

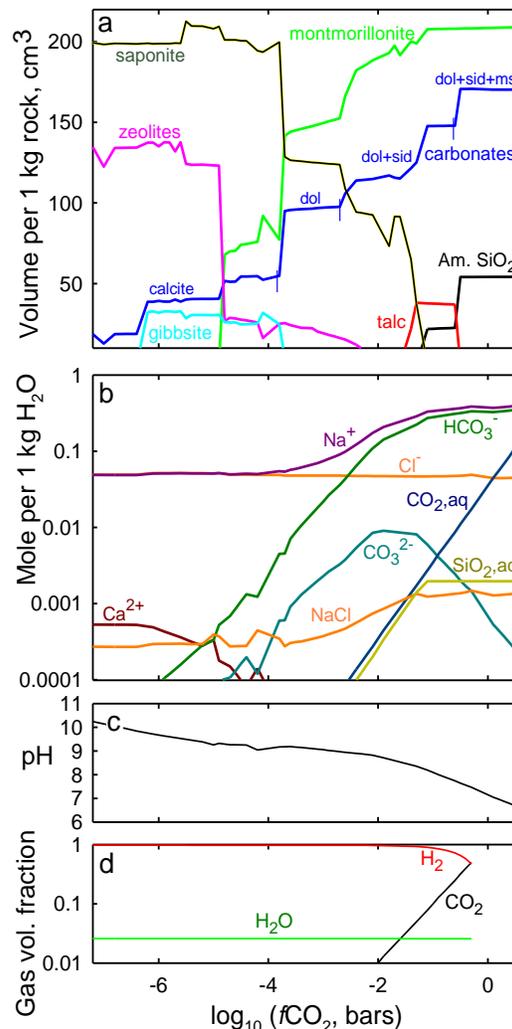
WATER-CO₂-BASALT INTERACTIONS ON TERRESTRIAL PLANETS AND EXOPLANETS. M. Yu. Zolotov, School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287-1404. E-mail: zolotov@asu.edu.

Introduction: Basalts are the most abundant surface rocks on terrestrial planets, and H₂O and CO₂ are the main products of volcanic degassing on Earth. In the Earth's history, water-CO₂-rock reactions affected speciation of atmospheric gases and surface waters, mineralogy of altered rocks and chemical sediments, and surface temperature [1, 2]. On Earth and Mars, masses and compositions of crustal carbonates provide constraints on past CO₂-bearing aqueous environments. On Mars, carbonates in weathering profiles [3] and some climate models [4] imply an early dense CO₂ atmosphere. Venus' current CO₂-rich atmosphere could reveal thermal decomposition of ancient water-deposited carbonates. CO₂-bearing habitable zone (HZ) exoplanets have been discussed as well [1, 2, 5-10]. The outstanding question is what atmospheric CO₂ can tell us about a HZ planet? Here we further evaluate chemistry and mineralogy of CO₂-bearing environments.

Models: We explore how water/CO₂/rock ratios, CO₂ fugacity ($f < 0.5$ MPa), temperature ($T < 200$ °C) and pressure ($P < 500$ MPa) affect compositions of solid, aqueous and gas phases through calculations of chemical equilibria in the water-CO₂-basalt system. Open system calculations are performed at fixed f CO₂. The rock is presented by Archaean magnesian basalt [11] in which all Fe is in ferrous (Fe²⁺) form. Formation of hydrocarbons is suppressed because their low- P formation is inhibited at $T < 200$ °C. Amounts of water and rock are referred to masses of surface water bodies and permeable rocks. The runs are performed with the *GEOCHEQ* code used elsewhere [e.g. 12].

Results: Secondary mineralogy and composition of aqueous and gas phases are non-linearly affected by water/CO₂/rock ratios and f CO₂ (Fig. 1). Systems with variable CO₂ content (x CO₂) and open systems with variable f CO₂ reveal roughly similar results. Increasing of x CO₂ or f CO₂ leads to sequential formation of carbonates (calcite, dolomite, siderite and sometimes magnesite). The increase in the carbonate content corresponds to formation of more Si/Al-rich solids. Sparse calcite coexists with Fe/Mg-rich smectites (saponite) and zeolites, while abundant Ca-Mg, Fe and Mg carbonates form with Si/Al-rich phyllosilicates and silica minerals (talc, beidellite, montmorillonite, kaolinite, amorphous silica). Formation of abundant silica at elevated $x(f)$ CO₂ corresponds to a maximum amount of carbonates (Fig. 1a). Further increase in $x(f)$ CO₂ does not cause formation of carbonates and favors dissolution of Fe and Mg carbonates in increasingly more acidic solution. In CO₂-poor systems, the rock strongly

Fig. 1. Chemical equilibrium speciation of the water-CO₂-basalt system as a function of f CO₂ at the water/rock mass ratio of 3, 25 °C and 1 bar total pressure. a, Mineralogy; b, aqueous solution, c, pH ; d, gas phase. Dol, dolomite; sid, siderite; ms, magnesite; am, SiO₂, amorphous silica; CO_{2,aq}, dissolved CO₂⁰.



affects composition and acidity (pH) of aqueous solution in which Na⁺ and Cl⁻ ions dominate. At elevated $x(f)$ CO₂ values, Na⁺, HCO₃⁻ and CO_{2,aq} dominate in solution and the pH is strongly affected by dissolved CO₂. The CO_{2,aq}/(HCO₃⁻ + CO₃²⁻) ratio increases as solution becomes more acidic (Fig. 1b,c). The gas phase consists of H₂, H₂O, and CO₂. CO₂ gas is abundant in equilibrium with low- pH solution and Si/Al-rich solids formed via an advanced alteration of basalt.

Deeper surface water reservoirs (higher water/rock ratios and pressures) accumulate more inorganic C and favor formation of Al/Si-rich phases at the water-rock interface. An increase in the water/rock mass ratio (e.g. beyond $\sim 10^4$ at 25 °C) causes sequential dissolution of carbonates and Si/Al-rich phases (talc, silica, montmorillonite, beidellite, kaolinite and then gibbsite/diaspore) in increasingly lower-*pH* solution (due to lesser concentrations of cations at a fixed $f\text{CO}_2$).

Could CO₂-rich atmospheres be common on HZ planets? The models suggest that atmospheres of terrestrial planets (early Venus, Earth and Mars) and HZ exoplanets with surface water may contain dense CO₂ atmospheres only if (1) a significant surface area is covered by a thick layer of minerals that are sparingly soluble in acidic solutions (silica, Al-rich clay minerals, Al hydroxide/oxyhydroxide), (2) the layer is impermeable and (3) a significant CO₂ mass is supplied. Although all three conditions may not be reached on a majority of terrestrial HZ planets, variations in occurrence, thickness and permeability of weathering crusts, and in CO₂ supply should affect atmospheric $f\text{CO}_2$.

Dense CO₂ atmospheres may not form if CO₂ is supplied by magma only. CO₂ is a low-solubility gas in silicate melts [13] and erupting basalts contain more than enough cations to trap all degassed CO₂ to carbonates. Though, CO₂ could be supplied by metamorphic decarbonatization (e.g. during a runaway greenhouse heating of past Venus' crust) and cometary ices.

Dense CO₂ atmospheres may not exist on terrestrial HZ planets with abundant surface water and active resurfacing by erosion, impacts and/or volcanism. A rapid aqueous deposition of carbonates in weathering crusts, lakes etc. could have prevented any prolonged existence of such atmospheres on early Earth, Mars and Venus. Such atmospheres may not exist on HZ planets with thin permeable layers of surface Si/Al-rich phases because carbonates could precipitate in middle parts of weathering profiles from neutralized solutions on land [3, 12] and below water reservoirs [8]. Subduction, burial or other submergence [e.g. 1, 2, 9] of carbonate-bearing rocks isolate CO₂ in temporal crustal reservoirs that compose a majority of planetary CO₂ abundance.

Common HZ planets with deep water oceans may not have dense CO₂ atmospheres as well. A significant amount of CO₂ could be dissolved in cold pressurized waters [7, 10, this work], especially in alkaline Na-rich solutions formed through water-rock interaction ('soda oceans'). Elevated pressures beneath ocean floors suppress silicate melting and degassing of magmas, if they form. Huge masses of cometary CO₂ are needed to acidify deep oceans and form Si/Al-rich minerals at the ocean floors. CO₂ hydrates could form at the bottom of low-*pH* oceans [10]. Though, high pressure and a limited volcanic/erosional/impact resurfacing at deep oce-

anic floors favor formation of low-permeability layers that limit water-rock interaction and trapping of inorganic carbon species in carbonates.

Desert HZ planets with sparse surface water bodies, rare rains and a rapid CO₂ supply could have CO₂-rich atmospheres. As on today's Venus, high-pressure CO₂-rich atmospheres could indicate kinetically suppressed trapping of degassed CO₂ without liquid water.

Elevated temperature decreases CO₂ solubility in water but favors precipitation of carbonates (by both thermodynamic and kinetic reasons) that stabilizes the greenhouse temperature [e.g. 1, 2]. Overall, dense CO₂ atmospheres could be less likely on planets with warm oceans.

Mineralogy could reveal CO₂-rich environments: A presence of silica and/or Si/Al-rich minerals in aqueously-deposited geological formations may indicate elevated CO₂/(rock + water) ratios and $f\text{CO}_2$ at the time of precipitation. In the solar system, possible examples are Archean SiO₂-rich banded iron formations [14], upper parts of Noachian weathering profiles on Mars [12, 15] and a subsurface water ocean on Enceladus that emits icy grains with Na carbonates and silica [16, 17]. A detection of Si/Al-rich chemical sediments on Venus' tessera terrains could be indicative of past CO₂-rich aqueous environments, and a detection of Na-rich salt deposits or flows (e.g. in channels [18]) may inform about past seas [19]. Likewise, a direct or indirect detection of abundant Si/Al-rich minerals and carbonates on Venus-like exoplanets could be interpreted in terms of past CO₂-rich aqueous processes.

References: [1] Kasting J. F. and Catling D. (2003) *Annu. Rev. Astron. Astrophys.*, 41, 429–463. [2] Kasting J. F. et al. (1993) *Icarus*, 101, 108–128. [3] Bulter B. et al. (2019) *JGR-P*, 124, 989–1007. [4] Wordsworth R. D. (2016) *Annu. Rev. Earth Planet. Sci.*, 44, 381–408. [5] Abbot D. S. et al. (2012) *Astrophys. J.*, 756, 178–191. [6] Kitzmann D. et al. (2015) *MNRAS*, 452, 3752–3758. [7] Levi A. et al. (2016) *Astrophys. J.*, 838, 24. [8] Krissansen-Totton J. et al. (2018) *PNAS*, 115, 4105–4110. [9] Foley B. J. and Smye A. J. (2018) *Astrobiology*, 18, 873–896. [10] Marounina N. and Rogers L. A. (2019) arXiv:1904.10458. [11] BVTP Project (1981) Lunar and Planetary Institute. page 16, #1. [12] Zolotov M. Yu. and Mironenko M. V. (2016) *Icarus*, 275, 203–220. [13] Lowenstern J. B. (1999) *Mineralium Deposita*, 36, 490–502. [14] Bekker A. et al. (2014) *Treatise on Geochemistry*, 2nd ed., vol. 9, 561–628. [15] Carter J. et al. (2015) *Icarus*, 248, 373–382. [16] Postberg F. et al. (2011) *Nature*, 474, 620–622. [17] Hsu H-W. et al., *Nature*, 519, 207–210. [18] Baker V. R. et al. (1997) In: *Venus II*, 757–793. University of Arizona Press. [19] Zolotov M. Yu. (2019) In: *Oxford Research Encyclopedia of Planetary Science*. Doi:10.1093/acrefore/9780190647926.013.14