

PHASE EQUILIBRIA MODELING OF LOW-GRADE METAMORPHIC MARTIAN ROCKS. J. Semprich¹, S. P. Schwenzer¹, A. H. Treiman². ¹School of Environment, Technology, Engineering and Mathematics, The Open University, Walton Hall, Milton Keynes, MK7 6AA, UK, ² Lunar and Planetary Institute, USRA, 3600 Bay Area Blvd., Houston TX 77085, USA.

Introduction: In addition to igneous rocks, numerous alteration products have been identified on Mars including clay minerals, chlorite, mica, prehnite, zeolites, serpentine, carbonate, sulphates, hydrated silica, and oxides [1], indicative of multiple and diverse aqueous activity and environments ranging from Martian surface conditions to deeper crustal levels. While a substantial part of the observed alteration products can be associated with surface weathering processes, evaporation, diagenesis, and impact-generated hydrothermal systems as predicted by thermochemical models [2-7], certain minerals such as prehnite require higher temperatures (200–400 °C) and are therefore indicative of low-grade metamorphic or hydrothermal alteration of mafic rocks at depth prior to being exposed by cratering [8,9]. Since metamorphic rocks seem to be more widespread on Mars than initially predicted and are expected from thermochemical constraints to form larger parts of the lower crust, understanding their formation conditions and distribution provides useful information about the composition and evolution of the Martian crust. A number of thermochemical studies have predicted the formation of alteration minerals using basaltic and ultramafic protoliths reacting with hydrothermal fluids [2-7], but focused on temperatures below 300 °C, relatively high water to rock ratios, and pressures equating to less than 10 km in Martian crustal depth beneath the surface. Furthermore, generic phase diagrams for terrestrial mafic and ultramafic rocks have been used for the recognition of low-grade metamorphic assemblages [1,10], or the plotting of Martian rock compositions [9]. Phase diagrams established for terrestrial rocks, however, may not always adequately represent Martian basalts due to their compositional differences influencing mineral stability and consequently the metamorphic facies. The aim of this study is to provide compositionally and pressure-temperature dependent phase assemblages for low-grade metamorphic Martian crustal rocks using a variety of protolith compositions and comparing them to terrestrial analogs.

Method: All phase diagrams have been calculated with the Gibbs free energy minimization software Perple_X 6.7.5 [11] using an internally consistent thermodynamic data set [12, and 2002 update]. For simplicity, our calculations assume iron to be divalent and fluid as pure H₂O resulting in the system TiO₂-Na₂O-CaO-K₂O-FeO-MgO-Al₂O₃-SiO₂-H₂O (TiNCKFMASH) for the P-T range of 0.001–0.5 GPa and 150–450 °C.

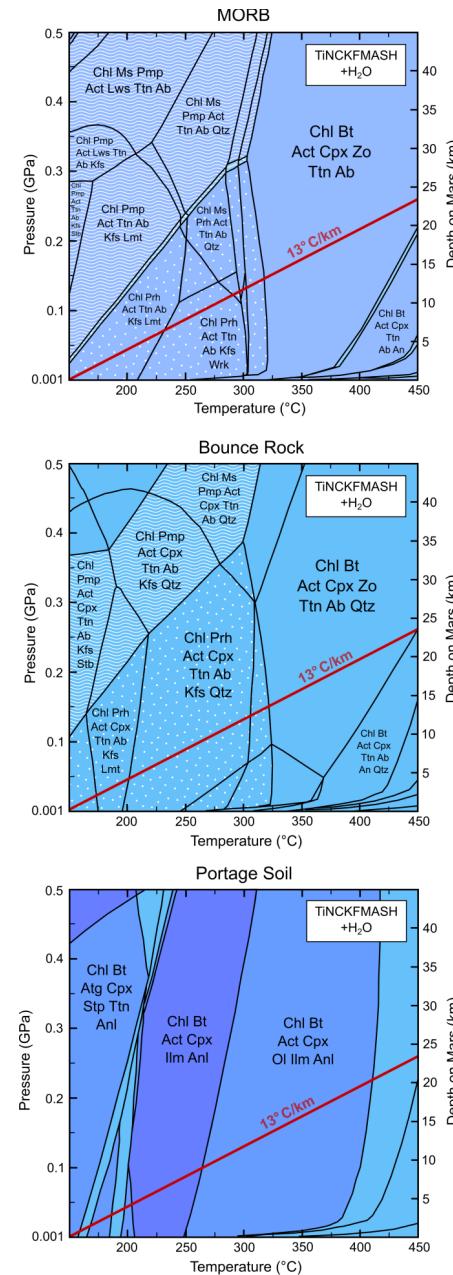


Fig. 1. P-T pseudosections for water-saturated MORB, Bounce Rock and Portage soil compositions. Mineral abbreviations in appendix. Dotted area represents prehnite, and wavy area pumpellyite stability fields. A possible Martian geotherm of 13 °C/km is shown by the red line

We used the following solid solutions: clinopyroxene and olivine [12]; chlorite, ilmenite, and white mica [13]; actinolite, pumpellyite, and stilpnomelane [14];

biotite [15]; antigorite [16]. Due to plagioclase being nearly pure albite at low $P-T$ conditions, no solid-solution model was specified. We calculated sections of a phase diagram for a specified composition, so-called pseudosections, using water-saturated compositions (Table 1) of an average MORB [17], a measurement of Bounce rock (interior) by Opportunity [18], representative for meteorite basalts, and Portage soil obtained in Gale Crater by Curiosity [19]. The depth scale was calculated with the formula $P = \rho gh$ using an average crustal density of 2960 kg/m^3 and g of 3.727 m/s^2 [20]. A geotherm of $13 \text{ }^\circ\text{C/km}$ [21] has been added.

Table 1: Rock compositions used for calculation of pseudosections

	MORB [17]	Bounce Rock [18]	Portage [19]
wt.%			
SiO ₂	50.42	51.6	43.88
TiO ₂	1.53	0.74	1.19
Al ₂ O ₃	15.13	10.5	9.43
FeO	9.81	14.4	19.19
MgO	7.76	6.8	8.69
CaO	11.35	12.1	7.28
Na ₂ O	2.83	1.7	2.72
K ₂ O	0.14	0.1	0.49

Results: MORB and Bounce Rock are compositionally similar and therefore show the typical very low-grade to low-grade metamorphic phases including zeolites, pumpellyite, prehnite, chlorite and actinolite. Due to the lower Al₂O₃ content of Bounce Rock, however, the stability fields of both pumpellyite and zeolites are reduced at the expense of prehnite and clinopyroxene. The Portage soil composition has significantly lower silica and much higher FeO than both MORB and Bounce Rock. As a result, neither prehnite nor pumpellyite are stable while minerals typical for ultramafic metamorphic rocks such as antigorite (serpentine), olivine and ilmenite are abundant phases. While MORB and Bounce Rock show a variety of zeolites such as laumontite, stilbite and wairakite, the predominant zeolite mineral in the less silica-rich portage soil is analcime.

Discussion: The prehnite-pumpellyite stability field is extremely small or absent for basaltic compositions, possibly due to problems with the available thermodynamic data. However, the pumpellyite stability field is not reached with a $13 \text{ }^\circ\text{C}$ geotherm. Calculating with ferrous iron is a reasonable approach for basalts, but portage soil is expected to contain larger amounts of ferric iron, which has to be addressed in future re-

search. If the fluid were not pure H₂O but a brine, additional phases such as carbonates, sulfates and possibly phosphates are expected. Our phase diagrams are in accordance with the detected prehnite-chlorite assemblages for basaltic rocks as well as serpentine and analcime for silica-poor compositions [8]. The detection of zeolites by remote sensing, however, seems to be hindered by the presence of other metamorphic minerals.

Conclusions and outlook: Compositional differences of Martian mafic and ultramafic rocks strongly influence the mineral stability fields and low-grade metamorphic facies. While some compositions such as Bounce Rock, resemble terrestrial basalts in mineralogy, phase stability fields are very sensitive to even small compositional protolith variations. Although the presented pseudosections already emphasize the importance of pressure-temperature and compositional dependent phase diagrams for a better understanding of Martian subsurface rocks, additional aspects such as more protolith compositions, varying water content, variations in fluid compositions as well as oxidation states remain to be explored.

Appendix: Mineral abbreviations: Act – actinolite, Ab – albite, Anl – analcime, An – anorthite, Atg – antigorite, Bt – biotite, Chl – chlorite, Cpx – clinopyroxene, Ilm – ilmenite, Kfs – K-feldspar, Lmt – laumontite, Lws – lawsonite, Ms – muscovite, Ol – olivine, Prh – prehnite, Pmp – pumpellyite, Qtz – quartz, Stb – stilbite, Stp – stilpnomelane, Ttn – titanite, Wrk – wairakite, Zo – zoisite

- References:** [1] Ehlmann, B.L. et al. (2009) *JGR*, 114, E00D08. [2] Bridges, J. C. and Schwenzer, S. P. (2012) *EPSL*, 359–360, 117–123. [3] Filiberto, J. and Schwenzer, S. P. (2013) *MAPS*, 48, 1937–1957. [4] Schwenzer, S. P. and Kring, D. A. (2013) *Icarus*, 226, 487–496. [5] Bridges, J. C. et al. (2015) *JGR*, 120, 2014JE004757. [6] Schwenzer, S. P. et al. (2016) *MAPS*, 51, 2175–2202. [7] Zolotov, M. Y. and Mironenko, M. V. (2016) *Icarus*, 275, 203–220. [8] Ehlmann, B. L., et. al. (2011) *Clays Clay Miner*, 59, 359–377. [9] McSween, H. Y. et al. (2015) *MAPS*, 50, 590–603. [10] Viviano, C. E. et al (2013) *JGR*, 118, 1858–1872. [11] Connolly, J. A. D. (2005) *EPSL*, 236, 524–541. [12] Holland, T. J. B. and Powell, R. (1998) *JMG*, 16, 309–343. [13] White, R. W. et al. (2014) *JMG*, 32, 261–286. [14] Massonne, H.-J. and Willner, A.P. (2008) *EJM*, 20, 867–879. [15] Tajčmanová, L. et al. (2009) *JMG*, 27, 153–165. [16] Padron-Navarta, J. A. et al. (2013), *Lithos*, 178, 186–196. [17] Gale, A., et al. (2013) *GGG*, 14, 489–518. [18] Zipfel, J. et al. (2011) *MAPS*, 46, 1–20. [19] Schmidt, M. E. et al. (2014) *JGR*, 119, 2013JE004481. [20] Turcotte, D. L., et al. (2002), *JGR*, 107, 5091. [21] Babeyko, A. Y. and Zharkov, V. N. (2000) *PEPI*, 117, 421–435.