

LOW-GRADE METAMORPHIC PHASES ON MARS AS A FUNCTION OF CO₂-H₂O FLUID COMPOSITIONS. J. Semprich¹, A. H. Treiman¹, J. Filiberto¹, S. P. Schwenzer², ¹Lunar and Planetary Institute, USRA, 3600 Bay Area Blvd, Houston TX 77058, USA. ² School of Environment, Earth and Ecosystem Sciences, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK. Corresponding author: jsemprich@lpi.usra.edu

Introduction: Mars has an abundance of hydrous phases, which are predominantly associated with surface or near-surface processes [1]. However, observed minerals such as prehnite, epidote, and serpentine, are indicative of low-grade metamorphic conditions and therefore must have formed at elevated temperatures either along a geothermal gradient or as a result of hydrothermal systems (impact- or volcanic-induced) [2,3]. The conditions required for the formation of low-grade metamorphic phases have been previously investigated via phase equilibria calculations assuming the fluid to be pure H₂O [4]. While this is likely a valid assumption for subsurface metamorphic fluids, the stabilities of some phases, particularly Ca-Al silicates are sensitive to CO₂ in the fluid phase. Here, we investigate the effect of H₂O-CO₂ fluid compositions on a shergottite-like martian basaltic composition and an ultramafic cumulate composition.

Methods: Phase diagrams were calculated with the Gibbs free energy minimization software *Perple_X* 6.8.4 [5] using an internally consistent thermodynamic data set [6, and 2002 update] following our previous approach. MnO, Cr₂O₃, and P₂O₅ were excluded from the calculation because of their low abundances and/or limitations of solid solution models. Thus, our calculation are all in the system TiO₂-Na₂O-CaO-K₂O-FeO-MgO-Al₂O₃-SiO₂-O₂ (TiNCKFMASO) + fluid. Oxidation state is represented by O₂, which was set at a fixed value of 0.12 rather than a buffer to account for Fe³⁺-bearing phases. For properties of the fluid phase, we used a compensated Redlich-Kwong (CORK) equation of state [6]. The following solid-solution models were used: clinopyroxene, olivine, dolomite, and magnesite [6]; pumpellyite and actinolite [7]; chlorite and white mica [8]; epidote [9]; biotite [10]; antigorite [11]; K-feldspar [12]; plagioclase [13]. Talc and brucite were assumed to be ideal solutions; calcite, prehnite, stilbite, and laumontite were treated as pure phases. Andradite and vesuvianite were excluded. We used the compositions of Bounce Rock [14] and the cumulate ALH A77005 [15]. Mineral abundances were then extracted along a 20 °C/km geotherm for X_{CO₂} of 0, 0.0005, and 0.05.

Results:

Variations with CO₂ in Bounce Rock. While prehnite is stable from 170-290 °C under pure H₂O (Fig. 1a), its stability is reduced significantly for X_{CO₂} as low as 0.0005 (Fig. 1b) and it is only present at

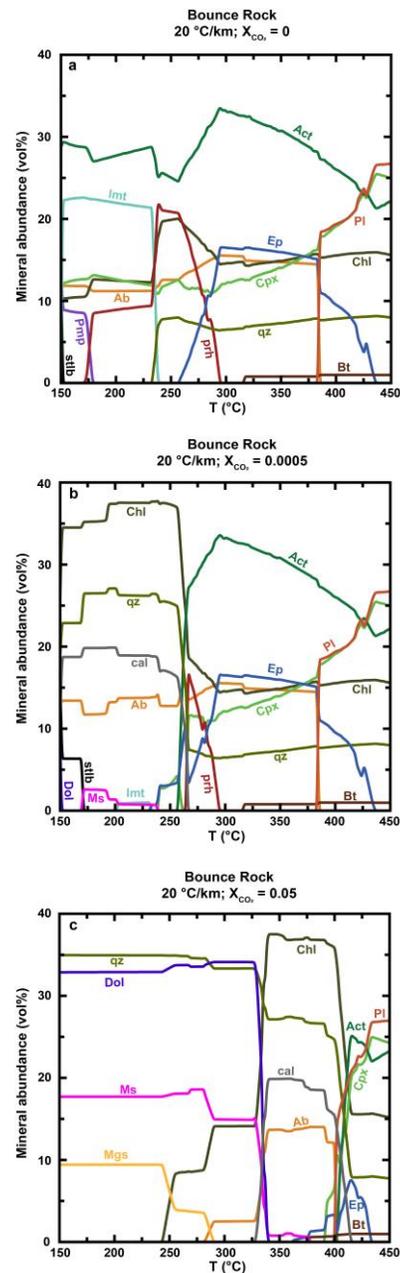


Figure 1. Mineral abundances (vol %) of phases along a 20 °C/km geotherm for the composition of Bounce Rock at fluid saturated conditions with X_{CO₂} of 0 (a), 0.0005 (b), and 0.05(c). Composition in wt %: 51.6 SiO₂, 0.74 TiO₂, 10.5 Al₂O₃, 14.4 FeO^T, 6.8 MgO, 12.1 CaO, 1.7 Na₂O, 0.1 K₂O. Mineral abbreviations in appendix.

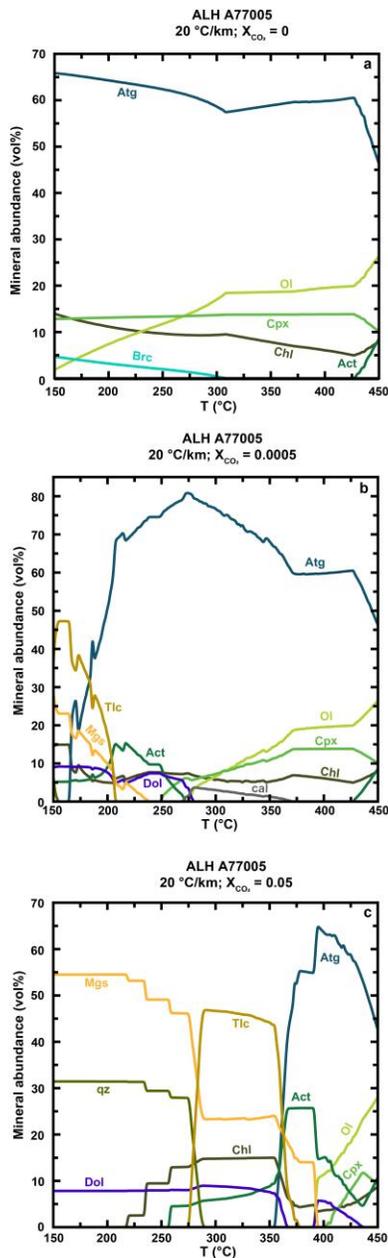


Figure 2. Mineral abundances (vol %) of phases along a 20 °C/km geotherm for the composition of a cumulate (ALH A77005) at fluid saturated conditions with X_{CO₂} of 0 (a), 0.0005 (b), and 0.05(c). Composition in wt %: 42.2 SiO₂, 0.39 TiO₂, 2.9 Al₂O₃, 20.1 FeO^T, 28.2 MgO, 3.2 CaO, 0.47 Na₂O. Mineral abbreviations in appendix.

temperatures above 250 °C. At X_{CO₂} = 0.05, prehnite is not stable (Fig. 1c). With increasing CO₂, the mineral assemblage becomes dominated by quartz, dolomite, magnesite, and muscovite at the expense of the pure H₂O assemblage of prehnite, actinolite, clinopyroxene, and zeolites.

Variations with CO₂ in the cumulate. The metamorphosed cumulate is mostly antigorite (serpentine) at H₂O-saturated conditions (Fig. 2a). At X_{CO₂} = 0.0005 and T <~ 250 °C (Fig. 2b), talc, magnesite, and dolomite dominate. At X_{CO₂} = 0.05 (Fig. 2c), the CO₂-free phase assemblage of antigorite, chlorite, olivine, clinopyroxene, and brucite is replaced by magnesite, quartz and dolomite (e.g., the rock listwanite).

Interpretation: Our results demonstrate that small amounts of CO₂ in the metamorphic fluid change the mineralogy significantly towards quartz- and carbonate-dominated assemblages, in both basaltic and ultramafic martian compositions. This is consistent with studies on Earth, where prehnite and zeolite form at low X_{CO₂} [16, 17]. In regions on Mars where prehnite has been detected, fluids could therefore not have contained significant amounts of CO₂. This may either be due to initially low CO₂ in martian subsurface fluids, not in contact with the martian atmosphere, or, alternatively, prehnite may have formed as a result of CO₂ degassing within a hydrothermal system from hot alkali chloride waters [18]. Similar fluids have been proposed based on Nakhilite melt inclusions [e.g., 19].

References: [1] Ehlmann B. L. et al. (2009) *JGR*, 114, E00D08. [2] McSween H. Y. et al. (2015) *MaPS*, 50, 590-603. [3] Schwenzer S. P. and Kring D. A. (2013) *Icarus*, 226, 487-496. [4] Semprich J. et al. submitted to *JGR-Planets*. [5] Connolly J. A. D. (2005) *EPSL*, 236, 524-541. [6] Holland T. J. B. and Powell R. (1998) *JMG*, 16, 309-343. [7] Massonne H.-J. and Willner, A.P. (2008) *EJM*, 20, 867-879. [8] White R. W. et al. (2014) *JMG*, 32, 261-286. [9] Holland T. J. B. and Powell R. (2011) *JMG*, 29, 333-383. [10] Tajčmanová, L. et al. (2009) *JMG*, 27, 153-165. [11] Padrón-Navarta J. A. et al. (2013), *Lithos*, 178, 186-196. [12] Thompson J. B. and Waldbaum D. R. (1969) *AmMin*, 54, 811-838. [13] Newton R. C. et al. (1980) *GeochimCosmo*, 44, 933-941. [14] Zipfel, J. et al. (2011) *MAPS*, 46, 1-20. [15] Lodders, K. (1998) *MaPS*, 33, A183-A190. [16] Digel S. D. and Gordron T. M. in Schiffman P. and Day H. W. (1995) *GeoSocAm Special Paper*, 296. [17] Thompson A. B. (1971) *ContribMinPet*, 33, 145-161. [18] Wheeler R.S. et al. (2001) *MinMag*, 65, 397-406. [19] Filiberto J. et al. (2014) *EPSL*, 401, 110-115.

Appendix: Mineral abbreviations: Act – actinolite, Ab – albite, Atg – antigorite, Brc – brucite, Bt – biotite, cal – calcite, Chl – chlorite, Cpx – clinopyroxene, Dol – dolomite, Ep – epidote, lmt – laumontite, Mgs – magnesite, Ms – muscovite, Pl – plagioclase, Pmp – pumpellyite, prh – prehnite, qz – quartz, stlb – stilbite, Tlc – talc. Capitalized: solid solution; lower case: pure phases.