot and relatively inhospitable to life, the Cambrian explosion of life forms may have been a natural consequence of the gradual subsidence of the volatile influx rate. As the concentration of greenhouse gasses in Earth's atmosphere declined, the climate cooled, and an environment more hospitable to life emerged.

As Frank (1990) has pointed out, it is difficult to envision a mechanism which could deliver volatiles to Earth in a manner consistent with the inferred presence of small comets. A nearly unique set of circumstance is needed. If a regular delivery of volatiles was necessary for the emergence and maintenance of life on Earth, then life in the universe may be more uncommon than previously thought (Frank, 1990). Instead of a robust process which mediates its environment (Lovelock, 1979), life may be a delicate and chance phenomenon that springs up for short periods of time under fortuitous circumstances.

References

- Ahrens, T.J., 1989. Water storage in the mantle. *Nature* 342, 122–123.
- Alvarez, L.W., Alvarez, W., Asaro, F., Michel, H.V., 1980. Extraterrestrial cause for the Cretaceous–Tertiary extinction: experimental results and theoretical interpretation. *Science* 208, 1095–1108.
- Anders, E., 1989. Pre-biotic organic matter from comets and asteroids. *Nature* 342, 255–257.
- Baker, V.R., 1982. The channels of Mars. Univ. Texas Press, Austin, TX, 198 pp.
- Bebout, G.E., 1995. The impact of subduction-zone metamorphism on mantle–ocean chemical cycling. *Chem. Geol.* 126, 191–218.
- Berner, R.A., 1990. Atmospheric carbon dioxide levels over Phanerozoic time. *Science* 249, 1382–1386.
- Bice, D.M., Newton, C.R., McCauley, S., Reiners, P.W., McRoberts, C.A., 1992. Shocked quartz at the Triassic–Jurassic boundary in Italy. *Science* 255, 443–446.
- Blanchon, P., Shaw, J., 1995. Reef drowning during the last deglaciation: evidence for catastrophic sea-level rise and ice-sheet collapse. *Geology* 23, 4–8.
- Boersma, A., 1984. Campanian through paleocene paleotemperature and carbon isotope sequence and the Cretaceous–Tertiary boundary in the Atlantic Ocean. In: Berggren, W.A., Van Couvering, J.A. (Eds.), *Catastrophes and Earth History*. Princeton Univ. Press, Princeton, NJ, pp. 247–277.
- Bose, K., Navrotsky, A., 1998. Thermochemistry and phase equilibria of hydrous phases in the system $\text{MgO-SiO}_2\text{-H}_2\text{O}$: implications for volatile transport to the mantle. *J. Geophys. Res.* 103, 9713–9719.
- Broecker, W.S., 1997a. Will our ride into the greenhouse future be a smooth one? *GSA Today* 7 (5), 1–7.
- Broecker, W.S., 1997b. Thermohaline circulation, the Achilles Heel of our climate system: will man-made CO_2 upset the current balance? *Science* 278, 1582–1588.
- Broecker, W.S., Bond, G., Klas, M., 1990. A salt oscillator in the glacial Atlantic? 1. The concept. *Paleoceanography* 5, 469–477.
- Carslaw, H.S., Jaeger, J.C., 1959. *Conduction of Heat in Solids*, 2nd ed. Oxford Univ. Press, Oxford, 510 pp.
- Chubb, T.A., 1986. Comment on the paper “On the influx of small comets into the Earth's upper atmosphere I. Observations”. *Geophys. Res. Lett.* 13, 1075–1077.
- Chyba, C., Sagan, C., 1992. Endogenous production, exogenous delivery and impact-shock synthesis of organic molecules: an inventory for the origins of life. *Nature* 355, 125–132.
- Chyba, C.F., Owen, T.C., Ip, W.-H., 1994. Impact delivery of volatiles and organic molecules to Earth. In: Gehrels, T. (Ed.), *Hazards Due to Comets and Asteroids*. Univ. Arizona Press, Tuscon, AZ, pp. 9–58.
- Cubasch, U., Cess, R.D., 1990. Processes and modelling. In: Houghton, J.T. et al. (Eds.), *Climate Change, The IPCC Scientific Assessment*. Cambridge Univ. Press, Cambridge, pp. 69–91.
- Dansgaard, W., Johnsen, S.J., Clausen, H.B., Dahl-Jensen, D., Gundestrup, N.S., Hammer, C.U., Hvidbert, C.S., Steffensen, J.P., Sveinbjörnsdóttir, A.E., Jouzel, J., Bond, G., 1993. Evidence for general instability of past climate from a 250-kyr ice-core record. *Nature* 364, 218–220.

- Davis, P.M., 1986. Comment on the letter "On the influx of small comets into the Earth's upper atmosphere". *Geophys. Res. Lett.* 13, 1181–1182.
- Davis, M., Hut, P., Muller, R.A., 1984. Extinction of species by periodic comet showers. *Nature* 308, 715–717.
- Dessler, A.J., 1991. The small-comet hypothesis. *Rev. Geophys.* 29, 355–382.
- Dickens, G.R., Castillo, M.M., Walker, J.C.G., 1997. A blast of gas in the latest Paleocene: simulating first-order effects of massive dissociation of oceanic methane hydrate. *Geology* 25, 259–262.
- Donahue, T.M., 1986. Comment on the paper "On the influx of small comets into the Earth's upper atmosphere II. Interpretation". *Geophys. Res. Lett.* 13, 555–557.
- Edwards, R.L., Cheng, H., Murrell, M.T., Goldstein, S.J., 1997. Protactinium-231 dating of carbonates by thermal ionization mass spectrometry: implications for Quaternary climate change. *Science* 276, 782–786.
- Evans, D.A., Beukes, N.J., Kirschvink, J.L., 1997. Low-latitude glaciation in the Palaeoproterozoic era. *Nature* 386, 262–266.
- Farley, K.A., Patterson, D.B., 1995. A 100-kyr periodicity in the flux of extraterrestrial ^3He to the sea floor. *Nature* 378, 600–603.
- Fisher, D.M., 1996. Fabrics and veins in the forearc: a record of cyclic fluid flow at depths of <15 km. In: Bebout, G.E. et al., (Eds.), *Subduction Top to Bottom*. Am. Geophys. Union Geophys. Monogr. 96, 75–89.
- Frakes, L.A., Francis, J.E., Syktus, J.I., 1992. *Climate Modes of the Phanerozoic*. Cambridge Univ. Press, Cambridge, 274 pp.
- Frank, L.A., 1990. *The Big Splash*. Carol Pub. Group, Seacacus, NJ, 255 pp.
- Frank, L.A., Sigwarth, J.B., 1993. Atmospheric holes and small comets. *Rev. Geophys.* 31, 1–28.
- Frank, L.A., Sigwarth, J.B., 1997a. Transient decreases of Earth's far-ultraviolet dayglow. *Geophys. Res. Lett.* 24, 2423–2426.
- Frank, L.A., Sigwarth, J.B., 1997b. Simultaneous observations of transient decreases of Earth's far-ultraviolet dayglow with two cameras. *Geophys. Res. Lett.* 24, 2427–2430.
- Frank, L.A., Sigwarth, J.B., 1997c. Detection of atomic oxygen trails of small comets in the vicinity of Earth. *Geophys. Res. Lett.* 24, 2431–2434.
- Frank, L.A., Sigwarth, J.B., 1997d. Trails of OH emissions from small comets near Earth. *Geophys. Res. Lett.* 24, 2435–2438.
- Frank, L.A., Sigwarth, J.B., 1998. Atmospheric holes: instrumental and geophysical effects. *J. Geophys. Res.* (in press).
- Frank, L.A., Sigwarth, J.B., Craven, J.D., 1986. On the influx of small comets into the Earth's upper atmosphere II: interpretation. *Geophys. Res. Lett.* 13, 307–310.
- Frank, L.A., Sigwarth, J.B., Craven, J.D., 1987. Reply to "Comment on 'On the Influx of Small Comets into the Earth's Upper Atmosphere, II. Interpretation' by L.A. Frank, J.B. Sigwarth and J.D. Craven" by J.T. Wasson and F.T. Kyte. *Geophys. Res. Lett.* 14, 781–782.
- Goodfriend, G.A., Mitterer, R.M., 1993. A 45,000-yr record of a tropical lowland biota: the land snail fauna from cave sediments at Coco Ree, Jamaica. *Geol. Soc. Am. Bull.* 105, 18–29.
- Grier, J.A., McEwen, A.S., 1997. The small-comet hypothesis: an upper limit to the current impact rate on the Moon. *Geophys. Res. Lett.* 24, 3105–3108.
- Grotes, P.M., Stulver, M., White, J.W.C., Johnsen, S., Jouzel, J., 1993. Comparison of oxygen isotope records from the GISP2 and GRIP Greenland ice cores. *Nature* 366, 552–554.
- Hallam, A., 1992. *Phanerozoic Sea-level Changes*. Columbia Univ. Press, New York, NY, 266 pp.
- Hannegan, B., Olsen, S., Prather, M., Zhu, X., Rind, D., Lerner, J., 1998. The dry stratosphere: a limit on cometary water influx. *Geophys. Res. Lett.* 25, 1649–1652.
- Hays, J.D., Imbrie, J., Shackleton, N.J., 1976. Variations in the Earth's orbit: pacemaker of the ice ages. *Science* 194, 1121–1132.
- Hills, J.G., 1981. Comet showers and the steady-state infall of comets from the Oort cloud. *Astron. J.* 86, 1730–1740.
- Hsu, K.J., McKenzie, J.A., 1985. A 'Strangelove' ocean in the earliest Tertiary. In: Sundquist, E.T., Broecker, W.S. (Eds.), *The Carbon Cycle and Atmospheric CO₂: Natural Variations Archean to Present*. Am. Geophys. Union Geophys. Monogr. 32, 487–492.
- Imbrie, J., Hays, J.D., Martinson, D.G., McIntyre, A., Mix, A.C., Morley, J.J., Pisias, N.G., Prell, W.L., Shackleton, N.J., 1984. The orbital theory of Pleistocene climate: support from a revised chronology of the marine $\delta^{18}\text{O}$ record. In: Berger, A. et al. (Eds.), *Milankovitch and Climate, Part 1*. Reidel, Norwell, MA, pp. 269–305.
- Imbrie, J., Boyle, E.A., Clemens, S.C., Duffy, A., Howard, W.R., Kukla, G., Kutzbach, J., Martinson, D.G., McIntyre, A., Mix, A.C., Molino, B., Morley, J.J., Peterson, L.C., Pisias, N.G., Prell, W.L., Raymo, M.E., Shackleton, N.J., Toggweiler, J.R., 1992. On the structure and origin of major glaciation cycles 1. linear responses to Milankovitch forcing. *Paleoceanography* 7, 701–738.
- Imbrie, J., Berger, A., Boyle, E.A., Clemens, S.C., Duffy, A., Howard, W.R., Kukla, G., Kutzbach, J., Martinson, D.G., McIntyre, A., Mix, A.C., Molino, B., Morley, J.J., Peterson, L.C., Pisias, N.G., Prell, W.L., Raymo, M.E., Shackleton, N.J., Toggweiler, J.R., 1993a. On the structure and origin of major glaciation cycles 2. the 100,000-year cycle. *Paleoceanography* 8, 699–735.
- Imbrie, J., Mix, A.C., Martinson, D.G., 1993b. Milankovitch theory viewed from Devil's Hole. *Nature* 363, 531–533.
- Kennett, J.P., Stott, L.D., 1991. Abrupt deep-sea warming, palaeoceanographic changes and benthic extinctions at the end of the Palaeocene. *Nature* 353, 225–229.
- Knauth, L.P., Clemens, P.L., 1995. Climatic temperature history of the Earth based on isotopic analyses of cherts. *Geol. Soc. Am. Abstr. Progr.* 27 (6), A205.
- Knauth, L.P., Lowe, D.R., 1978. Oxygen isotope geochemistry of cherts from the Onverwacht group (3.4 billion years), Transvaal, South Africa, with implications for secular variations in the isotopic composition of cherts. *Earth Planet. Sci. Lett.* 41, 209–222.
- Kortenkamp, S.J., Dermott, S.F., 1998. A 100,000-year periodicity in the accretion rate of interplanetary dust. *Science* 280, 874–876.

- Lebedinets, V.N., Kurbanmuradov, O., 1992. The role of cometary and meteoritic matter in the genesis of noctilucent clouds. *Astron. Vestn.* 26, 83–92, in Russian.
- Lovelock, J.E., 1979. *Gaia, a New Look at Life on Earth*. Oxford Univ. Press, Oxford, 157 pp.
- Matese, J.J., Whitmire, D.P., 1996. Tidal imprint of distant galactic matter on the Oort comet cloud. *Astrophys. J. Lett.* 472, L41–L43.
- Meade, C., Jeanloz, R., 1991. Deep-focus earthquakes and recycling of water into the Earth's mantle. *Science* 252, 68–72.
- Milankovitch, M., 1930. *Mathematische Klimalehre und Astronomische Theorie der Klimaschwankungen*. Borntraeger, Berlin, 176 pp.
- Miller, G.H., Magee, J.W., Jull, A.J.T., 1997. Low-latitude glacial cooling in the southern hemisphere from amino-acid racemization in emu eggshells. *Nature* 385, 241–244.
- Muller, R.A., MacDonald, G.J., 1995. Glacial cycles and orbital inclinations. *Nature* 377, 107.
- Muller, R.A., MacDonald, G.J., 1997a. Simultaneous presence of orbital inclination and eccentricity in proxy climate records from Ocean Drilling Program Site 806. *Geology* 25, 3–6.
- Muller, R.A., MacDonald, G.J., 1997b. Glacial cycles and astronomical forcing. *Science* 277, 215–218.
- Muzio, L.J., Kramlich, J.C., 1988. An artifact in the measurement of N₂O from combustion sources. *Geophys. Res. Lett.* 15, 1369–1372.
- Nakamura, Y., Oberst, J., Clifford, S.M., Bills, B.G., 1986. Comment on the letter "On the influx of small comets into the Earth's upper atmosphere". *Geophys. Res. Lett.* 13, 1184–1185.
- Nicholls, N., Gruza, G.V., Jouzel, J., Karl, T.R., Ogallo, L.A., Parker, D.E., 1996. Observed climate variability and change. In: Houghton, J.T. et al. (Eds.), *Climate Change 1995, The Science of Climate Change*. Cambridge Univ. Press, Cambridge, pp. 133–192.
- Nolet, G., Zielhuis, A., 1994. Low S velocities under the Tornquist–Teisseyre zone: evidence for water injection into the transition zone by subduction. *J. Geophys. Res.* 99, 15813–15820.
- Nozette, S., Lichtenberg, C.L., Spudis, P., Bonner, R., Ort, W., Malaret, E., Robinson, M., Shoemaker, E.M., 1996. The Clementine bistatic radar experiment. *Science* 274, 1495–1498.
- Parks, G., Brittnacher, M., Chen, L.J., Elsen, R., McCarthy, M., Germany, G., Spann, J., 1997. Does the UVI on Polar detect cosmic snowballs? *Geophys. Res. Lett.* 24, 3109–3112.
- Parks, G., Brittnacher, M., Elsen, R., McCarthy, M., O'Meara, J.M., Germany, G., Spann, J., 1998. Comparison of dark pixels observed by VIS and UVI in dayglow images. *Geophys. Res. Lett.* 25, 3063–3066.
- Peucker-Ehrenbrink, B., 1996. Accretion of extraterrestrial matter during the last 80 million years and its effect on the marine osmium isotope record. *Geochim. Cosmochim. Acta* 60, 3187–3196.
- Rampino, M.R., 1994. Tillites, diamictites, and ballistic ejecta of large impacts. *J. Geol.* 102, 439–456.
- Rampino, M.R., Haggerty, B.M., 1996. Impact crises and mass extinctions: a working hypothesis. In: Ryder, G. et al. (Eds.), *The Cretaceous–Tertiary Event and Other Catastrophes in Earth History*. Geol. Soc. Am. Spec. Pap. 307, 11–30.
- Raymo, M.E., Ruddiman, W.F., 1992. Tectonic forcing of late Cenozoic climate. *Nature* 359, 117–122.
- Raymo, M.E., Ruddiman, W.F., Froelich, P.N., 1988. Influence of late Cenozoic mountain building on ocean geochemical cycles. *Geology* 16, 649–653.
- Raynaud, D., Jouzel, J., Barnola, J.M., Chappellaz, J., Delmas, R.J., Lorius, C., 1993. The ice record of greenhouse gases. *Science* 259, 926–934.
- Rizk, B., Dessler, A.J., 1997. Small comets: naked-eye visibility. *Geophys. Res. Lett.* 24, 3121–3124.
- Rubey, W.W., 1951. Geologic history of sea water, an attempt to state the problem. *Bull. Geol. Soc. Am.* 62, 1111–1148.
- Rye, R., Kuo, P.H., Holland, H.D., 1995. Atmospheric carbon dioxide concentrations before 2.2 billions years ago. *Nature* 378, 603–605.
- Schimel, D., 26 others, Radiative forcing of climate change. In: Houghton, J.T. et al. (Eds.), *Climate Change 1995, The Science of Climate Change*. Cambridge Univ. Press, Cambridge, pp. 65–131.
- Shaffer, J.A., Cerveny, R.S., Dorn, R.I., 1996. Radiation windows as indicators of an astronomical influence on the Devil's Hole chronology. *Geology* 24, 1017–1020.
- Slade, M.A., Butler, B.J., Muhleman, D.O., 1992. Mercury radar imaging: evidence for polar ice. *Science* 258, 635–640.
- Smyth, J.R., 1994. A crystallographic model for hydrous wadsleyite (B-Mg₂SiO₄): An ocean in the Earth's interior? *Am. Mineral.* 79, 1021–1024.
- Summers, M.E., Conway, R.R., Siskind, D.E., Stevens, M.H., Offermann, D., Riese, M., Preusse, D.F., Strobel III, J.M.R., 1997. Implications of satellite OH observations for middle atmospheric H₂O and Ozone. *Science* 277, 1967–1970.
- Sundquist, E.T., 1993. The global carbon dioxide budget. *Science* 259, 934–941.
- Swisher III, C.C., Grajales-Nishimura, J.M., Montanari, A., Margolis, S.V., Claeys, P., Alvarez, W., Renne, P., Cedillo-Pardo, E., Maurrasse, F.J.-M.R., Curtis, G.H., Smit, J., McWilliams, M.O., 1992. Coeval ⁴⁰Ar/³⁰Ar ages of 65.0 million years ago from Chicxulub crater melt rock and Cretaceous–Tertiary boundary tektites. *Science* 257, 954–958.
- Thomas, E., Shackleton, N.J., 1996. The Paleocene–Eocene benthic foraminiferal extinction and stable isotope anomalies. In: Knox, R.W. O'B. et al. (Eds.), *Correlation of the Early Paleogene in Northwest Europe*. Geol. Soc. Spec. Publ. 101, 401–441.
- Toon, O.B., Turco, R.P., Covey, C., 1997. Environmental perturbations caused by the impacts of asteroids and comets. *Rev. Geophys.* 35, 41–78.
- Torgersen, T., Drenkard, S., Stute, M., Schlosser, P., Shapiro, A., 1995. Mantle helium in ground waters of eastern North America: time and space constraints on sources. *Geology* 23, 675–678.
- Tuncel, G., Zoller, W.H., 1987. Atmospheric iridium at the South

- Pole as a measure of the meteoritic component. *Nature* 329, 703–705.
- Turco, R.P., Toon, O.B., Park, C., Whitten, R.C., Pollack, J.B., 1982. An analysis of the physical, chemical, optical, and historical impacts of the 1908 Tunguska Meteor Fall. *Icarus* 50, 1–52.
- Vail, P.R., Mitchum, R.M., Jr., Thompson III, S., 1977. Seismic stratigraphy and global changes of sea level, Part 3: relative changes of sea level from coastal onlap. In: Payton, C.E. (Ed.), *Seismic Stratigraphy — Applications to Hydrocarbon Exploration*. Am. Assoc. Pet. Geol. Mem. 26, 83–97.
- Weissman, P.R., 1986. The Oort cloud and the galaxy: dynamical interactions. In: Smoluchowski, R. et al. (Eds.), *The Galaxy and the Solar System*. Univ. Arizona Press, Tucson, AZ, pp. 204–237.
- Winograd, I.J., Coplen, T.B., Landwehr, J.M., Riggs, A.C., Ludwig, K.R., Szabo, B.J., Kolesar, P.T., Revesz, K.M., 1992. Continuous 500,00-year climate record from vein calcite in Devil's Hole, Nevada. *Science* 258, 255–260.
- Winograd, I.J., Landwehr, J.M., Ludwig, K.R., Coplen, T.B., Riggs, A.C., 1997. Duration and structure of the past four interglaciations. *Quat. Res.* 48, 141–154.