



Time to Accumulate Chloride Ions in the World's Oceans

Creationism's Young Earth Not Supported

INTRODUCTION

Some "creation scientists" claim that the earth is only about 6000 years old, but this assertion is not based on science. They also object to using radiometric isotopic age-dating methods to determine the age of the earth, which calculate ages of about 4.54 billion years (Newman 1997). It is easy to counter these arguments, of course, if the earth can be shown to be billions of years old by some other method in addition to the isotopic age dating. One such method used early in the study of the age of the earth was based on observing the rate at which the world's rivers brought in dissolved sodium ions (Na^+) and then calculating how long it would take to make the world's oceans as salty as they are now, based on this rate of accumulation. In 1899, John Jolly estimated this time to be about 100 million years (Birkeland and Larson 1989). But then researchers realized that this estimate had a number of problems. The rate at which Na^+ ions were transported to the world's oceans was probably not constant, and many of the Na^+ ions came from recycled salt. Furthermore, the ocean waters probably reached a certain limit of Na^+ ion content but no more because many of these Na^+ ions were incorporated in clay and other minerals and thus removed from the ocean water. Therefore, the earth was *older* than 100 million years, but how much older could not be determined, so this method of estimating the age of the earth was abandoned. However, if the chloride ion (Cl^-) content in sea water is used instead of the Na^+ ion and if the origin of the Cl^- ions can be determined, then an estimate of the time that it takes to make all salt, both in the oceans and on the continents, can be calculated.

SOURCES OF SALTS AND THE CHLORIDE ION

It has been generally assumed that the Cl^- ion in salts in the oceans results from the weathering of igneous rocks, which produces dissolved ions that are transported to lakes or to the oceans. For example, each

year four rivers surrounding the Great Salt Lake in Utah bring in about 2.9 million acre-feet of rain water which carries about 8.82×10^9 kilograms of dissolved salts to the lake. Each year all this water evaporates in the summer, so these salts are added to the lake beds (UGS nd).

Although some Cl^- ions in the salts in the Great Salt Lake could be newly derived from the weathering of igneous rocks in adjacent mountains, it is likely that much of the Cl^- ion content came from recycled salt (NaCl) released during the erosion of marine sandstones of Paleozoic, Mesozoic, or Cenozoic age in the surrounding area. Furthermore, in various places around the world, there are local thick layers of salt (some more than 1 kilometer thick) that are interlayered with the marine sandstones. Salt in all of these places must have been in the oceans at one time but is now on the continents. Therefore, when we calculate the amount of salt in the oceans as a basis for estimating the age of the earth, we have to include these ions as a part of the salt "in the oceans" because they were originally located there. On that basis, a source for the Cl^- ions in this salt must also be accounted for in addition to the *present* Cl^- ions in the oceans.

That ultimate source for the Cl^- ions in the present oceans, marine sediments on the continents, and thick salt beds could be from the older Precambrian rocks that underlie the Paleozoic, Mesozoic, and Cenozoic sedimentary rocks. The structure of the underlying Precambrian igneous and metamorphic rocks reveals evidence of extensive erosion of former continental mountains that once projected with high elevations above sea level, just like the elevations of the present mountains. These mountains would have had deep roots. That is, the relatively low densities of the rocks in the mountains would have caused them to float like icebergs atop the underlying denser mantle with most of their volume below sea level, extending to deep roots. Through a long period of geologic time and after periods of isostatic uplift, these mountains were eroded down to their roots and planed off so the Paleozoic, Mesozoic, and Cenozoic rocks were deposited on top of them. The average total thicknesses of these ancient Precambrian eroded masses must have been at least 20 to 30 kilometers because only at such thicknesses (depths) and high temperatures as occur there can

Lorence G Collins is a retired professor of geology who has written extensively to promote general knowledge about geology and to counter arguments by anti-evolutionists. Two of his articles for RNCSE can also be found on-line at his website <<http://www.csun.edu/~vcge005/creation.html>>.

– More Than 3.6 Billion Years

Lorence G Collins, California State University, Northridge

the kinds and compositions of minerals in these exposed rocks be formed (Winter 2001).

AMOUNT OF CHLORIDE OBTAINED FROM PRECAMBRIAN ROCKS

If 25 kilometers (km) is chosen as the average thickness (most measures fall between 20 and 30 km) for the depth of erosion for a volume of Precambrian igneous and metamorphic rocks in the area occupied by the continents, and if the average density of these rocks is 2.9 grams/cubic centimeter (g/cc), and if these rocks contain 130 parts per million (ppm) Cl^- (Table 1), the amount of Cl^- in this volume is 3.4974×10^{20} g. But the amount of Cl^- in the world's oceans is 2.6715×10^{22} g (see Table 3 for details of these calculations).

TABLE 1

Comparison of the abundance in parts per million of the eight most common elements in the earth's crust to the abundance of the element chlorine (Klein and Hurlbut 1977).

Element	Symbol	Abundance (ppm)
Oxygen	O	466 000
Silicon	Si	277 200
Aluminum	Al	81 300
Iron	Fe	50 000
Calcium	Ca	36 300
Sodium	Na	28 300
Potassium	K	25 900
Magnesium	Mg	20 900
Chlorine	Cl	130

Therefore, the amount of Cl^- in the world's oceans is about 19 times more than can be produced from a 25-km-thick tablet of continental crustal rocks. In fact, the thickness of original rock necessary to produce the amount of Cl^- presently in the oceans would have to have been 475 km, which is a depth many times greater than would ever be possible to erode. Furthermore, even greater thicknesses would be needed to account for the additional amount of Cl^- in salt in the marine sandstones and in the pure salt layers that lie on top of the Precambrian rocks. Therefore, erosion of continental rocks is far from being an adequate source for the large quantity of Cl^-

ions in the world's oceans. In comparison, the amount of Na^+ in a 25-km-thick mass of continental rocks is many times more than adequate, since it makes up 2.83% of the earth's crust (Table 1). Obviously, this amount of Cl^- in the oceans requires another Cl^- ion source besides Precambrian igneous and metamorphic crustal rocks.

MANTLE PROCESSES

The scientific explanation for the origin of the earth is that it accreted from planetesimals that collided and melted. Relatively heavy iron and nickel sank to the core of the earth, and the lighter elements, consisting mostly of oxygen and silicon, but including lesser amounts of six other metallic elements and even smaller amounts of Cl^- (Table 1), floated up and crystallized as silicate minerals in the outer mantle (Winter 2001). The abundant large O^{2-} ions (1.40 Å; $1\text{Å} = 10^{-8}$ cm) and tiny Si^{4+} ions (0.42 Å) occur in silicate lattices in which four O^{2-} ions surround one Si^{4+} in tetrahedral arrangements, and the other metallic ions fill the interstices outside the tetrahedra to obtain electrical balance. On the other hand, the Cl^- ion with its large (1.81 Å) size (Table 2) does not fit into the lattices and is relatively unstable deep in the mantle at the high pressures that occur there. Consequently, when the outer mantle was first formed, most of the estimated primordial 2.2×10^{25} g Cl^- was concentrated in the outermost parts of the mantle (Graedel and Keene 1996). Moreover, throughout this period, the Cl^- ions, because of their large sizes, continued to be squeezed out of dense silicate minerals in the mantle and migrated upward as a highly volatile gas, hydrogen chloride (HCl). At the earth's surface much of this HCl was expelled during volcanic eruptions. Today, we estimate that 7.8×10^{12} g HCl are expelled annually into the atmosphere by volcanic eruptions (Mattox and Cadle 1980), and of this amount, the Cl^- ion is 7.5863×10^{12} g. Therefore, volcanoes contribute large quantities of Cl^- ions that are scattered throughout the world in acid deposition. This is another way that Cl^- ions can become a part of the salts in the Great Salt Lake or be accumulated in the oceans.

TABLE 2

Comparison of the relative sizes (radii) of ions in angstroms.

Ion	Size
Si^{4+}	0.42 Å
Al^{3+}	0.51 Å
Mg^{2+}	0.66 Å
Fe^{2+}	0.74 Å
Na^+	0.97 Å
Ca^{2+}	0.99 Å
K^+	1.33 Å
O^{2-}	1.40 Å
Cl^-	1.81 Å

TABLE 3 Calculations for determining the abundance of Cl^- ions in Precambrian crustal rocks in comparison to the abundance of Cl^- ions in the world's oceans.

Abundance of Cl^- ions in Precambrian rocks:

Volume of Precambrian rocks (thickness x area of continents):
 $(25 \text{ km}; 2.5 \times 10^6 \text{ cm}) \times (1.4843 \times 10^{18} \text{ cm}^2)$ (Enchanted Learning nd) = $9.2769 \times 10^{23} \text{ cc}$.

Mass of rock in this volume: (density x volume):
 $2.9 \text{ g/cc} \times 9.2769 \times 10^{23} \text{ cc} = 2.6903 \times 10^{24} \text{ g}$.

Amount of Cl^- in this mass:
 0.00013 (relative abundance of Cl^- ; Table 1) $\times 2.6903 \times 10^{24} \text{ g} = 3.4974 \times 10^{20} \text{ g Cl}^-$.

Abundance of Cl^- ions in the world's oceans:

Mass of Cl^- ions per cc of sea water: mass of salts/cc
 $(0.03528 \text{ g/cc}) \times \text{Cl}^- \% (0.553) = 0.0195 \text{ g Cl}^-/\text{cc}$ (UCAR 2002).

Mass of Cl^- ions in the world's oceans:
 $0.0195 \text{ g Cl}^-/\text{cc} \times 1.37 \times 10^{21} \text{ cc}$ (volume of the world's oceans; Duxbury 2000) = $2.6715 \times 10^{22} \text{ g Cl}^-$.

TOTAL TIME TO MAKE ALL CHLORIDE IONS

Because the annual amount of Cl^- ions that is expelled into the atmosphere is known ($7.5863 \times 10^{12} \text{ g}$), this value can be used to calculate the time for Cl^- ions to have accumulated in the world's oceans through volcanic eruptions. Dividing $2.6715 \times 10^{22} \text{ g}$ by $7.5863 \times 10^{12} \text{ g}$ gives the number of years to be about 3.5 billion years. However, the amount of Cl^- ions in the world's oceans ($2.6715 \times 10^{22} \text{ g}$) also includes the $3.4974 \times 10^{20} \text{ g}$ of Cl^- ions that were eroded from the 25-km-thick Precambrian tablet (Table 3). This contribution of Cl^- ions from this tablet would subtract from the 3.5 billion years. The proportion of Cl^- ions contributed from the continental rocks is only $\frac{1}{90}$ th of the total in the world's oceans and subtracts only 0.046 billion years. So we now have a rough estimate of 3.316 billion years.

TABLE 4 Calculations for obtaining the time to form the Cl^- ions in rock salt (NaCl) in continental rocks.

Volume of sedimentary rocks:
 $0.66 \times 1.4843 \times 10^{18} \text{ cm}^2$ (continental area) $\times 1.8 \times 10^5 \text{ cm}$ (thickness) = $1.7633 \times 10^{23} \text{ cc}$.

Volume of NaCl in sedimentary rocks:
 $0.01 \times 1.7633 \times 10^{23} \text{ cc} = 1.7633 \times 10^{21} \text{ cc}$.

Mass of NaCl (density x volume):
 $2.16 \text{ g/cc} \times 1.7633 \times 10^{21} \text{ cc} = 3.8087 \times 10^{21} \text{ g}$.

Mass of Cl^- ions in NaCl:
 0.6065 (percent Cl^-) $\times 3.8087 \times 10^{21} \text{ g}$ (mass of NaCl) = $2.31 \times 10^{21} \text{ g Cl}^-$.

Added time for first Cl^- ions in NaCl:
 $2.31 \times 10^{21} \text{ g of Cl}^- \div 7.5863 \times 10^{12} \text{ g/year} = 0.3045 \text{ billion years}$.

However, there are other factors to be considered in determining the amount of time needed to deposit all the salt present on the earth. For example, although more than $2.6715 \times 10^{22} \text{ g}$ of Cl^- have been released into the oceans, the above calculations have not taken into account the evaporite rock salt (NaCl) deposits on the continents, which must have formed from

deposition of Cl^- ions in former ancient isolated marine seas that evaporated. No one has estimated their volumes, but from the abundance of various sedimentary rocks, the approximate volumes can be deduced. The sedimentary rocks on the continents consist of mostly shales, sandstones, and limestones (greater than 95% and perhaps as much as 99%) (Blatt 1982). The remaining rock types (1-5%) are phosphorites, coal and other organic deposits, banded iron formations, volcanoclastic rocks (ash beds), chert, gypsum, and rock salt. On that basis, a reasonable estimate for the volume of rock salt is about 1% of the volume of sedimentary rocks.

Of the continental surface area, 66% is covered by sedimentary rocks, and the average thickness of all these sedimentary rocks is $1.8 \times 10^5 \text{ cm}$ (Blatt 1982). Therefore, the average volume of sedimentary rocks is $1.7633 \times 10^{23} \text{ cc}$, and 1% of this is $1.7633 \times 10^{21} \text{ cc}$. On the basis that NaCl has a density of 2.16 g/cc, the mass of the Cl^- ions in this volume is $2.31 \times 10^{21} \text{ g}$. This additional amount of Cl^- ions must be provided by Cl^- ions coming up from the mantle, and the amount of additional time required to produce that amount is 0.3045 billion years (see Table 4 for these calculations). Although there are more Cl^- ions on the continents in the troposphere, glaciers and ice masses, soil, ground water, fresh water lakes and rivers, and other sources (Graedel and Keene 1996), these amounts are so small that accounting for them does not change the time except in the fourth decimal point. Nevertheless, adding 0.3045 to 3.316 suggests that the time for all Cl^- ions to have accumulated on the earth in the oceans and in evaporite deposits is about 3.6 billion years.

OTHER FACTORS INCREASING THE TIME FOR ACCUMULATION OF CHLORIDE IONS

Some Cl^- in the world's oceans has been recycled into and then out of the crust because of plate tectonics. Therefore, the Cl^- in the world's oceans now does not include just the Cl^- ions that migrated into the oceans since the earth was formed. Since the Jurassic Period or as far back as the Precambrian, some Cl^- ions in the oceans have been carried down with sea water into the mantle by the subduction of basaltic oceanic plates. Both the water and the soluble Cl^- ions are released from the slabs and rise through the crust. The water facilitates the melting of the crustal rocks above the subducting slab to create magmas, and such magmas were injected into the Precambrian crust as well as into overlying Paleozoic, Mesozoic, and Cenozoic sedimentary rocks (Collins 1999). The solidified magmas might be expected to trap the Cl^- ions and prevent their use for estimating times of formation, but the large size (1.81 \AA) of the Cl^- ion allows only a little to be trapped. Consequently, the igneous rocks contain Cl^- only in parts per million. For example, the standard biotite granite G-2 contains 70 ppm Cl^- (USGS 1995). Taking into account the amount of Cl^- ions stored in the continental igneous rocks that have not been eroded away to their roots, as well as those that have, can affect the estimated time for Cl^- ions to accumulate in

the world's oceans by only an insignificant time. On the other hand, the time for recycling would affect the age estimate because only the Cl^- ions in the world's oceans are used in the calculations and not the time while some are being recycled. The recycling would have been slow because the oceanic plates move only 1–10 cm per year (Huang 2001) and because the widths of the plates that were subducted can be more than 9000 km (Birkeland and Larson 1989). The times involved when many Cl^- ions were being recycled during all subduction periods (including those in the Precambrian) are not included in the 3.6-billion-year age, and, therefore, an additional unknown period of time should be added to the 3.6 billion years. For example, if the average motion of the oceanic plates since the Pacific Ocean first split apart in the mid-ocean in the Jurassic Period is 5 cm per year and if the plates have moved 9000 km to the present time, the time for these movements is 0.18 billion years. This would make the total age of the Cl^- ions in the ocean about 3.78 billion years. Add similar times to this age for movements of crustal plates during older (Precambrian) subduction periods, and ages in excess of 4 billion years could be possible.

At any rate, the calculated 3.6 billion years for the minimum age of the earth is far greater than the often-quoted creationists' age of 6000–10 000 years. The time required for Cl^- ions to accumulate in the world's oceans and on the continent of 3.6 or more billion years is plausible and agrees with radiometric dates for Precambrian rocks. Some rocks have been dated as being 3.7 to 3.8 billion years old, and the oldest rock found near Great Slave Lake in Canada has been dated as being 4.03 billion years old. Furthermore, detrital zircon crystals in Precambrian metasedimentary rock in Australia are dated to be 4.3–4.4 billion years old (Newman 1997).

WHY CHLORIDE IONS ACCUMULATE

In order to use the abundance of Cl^- ions in the world's oceans as a means of calculating the age of the earth, these ions must have special properties that allow them to accumulate gradually. When the abundance of Na^+ (28 300 ppm) is compared to that of Cl^- (130 ppm) in crustal rocks (Table 1), the relatively smaller amount of Na^+ (30.8%) compared to the amount of Cl^- (55.3%) in sea water (Table 5) is far out of proportion and in a reverse relationship to what we would expect (UCAR 2002). That is, the extremely scarce Cl^- ion in Precambrian rocks has accumulated in the oceans and is the dominant ion, instead of the much more abundant Na^+ ion. Without knowing that huge amounts of Cl^- ions came up from the mantle below the Precambrian rocks, this reversal seems enigmatic. Why do the Cl^- ions accumulate to such a greater extent than Na^+ ions?

In contrast to the Cl^- ion, the other soluble elements (as ions) in sea water, such as sodium (Na), magnesium (Mg), sulfur (S), calcium (Ca), and potassium (K), do not accumulate to the extent that Cl^- ions do because they either become subtracted by sea animals to form their carbonate shells and skeletons (that later compose limestones) or are incorporated in the crystal structures of clay or other minerals. Both Na^+ and

Cl^- ions, however, are particularly soluble in water because water is an asymmetric molecule in which one end has a positive charge and the other a negative charge. Because of the polar nature of water, many water molecules orient their positive ends to surround the negative Cl^- ions, and many other water molecules orient their negative ends to surround the positive Na^+ ions. Because the Na^+ ion is relatively tiny (a sphere whose radius is 0.97 Å), fewer polar water molecules can surround it in comparison to the Cl^- ion whose sphere has a radius of 1.81 Å and whose greater surface area allows many more polar water molecules to surround it. This relationship between water and a Cl^- ion causes it to be extremely soluble ... and more soluble than the Na^+ ion.

The high solubility of the Cl^- ion, the lack of incorporation of Cl^- ions by sea animals, and the large (1.81 Å) size of the Cl^- ion which prevents it from being incorporated into other minerals ensure that the Cl^- ions remain in solution and accumulate in the oceans unless the water containing them is evaporated. On the basis of these characteristics, the thick salt (NaCl) beds (some more than 1 kilometer thick) that occur, for example, in China, Great Britain, United States, the former USSR, Germany, Canada, and Mexico, and which are interlayered with the supposed "Noachian Flood" deposits, provide strong evidence that all sedimentary rocks in the geologic column cannot have been deposited during the alleged global Flood lasting one year. The reason is that the geologic column must contain arid periods that allowed isolated salty seas to evaporate and precipitate their Na^+ and Cl^- ions (and other salts) into these thick salt beds. That cannot happen while water in the Noachian Flood is supposedly covering the whole earth. Furthermore, these salt beds are interlayered with other evaporite deposits, such as gypsum beds, chemically precipitated calcium carbonate (limestone), and other salts that are deposited sequentially in the proper order according to their ions' saturation points as water evaporates, and then these ions begin to precipitate (Birkeland and Larson 1989). Moreover, these salt beds are also interlayered with red beds (former muds) that contain oxidized iron (which indicates exposure to oxygen in the atmosphere), and these red beds have mud cracks that are characteristic of drying conditions in deserts. If creation scientists were to claim that the salt beds were formed during the Noachian Flood from the eruption of hot hydrothermal salt solutions from the mantle, this hypothesis would not make any scientific sense. Any erupting hot water salt solutions would have mixed with the Flood waters, and their Cl^- ions, which are very soluble, would have been disseminated and diluted in the water, preventing precipitation.

VALIDITY OF CALCULATIONS

The value of 3.6 to 4 billion years for the time of the accumulation of Cl^- ions in the world's oceans is based on the present annual rate at which HCl is erupted from volcanoes. Obviously, this rate has not been constant through time. The amount of emerging

TABLE 5

Percent of each element occurring as ions in sea water (UCAR 2002).

Element	Percent of All Dissolved Ions
Cl	55.3
Na	30.8
Mg	3.7
S	2.6
Ca	1.2
K	1.1

HCl in volcanoes is a function of several variables including the number of volcanoes at a given time, frequency of eruption during a year, activity of volcanoes through long periods of time (including periods of dormancy), and the rate at which HCl moves up from the mantle to be expelled by the volcanoes. Volcanoes erupt from mid-ocean spreading centers as well as on continents above subducting plates, so emergence of HCl from the mantle can be expected throughout most of geologic history. However, plate tectonics has been intermittent through time. During the Precambrian Era, rafted continental plates have collided, and plate movements have stopped for a while. But the earth is a restless planet, and the continents split apart again, and these back-and-forth rafted movements of continents are repeated over and over. When the plates are not moving, few volcanoes erupt, so the release of HCl could be at a much slower rate. Slow rates would *increase* the time it takes for Cl⁻ ions to accumulate in the world's oceans; fast rates would shorten the time. The slow rates, particularly early in the earth's history, could make the value for the first appearance of the Cl⁻ ions to be more than 3.6 billion years. In any case, the 3.6-billion-year value (or as much as 4 billion years if recycling during subduction is included) is an approximation of the time for the accumulation of all the Cl⁻ ions in the world's oceans. Whatever the real value is, it is certainly not in *thousands* of years but *billions* of years.

CONCLUSIONS

The instability of the Cl⁻ ions in the mantle because of their large (1.81 Å) size (which causes them to rise toward the earth's surface) and the relative inability for the rising Cl⁻ ions to precipitate abundantly in granitic crustal rocks (only 130 parts per million) explain why the Cl⁻ ions are mostly expelled during volcanic eruptions in escaping HCl gas and then accumulate in the world's oceans. This process would have taken at least 3.6 billion years, indicating that the world's *oceans* are billions of years old and that the earth itself must be older. Therefore, the Cl⁻ ions in the oceans could not have been deposited in 6000 years or during the Noachian Flood without a suspension of natural laws and processes. Thus the only way to produce these concentrations of salt in the world's oceans during these short periods of time is to invoke a miracle. Of course, there is no argument against a miracle, but neither does a miracle provide any scientific evidence.

Biblical stories, such as that of the Noachian Flood, were written to make a theological point without regard for science. As Pope John Paul II has pointed out, the Bible is not intended to be a science text, and science is not in conflict with the biblical message (John Paul II 1996). The Hebrew story-telling style of writing that described the Noachian Flood is quite acceptable and valid for the audience which was addressed by the author of Genesis. Who at that time would have the knowledge to understand a scientific explanation? What is important is that the theological messages that are presented in Genesis can be just as meaningful for the biblical people, who were not trained in science, as they can be for any scientist living today.

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AUTHOR'S ADDRESS

Lorence G Collins
 Department of Geological Sciences
 California State University, Northridge
 Northridge CA 91330-8266
 lorencec@sysmatrix.net

OOPS

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