Science Advances NAAAS

Supplementary Materials for

A heterogeneous mantle and crustal structure formed during the early differentiation of Mars

James M. D. Day *et al.*

Corresponding author: James M. D. Day, jmdday@ucsd.edu

Sci. Adv. **10**, eadn9830 (2024) DOI: 10.1126/sciadv.adn9830

The PDF file includes:

Information on modeling in Figure 1 Figs. S1 to S3 Legends for tables S1 to S5 References

Other Supplementary Material for this manuscript includes the following:

Tables S1 to S5

Tables S4 and *S5* represent compilations of available literature data for HSE abundances and Os isotopes, and S isotopes, respectively.

Modelling in Figure 1

Shown are two crystallization models. For modelling, it was assumed fractionation was driven by crystallization of olivine. Two sets of bulk partition coefficients were applied to the models: solely olivine crystallization (pyroxene partition coefficients are similar to or lower than olivine) and mixtures of olivine, Cr-spinel and sulfide crystallization. Even at an extreme of 10% olivine fractionation, HSE compositions cannot be explained by crystallization of this phase alone. Better fits come from mineral assemblages where a maximum of 10% olivine (\pm clinopyroxene) is fractionally crystallized with proportions of 0.98 olivine, 0.019 Cr-spinel and 0.001 sulfide. The HSE support crystallization of an olivine (\pm clinopyroxene)-dominated assemblage, but with minor spinel and sulfide co-crystallization.

Model 1 assumes melting from a depleted martian mantle (lithosphere) source, followed by fractional crystallization, and shows the results for 0-10% olivine crystallization with cocrystallization of Cr-spinel and sulfide, in the proportions 0.98-0.94 olivine, 0.02-0.06 Cr-spinel, with <0.001 sulfide, using the partition coefficients compiled in Table 4 of *(26)*. Model 2 shows continued fractional crystallization after removal of a dunite cumulate component in the same mineral proportions. Model 1 reproduces chassignite compositions reasonably well. Model 2 does not reproduce the Pd in nakhlites as well, but model fits are strongly affected by the partition coefficients, which are empirical estimates from terrestrial, not martian magmas. Consequently, *f*O2 and other intensive parameters for the magmas are likely to be important *(38)*. Martian mantle normalization is from *(32)*.

Fig. S1

Total alkali versus silica diagram for martian meteorites. Data for nakhlites, chassignites and ALH 84001 are presented in *Table S2*, or can be found in *(16)*. NWA 7034 data from *(19)* and Mars Exploration Rover (MER) field from *(4)*.

Fig. S2

Plots of MgO versus Cr for (a) chassignites, nakhlites and ALH 84001 and (b) only for nakhlites. Chassignites have MgO and Cr compositions consistent with accumulation of olivine and spinel. ALH 84001 is less MgO-rich, consistent with being an orthopyroxenite. Nakhlites are cumulative rocks containing augite and are broadly basaltic (*Fig. S1*), but their Mg-Cr systematics can be modelled by removal of olivine/clinopyroxene and spinel. Partition coefficients for modelling are from *(49)*.

Fig. S3

Incompatible trace element (ITE) diagrams normalized to (a) CI chondrite and (b) double normalized to CI chondrite and then Sm. The similarity of ITE patterns for nakhlites and chassignites are clear in (b), whereas ALH 84001 is more similar in composition to shergottites. Data for nakhlites, chassignites and ALH 84001 are presented in *Table S2*, or can be found in *(16)*.

Table S1: Highly siderophile element abundances (in ng/g) and ¹⁸⁷Re-¹⁸⁷Os for nakhlites, chassignites and ALHA 84001.

Table S2: Bulk rock major- and trace-element abundance data for nakhlites, chassignites and ALH 84001.

Table S3: Blank contributions to samples analyzed in this study.

Table S4: Highly siderophile element abundances (in ng/g) and ¹⁸⁷Re-¹⁸⁷Os for nakhlites, chassignites and ALHA 84001, including published data, shown in *italics*.

Table S5: Osmium isotopes and S isotopes for nakhlites, chassignites and ALHA 84001.

REFERENCES AND NOTES

- 1. H. Y. McSween Jr., Petrology on Mars. *Am. Mineral.* **100**, 2380–2395 (2015).
- 2. T. J. Lapen, M. Righter, A. D. Brandon, V. Debaille, B. L. Beard, J. T. Shafer, A. H. Peslier, A younger age for ALH84001 and its geochemical link to shergottite sources in Mars. *Science* **328**, 347–351 (2010).
- 3. L. C. Bouvier, M. M. Costa, J. N. Connelly, N. K. Jensen, D. Wielandt, M. Storey, A. A. Nemchin, M. J. Whitehouse, J. F. Snape, J. J. Bellucci, Evidence for extremely rapid magma ocean crystallization and crust formation on Mars. *Nature* **558**, 586–589 (2018).
- 4. A. Udry, G. H. Howarth, C. D. K. Herd, J. M. D. Day, T. Lapen, J. Filiberto, What martian meteorites reveal about the interior and surface of Mars. *J. Geophys. Res. Planets* **125**, e2020JE006523 (2020).
- 5. N. Dauphas, A. Pourmand, Hf–W–Th evidence for rapid growth of Mars and its status as a planetary embryo. *Nature* **473**, 489–492 (2011).
- 6. V. Debaille, A. D. Brandon, Q. Z. Yin, B. Jacobsen, Coupled $^{142}Nd-^{143}Nd$ evidence for a protracted magma ocean in Mars. *Nature* **450**, 525–528 (2007).
- 7. Z. Deng, F. Moynier, J. Villeneuve, N. K. Jensen, D. Liu, P. Cartigny, T. Mikouchi, J. Siebert, A. Agranier, M. Chaussidon, M. Bizzarro, Early oxidation of the martian crust triggered by impacts. *Sci. Adv.* **6**, eabc4941 (2020).
- 8. J. W. Valley, J. M. Eiler, C. M. Graham, E. K. Gibson, C. S. Romanek, E. M. Stolper, Lowtemperature carbonate concretions in the Martian meteorite ALH84001: Evidence from stable isotopes and mineralogy. *Science* **275**, 1633–1638 (1997).
- 9. H. B. Franz, S.-T. Kim, J. Farquhar, J. M. D. Day, R. C. Economos, K. D. McKeegan, A. K. Schmitt, A. J. Irving, J. Hoek, J. Dottin, isotopic links between atmospheric chemistry and the deep sulphur cycle on Mars. *Nature* **508**, 364–368 (2014).
- 10. J. J. Barnes, F. M. McCubbin, A. R. Santos, J. M. D. Day, J. W. Boyce, S. P. Schwenzer, U. Ott, I. A. Franchi, S. Messenger, M. Anand, C. B. Agee, Multiple early-formed water reservoirs in the interior of Mars. *Nat. Geosci.* **13**, 260–264 (2020).
- 11. D. S. McKay, E. K. Gibson Jr., K. L. Thomas-Keprta, H. Vali, C. S. Romanek, S. J. Clemett, X. D. Chillier, C. R. Maechling, R. N. Zare, Search for past life on Mars: Possible relic biogenic activity in Martian meteorite ALH84001. *Science* **273**, 924–930 (1996).
- 12. A. H. Treiman, The nakhlite meteorites: Augite-rich igneous rocks from Mars. *Geochemistry* **65**, 203–270 (2005).
- 13. R. J. Floran, M. Prinz, P. F. Hlava, K. Keil, C. E. Nehru, J. R. Hinthorne, The Chassigny meteorite: A cumulate dunite with hydrous amphibole-bearing melt inclusions. *Geochim. Cosmochim. Acta* **42**, 1213–1229 (1978).
- 14. A. Udry, J. M. D. Day, 1.34 billion-year-old magmatism on Mars evaluated from the co-genetic nakhlite and chassignite meteorites. *Geochim. Cosmochim. Acta* **238**, 292–315 (2018).
- 15. B. E. Cohen, D. F. Mark, W. S. Cassata, M. R. Lee, T. Tomkinson, C. L. Smith, Taking the pulse of Mars via dating of a plume-fed volcano. *Nat. Commun.* **8**, 640 (2017).
- 16. J. M. D. Day, K. T. Tait, A. Udry, F. Moynier, Y. Liu, C. R. Neal, Martian magmatism from plume metasomatized mantle. *Nat. Commun.* **9**, 4799 (2018).
- 17. M. Wadhwa, G. Crozaz, Trace and minor elements in minerals of nakhlites and Chassigny: Clues to their petrogenesis. *Geochim. Cosmochim. Acta* **59**, 3629–3645 (1995).
- 18. A. H. Treiman, A petrographic history of Martian meteorite ALH84001: Two shocks and an ancient age. *Meteoritics* **30**, 294–302 (1995).
- 19. C. B. Agee, N. V. Wilson, F. M. McCubbin, K. Ziegler, V. J. Polyak, Z. D. Sharp, Y. Asmerom, M. H. Nunn, R. Shaheen, M. H. Thiemens, A. Steele, Unique meteorite from early Amazonian Mars: Water-rich basaltic breccia Northwest Africa 7034. *Science* **339**, 780–785 (2013).
- 20. A. D. Brandon, R. J. Walker, J. W. Morgan, G. G. Goles, Re-Os isotopic evidence for early differentiation of the Martian mantle. *Geochim. Cosmochim. Acta* **64**, 4083–4095 (2000).
- 21. J. H. Jones, C. R. Neal, J. C. Ely, Signatures of the highly siderophile elements in the SNC meteorites and Mars: A review and petrologic synthesis. *Chem. Geol.* **196**, 5–25 (2003).
- 22. C. W. Dale, K. W. Burton, R. C. Greenwood, A. Gannoun, J. Wade, B. J. Wood, D. G. Pearson, Late accretion on the earliest planetesimals revealed by the highly siderophile elements. *Science* **336**, 72–75 (2012).
- 23. N. Mari, A. J. V. Riches, L. J. Hallis, Y. Marrocchi, J. Villeneuve, P. Gleissner, H. Becker, M. R. Lee, Syneruptive incorporation of martian surface sulphur in the nakhlite lava flows revealed by S and Os isotopes and highly siderophile elements: Implication for mantle sources in Mars. *Geochim. Cosmochim. Acta* **266**, 416–434 (2019).
- 24. S. Goderis, A. D. Brandon, B. Mayer, M. Humayun, Ancient impactor components preserved and reworked in martian regolith breccia Northwest Africa 7034. *Geochim. Cosmochim. Acta* **191**, 203–215 (2016).
- 25. S. R. Ramsey, A. M. Ostwald, A. Udry, E. O'Neal, J. M. D. Day, Z. Wilbur, J. J. Barnes, S. Griffin, Northwest africa 13669, a re-equilibrated nakhlite from a previously unsampled portion of the nakhlite igneous complex. *Meteorit. Planet. Sci.* **59**, 134–170 (2024).
- 26. J. M. D. Day, Hotspot volcanism and highly siderophile elements. *Chem. Geol.* **341**, 50–74 (2013).
- 27. B. J. Peters, J. M. D. Day, L. A. Taylor, Early mantle heterogeneities in the Réunion hotspot source inferred from highly siderophile elements in cumulate xenoliths. *Earth Planet. Sci. Lett.* **448**, 150–160 (2016).
- 28. J. M. D. Day, R. J. Walker, O. B. James, I. S. Puchtel, Osmium isotope and highly siderophile element systematics of the lunar crust. *Earth Planet. Sci. Lett.* **289**, 595–605 (2010).
- 29. J. M. D. Day, A. D. Brandon, R. J. Walker, Highly siderophile elements in Earth, Mars, the Moon, and asteroids. *Rev. Mineral. Geochem.* **81**, 161–238 (2016).
- 30. F. M. McCubbin, S. M. Elardo, C. K. Shearer Jr., A. Smirnov, E. H. Hauri, D. S. Draper, A petrogenetic model for the comagmatic origin of chassignites and nakhlites: Inferences from chlorine-rich minerals, petrology, and geochemistry. *Meteorit. Planet. Sci.* **48**, 819–853 (2013).
- 31. M. Humayun, S. Yang, A. J. Irving, R. H. Hewins, B. Zanda, K. Righter, A. H. Peslier, "Tin abundances require that chassignites originated from multiple magmatic bodies distinct from nakhlites" in *Lunar and Planetary Science Conference* (No. JSC-E-DAA-TN77055, NASA, 2020).
- 32. K. T. Tait, J. M. D. Day, Chondritic late accretion to Mars and the nature of shergottite reservoirs. *Earth Planet. Sci. Lett.* **494**, 99–108 (2018).
- 33. J. Filiberto, Experimental constraints on the parental liquid of the Chassigny meteorite: A possible link between the Chassigny meteorite and a Martian Gusev basalt. *Geochim. Cosmochim. Acta* **72**, 690–701 (2008).
- 34. R. P. Harvey, H. Y. McSween Jr., Petrogenesis of the nakhlite meteorites: Evidence from cumulate mineral zoning. *Geochim. Cosmochim. Acta* **56**, 1655–1663 (1992).
- 35. K. R. Stockstill, H. Y. McSween Jr., R. J. Bodnar, Melt inclusions in augite of the Nakhla Martian meteorite: Evidence for basaltic parental melt. *Meteorit. Planet. Sci.* **40**, 377–396 (2005).
- 36. V. Sautter, M. J. Toplis, J. P. Lorand, M. Macri, Melt inclusions in augite from the nakhlite meteorites: A reassessment of nakhlite parental melt and implications for petrogenesis. *Meteorit. Planet. Sci.* **47**, 330–344 (2012).
- 37. J. M. Brenan, N. R. Bennett, Z. Zajacz, Experimental results on fractionation of the highly siderophile elements (HSE) at variable pressures and temperatures during planetary and magmatic differentiation. *Rev. Mineral. Geochem.* **81**, 1–87 (2016).
- 38. M. Paquet, J. M. D. Day, A. Udry, R. Hattingh, B. Kumler, R. R. Rahbi, K. T. Tait, C. R. Neal, highly siderophile elements in shergottite sulfides and the sulfur content of the martian mantle. *Geochim. Cosmochim. Acta* **293**, 379–398 (2021).
- 39. J. Farquhar, S. T. Kim, A. Masterson, Implications from sulfur isotopes of the Nakhla meteorite for the origin of sulfate on Mars. *Earth Planet. Sci. Lett.* **264**, 1–8 (2007).
- 40. J. W. Dottin, J. Labidi, J. Farquhar, P. Piccoli, M. C. Liu, K. D. McKeegan, Evidence for oxidation at the base of the nakhlite pile by reduction of sulfate salts at the time of lava emplacement. *Geochim. Cosmochim. Acta* **239**, 186–197 (2018).
- 41. J. M. D. Day, L. A. Taylor, C. Floss, H. Y. McSween Jr., Petrology and chemistry of MIL 03346 and its significance in understanding the petrogenesis of nakhlites on Mars. *Meteorit. Planet. Sci.* **41**, 581–606 (2006).
- 42. A. Udry, H. Y. McSween Jr., P. Lecumberri-Sanchez, R. J. Bodnar, Paired nakhlites MIL 090030, 090032, 090136, and 03346: Insights into the Miller Range parent meteorite. *Meteorit. Planet. Sci.* **47**, 1575–1589 (2012).
- 43. A. D. Brandon, I. S. Puchtel, R. J. Walker, J. M. D. Day, A. J. Irving, L. A. Taylor, Evolution of the martian mantle inferred from the 187 Re- 187 Os isotope and highly siderophile element abundance systematics of shergottite meteorites. *Geochim. Cosmochim. Acta* **76**, 206–235 (2012).
- 44. C. D. Herd, E. L. Walton, C. B. Agee, N. Muttik, K. Ziegler, C. K. Shearer, A. S. Bell, A. R. Santos, P. V. Burger, J. I. Simon, M. J. Tappa, The Northwest Africa 8159 martian meteorite: Expanding the martian sample suite to the early Amazonian. *Geochim. Cosmochim. Acta* **218**, 1– 26 (2017).
- 45. T. J. Lapen, M. Righter, R. Andreasen, A. J. Irving, A. M. Satkoski, B. L. Beard, K. Nishiizumi, A. T. Jull, M. W. Caffee, Two billion years of magmatism recorded from a single Mars meteorite ejection site. *Sci. Adv.* **3**, e1600922 (2017).
- 46. J. A. Barrat, P. La Bachèlery, La Réunion Island dunites as analogs of the Martian chassignites: Tracking trapped melts with incompatible trace elements. *Lithos* **344–345**, 452–463 (2019).
- 47. J. M. D. Day, C. L. Waters, B. F. Schaefer, R. J. Walker, S. Turner, Use of hydrofluoric acid desilicification in the determination of highly siderophile element abundances and Re-Pt-Os isotope systematics in mafic-ultramafic rocks. *Geostand. Geoanal. Res.* **40**, 49–65 (2016).
- 48. J. M. D. Day, K. L. Nutt, B. Mendenhall, B. J. Peters, Temporally variable crustal contributions to primitive mantle-derived Columbia River Basalt Group magmas. *Chem. Geol.* **572**, 120197 (2021).
- 49. A. E. Ringwood, Special papers-apollo 11 symposium: Petrogenesis of apollo 11 basalts and implications for lunar origin. *J. Geophys. Res.* **75**, 6453–6479 (1970).
- 50. S. B. Shirey, R. J. Walker, The Re-OsISOTOPE system in cosmochemistry and hightemperature geochemistry. *Annu. Rev. Earth Planet. Sci.* **26**, 423–500 (1998).
- 51. J. P. Greenwood, L. R. Riciputi, H. Y. McSween Jr., L. A. Taylor, Modified sulfur isotopic compositions of sulfides in the nakhlites and Chassigny. *Geochim. Cosmochim. Acta* **64**, 1121– 1131 (2000).