

**Atmosphere/magma ocean interactions: Consequences for planetary differentiation and volatile evolution.**

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**Introduction:** It is well-known that interactions between magma oceans and their overlying atmospheres are key to early planetary differentiation and the development of principle volatile reservoirs in terrestrial planets [1-2]. The vapor pressure imposed by the atmospheres can dissolve significant volatiles in magma oceans (MO), which may constitute a significant initial inventory in planetary mantles and potentially deliver appreciable light elements to planetary cores. Those volatiles not dissolved in the MO can form a thick atmosphere which modulates the thermal evolution of the early partially molten planet. Sequestration in MO limit the loss of planetary volatiles by impact ablation. Thus it is a key step in establishment of primitive geochemical reservoirs, influences the dynamics of planetary interiors, and determines the evolution of early planetary atmospheres and climate. Yet, the consequences of magma ocean (MO) processes for the distribution of volatiles in early terrestrial planets are poorly understood.

**MO atmospheres:** It remains uncertain whether atmospheres above MO in terrestrial planets are thick or thin, and whether they are oxidized or reduced. Thick atmospheres may or may not survive giant impacts [3], and so MO formed by giant impacts may or may not have appreciable overlying atmospheres. Whether they do depends on whether the atmospheres can be replenished by subsequent MO degassing from the silicate portion of the planet, which is less likely to be devolatilized in the impact process. Planets that do not experience giant impacts (Mars?) likely retain thick atmospheres overlying a MO. The original lunar atmosphere has been little-discussed, but if any of the H documented in materials from the lunar interior is truly juvenile, then some H-rich atmosphere must have persisted at least until formation of the anorthosite carapace. A key consideration may be that the thickness of overlying atmospheres controls the time-scale of crystallization, which in turn may strongly influence the efficiency of fractionation in MOs.

MO have dramatically different relations to their overlying atmospheres depending on whether the surface conditions are oxidized or reduced [4,5]. Owing to higher magmatic solubilities, oxidized (H<sub>2</sub>O-CO<sub>2</sub>) atmospheres impart a much larger inventory into underlying MO than reduced CO-H<sub>2</sub> atmospheres. For example, for a terrestrial whole-mantle MO overlain by 100 bars H<sub>2</sub>O in an H<sub>2</sub>O-CO<sub>2</sub> atmosphere, 97% of the total H not in the core will be dissolved in the mantle, but for the same mass of H in a reduced CO-H<sub>2</sub>

atmosphere at IW-2, only 40% of the total H will be in the MO. This is owing to the lower solubility of H<sub>2</sub> in magma compared to H<sub>2</sub>O [4], but also to the lower total pressure imposed by less massive H<sub>2</sub> vs. H<sub>2</sub>O vapor. For C, solubilities are less certain, particularly for reduced conditions, but provisionally about 30% would be in the MO in the oxidized case and about 8% under reducing conditions.

**Atmosphere/MO/early mantle volatile partitioning:** Magma oceans largely degas as they crystallize, possibly resulting in a nearly volatile-free mantle when a solid silicate planet is first established. However, a number of processes may aid retention of volatiles during magma ocean solidification:

1. If magma ocean crystallization begins at intermediate depths, all of the volatiles dissolved at greater depth will be sequestered. For example, if on Earth a crystallization of a whole-mantle MO began at 70 GPa (~1700 km depth) [6], then 25% of the volatiles dissolved in the MO would be retained. Thus, for a MO below an H<sub>2</sub>O-CO<sub>2</sub> atmosphere, about 25% of the H<sub>2</sub>O and 10% of the CO<sub>2</sub> of all the volatiles not incorporated in the core would be held initially in the deep mantle. In addition to being a significant reservoir of C-H-O volatiles, this deep mantle layer is a likely initial repository of much of the non-radiogenic noble gases (<sup>3</sup>He, <sup>36</sup>Ar, etc.) in Earth's mantle.

2. MO crystallization processes are poorly understood, but if crystal-liquid separation from accumulated mushes is inefficient, then significant volatiles may be stored with trapped liquid. Layered mafic intrusions may provide some insight. In layered mafic intrusions, the fraction of trapped liquid increases with increasing crystallization rate, reaching ~40% for orthocumulates formed in regions where crystals accumulate on magma chamber floors at rates >1 m/year [7]. Crystal accumulation rates should be similarly high or higher for magma oceans (e.g., ~3 m/year for a whole-mantle MO on Earth that crystallizes in 1 Ma). This could result in up to 69 and ~14% of the H and C in the MO-atmosphere system to be retained following crystallization. However, the dynamics of crystallization in MOs are not likely the same as for layered mafic intrusions, and trapped liquid fractions closer to 10% seem likely [8], resulting in retention of 23% of the H and 4% of C. The higher percentages of H compared to C are owing to the greater solubility of H<sub>2</sub>O compared to CO<sub>2</sub>. If the overlying MO is reduced, percentages of both H and C retained in the solidified mantle will be diminished considerably.

3. Volatile-rich phases may saturate during MO crystallization. Recently it has been proposed that MO may become saturated in a C-rich phase (Fe-alloy, carbide liquid or diamond) during crystallization, thereby creating a carbon pump that could store appreciable C in a solidifying MO [8,9]. Hirschmann [8] emphasized the importance of redox gradients in creating a carbon pump, whereas Dasgupta et al. [9] considered only the role of diminished C concentrations in silicate magmas with pressure. The trouble with this latter scenario is that it does not account for the very low C solubility in magmas in the presence of a reduced vapor. For example, an atmosphere amounting to 100 bars CO<sub>2</sub>+100 bars H<sub>2</sub>O, once reduced to oxygen fugacities appropriate for saturation in a carbide liquid (e.g., IW-1.5) will likely have <5 ppm C dissolved as carbonate (<1 ppm), CH<sub>4</sub>, and CO (<3 ppm) species combined [10,11]. Such low dissolved C concentrations may not be sufficient to force saturation in a C-rich phase at reasonable depths (though experiments at very high pressure are lacking). Thus, it is unclear whether this mechanism can function unless the MO-atmosphere interface is comparatively oxidized, promoting significant C dissolution, whilst the MO is more reduced at depth, allowing saturation in a C-rich phase at low C concentration.

4. During MO crystallization, some of the volatiles can be partitioned into mantle silicates. Most importantly, partitioning of H into transition-zone minerals, wadsleyite and ringwoodite, could potentially sequester significant H, with upper and lower mantle silicates retaining less [2,12]. However, C is in large part rejected from principle mantle silicates: recent mineral/melt partition coefficients measured for upper mantle minerals suggest values near 10<sup>-4</sup> [13]. Whilst an order of magnitude higher than previous measurements [14], these still suggest negligible retention of C in mantle silicates.

**Discussion:** In the processes considered above, the masses of volatiles incorporated during MO solidification are proportional to the total amount of volatiles in the MO-atmosphere system. This inventory could be considerably larger than the volatiles remaining today in the bulk silicate Earth (BSE: mantle+crust+fluid envelopes) if there was substantial subsequent loss owing to impact ablation. Thus, the percentages above could be relative to an earlier, more volatile-rich reservoir and may represent a significant portion of the volatiles presently in the BSE.

Although the processes described above suggest that significant volatiles may be incorporated in the terrestrial planets through MO processing, in cases (1), (2), and (4) these processes favor retention of H<sub>2</sub>O compared to C. This contrasts with the low H/C ratio

of the modern terrestrial mantle [15]. H/C ratios of other planets are not well constrained. Apart from recycling of surface carbon, saturation in a C-rich phase (process 3) is the only mechanism by which a comparatively C-rich mantle might arise. The H/C ratios of other terrestrial interiors remain open to question. Because the interiors of Mars and the Moon are reduced compared to that of the Earth, saturation in a C-rich phase might be more likely, though there is the possibility that instead reduced conditions extracted effectively all interior carbon to the core.

If Earth lost much of its volatiles during a giant impact and regained them chiefly through accretion of a late veneer, then processing of volatiles in a magma ocean is of lesser consequence for Earth (but remains important for planets that either received a smaller proportion of late veneer or did not have a recycling mechanism capable of injecting late veneer volatiles into their interiors). However, following a giant impact, a significant fraction of the volatiles, previously buried in Earth's deep mantle (including H, C, and rare gasses) were likely retained; the abundances of these may depend on the masses sequestered during solidification of earlier magma ocean episodes. Significant volatile retention is likely required, as volatile derivation solely from a late veneer does not account for key elemental and isotopic ratio characteristics of Earth [16,17].

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