

SULFUR SPECIES FROM VOLCANIC OUTGASSING ON MARS: POTENTIAL SIGNATURES IN GEOMORPHOLOGY. *M. A. Kreslavsky^{1,2} and J. W. Head¹*, ¹Dept. Geol. Sci., Brown University, Providence, RI, USA, kreslavsky@brown.edu, ²Astron. Inst., Karazin National University, Kharkov, Ukraine.

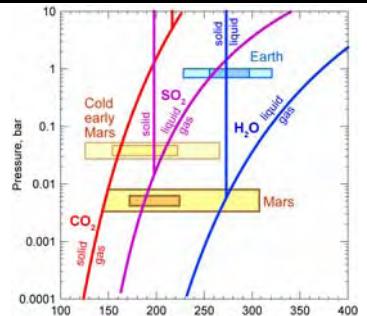
Introduction: The geological record unequivocally indicates that volcanism occurred throughout the geological history of Mars, and was especially active in early history (Hesperian and Noachian). Volcanism is always accompanied by release of gases; volcanic gases usually include much sulfur, mostly in the form of H₂S and SO₂. A chain of photochemical reactions in the middle atmosphere [1] quickly oxidizes H₂S to SO₂, and more slowly, SO₂ to SO₃, which picks up water vapor, forms sulfuric acid H₂SO₄, which, in turn, precipitates, chemically reacts with surface material and forms sulfates. For trace amounts of atmospheric sulfur species, their characteristic photochemical lifetime is ~40 days [2]. Larger amounts of atmospheric S would lead to removal of H₂O vapor with precipitating H₂SO₄ and slowing the process down. Colder climate conditions would further significantly lessen atmospheric H₂O. Photolysis of SO₃ and H₂SO₄ ignored in [1, 2] may become important dryer atmosphere and further slow down removal of SO₂. In an ultimate case of very cold and dry world, on Io, SO₂ forms stable surficial deposits in dynamic equilibrium with very thin SO₂ atmosphere [5]. Thus, it seems plausible that SO₂ could persist for rather long time under dry cold climate conditions.

Under warm and wet climate conditions, atmospheric S quickly precipitates to form dilute aqueous solutions of H₂SO₄. Due to their chemical reactivity, these solutions, if they flowed on the surface, would erode it at somewhat higher rates than pure water. This difference is quantitatively small and is unlikely to be observed in the geomorphology. In contrast, under cold climate conditions, like now or colder (which can be the case on early Mars due to lower luminosity of the Sun), the precipitation of S species could have very interesting and specific geomorphological effects. Here we qualitatively review these possible effects.

Sulfur dioxide glaciers: The phase diagram of SO₂ is shown in Fig. 1. SO₂ is somewhat less volatile than CO₂ and much more volatile than H₂O. If abundant in the atmosphere, SO₂ would form extensive seasonal deposits in the winter hemisphere and cycle seasonally (and under some conditions, diurnally) between the surface and the atmosphere. If the climate is dry enough, and SO₂ can persist for decades before being totally oxidized, the annual accumulation of solid SO₂ may lead to thick deposits locally and to formation of flowing glaciers. Such glaciers should behave in a manner similar to terrestrial cold-based glaciers.

Surface run-off of liquid sulfur dioxide: The present atmospheric pressure is lower than the SO₂ triple point pressure of ~14 mbar (Fig. 1), and SO₂ cannot exist in liquid form. Let us speculate, however, about a cold early Mars with relatively thick highly volatile (nitrogen) primordial atmosphere (Fig. 1). In this case, seasonal or diurnal cycling of SO₂ may include melting and surface runoff. It is instructive to compare the present-day H₂O cycle with this hypothetical SO₂ cycle on a cold early Mars. Although metastable liquid water can exist presently on the martian surface [3] (and probably does exist in special locations during short periods), no substantial surface runoff is observed, because (1) the atmosphere is so cold that it cannot bear much H₂O vapor, the seasonal deposits of solid H₂O ice are too thin, and the amount of H₂O that can potentially be in liquid form is too small, and (2) due to low ambient pressure, metastable liquid H₂O evaporates very quickly, even if its temperature is below the boiling point. In the case of SO₂, (1) the saturation pressure is much higher (Fig. 1), and the atmosphere can bear and deposit (seasonally or even diurnally) much larger amounts of the solid phase, which is then susceptible to seasonal or diurnal melting; (2) since the molecular mass of SO₂ is much higher than the mean molecular mass of the atmosphere, the vapor above the liquid phase would not convect, which would significantly decrease evaporation rates. Thus, unlike the present-day H₂O, SO₂ could occur in its liquid phase at the surface in appreciable amounts for appreciable time periods, flow and leave morphological traces of fluvial erosion. If the atmospheric pressure on cold early Mars was higher, the liquid phase would be metastable in a wider range of temperatures, and well-developed SO₂-based hydrological cycle with extensive surface run-off could exist.

Fig. 1. Phase diagrams of CO₂, SO₂, H₂O; boxes show ranges of surface conditions and year-average surface conditions on Mars, hypothetical cold early Mars with 50 mbar N₂ atmosphere, and the Earth.



Greenhouse effect and sulfur dioxide stability: All the above statements about SO₂ glaciers and surface runoff are based on consideration of the phase

diagram only and are highly speculative. Only numerical quantitative atmospheric models can show the extent of the SO₂ cycling outlined above. Another important problem that must be resolved before any early runoff features can be attributed to liquid SO₂ is its atmospheric lifetime on a cold early Mars. SO₂ is a greenhouse gas. It can trigger a run-away greenhouse effect, when rising temperature converts all solid SO₂ into gaseous phase, which enhances the effect and leads to even higher temperatures. The temperature rise would enhance evaporation of H₂O, which would facilitate precipitation of H₂SO₄ and removal of SO₂. New photochemical models for sulfur species coupled with climate models are necessary to estimate the lifetime of SO₂ on a cold early Mars and assess the potential for the processes outlined above.

Surface runoff of liquid sulfuric acid and its aqueous solutions: All atmospheric sulfur originating from volcanic outgassing ultimately precipitates as H₂SO₄. This can potentially have profound effects on geomorphology. H₂SO₄ has a much lower vapor saturation pressure than H₂O; pure H₂SO₄ melts at ~283 K; aqueous solutions of H₂SO₄ have much lower melting points, the minimum is as low as ~197 K for ~39% concentration. This means that under the present climate conditions, precipitation of H₂SO₄ on ice or ice-rich soil would cause day-time transient melting almost everywhere on the planet. Metastable cold concentrated aqueous solutions of H₂SO₄ would have much lower H₂O evaporation rates and much longer lifetimes than pure liquid H₂O; unlike water, concentrated sulfuric acid would flow on present-day Mars. Concentrated solutions flowing over frozen ice-rich soil would very effectively extract H₂O from the soil until the solution reaches its concentration limit for a given temperature. Due to this drying action, concentrated acidic flows would erode ice-rich frozen soil very effectively, at much higher rates than due to simple mechanical erosion.

Salts have long been recognized as solutes capable of reducing the melting point of water and facilitating surface runoff on Mars. H₂SO₄, acting in the same way, has some principle distinctions: 1) H₂SO₄ can reduce the melting point much lower; 2) H₂SO₄ can appear literally from the air, at new locations, in other words, new H₂SO₄ can melt old ice, while old salts can melt only new ice; 3) being rather volatile, H₂SO₄ can recycle in principle. The low saturation vapor pressure makes H₂SO₄ recycling rather slow. The potential role of such recycling depends on the rates of chemical interaction of concentrated H₂SO₄ solutions with minerals at low temperatures and requires special quantitative analysis.

Turning to early Mars with its high volcanic outgassing rates, we conclude that H₂SO₄ may play an

important role in the formation of morphological features suggestive of fluid runoff under cold climate conditions. Another important aspect is that cold climate facilitates persistence of concentrated solutions, while under a warm, wet climate, dilute solutions would be typical. Jarosite identified at the Opportunity landing site is mineralogical evidence for aqueous processes under acid-sulfate conditions with low pH [4]. The latter correspond better to cold, rather than warm, climate conditions.

Subglacial runoff of concentrated aqueous solutions of sulfuric acid: Concentrated solutions of H₂SO₄ have a high density, much higher than the density of H₂O ice. If H₂SO₄ precipitates on a flat surface of an ice sheet, it would form drops of concentrated solution; if the ice temperature exceeds 197 K, these drops will melt through the ice sheet, reach its base, coalesce, and the liquid would flow and pond. This sub-ice flow could lead to distinctive geomorphic features. This situation has one principle distinction. Under typical terrestrial conditions, subglacier water flow is caused by basal melting of the ice; as a rule, such glaciers are characterized by very high strain at the ice base, which effectively scours and erases features formed by the water flow. Under martian cold conditions, flow of concentrated acidic solutions (as well as brines) can occur beneath cold-based glaciers and ice sheets, where the basal ice temperature is far below the melting point, and the strain at the base is minimal (ice is "frozen on" the base), and the flow features are well preserved.

Conclusions: Under cold martian climate conditions, ejection of volcanic sulfur species into the atmosphere can potentially lead to distinctive geomorphologic effects. Sulfuric acid, the ultimate result of photochemical alteration of sulfuric species in the atmosphere, facilitates surface runoff of low-freezing fluids and favors sub-ice flow in cold-based conditions. Sulfur dioxide, if its photochemical life time under cold climate is long enough, could also produce glaciers and surface runoff. Quantitative models of different aspects of these processes are needed to assess the role of sulfur species in the formation of features actually observed on Mars and assess the implications for climate in the past.

References: [1] Wong, A.-S. et al. (2003) *JGR* 108, 5026, doi:10.1029/2002JE002003. [2] Wong, A.-S. et al. (2004) *JGR* 109, E01007, doi:10.1029/2003JE002210. [3] Hecht, M. (2002) *Icarus* 156, 373-386. [4] Morris R. V. et al. (2006) *JGR* 111, E12S15. [5] Nash D. B., Betts B. H. (1998) In: *Solar System Ices*, Kluwer, 607