THE FIRST BILLION YEARS OF MARTIAN HISTORY AS SEEN FROM THE SNC METEORITES: A REVIEW. J.H. Jones, SR, NASA/JSC, Houston, TX 77058 (jjones2@ems.jsc.nasa.gov).

**Introduction:** There are currently 28 known, distinct samples of Mars that have been liberated from that planet by impacts and subsequently delivered to the Earth. The formation ages of these samples range from 4.5 b.y. to 180 m.y. Collectively, these samples are called SNC meteorites after the major petrologic subdivisions: Shergottite, Nakhlitite, Chassigny. Texturally, most of these meteorites are cumulates or partial cumulates. However, a few may represent real melt compositions: EET79001B, Y9800459, QUE94201, and the groundmass of EET79001A.

**Early Differentiation:** The whole-rock Rb-Sr isochron for the shergottites is indistinguishable from the age of the solar system ~4.5 b.y. Therefore, martian differentiation occurred very early. Because the Sm-Nd system contains two chronometers, it is possible to produce a concordia diagram, conceptually similar to that for the U-Pb system (i.e., the loci of points for which two chronometers both yield the same age). Several shergottites define a time of differentiation of 4.53 b.y. on this Sm-Nd concordia. Finally, both shergottites and nakhlites have $^{182}$W isotope anomalies from the decay of short-lived $^{182}$Hf which has a half-life of 9 m.y. Therefore, differentiation and fractionation of W and Hf must have occurred within the first 50 m.y. of martian history. Therefore, it is clear that Mars differentiated very early. Additionally, the source regions of the shergottites and nakhlites are so depleted in radioactive heat-producing elements that producing young (<1 b.y.) basalts becomes problematic.

**Style of Differentiation:** Early martian differentiation was thorough and pervasive. All the SNC meteorites are basaltic and all are believed to originate from depleted source regions. There are at least two types of martian mantle: the somewhat depleted nakhlite source region and the very depleted shergottite source region. One measure of depletion is the value of $^{143}$Nd, which gives the time integrated deviation of the source’s Sm/Nd ratio from chondritic (i.e., undifferentiated). Light REE (LREE) depleted source regions have positive $^{143}$Nd and LREE enriched sources have negative $^{143}$Nd. The nakhlite source has a present-day $^{143}$Nd of ~+20 and the shergottite source has a present-day $^{143}$Nd of ~+50. For comparison, the terrestrial depleted MORB mantle has an $^{143}$Nd of +10 to 12. Therefore, even the nakhlite mantle is either twice as depleted as the MORB mantle or has been similarly depleted for twice as long, the latter being more likely.

In addition, there are Nd and Hf isotopic similarities between SNC and mare basalt source regions. This seems to indicate that the early differentiation processes for the Moon and Mars were similar. It is widely thought that the Moon differentiated via a magma ocean. Therefore, if the Moon experienced a magma ocean, it is likely that Mars did as well.

**Core Formation:** The moment of inertia of Mars indicates that it has a metallic core and the SNC meteorites are depleted in siderophile elements. The $^{182}$W isotopic anomalies discussed above probably arise because W went into the core and consequently raised the Hf/W ratio of the martian mantle. Therefore, core formation must have occurred in the first 50 m.y. of martian history, before $^{182}$Hf became extinct.

**Atmospheric Evolution:** There are at least two reservoirs of martian noble gases, the atmosphere and the mantle. The atmosphere contains isotopically fractionated gases and the mantle contains unfractionated noble gases. Within the SNC suite, the atmosphere is best sampled by glassy shock melts in EET79001A (i.e., “Lithology C”) and the interior mantle gases are best represented by Chassigny. One process (hydrodynamic escape?) fractionated Xe isotopes and later loss processes, such as Jeans escape and interactions between the Mars atmosphere and the solar wind, fractionated the light noble gases. The exception to this rule is Kr, which was apparently quantitatively removed during the early Xe fractionation process but was too heavy to be influenced by Jeans escape or solar wind interactions. Thus, Kr in the Mars atmosphere is solar in composition, as is the Xe in Chassigny. Thus, the inference is that martian noble gases were initially solar in their isotopic compositions.

The story that Xe tells about Mars is complicated. The impressive similarity between the Xe isotopic compositions of terrestrial and martian air tempts one to conclude that this isotopic composition is a real solar system component and not the result of an indigenous fractionation process. However, the similarity between terrestrial and martian Xe is not exact and good arguments have been made against the component model.

Even so, there remain puzzling issues with the hydrodynamic escape model. One problem is that the amount of outgassing of Xe from the martian mantle
must be low enough that the isotopic fractionation signature of hydrodynamic escape is not overwhelmed. Some outgassing is permitted if the original degree of isotopic fractionation was larger than presently observed. And outgassing is required for the other noble gases. Possibly, the early differentiation events described above depleted the mantle of its Xe [i.e., Xe acted extremely incompatibly during these events]. However, Chassigny [the type locality of martian mantle Xe] is not particularly depleted in Xe, suggesting that there are still significant quantities of mantle Xe.

Other mass balancing acts are also required for Xe. For example, there is a large $^{129}$Xe anomaly from the decay of short-lived $^{129}$I (half-life 16 m.y.) but little or no signature of longer-lived $^{244}$Pu (half life 82 m.y.). Therefore, the amount of residual Xe + later outgassed Xe must be much greater than the amount of fissionigenic Xe from $^{244}$Pu.

Note, however, that some of these possible difficulties disappear if hydrodynamic escape occurs later. If Xe is isotopically fractionated after $^{129}$I and $^{244}$Pu are extinct, then we do not have to worry about Pu Xe, for example, swamping out the residual Xe in the atmosphere, assuming that this fissionigenic Xe has already been outgassed. However, this model is at odds with stellar evolution models if the sun is called ancient. Within the SNC data array the second reservoir (low $\delta^D$) is best approximated by the carbonate in ALH84001, which is ~4 b.y. in age. By inference, the hydrothermal alteration products in the nakhlites also contain a component from this low $\delta^D$ reservoir. The high $\delta^D$ reservoir is best approximated by high temperature releases from QUE94201, Zagami, and Shergotty. Shergotty and Zagami are thought to have assimilated significant amounts of martian crust during their petrogenesis, but QUE94201 shows no evidence of this. Therefore, how these meteorites obtained this volatile element signature is unknown. Possibly, the shergottite mantle has a different volatile element signature than the Chassigny-nakhlite mantle. Possibly this high $\delta^D$ reservoir contains water that was isotopically fractionated during the waning phase of hydrothermal escape.

Reservoirs of Water: There are two obvious reservoirs of water on Mars in terms of distinctive isotopic composition, the atmosphere and the mantle. The atmosphere we know about and it has a large positive D/H ratio ($\delta^D \sim +4500\%$). The mantle is another issue. I and others have argued that the martian mantle [and basalts from that mantle] are likely very dry. However, since Chassigny is the type locality for mantle Xe, it is of interest to see what, if any, water it contains. The answer is that Chassigny has about 350 ppm water and a $\delta^D$ of $-50\%$. What this means for the Chassigny mantle is difficult. If Chassigny is 90% anhydrous cumulate of a 5% partial melt, then the martian mantle contained about 175 ppm water. To better constrain this concentration, better models both for the petrogenesis of Chassigny and the siting of Chassigny water would be required.

However, it now seems likely that there are at least two other reservoirs of martian water, perhaps the dominant reservoirs. Unlike our experience with Xe, where we are conditioned to expect mixing between the atmospheric and mantle reservoirs, most SNC meteorites show a mixing pattern that is nearly orthogonal to an atmospheric-mantle trend. On a $\delta^D$ vs. $\delta^{13}$C diagram, nakhlites and shergottites define a mixing line from a high $\delta^D$ ($\sim +1500\%$) – low $\delta^{13}$C ($\sim -30\%$) reservoir to a low $\delta^D$ ($\sim 0\%$) – high $\delta^{13}$C ($\sim +50\%$) reservoir. The physical nature of these reservoirs is unknown. However, they appear to be ancient. Within the SNC data array the second reservoir (low $\delta^D$) is best approximated by the carbonate in ALH84001, which is ~4 b.y. in age. By inference, the hydrothermal alteration products in the nakhlites also contain a component from this low $\delta^D$ reservoir. The high $\delta^D$ reservoir is best approximated by high temperature releases from QUE94201, Zagami, and Shergotty. Shergotty and Zagami are thought to have assimilated significant amounts of martian crust during their petrogenesis, but QUE94201 shows no evidence of this. Therefore, how these meteorites obtained this volatile element signature is unknown. Possibly, the shergottite mantle has a different volatile element signature than the Chassigny-nakhlite mantle. Possibly this high $\delta^D$ reservoir contains water that was isotopically fractionated during the waning phase of hydrothermal escape.

In my view it is most likely that both of these reservoirs have interacted with the martian atmosphere. Unless Mars received its volatiles from a source very different from that of the Earth, the large $\delta^D$ of $\sim +1500\%$ is otherwise hard to understand. Similarly, the high $\delta^{13}$C of $\sim +50\%$ of the second reservoir is very much like that inferred for atmospheric CO$_2$. The alteration products in the nakhlites and the hydrothermally deposited carbonate in ALH84001 make it likely that the low $\delta^D$ reservoir is water rich. Thus, interactions between it and the atmosphere could have affected $\delta^{13}$C without affecting $\delta^D$. For the high $\delta^D$ reservoir, if martian magmas are typically dry, then it might be easier to reset $\delta^D$ than $\delta^{13}$C. To better address these issues it would be useful to have $\delta^{13}$C, $\delta^D$, and noble gases measured on the same temperature releases.