Rare-earth-element minerals in martian breccia meteorite NWA 7034 and 7533: Implications for fluid-rock interaction in the martian crust.

Yang Liu^{1,*}, Chi Ma², John Beckett², Yang Chen¹, and Yunbin Guan²

¹Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA.

²Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA.

Abstract

Paired martian breccia meteorites, Northwest Africa (NWA) 7034 and 7533, are the first martian rocks found to contain rare-earth-element (REE) phosphates and silicates. The most common occurrence is as clusters of anhedral monazite-(Ce) inclusions in apatite. Occasionally, zoned, irregular merrillite inclusions are also present in apatite. Monazite-bearing apatite is sometimes associated with alkali-feldspar and Fe-oxide. Apatite near merrillite and monazite generally contains more F and OH (F-rich region) than the main chlorapatite host and forms irregular boundaries with it. Locally, the composition of F-rich regions can reach pure fluorapatite. The chlorapatite hosts are similar in composition to isolated apatite without monazite inclusions, and to euhedral apatite in lithic clasts. The U-Th-total Pb ages of monazite in three apatite are 1.0 ± 0.4 Ga (2σ), 1.1 ± 0.5 Ga (2σ), and 2.8 ± 0.7 Ga (2σ), confirming a martian origin. The texture and composition of monazite inclusions are mostly consistent with their formation by the dissolution of apatite and/or merrillite by fluid at elevated temperatures (>100 °C).

In NWA 7034, we observed a monazite-chevkinite-perrierite-bearing benmoreite or trachyandesite clast. Anhedral monazite and chevkinite-perrierite grains occur in a matrix of sub-micrometer REE-phases and silicates inside the clast. Monazite-(Ce) and -(Nd) and

chevkinite-perrierite-(Ce) and -(Nd) display unusual La and Ce depletion relative to Sm and Nd. In addition, one xenotime-(Y)-bearing pyrite-ilmenite-zircon clast with small amounts of feldspar and augite occurs in NWA 7034. One xenotime crystal was observed at the edge of an altered zircon grain, and a cluster of xenotime crystals resides in a mixture of alteration materials. Pyrite, ilmenite, and zircon in this clast are all highly altered, zircon being the most likely source of Y and HREE now present in xenotime. The association of xenotime with zircon, low U and Th contents, and the low Yb content relative to Gd and Dy in xenotime suggest the possible formation of xenotime as a byproduct of fluid-zircon reactions.

On the basis of relatively fresh apatite grains and lithic clasts in the same samples, we propose that the fluid-rock/mineral reactions occurred in the source rocks before their inclusion in NWA 7034 and 7533. Additionally, monazite-bearing apatite and REE-mineral-bearing clasts are possibly derived from different crustal origins. Thus, our results imply the wide-occurrence of hydrothermal fluids in the martian crust at 1 Ga or older, which were probably induced by impacts or large igneous intrusions.

Keywords: Martian crust, hydrothermal fluid, monazite, xenotime, chevkinite-perrierite, trachyandesite, resource

Introduction

Monazite and xenotime (REE-phosphates) and chevkinite-perrierite (REE-silicate) are common minor constituents in a wide range of terrestrial rocks and are commercially important repositories for the REE (e.g., Overstreet, 1967; Hetherington et al., 2008; Macdonald et al., 2009; Chakhmouradian and Wall, 2012; Catlos, 2013; Muhling et al., 2014; and additional citations in the supplementary file). These minerals are resistant to surface weathering on the Earth (e.g., Overstreet, 1967; Montel et al., 2011 in the supplementary file), and can precipitate when other, less stable, REE-bearing phases are altered or destroyed (e.g., Harlov, 2011, 2015).

Rare-earth-element minerals are quite rare in extraterrestrial samples from small planetary bodies, appearing only in a howardite and some Apollo samples (e.g., Lovering et al., 1974; Yagi et al., 1978; Jolliff, 1993; see also supplementary citations). Partly, this reflects a paucity of evolved igneous rocks and active, high-temperature fluids in the moon and other environments sampled by meteorites. Martian regolith breccia NWA 7034 and two pairs (NWA 7475 and 7533) are the first martian rocks shown to contain monazite inclusions in apatite (Liu and Ma, 2014; Yin et al., 2014). We also reported monazite-chevkinite-perrierite in a lithic clast in NWA 7034 (Liu and Ma, 2015). This is the first report of chevkinite-perrierite in a martian rock and the second report in an extra-terrestrial sample, lunar basalt 10047 (Muhling et al., 2014) being the other. Xenotime in NWA 7034 is the first reported occurrence in an extraterrestrial sample (Liu and Ma, 2015).

Most martian meteorites are igneous rocks that constitute a small fraction of the martian surface. Meteorite NWA 7034 and its pairings (NWA 7475, 7533, 7906, 7907, 8114, 8159, 8674) can be regarded as the first rocks in the martian meteorite collection that are typical of material at the surface of Mars (Agee et al., 2013). They consist of abundant alkali-feldspar, plagioclase

(An₆₀-An₁₀) and pyroxenes (mostly pigeonite and augite), with minor constituents including magnetite (+ maghemite component + rutile exsolution), pyrite, zircon and phosphate minerals (e.g., Agee et al., 2013; Humayun et al., 2013; Santos et al., 2015; Wittmann et al., 2015). Clasts in NWA 7034 and 7533 have been matched with float rock observed by surface missions (Santos et al., 2015; Grotzinger et al., 2015). Here, we concentrate on the textural and chemical properties of REE-minerals in NWA 7034 and 7533, and explore implications for evolution of the martian crust and its fluid environments.

Samples and Methods

Samples. We studied six sections from NWA 7034 and 7533 (Fig. S1). Two polished sections of NWA 7034 were allocated by the Institute of Meteoritics at the University of New Mexico. A separate part slice (0.94 gram) of NWA 7034, from the same individual that supplied the New Mexico collection, was obtained at JPL. Two polished sections were prepared from this slice. In addition, two polished thin sections of NWA 7533 from the California Institute of Technology (Caltech) were included in this study.

Analytical Techniques. Reflected light images of all sections were collected using Leica DM2500 petrographic microscopes at JPL. Backscattered electron (BSE) and cathodoluminescence (CL) images were collected using a field-emission scanning electron microscope (FE-SEM, ZEISS 1550 VP) at Caltech.

For the monazite-chevkinite-perrierite-bearing clast, the composition of sub-micrometer-sized REE-minerals was determined using the FE-SEM at 15 kV voltage and an Oxford X-Max SDD Energy Dispersive Spectrometer (EDS) with internal standards and the XPP matrix correction procedure.

Silicates, Fe-oxides and sulfide in the monazite-chevkinite-perrierite-bearing clast and the xenotime-bearing clast were analyzed using a JEOL JXA-8200 electron microprobe (EMP). Analytical conditions include a beam of 15 kV voltage and 20 nA current with a diameter of 2 or 5 μm (varied depending on the sample size). The counting times for each element were 20 s on peak and 10 s on each background.

Apatite was analyzed under conditions optimized for determining F and Cl concentrations. We used a voltage of 15 kV and a 10-25 nA beam current with a beam diameter of 2 to 10 μm (variable to fit the size of the grain). Counting time for each element is 20 s. We also collected F $K\alpha$, Cl $K\alpha$, P $K\alpha$, Fe $K\alpha$ and Ce $L\alpha$ maps of a few monazite-bearing apatite grains under 15 kV, 10-25 nA, a 1 μm diameter beam, and a step size of 0.5 μm with a dwell time of 100 ms at each step.

The REE concentrations of monazite inclusions, xenotime, merrillite and apatite were analyzed using a 1 μm diameter beam at 15 kV and 25 nA. On-peak counting times for most elements ($K\alpha$ lines for P, Na, Ca; $L\alpha$ lines for Y and REE) were 20 s, with 30 s for Pr, 50 s for Er and Yb, and 60 s for Mg. Interferences of $L\alpha$ peaks of each REE for other REE were corrected using the mean atomic number (MAN) method of Donovan and Tingle (1996). Both natural and synthetic standards were used for standardization and the resulting detection limits are listed in Table 1. Ytterbium in monazite and La, Ce, and Pr in xenotime were generally below detection. The analyzed grains of REE-minerals are all very small ($< \sim 1.5 \mu\text{m}$ in at least one direction), necessitating the use of 15 kV (versus e.g., 25 kV) to minimize activation volume. The small grain sizes also made it impossible to assess homogeneity or precision for individual grains. We estimated relative errors (1σ) based on counting statistics, 0.5-8 % relative for most elements except for Na, Er, Eu (15-18 % relative), and Yb (~ 30 % relative) in monazite, and Na, Mg (~ 11 % rela-

110 tive), and Ce (~30 % relative) in xenotime. Owing to the small size of monazite inclusions, the
111 apatite composition was used for removing host contamination in monazite analysis (see below).

112 The U, Th, Pb and Y concentration of monazite inclusions, xenotime, and zircons were meas-
113 ured using a 1 μm beam at 15 kV voltage and a 100 nA current. Counting times were 200 s on
114 peak and 100 s on each background. Y was included to correct counts of Pb $M\alpha$ for interference
115 by Y $L\gamma$. Apatite hosts and merrillite were also analyzed using these conditions but their contri-
116 butions to the monazite data were negligible (Table 2). Results and detection limits are reported
117 in Table 2.

118 *Volatile abundances and D/H in apatite using SIMS.* Volatile abundances (H, Cl, F, S) of iso-
119 lated monazite-bearing phosphates in NWA 7034 and 7533, and monazite-free phosphates in
120 NWA 7533 were analyzed using a Cameca IMS-7f GEO secondary ion mass spectrometer
121 (SIMS) at Caltech with a 10 keV Cs^+ primary beam of 5 nA current and following a procedure
122 similar to that of Boyce et al. (2010). A normal-incidence electron gun of -10 keV was used for
123 sample charging compensation. The areas of interest (20 x 20 μm) were rastered with the prima-
124 ry beam for ~3-5 minutes to remove the conductive carbon coating. Negative secondary ions of
125 -10 keV were then collected under a mass resolving power (MRP) of ~5000, to separate $^{16}\text{O}^1\text{H}^-$
126 from $^{17}\text{O}^-$. Ion images of $^{12}\text{C}^-$ and $^{16}\text{O}^1\text{H}^-$ were used to avoid hot spots and cracks. Secondary
127 ion signals were sampled only from the central ~10 x 10 μm portion of the analyzed areas limited
128 by a field aperture and further reduced with an electronic gate of 64%. Negative ions of $^{12}\text{C}^-$,
129 $^{16}\text{O}^1\text{H}^-$, $^{18}\text{O}^-$, $^{19}\text{F}^-$ and $^{31}\text{P}^-$ were measured for 10 cycles, each with a 2 s counting time for $^{12}\text{C}^-$ and
130 1 s for other species. The OH contents in phosphates were quantified using natural apatite stand-
131 ards with OH equivalent to 0.03 to 0.57 wt% H_2O from Boyce et al. (2010) and McCubbin et al.
132 (2010).

Hydrogen isotope measurements were conducted on the same spots as for the ion species described above using similar primary beam conditions (Cs^+ , 10 keV, 5 nA). The beam was rastered over a $20 \times 20 \mu\text{m}$ area for ~ 3 minutes to remove the conductive carbon coating. Since $^1\text{H}_2^-$ does not contribute significantly to D^- , the mass spectrometer was set for a low mass resolution (MRP ~ 550). Ion imaging of $^1\text{H}^-$ was used to locate the previously analyzed spots. The $^1\text{H}^-$ and D^- ions were collected for 1 s and 10 s, respectively, for 33-100 cycles. The setups of the field aperture and electronic gate are similar to those for OH analysis, to avoid possible contaminations and contributions from crater edges. A Durango apatite with δD of $-120 \pm 5\text{‰}$ (VSMOW, Greenwood et al., 2011) was used to examine the instrumental mass fractionation (IMF) on D/H, and the isotope data presented here have been corrected for background contributions and IMF.

Results

Monazite, $(\text{LREE})\text{PO}_4$, occurs most commonly as clusters of minute inclusions within isolated apatite grains, although it also occurs in lithic clasts (Fig. 1, S3, S4). In addition, we observed one example of REE silicate, chevkinite-perrierite, with monazite in a lithic clast (Fig. 2); and one example of xenotime, $(\text{Y,HREE})\text{PO}_4$, in a pyrite-ilmenite clast (Fig. 3). All of the observed REE-mineral grains are small ($< 1.5 \mu\text{m}$ in at least one direction) so that analyses invariably include contributions from surrounding phases. In the following sections, we first describe our procedures for constraining compositions of REE minerals from EMP and SEM-EDS analyses and then describe each style of occurrence for the REE-minerals in NWA 7034 and 7533. Data for REE-minerals after correction and normalization are reported in Tables 1, 3, and 4. Concentrations of U, Th, and Pb in monazite inclusions and xenotime are given in Table 2.

Contamination of EMP and SEM-EDS analyses by surrounding material. Because of the contamination of small grain sizes for REE-minerals in NWA 7034 and 7533 by surrounding material, it is important to first process the as-acquired analyses to isolate compositions of the target grains. We used the following procedure to correct the analysis of an REE mineral for contamination by the host apatite or other adjacent minerals. Analyses of Th, U and Pb were not corrected using these procedures as the concentrations in apatite are low and only ratios of these elements were needed to compute ages.

For EMP analysis of monazite inclusions in apatite, contamination from the host apatite was subtracted by adjusting the amount of apatite removed until the stoichiometry of the corrected data was as close as possible to 2.00 cations per 4 oxygens without any of the corrected oxide concentrations becoming negative. The apatite-corrected oxide wt%s were then renormalized to 100% (Table 1). The corrected monazite formulae yield cation totals of 2.01 to 2.02 per 4 oxygens with 0.99-1.02 cations for P (Fig. S2). Because of the low abundances of REE in apatite (Table S1), our correction procedure increased the inferred REE concentrations in monazite by a factor of 1.2-2.5, without significantly changing the relative ratios.

For the complex intergrowths of monazite and chevkinite-perrierite in the lithic clast (Fig. 2), we followed the same correction procedure but used analyses of adjacent matrix to make the corrections (Table 3). A small amount of the matrix was subtracted from the measured monazite data until the cation sum of the corrected data was as close to 2.00 as possible without rendering any oxide wt% negative. The corrected monazite analyses have 0.94-0.98 cations of P and a sum total of 2.02-2.05 cations on a 4 oxygen basis (Table 3, Fig. S2). The general formula for chevkinite-perrierite is $A_4BC_2D_2Si_4O_{22}$ where A = REE, Y, Ca, Sr, Th; B = Fe^{2+} , Mn, Mg; C = Ti, Al, Fe^{3+} , Fe^{2+} , Cr, Mn, Mg, Zr, Hf, Nb; D = Ti. The correction routine using matrix data

aimed to obtain Si close to 4.000 and Ti > 2.00. The corrected data yielded cation totals of 13.3-13.4 with A-site occupancies of 3.9-4.4 and B+C-site sums of 2.9-3.2 cations, respectively).

The EMP analysis of xenotime crystals yielded low totals, but good stoichiometry relative to the expected formula of (Y, REE)PO₄ (i.e., ~2 cations per 4 oxygens; Table 4). Given the good stoichiometry, the low totals are likely a result of missing elements contributed by surrounding alteration materials. We renormalized the oxide percentages to 100% (Table 4). Compositions of pyrite and ilmenite from the same clast are also included in Table 4.

Monazite inclusions in apatite. Monazite is the most common REE-mineral in NWA 7034 and 7533, occurring mostly as minute inclusions in isolated chlorapatite (Fig. 1, S3). There are ~390 isolated apatite grains with the smallest dimension >30 µm in six polished sections (~100 to ~150 mm²), and detailed examinations of two sections with 121 and 39 grains, respectively, suggest ≤10% of them contain monazite inclusions. Among the apatite grains of larger size (smallest dimension >100 µm, n = 19) in six sections, two grains contain irregular cores of zoned merrillite (Fig. 1c, S3b), similar in appearance to the example described by Shearer et al. (2015), and one grain contains a symplectic intergrowth of monazite and F-rich apatite rimmed by REE-merrillite (Fig. S3a). In addition to monazite in isolated apatite crystals, two clasts of >100 µm contain monazite-bearing subhedral apatite (≥50 area% of the clast) and alkali feldspar with minor Fe-oxides (Fig. S4). In contrast, apatite in igneous clasts (of >100 µm, Fig. S5) in the six sections (<10 igneous clasts per section) contains no monazite (e.g., Fig. S5). Examination of igneous clasts shown in Santos et al. (2015) and Wittmann et al. (2015) suggests a similar observation. Some of monazite-bearing chlorapatite grains also display Fe-O veins that are not associated with monazite inclusions or F-rich regions, but cross-cut merrillite inclusions, if present (Fig. 1a, 1c, S3b, S4). Monazite-free apatite grains also contain Fe-rich veins (Fig. S5b-c).

All monazite-bearing apatites display irregular cathodoluminescence (CL) patches (Fig. 1, S3, S4), which differs from those showing no inclusions (homogeneous or monotonically zoned, Fig. S5). Apatite in the immediate vicinity of monazite shows a dark CL. Compositions of the monazite-bearing apatite are broadly similar to apatite in lithic clasts and grains without monazite inclusions (Fig. 4). However, F K α and Cl K α maps of monazite-bearing apatites show that dark CL zones are associated with elevated F, which form irregular boundaries with the Cl-rich region with bright CL (Fig. 1). For apatite grains containing both monazite and merrillite, the apatite near merrillite is more F-rich than that near monazite, reaching essentially pure fluorapatite (Fig. 1 and 4, Table S1). Fluorapatites have not been reported previously in NWA 7034 and they are rare for martian samples (e.g., McCubbin and Jones, 2015). Thorium, U, and Pb contents of chlorapatite are generally below the detection limits of 109 ppm, 115 ppm and 92 ppm, respectively.

Merrillite inclusions in apatite vary from Na-rich and REE-poor in the core {e.g., Mg_{0.99}[Ca_{8.8-8.9}(YREE)_{0.2}]Na_{0.7}(PO₄)₇}, to Na-poor and REE-rich near the contact with apatite, {Mg_{0.97}[Ca_{8.1}(YREE)_{0.9}]Na_{0.06}(PO₄)₇, Fig. 1c, Table S3b}. Santos et al. (2015) and Shearer et al. (2015) described a similar merrillite inclusion with more Fe, less Y and REE {Mg_{0.84}Fe_{0.23}[Ca_{9.1}(YREE)_{0.03}]Na_{0.6}(PO₄)₇}. However, they did not note the REE-rich merrillite and monazite inclusions. Monazite inclusions in merrillite-bearing apatites are largely found in the mantling apatite and, occasionally, in the REE-rich merrillite (Fig. 1c and S3b). Thorium, U, and Pb contents of REE-rich merrillite are below detection limits.

Analysis of OH contents and δ D of apatites can be compromised by the inclusion of terrestrial crack-filling materials within the analytical volume (see Supplementary Table S2 and Fig. S6). Excluding the points with high C counts, low δ D, and cracks, the SIMS count ratios of F/Cl form

a general positive correlation with OH/Cl, suggesting the F-rich portions of the chlorapatite contain higher OH contents than the Cl-rich regions (Table S2). The Na-merrillite in Fig. 2c contains less H₂O than the analyzed apatites [156 ± 5 (1 σ) ppm H₂O *versus* 298-1490 ppm] but with a similar δD [$+496 \pm 34\text{‰}$ (1 σ) *versus* $+48 - +1476\text{‰}$].

All of the monazite inclusions are monazite-Ce, [(Ce_{0.32}Nd_{0.19}La_{0.14}Y_{0.15})PO₄] on average; they contain minor Ca, Na and Mg, with the remaining REE summing to 0.1-0.2 cations (Table 1). The sum of all REE₂O₃ exceeds 60 wt%. Thorium, U and Pb contents of monazites inclusions, without correcting for apatite contamination, range from below detection limits to 1123 ppm, 1337 ppm, and 353 ppm, respectively, and the 1 σ analytical errors based on counting statistics range from 5-13% relative for Th, 5-9% for U, and 11-23% for Pb (Table 2). The U-Th-total Pb ages of monazite inclusions are 999 ± 195 Myr, 1094 ± 257 Myr, and 2770 ± 370 Myr (Table 2), calculated using the method of Montel et al. (1996). The 1 σ uncertainties of ages are estimated by propagating the 1 σ analytical uncertainties of Th, U, and Pb using the method of Williams et al. (1999), and the large values reflect the low concentrations of Th, U and Pb in monazites. The apatite hosts for monazite inclusions with 999 Myr and 2770 Myr ages contain noticeable concentrations of Th and U. Subtracting the apatite contamination for these two grains, assuming Y contents in the monazite is 11 wt% Y₂O₃, changes calculated ages to 1132 Myr and 2563 Myr, respectively, which are within the 1 σ uncertainties.

CI-chondrite-normalized REE abundances of monazite inclusions are characterized by an increasing depletion with increasing atomic number (Fig. 5a-b), as expected from the REE partitioning behavior between monazite and melt (e.g., Stepanov et al., 2012). Monazite inclusions display negative Eu anomalies of ~ 0.4 to 0.6 [$Eu_N/Eu^*_N = Eu_N / (Sm_N * Gd_N)^{0.5}$, where N refers to the CI-chondrite normalized abundance]. The normalized abundances of LREE in these mona-

zite are similar to each other with $(\text{La}/\text{Nd})_{\text{N}} = 1.2\text{-}1.8$, but the LREE are enriched over MREE and HREE with $(\text{La}/\text{Y})_{\text{N}} = 5\text{-}16$ and $(\text{La}/\text{Yb})_{\text{N}} = 25\text{-}35$. The REE-merrillite inclusion in the same apatite displays smaller enrichment of LREE over MREE and HREE [$(\text{La}/\text{Y})_{\text{N}} = 2.4\text{-}3.1$, $(\text{La}/\text{Yb})_{\text{N}} = 4.9\text{-}5.2$, Table 1]. Na-merrillite analyzed by Shearer et al. (2015) shows similar relative enrichments but with lower abundances.

Monazite-, and chevkinite-perrierite-bearing lithic clast. Among six polished sections, only one such clast was observed. This clast is about 300 μm by 400 μm . Based on the BSE image (Fig. 2), we estimate a mode of 72 vol.% Na-rich ($\text{Or}_{9\text{-}25}\text{Ab}_{85\text{-}68}$) and 17 % K-rich alkali-feldspar ($\text{Or}_{87\text{-}90}\text{Ab}_{11\text{-}8}$, Table S3), ~4 % apatite, 3 % augite ($\text{En}_{38\text{-}48}\text{Wo}_{42\text{-}38}$, Table S3), ~2 % intergrown monazite and chevkinite-perrierite (compositions in Table 3), ~1 % Fe oxide, and ~1 % zircon. The Na-rich and K-rich alkali-feldspars form irregular boundaries with each other. Based on the mineral mode, this clast can be classified as an alkali-feldspar syenite or trachyte. Using modal percentages and nominal densities, we estimated that the bulk composition of the clast has ~59 wt% SiO_2 and ~10 wt% $\text{Na}_2\text{O} + \text{K}_2\text{O}$; if this were a fair representation of a bulk igneous rock, it would be classified as a benmoreite (or trachyandesite as in Santo et al., 2015) and constitute the extreme silica-rich end of igneous rocks on Mars (see Stolper et al. 2013). This clast contains less pyroxenes than trachyandesite clasts reported by Santos et al. (2015), although compositions of feldspars and pyroxenes are comparable. Similar feldspar dominant clasts with magnetite were reported in a paired meteorite NWA 7475 by Wittmann et al. (2015), but details are not available.

The monazite and chevkinite-perrierite grains occur within a small region (~10 μm by 10 μm) inside the lithic last. This region consists of ≤ 1 μm -wide anhedral monazite and chevkinite-perrierite grains set in a finer-grained matrix of mixed silicates and submicron REE-minerals

(Fig. 2). Monazite and chevkinite-perrierite grains are both Ce- and Nd-rich, [(Ce, Nd, Sm, Y, La)PO₄] for monazite and [(Nd,Ce,Sm,Pr,La,Y,Ca)₄Fe₂(Ti,Al)₃Si₄O₂₂] for chevkinite-perrierite (Table 3). Following the scheme of Macdonald et al. (2012), the association of CaO (1.6-2.9 wt%) and FeO (10.1-7.5 wt%) places NWA 7034 REE-silicate grains in the chevkinite field (Fig. 6a), although an unambiguous identification requires structural analysis. Correlations among FeO, CaO-MgO-Al₂O₃, and Σ La₂O₃-Sm₂O₃ place NWA 7034 chevkinite-perrierite in the field of terrestrial mafic and intermediate igneous rocks (Fig. 6c), which is also consistent with the bulk composition of the clast.

The CI-chondrite-normalized REE patterns of monazite and chevkinite-perrierite in the lithic clast reveal distinctive La and Ce depletions relative to Pr and Nd with (La/Nd)_N = 0.2-0.4, which contrasts with the monotonic decrease from La to Nd in monazite inclusions and in most terrestrial samples, which have (La/Nd)_N >>1 (Fig. 5c - 6b). Such depletion is not an artifact of matrix subtraction as the depletion was present in both minerals and the matrix used for correction (Table 3). Both monazite and chevkinite-perrierite in the lithic clast show no clear Eu anomaly when Eu content is above the detection limit.

Xenotime. The xenotime-bearing clast contains severely altered pyrite, ilmenite and zircon (Fig. 3 and Table 4). Ilmenite contains ~16 mol% hematite, similar to compositions reported by Santos et al. (2015). Anhedral zircons with a crackled interior and no Cl excitation mainly reside in a zone that bisects the clast (Fig. 3a). The clast also contains a small lithic portion with perthite (Ab₈₅Or₉ in Ab₁₂Or₈₇ host) and interstitial anhedral augite (En₅₁Wo₂₇, Aug 2 in Fig. 3). Isolated diopside grains (En₃₆₋₄₁Wo₄₄₋₄₆) are scattered through the matrix of the clast (Aug1 in Fig. 3). One EMP analysis of the matrix shows a low total (83 wt%) with 77 wt% FeO (assuming all Fe is Fe²⁺), ~4 wt% SiO₂, 1 wt% MgO, 0.8 wt% CaO, and ~0.3 wt% TiO₂. SEM EDS

analysis of the matrix shows that it is highly variable, and can contain P_2O_5 , S, and Al_2O_3 at >1 wt% level.

A few subhedral to euhedral xenotime grains are located along a grain boundary between altered pyrites and in close proximity to a zircon grain (Fig. 3). The xenotime grain has an average formula of $(Y_{0.7}Dy_{0.09}Gd_{0.05}Er_{0.05})PO_4$. Concentrations of U and Pb are below EMP detection limits; the concentration of Th is 1292 ppm with 6% relative error (Table 2). The CI-chondrite-normalized REE abundances of NWA 7034 xenotime (Fig. 5d) display a characteristic depletion in LREE with a small negative Eu anomaly of 0.9.

Discussion

In the following sections, we evaluate the possible influence of terrestrial weathering, and, because NWA 7034 and 7533 are conglomerates with clasts of variable provenances, we assess the formation conditions of each texturally distinctive REE-mineral. In the absence of a framework (experimentally or field based) established by martian REE-minerals, terrestrial and lunar samples form the primary basis for assessing the formation of rare-earth minerals in NWA 7034 and 7533.

Terrestrial weathering. NWA 7034 and 7533 are desert finds with obvious signs of terrestrial alteration (e.g., Ca-carbonate in fractures). Neither the monazite-chevkinite-perrierite-bearing lithic clast, nor monazite inclusions in isolated apatites are associated with calcite veining or impact fractures that might have provided access to terrestrial fluids. Moreover, the ≥ 1 Ga ages of monazite inclusions and the positive δD values ($> +490$ ‰) of the apatite hosts lends strong support for these grains being of martian origin.

Xenotime resides in the alteration, similar to that of pyrite (Fig. 3). The terrestrial-like D/H values of pyrite alteration suggest that pyrite was likely altered on Earth (e.g., Lorand et al.,

2015). However, pyrite does not contain significant HREE as a viable source for xenotime. Zircons in the sample may have supplied Y, HREE and P, as these elements can substitute for Zr and Si (Finch and Hanchar, 2003) and zircons in the xenotime-bearing clast contain significant Y_2O_3 (2-5 wt%, Tables 2 and 4). Moreover, all zircons in the xenotime-bearing clast are highly altered as shown by their anhedral shapes (Fig. 3) and very weak cathodoluminescence (CL dark). Together with the observed intergrowth of a subhedral xenotime crystal in an altered zircon and the close association of the xenotime cluster with zircons, these observations indicate that xenotime grains precipitated from a fluid that reacted with zircon. If zircons in the clast were altered but not recrystallized on Mars, xenotime may form by terrestrial alteration of these zircons. However, it is unclear desert environment is efficient for xenotime formation. Furthermore, the zircons and apatite in NWA 7034 and 7533 show apparent annealing events of the sample at ~1.4 to 1.7 Ga, and some of zircons were metamict before annealing (Yin et al., 2014; Nemchin et al., 2014). Therefore, considering evidence from pyrite (Lorand et al., 2015) and monazite inclusions, xenotime is likely formed on Mars by hydrothermal alteration of metamict zircons. The compositions of monazite, chevkinite-perrierite and xenotime reflect those of martian environments.

Formation of monazite inclusions in apatite in NWA 7034 and 7533.

Based on our results, monazite clusters in F-rich regions of NWA 7034 and 7533 apatite, the CL texture and F distribution of apatite, and the low Th and U contents of monazite inclusions are most consistent with the formation of monazite inclusions in apatite in these samples through secondary process, involving hydrothermal/metasomatic fluid interaction with chlorapatite. The F-rich regions in apatite from NWA 7034 and 7533 do not cross-cut the chlorapatite host (e.g., Fig. 1, S3, and S4), suggesting additional chlorapatite precipitation after the fluid-apatite reac-

tion. Monazite precipitation likely occurred before apatite was enclosed in NWA 7034 and 7533 because of the common occurrence of fresh isolated apatite grains and igneous apatite in lithic clasts. In contrast, Fe-O veins cross-cut apatite (Fig. 1c and S3b), whether with or without monazite and merrillite inclusions, suggesting they formed after the formation of monazite.

Dissolution of apatite and precipitation of monazite by a metasomatic or hydrothermal fluid at temperatures $>100^{\circ}\text{C}$ has been proposed to be the formation mechanism for monazite inclusions in terrestrial apatite found in a wide range of rock types (e.g., Boudreau and McCallum, 1990; Harlov et al., 2002; Harlov, 2011; and supplementary citations). In terrestrial examples, alteration of chlorapatite produces F- and OH-rich apatite (e.g., Boudreau and McCallum, 1990; Harlov et al., 2002), and monazite with generally low U and Th contents (Harlov, 2015). Models and experiments show that aqueous fluids (pure H_2O , or F-bearing, or pure CO_2) of neutral pH can induce monazite inclusions in chlorapatite and result in acidic fluids (e.g., Boudreau and McCallum, 1990; Harlov et al., 2002; and supplementary citations). However, the experiment using pure CO_2 did not produce observable changes in chlorapatite hosts (Harlov et al., 2002). Therefore, although martian atmosphere is mostly CO_2 rich since 4.0 Ga ago, the fluid that altered the chlorapatite in NWA 7034 and 7533 is likely aqueous with F and Cl.

The chemistry of monazite inclusions formed by dissolution/precipitation is controlled by the host phases (Harlov, 2015). Terrestrial monazite inclusions show strong MREE-HREE depletions with $(\text{La/Y})_{\text{N}}$ of 31-800, whereas the unaltered apatite displays $(\text{La/Y})_{\text{N}}$ of 2.3-35 (e.g., Boudreau and McCallum, 1990; Harlov et al., 2002). Martian monazite inclusions show less MREE-HREE depletion with $(\text{La/Y})_{\text{N}}$ of 5-16 (Fig. 5b), where as the host apatite contains $(\text{La/Y})_{\text{N}}$ of 2.4. The strong MREE-HREE depletion in terrestrial samples can be reproduced experimentally (e.g., Harlov et al., 2002; and Harlov and Föster, 2003 in supplementary citations).

Therefore, the MREE-HREE depletion in martian monazite may reflect different temperatures, pressures, or fluid compositions. In the case that merrillite is also present, it is possible that a fluid reacted with both apatite and merrillite. This is supported by the presence of F-rich apatite cross-cutting merrillite (Fig. 1c, S3). However, experimental studies of monazite formation from fluid-merrillite reactions have not been conducted.

Formation of monazite and chevkinite-perrierite in the lithic clast.

The CI-chondrite-normalized REE patterns of monazite and chevkinite-perrierite in the lithic clast (Fig. 2) differ fundamentally from monazite inclusions in isolated apatite grains, suggesting a different origin. The textural association of monazite and chevkinite-perrierite in NWA 7034 is uncommon in terrestrial rocks and the La-Ce depletion relative to Pr and Nd in monazite and chevkinite-perrierite in NWA 7034 is rare for both phases in terrestrial igneous rocks (e.g., MacDonald et al., 2012; Muhling et al., 2014; and supplementary citations); LREE depletions are observed in detrital monazite grains of suspected metamorphic origin (Triantafyllidis et al., 2010), and for chevkinite-perrierite in some gneisses and granulite-facies rocks described by Belkin et al. (2009).

Coexisting anhedral monazite and chevkinite-perrierite in a matrix containing REE-phases and silicates in NWA 7034 (Fig. 2) can, in principle, have formed as the breakdown products of a pre-existing phase. Based on observed modes, phase compositions by EDS, the area with monazite and chevkinite-perrierite has an aluminosilicate bulk-composition, with CaO, FeO, TiO₂, P₂O₅, and LREE as the principal components (Table 3). The unstable condition of this pre-existing phase could be induced by changes in temperature and pressure, or the introduction of a fluid.

Formation of xenotime in a lithic clast.

The xenotime-bearing pyrite-ilmenite clast is a rare type in NWA 7034 and paired rocks, as previous studies have not reported similar clasts (Santos et al., 2015; Wittmann et al., 2015) and we observed only one in the six sections we studied. As discussed above, we regard that xenotime is most likely formed by hydrothermal alteration on Mars. The low Th and U concentrations of NWA 7034 xenotime are consistent with terrestrial xenotime of a non-igneous origin (Hetherington et al., 2008; Tartèse et al. 2015). In terrestrial rocks, hydrothermal and metamorphic xenotime generally contains lower Yb relative to Gd and Dy than do igneous grains (e.g., Tartèse et al. 2015). The composition of xenotime in NWA 7034 lies at the low Yb end of the terrestrial field (Fig. 3c), similar to terrestrial hydrothermal and metamorphic occurrences.

Experiments show that zircon dissolution is substantially faster in fluids with neutral to high pH than it is in pure H₂O (e.g., Ayers et al, 2012). Lorand et al. (2015) postulated the presence of high pH (6 < pH < 10) H₂S-HS-rich fluids from which NWA7533 pyrite precipitated at 400-500 °C. Based on disturbances in the U-Pb isotopic system of zircons, Lorand et al. (2015) further suggested pyrite formation at ~1.4 Ga. Additional ages of zircons suggest the disturbance may have occurred at 1.7 Ga and ~1.4 Ga, the younger age roughly coeval with the ~1.35 Ga formation age of phosphates with and without monazite in NWA 7034 and 7533 (Humayun et al., 2014; Yin et al., 2014; Bellucci et al., 2015). The presence of altered pyrite in the xenotime-bearing clast in association with altered zircon may be a consequence of a high pH S-rich fluid that also induced xenotime formation. If so, further insight could be gained through solution (apatite-merrillite) – precipitation (monazite) experiments using Lorand et al.'s (2015) proposed fluids as a starting point.

Implication of martian crustal environments

As discussed above, monazite inclusions and xenotime are most likely formed through fluid-phosphate and fluid-rock reactions at elevated temperatures. We propose that the alteration occurred in the source rocks before their incorporation into NWA 7304/7533, because 1) other igneous clasts with apatite of similar composition in these samples do not display the same type of alteration that formed monazite [examples in Fig. S5 and those in Santos et al. (2015) and Wittmann et al. (2015)]; 2) the presence of unaltered apatite of the same composition as monazite-hosting apatite in NWA 7034 and 7533; and 3) monazite inclusions are not associated with terrestrial weathering. Considering that the monazite-bearing apatite, the monazite-chevkinite-perrierite-bearing trachyandesite (no pyrite) and the xenotime-bearing clast are likely to be derived from different protoliths, our results further suggest the existence of hydrothermal events in different locations within the martian crust. An alternative scenario in which alteration of apatite and zircons in the xenotime-bearing clast occurred after assembly of the NWA 7034 breccia seems much less likely because of the absence of any cross-cutting veins indicating the existence of the required fluids.

Among martian meteorites, only nakhlites of a comparable age (~1.3 Ga, Nyquist et al., 2001) host direct evidence for aqueous alteration (e.g., Treiman et al., 1993; Bridges and Schwenzer, 2012 in supplementary citations). However, the clay minerals and evaporites found in fractures in these meteorites are thought to have formed at a later time by fluids liberated from nearby impacts (e.g., Treiman et al., 1993). The hydrogen isotope compositions of monazite-bearing apatite ($\delta D = +496 - +870\text{‰}$) in NWA 7034 and 7533 are broadly similar to high values observed by Hallis et al. (2012) in the Fe-rich clay in Nakhla ($\delta D = +1165 \pm 86\text{‰}$), consistent with a martian crustal fluid.

Ages of two monazite inclusions from this study (1.0 and 1.1 Ga) are broadly similar to the formation of merrillite and apatite (1.35 Ga, Yin et al., 2014; Bellucci et al., 2015), as well as resetting ages of zircons (1.4-1.7 Ga) in NWA 7034 and 7533 (Nemchin et al., 2014; Yin et al., 2014). The much older date of one monazite inclusion (~2.8 Ga) indicates that at least some material in the source region of the NWA 7034 breccia survived the hydrothermal events from 1.0-1.7 Ga. Since NWA 7034 and pairs appear to have sampled diverse rock types, we hypothesize that hydrothermal events were wide-spread in the martian crust at ≥ 1 Ga. The fluid of elevated temperature may be derived from multiple large impacts or magmatic intrusion(s).

Low-grade metamorphism (diagenesis to prehnite facies) and hydrothermal alteration of the martian crust occurred on Mars in both Noachian and Hesperian periods based on various hydrated silicates detected from orbit, reflecting possible impacts or magmatic activity (Ehlmann et al., 2011). In NWA 7034 and 7533, metasomatic and metamorphic indicator phases such as serpentine, prehnite, or opaline silica are absent, although Muttik et al. (2014) reported fine-grained saponite (<50 nm) of uncertain origin along pyroxene boundaries. Rare-earth-element minerals in NWA 7034 and 7533 provide indirect evidence of hydrothermal activities at >1 Ga, that occurred at least locally in the relatively cold Mars of the Amazonian period. Local sources of heat could be sufficient to produce these phases; metamorphic events of regional significance are not required.

REE-minerals in NWA 7034 and 7533 have important ramifications for Mars exploration. We know from orbital and landing missions that the martian crust is enriched in alkali elements (e.g., McSween et al., 2009). The MSL mission, for example, has identified highly evolved rocks with high alkali contents, some of which are similar to the clasts of NWA 7034 and pairs (e.g., Grotzinger et al., 2015). Our results of REE-minerals in NWA 7034 and 7533 (e.g., the

trachyandesite clast) demonstrate that REE-minerals may be a minor but important component in martian crust and, as on the Earth, they can be locally important ore minerals (Chakhmouradian and Wall, 2012). Several studies hypothesize that impact craters could generate the hydrothermal environments necessary for the formation and deposit of ore minerals (e.g., West and Clarke, 2010). Our finding of these minerals forming with hydrothermal fluids emphasizes impact craters being the potential sites for finding resources.

Summary

We report monazite-(Ce) inclusions in apatite, monazite-(Ce,Nd) and chevkinite-perrierite-(Ce,Nd) in a trachyandesite clast, and xenotime-(Y) in a pyrite-ilmenite-zircon clast in martian breccia meteorites NWA 7034 and 7533. The most common occurrence is anhedral monazite-(Ce) inclusions in apatite. Occasionally, monazite-bearing apatite also contains zoned, irregular merrillite inclusions (Na-rich center to REE-rich rims). Monazite-bearing apatite is also occasionally associated with alkali-feldspar and oxide. Cathodoluminescence imaging and X-ray maps of monazite-bearing apatite reveal F-rich apatite mantles monazite or merrillite inclusions and cross-cuts merrillite inclusions, also forms irregular boundaries with the chlorapatite host. Near merrillite, they can be virtually pure fluorapatite. Outer portions of apatite hosts are chlorapatite, similar to detrital apatite grains or euhedral crystals in lithic clasts in the same sample. The U-Th-Pb contents of monazite are low (summing to <1 wt%), and those above detection limits suggest they form on Mars at ~1 Ga or older. Based on petrographic context, terrestrial data and the chemistry of martian monazite inclusions, the most likely formation mechanism is precipitation associated with dissolution of merrillite and/or apatite by a fluid at elevated temperatures (>100 °C).

Anhedral monazite-(Ce, Nd) and chevkinite-perrierite-(Ce, Nd) are intergrown in a matrix of submicron REE-phases and silicates included in a trachyandesite clast. Monazite and chevkinite-perrierite display unusual La and Ce depletions relative to Sm and Nd $[(\text{La}/\text{Nd})_{\text{N}} = 0.2-0.4]$, the opposite for monazite inclusions and those in most terrestrial occurrences, which have $(\text{La}/\text{Nd})_{\text{N}} \gg 1$.

Xenotime-(Y) resides in a highly altered pyrite-ilmenite-zircon clast with a small amount of silicate. Xenotime contains low U and Th, and low Yb relative to Gd and Dy, a feature typical of hydrothermally formed xenotime on the Earth. Zircons are the most likely source of Y and HREE. The highly altered zircon suggests that Y and HREE may be released from zircon through reaction with fluid.

On the basis of relatively fresh apatite grains and lithic clasts, we propose that fluid-rock/apatite reactions occurred in the source rocks prior to their inclusion in NWA 7034 and 7533. Our results imply the presence of hydrothermal fluids in the martian crust at 1 Ga or older, which were induced by either impacts or large igneous intrusions. The potential association of REE mineralization with impacts suggests concentrated REE-mineral deposits (potential re-source) may occur near impact craters.

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Table 1. Representative composition of monazite (corrected for apatite contamination) and merrillite inclusions in apatite.¹

Monazite Inclusions ²							Merrillite Inclusions (Fig. 1c)					
wt%	NWA 7034 (Fig. 1b)			NWA 7533 (Fig. 1c)			Na-mer		REE-mer			d.l. (wt%)
P ₂ O ₅	31.9	32.5	31.0	32.0	31.6	30.7	44.6	44.8	42.4	42.8	45.2	0.06
Na ₂ O	0.12	0.13	0.16	0.14	0.04	0.07	2.04	2.03	0.16	0.18	1.98	0.03
MgO	0.14	0.21	0.22	0.21	0.81	0.30	3.59	3.58	3.35	3.34	3.59	0.01
CaO	1.25	1.79	0.10	0.88	0.13	0.12	45.1	44.9	39.1	39.7	44.8	0.03
Y ₂ O ₃	4.96	5.47	7.85	6.11	8.61	10.8	0.81	0.61	3.12	2.71	0.66	0.12
La ₂ O ₃	11.3	10.4	9.61	10.4	9.64	8.31	0.27	0.28	1.06	1.20	0.29	0.04
Ce ₂ O ₃	25.1	24.2	23.9	24.7	23.1	20.5	0.76	0.79	2.86	3.18	0.73	0.04
Pr ₂ O ₃	2.95	2.90	3.21	3.29	3.07	2.67	0.10	0.13	0.37	0.48	0.12	0.03
Nd ₂ O ₃	14.3	13.7	14.4	13.7	14.0	14.5	0.51	0.49	2.01	2.13	0.53	0.04
Sm ₂ O ₃	2.97	3.01	2.89	3.05	3.15	3.82	0.18	0.15	0.59	0.51	0.13	0.09
Eu ₂ O ₃	0.57	0.59	0.54	0.53	0.57	0.71	b.d.	b.d.	0.12	b.d.	b.d.	0.09
Gd ₂ O ₃	2.63	2.55	3.16	2.68	2.46	3.66	0.17	0.15	0.64	0.61	0.11	0.10
Dy ₂ O ₃	1.25	1.82	2.01	1.50	1.87	2.60	0.14	0.16	0.53	0.59	0.18	0.11
Er ₂ O ₃	0.45	0.58	0.71	0.55	0.66	1.12	0.08	0.04	0.27	0.19	b.d.	0.10
Yb ₂ O ₃	b.d.	0.20	0.21	0.19	0.26	0.23	0.12	b.d.	0.15	0.16	b.d.	0.10
Total	100	100	100	100	100	100	98.4	98.2	96.7	97.8	98.5	
Apt re- moved	0.25	0.61	0.64	0.21	0.36	0.67						
Cation	<i>4O</i>	<i>4O</i>	<i>4O</i>	<i>4O</i>	<i>4O</i>	<i>4O</i>	<i>28O</i>	<i>28O</i>	<i>28O</i>	<i>28O</i>	<i>28O</i>	
P	1.015	1.020	0.999	1.015	1.002	0.986	6.957	6.988	6.988	6.985	7.017	
Na	0.009	0.010	0.012	0.010	0.003	0.005	0.730	0.727	0.059	0.066	0.704	
Mg	0.008	0.012	0.013	0.012	0.045	0.017	0.987	0.982	0.972	0.961	0.981	
Ca	0.050	0.071	0.004	0.035	0.005	0.005	8.909	8.868	8.153	8.190	8.811	
Y	0.099	0.108	0.159	0.122	0.172	0.218	0.079	0.060	0.323	0.278	0.065	
La	0.157	0.142	0.135	0.144	0.133	0.117	0.018	0.019	0.076	0.085	0.020	
Ce	0.345	0.328	0.333	0.339	0.316	0.285	0.051	0.053	0.204	0.224	0.049	
Pr	0.040	0.039	0.045	0.045	0.042	0.037	0.034	0.032	0.139	0.146	0.034	
Nd	0.192	0.181	0.195	0.184	0.187	0.197	0.006	0.009	0.026	0.034	0.008	
Sm	0.038	0.039	0.038	0.039	0.041	0.050	0.012	0.010	0.040	0.034	0.008	
Eu	0.007	0.008	0.007	0.007	0.007	0.009	0.010	0.009	0.041	0.039	0.007	
Gd	0.033	0.031	0.040	0.033	0.031	0.046	0.008	0.010	0.033	0.037	0.010	
Dy	0.015	0.022	0.025	0.018	0.023	0.032	0.005	0.002	0.016	0.012	0.003	
Er	0.005	0.007	0.009	0.006	0.008	0.013	0.007	0.004	0.009	0.009	0.004	
Yb	0.001	0.002	0.002	0.002	0.003	0.003	0.005	0.004	0.000	0.030	0.004	
Total	2.016	2.020	2.014	2.012	2.018	2.020	17.8	17.8	17.1	17.1	17.7	
H ₂ O (ppm) ³							156±5					
δD (‰) ³							+496 ±68					

¹ b.d., below detection. d.l. is the detection limit at 99% confidence calculated based on counting statistics using the Probe for EMPA program.

² Monazite data are renormalized after removing apatite host contamination (see text). The fraction of apatite removed is given.

³ SIMS analysis for OH and δD with 1σ uncertainties. δD (‰) is calculated as [(D/H)_{sample}/(D/H)_{VSMOW} - 1]*1000.

Table 2. Concentrations of Th, U, Pb and Y in selected monazite inclusions (no correction for apatite contamination), xenotime, and calculated ages¹.

Detection limit (ppm)			109		115		92		170	
			Th	1 σ	U	1 σ	Pb	1 σ	Y	1 σ
Age (Ma)	1 σ (Ma)		ppm	%	ppm	%	ppm	%	wt%	%
<i>Monazite (Mnz) in apatite (ap) Fig. 1b</i>										
7034 Mnz	1094	257	1123	5	708	7	177	23	0.44	2
7034 Cl-ap			b.d.		b.d.		b.d.		b.d.	
<i>Monazite in apatite in Fig. S3c3</i>										
7034 Mnz			700	8	1136	4	b.d.		8.48	0.3
<i>Monazite in apatite in Fig. S3c4</i>										
7034 Mnz	2770	370	439	11	536	9	353	11	2.37	1
7034 Cl-ap			350	13	b.d.		b.d.		0.098	
<i>Monazite-merrillite(mer) in apatite in Fig. 1c</i>										
7533 Mnz	999	195	802	7	1337	5	243	19	4.26	0.5
7533 RE_mer			b.d.		b.d.		b.d.		2.33	0.7
7533 Cl-ap			237	19	300	16	b.d.		b.d.	
7533 Cl-ap			b.d.		b.d.		b.d.		b.d.	
7533 F-ap			b.d.		b.d.		b.d.		0.12	
<i>Monazite-merrillite in apatite in Fig. S3a</i>										
7533 Mnz			b.d.		1009	6	b.d.		5.93	0.4
7533 Mnz			b.d.		b.d.		b.d.		4.69	0.4
7533 Cl-ap			b.d.		b.d.		b.d.		0.051	15
<i>Monazite in apatite associated with the lithic clast Fig. S4a</i>										
7034 Mnz			284	17	254	21	b.d.		2.79	0.6
7034 Cl-ap			296	15	b.d.		346	12	0.12	6
<i>Xenotime (Xtm) in Fig. 3</i>										
Zircon (Zrn)			732		b.d.		b.d.		4.05	0.4
Xtm			b.d.		b.d.		1014	6	23.3	0.2
<i>Other Zircon²</i>										
Isolated grain with no alteration			b.d.		b.d.		b.d.		0.093	10
Grain with dark CL and round inclusions			245		b.d.		b.d.		0.23	4

¹The 1 σ uncertainties for elemental concentrations were derived from counting statistics. The 1 σ uncertainties of ages were calculated by error propagation. b.d., below detection.

Table 3. Representative SEM EDS analysis of monazite (Mnz) and chevkinite-perrierite (C-P) in Figure 2 after correction for matrix contamination.

Point ²	Mnz 1	Mnz 2	Mnz 3	Mnz 4	C-P 1	C-P 2	C-P 3	Matrix ²	Recon. ⁴
P ₂ O ₅ (wt%)	30.6	28.4	26.9	25.9			1.71	0.99	2.52
Na ₂ O								2.26	1.98
MgO					1.26	1.30	1.25	0.67	0.67
CaO	0.03	0.58	0.42		1.89	2.88	1.59	6.66	5.96
Al ₂ O ₃	0.62		0.13	0.48	3.52	3.40	4.34	17.7	15.8
SiO ₂	0.33	1.58	0.01	0.98	19.3	19.5	19.8	43.1	39.2
TiO ₂					14.7	15.6	13.1	4.10	4.62
FeO					9.88	7.50	10.1	3.42	3.69
Y ₂ O ₃	4.35	2.40	1.21	2.38	3.48	3.61	1.97	2.15	2.36
La ₂ O ₃	4.10	4.15	5.05	2.71			3.64		0.22
Ce ₂ O ₃	23.4	23.0	27.4	23.3	15.1	13.6	18.3	5.80	7.39
Pr ₂ O ₃	3.77	3.82	5.97	4.63	3.86	3.70	2.19	1.54	1.82
Nd ₂ O ₃	27.6	24.6	25.0	24.4	18.9	18.9	18.2	7.20	9.12
Sm ₂ O ₃	5.27	7.59	5.06	5.26	5.50	5.62	3.81	3.21	3.48
Eu ₂ O ₃		1.23	1.61						
Gd ₂ O ₃		2.74	1.26	3.56	2.65	4.40		1.22	1.26
Dy ₂ O ₃				3.00					
Ho ₂ O ₃				3.42					
Er ₂ O ₃									
Tm ₂ O ₃									
Yb ₂ O ₃									
Total	100	100	100	100	100	100	100	100	100
Fraction of Matrix removed	0.20	0	0.06	0.12	0.04	0.15	0.08		
Cation	<i>40</i>	<i>40</i>	<i>40</i>	<i>40</i>	<i>220</i>	<i>220</i>	<i>220</i>		
P	0.989	0.943	0.937	0.904			0.292		
Na									
Mg					0.390	0.401	0.378		
Ca	0.001	0.025	0.019		0.417	0.634	0.344		
Al	0.028		0.007	0.023	0.855	0.821	1.030		
Si	0.013	0.062		0.040	3.996	3.997	3.998		
Ti					2.274	2.408	1.985		
Fe					1.706	1.285	1.694		
Y	0.089	0.050	0.027	0.052	0.383	0.393	0.211		
La	0.058	0.060	0.077	0.041			0.271		
Ce	0.327	0.331	0.413	0.352	1.137	1.017	1.350		
Pr	0.052	0.055	0.090	0.070	0.290	0.276	0.160		
Nd	0.377	0.345	0.368	0.359	1.394	1.379	1.306		
Sm	0.069	0.103	0.072	0.075	0.391	0.397	0.264		
Eu		0.016	0.023						
Gd		0.036	0.017	0.049	0.181	0.299			
Dy				0.040					
Ho				0.045					
Er									
Tm									
Yb									
Total	2.003	2.025	2.048	2.051	13.4	13.3	13.3		

¹Analytical points are shown in Figure 2. ²Matrix composition was analyzed using an area scan as shown in Figure 2. ³Reconstructed composition was estimated based modal analysis of the region in Figure 2b with ~5 wt% monazite, 7 wt% chevkinite-perrierite, and 90 wt% matrix.

Table 4. Representative EMP and SEM EDS analysis of minerals in Figure 3.

EMP ¹			EMP ²						EDS		EMP	
wt%	Xtm	Xtm	Ilm ³		Aug1	Aug2	Fsp1	Fsp2	Zrn		Py	
P ₂ O ₅	37.6	36.2	SiO ₂	0.05	50.7	54.0	67.0	65.1	SiO ₂	31.1	Fe	47.1
Na ₂ O	0.19	0.12	TiO ₂	44.6	0.68	0.64			TiO ₂		S	53.4
MgO	0.07	0.08	Al ₂ O ₃	0.06	1.94	5.42	19.0	18.5	Al ₂ O ₃	0.56		
CaO	1.18	0.81	CaO	0.09	23.0	11.1	1.38	0.31	CaO	0.25		
			FeO ^T		9.15	11.6	0.28	0.87	FeO ^T	2.17		
Y ₂ O ₃	37.8	41.0	Fe ₂ O ₃	17.2					MnO			
Nd ₂ O ₃	0.43	0.51	FeO	29.2					MgO			
Sm ₂ O ₃	1.25	1.27	MnO	2.57	0.12	0.44			Na ₂ O			
Gd ₂ O ₃	5.28	4.34	MgO	4.40	13.9	14.9			K ₂ O			
Dy ₂ O ₃	8.09	8.18	Na ₂ O	<0.02	0.22	0.51	9.77	1.27	ZrO ₂	63.0		
Er ₂ O ₃	5.74	4.55	K ₂ O	<0.01	0.06	0.68	1.53	14.4	HfO ₂	1.02		
Yb ₂ O ₃	2.42	2.69	BaO	0.90			<0.04	0.05	Y ₂ O ₃	1.94		
Total	100	100	Total	98.8	99.8	99.4	99.9	100.9	Total	100	Total	100.5
Cation	40	40		30	60	60	80	80		40	atom%	
P	1.039	1.012	Si	0.001	1.911	1.980	2.955	2.978	Si	0.967	Fe	33.6
Na	0.012	0.007	Ti	0.837	0.019	0.018			Ti		S	66.4
Mg	0.003	0.004	Al	0.002	0.086	0.234	1.035	0.997	Al	0.020		
Ca	0.041	0.029	Fe ^T		0.288	0.355	0.010	0.049	Fe	0.056		
Y	0.656	0.722	Fe ³⁺	0.323					Mn			
Nd	0.005	0.006	Fe ²⁺	0.608					Mg			
Sm	0.014	0.014	Mn	0.058	0.004	0.014			Ca	0.008		
Gd	0.057	0.048	Mg	0.164	0.782	0.815			Na			
Dy	0.085	0.087	Ca	0.002	0.927	0.435	0.065	0.015	K			
Ho			Na	0	0.016	0.037	0.835	0.115	Zr	0.953		
Er	0.059	0.047	K	0	0.003	0.032	0.086	0.843	Hf	0.009		
Yb	0.024	0.027	Ba	0.009				0	Y	0.016		
Total	1.997	2.008		2.000	4.036	3.919	4.987	4.998		2.029		
					En	39	51	Ab	85	12		
					Wo	46	27	Or	9	87		

¹ Original EMP totals of xenotime (Xtm) are low (68 to 80 wt%), but the calculated formula are close to the expected value, suggesting that the low totals are caused by small sizes and a non-phosphate matrix. Here we reported oxide data normalized to 100%.

² Detection limits for silicates (Aug, augite; Fsp, feldspar) are the same as in [Table S3](#).

$^3\text{FeO}^{\text{T}}$ is total iron assuming all Fe is Fe^{2+} . For ilmenite, Fe^{3+} was estimated by charge balance, which corresponds to a hematite component of ~16 mol%.

Fig. 1a

Fig. 1b

Fig. 1c

Figure 1. BSE, CL, and composite elemental X-ray maps of monazite-(Ce)-bearing chlorapatite (Ap) grains. Host apatite grains are sensitive to electron probe beams (circular spots in BSE, dark ones in CL images). (a) A monazite-bearing chlorapatite in NWA 7034, its upper top region showing Fe-oxide veins. Monazite (Mnz) inclusions are in the F-rich region. (b) A subhedral monazite-bearing chlorapatite in NWA 7034. The high magnification image of the red box shows the anhedral shape of monazite. (c) Chlorapatite with an irregular merrillite (Mer) that enriches in REE (RE-mer) toward the boundary with apatite. F-rich apatite cross-cuts and surrounds merrillite. Monazite grains are located in RE-mer and in F-rich apatite (Fig. S3), and show no association with the Fe-rich veins. Numbers in BSE images label the EMP locations of host apatite reported in Table S1.

Figure 2. BSE images of the monazite (Mnz) and chevkinite-perrierite (C-P) bearing lithic clast. (a) Overview of the clast, consisting of feldspar (Fsp), augite (Aug), chlorapatite (Cl-Ap), and zircon (Zrn). Numbers in the images mark the EMP analysis of silicates in [Table S3](#). The red box marks the location of (b), the area with monazite and chevkinite-perrierite. (c) An enlarged image of the area in (b). Numbers mark the SEM-EDS analysis in [Table 3](#). Box outlines the matrix analyzed.

Figure 3. BSE images of a xenotime-(Y) (Xtm) and zircon (Zrn) bearing clast in NWA 7034 (a-b) and compositions of xenotime compared to lunar and terrestrial examples (c). (a) Overview of the clast. Zircons are circled in red dotted curves. Compositions of minerals are listed in Table 4. Aug, augite; Fsp, feldspar; Ilm, ilmenite; Py, pyrite. (b) Enlarged image of the area in the red box in (a), showing clusters of xenotime and a xenotime in zircon. (c) Ternary plot of molar Gd, Dy, and Yb in NWA 7034 xenotime (stars) and terrestrial occurrences (colored dots, triangles and squares are from Tartèse et al., 2015). The gray arrow shows the suggestion by Tartèse et al. (2015) that Yb is generally lowest in hydrothermal xenotime, and highest in igneous xenotime, and intermediate for metamorphic and diagenetic grains.

Figure 4. Apatite in NWA 7034 and 7533, compared to those from other NWA 7034 apatite and those in other martian meteorites (McCubbin and Jones, 2015).

Figure 5. The REE and Y abundances in monazite inclusions and xenotime, normalized to the CI-chondrite (Anders and Grevesse, 1989). Y is plotted in place of Ho, which has a similar ionic radius but was not analyzed. Analytical precisions calculated using counting statistics are shown in (a) if larger than symbols, but omitted in others for clarity. The horizontal lines with a downward arrow indicate the EMP detection limit for that element. Dashed lines indicate missing elements. (a) Monazite inclusions in NWA 7034/7533 compared to granites in Zhu and O’Nions (1999), and lunar samples (Lovering et al., 1974; Jolliff, 1993). (b) Monazite inclusions compared to monazite inclusions in fluorapatite (Harlov, 2011) and chlorapatite (Boudreau and McCallum, 1990). (c) Monazite in NWA 7034 clast (Fig. 2) compared to those in terrestrial igneous and metamorphic rocks (Spear and Pyle, 2002; Catlos 2013). (d) NWA 7034 xenotime compared to those in pegmatites and metamorphic rocks in Spear and Pyle (2002).

Figure 6. Chemistry of NWA 7034 chevkinite-perrierite. (a) FeO and CaO in chevkinite-perrierite. The solid line separating chevkinite and perrierite is suggested by Macdonald et al. (2012). (b) The REE and Y abundances in chevkinite-perrierite are normalized to the CI-chondrite (Anders and Grevesse, 1989) and compared to the literature data. (c) Comparison of NWA 7034 chevkinite-perrierite with the literature data. Data source: Macdonald et al. (2012), Muhling et al. (2014), and additional references in the supplementary file.