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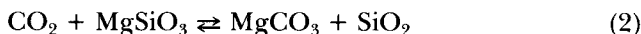
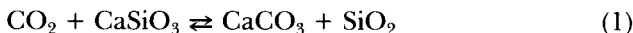
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A. G. HÖGBOM AND THE DEVELOPMENT OF THE CONCEPT OF THE GEOCHEMICAL CARBON CYCLE

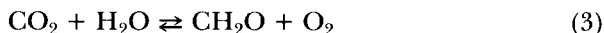
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It is generally agreed that the level of atmospheric CO₂ on the time scale of millions of years is controlled mainly by a combination of degassing from the Earth's interior balanced by the uptake of CO₂ via the weathering of Ca and Mg silicate minerals. The CO₂ is converted to dissolved HCO₃⁻ during weathering, and this carbon is carried to the sea by rivers and precipitated there as Ca and Mg carbonate minerals. Credit for formulating this silicate-carbonate subcycle is often given to Urey (1952) who wrote the reactions:



These reactions, which are commonly referred to as the Urey reactions (Berner, Lasaga, and Garrels, 1983; Berner, 1991), going from left-to-right represent CO₂ removal via weathering and carbonate precipitation and going from right-to-left represent degassing due to the thermal decarbonation of the carbonates after burial to sufficient depths. Added to the Urey reactions should also be the organic carbon subcycle which exerts an important additional control on atmospheric CO₂ level. This involves the removal of CO₂ from the atmosphere by the burial of organic matter in sediments and the weathering of organic matter (or its thermal decomposition) which returns the CO₂. The appropriate reactions are:



Together reactions (1) to (3) regulate CO₂ on a multimillion year time scale and are the basis for the *geochemical, or long term, carbon cycle*.

Control of atmospheric CO₂ by weathering and degassing certainly is not original with Urey. Several authors (Plass, 1956; Raymo, 1991) have cited the much earlier work of Chamberlin (1899a) who formulated these reactions in words, without writing them out in chemical symbolism. Chamberlin emphasized the importance of changes in CO₂ level over geologic time due to changes in the area and especially elevation of continental areas undergoing CO₂ uptake via weathering. However, he also mentioned CO₂ uptake via organic matter burial and emphasized

varying rates of volcanism as an additional source of CO₂ variation over time.

Chamberlin's interest in CO₂ was based on the contemporary work of Arrhenius (1896) who showed that atmospheric CO₂ could act as a greenhouse gas to warm the Earth. (Actually, Arrhenius was one of the first to calculate the magnitude of the CO₂ greenhouse effect on global temperature, and his results amazingly are not much different from the highly sophisticated calculations made today by general circulation modeling.) A lowering of CO₂ via enhanced weathering accompanying mountain uplift was cited by Chamberlin as a major cause of past glaciations. However, in a companion paper (Chamberlin, 1899b), he found difficulty in the timing of mountain uplift with the inception of the Permo-Carboniferous glaciation and was forced also to call upon enhanced burial of organic matter accompanying coal formation (reaction 3 above going from left-to-right) to help explain this major glacial event.

Chamberlin (1899a) also cites a shorter-term carbon cycle. This consists of storage in the oceans of dissolved HCO₃⁻, produced by the weathering of either carbonates or silicates, which results in a lowering of the level of CO₂ in the atmosphere. Added to this is greenhouse cooling of the oceans, due to lowered CO₂, resulting in enhanced CO₂ solubility and further lowering of the atmospheric concentration, a positive feedback effect. This oceanic carbon storage, which cannot persist for more than a few hundred thousand years because of buffering by inorganic CaCO₃ dissolution and precipitation, is the basis of several short term carbon cycle models including the so-called coral reef hypotheses for CO₂ changes during the Pleistocene (Berger, 1982; Opdyke and Walker, 1992).

In my research I have discovered that much of Chamberlin's work was not original but was based on the earlier work of a Swedish chemist, A.G. Högbom. Chamberlin was familiar with Högbom's work, and he credits Högbom accordingly, but this is often missed by readers of Chamberlin's work. For example Chamberlin, referring to atmospheric CO₂, states:

Professor Högbom has made a valuable contribution to the general doctrine of consumption and supply (Chamberlin, 1899a, p. 548)

Actually it was Chamberlin's purpose to extend Arrhenius and Högbom's ideas to geology by identifying specific periods in time when the geochemical carbon cycle was out of balance and when glaciation occurred due to a reduced greenhouse effect. Chamberlin did introduce the importance of mountain uplift to weathering, but practically all the chemical reasoning given by Chamberlin (and more) can be found in a paper previously published in Swedish by Högbom (Högbom, 1894), much of which is quoted and translated into English by Arrhenius (1896).

Several quotations from Högbom (1894) support this contention. (Translation from the Swedish here is mainly by Arrhenius with corrections and additions by my colleague, George Veronis. Note that CO₂ is

referred to as carbonic acid, and quotes in italics are my additions). The quotations are:

1. With respect to CO₂ variations due to changes in weathering rate:

As the process of weathering has consumed quantities of carbonic acid many thousand times greater than the amount now disposable in the air, and as this process from different geographical, climatological and other causes has in all likelihood proceeded with very different intensity at different epochs, the probability of important variations in the quantity of carbonic acid [*over time*] seems to be very great . . . (Arrhenius quoting Högbom, p. 271)

2. With respect to *all possible* inputs and outputs of atmospheric CO₂:

Carbonic acid is supplied to the atmosphere by the following processes: (1) volcanic exhalations and geological phenomena connected therewith; (2) combustion of carbonaceous meteorites in the higher regions of the atmosphere; (3) combustion and decay of organic bodies [*later he describes fossil fuel burning as well as the weathering of organics*]; (4) decomposition of carbonates; (5) release of CO₂ dissolved in seawater because of temperature increase or reduction of atmospheric CO₂ partial pressure; (6) liberation of carbonic acid mechanically enclosed in minerals on their fracture or decomposition [*mainly volcanic exhalations*]. The carbonic acid of the air is consumed chiefly by the following processes: (7) formation of carbonates from silicates on weathering; (8) the consumption of carbonic acid by vegetative processes [*for long term effects he later discusses organic matter burial*]; (9) the absorption of CO₂ in the sea. (Arrhenius quoting Högbom, p. 272, with the addition of items (5) and (9) from the Veronis translation—items 5-9 are renumbered here.)

3. With respect to *main* inputs and outputs and the balance between them:

As the enormous quantities of carbonic acid (representing a pressure of many atmospheres) that are now fixed in the limestone of the earth's crust cannot be conceived to have existed in the air but as an insignificant fraction of the whole at any one time since organic life appeared on the globe, and since therefore the consumption through weathering and formation of carbonates must have been compensated by means of continuous supply, we must regard volcanic exhalations as the chief source of carbonic acid for the atmosphere. (Arrhenius quoting Högbom, p. 272—my underlining added).

Here I have added underlining to emphasize that consumption by weathering on a million year time scale must be matched closely by supply via volcanism (and metamorphism). This important point unfortunately is too often ignored by present day workers on the carbon cycle.

4. With regard to volcanic degassing over time:

Just as single volcanoes have their periods of variation with alternating relative rest and intense activity, in the same manner the globe as a whole seems in certain geological epochs to have exhibited a more violent and general volcanic activity, whilst other epochs have been marked by comparative quiescence of the volcanic forces. It seems therefore probable that the quantity of carbonic acid in the air has undergone nearly simultaneous variations, or at least that this factor has had an important influence. (Arrhenius quoting Högbom, p. 272-283).

5. Högbom also discusses the role of the ocean, plants, and weathering as a buffer against atmospheric CO₂ changes. This buffering process is important in the short term carbon cycle which is of great interest today

because of the rise of atmospheric CO_2 due to the burning of fossil fuels. According to the Veronis translation (a passage omitted by Arrhenius) Högbom states:

Suppose eg. that a sudden addition of CO_2 , by an amount equal to that already existing in the atmosphere, should take place in one way or another. By this act the CO_2 in the atmosphere would not at all be doubled because the major part of the addition would be offset by increased CO_2 absorption in seawater because of the increased partial pressure. Therefore, the increase of CO_2 in the atmosphere would be insignificant. On top of that the increase of absorption of CO_2 in the minerals and increase in the biosphere would make the CO_2 increase in the atmosphere negligible. A similar tendency to maintain the equilibrium would occur if there were a decrease of the CO_2 in the atmosphere.

Högbom also goes on to discuss the buffering of the oceans with respect to HCO_3^- storage due to CaCO_3 precipitation, an idea further elaborated by Chamberlin, as discussed above. Högbom's buffering ideas are now generally accepted, but they are not as perfect as he states because changes in atmospheric CO_2 that have occurred due to the burning of fossil fuels, for example, are not "negligible."

Högbom does make one major error. He assumes that carbonates once formed are not subsequently decarbonated, so that the total mass of carbonates must be increasing with time. Carbon dioxide of presumably primitive origin simply comes out of the Earth and is fixed for all time as carbonates. This idea has been adopted in the modeling of Budyko, Ronov, and Yanshin (1987) but is refuted by simple mass-balance considerations (Koster van Gross, 1988). Burial of CaCO_3 and subsequent mobilization of CO_2 by thermal breakdown of CaCO_3 via metamorphism, or by melting in the mantle, are important processes for recycling CO_2 , in other words, Urey reactions (1) and (2) going from right-to-left. Following Högbom, Chamberlin also makes the same mistake. He ascribes degassing to the release of CO_2 contained in some unspecified manner (occluded?) in buried "crystalline" rocks and not directly to the thermal decarbonation of carbonates. In other words he also does not call upon the Urey reactions.

In summary, A. G. Högbom was a true innovator, and his contributions to many of the ideas related to the global carbon cycle, both long term and short term, have not been appreciated. Since his work is cited in translation in the paper by Arrhenius (1896) his ideas about the carbon cycle, when rarely mentioned, are erroneously attributed to Arrhenius. Furthermore, the work of T. C. Chamberlin, which is much more commonly cited, is based heavily on the earlier work of Högbom, and, accordingly greater credit should be given to Högbom. Finally, the so-called Urey reactions, (1) and (2) above, represent to a large degree the codification of the thinking of this innovator of more than a half century earlier. Perhaps it is time that these reactions be redesignated as the Högbom-Urey reactions.

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