CHEMISTRY AND ACCRETION OF EARTH AND MARS. H. Wänke and G. Dreibus, Max-Planck-Institut für Chemie, Searstrasse 23, 6500 Mainz, F.R. Germany

EARTH: The high abundance of siderophile elements in the Earth's mantle excludes all models which require chemical equilibrium between primitive mantle material and a pure metal FeNi phase. Furthermore, the C1 neutralized abundances of moderately siderophile elements (Ga, Cu, W, Co, Ni) and of moderately volatile elements (Na, K, Rb, F, Zn, In) in the Earth's mantle agree within about a factor of 2 (ref.1). Elements more siderophile than Ni are somewhat more depleted as are elements with higher volatility than Na and K. To account for the observed elemental abundance pattern of the Earth's mantle an inhomogeneous accretion model was set up by Wänke (2). A similar model was briefly visualized by Anders (3) and also favoured by Ringwood (4).

According to the model outlined by Wänke (2), accretion of the Earth started with highly reduced material free of volatile and moderately volatile elements but containing all other elements in C1 abundance ratios. This component A contained all siderophile elements as metals or sulfides (including W and in part also Si, Cr, Mn, and V). It was assumed that core formation occurred contemporaneously with accretion. After accretion of about 2/3 of the Earth and more oxidized material (Fe, Co, Ni, Co, Ga, W, etc. and all lithophile elements as oxides) was added, containing all elements including moderately volatile elements in about C1 abundances (component B). Further support for this model results from the work of Newsom and Palme (5), based on the study of abundances of Ho and W in the Earth's mantle.

Mixing of the originally FeO-free mantle with component B is explained in the following way. For the whole Earth the energy retained during accretion (6) is about $1.8 \times 10^{33}$ J, the energy released during core formation is $1.5 \times 10^{33}$ J (7) and the energy produced during 4.55 by the decay of K, Th, and U is $1.2 \times 10^{33}$ J, i.e. about 75% of the total energy are released during accretion. As for the accretion time the estimates are in the 1 to range (8) of the age of the Earth the energy output during accretion was about 300 times the mean energy output by the decay of the radioactive elements. Today the turnover time of the Earth's mantle by convection is in the order of some 10^9 years. Hence, the turnover time of the Earth's mantle during accretion is estimated to be less than 10^9 yrs., a value small relative to the accretion time of about 3 x 10^9 yrs.

Component B was obviously added to a vigorously convecting mantle which was molten to a depth of several hundred kilometers (6). We have no doubt that such a scenario required additional time. The mixture of the originally FeO-free mantle with component B from the region outside of the Mars' orbit was added only at a late phase of the accretion as the transfer of material to be responsible for the Earth's inhomogeneity. We suggest that component A and component B were mixed in about 5-10% of Earth's mass, a factor of 5 lower as compared to the Earth. In the case of the Earth material of component B was added only at a late phase of the accretion as the transfer of material from the region outside of the Mars' orbit required additional time. As this transfer may be influenced by the perturbation effect of Jupiter it may be coupled with the formation time of Jupiter. Thus material of component B reached the Earth's orbit with relatively high geocentric velocities resulting in a low cross section of the Earth. Hence we expect for Venus almost the same portion of component B as for the Earth.

MARS: From the data on SNC meteorites (9), and various element correlations observed for these meteorites, we find a mantle composition for their parent body (SPB) as shown in the figure. According to recent studies (10) SPB must be planet Mars. However, while for the Earth a mixing ratio of component A to component B was estimated to about 85-15, on the SPB, i.e. on Mars the mixing ratio is about 65:35. Close inspection of the data indicates that Mars probably accreted like the Earth from two chemically different components which, however, had the chance to equilibrate with each other to a large extent before core formation (i.e. almost homogeneous accretion). Sulfur supplied by component B was responsible that a sulfur-rich FeNi alloy formed, leading to a sulfide-silicate equilibrium. During core formation extraction of elements from the mantle took place according to their sulfide-silicate partition coefficients rather than their metal-silicate partition coefficients. The sulfide-silicate partition coefficients are low for W and Ga and high for Cu, Co, and Ni. Hence, a large fraction of W from components A and B remained in the mantle, while large portions of Co, Ni and also Zn were extracted as sulfides.

VOLATILES: We now turn to the question of a possible loss of volatiles from the Earth after accretion. Sakaiya et al. (11) suggested depletion factors in the order of $10^4$. Anders and Oenema (12) neglect any such loss and proposed 6.3% of C3V material to be responsible for the Earth's inventory of volatiles. This would yield 12,000 b.y. to accrete the observed abundance quite well (see below). To account for the abundance of oxidized moderately siderophiles as well as moderately lithophiles of the Earth, we have proposed admixture of component B with a composition similar to C1. Clearly, component B may have been
CHEMISTRY AND ACCRETION OF EARTH AND MARS

Wänke, H. and Dreibus, G.

depicted for the most volatile elements prior to accretion. Neglecting such a depletion we can estimate upper limits for a possible "excess" of volatiles prior to their hypothetical loss. About 50 % of the Earth's inventory of K and U reside in the crust. For the equally incompatible halogen C1, Br, and I the crustal partition may be equal or more likely higher. The crustal abundance alone yield for C1 of 5 ppm (13) compared to 102 ppm from 15 % C1. The resulting depletion factor for C1 of 13 may be somewhat too high due to a lower than 100 % release. A C1: H2O concentration (14) of 7.2 % yields 1.1 % H2O, an amount 33 times exceeding the crustal abundance. However, H2O could have been used up by the reaction Fe + H2O = FeO + H2, raising the FeO content from 3.5 % to 7.8 %, a value not unreasonable for the early Earth (15). One may argue that this "excess" C1 was trapped in the core by some alloy, either still present at this stage or formed by disproportionation (3FeO = Fe + Fe2O3) (16). A portion of 15 % C1 material yields 13 x 10^6 g 36Ar/g (17), compared to 2.3 x 10^6 g 36Ar/g present in the Earth's atmosphere. Assuming 100 % release, we find a depletion factor of 5.7 for 36Ar, resp. 3.8 for 40Ar.

C1 halogen abundances agree well with the solar values, however for rare gases the absolute abundances as well as the abundance ratios in C1 differ from the solar values by large factors. Hence, the absolute abundances of rare gases in component B could also have been considerably higher compared to those observed today in C1 chondrites. For the halogens the depletion due to escape after accretion comes close to a factor of 10. The removal must be mass independent as C1, Br and I (10) (as well as 40Ar and 86Kr) are present on the Earth in C1 abundance ratios. Because of the larger affinity of halogens to silicate matter, the depletion factor for rare gases could be considerably higher. In the case of Mars the rare gas depletion factor amounts to more than 100 times the terrestrial value (19). Aside the lower gravity this might be due to the large amounts of H2, produced by the equilibration of component A and B.

ORIGIN OF COMPONENT A AND B: The required difference in oxygen fugacity of component A and B for the models for the solar nebula is easy to visualize a scenario in which loss of H2 from certain regions of the solar nebula is more rapid than that of H2O which could be held back in form of ice grains. The high depletion of moderately volatile elements such as Na, K, F, etc. on Earth and Mars is a more severe constraint. Temperatures of about 1000 K are required to fractionate these elements from the more refractory ones. According to current models such temperatures will not be reached in most parts of the solar nebula (20).

We have previously tried to visualize a solar nebula in which the only fractionation of importance was that of water (21). Water would only be added in appreciable quantities to planetesimals in regions where water occurred in form of ice or hydrates. Carbon seems to be the most abundant element present in solid form in interstellar matter either in form of graphite (22) and/or in form of "refractory" organic compounds (23). Hence, in planetesimals accreted from unaltered interstellar material, the abundance of carbon may be comparable to that of silicon. Depending on the accretion temperature, planetesimals would or would not contain H2O. In the absence of water (inner part of the solar nebula) primary objects heated by the decay energy of 26Al and by chemical energy become strongly reduced by carbon. Hence, not only FeH, but also large amounts of Cr, Mn, V as well as some Si will be converted into metals or sulfides. These primary objects will have molten interiors, however, because of their low surface temperature only highly volatile compounds can be lost during this stage. Collisions of objects with molten interiors will produce many droplets (chondrules) which loose volatiles and moderately volatiles very effectively (24,25). As a result the vaporized portion will be in form of very fine material which is separated from the larger chondrules ("amorphous metal and silicate", ref. 26). Hence, reduction and loss of volatiles are two steps of one process. Component A could be generated in this way. Planetesimals containing large amounts of H2O will only reach considerably lower temperatures as the heat sources will mainly be used up for the evaporation of H2O and the reaction C + 2H2O = CO2 + H2. Highly oxidized planetesimals which retained most of their volatiles and being compositionally similar to C1 chondrites will result (component B). Thus we might have a scenario which fulfills the conditions of the accretion history of the Earth and Mars and which results in an increase of the bulk oxygen content from planet Mercury to Mars.

We would like to underline that the two components as described here have to be taken as an approximation towards reality. The process responsible for the creation of component A (reduction accompanied by removal of volatile and moderately volatile elements) will not always lead to the visualized and products. However it seems that the actual situation can be successfully described in form of two components which physically should be addressed as endmembers of a fractionation sequence. Removal by volatilization may in many cases only affect the more volatile elements up to S, P, etc., but not Na and K.