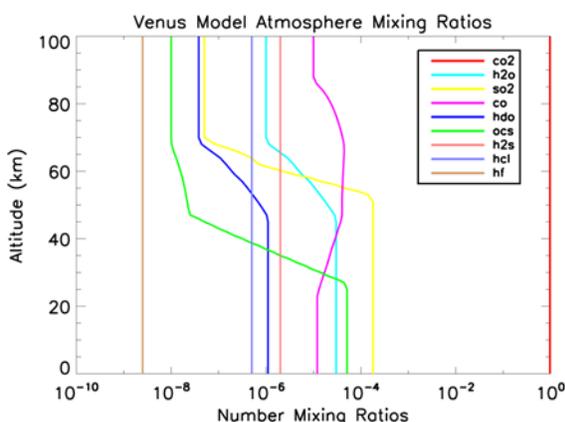


**THE ROLE OF SULFUR IN DETECTING RECENT CLIMATE CHANGE ON VENUS.** M. A. Bullock<sup>1</sup> and D. H. Grinspoon<sup>2</sup>, <sup>1</sup>Southwest Research Institute, 1050 Walnut St., Suite 300, Boulder, CO 80302 (bullock@boulder.swri.edu), <sup>2</sup>Denver Museum of Nature & Science, Denver, CO (david.grinspoon@dmns.org).

**Introduction:** Even with the extremely limited data on the deep atmosphere and surface of Venus, it is clear that chemical reactions are vigorous near the surface. The evidence for this are the steep gradients in sub-cloud mixing ratios that have been observed for CO, SO<sub>2</sub>, OCS and other trace species (Fig. 1). Moreover, due to the high temperatures and pressures at the surface, it is also likely that reactions between atmospheric gases and surface minerals are ongoing, influencing global chemical cycles and the composition of the near-surface crust.



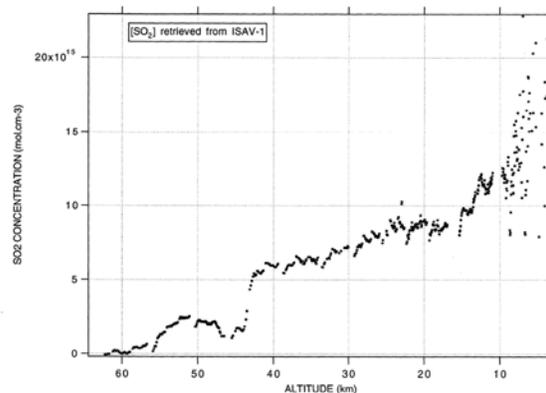
**Figure 1.** Atmospheric mixing ratios of the nine most abundant gases in the Venus atmosphere. Note the strong gradients in OCS, CO, and SO<sub>2</sub> beneath the clouds.

**Atmospheric SO<sub>2</sub>:** Of particular interest are the sulfur gases, since extrapolation of the Pioneer Venus GCMS results from 22 km indicate that SO<sub>2</sub> abundance near the surface is about 180 ppm. Furthermore, laboratory work has shown that the equilibrium abundance of this gas should be about 2 ppm, but that it reacts rapidly with carbonates under Venus like conditions. These experiments led Fegley and Prinn [1] to conclude that the residence time of SO<sub>2</sub> in the Venus atmosphere was about 2 My, and that volcanism at a rate of 0.4 to 11 km<sup>3</sup>/year is presently necessary to sustain the clouds. Using these laboratory data, reaction/diffusion calculations to model the transport of atmospheric gases to fresh reaction sites within the surface, and a simple microphysical cloud model, Bullock and Grinspoon further refined the estimate of SO<sub>2</sub> atmospheric residence time to be about 30 My [2]. An independent analysis of the present-day volcanic rate, from the observed incidence of crater embayment and

a Monte Carlo cratering and volcanic activity model, concluded that the recent volcanic rate on Venus has to be on the order of 0.4 km<sup>3</sup>/yr [3].

Given the above, it is reasonable to conclude that if volcanism ever ceased or severely declined on Venus for 50 My, SO<sub>2</sub> could have been drawn down into the surface and the clouds would have dissipated. Venus' appearance in Earth's night sky would have been dramatically affected, since its albedo would have decreased from 0.8 to 0.4. Surprisingly, however, climate models show that Venus would have not gotten hotter, since Rayleigh scattering by the thick atmosphere would have kept 40% of the incident light reflecting into space, and because the clouds themselves are a potent greenhouse agent [2].

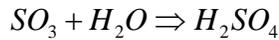
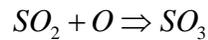
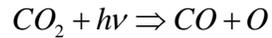
There are several problems and opportunities with this proposed SO<sub>2</sub> scenario. One of the most interesting comes from observations of SO<sub>2</sub> much lower in the atmosphere, near 12 km, from the Vega UV spectrometers. Bertaux and colleagues showed that SO<sub>2</sub> mixing ratio declines dramatically towards the surface (Fig. 2), and approaches something like the equilibrium value over carbonate [4]. Although this would indicate that reactions between atmospheric SO<sub>2</sub> and the surface are not occurring, it also means that an explanation for the atmospheric reactions that are responsible for such a wholesale destruction of SO<sub>2</sub> in the deep atmosphere is necessary. There were numerous problems with the UV spectrometers on the Vega descent probes however. New data from a deep atmosphere probe will be necessary to resolve this issue.



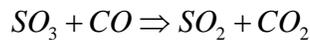
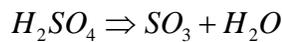
**Figure 2.** Vertical profile of SO<sub>2</sub> number density retrieved by the Vega 1 UV spectrometer. From [4].

**The Venus Sulfur Cycle:** Sulfur gases exist in the Venus atmosphere in significant quantities at the full

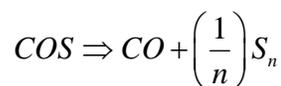
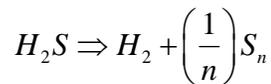
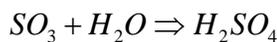
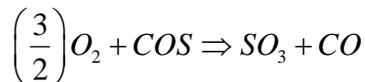
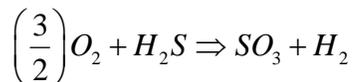
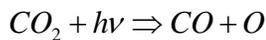
range of oxidation states, from  $H_2S$  to  $SO_3$ . The Venus sulfur cycle is often divided into three subcycles. The *fast atmospheric cycle* transfers sulfur between vapor and sulfuric acid liquid aerosol reservoirs. Above and within the clouds, it is driven by photochemistry and produces sulfuric acid cloud aerosols via the net reactions:



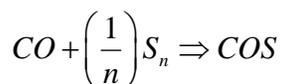
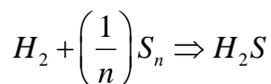
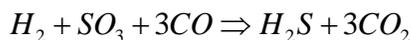
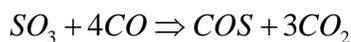
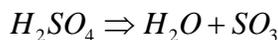
In the hot sub-cloud region sulfur to its largest reservoir,  $SO_2$ . The net reactions can be written:



The *slow atmospheric cycle* transfers sulfur between liquid acidic aerosols and sulfur gases of different oxidation states. Within the clouds,



Below the clouds, the return reactions are:



The third, or *geologic cycle*, produces atmospheric  $H_2S$  and  $COS$  from the oxidation of pyrite [6], and draws down  $SO_2$  from its reaction with carbonate, as discussed above.

Yung and Liang recently made the point that the transfer of sulfur between atmospheric reservoirs ( $SO_2$ ,  $OCS$ , and allotropes of  $S$ ) is enormous: At least 1000 times greater than any plausible surface source or sink [5]. All these potential atmospheric and surface reactions involving sulfur make the sulfur cycle on Venus complex, but they also hold the promise that sulfur itself may be a key marker of recent changes in Venus' climate.

**Detecting Climate Change with New Missions to Venus:** New missions to the surface of Venus will make it possible to soon test hypotheses about the current rate of volcanism on Venus, the longevity of its clouds, and to test for epochs of recent climate change [7]. Isotopic ratio measurements of  $^{32}S/^{33}S/^{34}S$  within  $SO_2$  and  $OCS$  can definitively say whether all  $S$  has undergone mass independent fractionation, and hence was derived exclusively from photochemistry in the upper atmosphere. Landed imagery, at resolutions 5-10 times better than the spectacular Venera 14 images (Fig 3), and at a range of carefully selected colors, can look for layering and compositional changes indicative of climate change. Changes in diffusive regime, and hence climate and chemistry, can be detected by elemental, chemical, and mineralogical analysis of material from the surface and from a few cm below the surface. Finally, the exciting opportunities to map the surface in 3 narrow windows near  $1 \mu m$  hold the promise to discriminate compositional and hence possible weathering history changes in different terrains.



**Figure 3.** Surface image of Venus from Venera 14. Layered slabs are evident, with layers on scales of cm.

[1] Fegley, B. and R.G. Prinn (1989) *Nature* 337, 55-58. [2] Bullock, M.A. and D.H. Grinspoon (2001) *Icarus* 150, 19-37. [3] Bullock, M.A., D.H. Grinspoon, and J.W. Head (1993) *GRL* 20, 2147-2150. [4] Bertaux, J.L., et al. (1996) *JGR* 101, 12,709-12,745. [5] Yung, Y.L. and M. Liang (2008) *B.A.A.S.* 40, Abstract 62.05. [6] Fegley, B., et al. (1997) in *Venus II*, University of Arizona Press, 591-636. [7] Bullock, M.A., et al. (2008) *B.A.A.S.* 40 Abstract 32.08.