Regolith breccia Northwest Africa 7533: Mineralogy and petrology with implications for early Mars

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Abstract—Northwest Africa 7533, a polymict Martian breccia, consists of fine-grained clast-laden melt particles and microcrystalline matrix. While both melt and matrix contain medium-grained noritic-monzonitic material and crystal clasts, the matrix also contains lithic clasts with zoned pigeonite and augite plus two feldspars, microbasaltic clasts, vitrophyric and microcrystalline spherules, and shards. The clast-laden melt rocks contain clump-like aggregates of orthopyroxene surrounded by aureoles of plagioclase. Some shards of vesicular melt rocks resemble the pyroxene-plagioclase clump-aureole structures. Submicron size matrix grains show some triple junctions, but most are irregular with high intergranular porosity. The noritic-monzonitic rocks contain exsolved pyroxenes and perthitic intergrowths, and cooled more slowly than rocks with zoned-pyroxene or fine grain size. Noritic material contains orthopyroxene or inverted pigeonite, augite, calcic to intermediate plagioclase, and chromite to Cr-bearing magnetite; monzonitic clasts contain augite, sodic plagioclase, K feldspar, Ti-bearing magnetite, ilmenite, chlorapatite, and zircon. These feldspathic rocks show similarities to some rocks at Gale Crater like Black Trout, Mara, and Jake M. The most magnesian orthopyroxene clasts are close to ALH84001 orthopyroxene in composition. All these materials are enriched in siderophile elements, indicating impact melting and incorporation of a projectile component, except for Ni-poor pyroxene clasts which are from pristine rocks. Clast-laden melt rocks, spherules, shards, and siderophile element contents indicate formation of NWA 7533 as a regolith breccia. The zircons, mainly derived from monzonitic (melt) rocks, crystallized at 4.43 ± 0.03 Ga (Humayun et al. 2013) and a 147Sm-143Nd isochron for NWA 7034 yielding 4.42 ± 0.07 Ga (Nyquist et al. 2016) defines the crystallization age of all its igneous portions. The zircon from the monzonitic rocks has a higher Δ17O than other Martian
meteorites explained in part by assimilation of regolith materials enriched during surface alteration (Nemchin et al. 2014). This record of protolith interaction with atmosphere-hydrosphere during regolith formation before melting demonstrates a thin atmosphere, a wet early surface environment on Mars, and an evolved crust likely to have contaminated younger extrusive rocks. The latest events recorded when the breccia was on Mars are resetting of apatite, much feldspar and some zircons at 1.35–1.4 Ga (Bellucci et al. 2015), and formation of Ni-bearing pyrite veins during or shortly after this disturbance (Lorand et al. 2015).

INTRODUCTION

Since the Viking mission (1976), a vast amount of information has been obtained on Mars. Its geology and geochemistry have been studied using orbiters, rovers, and the SNC meteorites. Orbiting visible/infrared spectrometers, for example, OMEGA/MEx, have led to the production of global maps showing the distribution of olivine, pyroxene, hydrated minerals, and ferric iron oxides (Mustard et al. 2005; Poulet et al. 2005, 2007; Ody et al. 2012). Infrared detection of plagioclase and its variability has clarified rock types: TES spectra suggested that the crust of Mars was not purely basaltic (Bandfield et al. 2000; McSween et al. 2003), and CRISM spectra (Carter and Poulet 2013; Wray et al. 2013) indicated plagioclase-rich rocks showing that magmatic evolution must have been complex. Oxides of ferric iron are dominant in the spectra for the northern hemisphere while abundant orthopyroxene is found only in the southern heavily cratered uplands of Noachian age. Maps of secondary minerals have given rise to the concept of changing climate and alteration style with time (Bibring et al. 2006), with the more abundant evidence of (less acid) water in the Noachian (phyllosian alteration), making this period the most favorable for the development of life. More recently, higher resolution spectral data have given detailed pictures of local geologic history (Murchie et al. 2009). Carter et al. (2013) reported occurrences of 10 hydrated minerals, including the discovery of epidote, giving evidence for hydrothermal activity. The residual heat associated with large impact craters is likely to have generated hydrothermal systems, possibly accompanied by freezing of crater lakes, with interesting biochemical possibilities (Newsom 1980; Osinski et al. 2001, 2013; Abramov and Kring 2005).

Rovers have provided in situ bulk rock analyses on Mars (e.g., McSween et al. 2009; Sautter et al. 2016). Basaltic andesite was found in Ares Vallis by the Pathfinder mission (McSween et al. 1999, 2003) and picritic basalt at Gusev by Spirit (Gellert et al. 2004). These rocks are usually interpreted as volcanic in nature, but there is always the question of whether the analyses represent pristine or altered volcanic rocks, or volcanic debris in sedimentary rocks, or impact rocks (Ashley and Delaney 1999; McSween et al. 2003; Schultz and Mustard 2004). Curiosity is currently making many fascinating observations at Gale Crater. These include descriptions of polymict fragmentary two-feldspar-rich rocks of either sedimentary or impact origin (Mangold et al. 2013), and analyses of a rock with the chemistry of mugearite, that is, basaltic trachyandesite (Gellert et al. 2013; Stolper et al. 2013; Schmidt et al. 2014). Sautter et al. (2014) have described many feldspar-rich samples, and have deconvolved the data using major-element ratios to show that orthopyroxene, augite, plagioclase, and orthoclase are present.

Martian meteorites have been subjected to very complete analysis, particularly of isotope abundances, which cannot be measured by rovers, and their parent magmas yield information on the mantle of Mars (e.g., Debaille et al. 2007). They might constitute an inverse ground truth for rover analyses where sample preparation and instrument calibration may be difficult. However, the SNC meteorites differ geochemically in some respects from Martian surface materials analyzed in situ (e.g., McSween et al. 2003). Matches between shergottite and surface spectral signatures have been reported for certain regions (Ody et al. 2015). However, the largest group of Martian meteorites, the shergottites, has very young radiometric ages, whereas basalts mineralogically similar to shergottites emplaced in Gusev Crater in the Hesperian date from ~3.65 Ga based on crater counting (Greeley et al. 2005; McSween et al. 2006). Mineral isochrons for the shergottites give very young ages, typically <200 Ma (Nyquist et al. 2001; Borg et al. 2005; Bouvier et al. 2008; Niihara et al. 2012), and they may therefore come from such very restricted regions. There has been controversy over the formation ages of shergottites (Bouvier et al. 2008) but young ages have recently been confirmed by dating Zr-rich phases in shergottites (Niihara et al. 2012; Moser et al. 2013). Based on crater counting on high-resolution images, volcanic calderas on Mars vary greatly in age (Robbins et al. 2011). Volcanism continued until a little
over a hundred million years ago in a few volcanoes like Olympus Mons. Only the ancient orthopyroxenite ALH 84001, dated at 4.1 Ga (Bouvier et al. 2009; Lapen et al. 2010), has been a candidate to represent the Noachian of the cratered southern uplands. Ody et al. (2015) discuss possible occurrences of similar orthopyroxene-bearing rocks on the Noachian surface. These cratered highlands make up nearly half the surface of Mars, and most of the largest impact structures occur in the oldest part of it (Tanaka et al. 2014). It is surprising that ancient Martian meteorites are not more common and, in view of the extent of the early heavy bombardment on Mars, that breccias have not been prominent among Martian meteorites. This may be related to the efficiency of ejection of weakly lithified material (Hartmann and Barlow 2006).

The first Martian breccia meteorite identified was Northwest Africa 7034 (Agee et al. 2012, 2013; Ziegler et al. 2013; Cartwright et al. 2014) and shortly afterward we obtained Northwest Africa 7533 (Hewins et al. 2013a; Humayun et al. 2013), the subject of this paper. These meteorites, and NWA 7475, NWA 7906, NWA 7907, NWA 8114, NWA 8171 (Korotev et al. 2013; Wittmann et al. 2013a, 2015; Hofmann et al. 2014; MacArthur et al. 2015) are paired. These breccia meteorites are very different from the SNC meteorites, as are known Martian surface rocks (McSween et al. 2003; Stolper et al. 2013; Sautter et al. 2014) and, because of the diverse clast suite, can potentially yield much information on the early crust of Mars. They form an important window on a previously unsampled and probably major lithologic unit of Mars. A first impression of NWA 7533, with which we concurred, was that it was "fiendishly complex" (McSween 2013). However, we are now inclined to agree with Simonds et al. (1977) that "breccias aren't so bad after all." NWA 7533 has yielded evidence of formation in a regolith, of the nature of early crustal reservoirs, of zircon crystallization at 4.428 Ga, and of atmosphere-hydrosphere-surface interaction before this time (Hewins et al. 2013a, 2013b; Humayun et al. 2013; Nemchin et al. 2014). We therefore present here an account of the petrologic components in this polymict breccia in the context of the new discoveries stemming from this important find.

**SAMPLES AND METHODS**

A 17 g sample of NWA 7533 was cut without using any lubricating fluids (no water) at the Muséum National d'Histoire Naturelle (MNHN). Seven polished sections (7533-1 to -7) and one doubly polished transparent thick section (7533-LM, ≥50 μm, unmounted) were prepared and studied using optical microscopy, scanning electron microscopy (SEM), and electron probe microanalyzer (EPMA). They are in part serial polished sections, usually too thick for identifying the same object in two sections. Backscattered electron (BSE) maps and images of selected clasts were made at MNHN using a Tescan VEGA II LSU SEM in conventional mode (mainly 15 keV and <20 nA), and minerals were characterized with an SD3 (Bruker) EDS detector. A Zeiss Sigma field emission SEM with GEMINI technology using a SmartSEM® interface and an Oxford 50 mm² detector was used at Laboratoire de Géologie, Ecole Normale Supérieure, Paris; high-resolution imaging was done on polished sections 7533-1 and -2 at 15 keV and 8.4 nA. X-ray maps were made on both SEM instruments. All quantitative mineral analyses were made by wavelength-dispersive spectrometry on the Cameca SXFive electron microprobe at the Université Paris VI, generally using 15 keV and 10 nA. For analysis of Ni in silicates, we used 20 kV and 300 nA, counting for 100 s on three WDS simultaneously (Hewins et al. 2014). San Carlos, Chassigny, and Eagle Station olivines and Tatahouine pyroxene (Jarosewich et al. 1980; Smith et al. 1983; Barrat et al. 1999; El Goresy et al. 1999; De Hoog et al. 2010), were analyzed as internal standards. The detection limit, based on count rates on peak and background above and below the peak, is a probability function considering the risk of treating positive as zero, and vice versa, at the 95% confidence level, and is 24 ppm Ni in our pyroxene.

Powder diffraction data were collected on a Bruker D2 Phaser diffractometer equipped with a Lynxeye CCD detector. X-rays, were generated by a copper cathode (λ = 1.54060 Å – 30 kV/10 mA) and the Kα radiations isolated with a Cu Kβ filter. The sample holder rotation speed was 20 rotations/min and a numeric filter was applied to the data set in order to minimize the iron fluorescence contribution.

Transmission infrared spectra were measured on 7533-LM in an environmental cell with a Bruker Hyperion FTIR spectrometer in the 500–4000 cm⁻¹ range with a 4 cm⁻¹ resolution. Diffuse visible and near infrared reflectance spectra were measured using the spectrophoto-goniometer available at IPAG.

Three fine-grained matrix areas were extracted as focused ion beam (FIB) sections (~100 nm thick) using an FEI Strata DB 235 at IEMN at the University of Lille, France. They were studied by transmission electron microscopy (TEM) with an FEI Tecnai G2-20 Twin (LaB6, 200 kV) and a Philips CM30 (LaB6, 300 kV) at the electron microscopy center of the University of Lille, France. Both instruments use an energy dispersive spectrometer (EDS) for elemental microanalysis.
D/H ratios of pyrite alteration products were analyzed on 7533-LM on the NanoSIMS installed at MNHN Paris by Lorand et al. (2015). A 30 pA Cs⁺ primary beam was used to collect H⁻ and D⁻ secondary ions in multicolonction mode on a 20 × 20 µm² surface area at a raster speed of 1 ms/pixel. Instrumental fractionation was corrected using a terrestrial goethite sample with a D/H isotopic composition of ~−150‰.

One polished section 7533-3 was studied by laser ablation inductively coupled plasma–mass spectrometry (LA-ICP-MS) for elemental abundances. Analyses were performed with a New Wave UP193FX (193 nm) excimer laser ablation system coupled to a Thermo Element XR at the Plasma Analytical Facility, FSU. A total of 73 elements, including all major elements (Humayun et al. 2010), S and Cl, were determined simultaneously in low-resolution mode using methods previously described (Humayun et al. 2007; Gaboardi and Humayun 2009). Standardization utilized 6 MPI-DING glasses, 3 USGS silicate glasses, NIST SRM 610, SRM 1263a steel, the iron meteorites North Chile (Filomena) and Hoba, and a pyrite (for S). Beam spots were 50–150 µm ablated at 50 Hz, using either spot or raster mode.

Zr-rich phases were located by X-ray mapping of 7533-4 and analyzed by SIMS. U-Pb isotopic analyses of zircon were performed on a sensitive high-resolution ion microprobe (SHRIMP II) at Curtin University, as described in Humayun et al. (2013). Oxygen isotope ratios were obtained using a Cameca IMS1480 ion microprobe at the Swedish Museum of Natural History (Nemchin et al. 2014) using 1 nA Cs⁺ primary beam with an impact energy of 20 kV and operating at a mass resolution sufficient to resolve 17O⁻¹¹ from 16O⁻¹⁻ (M/ΔM = 7500). The U-Pb apatite analyses were performed on the same instrument with a −13 kV molecular oxygen beam and operating at a mass resolution (M/ΔM) of 5400 (Bellucci et al. 2015). The Pb isotopic composition of plagioclase and alkali feldspar were determined using a 9 nA O₂⁻ primary beam and a mass resolution of 4860 (M/ΔM).

PROVENANCE OF THE METEORITE

The NWA 7533 breccia has mineralogical, chemical, and isotopic properties consistent with a Martian origin and similar to those of NWA 7034 and NWA 7475 (Agee et al. 2013; Hewins et al. 2013a, 2013b; Humayun et al. 2013; Nemchin et al. 2014; Wittmann et al. 2015). The bulk oxygen isotopic composition by IR-laser fluorination/mass spectrometry are δ²⁰⁸O = 5.92; δ¹⁸O = 3.65; Δ¹⁷O = 0.57 (all per mil) and the magnetic susceptibility, log X = 4.45 (Gattacceca, personal communication), are indistinguishable from NWA 7034 values (Agee et al. 2013). This material is very different from the SNC meteorites (Agee et al. 2013; Hewins et al. 2013a, 2013b; Humayun et al. 2013), as are many Martian surface rocks analyzed by rovers (McSween et al. 2009; Stolper et al. 2013; Sautter et al. 2014).

Noble gas isotope data show the presence of a trapped gas component in NWA 7034 like the modern Martian atmosphere (Cartwright et al. 2014) and this is the clearest isotopic evidence for a Martian origin for these regolith breccias. The oxygen isotope data are complex: an orthopyroxene mineral separate exhibited Δ¹⁷O of 0.33‰, indistinguishable from SNC compositions (Ziegler et al. 2013), confirming a Martian origin. However, there is an overall trend of increasing Δ¹⁷O with increasing δ¹⁸O in NWA 7034 separates, toward the composition of known Martian alteration phases, and Nemchin et al. (2014) found Δ¹⁷O values in NWA 7533 zircons ranging from within error of the Mars Fractionation Line (MFL) to +2.16 ± 0.56‰. We discuss below the implications for the Martian atmosphere and regolith. The FeO/MnO ratio for all pyroxenes in NWA 7533 is ~34, except for those in clast-laden melt rocks (see below), like that of ALH 84001 pyroxene, and this is also a Martian signature.

The bulk breccia composition is equivalent to alkali basalt formed by 4% partial melting of primitive mantle (Humayun et al. 2013) recycled into a suite of rocks in this early crust. It cannot be said to be simply basaltic, in that it contains pyroxenitic, noritic, and monzonitic material. It is not simply related to the SNC meteorites: they contain olivine, except for the most fractionated shergottites, whereas olivine is almost entirely absent from the breccia. SNC are volcanic and subvolcanic rocks, but NWA 7533 contains material deposited on the surface, such as melt spherules, and lithic clasts of rocks crystallized at depths possibly up to kilometers. Noritic clasts in the breccia contain inferred pigeonite (whereas pigeonite is widely preserved in SNC) with exsolution lamellae many microns thick, compared to only hundreds of nanometers in SNC pyroxenes. The breccia contains higher concentrations of siderophile elements than the SNC, for the same Mg content (Humayun et al. 2013), and its sulfides are of hydrothermal origin (pyrite) rather than magmatic origin (pyrrhotite) in the SNC (Lorand et al. 2015). While the SNC are relatively young rocks (Amazonian), this black and white breccia NWA 7533 is a major repository of geochemical information on early Mars, along with ALH 84001, and some of the rocks analyzed by Curiosity at Gale Crater. As it is very diverse lithologically, we sketch our view of the breccia and its components in Fig. 1. We present below observations and data first for the matrix, followed by sections on
spherules and shards, lithic and crystal clasts. The lithic material is described in a sequence of increasing grain size: clast-laden melt rocks, microbasaltic clasts, clasts with zoned pyroxenes, and noritic- monzonitic clasts.

THE BRECCIA COMPONENTS AND MATRIX

The breccia is complex with a variety of crystal clasts, inclusions, and crystal types, contained in breccia matrix and in aphanitic melt rock bodies. We discuss the matrix here and subsequently present results by lithological type of object. A cut slab is shown in Fig. S1 in supporting information and an Mg Kα X-ray map of a polished section (7533-2) in Fig. 2, in which feldspars are dark gray and pyroxenes are medium to light gray. Both show spherules, melt rock bodies, lithic clasts, and crystal clasts. Figure 2 shows a feldspar-rich melt spherule 3 mm in diameter and a spherule fragment with olivine and pyroxene dendrites, estimated at about 6 mm in former diameter, as well as smaller crystal and monzonitic and microbasaltic lithic clasts. The hosts of the smaller clasts are twofold, clast-laden aphanitic bodies and matrix, which are hard to distinguish at this scale, although breccia matrix tends to be brighter, that is, more Mg-rich (Fig. 2). The aphanitic bodies, interpreted below as clast-laden melt rocks with fine-grained igneous textures (~10 μm crystals), and other clasts are embedded in very fine-grained (~1 μm) compact crystalline breccia matrix.

The melt rock bodies, spherules, and lithic clasts occur with crystal clasts down to at least 5 μm, all supported by a matrix with 200 nm to 2 μm grains. This matrix is crystalline and annealed, rather than a clastic aggregate, and it was studied in detail by field emission (FE) SEM in sections 7533-1 and -2. It is composed mainly of anhedral micron-sized plagioclase feldspar, with pyroxene grains down to a few hundred nm surrounding and embedded in feldspar (Figs. 3a and S2 in supporting information). The pyroxene is somewhat clustered into tiny aggregates (Fig. S2d) between plagioclase grains. Fe-rich phases, especially magnetite and probably maghemite, may be symplectitic or lacy, and are irregularly distributed in the matrix, especially in pyroxene. Microprobe analyses of minerals in the matrix are of low quality because of the small grain size although they are sufficient to identify pyroxenes and calcic plagioclase similar to those in the melt rocks. Analytical transmission electron microscope (ATEM EDS) analyses are shown in Table S1 in supporting information. For plagioclase, they suffer from low cation totals. Since Ca correlates well with Si and Al, but Na does not, likely due to migration under the TEM beam, endmembers were calculated using Si and Al atoms per formula unit (a.f.u.) to define An, for example, An% = 100*(Al a.f.u −1), K to define Or, and obtaining Ab by difference. The matrix also contains some vugs (Lorand et al. 2015; Leroux et al. 2015) associated with pyrite veins.
The matrix was also studied by TEM on FIB sections (Figs. 3b and S2c). It is a granoblastic assemblage with low-Ca pyroxene and feldspar grains with an average grain size close to 300 nm (Leroux et al. 2015). Although some well-equilibrated triple junctions are observed, as for NWA 7034 (Muttik et al. 2014a), most grains have preserved an irregular morphology. Intergranular porosity is also high, in particular, at triple junctions (Figs. 3b and S2c). The low-Ca pyroxenes range from En$_{64}$ to En$_{74}$ and contain a high density of planar defects on (100) corresponding to thin alternating domains of clino- and orthopyroxene. Most of the feldspar grains are plagioclase (from An$_{14}$ to An$_{57}$) with minor alkali feldspar. Three grains of Cl-rich apatite >1 μm in size are present in the FIB section and one of them contains dislocations organized along regular subgrain boundaries or deformation bands. Fe-oxides, for which the electron diffraction patterns are compatible with magnetite and maghemite, are distributed throughout the matrix. The grain size ranges from 1 μm to a few nm. Large Fe-oxides are located in the pyroxene-feldspar grain boundaries, including triple junctions, and the smaller ones may occur within the pyroxene grain interiors. Most of the grain boundaries are unusually thick (10–20 nm) and filled with a low-density amorphous material very sensitive to the electron beam (Fig. S2). The composition of the grain boundaries is close to those of the adjacent minerals but enrichments in SiO$_2$, Al$_2$O$_3$, CaO, and Cl were frequently detected (Leroux et al. 2015). The amorphous state could be the result of beam damage and, because of a smectite-like composition, the high e-beam sensitivity could be due to the presence of water. The amorphous material may be related to the decomposition of pyroxene into silica and Fe-oxide that has been identified in pyroxene clasts (Leroux et al. 2016), but another plausible explanation is alteration in hot desert conditions (Leroux et al. 2015). HRTEM analyses of the matrix of NWA 7034 also showed minor phyllosilicates (<50 nm) on pyroxene grain boundaries (Muttik et al. 2014a; LPSC 2763), but the identification of phyllosilicates was not confirmed in this study.

**FINE-GRAINED CLASTS**

**Clast-Laden Impact Melt Rock**

The largest objects (~1 cm) in NWA 7533 are smooth or angular fine-grained melt bodies (Fig. 2), containing lithic and crystal fragments. They include oval and aerodynamically shaped bodies (Hewins et al. 2013a; Humayun et al. 2013), which are particles of clast-laden melt rocks (Grieve et al. 1974; Simonds 1975). Similar material, clast-rich amoeboid vitrophyre, is the dominant component in NWA 7475 (Wittmann et al. 2015), and the “plumose” groundmass with clasts described in NWA 7034 (Agee et al. 2013) is probably the same. A croissant-shaped body in 7533-1 appears to be sculpted by transport while partially molten (Humayun et al. 2013). The melt rock is a fine-grained plagioclase -pyroxene igneous rock mainly with subophitic texture and the aspect ratio of the plagioclase laths (mostly 1–2 μm wide) is ~10. Where pyroxene grains are parallel to plagioclase laths, the texture is more fasciculate. The textures of the melt rock are shown in Figs. 4a–d and S3 in supporting information. Finer grained melt rocks have abundant small crystal clasts (Fig. 4a), angular to more rounded than in breccia matrix. Coarser grain size (~30 μm long)
is associated with fewer crystal clasts and the presence of lithic clasts (Fig. 4b). Angular lithic clasts in the melt rock are up to ~1 mm long.

The finer grained melt rocks are remarkable in containing ellipsoidal aggregates or clusters of orthopyroxene granules or dendrites (with embedded magnetite, chromite, ilmenite, or pyrite) surrounded by rings of plagioclase laths which radiate outward from the pyroxene cluster (Figs. 4a and 4c). We have described examples of this pyroxene-plagioclase association as clot-aureole structures (Hewins et al. 2013a; Humayun et al. 2013). The most obvious ellipsoidal objects are around 100 μm in size, but many smaller ones (down to ~30 μm) are recognized in X-ray maps (Figs. 4c, S3c, and S3d), especially Si Kα and RGB composite images (Fig. S4a) extend into the plagioclase aureoles, in which plagioclase laths extend into the groundmass. The pyroxene dendrites may be attached to the pyroxene of the groundmass. A Ca Kα map demonstrates that all the fractures in the clumps (dark in Figs. 4c and 4d) are filled with calcite (Fig. S4c). Figures S3c, S3d, and S4b also show chemical heterogeneity in the groundmass, with Mg-versus Al-rich zones or schlieren. Zones with few clumps are richer in plagioclase and poorer in pyroxene, that is, more Al-rich, than zones with many clumps, which are Mg-rich.

Microprobe analysis of minerals in the groundmass of the melt rock is difficult because of the small grain size. Good analyses of pyroxene, however, are
consistently magnesian and show moderate Al\textsubscript{2}O\textsubscript{3} (2–3 wt\%) and TiO\textsubscript{2} (up to 1 wt\%) contents. The results are shown in the pyroxene quadrilateral (Fig. 5a) and Table S2 in supporting information. The analyses for 12 melt bodies in 4 sections are very similar and have a nearly constant Mg number of 69 ± 2. The continuity in Ca concentrations (Wo 1.8 – 47.4) suggests mixtures of orthopyroxene and augite, which is confirmed by BSE and X-ray images. However, the clumps are dominantly orthopyroxene En\textsubscript{68.1} ± 1.3Fs\textsubscript{29.5} ± 1.3Wo\textsubscript{2.4} ± 0.3, whereas the groundmass pyroxene is on average more Ca-rich (En\textsubscript{52.3} ± 6.1Fs\textsubscript{23.3} ± 4.3Wo\textsubscript{24.4} ± 12.9). The clump orthopyroxene is close in major-element composition to ALH 84001 orthopyroxene, which we show in this (Fig. 5a) and subsequent pyroxene quadrilaterals to emphasize similarities (and differences in the case of the more fractionated rocks). However, it is more Al-rich (2.9 ± 0.9 wt\% Al\textsubscript{2}O\textsubscript{3}) than ALH 84001 pyroxene and other orthopyroxenes in the breccia, and also extremely Cr-poor (0.03 wt\% Cr\textsubscript{2}O\textsubscript{3}). Furthermore, whereas pyroxene in the breccia generally has an FeO/MnO ratio of ~34, with scattered high Mn exceptions, pyroxene in the clast-laden melt rocks is consistently more Mn-rich than this typically Martian value, with an FeO/MnO ratio of ~25 (Fig. 5b). The plagioclase is mainly andesine, An\textsubscript{56–32} (An\textsubscript{41} ± 7), and not significantly different in the aureoles surrounding the clumps than in the groundmass (Fig. 5c, Table S3 in supporting information). It is similar in composition to that in the less fractionated lithic clasts.

**Shards and Melt Spherules**

Orthopyroxene-rich objects probably related to the melt rock clumps occur as clasts in the meteorite matrix, and tend to have an irregular or polygonal form. Most have concave surfaces bounded by plagioclase with the orthopyroxene dendrites in the interior (Figs. 6a and S5a in supporting information). These appear to be shards of fine-grained vesicular melt rock or devitrified glass. Other shard-like clasts have a foliated or spherulitic appearance. Rare small spherules resembling droplets of the clump material are described below. The mineral compositions of the shards are like those of the clumps, and some are included in Tables S2, S3, and Fig. 5.

Large melt spherules are prominent on the sawn surfaces of this breccia (e.g., Figs. 2 and S1) and of paired meteorites (e.g., Agee et al. [2012] fig. 1; Wittmann et al. 2015 fig. 1). The spherules can be grouped into three types: vitrophyric, crystalline, and altered. The largest spherules (diameters of several mm) are vitrophyric, although their groundmass is not glassy but finely crystalline (grain size 1–5 μm) with pyroxene and feldspar laths in fine spherulitic to variolitic textures (e.g., Figs. 6b–d). The spherule 7533-2-2 in Figs. 6b and 6c is 3 mm in diameter, with a groundmass speckled with submicron Fe-rich phase(s), including Cr-bearing magnetite and chromite, especially just under its surface, and it develops coarsely crystalline patches near its borders. It has no large dendrites and is traversed by
veins of plagioclase and hyalophane (Figs. 6b and 6c) consistent with hydrothermal activity. Another veined feldspar-rich spherule (7533-7-sph1; Fig. S5b) has a Na-depleted signature consistent with melting of an altered, clay-bearing protolith (Humayun et al. 2014c). Oval objects with a patchy texture, in some cases with a vitrophyric interior region, have more coarsely crystalline dendritic/spherulitic borders with pigeonite and subcalcic augite (Fig. S5b), in turn coated with probable accretionary rims. Similarly, spherules in NWA 7475 tend to preserve quenched mesostasis in their interiors (Wittmann et al. 2015). Sampling of nonequatorial sections of larger spherules and differences in alteration may account for variations in the appearance of spherules, which require detailed study.

Olivine occurs in NWA 7533 only in one melt spherule 74533-2-2 (Fig. 2) as long chain dendrites (Fig. 6d) along with long pyroxene dendrites. In NWA 7034, olivine dendrites occur in a large partial spherule, but also as one grain in a microbasalt, probably in reaction relationship with pyroxene (Santos et al. 2015a). Plagioclase occurs as small insets in the olivine dendrites. The olivine dendrites are bordered by orthopyroxene that is continuous with pyroxene alternating with plagioclase in the spherulitic groundmass (Fig. 6d). A similar object from NWA 7034, a vitrophyre with olivine dendrites (Agee et al. 2013; Udry et al. 2014), has a high Na/K ratio and resembles the more basaltic components of the breccia. The derivation of the spherules from both clay-rich and
basaltic sources suggests an analogy with S-type and I-type granites. Smaller spherules (a few hundred μm in diameter) are more coarsely crystalline. In texture and mineralogy, these show resemblances to aspects of clast-laden melt rocks, for example, clumps and groundmass (Figs. S5c and S5d).

Mineral compositions for spherules are shown in Fig. 7, and Tables S4 and S5 in supporting information. For olivine-bearing spherules, olivine (Fo_{74-65}) and pyroxene (En_{69}Wo_{2-En_{63}}Wo_{3}) compositions are shown in Fig. 7a, along with selected data for the similar material in NWA 7034 (Agee et al. 2013; Udry et al. 2014). The pyroxene in the latter is similar (En_{71}Wo_{2-En_{49}}Wo_{9}) but more zoned, and the olivine is more ferroan (Fo_{65-53}; Udry et al. 2014) than that in 7533-2-2. Pyroxenes from a small finely crystalline spherule, 7533-1-ENS (see Fig. 10c), are also shown: they are orthopyroxene En_{71,9}Fs_{25,6}Wo_{2,5} and augite En_{35,1}Fs_{18,0}Wo_{46,9}. As shown in Fig. 7a, the orthopyroxene in the small spherule is similar to that in the vitrophyric spherules in 7533-2 and -7, as is its plagioclase, but augite has also crystallized. The orthopyroxene is in all cases quite close in composition to that of ALH 84001.

For the 3 mm extremely fine-grained spherule in section 2, we have only vein feldspar analyses, in part mixtures of plagioclase An_{41,8}Ab_{23,5}Or_{30,6}Ch_{0,3} and halloysite An_{4,5}Ab_{20,4}Or_{63,7}Ch_{11,4}. These are shown in Figs. 7b and 7c, along with plagioclase from four other spherules, none of which have Ba-rich feldspar. The vein feldspar in 7533-7-1 is mainly plagioclase similar in composition to all the other plagioclase, for example, the spherule with olivine dendrites (An_{33,8}Ab_{62,6}Or_{3,6}) and the small 7533-1 ENS plagioclase An_{39,6}Ab_{58,5}Or_{1,9}. The latter also contains chromite Sp_{19,1}Chr_{56,8}Us_{1,4}Mg_{2,4}. Analyses of oxide minerals for spherules and all other clast types are shown in Table S6 in supporting information.

**Fine-Grained Igneous Clasts**

NWA 7533 contains basaltic clasts with grains ~50 μm to ~100 μm (Fig. 8) and subophitic to granoblastic textures, which we have called microbasalts (Hewins et al. 2013a) and analyzed samples plot in the basalt field of an SiO_{2}-Na_{2}O+K_{2}O plot (Humayun et al. 2013). Similar clasts in NWA 7034 were called igneous clasts by Santos et al. (2015a) who classified them as basaltic, andesitic, etc., based on their bulk compositions. They contain pyroxenes, plagioclase, oxide minerals, chlorapatite, and in some cases K feldspar. They are coarser grained than the groundmass of the clast-laden melt rocks, and, according to Santos et al. (2015a, 2015b) have grains typically 200 μm or less in their longest dimension. Crystal clasts are rare in this material, but their occasional presence (Fig. S6a in supporting information) suggests that the microbasalt is clast-poor impact melt, and both of them have similar basaltic and Ni-Ir-rich bulk compositions (Humayun et al. 2013). The microbasalt is not observed as clasts within the clast-laden melt rock. The subophitic texture is illustrated in Figs. 8a and 8b, where pyroxene grains are molded around euhedral plagioclase laths. Plagioclase laths are irregular in size and distribution, with trachytic patches where they are subparallel, in which case a pyroxene grain (pigeonite in Fig. 8b) may range from poikilitic to apparently interstitial. There are also clasts with metamorphic (granoblastic) textures with anhedral plagioclase and chains of pyroxene crystals as shown in Fig. 8c.
The microbasalts, like the clast-laden melt rocks, may contain magnesian orthopyroxene, but pigeonite is also identified with certainty (Table S7 in supporting information). The presence of orthopyroxene versus pigeonite does not correspond to metamorphic versus igneous texture, and the two phases have a similar range of Fe/Mg ratios. All microbasalt pyroxenes are plotted in Fig. 9a showing that their most magnesian compositions are close to those of ALH 84001, and of melt rock pyroxenes. Pyroxene compositions for individual clasts in six polished sections are shown and discussed in Fig. S7 in supporting information. The rocks tend to have either orthopyroxene or pigeonite, with only one clast augite-rich. Orthopyroxene extends to more Mg-rich compositions than pigeonite but otherwise the composition ranges are similar. One clast, 7533-2-84, has both zoned pigeonite and zoned augite, like coarser grained rocks described below and shergottites.

Plagioclase has a composition range of An\textsubscript{55-23} in 15 clasts of microbasalt from 5 sections, with little variation between clasts or in %Or (Fig. 9b; Table S8 in supporting information). A sixteenth clast, 7533-2-84, the one with zoned pigeonite and augite; however, it has a similar range of Ca/Na ratios (An\textsubscript{50-24}) but is enriched in K, up to Or\textsubscript{22} (Fig. 9b), probably due to small grains or exsolution blebs of K feldspar in andesine. A seventeenth clast (7533-7-MH4; Fig. S6b) contains discrete K feldspar (Or\textsubscript{84}; Fig. 9b); its pyroxene is also fractionated although it is orthopyroxene. Such clasts may have basaltic andesite major-element compositions (Santos et al. 2015a, 2015b) and they have mineralogical similarities to the medium-grained rocks with zoned pyroxenes discussed below. Fe-rich oxide compositions are shown in Fig. 9c and Table S6. The spinel is Fe-rich, but contains significant Cr and Ti, with a composition range Ch\textsubscript{11-13} and Us\textsubscript{1-29} with an outlier at Us\textsubscript{63}.

Fig. 8. BSE images showing textures of microbasalts: (a) subophitic 7533-2-cent3; (b) poikilitic-intersertal 7533-4-L; (c) granoblastic 7533-1-obj2. (d) Mg Kz image of layered sedimentary clast containing pyroxene (light gray) and feldspar (dark gray) with mudstone-size and clay-size layers.
magnetite and ilmenite are present and, as for other ilmenite-rich clast types (zoned-pyroxene and monzonitic), indicate \( f_O^2 \) 2–3 log units above the FMQ buffer (Table S9 in supporting information).

**Sedimentary Clasts**

Fine-grained clasts in NWA 7533 with layers a few hundred microns in thickness are interpreted as sedimentary in origin. They have clastic textures unlike the granoblastic texture of the fine matrix, with the smallest pyroxene grains independent and not molded around anhedral plagioclase grains. Variations in grain size and mineral abundance (pyroxene versus feldspar) are responsible for this lamination or bedding. One such clast is observed in 7533-2 (Fig. 1b) immediately below and to the left of the 3 mm spherule. A more detailed image, also an Mg K\( \alpha \) map, is given in Fig. 8d, which shows layers of clay-size particles (<4 \( \mu \)m) probably transported in suspension alternating with layers of very fine siltstone- or mudstone-size particles (4–64 \( \mu \)m). The latter are very poorly sorted with both clay-size and larger particles, mainly crystal clasts, up to 100 \( \mu \)m. Indeed, the two flat igneous “pebbles” (2-1521 and 2-84) appear to be part of the sedimentary sequence, as shown in the BSE image Fig. S8 in supporting information. Both BSE and Mg K\( \alpha \) show that there are alternating pyroxene- and plagioclase-rich layers. Similar lithic clasts, with ~100 \( \mu \)m layers, have been observed in NWA 7475 (Wittmann et al. 2015; fig. 17c). The finest grains are similar in size to observed atmospheric dust grains (Lemmon et al. 2004) and we concur with Wittmann et al. (2015) that these may have been eolian dust deposits.

**MEDIUM-GRAINED LITHIC CLASTS**

A major distinction in clast types in the breccia is between fine-grained type described above and those with 1–2 mm grains. We have no barometry for these rocks but they have coarser exsolution features in pyroxene and alkali feldspar than the subvolcanic/hypabyssal SNC meteorites. This suggests slow cooling and we have chosen to use plutonic rock names: they are mainly noritic to monzonitic fragments (Hewins et al. 2013a; Humayun et al. 2013). Plutonic rocks are normally classified by abundance of minerals but here typical crystals and crystal fragments are ~1 mm long and small clasts may be made up of only a few of the possible phases. We have used a combination of phase compositions and associations to make a classification, and use adjectives rather than names to indicate uncertainty in modal abundances. For example, as we are not sure of the K feldspar abundance, some monzonitic clasts could be syenites or diorites. Ca-poor pyroxene is the key mineral for noritic clasts and K feldspar for monzonitic clasts, and both may contain augite and plagioclase. In the absence of the key minerals, plagioclase composition (more calcic in noritic
clasts, more sodic in monzonitic clasts) and spinel composition (Cr-bearing in noritic clasts and Ti-bearing in monzonitic clasts) can be used. Crystal clasts also give clues to lithologic types, and the presence of magnesian orthopyroxene suggests a source from orthopyroxenites (see below). However, in addition to plutonic material, there is a minority of clasts whose strongly zoned pyroxenes suggest a near-surface origin, and we discuss these first.

Clasts with Zoned Pyroxenes

Four clasts contain zoned pyroxenes, pigeonite and augite with no exsolution (Table S10 in supporting information), like those in shergottites and in microbasalt 7533-2-84, plus two feldspar phases and abundant chlorapatite (analyses of phosphates from all clasts types are given in Table S19 in supporting information). NWA 7533-4-K and 7533-1-12 shown in Figs. 10a and 10b, respectively, contain up to 1 mm pyroxene and 500 µm chlorapatite. Accessory phases include Ti-magnetite, ilmenite, a TiO₂ phase, plus late hydrothermal pyrite, and terrestrial alteration in the form of Fe oxyhydroxides and veins with calcite. Clast 1–12 is similar to but has less augite than 4-K.

The feldspars in the medium-grained clasts (Table S11 in supporting information) are very sodic plagioclase An₃₅–₁₈, and homogeneous orthoclase or sanidine Or₆₉–₈₈ (Fig. 11a). The plagioclase in microbasaltic clast 7533-2-84 is also shown; with An₂₀–₂₄ it is more calcic but overlapping the plagioclase in the clasts with zoned pyroxenes. Discrete orthoclase was not recognized in the microbasalt but spikes in the K content of “plagioclase” (Or₂₂) indicate overlaps of the two phases. Oxide phases in the medium-grained clasts (Tables S6 and S9) are Ti magnetite notably poor in Cr, Sp₃₋₅Chr₀.₅–₀.₁UsP₂₃–₁₂Mg₂₆–₁₂, and ilmenite Ilm₈₀–₉₁Hem₁₈–₈. Spinel compositions are plotted in Fig. 11b.

The pyroxene compositions of these clasts are shown all together in Fig. 11c, again with microbasaltic clast 7533-2-84 that has similar mineral compositions despite its texture, and separately in Fig. S9 in supporting information. In clast 4-K, the pyroxenes are pigeonite En₆₀–₃₆Fs₃₁–₅₀Wo₉₈–₁₄ and augite En₄₈–₂₃Fs₅₁–₃₉Wo₂₈–₃₈ (Figs. 11c and S7), like those of shergottites. The unusual microbasalt clast 7533-2-84, with a range of pigeonite compositions, is seen in Fig. S9 to have pigeonite and augite compositions more magnesian on average than, but overlapping with, the compositions of pyroxenes in the four zoned-pyroxene clasts. Some noritic-monzonitic clasts containing both unzoned pigeonite and K feldspar may be related to the zoned-pyroxene rocks.

Noritic-Monzonitic Clasts

Clasts with orthopyroxene or inverted pigeonite, and plagioclase (An₉₅–₇₀), plus augite, Cr-Ti-magnetite, and rarely alkali feldspar, are classed as noritic; those with alkali feldspar as well as plagioclase (An₂₃–₃₀) and augite, plus rare inverted pigeonite, abundant chlorapatite, Ti-bearing magnetite, ilmenite, and zircon, as monzonitic. Orthopyroxene including inverted pigeonite is more abundant in the noritic clasts and augite in the monzonitic clasts, but there is considerable overlap in pyroxene compositions.
between the two types, with pyroxene in monzonite only slightly more ferroan on average. Concentrations of siderophile elements in these clasts indicate crystallization from impact melts (Humayun et al. 2013).

Noritic clasts apparently representing rocks with hypidiomorphic granular textures (Turner and Verhoogen 1951) are illustrated in Figs. 12a, 12b, and S10 in supporting information. The Ca-poor pyroxene may be homogeneous orthopyroxene (Figs. 12b, S10a, and S10b), but inverted pigeonite (Fig. 12a) and rarely pigeonite also occurs (Fig. S10c). Fresher orthopyroxene is more ferroan, and dusty speckled orthopyroxene is more magnesian (OF and OM in Fig. S10a). Augite can be single phase (Fig. S10a), or exsolved (Fig. S10b). Most of the augite grains coexisting with orthopyroxene in other clasts equilibrated at temperatures (Lindsley and Andersen 1983) of 800–900 °C (Fig. S11 in supporting information). Chromite-magnetite is common, and accessories include zircon (Fig. S10a) and chlorapatite (in rare cases overgrown on merrillite or containing lacy monazite, as in Fig. S10c, Table S19).

Monzonitic clasts contain either two homogeneous feldspar phases (Fig. 12d) or plagioclase plus intergrowths (perthitic or antiperthitic; Figs. 12c and 12e). The minority phase occurs as irregularly distributed ragged lamellae or flames. As perthitic feldspar is found only in monzonitic clasts, a crystal clast of perthitic feldspar is automatically monzonitic (Fig. 12c). Most clasts contain subhedral to anhedral augite, partly molded around feldspar grains, but there is also peculiar stringy augite interstitial or subophitic to alkali feldspar laths (Fig. 12e). Euhedral chlorapatite is abundant. Zircon, although present in some noritic clasts, is more abundant in the monzonitic ones (Figs. 12c–e), as is baddeleyite (Fig. 22 discussed below).

Individual mineral analyses are given in Tables S12, S13, S6, and S9, and Fig. S12 in supporting information. Average mineral compositions for lithic clasts are shown in Fig. 13a (feldspars), 13b (pyroxenes), and 13c (spinelS). The separation into two groups is seen well in the feldspar triangle (Fig. 13a), where there is one exception of K feldspar coexisting with calcic plagioclase. Another case of intermediate properties is shown where low calcium pyroxene coexists with calcic plagioclase. Oxide minerals, if present, also serve to distinguish the rock types. Spinel in noritic rocks is Cr-rich or Cr-bearing, whereas those in monzonitic rocks are Ti-bearing (Fig. 13c). SpinelS are also more Al-rich in noritic clasts, up to Sp24. There is a small overlap of the two spinel trends near the magnetite pole.

The monzonitic fragments are enriched in K, REE, P, Ti, Cl, and Zr and contain zircon, and occasionally baddeleyite (Humayun et al. 2013) that have provided a crystallization age for the noritic-monzonitic rocks, as discussed below. Compositions of minerals associated

![Fig. 11. Mineral compositions for four zoned-pyroxene clasts and for 7533-2-84, a slightly fractionated microbasaltic clast; (a) feldspars, (b) Ti-bearing spinels, (c) pigeonite and augite.](image-url)
with zircons are included in Tables S12, S13, and S6. Zircon Z1 (Fig. S10a) is almost completely included by a 300 μm clast rich in pyroxene that is dominantly a fractured ferroan orthopyroxene grain (En_{45.3}Fs_{52.1}Wo_{2.6}). The clast also contains two small grains of plagioclase (An_{39.5}Ab_{57.8}Or_{2.6}) and Cr-bearing magnetite Sp_{3.59}Cr_{1.40}Us_{0.14}Mg_{79.54}. This assemblage is characteristic of the noritic clasts in NWA7533. Zircon Z2 (Fig. S12c) is a skeletal, hopper-shaped crystal (Humayun et al. 2013; Fig. S2) inside a shard of antiperthite. Its shape suggests rapid growth, possibly due to supercooling of the melt. The antiperthite has a bulk composition of An_{2.8}Ab_{69.6}Or_{28.6}, with host An_{2.0}Ab_{96.0}Or_{2.0} and lamellae An_{1.7}Ab_{14.2}Or_{84.1}. Similar feldspars are found in monzonitic clasts in NWA7533 and their exsolution suggests formation at depth, although the patchiness of the coarse lamellae may indicate hydrothermal or deuteric modification, making them unsuitable for cooling rate determination. Figure 12e shows a third monzonitic clast with two analyzed zircons Z5 and Z6, and a fourth baddelyite-bearing monzonitic clast (discussed below in Fig. 22) yields age information from four phases (Humayun et al. 2013; Bellucci et al. 2015).
Individual single-phase feldspar analyses (Table S13) are shown in Fig. 14, along with representative tie-lines for coexisting plagioclase and orthoclase. Tie-lines for exsolved phases in perthite and antiperthite are also shown. Two unusual clasts are shown separately. One (7533-5 C) contains both Ca- and Na-rich plagioclase, suggesting alteration.

Fe-Ti-P-Rich Clasts (FTP)

The second uncommon clast type containing abundant ilmenite and chlorapatite blades, an Fe-, Ti-, and P-rich FTP (Agee et al. 2013; Santos et al. 2015a, 2015b; Nyquist et al. 2016), has only albite-rich feldspar (Fig. 14). However, the analyses of three grains of this anorthoclase feldspar extend between the most sodic plagioclase and bulk antiperthite compositions, resembling a segment of the continuous crystallization trend from plagioclase to alkali feldspar found in some alkali basalts (e.g., Keil et al. 1972). The FTP clasts in our sections are too small and too rare for detailed study.

Crystal Clasts and Rock Types

Crystal clasts are angular anhedral grains distinct from the igneous or metamorphic textured material containing them. The bigger clasts (up to ~2 mm) are dominantly crystal clasts (pyroxenes and feldspars, as well as magnetite-chromite and chlorapatite). Those analyzed are mainly >100 \( \mu \)m, so there are very few derived from the finer grained materials. The compositions of crystal clasts of orthopyroxene, pigeonite, and augite (Table S14) are shown in the pyroxene quadrilateral (Fig. 15). Their average FeO/MnO ratio is 34.5 ± 6. Note that most of the compositions are like those of the noritic-monzonitic rocks, but that the orthopyroxene extends to more magnesian compositions. Orthopyroxene with En\(_{80-74}\) has not been seen attached to plagioclase, although it may be associated with augite and/or chromite. We assume such orthopyroxene-dominated clasts represent orthopyroxenites, and treat them below with crystal clasts.

ALH 84001 (Mittlefehldt 1994) has orthopyroxene compositions falling close to the range of the breccia pyroxenes not known to coexist with plagioclase. The orthopyroxene minor element concentrations of orthopyroxenite ALH 84001 fall in the center of the clouds for NWA 7533 crystal clast orthopyroxene, while its augite on the other hand is at the extremity of the breccia augite range (Fig. S13 in supporting information), probably because augite is a minor phase in ALH 84001 and thus contributions of augite from similar or more magnesian orthopyroxenites to the polymict breccia would be negligible.

To investigate the question of clast provenance, and the possibility of pristine clasts, for example, of orthopyroxenite, we identified the carriers of Ni in the
breccia. The most Ni-rich phase is pyrite with up to 4.5 wt% Ni (Lorand et al. 2015), but this occurs as an accessory mineral. Spinel (chromite-magnetite) is more abundant, and is found in the matrix and most clasts. The more Fe-rich spinels contain \( \sim 0.3 \) wt% NiO (Hewins et al. 2013a, 2013b), and Cr-rich spinels have lower (<1000 ppm) Ni contents (Fig. 16a), approaching those for chromite in ALH 84001 (Gleason et al. 1997).

Ni analyses for silicates are given in Table S15 in supporting information. The Ni contents of silicate standards (Jarosewich et al. 1980; Smith et al. 1983; Barrat et al. 1999; El Goresy et al. 1999; De Hoog et al. 2010) were easily measured at 20 KeV with error bars (SD of replicates) bracketing literature values for those with the lowest concentrations, olivine in Eagle Station and orthopyroxene in Tatahouine (Fig. 16b). The average compositions of 11 orthopyroxene crystal clasts (plus one augite and two pigeonites), plus pyroxenes in lithic clasts, are shown in Fig. 16c. Excluding two high values (possibly from noritic rocks), the crystal clasts, mostly magnesian orthopyroxene, have Ni concentrations (mean 21 ppm, SD 13) close to the detection limit and to the Ni content of orthopyroxene from ALH 84001, consistent with an origin in pristine crustal rocks. The pyroxenes in plagioclase-bearing lithic clasts have between 100 and 800 ppm Ni, mean 299, SD 184 (excluding 2 clasts with low values), like those in the groundmass of clast-laden melt rock.

Inverted pigeonite is common as crystal clasts, but augite with exsolved Ca-poor pyroxene is less abundant (Hewins et al. 2013a, 2013b; Humayun et al. 2013). Lamellae are generally up to about 8 \( \mu \text{m} \) wide (Figs. S14a and S14b in supporting information). Exceptionally they are \( \sim 50 \) \( \mu \text{m} \) wide (Fig. S14c). Analyses of hosts and lamellae are given in Table S16 in supporting information. Composition profiles across the inverted pigeonite and augite of Figs. S14a and S14b are shown in Figs. 17a and 17b. These are top-hat profiles, with no concentration gradients. Compositions of coexisting phases are shown in the pyroxene quadrilateral and of augite in the Lindsley-Andersen geothermometer plot (Figs. S15a and S15b in supporting information). Despite the equilibrium suggested by the top-hat profiles, the estimated temperatures range from 700 to 900 °C, possibly due to excavation of hot rocks.
Feldspar clasts (Table S17 in supporting information) include plagioclase An\textasciitilde{54–31}, anorthoclase, K feldspar, plus perthite and antiperthite (Table S18 in supporting information) and their compositions are plotted in Fig. S15c. It is striking that the sodic plagioclase (An \textasciitilde{<30}) of the monzonitic clasts is not represented in the clasts analyzed. Perhaps there is a sampling bias because such compositions are inconspicuous relative to the brighter (higher Z) more calcic plagioclase and the two-tone perthites. However, the most calcic plagioclases of the noritic clasts are also missing, with the modes of the two distributions similar (Ab\textasciitilde{50–60}), so this may just reflect the low number of analyses of clast feldspars.

**ALTERATION AND VEINS**

**Pyroxene Alteration**

In some pyroxene clasts, in many cases those showing exsolution, magnetite is observed as small grains in conjunction with a silica phase. In some cases, magnetite is abundant, but silica cannot be located (e.g., Fig. S14c). This grain shows extremely coarse lamellae, indicating very slow cooling, and has somewhat kinked cleavage, fracturing, and very irregular exsolution lamellae, suggestive of annealing.
In lithic clasts, a pyroxene phase may show a striking bimodal composition distribution indicating disequilibrium in the pyroxene assemblage, as illustrated in Fig. S16 in supporting information (Table S16). For example, the orthopyroxene crystals of clast 7533-4 Z1 in Fig. S10a are both high-Z (OF) and low-Z (OM), respectively OF (En₄₃) and OM (En₆₃) in the figure. Augite in this clast is speckled with Fe-rich material, and gives both stoichiometric and nonstoichiometric (near the large concordant zircon) analyses. Similarly 7533-1-obj D with a distribution of pigeonite compositions like those in zoned-pyroxene lithic clasts, shows wispy patches of magnesian pigeonite in ferroan pigeonite (not zoning). Lithic clast 7533-2-2229 contains augite, which is more magnesian than expected for the coexisting orthopyroxene. In 7533-4 clast Z4-Z12 augite En₁₃Wo₄₀ contains a patch of salitic augite En₄₂Wo₄₉ (Fig. S16). The magnesian pyroxenes are often patchy or vein-like and appear secondary, possibly as a result of oxidation causing the Fe-rich speckling. They are dark and tend to follow cleavage (Fig. S4). They show low Fe/Mn consistent with oxidation. Similar alteration of pyroxene is described by Santos et al. (2015a, fig. 17), and Lorand et al. (2015); and Wittmann et al. (2015, fig. 14a) describe a discordant vein of salitic augite En₃₇Fs₁₅Wo₄₈ in orthopyroxene.

**Pyrite Veins and Oxyhydroxide**

None of the rock types sampled by NWA 7533 contains magmatic sulfides, except for very rare grains of pyrrhotite totally enclosed in plagioclase. Pyrite is present, however, and was fractured and subsequently altered to oxyhydroxide (Fig. 18a). Some crystals of pyrite that contain mineral inclusions must have grown when the breccia was incompletely lithified. Fine-grained matrix, clast-laden impact melt rocks, melt spherules, microbasalts, medium grained-lithic clasts, and crystal clasts are all cut by fractures or veins containing euhedral pyrite (Lorand et al. 2015). Euhedral pyrite also occurs as a late mineral in vugs (Fig. 18b.) S-rich hydrothermal fluids were injected during lithification of the breccia and after the breccia became brittle, generating vein systems by hydraulic fracturing (Lorand et al. 2015). Pyrite veins or fractures are of late origin but predate an impact event that shocked pyrite in NWA 7533 (see below).

Pyrite displays mixed signatures, preserving refractory metals (PGE, Re) as rare micronuggets mostly inherited from repeated meteorite bombardment while less resistant refractory metals (Mo and Re) were redistributed by late alteration (Lorand et al. 2015, 2016). It contains up to 4.5% Ni that, in association with magnetite, indicates a temperature up to 500 °C, fO₂ > FMQ+2, and near-neutral solutions (Lorand et al. 2015). Os-Ir-rich particles (200–700 nm) were found in altered pyrite, converted from the parental meteoritic phases into As-S rich phases by hydrothermal sulfurization reactions (Lorand et al. 2015, 2016).

The fracture systems interpreted as a penultimate event on Mars would also have allowed the passage of fluids on Earth, which we argue below caused the partial to complete replacement of pyrite by Fe oxyhydroxides. There are micro- and nano-scale Fe-rich phases in the breccia, difficult to identify because of grain size, although many have been identified by different techniques. We identified maghemite by XRD, as did Agee et al. (2013) for NWA 7034, which was
confirmed by FTIR (Muttik et al. 2014b). Goethite was identified in NWA 7034 by Mössbauer spectroscopy (Gattacceca et al. 2014). Beck et al. (2015) identified ferrihydrite in NWA 7533 by IR spectroscopy. EMP analyses of the pyrite pseudomorphs show that these have compositions similar to that of goethite, but containing ~4% SiO₂ (Table S20 in supporting information). The silica is seen in TEM images as nanolayers (Lorand et al. 2015). Electron diffraction shows that the structure of the replacement phase is compatible with hematite, but other iron-oxides or oxyhydroxides cannot be excluded (Lorand et al. 2015). Muttik et al. (2014b) showed the banded structure and identified the phase as maghemite from HRTEM, although maghemite normally has low water contents. If the main phase is anhydrous oxide, the low EMP totals must be explained by porosity and/or a hydrated phase, possibly silica as a gel. NanoSIMS imaging of the Fe oxyhydroxides indicates a terrestrial δD value of 10 ± 85‰ with respect to SMOW, similar to values for NWA 7034 (Liu et al. 2014), requiring alteration by terrestrial water, which explains gradients in pyrite replacement from fusion crust to the interior of the meteorite (Lorand et al. 2015). Alteration of pyrite in the desert would have yielded acidic pore fluid that could have caused alteration along grain boundaries in the fine-grained matrix, possibly producing the amorphous material filling them.

**Feldspar and Calcite Veins**

The large olivine-free melt spherules are cut by veins (Figs. 6b and 6c and S5b) but they do not continue into the material outside the spherules, unlike those cutting the pyroxene-plagioclase cluster-aureole structures in clast-laden melt rocks. This alteration probably occurred before the consolidation of the breccia. The veins contain two feldspars, intermediate plagioclase like that in the spherules and Ba-rich K feldspar (hyalophane) in one case (0–14 mole% Cn, Fig. 7) and Ba-poor K feldspar in another (0–3 mole% Cn), in addition to several pyrite crystals. Terrestrial hyalophane is dominantly a hydrothermal mineral (McSwiggen et al. 1994).

Calcite veins cut all components of the breccia, and in some cases calcite was deposited in sulfide-filled fractures, where it is in contact with the oxyhydroxide replacing pyrite (Lorand et al. 2015). We show examples in clump-aureole structures and in an inverted pigeonite clast (Figs. S4 and S14c). Calcite in NWA 7034 is inferred to have a terrestrial oxygen isotopic composition (Agee et al. 2013) although the fractures in the pyroxene clumps appear to predate the fall to Earth.

**Shock Effects**

Despite a probable major reheating at 1.35–1.4 Ga, and the later removal of the breccia from the surface of Mars, NWA 7533 shows only weak shock effects (after the impact melting events). These are primarily intense fracturing of the crystals, particularly of plagioclase. NWA 7533 lacks two of the most useful shock indicator phases, olivine, and quartz. Feldspars in some cases have a crackled appearance resembling perlitic fracturing, and may be deficient in Na cations. Maskelynite has not been observed. A TEM investigation of augite showed (100) mechanical twins which have accommodated the plastic deformation, and shear of the exsolution lamellae crossed by the twins, which can be activated at relatively low shock intensity (Leroux et al. 2016). Shock markers in pyroxene such as twinning on (001), mosaicism, planar deformation features were not observed, although Wittmann et al. (2015) reported undulatory extinction and mechanical twinning in some orthopyroxene clasts in NWA 7475. The most strongly shocked clasts they observed had reduced birefringence and shock melt veins. The generally low shock intensity in the breccias is in strong contrast to that of SNC meteorites (e.g., El Goresy et al. 2013).

The most distinctive sign of shock is found in pyrite. This fragile mineral shows planar elements (fig. 18a in Lorand et al. 2015) resembling planar deformation features (PDF). Pyrite also shows fracture networks, and disruption into subgrains. Pyrite occurring in veins or fractures postdates all rock types in the breccia, and other late phases appear to be terrestrial. Pyrite appears to be the last phase to crystallize in the breccia on Mars, so that the shock creating its planar fractures was a very late event, possibly related to the excavation event (Lorand et al. 2015).

**DISCUSSION**

**Classification of the Breccia**

There are well-developed classification schemes for breccias from the Earth and the Moon (Stöffler et al. 1980; French 1998; and particularly Stöffler and Grieve 2007). NWA 7533 contains crystal and lithic clasts derived from pyroxenitic to monzonitic source rocks, making the breccia distinctly polymict. The dark melt bodies up to ~1 cm embedded in its fine matrix are its most prominent feature (Fig. 2) and have the distinctive textures of clast-laden impact melt rocks (Hewins et al. 2013a). Similar objects in NWA 7475 were described as clast-rich amoeboid vitrophyres (Wittmann et al. 2015).
Such rocks were recognized in relation to both lunar and terrestrial cratering shortly after the Apollo program (Grieve et al. 1974; Simonds 1975; Stöffler and Grieve 1994) and are widespread in both lunar and other meteorites (Warren et al. 2005; Hudgins et al. 2007; Schmieder et al. 2016). Broadly speaking, NWA 7533 is a polymict breccia containing melt particles, that is, compared to terrestrial rocks it is suevite-like: it consists of fine matrix with melt rock bodies in it (Hewins et al. 2013b). However, it contains both clast-rich and clast-free impact melt rocks, with the latter sometimes enclosed in the former (e.g., Fig. 4d), as in “cored bombs.” Thus, the monzonitic and noritic xenoliths are an older generation, indicating at least two impact melting events, the former at ~4.43 Ga. This evidence is consistent with an origin for NWA 7533 as a regolith breccia (Stöffler and Grieve 2007).

In regolith breccias, surface fines are important and the matrix in NWA 7533 (Fig. 3) is finely crystalline, containing submicron grains (Hewins et al. 2013a; Muttilk et al. 2014a; Leroux et al. 2015). Although dust grains could be part of impact ejecta (Wittmann et al. 2015), Humayun et al. (2013) also proposed on geochemical grounds that this breccia is derived in part from wind-blown dust. The presence of vesicular shards (Fig. 6a) is also consistent with a surficial origin. Several kinds of melt spherules up to 6 mm in apparent diameter are present (Figs. 2 and 6), and they are typical of a surface origin as in regolith breccias (Stöffler et al. 1980; French 1998), but can be formed by volcanic fire fountains or deposited as ejecta from large craters (French 1998). Siderophile element concentrations in NWA 7533 components require ~5% chondritic component and confirm an impact origin for the melt rocks, including the older monzonitic-noritic clasts, and for at least some of the spherules (Humayun et al. 2013; Udry et al. 2014). The similarity to Gusev soils (Humayun et al. 2013) is also consistent with an origin as a regolith breccia. Rather than a simple regolith breccia, however, NWA 7034, 7475, and 7533 may be a suevitic breccia formed by recycling of regolith and bedrock during a large event depositing the clast-laden melt rock splashes (Wittmann et al. 2015).

Despite previous lack of evidence of impact melts in SNC meteorites, except as shock veins, inevitably they must exist on Mars, given the scale of cratering. Impact melt flows can be recognized at very young craters, like Pangboche on Olympus Mons (Mouginis-Mark 2015). Many Mars surface features formed since the late Hesperian, such as dark dunes, dark layers in crater floor deposits, and dark streaks, can be interpreted in terms of impact melt breccias and glassy impact debris (Schultz and Mustard 2004). For large complex craters, the long-lived heat particularly associated with impact melt sheets can give rise to hydrothermal systems (Newcom 1980; Osinski et al. 2001, 2013). Impact structures are associated with 55% of the occurrences of hydrous minerals prevalent in the phyllosian alteration of the PreNoachian (Carter et al. 2013). Although hydrous minerals are not abundant in the breccia (Muttik et al. 2014b), there is petrological evidence of hydrous precursors for spherules and melt rocks (Humayun et al. 2014a, 2014b, 2014e) and oxygen isotope evidence of melt-fluid-atmosphere interaction in the zircons of noritic and monzonitic melt rocks (Nemchin et al. 2014). The high Δ¹⁷O of the zircons indicates mass-independent fractionation in the atmosphere, and due to weathering or hydrothermal alteration, this signature was incorporated into the protoliths of the melt rocks which crystallized the zircons at 4.43 Ga.

Mars regolith breccias should differ from lunar and meteorite regolith breccias, because of a lack of gardening by micrometeorite impacts (Stöffler and Grieve 2007), and of implanted solar wind (Bogard et al. 1973; Wieler 1998). Indeed, the absence of agglutinates in NWA 7533 is explained by the filtering effect of the Martian atmosphere on small projectiles. Similarly, the Martian surface is shielded from the solar wind by the Martian atmosphere, so that the absence of solar wind and the presence of Martian atmospheric gases in this regolith breccia (Cartwright et al. 2014) is clear evidence of a Martian origin. There is evidence of multiple events, spherule deposition, and the accumulation of a meteoritic component on the surface, as for the Moon, but also interaction with the hydrosphere and atmosphere (Humayun et al. 2013; Nemchin et al. 2014). Assuming NWA 7533 is representative of the southern hemisphere, it represents a new kind of regolith breccia unique to early terrestrial planetary surfaces, providing clues to the nature of Hadean surfaces on Earth.

**Formation of Clast-Laden Melt Rocks**

The NWA 7533 breccia was not formed instantaneously: it is an accumulation of melt rock bodies and matrix, somewhat younger than the 4.43 Ga monzonitic clasts they both contain. Abundances of Ir and other siderophile elements indicate the presence of ~5% projectile component in most clasts, as in lunar breccias (Humayun et al. 2013). This contamination includes the monzonitic and microbasaltic fragments with normal igneous textures, except clasts from pristine orthopyroxenite (Hewins et al. 2014). The pervasive siderophile enrichment even in the melt rocks with pyroxene exsolution apparently formed at depth suggests a thick sequence of impact-generated rocks

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including mature regolith. Only the fine-grained clast-laden rock bodies have a texture characteristic of impact melting and some of them have sculpted forms as in suevitic breccias (Hewins et al. 2013a; Humayun et al. 2013). The presence of schlieren in impact glasses shows that melts formed in different locations can be intimately mixed during excavation (See et al. 1998), and heterogeneity in the groundmass of the melt rocks (Figs. S3 and S4) is consistent with this process. The presence of aligned ellipsoidal structures in a breccia clast in NWA 7034 section 3A,3 (Santos et al. 2015a; Figs. 8a and 8b), similar to the clump-aureole structures described above in clast-laden melt rocks, but deformed, suggests flow in melt rock before the end of solidification.

Several origins have been discussed for clast-laden melt rocks. For coarser grained impact melt rocks, superheated melt mixes with fractured target rock at the contact between the melt and the crater footwall. Melt jetted from the crater overtakes colder fragmental debris, the incorporation of which partially quenches it (Grieve et al. 1974; Simonds 1975). Such rocks were recognized in relation to both lunar and terrestrial cratering shortly after the Apollo program (Grieve et al. 1974; Simonds 1975; Stöffler and Grieve 1994) and are widespread in both lunar and other meteorites (Warren et al. 2005; Hudgins et al. 2007; Schmieder et al. 2016). Recent detailed investigations of terrestrial craters (Grieve et al. 2010; Stöffler et al. 2013) have indicated that suevites are not necessarily fallback or ejecta from the initial plume but can be generated phreomagmatically when hydrated rocks and/or water fall into impact melt pools. Vaporization at depth can cause explosive fragmentation of melt and mixing of melt splashes with solid debris. The presence of shards with concave surfaces (Fig. 6a) indicates vesiculation in the melt rocks. There are ample indications of the action of water on the precursors to the melt materials incorporated into NWA 7533. Thus, these early impacts were probably on a wet Pre-Noachian terrain with phyllosilicate weathering effects. Formation of clast-laden melt rocks may therefore be due to late contamination and phreatic eruptions of an impact melt pool. The large volume of Onaping breccias above the Sudbury Igneous Complex suggests that seawater reacted with the impact melt in the crater (Grieve et al. 2010). Evidence of wide spread occurrence of breccias like NWA 7533 in the Noachian would have interesting implications for water abundance, if the suevite analogy is correct.

**Clump-Aureole Structures in Clast-Laden Melt Rocks**

Although the clast-laden melt rocks are similar in many ways to those known on other planetary bodies (Grieve et al. 1974; Simonds 1975; Stöffler and Grieve 1994; Warren et al. 2005; Hudgins et al. 2007; Osinski et al. 2008), with textures characteristic of melts formed by impact, their oval somewhat spherulite-like clump-aureole structures (Figs. 4–5 and S2) are unique. Other phases in the orthopyroxene clusters may include chromite (early-forming), fine Fe-oxide dust, and (late-forming) pyrite. Even in low magnification, BSE images (Figs. S3f and S4a; Santos et al. 2015a, fig. 8) these melt rocks may be recognized by the presence of the dark plagioclase aureoles. Fractures partially filled with calcite (Figs. 4 and S4c) emanate from and cross in the clumps, and are at their thickest in the centers of the clumps suggesting pull apart by shrinkage as in septarian nodules. The groundmass to the clump-aureole structures contains plagioclase and more augite than orthopyroxene. The dominance of plagioclase laths in the texture of the melt rocks and local subophitic texture suggests that plagioclase is the equilibrium liquidus phase. We considered several possibilities for the origin of orthopyroxene clumps.

Inversion of clasts of a high-pressure phase such as majorite to pyroxene would explain its concentration, but in this case textural evidence of expansion rather than contraction should be present.

Thin reaction coronas of pyroxene grains may be observed around olivine and quartz clasts in melt rock and they may also contain plagioclase laths (Hewins 1984) or glass depleted in Fe and Mg (Grieve 1975). The clumps in NWA 7533 are unlikely to represent coronas from totally transformed relics, as olivine is rare and quartz has not been observed. However, the plagioclase aureoles in NWA 7533 probably formed in similar boundary layer liquids depleted by pyroxene crystallization.

Glass spherules are often encountered in proximal and distal impact ejecta deposits (French 1998; Wittmann et al. 2013b). Devitrified glass spherules are often surrounded by inward-growing fibro-radial feldspar (Simonson 2003). However, the clumps in NWA 7533 melt rocks are of different composition and the feldspar forms laths, not fibers, which like the pyroxene extend outwards into the melt groundmass (Figs. 4b and 4c). Aggregates of pyroxene like those in melt rock clumps occur in shards in the breccia, often with concave surfaces (Fig. 6a), consistent with vesiculated melts. The textural similarity suggests a similar crystallization process in both vesicle-rich and vesicle-free melt rocks.

In some cases, a large chromite grain in the center of the clump constitutes a possible nucleation site for orthopyroxene in a highly supercooled liquid, if nucleation of plagioclase was inhibited. However, in many other cases chromite is absent from the plane
exposed. Nucleation on unknown sites similar to the formation of spherulites remains a possibility. The similarity to textures in irregular fragments, concave fragments, and the pyroxene-rich vesicular shards supports this idea. Schlieren in impact glasses show mixing of melts formed in different locations (See et al. 1998). The heterogeneity in the groundmass (Fig. 5) and the similarity in pyroxene composition to that in ALH 84001 suggest the presence of melted orthopyroxenite. Rapid crystallization of these magnesian schlieren, supercooled by mixing with cold clasts, would be natural before the growth of plagioclase in the more aluminous groundmass. This chemical heterogeneity suggests assimilation by the impact melt with the clumps forming on unresorbed orthopyroxene relics, although overgrowths rather than clusters of grains would be expected.

Some small aggregates of micron-sized pyroxene are observed in breccia matrix (Fig. S2d) and some are traversed by cracks. On early Mars, alteration produced phyllosilicates including Fe-Mg clays (Bibring et al. 2006) and the phreomagmatic model of suevitic impact melt rocks (Grieve et al. 2010; Stöffler et al. 2013) involves addition of water or hydrated material into melts. Dehydration of altered mafic dust pellets might have led to shrinkage on heating before or after incorporation in the melt, and subsequent deposition of calcite in the fractures. Dust balls of pyroxene or altered pyroxene might survive better in the impact melt if dehydration occurred before incorporation. Thus, the clump-aureole structures may have formed by spherulitic growth on remnants of pyroxene or hydrated dust pellets.

Clast Bulk Compositions and Mars Surface Measurements

We have described clast-laden melt rocks, microbasalts generally free of clasts, and medium-grained noritic-monzonitic clasts. The siderophile element concentrations of all three indicate incorporation of a projectile component (Humayun et al. 2013). The high Ni in the pyroxenes of the noritic-monzonitic clasts of NWA 7533 is consistent with crystallization from impact melts, as proposed by Humayun et al. (2013). Ni from projectiles is not fractionated out of the silicate, due to high fO2 and low fS2 in the melt, indicated by the presence of magnetite and absence of magmatic sulfides (Lorand et al. 2015). Santos et al. (2015a) have shown that the bulk compositions of “microbasaltic” clasts in NWA 7034 are mostly basaltic but extend to mugearitic. Major-element ICP-MS data were acquired on NWA 7533 clasts (Humayun et al. 2013) (Table S1) and we show a diagram of silica vs. total alkalis (Fig. 19a). The fine-grained materials plot in the basaltic field, where many Gusev soils fall and where Agee et al. (2013) showed that the bulk composition of NWA 7034 (measured on fine-grained groundmass) plots.

There is partial overlap in composition between our fine-grained samples, but variation in Al/Si shows that microbasalts are closer to SNC meteorites than matrix and clast-laden melt rocks (fig. S4 in Humayun et al. 2013). This is probably due to mixing with feldspar clasts from the medium-grained noritic-monzonitic rocks, or similar rocks. The REE data (Fig. 19b) emphasize the overlap between our generally clast-free microbasalt and the clast-laden melt rocks, with the difference between the two being due to the absence or presence (surviving or digested) of clasts. The monzonitic rocks are distinctly higher in alkali (Fig. 19a) and REE (Fig. 19b) contents. In particular, one monzonitic sample (clast II) falls in the middle of the mugearite (basaltic trachy-andesite) field, and has a composition resembling that of sample Jake M. at Gale Crater (Stolper et al. 2013). Such rocks appear to be absent at Gusev.

Though the Curiosity rover is especially concerned with sedimentary rocks at Gale Crater, many rocks analyzed by ChemCam are highly feldspathic like lithic clasts in NWA 7533. Of course the rover has encountered a more diverse suite of rocks, including olivine-bearing and quartz(?)-bearing rocks not seen in the breccia, as well as the sedimentary rocks. Here, we examine the similarities between our monzonitic and noritic clasts and anhydrous samples analyzed by ChemCam with H lacking in the laser-induced breakdown spectra (LIBS). While individual grains can be imaged and identified by physical properties, laser data are generally of overlapping grains. The mixing lines in ratio diagrams can be used to extrapolate endmember single mineral compositions (Sautter et al. 2014, 2016). In Fig. 20a, we compare monzonitic clast II with Black Trout sample from Gale Crater (Sautter et al. 2014). Ideal augite, orthopyroxene, and olivine plot at 0.5, 1.0, and 2.0 on the (Fe+Mg)/Si axis; anorthite CaAl2Si2O8 plots at 1.0 and both albite NaAlSi3O8 and orthoclase KAlSi3O8 plot at 0.33 on the Al/Si axis. Our electron probe analyses of pyroxenes and feldspars plot on or near the axes, and can be identified by stoichiometry. The laser spot analyses, by ICP-MS (Humayun et al. 2013) and LIBS/ChemCam (Sautter et al. 2014) are generally mixtures of phases. For NWA 7533 clast II we also have a laser bulk analysis performed by rastering. The LIBS data for Black Trout clearly require the presence of two feldspars (similar to the intermediate-sodic plagioclase and alkali feldspar of the breccia) and also suggest the
presence of a silica-rich phase such as quartz. In Fig. 20b, we compare analyses of noritic clasts in the breccia with sample Mara (Sautter et al. 2014) from Gale Crater. Here, laser spots can be explained as mixtures of calcic plagioclase, augite, and orthopyroxene, possibly with a higher augite/orthopyroxene ratio in Mara than in the breccia norite. Matrix, melt rock, and microbasalt in NWA 7533, not shown here, are similarly noritic, but there the data points are pulled across the plagioclase-orthopyroxene tie-line by the presence of Fe-rich phases, especially chromite and magnetite.

The zoned-pyroxene clasts resemble enriched shergottites mineralogically. Although the clasts have the same composition ranges for pigeonite and augite as Shergotty, they differ from shergottites (even Los Angeles) in having abundant K feldspar. The nakhlites and chassignites are even more distinct in mineralogy. In addition the pyroxene in 7533-1-12 was analyzed for Ni (Table S15), and is Ni-rich with 486 ppm Ni, SD 229, the pigeonite having more Ni (648 ppm, SD 5 ppm) than the late subcalcic augite. Based on these data, the zoned-pyroxene rocks are likely to have incorporated projectile material, and to represent impact melts, like the other lithic clast types analyzed by LA-ICPMS (Humayun et al. 2013). Bellucci et al. (2015) found a U–Pb age for chlorapatite in clast 7533-4-K (their clast 1) of 1.357 ± 81 Ga. They also used Pb isotope measurements to show a model age near 4.43 Ga for one plagioclase and near 1.35 Ga for most feldspar in the same zoned-pyroxene lithic clast. Ody et al. (2015) report four locations with spectral signatures (strongly influenced by pyroxenes) matching basaltic shergottites in Sirenum Planum. Because of the Noachian age of this terrain, another possible interpretation of these spectra would be impact melt rocks rather than basaltic shergottites.

Along with the 4.43 Ga noritic-monzonitic impact melt clasts, NWA 7533 contains orthopyroxenes with low Ni contents. Many of these orthopyroxene clasts...
are Mg-rich with compositions not associated with plagioclase in lithic clasts. This suggests a pristine orthopyroxene crustal component, which resembles ALH 84001 in major and minor element abundances (Figs. 15 and S13). Orthopyroxene in NWA 7033 also has $\delta^{17}$O and $\delta^{18}$O very close to those of ALH 84001 (Franchi et al. 1999; Ziegler et al. 2013). Pyroxene clasts are not yet individually dated, although pyroxene separates in NWA 7034 have a crystallization age close to that of the zircon (Nyquist et al. 2016). ALH 84001 has an age of 4.1 Ga (Bouvier et al. 2009; Lapen et al. 2010), both indicating early Noachian terrain and suggesting an origin in the southern hemisphere. Ody et al. (2015) have examined orthopyroxene-rich terrains and found that the IR spectra indicate the presence of plagioclase, that is, noritic rocks, or an association of orthopyroxenite and norite, as in the breccia. Based on the clasts in NWA 7533, the noritic rocks might equally well be melt rocks or breccia as pristine norite.

The History of the Breccia

To understand the earliest history of Mars we must find the relative ages of major processes, such as the crystallization of earliest magmatic rocks and the transition from primary to secondary atmospheres. The timing of crust formation, the extent of the early heavy bombardment, and the onset of aqueous alteration have been uncertain (Carr and Head 2010; Fassett and Head 2011). There are over 40 impact basins with diameters $>400$ km in the Noachian (Hartmann 2005). Craters $>150$ km in diameter have been dated by crater counting and about 73% of them formed in the Early Noachian, that is, as a result of the early heavy bombardment completing accretion (Tanaka et al. 2014). Most of the formative events in Mars’ history occurred before the limit where crater counting becomes a viable dating tool, and has been consigned to the PreNoachian, that is, buried under the crater-saturated surface (Frey et al. 2003; Carr and Head 2010; Fassett and Head 2011; Tanaka and Hartmann 2012). Clearly impact breccias must be important in this story and the dating of NWA 7533 and NWA 7034 (Humayun et al. 2013; Nyquist et al. 2016) give us a unique glimpse of geological processes in this earliest time period.

Crystallization Absolute Ages

The monzonic fragments are enriched in K, REE, P, Ti, Cl, and Zr; and contain zircon, and occasionally baddeleyite, which have provided a crystallization age for the noritic-monzonitic rocks (Humayun et al. 2013). Zircon and baddeleyite in one noritic and four monzonic fragments, and others occurring as clasts or xenocrysts in fine-grained matrix and clast-laden melt rocks, were analyzed by SHRIMP. Two dated zircons Z2 and Z1 are shown in their respective noritic and monzonitic host in Figs. 12c and S10a, and described by Humayun et al. (2013, SOM). The morphology and oscillatory zoning of many such zircons (e.g., Z14, a matrix grain with a concordant age, Fig. S10d) suggest that such grains have crystallized during solidification of these rocks.

The crystallization age of the zircon in noritic-monzonitic clasts in NWA 7533 is 4.428 ± 0.025 Ga (Humayun et al. 2013) and zircons in NWA 7034 have similar ages (Tartèse et al. 2014; Yin et al. 2014). Similar crystallization ages were inferred for pyroxene and plagioclase based on Sm-Nd dating for NWA 7034 (Nyquist et al. 2016) and a common-Pb model age for plagioclase (Bellucci et al. 2015). For NWA 7533, the hosts to zircon and baddeleyite are matrix and noritic-monzonitic melt rocks. The least radiogenic Pb isotopic compositions measured in plagioclase and K feldspar lie within error of the 4.428 Ga Geochron, and hosts include monzonitic melt rock and medium-grained zoned-pyroxene melt rock. We conclude that the crystallization of medium-grained rocks was at ~4.4 Ga.

Relative Ages of Melt Rocks

The history of the breccia as well as it can currently be deciphered is outlined in Fig. 21. While an early age of crystallization is firmly established for the oldest components at ~4.35–4.43 Ga, the timing of assembly, and lithification or compaction age of the breccia is not well understood, at present. Lithification may be related to heating by initially hot components, compaction by impacts, and cementation by circulating fluids. We consider two possible models here.

(1) The lithification age is ~4.4 Ga. One could expect that the impact record of Mars should include a broad range of ages between 4.4–3.8 Ga, related to the late, heavy bombardment, as observed for the lunar breccias (Grange et al. 2013; Joy et al. 2014). The number of zircon grains dated is still relatively small, but no upper intercept age younger than 4.35 Ga has been observed (Humayun et al. 2013; Tartèse et al. 2014; Yin et al. 2014). One interpretation of this absence of post-4.35 Ga zircons is that the breccia was compacted at ~4.3 Ga, and that all subsequent disturbances recorded by zircons reflect later impacts or other geological events that affected the assembled breccia. This model implies rapid assembly and closure within the Pre-Noachian period. Certain aspects of this model are unsatisfactory, including that the abundant Fe-oxides are expected to form in the “siderikian” (Bibring et al. 2006), a time (~3.5 Ga) overlapping the Amazonian period (~3.0 Ga) of Martian history. However, the absence of excesses of
Cl, S, and Zn in the breccia (Humayun et al. 2013) may be consistent with a pre-theiikian age (>4.0 Ga) of lithification or at least alteration.

(2) The lithification age is ~1.4 Ga. Yin et al. (2014) argued that some of the zircon analyses at the lower intercept were actually concordant grains that crystallized from melts at ~1.4 Ga. This led them to interpret the lithification age of the breccia as ~1.4 Ga. This model of the assembly time cannot explain the absence of zircons between 4.35–1.4 Ga, but is more permissive to sampling a very wide range of Martian history (~3 Ga), even if not recorded by zircon-forming events. Resolving these two models is essential to fully reading the record of ancient Mars from this breccia.

The ages of components such as clast-laden melt rocks, microbasaltic melt rocks, and spherules are not strongly constrained like those of the monzonitic melt rocks. However, the zoned-pyroxene rocks, microbasalts, and clast-laden melt rocks differ from each other and noritic-monzonitic rocks mainly in clast abundance, grain size, and extent of fractionation. The microbasalts in part resemble zoned-pyroxene clasts in mineral compositions (Fig. 11) and the clast-laden rocks in containing clasts in a few cases (Fig. S6a). Furthermore, these components appear to have the same zircon and plagioclase crystallization ages as the monzonitic clasts (Nemchin et al. 2014; Yin et al. 2014; Bellucci et al. 2015; Santos et al. 2015a). Specifically, a clast in NWA 7034 with basaltic trachyandesite composition (Santos et al. 2015a), which forms part of the microbasaltic group of clasts, contains concordant and discordant zircons (4333 ± 38 Ma and 1434 ± 65 Ma; Yin et al. 2014); zoned-pyroxene clast 7533-4-K has a plagioclase model age near 4.5 Ga with apatite and K feldspar reset (Bellucci et al. 2015). However, the fine-grained melt rocks must have formed in a later impact event than the source rocks of the noritic and monzonitic melt rock clasts they contain (Fig. 4b), and the orthopyroxene clasts they contain, although not necessarily much later. Wittmann et al. (2015) suggested that the melt rock (“amoeboïd clast-rich vitrophyres”), spherules, and pulverized target rock were deposited in a single event, possibly at ~1.4 Ga. The zircon and feldspar age data cited above suggest that this event is followed closely after the crystallization of the medium-grained melt rocks. The occurrence of both igneous and annealed textures in microbasaltic clasts shows that some of them were metamorphosed before incorporation in the breccia. This suggests burial by hot debris and close formation in time in a series of impact deposits, the last of which formed the breccia. The new Sm-Nd dating of bulk breccia chips and mineral separates (Nyquist et al. 2016) yields an age of 4.42 ± 0.7 Ga, indistinguishable from the zircon crystallization ages and showing that all the rock types making up the breccia formed within a very short lapse of time.

Fig. 21. Schematic development of the breccia, showing two impact events slightly separated in time. 1) Regolith (reg) on primitive crust with felsic rocks (FLC) and orthopyroxenites (pxt). 2) Noritic-monzonitic impact melt rocks (NO-MO). 3) Microbasaltic and clast-laden melt rocks (MR).
Late Events

Despite the low level of shock in the breccia, there is evidence of late disturbances of the crystallization ages of the melt rocks. Imaging of some zircon grains (Z1 and Z2) reveals variable later degradation of internal structures as a result of damage induced by radioactive decay, consistent with discordant ages and annealing at ~1.7–1.4 Ga (Humayun et al. 2013). Some zircon U-Pb data for monzonitic clasts fall on a discordia line with a lower intercept of $1.712 \pm 85$ Myr indicating a major subsequent resetting, presumably by a later impact (Humayun et al. 2013). Re-examination of the lower intercept for NWA 7533 zircons shows that of the four zircons that plot near this intercept, the Pb-Pb ages of at least two of these zircon analyses (Z2, Fig. 21; Z3) yield lower intercepts of ~1.4–1.5 Ga. For NWA 7034, Yin et al. (2014) and Tartese et al. (2014) also report zircon resetting at ~1.4–1.5 Ga. The U-Pb isotopic compositions measured for the chlorapatite in NWA 7533 (Bellucci et al. 2015) yield a $1.357 \pm 81$ Ga age and in NWA 7034 (Yin et al. 2014) a $1.345 \pm 47$ Ga age. Feldspar Pb-Pb dating by Bellucci et al. (2015) also shows that some Pb-Pb model ages for plagioclase in lithic clasts are within error of 4.4 Ga, but K feldspar and plagioclase also have reset ages close to the 1.35 Ga Geochron.

Some monzonitic clasts and one zoned-pyroxene melt rock clast (NWA 7533-4 K) show both preserved crystallization ages and reset ages in different phases, demonstrated by data in figs. 3 and 4 of Bellucci et al. (2015). As an example of this, in Fig. 22 we show a monzonitic clast with baddeleyite $\geq 4.298 \pm 0.020$ Ga, plagioclase ~4.4 Ga, chlorapatite 1.357 ± 0.081, and K feldspar ~1.35 Ga ages (Humayun et al. 2013; Bellucci et al. 2015). This clast 7533-4-Z4 is referred to as clast 2 in Bellucci et al. (2015). Bellucci et al. (2015) proposed that this strong disturbance indicated by the isotope data was a thermal event related to impact in the Amazonian toward 1.35. The partially sintered sub-µm granoblastic texture (Muttik et al. 2014a; Leroux et al. 2015) is consistent with a moderate annealing intensity, corresponding to brief heating possibly during the 1.35 Ga event. The role of other disturbances in the isotopic record, and the ages of specific clast types, may need to be clarified, but the 1.35 Ga event probably represents the lithification of the breccia.

The latest breccia event before excavation, during and after annealing of the matrix, is hydrothermal activity depositing pyrite in vugs in matrix and in fractures cutting all facies of the breccia (Lorand et al. 2015). Pyrite precipitation in these oxidized rocks required T up to 400–500 °C and near-neutral rather than acidic solutions, possible because of the absence of magmatic sulfides in the breccia components and/or their protoliths (Lorand et al. 2015). The Martian origin of the pyrite is demonstrated by its fracturing caused by shock (Lorand et al. 2015), possibly during the launch event. Wittmann et al. (2015) using Fe and Th abundances, and the ~5 Ma exposure age of Cartwright et al. (2014), suggest one possible launch site for the breccias, the young rayed crater Gratteri. This crater has also been suggested as the source of ALH 84001 (Tornabene et al. 2006). NanoSIMS imaging of pyrite grains shows that Fe oxyhydroxides replacing them along their fractures exhibit a homogeneous terrestrial D/H ratio (Lorand et al. 2015). The average $d_D$ value (10 ± 85‰) indistinguishable from the terrestrial values, and calcite veins with terrestrial oxygen isotopic compositions (Agee et al. 2013), record the breccia’s relatively brief residence (typically thousands of years for desert meteorites) on Earth.

Implications for Conditions on Mars

Radiometric dating has yielded crystallization ages of 4.43–4.35 Ga for all rock types in the breccia (Humayun et al. 2013; Nyquist et al. 2016). Thus, a crustal reservoir containing debris from pristine igneous rocks heavily contaminated by projectiles was in place on Mars at 4.43 Ga, a little over 100 Ma after its
accretion. Debaille et al. (2007) showed that combined
$^{142}$Nd-143Nd isotope evidence in shergottites implies
mixing between two distinct source reservoirs formed at
4.535 Gyr and 4.457 Gyr ago and argued that the
younger reservoir was residual melt from a magma
ocean, rather than ancient crust. However, the
solidification of any magma ocean is thought to have
occurred within 5 to 10 Ma after Martian accretion
(Elkins-Tanton 2012), a much shorter time frame than the
30–110 Ma required by Debaille et al. (2007). The
eyoung crust rather than a late magma ocean reservoir is
available to contaminate and enrich shergottite magmas
emplaced through it. The Martian Nd isotope
systematics (Debaille et al. 2007) can be explained by
formation of this crust and depleted mantle, without the
need for a magma ocean (Agee et al. 2013; Humayun
et al. 2013). In that case, H$_2$O and CO$_2$ would have
been outgassed continuously during early crust
formation to form the (Pre-) Noachian atmosphere,
allowing element surface conditions (Nemchin et al.
2014). In this period of the most intense basin
formation, hydrothermal activity would have been
important, and could have promoted an extensive
aquifer even if surface material was frozen (Pope et al.
2006; Abramov and Mojzsis 2014).

**Oxygen Isotope Data**

An orthopyroxene mineral separate (Ziegler et al.
2013), likely to be Ni-poor orthopyroxene (Hewins
et al. 2014) from pristine orthopyroxenites like ALH
84001 (Mittlefehldt 1994), exhibited $\Delta^{17}$O of 0.33$_{\text{iso}}$,
indistinguishable from SNC compositions, and reflecting
mantle isotopic composition. There is an overall trend
of increasing $\Delta^{17}$O with increasing $\delta^{18}$O in NWA 7034
separates, toward the composition of known Martian
alteration phases. These $\Delta^{17}$O values were attributed to
photochemically induced isotope fractionation and transfer
of the atmospheric signal to rocks by surface
alteration (Farquhar and Johnston 2008). The Amazonian
and younger Martian atmosphere has been proposed to
have had a high $\Delta^{17}$O value of $>0.6$_{iso} (Farquhar and
Thiemens 2000; Ziegler et al. 2013; Shaheen et al. 2015).
The similar O isotopic compositions of ALH 84001 and
SNC alteration phases suggest that exchange with the
atmospheric reservoir occurred through most of Martian
history (Farquhar and Thiemens 2000).

The zircon crystals in NWA 7533 dated by the U-
Pb method were subsequently analyzed for O isotopes
(Nemchin et al. 2014). Different zircon grains show a
difference in $\Delta^{17}$O values, many higher than the SNC
values defining the Mars fractionation line. Some are
also higher than bulk NWA 7034 and magnetite
separate data (Ziegler et al. 2013), and include the
largest $\Delta^{17}$O reported from a Martian meteorite
(Nemchin et al. 2014). The zircons probably crystallized
from melts that had incorporated surface material with the
atmosphere-hydrosphere isotopic signature, although are also partly altered (the most extreme $\Delta^{17}$O values being found in metamict portions of the zircons with an age of $\sim$1.4 Ga). The excess of norite-
monzonite zircon $\Delta^{17}$O values over SNC values
(Nemchin et al. 2014) implies that the atmosphere was
thin enough to create reactive $^{17}$O species before impact
melting and zircon crystallization, and hydrated crust
was already present at 4.43 Ga (Humayun et al. 2013;
Nemchin et al. 2014).

**Early Aqueous Alteration**

All crystallization ages for clasts in NWA 7533 date
from the earliest Noachian (PreNoachian) characterized
by phyllosilicate alteration in remote sensing. Newsom
(1980) argued for the production of clays as well as
ferric hydroxides by hydrothermal alteration associated
with Martian impact melt sheets.

Geochemical evidence that the precursors of the
monzonites and some spherules were altered and clay-
rich (Humayun et al. 2013, 2014a, 2014b, 2014c) is
consistent with the zircon record of melt-hydrosphere-
atmosphere interaction (Nemchin et al. 2014). Humayun
et al. (2014c) have shown that spherules, although
themselves little altered, have alkali element ratios
(enrichments of K, Rb, Cs, and Tl and depletion in Na)
characteristic of terrestrial clay minerals and consistent
with a weathered source. Vesicular shards (Fig. 6a) also
indicate the presence of volatiles. The bulk compositions
(Humayun et al. 2013) also indicate degassing or
leaching of S from the precursors and the melt rocks
lack magmatic sulfides in consequence (Lorand et al.
2015). Thus, phyllosian conditions (Bibring et al. 2006)
are indicated before 4.43 Ga. However, there is no clear
evidence that phyllosilicates formed in the assembled
breccia in the Noachian, for although NWA 7034 does
contain clays, they occur as nanogranoblastic crystals in
the annealed matrix (Muttik et al. 2014a). Their
Martian origin is based on the observation that water
from NWA 7034 is Martian in oxygen isotope
composition (Agee et al. 2013). Possibly these are
annealed Pre-Noachian clay dust grains, but their time
of formation is not well defined.

Fractional crystallization of a Martian basalt
magma like those in Fig. 19 does not yield evolved
rocks like the zircon-bearing noritic-monzonitic clasts.
The various clast types in the breccia may be derived by
melting different Pre-Noachian protoliths with different
degrees of alteration or sedimentary geochemical
characteristics, rather than by fractionation of thick
melt sheets. If all the iron is ferrous, olivine will
crystallize instead of orthopyroxene and magnetite. The
magnetite-ilmenite assemblages in these rocks indicate oxygen fugacities at FMQ+2–3 log units (see below and Table S9) and show that the melt and therefore the protolith were highly oxidized. This oxidation, accomplished by weathering or alteration of olivine in precursors to serpentine + magnetite, explains the crystallization of pyroxene and magnetite in its stead in the noritic-monzonitic melt rocks (Humayun et al. 2014a, 2014b), although the high alkalis and high K/Na of the monzonitic rocks remain a problem in modeling.

NWA 7533 could possibly record global climate changes during the Noachian, Hesperian, and Amazonian periods with different weathering styles (phyllosian, theiikian, and siderikian; Bibring et al. 2006). However, the breccia does not contain the weathering sequence phyllosilicate/sulfate/anhydrous oxide and this suggests that local environmental effects might have countered the global-scale patterns. Murchie et al. (2009) describe both phyllosilicate-rich and silica-, sulfate-bearing layered deposits deposited on ancient cratered terrain. These deposits may both have formed from volcanic and impact glasses, but the phyllosilicates would have formed by abundant neutral fluid alteration, and the sulfates from more acid solutions. Thus, the general climatic transition may depend on local environmental conditions, due to variations in volcanic emissions and availability of S and/or water (Murchie et al. 2009). Either magmatic sulfide was virtually absent in NWA 7533 (Lorand et al. 2015) or sufficient water was present to remove S along with Cl and Zn in solution (Humayun et al. 2013). In addition, there is no record of the Hesperian (theiikian alteration style) in the dating. Fluid compositions and alteration phases may vary locally, but as similar breccias are probably widespread in the southern hemisphere this may also be a regional effect.

**Oxidation and Magnetics**

The magnetite-ilmenite temperature assemblage in lithic clasts in the breccia indicates a high fO2 of IW+2 to IW+3 log units at ~750 °C (Table S9). Pyroxene has been oxidized to magnetite plus silica (Leroux et al. 2016). Alteration of NWA 7533 lithic clasts includes disequilibrium pyroxene assemblages probably related to oxidation, and pyroxene decomposition into Mg-rich pyroxene, silica, and Fe-oxide (Leroux et al. 2015). This reaction requires a high temperature and a high oxygen fugacity, at least 2–3 log units above FMQ, consistent with a water-rich environment. Late-forming pyrite veins also formed at a minimum log fO2 of >FMQ+2 at 400–500 °C (Lorand et al. 2016) from near neutral (6 < pH<10), H2S-HS-rich fluids. Hydrothermal alteration under oxidizing conditions appears to have given rise to fine-grained Fe-rich phases influencing the magnetic properties of the breccia.

Alteration of spherules and melt rock clasts consists of a fine speckling with high-Z Fe-rich material, which is difficult to characterize in situ, and different techniques have identified different phases. The micro- and nanoscale Fe-rich phases indicated include maghemite, hematite, goethite, and ferrihydrite, a complication being the terrestrial alteration of pyrite. A poorly crystalline Fe–OH bearing mineral gives the best match to the IR spectrum of the breccia. IR and XANES measurements of NWA 7533 show that a strong 3 μm absorption band is due to Fe3+-OH, and corresponds to one observed in Mars surface spectra particularly of the dark areas (Beck et al. 2015). Although there are also terrestrial oxyhydroxides in the breccia these are confined to specific areas corresponding to former pyrite crystals and there must be a widespread occurrence of a phase like ferrihydrite on Mars. Abundant fine-grained magnetite and maghemite explain the breccia’s magnetic properties especially the high saturation remanence (Gattacceca et al. 2014).

Parts of the Noachian terrain display anomalies in crustal remanent magnetization reported by Acuña et al. (1999). This could be explained if the crust were constructed of certain SNC meteorites, but implausible thicknesses would be required, whereas only ~1 km of breccia could cause the observed remanent magnetism (Gattacceca et al. 2014). This is consistent with formation of the NWA 7533 breccia in the southern hemisphere while the Martian dynamo was active, that is, in the Noachian (Rochette et al. 2013; Gattacceca et al. 2014). Magnetic anomalies are restricted spatially but the 3 μm absorption indicating dust rich in Fe3+ is widespread on Mars. The source of the hydrated and oxidized dust covering may be the ancient breccias in the heavily cratered southern highlands eroded and transported by wind (Beck et al. 2015). The similar compositions of fine-grained materials in NWA 7533 and the soils of Gusev Crater (Humayun et al. 2013) is in accord with this idea.

**CONCLUSIONS**

NWA 7533 is a polymict Martian breccia paired with NWA 7034, 7475, 7906, 7907, 8114, and 8171. The abundance of fine-grained clast-laden melt rock bodies, spherules and shards, and their high siderophile element contents is consistent with classification as a regolith breccia. NWA 7533 is essentially a deposit of co-genetic melt particles differing texturally and chemically as a function of clast abundance. In addition, the breccia contains a (slightly) earlier generation of medium-grained noritic and monzonitic melt rocks. There is a paucity of material that can be interpreted as pristine crustal rock, although the low-Ni orthopyroxene clasts...
are interpreted as pristine orthopyroxenite of a deep-crustal origin similar to ALH 84001, a conclusion consistent with their low siderophile element abundances. The crystallization of the monzonite-noritic, zoned-pyroxene, and microbasaltic melt rocks occurred at \( \sim 4.43 \) Ga. Then orthopyroxenites crystallized in the Martian crust from before 4.43 Ga at least until 4.09 Ga (Lapan et al. 2010). The noritic and monzonitic clasts are essentially two-pyroxene and two-feldspar rocks, respectively, but can also be distinguished by plagioclase and spinel compositions. Exsolution in this clast suite pyroxene is coarser than in SNC meteorites, suggesting a thick sequence of impact melt rocks. The nanocrystalline matrix of the breccia was partly annealed, possibly in the \( \sim 1.35 \) Ga event disturbing K feldspar, chlorapatite, and zircon ages, but it preserves some porosity. Matrix and clasts are cut by pyrite veins, probably caused by this heating event. Oxygen isotopic analyses of zircon grains and the geochemistry of the fine-grained rocks show that the protoliths interacted with atmosphere-hydrosphere before melting. These breccias document the formation of evolved crust on Mars with a wet surface environment before 4.43 Ga.

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Additional supporting information may be found in the online version of this article:

**Fig. S1:** Sawed surface of a 2.5 cm wide slab of NWA 7533 with two melt spherules (black) and dark bodies of clast-laden melt rock; feldspathic clasts are light colored.

**Fig. S2:** Breccia matrix. a) Low magnification BSE view, with many crystal clasts (plagioclase dark gray, pyroxene medium gray). b) High magnification BSE image, with light orthopyroxene embedded in dark plagioclase. c) TEM image showing granoblastic texture with porosity on grain boundaries. d) BSE. Micron-sized medium gray orthopyroxene grains in a cluster like a dustball.

**Fig. S3:** Clast-laden melt rock BSE images. a) Somewhat rounded 40 μm clasts in subophitic fine-grained groundmass; (b) less fine-grained, fewer clasts; (c, d) Mg and Al Kα X-ray maps complementary to Fig. 4c showing pyroxene and plagioclase, light/dark and dark/light, respectively. These images show the clusters and aureoles very clearly, because of the enhanced contrast between pyroxene and plagioclase relative to BSE. In Mg Kα, the top half is seen to be an Mg-rich groundmass with radial orthopyroxene in the clumps. In the Al image, the groundmass laths are seen to be skeletal-dendritic and the aureole plagioclase is radial; the plagioclase lath abundance defines the schlieren. e) The fine-grained clast 2-84 (Fig. 8d) has zoned pigeonite and augite En66.4/pigeonite, and/or augite. e) The fine-grained clast 2-84 (Fig. 8d) has zoned pigeonite and augite En66.4/pigeonite, and/or augite. e) The fine-grained clast 2-84 (Fig. 8d) has zoned pigeonite and augite En66.4/pigeonite, and/or augite.  

**Fig. S4:** a) Detail of NWA 7533-1 showing crescent-shaped clast-laden melt rock body (MR), with crystal clasts, several clump-aureole structures (small dark ellipses), and also microbasalt (MB) and spherule (S). b) Red-green-blue coded X-ray (Mg, Al, Si, Kα) image of the clump-aureole structures (orthopyroxene clusters with plagioclase borders) in melt rock in Fig. 4c: orthopyroxene purple, augite dark purple (with orthopyroxene rims), plagioclase light blue; Fe-oxides and crack-filling calcite are black. Plagioclase-rich and pyroxene-rich schlieren are evident. c) Ca Kα map shows white calcite in fractures.

**Fig. S5:** BSE images of shards and spherules. a) Triangular shard with orthopyroxene surrounded by plagioclase in breccia matrix. b) Detail of large aphanitic spherule in NWA 7533-7 with feldspar veins and coarse crystals near the periphery. c, d) Small spherules containing pyroxene, plagioclase, chromite, and magnetite. Spherules (c) in 7533-LM and (d) in 7533-5 resemble orthopyroxene clumps.

**Fig. S6:** a) Microbasaltic clast in 7533-6, with two small lithic clasts near its center. b) Microbasaltic clast 7533-7-4, containing potash feldspar (K), as well as orthopyroxene (O), augite (A), and plagioclase.

**Fig. S7:** a–f) Pyroxene compositions for microbasalt. a) One clast E in 7533-4 with primary orthopyroxene only, and one with pigeonite only, 7533-4-L. Both phases have compositions extending to more Fe-rich values (En69–55/Wo3–1 and En66–49/Wo10) than for clast-laden melt rocks. b) In granoblastic clast 7533-1-obj2 (Fig. 8c) fine mixtures of orthopyroxene and augite are present with little variation in Fe/Mg ratio. Magnesian orthopyroxene En63.7/pigeonite Fs32.0/Wo4.3 with augite En49.3/augite Fs32.0/Wo5.4 indicates that primary pigeonite was originally present. Fe-Mg fractionation is recorded in the orthopyroxene, En67–55/Wo3–1. c, d) A crystallization sequence of orthopyroxene followed by pigeonite, and/or augite. e) The fine-grained clast 2-84 (which sits at the bottom of the sedimentary clast in Fig. 8d) has zoned pigeonite and augite En66.4–51.9/Fs38.8–37.3/Wo6.3–14.2 and augite En49.3–40.5/Fs17.8–22.2/Wo28.1–32.0, and is discussed below along with similar medium-grained rocks, that also have zoned pyroxenes like those of shergottites.

**Fig. S8:** BSE image of sedimentary clast in 7533-2. Border (white) established by locating the characteristic texture of breccia matrix using a 1.2 Gpix FEG SEM image of true dimensions ~6 × 9 m. Noritic clast 2-1521 at top and microbasaltic clast 2-84 at bottom are attached to the sedimentary layers.

**Fig. S9:** Individual pyroxene quadrilaterals for four small zoned-pyroxene lithic clasts and one microbasalt (7533-2:84), showing pigeonite with or without augite or subcalcic augite (clast size effect).

**Fig. S10:** BSE images. a) Noritic clast 7533-4-C with magnesian (OM) and ferroan (OF) orthopyroxene, augite (A), plagioclase (P), and Cr-bearing magnetite (M). Z is zircon Z1, which partially retains a concordant U-Pb age
despite dark speckled pyroxene alteration in the clast. b) Noritic clast 7533-4-C containing orthopyroxene (opx), augite (aug, with opx lamellae), plagioclase, and Cr-bearing magnetite. c) Noritic clast 2-nor7479X; Merrillite (Me) overgrown by chlorapatite (Ap); similar two-phosphate clasts are found in breccia matrix. Lacy monazite (Mo) in chlorapatite. Pigeonite (pig) with augite (exsolved and as alteration, associated with pyrite) and chromite. d) Igneously zoned zircon clast Z14 in breccia matrix (black) has concordant U-Pb age (Humayun et al. 2013).

Fig. S11: a) The coexisting pyroxenes of several noritic clasts (Table S14), including those in Figs. 12b, S10a, and S10b, are plotted. b) The augites after recalculation with IGPET for the Lindsley and Andersen (1983) geothermometer. We show separately clast NWA 7533-4-C (Fig. S10a) where the large augite, unlike the small orthopyroxene granules, is unmixed to more calcic augite and orthopyroxene lamellae. This thermometer is not rigorously applicable for moderate amounts of nonquadrilateral components and there is a risk of underestimating the Ca content of thin augite lamellae. Nevertheless clast C shows the expected behavior where igneous equilibration is about 300 °C higher than equilibration within the unmixed augite. However, most of the augite grains coexisting with orthopyroxene in the other clasts equilibrated at temperatures of 800–900 °C, little different from that of the augite lamellae in clast C. Exsolution in pyroxene crystal clasts is discussed below.

Fig. S12: Compositions of individual analyses of (a) feldspars and (b) pyroxenes in noritic and monzonitic clasts. Compositions for clasts of intermediate properties are not shown, for clarity.

Fig. S13: Minor elements in pyroxene crystal clasts in NWA 7533.

Fig. S14: Clasts with exsolution. a) Orthopyroxene with augite lamellae (BSE), 7533-1 -10. b) Augite with orthopyroxene lamellae (BSE), 7533-1-9. c) Coarsely exsolved pyroxene 7533-7-MH3. X-ray map Mg red, Fe blue, Ca green. Note tiny magnetite granules in host orthopyroxene (salmon), coarser magnetite (blue), irregular augite lamellae (greenish), and calcite veins (green). The dark lines are relics of LA-ICPMS work.

Fig. S15: Crystal clasts; (a) compositions of host and lamellae in pyroxenes, with (b) temperature estimates after Lindsley and Andersen (1983), and (c) compositions of feldspar crystal clasts.

Fig. S16: Examples of disequilibrium pyroxene assemblages due to oxidative alteration forming magnesian pyroxene. These are the clasts from 7533-4 shown in Fig. s10a and Fig. 22, plus 1-objD and 2-229.

Table S1: ATEM analyses (atom%) of pyroxenes and feldspars in fine-grained breccia matrix.

Table S2: Analyses of pyroxenes in clumps and groundmass of clast-laden melt rocks, and shards.

Table S3: Analyses of feldspars in aureoles to clumps and groundmass of clast-laden melt rocks, and shards.

Table S4: Analyses of olivine and pyroxene in spherules.

Table S5: Analyses of feldspars in spherules and veins in spherules.

Table S6: Analyses of spinel, ilmenite, and maghemite in lithic and crystal clasts.

Table S7: Analyses of pyroxenes in microbasaltic (melt rock) clasts.

Table S8: Analyses of feldpars in microbasaltic (melt rock) clasts.

Table S9: Magnetite-ilmenite geothermobarometry.

Table S10: Analyses of pigeonite and augite in lithic clasts with zoned pyroxenes.

Table S11: Analyses of feldspars in lithic clasts with zoned pyroxenes.

Table S12: Analyses of pyroxenes in noritic, monzonitic, and intermediate lithic clasts.

Table S13: Analyses of feldspars in noritic, monzonitic, and intermediate lithic clasts.

Table S14: Analyses of pyroxene crystal clasts.

Table S15: Pyroxenes and controls analyzed for Ni by EMP at 20 kV and 300 nA.

Table S16: Coexisting pyroxenes in equilibrated two-pyroxene rocks, in exsolved crystals, and in disequilibrium assemblages.

Table S17: Analyses of feldspar crystal clasts.

Table S18: Analyses of perthitic feldspar crystal clasts.

Table S19: Analyses of phosphates in lithic and crystal clasts.

Table S20: Analyses of oxyhydroxide in lithic and crystal clasts.