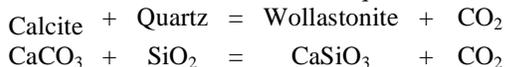


**ATMOSPHERES OF VENUS-LIKE PLANETS: STABILITY CONSTRAINTS ON MINERAL REACTION BUFFERS.** A. H. Treiman<sup>1</sup> and M. A. Bullock<sup>2</sup>, <sup>1</sup>Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston TX 77058 <treiman[at]lpi.usra.edu>, <sup>2</sup>Department of Space Studies, Southwest Research Institute, 1050 Walnut Street, Suite 300, Boulder CO 80302.

The composition of a planet's atmosphere can be buffered by chemical reactions with minerals at its surface [1-5]. The compositions of 'hot' thick exoplanet atmospheres can therefore act as probes of their planets' surface mineralogies and compositions. In the context of a planetary atmosphere, however, many potential buffering reactions are not stable and would lead to catastrophic greenhouse runaway or atmospheric collapse.

**Introduction:** In our solar system, mineral-atmosphere buffering is most relevant for Venus [2-5]. The T and CO<sub>2</sub> pressure at Venus' surface match a point on the mineral decarbonation equilibrium,



(Fig. 1), which has been suggested to buffer the CO<sub>2</sub> content of Venus' atmosphere [1-5]. The concept of atmospheric buffering by the surface has been applied to other gas species, such as sulfur gases, halogens, oxidation state (e.g., CO/CO<sub>2</sub>), etc. [2-6].

This particular reaction, calcite-quartz-wollastonite

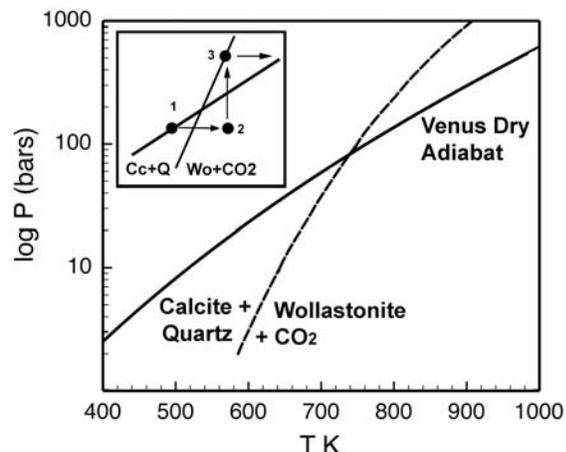


Fig. 1. Demonstration that the Cc-Q-Wo reaction cannot buffer CO<sub>2</sub> pressure in the Venus atmosphere. Main figure shows pressure-temperature trajectories for the dry adiabat of the Venus atmosphere and the reaction Cc-Q-Wo. Inset shows instability with respect to a T perturbation – see text.

(CcQWo) cannot buffer the CO<sub>2</sub> content Venus' atmosphere, because of the interplay between the atmosphere's temperature lapse rate and the reaction thermochemistry. A chemical buffer would act to damp out or diminish chemical perturbations in a system, so a buffer of Venus' atmosphere composition would oppose or diminish a change imposed on the atmosphere. The CcQWo reaction cannot, however, buffer the tem-

perature or CO<sub>2</sub> pressure of the Venus atmosphere (if Venus' surface actually has abundant wollastonite or calcite+quartz [7-9]); its operation at the Venus surface would amplify perturbations in temperature or pressure [10-13]. These effects are based on CcQWo achieving thermochemical equilibrium with the atmosphere. The kinetics of this reaction at Venus surface conditions are unknown, although other heterogeneous reactions have been shown to proceed rapidly [5,7,14] relative to geologic timescales.

**Reaction-Adiabatic Instability:** The atmosphere-reaction instability is illustrated in Figure 1 and its inset. Consider a spot on Venus' surface in the Cc+Q stability field, just above (in T) the reaction stability of Wo+CO<sub>2</sub> (Fig. 1 inset), and imagine a small increase in T (as from an increase in solar luminosity). The Cc+Q at that spot will react to form Wo+CO<sub>2</sub>, which increases the surface pressure. The increased pressure in turn increases the Venus greenhouse effect and hence surface T, returning the atmosphere to the dry adiabat but at a higher pressure and T. The increase in pressure and T causes Cc+Q that was initially at lower P&T (higher elevation) to react, releasing more CO<sub>2</sub> and further increasing pressure, the greenhouse effect, and therefore surface T. The process runs away until all Cc+Q has reacted and its carbon dioxide resides in a massive, high T atmosphere. The stair-steps of the Figure 1 inset are schematic – in reality, pressure and T at the Venus surface would follow a smooth trajectory, running away to high T until the Cc+Q was exhausted. In the converse case, a small decrease in T would lead to runaway production of Cc+Wo from Wo, and collapse of the CO<sub>2</sub> atmosphere.

**General Instability Criterion:** Generalizing this argument for any atmosphere that follows a dry adiabat, a surface-atmosphere reaction that produces a radiatively active gas species can buffer the abundance of that species only if the atmospheric lapse rate is greater than the P-T slope of the potential buffering reaction:

$$dP/d\Gamma_{(atm)} > dP/d\Gamma_{(rxn)}.$$

Applying the Clausius-Clapeyron equation and the expression for an adiabatic lapse rate, approximating the gases as ideal, and taking molar volumes for gases as much greater than those of solids, a solid-gas reaction can buffer an atmosphere's composition only if

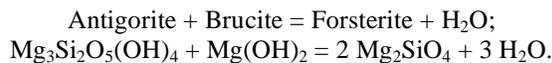
$$\bar{C}P_{(atm)}/\bar{V}_{(atm)} > \Delta\bar{H}_{(rxn)}/(T \cdot \bar{V}_{(gas)}).$$

For an atmosphere whose main constituent is the radiatively active gas species produced or consumed in the reaction, this relation simplifies to

$$\bar{C}p_{(gas)} \cdot T > \Delta\bar{H}_{(rxn)}.$$

**CO<sub>2</sub> Atmospheres:** Venusoid exoplanets will have massive CO<sub>2</sub> atmospheres and greenhouse-amplified surface temperatures, and thus other decarbonation reactions may act as potential CO<sub>2</sub> buffers (e.g., forsterite + CO<sub>2</sub> = enstatite + magnesite [3]). However, the  $\Delta\bar{H}_{(rxn)}$  values for likely decarbonation reactions are uniformly much greater than  $\bar{C}p_{(gas)} \cdot T$  at Venus-like T. Thus, it is unlikely that mineral-gas reactions at an exoplanet's surface could buffer the CO<sub>2</sub> pressure of its atmosphere.

**H<sub>2</sub>O Atmosphere:** The early Earth may have had a steam atmosphere [15,16], as might some comparable exoplanets. The H<sub>2</sub>O pressure of such an atmosphere could be buffered by reactions with its surface, e.g.:

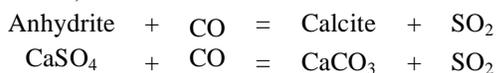


This and other dehydration reactions also fail the stability criterion above, and so it seems likely that the density of a steam atmosphere cannot be buffered by gas-mineral reactions at its surface.

**Minor Gas Species:** The above derivation applies also to minor gas species in an atmosphere, without the last simplification, i.e.:

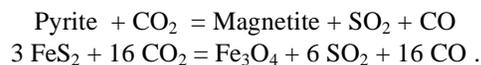
$$Cp_{(atm)} \cdot T > \Delta\bar{H}_{(rxn)} \cdot \left( \bar{V}_{(atm)} / \Delta\bar{V}_{(rxn)} \right)$$

For instance, SO<sub>2</sub> in Venus' atmosphere may be buffered or affected by reactions with the solid surface. The anhydrite-calcite reaction [4,14] cannot be a buffer for Venus, but is illustrative:



The reaction produces the radiatively active gas SO<sub>2</sub>, and consumes a radiatively inactive gas, so can contribute to increased greenhouse warming. It produces no net gases, so its  $\Delta\bar{V}_{(rxn)}$  is that for the solids, which is small and negative ( $-9 \text{ cm}^3 \cdot \text{mol}^{-1}$ ) because the molar volume of anhydrite (CaSO<sub>4</sub>) is greater than that of calcite (CaCO<sub>3</sub>). Thus, the inequality is satisfied and the reaction is a potential buffer of SO<sub>2</sub> in the atmosphere of a Venus-like planet.

**Mixed Radiatively Active Gases:** The SO<sub>2</sub> content of Venus' atmosphere might also be buffered by reactions involving iron oxide and sulfide on the surface [17-19], such as



The composition of Venus' lower atmosphere is close to that expected if this reaction were at equilibrium on the Venus surface [19]. Progress of this reaction (to the right) reduces the abundance of radiatively active gas molecules in the atmosphere (6 SO<sub>2</sub> minus 16 CO<sub>2</sub>). However, because SO<sub>2</sub> absorbs energy in the 2.1 to 2.7  $\mu\text{m}$  window between very broad CO<sub>2</sub> absorption bands, incremental changes in atmospheric SO<sub>2</sub> have more impact on the greenhouse than do changes in CO<sub>2</sub>. The oxidation of pyrite is therefore near an unstable equilibrium with respect to the Venus greenhouse effect. On Venus-like planets where CO<sub>2</sub> may not be the major atmospheric gas, however, pyrite oxidation could lead to a net decrease in the greenhouse, and the pyrite-magnetite reaction would pass the criterion as a potential buffering reaction. In general, the sensitivity of a particular terrestrial planet's atmosphere to a specific triatomic gas depends on the temperatures (and hence the peak of the Planck functions) of the host star and planetary surface, as well as on the specific composition of the atmosphere.

**Conclusions:** On a hot terrestrial (Venus-like) planet, the atmosphere composition can be strongly affected by chemical reactions with solids at its surface. Buffering of radiatively active gases is constrained by the interplay of reaction enthalpy and atmospheric lapse rate, so that some species (e.g., CO<sub>2</sub>, H<sub>2</sub>O) are not likely to be buffered.

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