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 fCO₂. 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 fCO₂ (Fig. 1). Systems with variable CO₂ content (xCO₂) and open systems with variable fCO₂ reveal roughly similar results. Increasing of xCO₂ or fCO₂ 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-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 affects composition and acidity (pH) of aqueous solution in which Na⁺ and Cl⁻ ions dominate. At elevated x(f) CO₂ values, Na⁺, HCO₃⁻ and CO₃²⁻ dominate in solution and the pH is strongly affected by dissolved CO₂. The CO₃²⁻/HCO₃⁻ 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.

Fig. 1. Chemical equilibrium speciation of the water-CO₂-basalt system as a function of fCO₂ 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; CO₂aq, dissolved CO₂⁰.
Higher 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 \(-10^{2}\) 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 \(f_{CO_2}\)).

Could \(CO_2\)-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 \(CO_2\) 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 \(CO_2\) 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 \(CO_2\) supply should affect atmospheric \(f_{CO_2}\).

Dense \(CO_2\) atmospheres may not form if \(CO_2\) is supplied by magma only. \(CO_2\) is a low-solubility gas in silicate melts [13] and erupting basalts contain more than enough cations to trap all degassed \(CO_2\) to carbonates. Though, \(CO_2\) could be supplied by metamorphic decarbonatization (e.g. during a runaway greenhouse heating of past Venus’ crust) and cometary ices.

Dense \(CO_2\) 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 \(CO_2\) in temporal crustal reservoirs that compose a majority of planetary \(CO_2\) abundance.

Common HZ planets with deep water oceans may not have dense \(CO_2\) atmospheres as well. A significant amount of \(CO_2\) 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 \(CO_2\) are needed to acidify deep oceans and form Si/Al-rich minerals at the ocean floors. \(CO_2\) hydrates could form at the bottom of low-\(pH\) oceans [10]. Though, high pressure and a limited volcanic/erosional/impact resurfacing at deep oce-