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Outgassed Water on Mars: Constraints from Melt Inclusions in SNC Meteorites

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The SNC (shergottite-nakhlite-chassignite) meteorites, thought to be igneous rocks from Mars, contain melt inclusions trapped at depth in early-formed crystals. Determination of the pre-eruptive water contents of SNC parental magmas from calculations of the solidification histories of these amphibole-bearing inclusions indicates that martian magmas commonly contained 1.4 percent water by weight. When combined with an estimate of the volume of igneous materials on Mars, this information suggests that the total amount of water outgassed since 3.9 billion years ago corresponds to global depths on the order of 200 meters. This value is significantly higher than previous geochemical estimates but lower than estimates based on erosion by floods. These results imply a wetter Mars interior than has been previously thought and support suggestions of significant outgassing before formation of a stable crust or heterogeneous accretion of a veneer of cometary matter.

Torrents of running water have scoured the ancient, heavily cratered crust of Mars to produce valley networks, and a variety of more recent features (softened terrain, pedestal craters, patterned ground) testify to the presence of subsurface water or ice (*1*). Under present atmospheric conditions, however, liquid water is unstable everywhere on the planet's surface, water ice is stable on the surface only at the poles, and only minute amounts of water vapor are present in the martian atmosphere. Although ice at the polar caps may be equivalent to a global average water depth of perhaps 20 m (*2*), most of the planet's water is probably hidden from view as permafrost or ground water. As much as 1000 m of globally distributed water could be stored within the upper 10 km of the crust (*3*). Because most of the water on Mars cannot be imaged by spacecraft, it is difficult to quantify the amount of water that has been outgassed.

One estimate of outgassed water, extrapolated from the amount of erosion caused by a large flood in the Chryse basin, corresponds to global depths of >440 m (*2*). This is a minimum estimate, because it was assumed that water carried its maximum sediment load. Even larger amounts of water are required by the proposed former existence of martian seas (*4*). (For comparison, Earth has outgassed enough water to cover its surface uniformily to a depth of 2700 m.)

A contrary view is provided by measurements of the total volume of igneous materials on Mars, which are the source of its outgassed water. A recent estimate, based on the assumption that martian magmas have water contents similar to those of typical terrestrial basaltic magmas (1% by weight), corresponds to a global water depth of 150 m (*5*).

Other, independent estimates are based on the composition of the martian atmosphere. Atmospheric hydrogen, nitrogen, and argon isotopic abundances suggest that the amounts of outgassed water were limited, corresponding to global depths of 3.6, 8 to 133, and 6 to 10 m, respectively (*6*). Atmospheric carbon and oxygen isotopic compositions are consistent with an outgassed water depth of perhaps 50 to 60 m (*7*). These values, however, rest on questionable assumptions that impact erosion of the atmosphere has been negligible, that ratios of noble to other gases were uniform among the terrestrial planets and remained unchanged during hydrodynamic escape, that escape rates for CO_2 and H_2O over time are adequately estimated, that climatic conditions in the past were similar to those of the present, and other complications (*8*).

The SNC meteorites are believed to be martian igneous rocks ejected during large impacts (*9*). Another estimate for the amount of outgassed water is based on a model for the bulk composition of the SNC meteorite parent body formulated from element ratios in the meteorites. Calculations of the original volatile inventory of this parent body suggest that it was significantly enriched in volatile elements and water relative to Earth, but the model assumes that most of its water was lost through reaction with metallic iron during core formation early in the planet's history (*10*). The water content of the martian mantle, calculated from ratios of the abundance of water to the abundances of other volatile species in bulk SNC meteorites and its solubility in magmas, is only 36 ppm (*11*). If all of this water were outgassed, it would form a global ocean 130 m deep. However, more reasonable degrees of outgassing imply that the amount of water was smaller, perhaps 10 to 20 m. This estimate depends critically on the assumption of homogeneous accretion by which Mars lost its original water through planet-wide equilibration, an accretion model different from that advocated for Earth.

These conflicting estimates for martian outgassed water can be reconciled in several ways: The measured volume of igneous materials presumably represents volcanic activity since 3.9 billion years ago, the time at which stable crust began to form. Any magmatism and outgassing before that time left no rock record, so this represents a minimum estimate. The addition of non-outgassed water through late accretion of a veneer of cometary material (*12*) could also explain the discrepancy between estimates based on igneous materials and those based on erosion by floods. The SNC parent body model can be reconciled with other water estimates if the need for homogeneous accretion is relaxed, so that not all water is lost through reaction with metallic iron. The lower atmospheric estimates can be understood if Mars lost part of its early atmosphere by impact erosion or hydrodynamic escape.

The estimate of martian outgassing based on the volume of volcanic materials represents a critical lower limit for the planet's water inventory, one that can be quantified further by a consideration of

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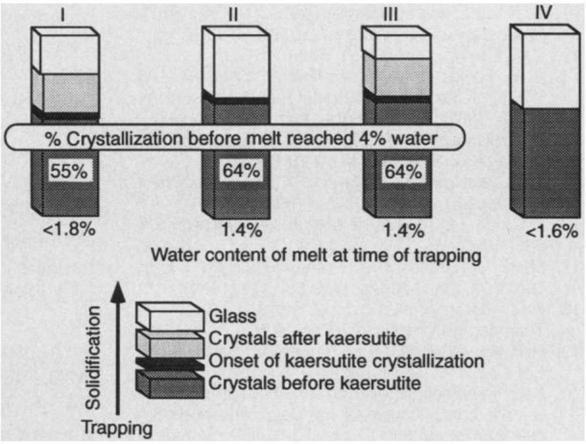

Fig. 1. Representative calculations of the solidification histories of trapped melt inclusions in four SNC meteorites; bar I, Shergotty (*23*); bar II, Governador Valadares (*19*); bar III, Chassigny (*17*); and bar IV, LEW88516 (*21*). The bars can be visualized as time lines, as indicated in the key at the bottom of the figure. The amount of crystallization before the onset of kaersutite crystallization (requiring 4% water) is indicated on each bar, and the corresponding as-trapped water content is shown below each bar. Inclusions in Shergotty (which crystallized an indeterminate amount of host pigeonite) and LEW88516 (which contain no amphibole) provide only upper limits.

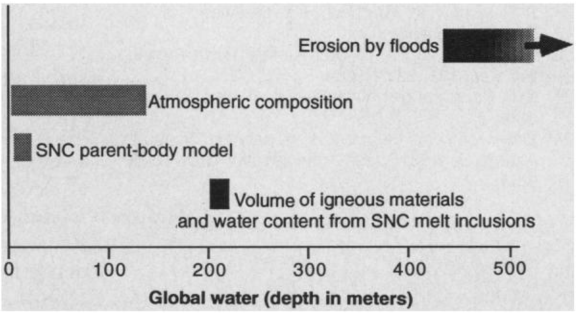

Fig. 2. Comparison of the amounts of martian outgassed water, based on various geological observations and geochemical measurements and models, with our results if magmas delivered 1.4% water to the surface.

SNC meteorites. The water contents of these meteorites, measured after precombustion to remove terrestrial contaminants, are small, in the range of 130 to 350 ppm (*13, 14*). But, because magmas emplaced on or near the martian surface are subject to vesiculation during ascent (because of low internal pressures on Mars) and desiccation by the dry atmosphere, bulk rock measurements probably cannot be used to infer valid estimates of magmatic water actually delivered to the surface. A further complication is that the oxygen isotopic composition of water released at high temperature from SNC meteorites suggests that some fraction of the water they contain is not magmatic (*14*) but may have been derived through later alteration by water already in the crust.

What is needed is an estimate of the water contents of SNC magmas before near-surface dehydration or contamination by crustal water. We therefore estimated the water contents of parental magmas for different SNC meteorites from the properties of melt inclusions. These inclusions were trapped in the cores of the earliest minerals to crystallize (*15*) at depth, and the minerals were then carried upward in magmas that solidified on or near the surface. Dissolved water within melt pockets in growing crystals was unlikely to have been affected by crystal boundary effects because of its high diffusivity in magma, and diffusive exchange between trapped and external water would have been sluggish in olivine and pyroxene host crystals (*16*).

Many of the inclusions contain daughter crystals of amphibole (kaersutite), a phase that does not appear in these meteorites outside of the inclusions. Phase equilibria for kaersutite (*17*) indicate that it is stable only at pressures above 1.5 kbar, corresponding to a depth on Mars of 11 km. Magma trapped at such a depth is unlikely to have experienced significant vesiculation or interaction with crustal water. Kaersutite in the inclusions is a hydrous amphibole, as confirmed by measurements of a significant hydrogen component and only minor halogen abundances (*18*). Kaersutite becomes a stable phase only when the water contents of inclusion melts reach approximately 4% by weight (*17*). From the extent of inclusion solidification before the onset of kaersutite crystallization, we can calculate the amount of water in each melt inclusion at the time of trapping.

We approximated the solidification histories of amphibole-bearing melt inclusions in four SNC meteorites using linear regression methods to solve a system of mass-balance equations, as described in (*19*) (Fig. 1). Plating of additional host mineral on the walls of the inclusion, as well as crystallization of daughter minerals within the inclusion, progressively increases the water content of the trapped melt until kaersutite forms. In the case of Shergotty and Chassigny, additional crystallization occurred after the onset of kaersutite crystallization. The Shergotty calculation provides only an upper limit to the water content in the trapped liquid, but 1.4% is a plausible value for this magma (*20*). Kaersutite has not been found in LEW88516 inclusions (*21*), so the calculation for this inclusion likewise indicates only an upper limit. As shown in Fig. 1, SNC magmas had approximately 1.4% water by weight at the time that inclusions were trapped, which would allow the melts to reach the required 4% water contents after 50 to 75% crystallization as closed systems.

Applying an average value of 1.4% water to estimates of the total volume of martian igneous materials (*5*), we can adjust the estimate of martian outgassed water upward to global depths of 210 m. Of course, this calculation depends critically on the assumptions that these SNC magmas are representative of Mars volcanism and that intrusions in the subsurface have outgassed. The almost complete dehydration of the nakhlites and Chassigny, which are unlikely to have been surficial flows (*9*), supports the latter assumption. This amount of water remains less than estimates from erosion by floods (Fig. 2), but it does provide a refined lower limit for martian water outgassed since 3.9 billion years ago.

Speculating about the water content of the SNC magma source region, that is, the martian mantle, is difficult, because we do not know the degree of melting of this source, nor do we know how much fractionation of primary magmas may have occurred en route to the surface. However, as noted by Johnson *et al.* (*17*), the 36 ppm of water estimated for the martian mantle (*11*) seems rather low, because it would imply that the degree of melting (0.2%) was implausibly small (if no fractionation occurred and water is perfectly incompatible). For a more reasonable 10% melting with no subsequent fractionation, a magma with 1.4% water would require a source region containing 1400 ppm water. This value is undoubtedly too high because SNC meteorites formed from fractionated magmas (*9*), but it does suggest that the interior of Mars is wetter than has been inferred from past geochemical models and is perhaps similar to the terrestrial mantle [thought to contain 150 to 350 ppm water (*22*)]. This conclusion is not surprising in light of the enrichment of other volatiles in Mars (*11*), but it may require incomplete reaction with iron during core formation. If only 20% of the original accreted water remained unreduced, the water content of the martian mantle would correspond to the abundances in the terrestrial mantle.

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Structural Relationship of Bacterial RecA Proteins to Recombination Proteins from Bacteriophage T4 and Yeast

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RecA protein is essential in eubacteria for homologous recombination and promotes the homologous pairing and strand exchange of DNA molecules in vitro. Recombination proteins with weak sequence similarity to bacterial RecA proteins have been identified in bacteriophage T4, yeast, and other higher organisms. Analysis of the primary sequence relationships of DMC1 from *Saccharomyces cerevisiae* and UvsX of T4 relative to the three-dimensional structure of RecA from *Escherichia coli* suggests that both proteins are structural homologs of bacterial RecA proteins. This analysis argues that proteins in this group are members of a single family that diverged from a common ancestor that existed prior to the divergence of prokaryotes and eukaryotes.

RecA protein plays a central role in recombination and DNA repair in prokaryotes. RecA forms a nucleoprotein filament and catalyzes adenosine 5′-triphosphate (ATP)–dependent recognition, pairing, and exchange of strands between two homologous DNA molecules (*1–4*). Bacterial RecA proteins are all closely related (56 to 100% sequence identity) (*2*). Bacteriophage T4 UvsX protein is more distantly related to the bacterial proteins ($\sim$20% amino acid identity) (*2, 5*) and has in vitro activities similar but not identical to those of RecA (*6–8*). In the yeast *S. cerevisiae*, three RecA-related proteins have been identified: DMC1, RAD51, and RAD57 (*9–11*). DMC1 has a meiosis-specific function required for meiotic recombination, synaptonemal complex formation, and progress through the meiotic divisions (*9*). The recombination role may be primary, and *dmc1* mutants accumulate recombination intermediates (double-stranded ends with 3′ single-stranded tails) compatible with a defect in strand invasion or exchange (*9*). RAD51 and RAD57 are required both for mitotic repair of DNA double-strand breaks and for full levels of meiotic recombination (*10, 11*). RAD51 and DMC1 are closely related to one another ($\sim$45% identity), have less similarity with prokaryotic RecA proteins ($\sim$20 to 30% identity), and are even less similar to T4 UvsX (*9, 11*). RAD57 also shows significant sequence similarity to RAD51 and RecA proteins (*12*). Very recently, *RAD51*-like genes have been identified in a number of higher organisms (*13, 14, 15*) and a *DMC1*-like gene has been identified in lily (*16*).

Although the primary sequence relationships among these proteins are suggestive, we have sought further evidence of an overall structural relationship among them by comparing the primary sequences of bacterial RecAs, yeast DMC1, and T4 UvsX with reference to the crystal structure of *E. coli* RecA protein (*17, 18*). One type of evidence for overall structural similarity among DMC1, UvsX, and RecA proteins is provided by mapping the primary sequences of the yeast and T4 proteins onto the tertiary structure of RecA. For DMC1, the primary sequence alignment used for this analysis was that derived previously in the absence of structural information (*9*) with a few minor modifications (Fig. 1). The DMC1-RecA comparison reveals several features that are compatible with an overall similarity in tertiary structure. (i) All of the small insertions and deletions present in the primary sequence alignment occur in surface loops or at the ends of α-helices (Fig. 2A). (ii) Larger insertions and deletions occur at the NH$_2$- and COOH-termini (Figs. 1 and 2A). DMC1 lacks the COOH-terminal portion of RecA protein and has 32 additional NH$_2$-terminal residues. In RecA protein, each of these regions represents a structural domain that protrudes away from the body of the protein in both the monomer and polymer (*17*). A proteolytic fragment of RecA protein lacking much of the COOH-terminal domain is proficient in strand exchange (*19*), and this domain may not be essential for homologous pairing and strand exchange but may instead be involved in the regulation of DNA binding and the SOS response in *E. coli* (*17, 20*). (iii) Charged residues occur on the surface of the protein, whereas hydrophobic residues occur mainly in the interior (Fig. 2B).

Similar conclusions pertain to UvsX. A published alignment of UvsX with RecA (*2*) showed the same general features as the

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