MARTIAN UNBOUND WATER INVENTORIES: CHANGES WITH TIME. Michael H. Carr[1] and James W. Head[2], [1]U. S. Geological Survey, Menlo Park, CA 94025 USA (carr@usgs.gov), [2]Department of Geological Sciences, Brown University, Providence RI 02912 USA (james_head@brown.edu).

Introduction: Formation of the widespread late-Noachian valley networks on Mars and large Hesperian flood features, if formed by water require significant water inventories [1]. Here we examine ways in which known water inventories may be reconciled with what may be required to form the water-worn features observed. We divide the water inventory into six parts: 1) water vapor in the atmosphere (inconsequential), 2) surface water ice (current polar ice deposits and surface snow and ice) [2], 3) shallow sequestered water ice (ice deposited during climate oscillations, but now buried by sublimation residues; latitude-dependent mantle [3], lobate debris aprons, lineated valley fill [4,5], pedestal and excess ejecta craters [7], etc.), 4) subsurface cryosphere [8] (that part of the global permafrost layer that contains water ice, including the Dorsa Argentaea Fm.[6]), 5) groundwater [9] (pore water below the base of the cryosphere), and 6) water sequestered in minerals [10] (water removed from the other five reservoirs by alteration and hydration, e.g., sulfates, phyllosilicates, etc.). Our concern here is mainly with unbound water. We consider that sequestered in minerals only insofar as it affects the unbound reservoir. We concentrate initially on surface ice, shallow sequestered ice and near-surface permafrost reservoirs. We first assess the present inventory, and then step backward to estimate the inventory at the end of the Hesperian, taking into account additions by outgassing and reductions by losses from the top of the atmosphere and to weathering.

Inventory: The two polar caps together contain approximately 3.2 x 10^6 km^3, or a 22 m global equivalent layer (GEL) [1]. To this must be added ground ice detected at high latitudes by ground penetrating radar [11], fresh impact craters [12] and the Phoenix lander [13]. Mouginot et al. [11] estimate that such ice deposits at depths less than 60-80 m. (a combination of regolith pore ice and sequestered ice) constitute another 10^6 km^3 or 7 m GEL. The Dorsa Argentaea Fm. is estimated to contain about 4 m GEL, raising to the known total to approximately 34 m GEL. The largest unknown is how much ground ice and groundwater exist at depths deeper than 60-80 m. The holding capacity of the megaregolith at these greater depths may be substantial. Estimates by Clifford [9] for the total megaregolith capacity range from 0.5 to 1.5 km GEL, but there is no data on the extent to which the available porosity is filled, nor to what degree this reservoir participates in surface processes. While Amazonian outflow channels, which probably form by eruption of groundwater, are rare, they do exist, as for example, Athabasca Vallis [14]. But the contrast between the abundance of outflow channels in the late Hesperian compared with their rarity in the Amazonian suggests either that the megaregolith had lost most of its water by the end of the Hesperian, that the cryosphere had thickened due to declining thermal fluxes [8], and/or that groundwater reservoirs were largely regional (centered on the Tharsis and Elysium regions [15]) as opposed to global. If we conservatively assume that the megaregolith deeper than 60-80 m contains 20 m GEL ice and water within pores, then we may at present have approximately 50-60 m of unbound, near-surface water. We view this as a minimum. The inventory could be much larger if a significant fraction of the available pore space is occupied by ground ice and groundwater [8,9].

To estimate the amount of water present at the end of the Hesperian we need to know the gains and losses of water over the last 3 billion years. Greeley [16] estimated that 14 m of water outgassed during the Amazonian from the measured exposures of Amazonian volcanic rocks, coupled with thickness estimates and an assumption of 1% by volumes of water, an assumption that is consistent with recent measures of the water content an Amazonian aged martian meteorite [17]. Water may be lost from the groundwater-ground ice inventory by reacting with the surface or escape from the upper atmosphere. Losses by reaction with the surface during the Amazonian appear to be trivially small. Phyllosilicate and hydrated sulfate bearing rocks are almost all pre-Amazonian and weathering of basalts at the Spirit landing site is confined to a thin veneer. Lammer et al. [18] estimate H and O losses from the present-day upper atmosphere and use the present-day losses to estimate losses over the last 3.5 Ga. Hydrogen losses depend, however, on the hydrogen mixing ratio in the lower atmosphere which in turn depends on obliquity. Mellon and Jakosky [19] suggest that the mixing ratio at 40^0 obliquity, the average for the last 3 Ga [20], would be two orders of magnitude higher than it is for the present obliquity. Thus estimates of H losses based on present-day losses may lead to significant underestimates of losses over geologic time. From O loss rates, which are unlikely to the significantly affected by obliquity, and assuming a 2:1 escape ratio of H and O, Lammer et al. [18] estimated that 30 m GEL of water could be lost from the exchangeable near-surface reservoir over the last 3 Ga . Combining this value with those above we estimate that at least 60-70 m GEL of unbound water could have been present near the surface at the end of the Hesperian. (50-60 m today, add 30 m lost, less 14 m outgassed). The figure would be much higher if a significant fraction of the pore space at depths below 80 m depth was filled.

Most of the large outflow channels are late Hesperian in age [1]. The amount of water required to cut the channels is poorly constrained in part because we do not know the sediment load. The largest outflow channel, Kasei Vallis, has an eroded volume of 7 x 10^5 km^3 or 4.9 m GEL, so with a sediment load of 20% approximately 25 m GEL would be required. Other outflow channels such as Tiu, Ares, Mangala and Maja are much smaller [1]. Possibly the largest uncertainty with respect to volumes eroded in the late Hesperian is the extent to which the volume of the canyons is the result of faulting, as opposed to erosion, and the extent to which the canyons enlarged during the Hesperian. There is abundant evidence of fluvial erosion and possible lakes within the canyons, particularly in the east [e.g., 21] but the amount of erosion is unclear. The minimum 60-70 m GEL at the end of the Hesperian is not inconsistent with what we know of the canyon and channel formation, but, if true, it implies that the volume of the canyons is largely tectonic and/or largely the result of events in the Noachian and early Hesperian. It is also roughly compatible with the volume enclosed by the proposed Deuteronilus Shoreline [22]. However, it falls far short of the volumes enclosed by the higher shorelines.

To derive the inventory at the end of the Noachian, we must know how much water was lost during the Hesperian. As before, we take loss of oxygen as the limiting factor. Lammer et al [18] estimate that ~5 m GEL equivalent oxygen would be lost from the top of the atmosphere between 3.7 and 3.0 Ga ago. To this must be added the oxygen lost by reaction with the surface. Kilometers-thick sulfate deposits [23] represent a significant sink for oxygen, but the total sulfate volume is not well known and whether the sulfates result from Hesperian oxidation or the leaching of sulfates that formed earlier, in the Noachian, is unclear. Nevertheless, loss of the equivalent of tens of meters of water through oxidation and hydration of sulfates during the Hesperian is not unreasonable during the Hesperian. These losses must be offset by outgassing gains during the Hesperian, estimated by Greeley [16] to be 27 m

A better estimate of the amount of water at the end of the Noachian may be provided by Tharsis. Phillips et al. [24] estimate that formation of Tharsis, which they argue was largely complete by the end of the Noachian, resulted in the outgassing of 120 m of water. How much of this was retained by the end of the Noachian would have depended on the time of formation. If Tharsis formed late in the Noachian most of the water would have been retained. If it formed early, then much of the water would have been lost by hydrodynamic escape, as would most of the water outgassed during formation of the crust. We have been discussing here the inventory of unbound water. Sequestered within Noachian rocks may be a substantial water inventory. Mustard et al. [10] estimate the potential size of the hydrous mineral crust reservoir on the basis of the presence and depth of hydrated minerals seen throughout Noachian aged terrains, to be in the range of 150-1800 GEL, but little of this water is likely to be available for surface processes such as fluvial erosion, glaciation and polar cap formation.

Conclusions: We conclude that a near-surface, unbound water inventory of several tens of meters GEL through the Hesperian and Amazonian is compatible with what we know about loss mechanisms and what we know about the geology, with some significant exceptions. If Mars had Hesperian oceans larger than that defined by the Deuteronilus shoreline, or if the canyons were formed largely by water erosion during the Hesperian, then there remain significant incompatibilities. This inventory does not include the potentially much larger inventory of water sequestered in Noachian aged minerals.

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