ATMOSPHERIC THICKNESS ON ANCIENT MARS: CONSTRAINTS FROM SNC METEORITES. J. C. Bridges[1] and I. P. Wright[1], [1]Planetary and Space Sciences Research Institute, Open University, Milton Keynes, UK, j.bridges@open.ac.uk.

Introduction: Mars atmospheric pCO_2 levels between 4.5-3.8 Ga have commonly been estimated at 1-3 bar [1,2] based on the existence of fluvial features or sedimentary rocks on the surface of Mars. Most of the original atmospheric CO_2 (90-95%) has been lost through impact erosion, sputtering processes associated with the solar wind and sequestration within the crust [3]. This has been correlated with isotopic fractionations identified within SNC meteorites [4]. Here we consider the amount of CO_2 that could be sequestered within the martian crust – using carbonate abundances in some SNC meteorites as a guide – in order to provide constraints on past atmospheric conditions and total CO_2 inventory.

Carbonate in SNC meteorites: Of the >32 currently known martian meteorites the 7 nakhlites and ALH 84001 contain evaporite mineral assemblages [5,6]. ALH 84001 contains ~1 vol% carbonate grains 100 μm diameter which are zoned from Ca-rich cores to Mg- and Fe-rich rims. They have a complex history, having undergone post-formational shock alteration but originally crystallised (3.9 Ga) rapidly (ie in days or weeks) from 25-150^{o}C brines [6,7]. The equivalent phases in the nakhlites (mainly Fe-rich smectite clays, Fe-carbonate, sulphates, halite) have been modelled as products of progressive brine evaporation through the nakhlite parent rocks. Such thermodynamically-based modelling can provide information about the composition of martian fluids and the pressure (pCO_2) of the atmosphere at the time of the fluid's activity. For instance, modelling brines associated with the nakhlites studied so far suggests that the atmospheric pressure of CO_2 at the time of the evaporite minerals' crystallisation was 50-100 mbar. Radiometric dating work [8] suggests that these evaporite assemblages are approximately 670 Ma. We use this modelling as a way of providing an estimate of pCO_2 in the Mars atmosphere 670 Ma.

Calculation of past pCO_2: We can calculate the past atmospheric pCO_2 on >3.8 Ga Mars (Table 1) by using the following observations. 1. The average abundance of martian carbonate in SNC meteorites varies up to 1 vol.% in ALH 84001 [6,9]. 2. ALH 84001 is Noachian in age (4.5 Ga rock crystallisation with carbonates 3.9 Ga, see [7]). This provides an estimate for average crustal abundances of carbonate (which we take here as $MgCO_3$, consistent with the composition of carbonate within ALH 84001). For instance, within the uppermost 1 km of the martian crust, for 1 vol. % $MgCO_3$, this is equivalent to 5.2 x 10^{19} mol or 2.3 x 10^{18} kg CO_2. Over the planet's surface this quantity on Mars is equivalent to an atmospheric pressure pCO_2 of 580 mbar. Some CO_2 may also be absorbed directly within the uppermost 1 km of Mars. Lesser amounts are present within the polar ice caps and the remnant caps are dominated by H_2O. Carbonate is assumed to be the largest crustal reservoir of carbon e.g. the regolith probably contains much less than 280 mbar of CO_2 in the form of ice [10].

A potential alternative to meteorites for estimating average carbonate abundances within the martian crust is to use thermal emission data from *Mars Global Surveyor* and *Mars Express*. The former has reported ~2 wt% $MgCO_3$ within martian dust [11], which if it is representative of the uppermost 1 km of crust is equivalent to 1200 mbar pCO_2. However, the OMEGA experiment onboard Mars Express, has not confirmed this during its current mapping phase [12].

The salt deposits of the Eagle Crater sedimentary layers contain sulphate but not carbonate. Similarly, the *Spirit* Lander has detected only possible traces of carbonate [13]. However, within an acid-sulphate fluid system, carbonate will be replaced by sulphate minerals and this is a likely explanation for the lack of any more than uncertain traces of carbonate being found by the MER rovers. Carbonate associated with the evaporative brines is expected to be present at deeper levels i.e. tens of meters to km depth in the crust.

About 56% of the martian surface (the ancient highlands in the southern hemisphere) consists of terrains of ancient, Noachian age. By using the concentration of carbonate within ALH 84001 and the proportion of Mars over which Noachian terrains are exposed in the ancient highlands, the equivalent of 2300 mbar pCO_2 is trapped within the 7 km depth layered units of the Noachian terrains. The 7 km figure is taken from the thickness of layered units exposed on the sides of Valles Marineris canyons. The photographic evidence of Mars [14] suggests that a large proportion of the ancient highlands may be underlain by layered rocks, some of which, but not all, will be sedimentary in origin deposited from flowing water and likely to contain carbonate. However, the SNCs show that igneous rocks on Mars also contain carbonate.

Such figures of trapped CO_2 are small in comparison with the amount of CO_2 trapped within the Earth's crust as carbonate, or present within the current Venusian atmosphere (about 90 bars) and can be considered a lower limit for ancient Mars. Assuming atmospheric losses due to impact and solar wind-related activity of 95% this suggests that the original pCO_2 was 45 bar pCO_2, with 2.3 bar pCO_2 being trapped within rocks over the course of the next 700 million years until 3.8 Ga. Based on the nature of the nakhlite secondary mineral assemblages, by 0.67 Ga pCO_2 was ~0.1 bar [6]. The 2300 mbar maximum atmospheric pressure during the Noachian is consistent with other estimates based on theoretical considerations of the pCO_2 necessary to produce enhanced surface temperatures and thus permit extensive fluvial activity [1,2].

Our calculations are based on carbonate abundances in an SNC meteorite. In reality this figure will vary considerably between different rocks on Mars. As this meteorite does not have a basaltic composition it is unlikely to be a major rock type within the uppermost crust of Mars. However, at least 8 SNC meteorites from 2 Mars localities contain carbonate therefore we believe it is reasonable to construct a model using them as a guide to crustal abundances.

Another way of calculating the original crustal and atmospheric inventory on Mars is to use the assumption that the terrestrial planets all had similar CO_2 outgassing histories in their early stages. If the outgassed CO_2 in the atmosphere of Earth had not been trapped by dissolution in the oceans and carbonate formation its surface atmospheric pressure would be about 70 bar [15]. The equivalent pressure on Mars is ~51 bar (taking Earth to have 3.6 times the surface area of Mars). If we assume 95% of this was lost on early Mars then ~2600 mbar would be atmosphere that remained, mainly being trapped as carbonate in Noachian crust. Thus we have a range of likely original CO_2 inventories from 45-51 bar and trapped CO_2 (mainly carbonate with atmosphere and ice) of 2300-2600 mbar.

Conclusions: 1. Using the abundances of carbonate in the Noachian martian meteorite ALH 84001 as a crustal average within the uppermost 7 km of the ancient highlands suggests that 2300 mbar pCO_2 could be trapped in this region.

2. Assuming the 2300 mbar was the residue left after atmospheric losses, the original Mars crustal and atmospheric inventory was approximately 45 bar pCO_2.

3. Alternatively, if Mars had a similar CO_2 inventory to Earth then there would have been 51 bar within the original Mars crust and atmosphere. If 95% of this was lost then 2600 mbar is the remaining pCO_2 that was trapped as carbonate in the ancient highlands with lesser amounts in near-surface ice or atmosphere.

4. By 670 Ma atmospheric pCO_2 had declined to approximately 50-100 mbar.

Table 1. Mars crustal and atmosphere CO_2 based on SNC meteorite carbonate abundances.

	Total Mars crust and atmosphere pCO_2 mbar	Atmosphere pCO_2 mbar
4.5- 3.8 Ga	45000 [1]	2300
0.67 Ga	2400 [2]	30-100 [3]
0 Ga	2230	0-30 [4]

pCO_2 calculated assuming area of Mars is 1.45 x 10^{14} m^2, gravitational constant 3.7 ms^{-2}, 1 vol. % $MgCO_3$ in crustal silicate (equivalent to 1 wt%), 56% of Mars surface (ancient highlands) underlain by layered rocks with 1 vol. % carbonate, crustal density 3 gcm^{-3}. The CO_2 within the total mass of carbonate in the top 7 km of crust in the ancient highlands is calculated as number of moles and then mass. This mass is then recalculated as a pressure over the entire surface of Mars. For an average crustal abundance of 1 vol% $MgCO_3$ and 7 km depth over the ancient highlands an equivalent pCO_2 of 2300 mbar is trapped.

[1] The total crustal inventory (i.e. carbonate, ice, atmosphere) based on assuming approximately 95% loss of CO_2 to space 4.5 to 3.8 Ga leaving the 2300 mbar atmosphere pCO_2 calculated here to be trapped within the crust as carbonate and up to 100 mbar pCO_2 within the atmosphere during the remainder of Mars history (i.e. 2300 mbar ÷ 0.05 = the 45 000 mbar inventory). [2] The 2400 mbar total inventory is the sum of 2300 mbar in [1] and 100 mbar atmospheric pCO_2 at 0.67 Ga [3]. [4] The variation of 0-30 mbar pCO_2 within the current epoch on Mars is the result of obliquity variations on an approximately million year cycle: high angles allowing more polar ice to be sublimed [16].

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