

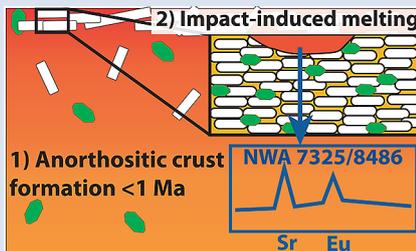
Evidence for anorthositic crust formed on an inner solar system planetesimal

P. Frossard^{1*}, M. Boyet¹, A. Bouvier^{2,3}, T. Hammouda¹, J. Monteux¹



doi: 10.7185/geochemlet.1921

Abstract



During the first million years of solar system history, planetesimals experienced extensive melting powered by the radioactive decay of ^{26}Al (Lee *et al.*, 1977). To date, the only known anorthositic crust on a solar system body is that of the Moon, formed by plagioclase flotation on top of the magma ocean (Wood *et al.*, 1970). Here we show evidence from the ungrouped achondrite meteorite Northwest Africa (NWA) 8486 that an anorthositic crust formed on a planetesimal very early in solar system history (<1.7 Ma). NWA 8486 displays the highest anomalies in Eu and Sr found in achondrites so far and, for the first time, this characteristic is also identified in clinopyroxene. Elemental modelling, together with calculated timescales for crystal settling, show that only

the melting of an anorthosite can produce NWA 8486 within the first 5 million years of solar system history. Our results indicate that such a differentiation scenario was achievable over short timescales within the inner solar system, and must have contributed to the making and elemental budget of the terrestrial planets.

Received 18 March 2019 | Accepted 14 August 2019 | Published 7 October 2019

Introduction

Over 80 ungrouped achondrites have been found in the past 20 years, enriching our collections with new types of meteoritic samples. Northwest Africa (NWA) 8486 is one of several paired stones, along with the ungrouped achondrites NWA 7325 and 8014, that have been found in the Sahara desert (Ruzicka *et al.*, 2017). They are plagioclase-rich cumulative gabbros that experienced remelting and fast cooling (Yang *et al.*, 2019), with a very peculiar calcic and magnesian mineralogy. NWA 8486 formed under reduced conditions, with an oxygen fugacity ($f\text{O}_2$) of 3.2 log units below the iron-wüstite (IW) buffer (Sutton *et al.*, 2017), and therefore likely originates from the inner solar system. Based on Cr, Ti and O isotopic compositions, NWA 7325/8486 have affinities with both acapulcoite-lodranite and ureilite groups (Barrat *et al.*, 2015; Weber *et al.*, 2016; Goodrich *et al.*, 2017). The Pb-Pb isochron age of 4563.4 ± 2.6 Ma, Al-Mg age of 4563.09 ± 0.26 Ma and initial Mg isotopic composition for NWA 7325 indicate that the parent material of this meteorite had to be formed within 1-2 Myr after Solar System formation (Koefoed *et al.*, 2016).

Eu and Sr Anomalies in NWA 7325/8486

We investigated major and trace element composition of NWA 8486 through *in situ* and in solution analyses. The mineral compositions of NWA 8486 are consistent with those of NWA

7325 (Barrat *et al.*, 2015; Weber *et al.*, 2016; Goodrich *et al.*, 2017), with $\text{An}_{88.7 \pm 3.0}\text{Ab}_{11.2 \pm 3.0}$ plagioclase, $\text{Wo}_{45.4 \pm 0.5}\text{En}_{53.4 \pm 0.5}\text{Fs}_{1.2 \pm 0.1}$ clinopyroxene and $\text{Fo}_{97.1 \pm 0.3}$ olivine. The modal compositions reported for different fragments of NWA 7325 vary (Barrat *et al.*, 2015; Weber *et al.*, 2016; Goodrich *et al.*, 2017), illustrating the heterogeneous distribution of the minerals at the centimetre scale. The fragment of NWA 8486 studied here contains the highest pyroxene modal content at 52 %, the lowest plagioclase content at 44 %, with the remaining 4 % consisting of olivine, sulphides and metal. The range reported for NWA 7325 is 30-44 % for pyroxene, 54-60 % for plagioclase and 2-15 % for olivine (Barrat *et al.*, 2015; Weber *et al.*, 2016; Goodrich *et al.*, 2017).

We report trace element abundances in mineral (plagioclase, pyroxene and olivine) and a whole rock powder of NWA 8486. Minerals were analysed either *in situ* or in solution after mechanical separation (Supplementary Information). The whole rock composition slightly differs from that of NWA 7325 from Barrat *et al.* (2015) as a consequence of different modal compositions (Fig. 1). Incompatible and moderately volatile elements are depleted in this meteorite, below $0.5 \times \text{CI}$ chondrites for the whole rock with the exceptions of Eu and Sr. Positive Eu and Sr anomalies (Eu/Eu^* and Sr/Sr^*) are present in each mineral phase with different magnitudes, from 1.8 to 6.5 in pyroxene and 450 to 1039 in plagioclase (Supplementary Information). Their amplitude in the whole rock is much higher than that measured in lunar anorthosites (Fig. 1).

1. Université Clermont Auvergne, CNRS, IRD, OPGC, Laboratoire Magmas et Volcans, F-63000 Clermont-Ferrand, France
2. Department of Earth Sciences, Centre for Planetary Science and Exploration, University of Western Ontario, Ontario, Canada
3. Bayerisches Geoinstitut, Universität Bayreuth, Germany
* Corresponding author (email: paul.frossard@uca.fr)



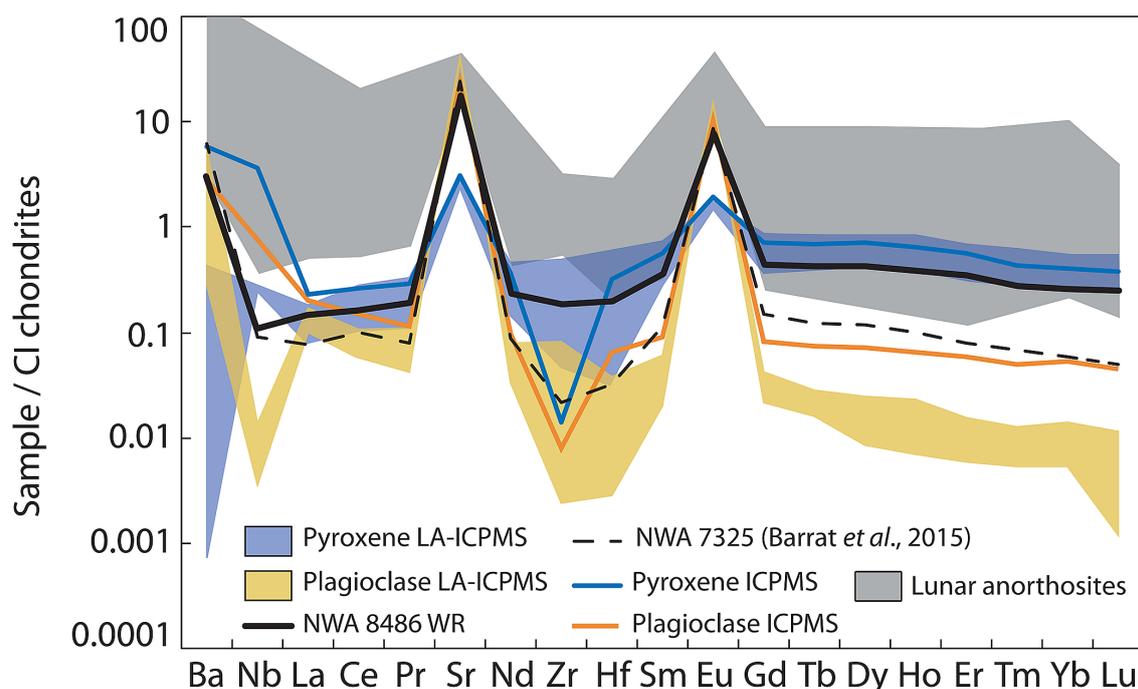


Figure 1 Trace element composition of NWA 8486 normalised to CI chondrites (Anders and Grevesse, 1989). All fractions exhibit Eu and Sr positive anomalies. NWA 7325 has a lower content for most incompatible elements compared to NWA 8486 owing to its modal enrichment in plagioclase. Lunar anorthosites are reported for comparison (data from Haskin *et al.*, 1973 and Norman *et al.*, 2003).

Europium changes valence in a continuum from a 3+ state to a 2+ state around the IW buffer (where $\text{Eu}^{3+}/\Sigma\text{Eu} = 0.5$) and in these conditions plagioclase preferentially incorporates Eu^{2+} in its lattice, resulting in an enrichment in Eu over the other trivalent rare earth elements (REE^{3+}). The similar plagioclase/melt partition coefficients of Sr^{2+} and Eu^{2+} arise from very close ionic radii. NWA 7325/8486 formed within an $f\text{O}_2$ of $\text{IW}-3.2 \pm 0.2$, which is more reduced than for lunar rocks that formed in a range of IW-2 to IW (Wadhwa, 2008; Sutton *et al.*, 2017). Despite their higher $f\text{O}_2$, lunar anorthosite plagioclases show similar Eu anomalies to reduced meteorites (Fig. S-4). Thus, even considering variations due to parental melt composition, there should be little difference between NWA 8486 and lunar anorthosite plagioclase compositions if they were formed under similar conditions. Although positive Eu and Sr anomalies are common in plagioclase, the present data are the first report of positive Eu and Sr anomalies in clinopyroxene in an achondritic meteorite. Europium partitioning in clinopyroxene changes depending on the composition of the system with Eu^{2+} being either similarly or less compatible than Eu^{3+} (Karner *et al.*, 2010). Therefore, the peculiar trace element inventory of NWA 8486 cannot be solely attributed to redox conditions.

Anorthosites as Source Rocks of NWA 7325/8486

NWA 8486 stands out as a unique meteorite when compared to the composition of other achondrites and lunar anorthosites. Pyroxene, plagioclase and whole rock data from all known types of achondrites define separate fields in an Eu_N/Sm_N versus Sr_N/Nd_N diagram (with $_N$ indicating concentrations normalised to corresponding CI chondrite abundances) (Fig. 2). The composition for NWA 8486 is shifted towards both higher Eu_N/Sm_N and Sr_N/Nd_N ratios compared to other planetary compositions. The rare felsic (Si-rich, evolved) achondrites GRA 06128/9 and Almahata Sitta (ALM-A clast) do not appear any different from other achondrites in terms of Eu and Sr

enrichments. Early occurrences of such felsic rocks have been related to partial melting of chondritic material instead of the multi-stage processes involved to form felsic crust on Earth (Day *et al.*, 2009; Bischoff *et al.*, 2014). Therefore, the particular composition of NWA 7325/8486 must be related to the melting of a specific source which was already enriched in Eu (relative to other REEs) and Sr. Barrat *et al.* (2015) suggested that impact melting of a gabbroic crust might produce such anomalies. In view of a homogeneous distribution of ^{26}Al in the solar system, Barrat *et al.* (2015) and Koefoed *et al.* (2016) calculated that the differentiation event for NWA 7325's parent body was ~1-2 Myr after formation of the solar system, while its crystallisation (from Pb-Pb chronometry) occurred within about 3 Myr after that. Considering the diopside-anorthite binary system at 1 atm (Osborn, 1942), the source of NWA 7325/8486 parent melt needs to be already enriched in plagioclase to reach the high plagioclase modal compositions for the meteorite, at least 48 % plagioclase to match NWA 8486. The modal composition of NWA 8486 lies on the eutectic point of the diagram. Thus, basaltic sources with low plagioclase content can produce eutectic compositions, but higher anorthite modes cannot be reached. We performed melting models of varied compositions and compared the compositions of these liquids with those in equilibrium with NWA 8486 minerals (Supplementary Information). The enrichment in Eu and the general depletion of incompatible elements are not reproduced with cumulate eucrite (Moore County) compositions (Fig. 3). The only possibility found to produce a parental magma enriched in both Eu and Sr is melting of a plagioclase-, Mg- and Ca-rich rock. Low degree melting (below 5 %) of an anorthosite (98 % anorthite) produces liquids corresponding to NWA 7325/8486 modes, but does not yield both high enough Eu anomalies and REE depletion. However, a higher pyroxene content can produce a larger amount of melt of eutectic composition. NWA 8486 features can be reproduced by 20-50 % melting of a pyroxene-rich anorthosite (Apollo noritic anorthosite 62236 with 20 % pyroxene) (Fig. 3). Anorthosites are therefore the most likely source for the parental magma of the NWA 7325/8486 suite.

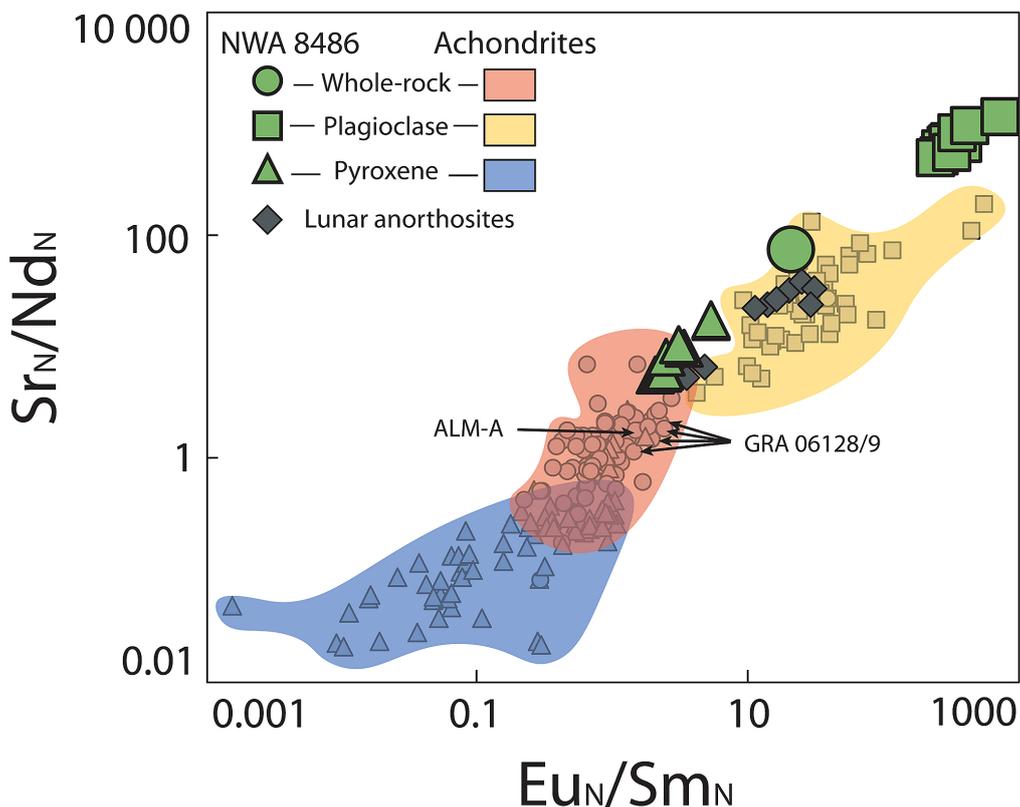


Figure 2 Eu/Sm and Sr/Nd ratios of achondrites and NWA 8486 normalised to CI chondrites (Anders and Grevesse, 1989). Overlap between the different fields is due to whole rocks mainly composed of pyroxene or plagioclase (e.g., aubrites, ureilites, lunar anorthosites). For each field group, NWA 8486 exhibits higher Eu_N/Sm_N and Sr_N/Nd_N . Only lunar anorthosites are similar to NWA 8486 whole rock, but they contain much more plagioclase than NWA 8486. See Supplementary Information for data sources.

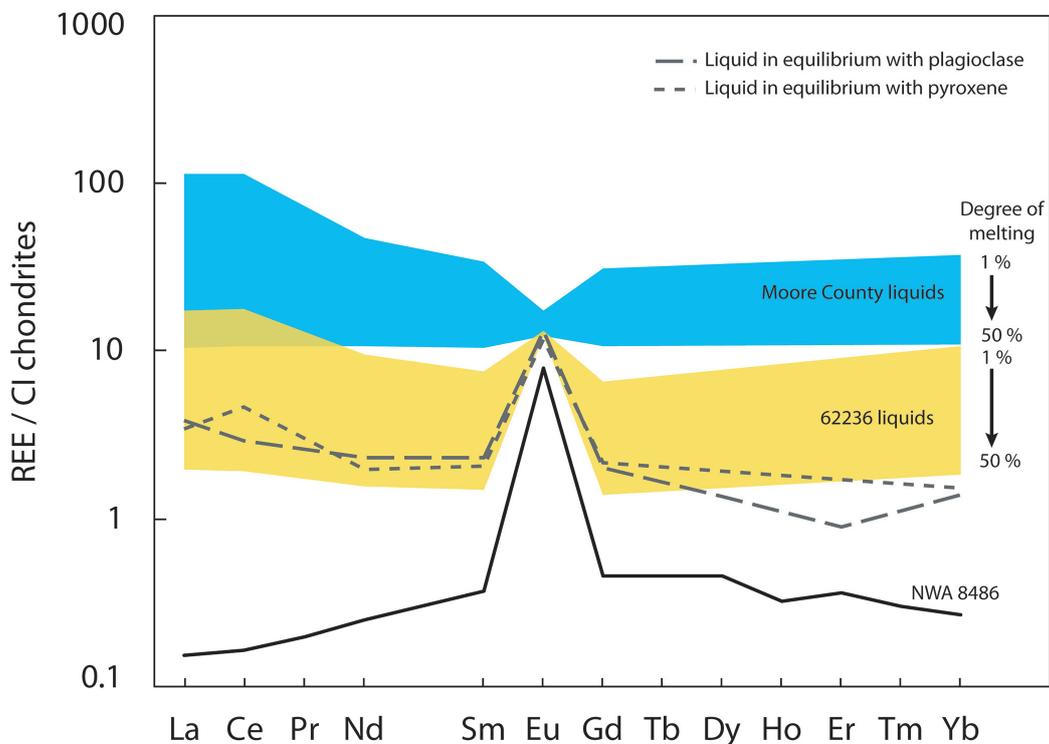


Figure 3 REE composition of liquids in equilibrium with NWA 8486 minerals (in grey dashed lines) compared to liquids modelled with compositions of the cumulate eucrite Moore County and the pyroxene-rich lunar anorthosite Apollo 62236, normalised to CI chondrites (Anders and Grevesse, 1989). A non-modal melting is considered, in agreement with petrological constraints, of eutectic proportions of 42 % plagioclase and 58 % pyroxene (Osborn, 1942). The range of composition of the liquids from 1 % to 50 % degree of melting is represented for each source composition. NWA 8486 whole rock composition is shown (black line) for comparison. See Supplementary Information for details on the model.

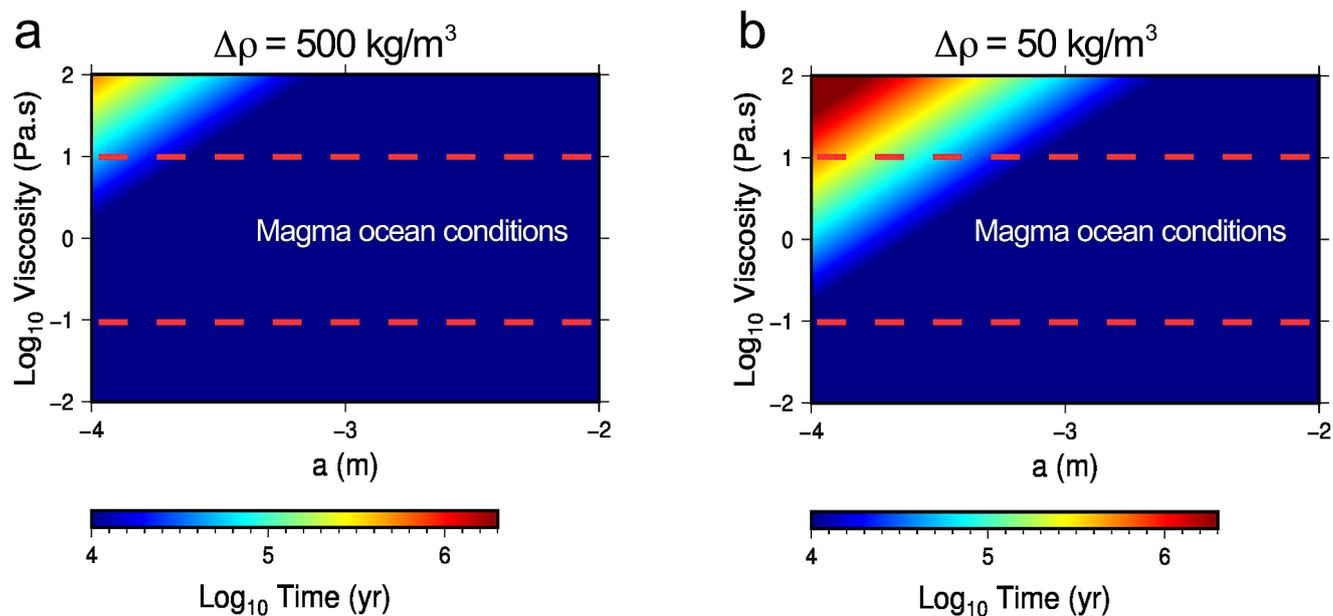


Figure 4 Time for plagioclase crystal ascent during the late stage of a magma ocean. This time is calculated for a range of viscosities (0.1 to 10 Pa.s), crystal diameters (a ; 100 μm to 1 cm) and density contrasts ($\Delta\rho$; 50 to 500 kg/m^3) between the crystal and the liquid phase. The time for a crystal to reach the surface of the magma ocean is represented with a colour scale ranging between 10 kyr (blue) and 2 Myr (red). Both panels show that the time of ascent of the crystal is a few tens of thousands of years in magma ocean conditions, except for small crystals around 100 μm and high viscosities of >10 Pa.s for which time of ascent is longer.

Timescales of Anorthosite Formation on Early Solar System Planetesimals

Anorthosites are associated with large magma systems that experience fractional crystallisation, in which plagioclase floats at the surface. Lunar anorthosites are derived from a magma ocean (MO) that formed subsequently to the Moon-forming impact event, but their petrogenesis model is still debated. Specific conditions are required for anorthositic crust formation (Albarède and Blichert-Toft, 2007). The body needs to be rather dry, as plagioclase formation is delayed in presence of water and would appear late in the crystallisation sequence (Elkins-Tanton, 2008). The size of the planetary body is also important as plagioclase is stable up to 1 GPa, which corresponds to a depth of 75 km for a Mars-like body or 200 km for a Moon-like body (Albarède and Blichert-Toft, 2007). Studies on Mercury's MO have shown that in very reduced conditions anorthite is denser than the melt and then may not float (Brown and Elkins-Tanton, 2009; Vander Kaaden and McCubbin, 2015). Crystal settling that enables anorthositic crust formation may be hindered by highly turbulent convection on small parent bodies with low gravity. Nonetheless, some authors have suggested that crystal settling can occur in such environments (Taylor *et al.*, 1993; Elkins-Tanton, 2012).

Geochemical modelling indicates that the NWA 7325/8486 source was most likely an anorthosite. Although Mercury may not be an analogue to NWA 7325/8486 parent body, it may represent an end member in terms of density and composition of the MO. Calculations have been carried out to constrain the timescales of formation of an anorthositic crust in a MO. The plagioclase formation occurs generally when the MO is crystallised by 70–80 vol. % (Supplementary Information). Assuming that the remaining molten material (≈ 20 vol. %) forms a buoyant layer over the solidified mantle and that 15 vol. % of the inner body is made of a metallic core, we can estimate the depth of the molten layer relative to the radius of the body (Supplementary Information). Considering that the rising velocity for plagioclase crystals in a MO

scales with a Stokes' Law settling velocity (Martin and Nokes, 1989), the time for a plagioclase crystal to reach the surface in a shallow MO can be assessed. The calculation yields that for the MO viscosity range (10^{-1} – 10^1 Pa.s, Dygert *et al.*, 2017) and density contrasts between crystal and magma (50–500 kg/m^3 , Brown and Elkins-Tanton, 2009; Dygert *et al.*, 2017), a crystal of at least 100 μm in diameter will reach the surface of the MO in a few tens of thousands of years (Fig. 4). The time of ascent of plagioclase is much smaller than the age of the first differentiation on NWA 7325/8486 estimated at 1.7 Ma using the ^{26}Al – ^{26}Mg systematics (Koefoed *et al.*, 2016). Therefore, we believe that NWA 7325/8486 is the first evidence of the formation and re-processing of an anorthositic crust on a planetesimal very early in the solar system.

If anorthosite could form quickly on planetesimals and magma oceans were common in the first few million years of the solar system, where are the anorthosites in the meteorite record? The reason for the absence of anorthositic crusts on achondrite parent bodies probably lies in their thermal and chemical evolution. The conditions necessary for magma oceans to form with anorthositic crusts may have been limited by the time and place of accretion (Greenwood *et al.*, 2012). Inner solar system planetesimals that accreted early were enriched in ^{26}Al and were thus more likely to have experienced magma ocean conditions (Grimm and McSween Jr, 1993). Iron meteorites are evidence of these processes. Their parent bodies were rather small (20 to 200 km; Chabot and Haack, 2006) and possibly formed within the terrestrial accretion zone below 1 AU before being scattered into the main asteroid belt. Silicate layers from these bodies have a low probability of survival in the chaotic early inner solar system (Bottke *et al.*, 2006; O'Neill and Palme, 2008). It is likely, then, that anorthositic crusts were formed in the inner solar system but rarely preserved. Material from these planetesimal silicate layers could have been subsequently added to the accreting terrestrial planets, providing a non-chondritic source for refractory lithophile elements.

Acknowledgements

We thank Dr. L. Garvie (Center for Meteorite Studies, Arizona State University) for the loan of NWA 8486, J.-L. Devidal for assistance with electron microprobe and LA-ICP-MS analyses, and J.-M. Hénot for assistance with SEM analyses. We also thank T. Withers for comments and J.-A. Barrat for enriching discussions on geochemical modelling. Helen Williams is acknowledged for editorial handling and Addi Bischoff and Stephen Elardo for constructive and thorough reviews that greatly improved the manuscript. This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (Grant Agreement No 682778 – ISOREE to MB), and NSERC Discovery Grant, Canada Research Chair, and the Canada Foundation for Innovation JELF programs (to AB). This is Laboratory of Excellence ClerVolc contribution number 369.

Editor: Helen Williams

Additional Information

Supplementary Information accompanies this letter at <http://www.geochemicalperspectivesletters.org/article1921>.



This work is distributed under the Creative Commons Attribution Non-Commercial No-Derivatives 4.0 License, which permits unre-

stricted distribution provided the original author and source are credited. The material may not be adapted (remixed, transformed or built upon) or used for commercial purposes without written permission from the author. Additional information is available at <http://www.geochemicalperspectivesletters.org/copyright-and-permissions>.

Cite this letter as: Frossard, P., Boyet, M., Bouvier, A., Hammouda, T., Monteux, J. (2019) Evidence for anorthositic crust formed on an inner solar system planetesimal. *Geochem. Persp. Let.* 11, 28–32.

References

- ALBARÈDE, F., Blichert-Toft, J. (2007) The split fate of the early Earth, Mars, Venus, and Moon. *Comptes Rendus Geosciences* 339, 917–927.
- ANDERS, E., GREVESSE, N. (1989) Abundances of the elements: Meteoritic and solar. *Geochimica et Cosmochimica Acta* 53, 197–214.
- BARRAT, J.-A., GREENWOOD, R.C., VERCHOVSKY, A.B., Gillet, P., Bollinger, C., Langlade, J.A., Liorzou, C., Franchi, I.A. (2015) Crustal differentiation in the early solar system: Clues from the unique achondrite Northwest Africa 7325 (NWA 7325). *Geochimica et Cosmochimica Acta* 168, 280–292.
- BISCHOFF, A., HORSTMANN, M., BARRAT, J.-A., CHAUSSIDON, M., Pack, A., Herwartz, D., Ward, D., Vollmer, C., Decker, S. (2014) Trachyandesitic volcanism in the early solar system. *Proceedings of the National Academy of Sciences* 111, 12689–12692.
- BOTTKE, W.F., NESVORNÝ, D., GRIMM, R.E., MORBIDELLI, A., O'BRIEN, D.P. (2006) Iron meteorites as remnants of planetesimals formed in the terrestrial planet region. *Nature* 439, 821–824.
- BROWN, S.M., ELKINS-TANTON, L.T. (2009) Compositions of Mercury's earliest crust from magma ocean models. *Earth and Planetary Science Letters* 286, 446–455.
- CHABOT, N., HAACK, H. (2006) Evolution of Asteroidal Cores. In: Lauretta, D.S., McSween Jr., H.Y. (Eds.) *Meteoritics and the Early Solar System II*. The University of Arizona Press, Tucson, 747–771.
- DAY, J.M., ASH, R.D., LIU, Y., BELLUCCI, J.J., RUMBLE III, D., McDONOUGH, W.F., WALKER, R.J., TAYLOR, L.A. (2009) Early formation of evolved asteroidal crust. *Nature* 457, 179–182.
- DYGERT, N., LIN, J., MARSHALL, E.W., KONO, Y., GARDNER, J.E. (2017) A low viscosity lunar magma ocean forms a stratified anorthitic flotation crust with mafic poor and rich units. *Geophysical Research Letters* 44, 11,282–11,291.
- ELKINS-TANTON, L.T. (2008) Linked magma ocean solidification and atmospheric growth for Earth and Mars. *Earth and Planetary Science Letters* 271, 181–191.
- ELKINS-TANTON, L.T. (2012) Magma oceans in the inner solar system. *Annual Review of Earth and Planetary Science* 40, 113–139.
- GOODRICH, C.A., KITA, N.T., YIN, Q.-Z., SANBORN, M.E., WILLIAMS, C.D., NAKASHIMA, D., LANE, M.D., BOYLE, S. (2017) Petrogenesis and Provenance of Ungrouped Achondrite Northwest Africa 7325 from Petrology, Trace Elements, Oxygen, Chromium and Titanium Isotopes, and Mid-IR Spectroscopy. *Geochimica et Cosmochimica Acta* 203, 381–403.
- GREENWOOD, R., FRANCHI, I., GIBSON, J., BENEDIX, G. (2012) Oxygen isotope variation in primitive achondrites: The influence of primordial, asteroidal and terrestrial processes. *Geochimica et Cosmochimica Acta* 94, 146–163.
- GRIMM, R.E., MCSWEEN JR, H.Y. (1993) Heliocentric zoning of the asteroid belt by aluminum-26 heating. *Science* 653–655.
- HASKIN, L. A., HELMKE P. A., BLANCHARD D. P., JACOBS J. W., TELANDER K. (1973) Major and trace elements abundances in samples from lunar highlands. *Proceedings of the Lunar Science Conference* 4, 1275–1296.
- KARNER, J.M., PAPIKE, J.J., SUTTON, S.R., BURGER, P.V., SHEARER, C.K., LE, L., NEWVILLE, M., CHOI, Y. (2010) Partitioning of Eu between augite and a highly spiked martian basalt composition as a function of oxygen fugacity (IW-1 to QFM): Determination of $\text{Eu}^{2+}/\text{Eu}^{3+}$ ratios by XANES. *American Mineralogist* 95, 410–413.
- KOEFOED, P., AMELIN, Y., YIN, Q.-Z., WIMPENNY, J., SANBORN, M.E., IZUKA, T., IRVING, A.J. (2016) U–Pb and Al–Mg systematics of the ungrouped achondrite Northwest Africa 7325. *Geochimica et Cosmochimica Acta* 183, 31–45.
- LEE, T., PAPANASTASSIOU, D., WASSERBURG, G. (1977) Aluminum-26 in the early solar system-Fossil or fuel. *Astrophysical Journal* 211, L107–L110.
- MARTIN, D., NOKES, R. (1989) A fluid-dynamical study of crystal settling in convecting magmas. *Journal of Petrology* 30, 1471–1500.
- NORMAN, M.D., BORG, L.E., NYQUIST, L.E., BOGARD, D.D. (2003) Chronology, geochemistry, and petrology of a ferroan noritic anorthositic clast from Descartes breccia 67215: Clues to the age, origin, structure, and impact history of the lunar crust. *Meteoritics and Planetary Science* 38, 645–661.
- O'NEILL, H.S.C., PALME, H. (2008) Collisional erosion and the non-chondritic composition of the terrestrial planets. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 366, 4205–4238.
- OSBORN, E.F. (1942) The system CaSiO_3 -diopside-anorthite. *American Journal of Science* 240, 751–788.
- RUZICKA, A., GROSSMAN, J., BOUVIER, A., AGEE, C.B. (2017) The Meteoritical Bulletin, No. 103. *Meteoritics and Planetary Science* 52, 1014.
- SUTTON, S.R., GOODRICH, C.A., WIRICK, S. (2017) Titanium, Vanadium and Chromium Valences in Silicates of Ungrouped Achondrite (NWA) 7325 and Ureilite Y-791538 Record Highly-Reduced Origins. *Geochimica et Cosmochimica Acta* 204, 313–330.
- TAYLOR, G.J., KEIL, K., MCCOY, T., HAACK, H., SCOTT, E.R. (1993) Asteroid differentiation: Pyroclastic volcanism to magma oceans. *Meteoritics* 28, 34–52.
- VANDER KAADEN, K.E., MCCUBBIN, F.M. (2015) Exotic crust formation on Mercury: Consequences of a shallow, FeO-poor mantle. *Journal of Geophysical Research: Planets* 120, 195–209.
- WADHWA, M. (2008) Redox conditions on small bodies, the Moon and Mars. *Reviews in Mineralogy and Geochemistry* 68, 493–510.
- WEBER, I., MORLOK, A., BISCHOFF, A., HIESINGER, H., WARD, D., JOY, K., CROWTHER, S., JASTRZEBSKI, N., GILMOUR, J., CLAY, P. (2016) Cosmochemical and spectroscopic properties of Northwest Africa 7325—A consortium study. *Meteoritics and Planetary Science* 51, 3–30.
- WOOD, J.A., DICKEY JR, J., MARVIN, U.B., POWELL, B. (1970) Lunar anorthosites and a geophysical model of the moon. *Geochimica et Cosmochimica Acta Supplements* 1, 965–988.
- YANG, J., ZHANG, C., MIYAHARA, M., TANG, X., GU, L., LIN, Y. (2019) Evidence for early impact on hot differentiated planetesimal from Al-rich micro-inclusions in ungrouped achondrite Northwest Africa 7325. *Geochimica et Cosmochimica Acta* 258, 310–335.

