

**LOW TEMPERATURE NEAR-SURFACE THERMOCHEMICAL MODELLING OF THE ALTERATION ASSEMBLAGE IN MARTIAN METEORITE ALH84001** M. Melwani Daswani<sup>1</sup>, S. P. Schwenzer<sup>1</sup>, I. P. Wright<sup>1</sup> and M. M. Grady<sup>1</sup>. <sup>1</sup>The Open University, Department of Physical Sciences, CEPSAR, Walton Hall, Milton Keynes MK7 6AA, UK, mohit.melwani-daswani@open.ac.uk.

**Introduction:** The origin of secondary carbonate minerals in the oldest known martian meteorite ALH84001 have been intensely debated in the literature, with widely different thermal origins considered: ranging from hydrothermal alteration (possibly impact-induced) [e.g. 1, 2, 3] to low temperature alteration conditions [e.g. 4, 5, 6]. Recent isotopic evidence suggests the carbonates precipitated from evaporating water at  $18 \pm 4$  °C under near-surface conditions [7].

Here, we aim to test this latter scenario with thermochemical modelling.

**Modelling method and conditions:** CHIM-XPT, a modelling software to compute reaction processes at 0.01 – 600 °C [8], was used here to carry out the aqueous alteration scenarios at 15, 20 and 25 °C; and pressures of 1 and 2 bar of atmospheric CO<sub>2</sub>. The water to rock ratio (W/R) was varied from 0.1 to 100,000 to obtain various alteration mineral precipitates. Isothermal evaporation scenarios where only water was evaporated were also modelled starting from W/R of 0.1, 0.5, 1 and 5.

The composition of the ALH84001 host rock was obtained from [9] and the secondary carbonate phases were not included in the initial unaltered rock composition. The composition of the starting fluid consisted of pure water equilibrated with 1 or 2 bar of atmospheric CO<sub>2</sub>. We chose these pressures, because they have been used as surface pressures in early martian climate models [10, 11].

**Results:** 15 °C. At both 1 and 2 bar of CO<sub>2</sub> pressure, the alteration assemblage as W/R decreases consists mostly of amphibole group minerals (ferroanthophyllite, tremolite, ferroactinolite) and phyllosilicates (serpentines, smectites, talc). A small amount of K-rich nontronite is formed in evaporation scenarios at  $W/R < 1.2$ . No carbonates were formed.

20 °C. At 1 bar CO<sub>2</sub>, a similar assemblage of phyllosilicates as those at 15 °C are found. However, at 2 bar CO<sub>2</sub>, a series of carbonate minerals precipitate at varying W/R. Calcite (CaCO<sub>3</sub>) precipitates at  $W/R > 60$ , ankerite (CaMg(CO<sub>3</sub>)<sub>2</sub>) at  $W/R > 300$  and siderite (FeCO<sub>3</sub>) at  $W/R > 500$ . Rhodochrosite (MnCO<sub>3</sub>) is present at  $W/R < 50$ , forming ~1% of the alteration assemblage. Fe-rich celadonite is formed both at 1 and 2 bar CO<sub>2</sub> at  $W/R < 0.5$ . In evaporation models beginning at  $W/R \geq 1$ , celadonite is not formed.

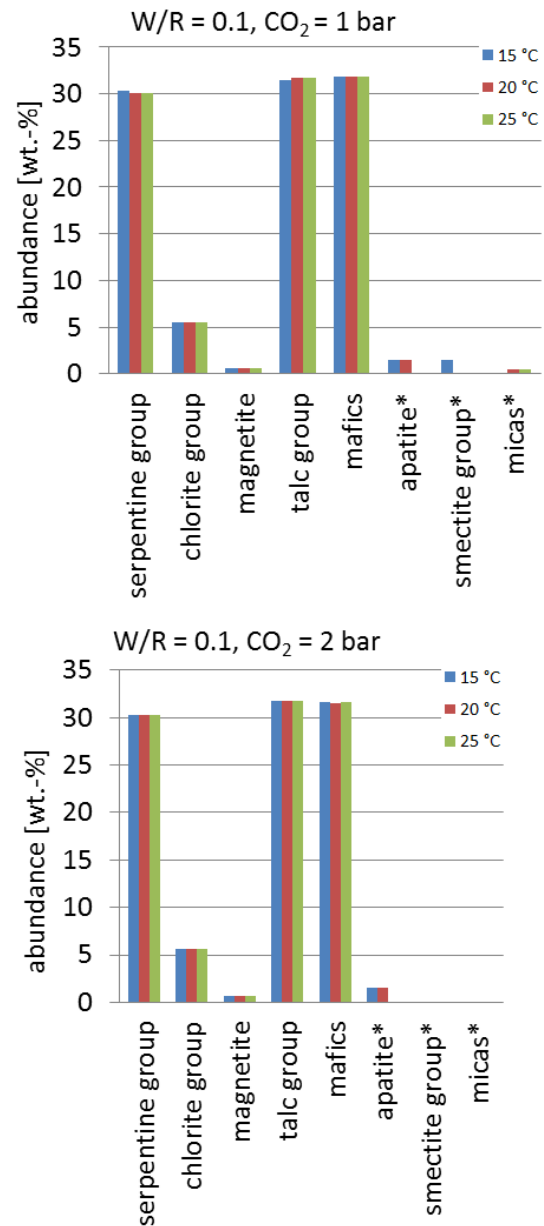


Figure 1. Mineral abundance after alteration of ALH84001 at  $W/R=0.1$ . Phases with (\*) are shown enhanced by a factor of 10.

25 °C. At 1 bar CO<sub>2</sub>, the composition and proportion of phyllosilicate phases is the same as that found at 20 °C. At 2 bar CO<sub>2</sub>, the same alteration phases occur, but small amounts of rhodochrosite (less than 0.5% of the mass of the alteration assemblage) form in addition

at  $W/R > 5$ . However, the other carbonates precipitated at 20 °C (ankerite, calcite and siderite) are absent. Fe-rich celadonite is found at  $W/R < 1$  at both  $CO_2$  pressures.

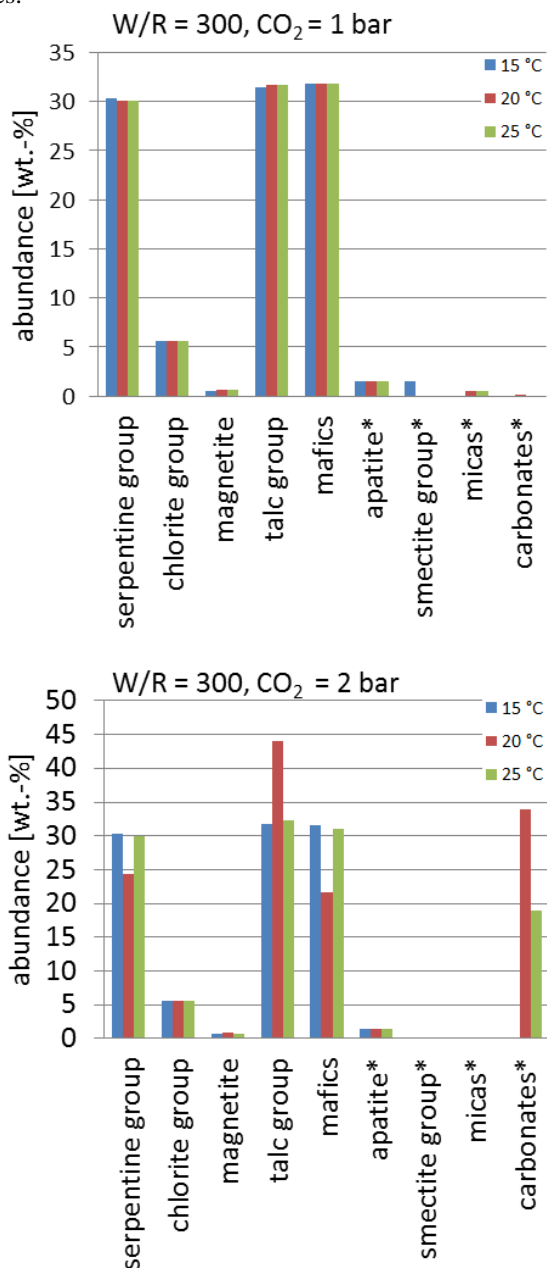


Figure 2. Mineral abundance after alteration of ALH84001 at  $W/R=300$ . Phases with (\*) are shown enhanced by a factor of 10.

Isothermal evaporation of water starting at  $W/R$  of 0.1, 0.5 and 1, and at 2 bar of  $CO_2$  pressure yielded small amounts of rhodochrosite. Evaporation starting at  $W/R=5$  did not yield any carbonates.

Figure 1 summarises the mineral phases found at low  $W/R$ , while figure 2 collects those at high  $W/R$ .

**Conclusions and discussion:** The results show that the precipitation of carbonates depends on the amount of  $CO_2$  in dissolution and the temperature of the system. The initial amount of  $CO_2$  dissolved is itself dependent on temperature.  $W/R$  has an impact on both the amount and type of carbonates formed.

Despite higher amounts of  $CO_2$  dissolved at 15 °C relative to the higher temperatures, carbonates in the system are soluble and do not precipitate. At 15 °C, atmospheric pressures of  $CO_2 > 2$  bar are necessary to precipitate carbonates in the system.

At 25 °C, not enough  $CO_2$  is dissolved in the fluid to form carbonates. Only evaporation of water yields concentrations high enough to precipitate carbonates at low  $W/R$  ratios.

In principle, the results are in agreement with a low temperature (~20 °C) and moderately high atmospheric  $CO_2$  pressure (~2 bar) formation of the carbonates in ALH84001, as seen by the suite of carbonates formed. The differing carbonate types in ALH84001 [e.g. 5] may reflect a changing  $W/R$  brought on by evaporation of the alteration fluid.

The formation of substantial amounts of secondary phyllosilicates while modelling the alteration of the ALH84001 host rock at low temperatures is however in disagreement with observations, as none are found in the meteorite. Moreover, sulfides in ALH84001 are also secondary in nature and are not formed in the alteration models, as the unaltered host rock does not contain sufficient sulfur. It therefore must be considered that the original alteration fluid contained species undefined in the model (including sulphate and carbonate ions) leached from rocks prior to the onset of alteration in the ALH84001 host rock and/or that the fluid might have contained a higher  $CO_2$ -pressure than assumed in this model.

**References:** [1] Golden D. C. (2001) et al. *Am Min*, 86, 370-375. [2] Treiman A. H. et al. (2002) *EPSL*, 204, 323-332. [3] Schwenzer S. P. and Kring D. A. (2009) *Met Soc LXXII*, Abstract #5262. [4] Valley J. W. et al. (1997) *Science* 275, 1633-1638. [5] Eiler J. M. et al. (2002) *GCA*, 66, 7, 1285-1303. [6] Socki et al. (2003) *LPS XXXIV*, Abstract #1938. [7] Halevy I. et al. (2011) *PNAS*, 108, 41, 16895-16899. [8] Reed M. H. et al. (2010): Users Guide for CHIM-XPT: A Program for Computing Reaction Processes in Aqueous-Mineral-Gas systems and MINTAB Guide. University of Oregon. [9] Mittlefehldt D. W. (1994) *Meteoritics*, 29, 214-221. [10] Wordsworth R. et al. (2013) *Icarus*, 222, 1-19. [11] Forget F. et al. (2013) *Icarus*, 222, 81-99.