aqueous Fe^{2+} ions. In pH 6 saline waters at 0°C, rates of oxidation of dissolved Fe^{2+} would have to exceed 14,000 ppm Fe m^{-2} yr^{-1} to maintain the P_{O_2} at 10^{-5} bar relative to $P_{CO_2} = 3.4 \times 10^{4}$ bar. If the P_{CO_2} was 1000x higher than present-day values (i.e., P_{CO_2} = 0.35 bar), a P_{O_2} of 10^{-5} bar could be achieved, supporting the suggestion [e.g., 9] that atmospheric pressure was higher earlier in Mars' history. On the other hand, the comparatively high P_{O_2} of the martian atmosphere would effectively oxidize the high concentrations of Fe^{2+} ions that could be present in very acidic solutions if such groundwaters occurred on Mars.

Generation of Acidic Groundwater: Oxygen in subsurface groundwater is consumed by oxidation of iron sulfides (e.g., $FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+$) and by oxidation of some of the Fe^{2+} ions (i.e., $Fe^{2+} + 1/4\ O_2 + 3/2\ H_2O \rightarrow FeOOH + 2\ H^+$) released during oxidation of sulfides and from dissolution of ferromagnesian silicates. Such ferrolysis reactions cause groundwater to become acidic, facilitating the dissolution of ferromagnesian silicates. Since Fe^{2+} ions are stabilized and are very slowly oxidized in low pH saline solutions, concentrations of dissolved ferrous iron increase (perhaps to as high as 1000 ppm) and may persist indefinitely in acidic groundwater (now permafrost on Mars). Oxidation to insoluble nanophase ferric oxides, oxyhydroxides, and hydroxysulfate minerals would occur rapidly when melt waters become oxygenated in contact with the atmosphere and when acid-buffering reactions occurred involving the formation of clay silicates. Such clay silicates include authigenic Mg-Fe saponites, which are also precipitated from acidic brines, and residual montmorillonites derived from leached basaltic feldspars. Environments on the present-day martian surface that are capable of precipitating ferric-bearing assemblages are equatorial melt waters and regions where sublimation of permafrost has induced the oxidation of Fe^{2+} ions after they were released in evaporite deposits. Oxidative weathering reactions in arid environments might have been more prevalent earlier in the history of Mars, however, by analogy with unique terrestrial environments in Australia.

Terrestrial Analogs: On Earth, natural acidic groundwater systems are comparatively rare but occur, nevertheless, when water seeps through mined sulfide and coal deposits. Outflows of such acid mine drainage water are invariably associated with ochrous ferric-bearing assemblages. On a much larger scale, oxidative weathering associated with acidic groundwater is occurring across the southern half of the Australian continent [10].

In the southeastern part of Western Australia, deep weathering of basement igneous rocks in the Yilgarn Block comprising Archean komatiitic basalts has yielded saline groundwater systems, drainage of which in a semi-arid climate has resulted in extensive playas [10–15]. The discharging water contains high concentrations of dissolved Al, Si, and Fe^{2+}, oxidation and hydrolysis of which generates very acidic groundwater (pH ≥ 2.8), as a result of the ferrolysis reactions. The acidity prevents the precipitation of aluminosilicate clay minerals. Instead, jarosite $[KFe_3(SO_4)_2(OH)_6]$-alunite $[KAl_3(SO_4)_2(OH)_6]$ assemblages are precipitated in the pH range 2.8–6 from solutions with ionic strengths ranging from 1 M to 5 M, occurring in evaporite deposits with gypsum and halite. Ferrihydrite, instead of jarosite-alunite assemblages, is deposited from groundwater depleted in dissolved K and Al. A similar situation may exist on Mars where groundwater associated with parent iron-rich komatiitic basaltic rocks may also have low Al and K contents.

Two stages were important in the development of the acidic hydrogeochemical and arid weathering environment of southern Australia. Initially, there were periods of laterization/ferric oxide deposition under a warm humid climate during the Tertiary. The laterite profiles are characterized by a surface duricrust of Fe and Al oxides over deep clay silicate zones depleted of alkali and alkaline Earth elements. Subsequently, periods of aridity and semi-aridity have continued to the present.

An explanation for the acidic saline groundwater systems on such a large scale and only in Australia lies in the recent climatic history of the continent. After the break from Antarctica began at 65 Ma, Australia moved into the subtropic region. The climate through the Eocene was humid and warm, much like that proposed on early Mars, and periods of laterization occurred. Laterite profiles became abundant in Western Australia on deeply weathered bedrock depleted in alkalis and alkaline earth elements, but enriched in Fe, Al, and Si. Little chemical weathering is now occurring on the Australian continent today due to arid conditions. However, periodic discharges of anoxic acidic groundwater into the arid environment and oxidation of the dissolved ferrous iron continue to generate ferric-bearing mineral assemblages in contact with the oxygenated atmosphere. A similar scenario may apply to the present-day surface of Mars, in which periodic precipitation of hydronium jarosite and ferrihydrite may be precursors to nanophase hematite identified in bright regions of the martian surface.

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MARS: NOACHIAN HYDROLOGY BY ITS STATISTICS AND TOPOLOGY.

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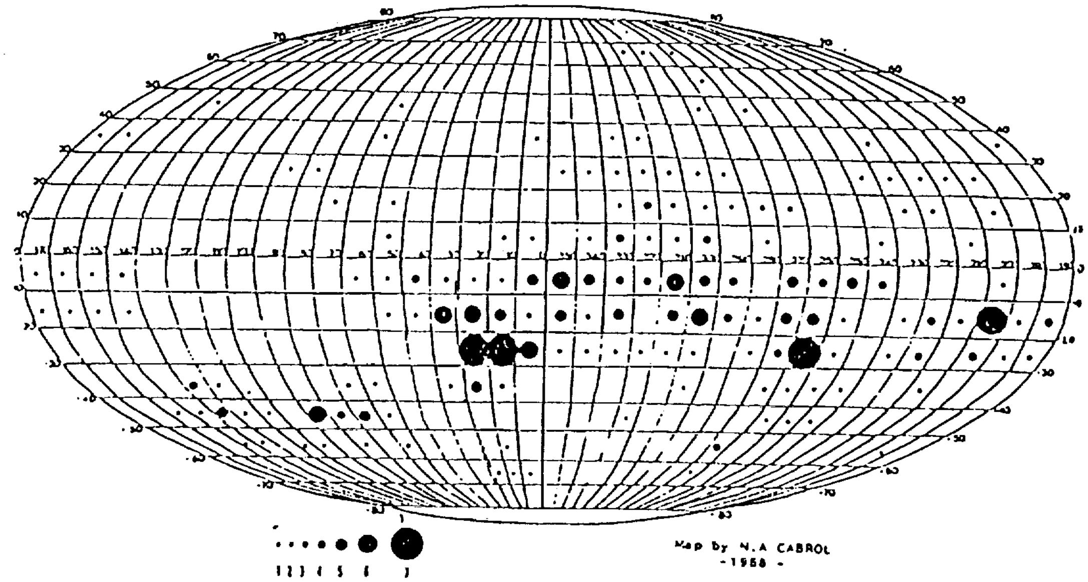
Discrimination between fluvial features generated by surface drainage and subsurface aquifer discharges will provide clues to the understanding of early Mars' climatic history. Our approach is to define the process of formation of the oldest fluvial valleys by statistical and topological analyses [1–3].

Formation of fluvial valley systems reached its highest statistical concentration during the Noachian Period. Nevertheless, they are a scarce phenomenom in martian history, localized on the craterized upland and subject to latitudinal distribution [1,4,5]. They occur sparsely on Noachian geological units with a weak distribution



dot	hw n°	dot	hw n°
1	1–5	5	31–40
2	6–10	6	41–80
3	11–20	7	above 81
4	21–30		

Fig. 1. Distribution of headwater density (hw) by 36 × 10^4 km^2.

density (Fig. 1), and appear in reduced isolated surface (around 5 × 10^3 km^2), filled by short streams (100–300 km length) [3].

Topological analysis of the internal organization of 71 surveyed Noachian fluvial valley networks also provides information on the mechanisms of formation.

The tributary hierarchization in these networks shows the specificity of an early martian hydrology. Compared with Earth-like surface drainage systems, which are characterized by a hierarchization of tributaries, martian networks are strongly characterized by typical short theater-headed tributaries with poorly dissected interfluves [6]. The relationship between the number of these headwater branches and the total number of branches of a given network (Fig. 2) provides arguments in favor of the formation of networks highly subject to their terminations. The topological analysis of the internal branch distribution shows common characteristics between most valley networks: (1) over 60% of headwater branches are short tributaries and (2) the relationship between the total branch lengths of a network and its delineation around the headwater system, including its outlet (designated here as drainage density K_d), combined with the planimetric relationship between the circumscribed surface and its perimeter (designated as drainage compacity K_c), shows a good concentration of the physiographic ratio K_d/K_c (Fig. 3). Symbolic of a martian network, the physiographic ratio is a geometric parameter independent of subsurface network geology and topography.

Statistics of terrestrial drainage basins show a mean value K_d = 0.05 and K_c = 1.3 (K_d/K_c = 0.04) compared with the martian value K_d = 0.1 and K_c = 1.4 (K_d/K_c = 0.07). This means that for an equivalent coefficient of compacity K_c, terrestrial drainage systems are twice as dense as the martian ones. The martian physiographic

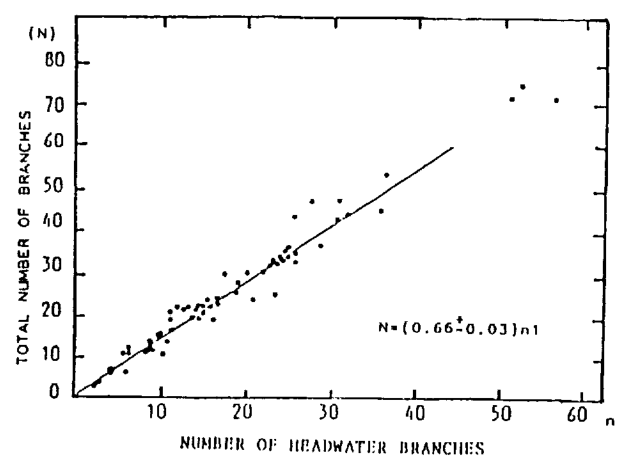


Fig. 2. Relationship between the number of headwater branches (n_1) and total number of branches.

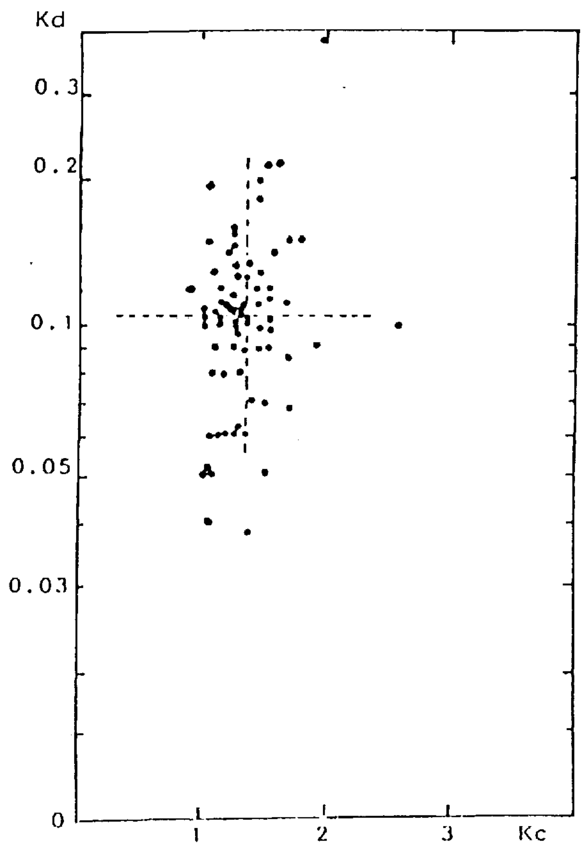


Fig 3. Each network is symbolized by its two physiographic parameters, drainage density (K_d) and drainage basin compacity (K_c).

coefficient is similar to that of terrestrial karst terrain drainage basins. This suggests that martian valley networks are developed on a substratum subject to structural constraints that determine the effectiveness of groundwater flow [7] circulation. The physiographic parameter is not representative of a wide runoff surface but more of reduced-area systems such as sapping valleys, the morphology of which is illustrated by the high frequencies of headwater localized in confined units. Given that major concerns are the history of water and the possibility of life, further investigations of ancient valley networks as unequivocal evidence of circulation of subsurface water will promise a significant advance in our knowledge of Mars.

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THE EVOLUTION OF THE EARLY MARTIAN CLIMATE AND THE INITIAL EMPLACEMENT OF CRUSTAL H_2O.

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Introduction: Given the geomorphic evidence for the widespread occurrence of water and ice in the early martian crust, and the difficulty involved in accounting for this distribution given the present climate, it has been suggested that the planet's early climate was originally more Earth-like, permitting the global emplacement of crustal H_2O by direct precipitation as snow or rain [1.2]. The resemblance of the martian valley networks to terrestrial runoff channels and their almost exclusive occurrence in the planet's ancient (~4-b.y.-old) heavily cratered terrain are often cited as evidence of just such a period. An alternative school of thought suggests that the early climate did not differ substantially from that of today. Advocates of this view find no compelling reason to invoke a warmer, wetter period to explain the origin of the valley networks. Rather, they cite evidence that the primary mechanism of valley formation was groundwater sapping, a process that does not require that surface water exist in equilibrium with the atmosphere [3–5]. However, while sapping may successfully explain the origin of the small valleys, it fails to address how the crust was initially charged with ice as the climate evolved toward its present state. Therefore, given the uncertainty regarding the environmental conditions that prevailed on early Mars, the initial emplacement of ground ice is considered here from two perspectives: (1) The early climate started warm and wet, but gradually cooled with time, and (2) the early climate never differed substantially from that of today.

Early Climate: Warm and Wet: The density and distribution of the valley networks throughout the heavily cratered terrain suggests that, regardless of whether early Mars started warm or cold, groundwater was abundant in the planet's early crust. However, given an initially warm start, an inevitable consequence of both the decline in Mars' internal heat flow and the transition to colder temperatures would have been the development of a freezing front within the regolith that propagated downward with time, creating a thermodynamic sink for any H_2O within the crust. Initially, water may have entered this developing region of frozen ground from both the atmosphere and underlying groundwater. However, as ice condensed within the near-surface pores, it effectively sealed off the deeper regolith from any further atmospheric supply. From that point on, the only source of water for the thickening cryosphere would have been the geothermally driven flux of vapor arising from the presence of groundwater at depth. Indeed, calculations by Clifford [6] indicate that a geothermal gradient as small as 15 K km^{-1} could supply the equivalent of 1 km of water from higher-temperature (higher vapor pressure) depths to the colder (lower vapor pressure) base of the cryosphere every 10^6–10^7 yr. Given the higher geothermal heat flow expected to have characterized the planet 4 b.y. ago, this supply of vapor may have been as much as 3–5 times greater in the past.

Pollack et al. [2] estimate that if the primary mechanism driving climate change was the removal of a massive (1–5-bar) CO_2 atmosphere by carbonate formation, then the transition from a warm to cold early climate must have taken between 1.5×10^7 to 6×10^7 years. For transition times this slow, the downward propagation of the freezing front at the base of the cryosphere is sufficiently small (when compared with the geothermally induced vapor flux arising