HIGH INPUT RATES OF MICROMETEORITIC SULFUR, "SMOKE" PARTICLES AND OLIGOELEMENTS ON THE EARLY EARTH. M.Maurette[1], A.Brack[2], J.Duprat[1], C. Engrand[1], G.Kurat[3]. [1]CSNSM, Bâtiment 104, 91405 Orsay−Campus, France; [2]CBM, Rue Charles Sadron, 45071 Orléans, France; [3]Naturhistorisches Museum, Postfach 417, A-1014, Wien, Austria.

Accretion of juvenile micrometeorites. Since the late 1999, we have been investigating the effects of the accretion of juvenile micrometeorites on the Earth, during the post-lunar period of the "*Late Heavy Bombardment*", in the framework of the conjuncture of Hartmann —coined as the *LHBomb* [1].

We use an "accretion" formula reported in a companion paper [2]. It is based on the following deductions: – the giant Mars sized impact that formed the Moon also blew off the complex pre-lunar atmosphere of our blue planet [3]; – the composition of the micrometeorite flux has been invariant with time [4]; – the relative variation of lunar cratering rate with time, as reported in figure 6.6 of Ref. 1, scales to that of the micrometeorite flux.

It allows the prediction of the total amounts of micrometeoritic species released on the early Earth mostly during the first ~100 Myr that followed the formation of the Moon, using the wt% content of a given species, ***A***, in Antarctic micrometeorites and the present day mass flux of micrometeorites, of about 40,000 tons/yr [5]. This formula is validated by the unexpected good fit between its predictions and the corresponding observations reported for both: – the total amounts of Ne, N_2, H_2O and CO_2 in the Earth's atmosphere [4]; – the iridium content of lunar samples [2]. We are, therefore, using it to tackle various problems.

High sulfur contents in micrometeorites from central Antarctica. Micrometeorites collected near the margin of the Antarctic ice sheet, around Cap-Prudhomme, at 6 km from the French station of Dumont d'Urville, showed anomalous low sulfur contents (~0.1%) with regard to those (~3%) measured in CM2 hydrous-carbonaceous chondrites — a relatively rare type of meteorites to which ~95% of the Antarctic micrometeorites are related. Micrometeoritic Fe−sulfides, which are the major host phases of sulfur in extraterrestrial material, could have been lost during either atmospheric entry or terrestrial weathering, involving the preferential leaching of Fe-sulfides.

This last assumption was confirmed by the collection of a new set of micrometeorites near the French−Italian "Concordia" station, in Central Antarctica. Micrometeorites deposited a few years ago in snow samples buried at a depth of ~50 cm were well shielded from weathering. They were recovered with the least destructive and cleanest technique available, which yielded unweathered micrometeorites, showing high sulfur contents of about 5% [6].

The two worlds of iron sulfides and thioesters. With the simple "maximizing" assumption that all sulfur from volatilized micrometeorites gets initially oxidized during atmospheric entry, like organic carbon, one ends up with an enormous initial input rate of SO_2 <u>in the thermosphere</u> (~10^{16} g/yr) that lasted about 100 Myr. This SO_2 input would be even larger than that of CO_2. For a comparison, one of the most intense historical volcanic eruptions (Laki in Iceland) lasted for ~9 months, and yielded ~10^{14} g of SO_2 [7].

We first wondered about the plausible contributions of this post-lunar SO_2 input in prebiotic chemistry. It was probably quickly transformed in the stratosphere to sulfate aerosols —i.e., mostly H_2SO_4 molecules with ~30% of water— that finally were deposited in the early oceans. A plausible reaction pathway to eliminate such an excess of sulfates requires the likely existence of abundant early hydrothermal sources. They functioned like the contemporary sources, as "reactors" converting sulfates dissolved in water into both huge deposits of iron sulfides and exhalations of H_2S [9].

This amount of reprocessed sulfides is just enormous. The upper limit of their mass (about $8x10^{23}$ g) is equivalent to a global ≈300 m-thick layer around the Earth. Thus, micrometeoritic sulfur could have intervened in prebiotic chemistry in at least two different ways. Sulfides are requested in the so-called sulfide "world" [10]. Moreover, FeS and H_2S can reduce CO_2 to organic sulfides (thiols), as demonstrated in laboratory simulation of hydrothermal synthetic reactions [10]. Methyl- and ethyl-thiols were the principal thiols formed along with smaller amounts of others containing up to five carbon atoms. Thiols can lead to thioesters, which probably activated important organic prebiotic chemical reactions [11].

Micrometeorites in post-lunar early climatic variations. A remarkable balance between the absorption and scattering of solar radiation by the early Earth allowed the gentle greenhouse effect that allowed the birth of life. But when was it triggered? It is likely that the Moon forming impact had suddenly blown off all atmospheric factors that ruled the pre-lunar greenhouse effect established before the formation of the Moon. Therefore, the huge release by micrometeorites of three powerful greenhouse gases (SO_2, H_2O, CO_2), during the first ~100 Myr of the post-lunar period, was probably one of the ruling factor of the new greenhouse effect, which was effective in the origin of life. They should have produced a marked heating of the Earth's surface.

How did the Earth manage to avoid a runaway greenhouse effect without the decisive help of the faint young Sun invoked in all previous models? Hunten et al [12] proposed that, today, climatic variations over the last ~10 Myr might have been triggered by a variable input of "meteoritic" smoke particles. This concept can be extended to the "micrometeoritic" smoke particles injected into the thermosphere by about 50% of the incoming flux of micrometeorites that volatilized upon atmospheric entry. The equivalent equilibrium thickness of the resulting permanent cloud of dust, which would have topped any underlying cloud system, was ≈120 µm, if its constituent dust particles took roughly ~4 years to reach the stratosphere —this residence time was deduced from radioactive aerosols injected at an elevation of 60 km [13]. As this is much larger than the wavelength of visible solar light, this high elevation "smoky" cloud could have reflected sunlight, thus contributing to counterbalance the heating effect of micrometeoritic greenhouse gases.

Micrometeoritic oligoelements during precambrian times. The accretion formula can be applied to oligoelements, such as iron, which play a "vital" role in cell metabolism at very low concentration levels. Blain [14] recently supported earlier views by Martin [15], who deduced that iron is necessary to the growth of phytoplankton, which might rule the exchange of CO_2 between the atmosphere and the oceans today. But the amount of this element in the oceans is amazingly small (i.e., a few 10^{-3} ppb at the centre of the Pacific Ocean). Johnson [16] convincingly argued that the contemporary micrometeorite flux would already deliver ~20% of this amount.

During the Precambrian period, it is believed that the amount of iron was much more important than today, due to Fe^{2+}, as present in a "slightly acidic solution of iron sulfates" [15]. During the peak of the *LHBomb*, the flux of micrometeoritic iron, which was ~10^6 times higher than to day, yielded a much larger concentration of iron in the oceans of about a few ppm. Later on, when the first life forms appeared in the oceans (somewhere between 4.2 and 3.9 Gyr ago) the micrometeorite iron flux was still between ~1800 and ~60 times more intense than today. The question arises whether these high iron contents constrained the evolution of early life forms along peculiar evolutionary tracks, leading to a preferential growth of some iron metabolising microorganisms, thriving in acidic early oceans fertilised by SO_2 and iron "falling from the sky", both delivered by the early micrometeorite flux?

References: [1] Hartmann (1999) *Moons and Planets*, 4th Edition (Wadsworth, Belmont), pp. 1-428; [2] Langevin and Maurette (2004) This abstract book; [3] Ahrens (1993) *Ann. Rev. Earth Planet Sci.* 21, 525-555; [4] Maurette et al (2003) In, Celnikier et al (Eds) *Frontiers of life* (Thê Gioi Publishers, Hanoï), pp. 7-22; [5] Love and Brownlee (1993) *Science* 262, 550-553; [6] Duprat et al (2003) *Lunar Planet. Sci*. 34, A1727 (CD-ROM); [7] Thordarson et al (1996) *Bull. Volc*. 58, 205-225; [8] Fouquet et al (1996) *Earth Planet. Sci*. 44, 147-162; [9] Wächtershaüser (1998) In, Brack A. (Ed.) *The molecular origin of Life* (Cambridge University Press), pp 206-218; [10] Heinen and Lauwers (1996) *Origins Life Evol. Biosphere* 26, 131-150; [11] De Duve (1998) In, *The molecular origin of Life* (Ed. A.Brack), pp. 219-235 (Cambridge University Press); [12] Hunten et al (1980) *J. Atmos. Sci*. 37, 1342-1357; [13] Leipunskii et al (1970) *J.Geophys.Res*. **75**, 3569-3574; [14] Blain (1996) *La Recherche* 287, 56•60; [15] Martin (1990) *Paleoceanography* 5, 1-13; [16] Johnson (2001) *Global Biogeochemical cycles* 15, 61-63.

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