# **RESEARCH ARTICLE**

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# Formation of ferroan dacite by lunar silicic volcanism recorded in a meteorite from the Moon



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#### Abstract

An igneous clast from the Northwest Africa 773 (NWA 773) clan of lunar meteorites formed by silicic volcanism on the Moon. The clast was identified in Northwest Africa 2727 (NWA 2727), which is included in the NWA 773 clan. Over 80 mode% of the clast consists of silica + plagioclase + K-Ba-feldspar. The silica phases cristobalite, tridymite, and quartz are all present in the clast, indicating rapid cooling at low pressure in agreement with a volcanic setting. This clast is characterized as a dacite on the basis of mineral modes and whole-rock chemical composition. Olivine and pyroxene in the clast have high Fe/Mg ratios (olivine Fe# > 99, pyroxene Fe# > 99; with Fe# = molar Fe/(Fe +Mg)  $\times$  100), suggesting crystallization from a residual liquid after fractionation of more magnesian silicates. The clast is similar in some respects to ferroan gabbro alkaline-phase-ferroan (FG/ARFe) clasts that are inferred to be comagmatic with olivine gabbro (OG) and other mafic lithologies of the NWA 773 clan. However, the high silica concentration and dominance of apatite as the main Ca-phosphate (no merrillite was identified) are distinct from the FG/ARFe clasts. Thus, the dacite clast probably crystallized in a magmatic setting that was independent of the OG and FG/ARFe lithologies. The mafic major element composition, young age, and high KREEP-content of the NWA 773 clan have been used previously to infer an origin from the Procellarum-KREEP terrane (PKT) on the nearside of the Moon. Several candidates for silicic volcanism/plutonism have been identified in the PKT (e.g., Gruithuisen Domes, Hansteen alpha, Lassell Massif). The presence of the dacite lithology provides additional support for an origin in or around PKT for meteorites of the NWA 773 clan, and for complex igneous activity in PKT region.

Keywords: Moon, Mineralogy, Petrology, Volcanology, Silicic volcanism

#### Introduction

On Earth, igneous processes in diverse geochemical settings have resulted in wide compositional ranges of mafic to silicic rocks which form the crust. In contrast, the surface of the Moon is dominated by anorthositic rocks in the highlands and basaltic rocks in the lowlands. Anorthosites of the lunar highlands are interpreted as flotation cumulates from the lunar magma ocean (Warren 1985). Lunar basalts form by volcanic eruptions from the interior after partial melting in the mantle and are concentrated on the nearside of the

Moon, in and near the Procellarum-KREEP Terrane (PKT, with KREEP indicating enrichment in K, rare earth elements, and P) (Jolliff et al. 2000; Grove and Krawczynski 2009). Though the absolute age (or ages) of anorthosites in the highlands has been a topic of recent research (e.g., Borg et al. 2011; Barboni et al. 2017), it has been well established both from crater frequency counting and isotopic ages that basalts of the lunar lowlands (maria) are younger than the highlands anorthosites (e.g., Nyquist and Shih 1992; Hiesinger et al. 2003, 2010; Morota et al. 2011; Snape et al. 2016). For the most part, the anorthosites have crystallization ages prior to 4.3 Ga, whereas the main pulse of mare volcanism occurred from 3.9 to 3.2 Ga. Isotopic crystallization ages for a few lunar basalts are as young as 2.9–3.0 Ga (Borg et al. 2009; Elardo et al. 2014), and crater counts indicate that basaltic

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volcanism continued in the PKT to at least 1.5 Ga (Hiesinger et al. 2003; Morota et al. 2011).

In contrast to basalts and anorthosites, granitic rocks are rare on the Moon, comprising well under 0.1% by mass of the Apollo collection as reported by Seddio et al. (2015). Nonetheless, the presence of granitic rocks is an indicator of compositional evolution by igneous processes in the Moon. Some candidates for localities where the lunar silicic rocks occur have been identified from remote sensing data sets that combine infrared spectroscopy, gamma-ray spectroscopy, and topography. Gruithuisen Domes, Hansteen alpha, and Lassell Massif have infrared spectra indicating silica-rich compositions (Glotch et al. 2010) and are located in the PKT, which as described above, has a long-term history of volcanism on the Moon. Gruithuisen domes and Hansteen alpha are topographic highs, indicating that they may have formed from rhyolitic volcanism, whereas intrusive granites may be exposed at Lassell and parts of Aristarchus crater (see Head and McCord 1978 and Hawke et al. 2003, in addition to Glotch et al. 2010).

Some of the processes that have been linked to the origin of silicic rocks on the Moon include (1) underplating of crust by basaltic magma and low-degree partial melting of crustal rocks (e.g., Hagerty et al. 2006; Glotch et al. 2010); (2) silicate liquid immiscibility resulting in co-existence of FeO-rich mafic and SiO2-alkali-rich liquids (e.g., Rutherford et al. 1976; Fagan et al. 2014); and (3) fractional crystallization of basaltic liquid (e.g., Seddio et al. 2013). Similar processes play roles during granite formation on the Earth, but plate tectonics, terrestrial weathering and sedimentation, and high-water pressures in the crust have dramatic effects on formation of terrestrial granitic rocks (e.g., Tatsumi 2000; Weinberg and Hasalová 2015). In the case of Earth, granite formation is often associated with wet conditions during various stages of melting and crystallization (Campbell and Taylor 1983; Brown 2013). However, terrestrial Atype or ferroan granitoids are characterized by more anhydrous conditions (Frost and Frost 2011), and share some similarities in mineralogy, chemistry, and possibly origin with granitic rocks on differentiated bodies other than the Earth (Bonin 2012). Based on the andesitic meteorites Graves Nunatak 06128/9 (GRA 06128/9; Day et al. 2009), Northwest Africa 11119 (NWA 11119; Srinivasan et al. 2018), and trachyandesite ALM-A from the Almahata Sitta ureilite strewn field (Bischoff et al. 2014), it is known that silica-rich volcanism occurred in the early solar system, within a few million years of Ca-Alrich inclusions. From study of meteorites from asteroid 4 Vesta, dacite formation occurred on Vesta by crustal partial melting (Hahn Jr. et al. 2017). Therefore, silicic igneous rocks formed by conditions and processes distinct from the settings typical of Earth. Petrologic description of samples of lunar silicic rocks is an essential step toward evaluating the igneous processes that led to granite formation on the Moon and other celestial bodies.

Here, we have found a silicic clast in the lunar meteorite breccia Northwest Africa 2727 (NWA 2727), which is included in the NWA 773 clan of lunar meteorites (Jolliff et al. 2007; Nagaoka et al. 2019). NWA 773 clan meteorites share a distinctive olivine gabbro (OG) lithology (Fagan et al. 2003; Jolliff et al. 2003; Zhang et al. 2011; Valencia et al. 2019). In addition to the OG lithology, the NWA 773 clan contains a variety of basaltic clasts, feldspar + pyroxene gabbro, olivine-pyroxene-silica symplectites, and silica-bearing alkaline-phase-ferroan (ARFe) clasts. Several of these clast-types have been linked together to form during a common igneous differentiation suite (Fagan et al. 2014; Shaulis et al. 2017; Valencia et al. 2019). The likely parental material of the differentiation suite had a very low-Ti mafic and KREEP-bearing composition similar to green picritic glass from Apollo 14 site (Jolliff et al. 2003; Valencia et al. 2019). As discussed above, several candidates for silicic magmatism have been identified in the PKT (Glotch et al. 2010 and references therein). In this study, we describe the mineralogical and petrological characteristics of the silicic clast to constrain its origin. Furthermore, we compare the silicic clast with other silica-bearing lithic clasts of the NWA 773 clan and other lunar and terrestrial samples to consider implications of the clast for the origin of silica-bearing igneous rocks in general.

# Methods/Experimental

# NWA 2727, a member of the NWA 773 clan of lunar meteorites

Lunar meteorite NWA 2727 was found in Morocco or Algeria in 2005 (Connolly et al. 2006), and is a polymict, mafic breccia belonging to the NWA 773 clan (Bunch et al. 2006; Zeigler et al. 2007; Kayama et al. 2018; Valencia et al. 2019). As a whole, the NWA 773 clan consists of a coarsegrained regolith breccia with variable abundances of gabbroic and basaltic lithologies (Valencia et al. 2019). The gabbroic lithologies were roughly divided into three types (Fagan et al. 2003, 2014; Jolliff et al. 2003; Zhang et al. 2011; Valencia et al. 2019): olivine gabbro (OG, an olivine-pyroxeneplagioclase-rich rock); anorthositic gabbro (AG, plagioclase-rich rock with some pyroxene); and ferroan gabbro (FG, a group of lithologies all having high Fe# = molar Fe/[Fe + Mg]; see below). OG clasts in NWA 773 clan have been well characterized by previous studies (Fagan et al. 2003; Jolliff et al. 2003; Zhang et al. 2011; Nagaoka et al. 2015; Valencia et al. 2019). Isotopic Sm-Nd isochron ages of the OG lithology have been analyzed by Borg et al. (2009), who reported an age of  $2.99 \pm 0.03$  Ga, and by Nyquist et al. (2009), reporting an age of  $3.10 \pm 0.05$  Ga. Isotopic analyses of baddeleyite crystals in the OG lithology and in other types of clasts yield Pb-Pb ages near 3.1 Ga (Zhang et al. 2011; Shaulis et al. 2017). In contrast, a zircon crystal from the NWA 773 breccia has a U-Pb age of 3.958 ± 0.018 Ga (Shaulis et al. 2017). The AG lithology consists mostly of plagioclase and pyroxene. Anorthositic gabbro clasts have cumulate texture consisting of coarse crystals of anhedral plagioclase intergrown with pyroxene (Valencia et al. 2019). Although FG is variable in mineral assemblage, mineral zoning, and texture, the ferroan composition of mafic minerals is common in the FG lithology. The following ferroan lithologies are included in FG group (Valencia et al. 2019): pyroxene gabbro, symplectite clasts, and alkaline-phase-ferroan (ARFe) clasts (Fagan et al. 2003, 2014; Jolliff et al. 2003). The pyroxene gabbro is dominated by zoned pyroxene and usually contains plagioclase feldspar as well. Symplectite clasts consist of fine, curved intergrown favalite, hedenbergite, and silica. Even though silica occurs as a characteristic phase of the symplectite lithology, the symplectite also contains fayalite and is not SiO<sub>2</sub>-rich in its bulk composition. Fayalite and silica also occur together in the ARFe lithology, but they form coarser crystals instead of symplectic intergrowths; in addition, the ARFe clasts contain K-Ba-feldspar and/or feldspathic glass along with merrillite, ± apatite, ± ilmenite, and ± hedenbergitic pyroxene.

These three gabbros (OG, AG, FG) formed from a comagmatic sequence of crystallization (Fagan et al. 2014; Shaulis et al. 2017; Valencia et al. 2019). Furthermore, olivine phyric basalt (OPB) is a clast-type included in several NWA 773 clan meteorites, and is interpreted as co-magmatic with the three gabbros (Valencia et al. 2019). NWA 2727 includes clasts of all of the four lithologies described above (OG, AG, FG, OPB), as reported by Valencia et al. (2019).

In addition to the OPB, other types of basaltic clasts with pyroxene phenocrysts have been found in the NWA 773 clan. Basalts with pyroxene phenocrysts in fine pyroxene+ feldspar groundmass occur in NWA 773 (Fagan et al. 2003, see their "straw-textured clast") and in NWA 2727 (Kayama et al. 2018). Anhedral quartz single crystals (10 to 20  $\mu m$  in radius) are present in clinopyroxene-phyric basalt (CPB) clasts in NWA 2727 (Kayama et al. 2018). The presence of multiple types of basalts indicates that some clasts of the NWA 773 clan formed initially from variable types of volcanism.

The NWA 773 clan shares (1) mafic minerals and major element composition; (2) isotopic ages of 3.0 to 3.1 Ga for the most part, though some clasts in the breccia are older; and (3) KREEP-rich minor element composition (Fagan et al. 2003; Jolliff et al. 2003; Zhang et al. 2011; Valencia et al. 2019). On the basis of mafic composition, geochemical KREEP signature, and young crystallization age, NWA 773 clan is considered to originate from PKT (Jolliff et al. 2003).

#### Analytical methods for mineralogy and petrology

The polished thin section (PTS) of NWA 2727 was investigated by a combination of petrographic and chemical microanalyses including electron microprobe spectroscopy and scanning electron microscope imaging and mapping. Thin-section scale back-scattered electron (BSE) images and X-ray elemental maps were collected by an electron probe micro-analyzer (EPMA) (JEOL JXA-8900) at Kobe University. Clast-scale BSE images and X-ray elemental maps of the silicic clast were captured using the Hitachi S-3000 N scanning electron microscope (SEM) and JEOL JXA-8900 EPMA at Waseda University. These X-ray elemental images were adjusted and combined using an imaging analytical tool (Adobe Photoshop®). Photoshop was also used to estimate the area fraction (mode) of minerals from elemental maps covering approximately 3 mm<sup>2</sup> in the silicic clast by counting pixels of each phase, which is taken to be proportional to the volume fraction. Mineral phases and modes were identified and determined based on the combined X-ray element maps.

Quantitative analyses of minerals in the silicic clast were performed by wavelength dispersive spectroscopy using a JEOL JXA-8900 EPMA at Waseda University with (1) an accelerating voltage of 15 kV and a probe current of  $2.0 \times 10^{-8}$  A for feldspar, silica, pyroxene, olivine, and Fe-oxide, and (2) 7 kV and  $2.0 \times 10^{-8}$  A for Caphosphate. Quantitative major element analyses were determined for the silicates and Fe-oxide; the main goal of the Ca-phosphate analyses was to use Ca/P ratios to distinguish apatite from merrillite. During electron irradiation using EPMA, alkali feldspar crystals showed blue cathodoluminescence that faded during exposure to the electron beam. Well-characterized oxides, silicates, and phosphates were used as standards. Approximate lower limits of detection for the 15 kV analyses are as follows (in wt%): Na<sub>2</sub>O = 0.02; MgO = 0.02; Al<sub>2</sub>O<sub>3</sub> = 0.03; SiO<sub>2</sub> = 0.04;  $P_2O_5 = 0.03$ ;  $K_2O = 0.01$ ; CaO = 0.02;  $TiO_2 = 0.05$ ;  $Cr_2O_3 = 0.04$ ; MnO = 0.05; FeO = 0.06; BaO = 0.03. Only data with analytical totals of 98-102 wt% with close fits to the mineral stoichiometries were selected in this paper.

Laser micro-Raman spectroscopy was carried out to identify minerals using Thermo Electron (Nicolet Almega XR) with the 532 nm excitation line of the Nd:YAG laser at Okayama University of Science. The source laser power was set at 20 mW on the sample with a  $\sim 2~\mu m$  spot diameter. Raman spectra of minerals were collected with the wavenumber range from 150 to 800 cm $^{-1}$  with step size of 1 cm $^{-1}$ . Raman intensity mapping was measured along the X and Y directions with 30  $\mu m$  step sizes. In the Raman maps, the integral intensities of the main bands for each mineral were extracted from the spectral data of each measuring point to observe distributions of minerals. The Raman data were collected in five accumulations of 60 s

for the spectra and three accumulations of 30 s exposure time for mapping. All the spectral data were calibrated by monitoring the position of the O-Si-O bending vibration (464 cm<sup>-1</sup>) in reference standard quartz of high optical grade before and after each measurement. Detailed information on the Raman spectroscopy is shown in Kayama et al. (2018).

#### **Results**

### Petrography

Figure 1 shows false-color elemental mapping of Al (red), Mg (green), and Fe (blue)  $K\alpha$  x-rays, and distinguishes the main minerals of NWA 2727, as shown in the following colors: light green and blue colors indicate olivine; dark green and blue colors indicate pyroxene; red color indicates plagioclase. The PTS contains several types of clasts identified as mafic lithologies including OG, AG, FG (pyroxene gabbro), OPB, and the silicic clast (Fig. 1). The diversity of clast-types in our polished thin section (PTS) is consistent with previous work on NWA 2727, except for the silicic clast, which has not been described previously (Bunch et al. 2006; Zeigler et al. 2007; Valencia et al. 2019). Petrological descriptions of each lithology in the PTS are summarized below.

The OG lithology consists mostly of olivine and pyroxene with plagioclase. Large and small varieties of OG clasts are included in the PTS. The largest OG clast in this PTS is  $8.0 \times 6.2$  mm in size (Fig. 2a). Olivine (light green grains in Fig. 2a; 57 vol%) is the most abundant mineral in this OG clast. Olivine occurs as subhedral to euhedral crystals ranging from 100 µm up to 1.8 mm across. Several grains of olivine are over 1 mm across. Pyroxene (dark green grains in Fig. 2a; 25 vol%) is the second most abundant mineral. Pyroxene crystals in the OG also are coarse, with grain sizes up to 1 mm across. Anhedral crystals of plagioclase (red in Fig. 2a; 16 vol%) typically occur between coarse olivine and pyroxene. Plagioclase often appears elongate in the OG clast, with grain sizes up to  $1.3 \times 0.3$  mm. Large olivine crystals with pyroxene and plagioclase filling interstices indicate the cumulate texture. Fe-oxides occur in trace abundances in the OG clast, and are located between coarse minerals. Silica minerals are not found in the OG clast. These petrological features are similar to other OG clasts in the NWA 773 clan (Fagan et al. 2003; Jolliff et al. 2003; Zhang et al. 2011; Nagaoka et al. 2015; Valencia et al. 2019).

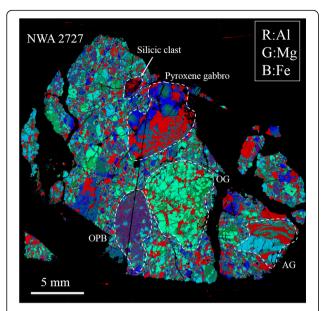
The AG has a cumulate texture and is dominated by plagioclase and pyroxene (Valencia et al. 2019). One plagioclase-rich clast with texture similar to the AG was identified in the PTS. The clast is  $4.4 \times 4.3$  mm in size in this PTS (Fig. 2b). Plagioclase (red in Fig. 2b; 35 vol%) occurs as elongate-appearing crystals, with grain sizes up to  $2.1 \times 0.5$  mm. Plagioclase in the clast (35 vol%) is more abundant than in the OG lithology (16 vol%).

Pyroxene (dark green in Fig. 2b; 27 vol%) forms elongate crystals between coarser plagioclase. Olivine (light blue in Fig. 2b; 36 vol%) shows some euhedral crystal faces, with grain sizes ranging from 0.3 to 2 mm across. Silica minerals were not identified. The mineral assemblage of this clast is similar to that of the OG, but the mineral textures and modal abundances are different. Plagioclase in this clast is much more abundant than in OG clasts. This clast has coarse laths of anhedral plagioclase intergrown with pyroxene similar to the cumulate texture of AG as described by Valencia et al. (2019). Therefore, the plagioclase-rich clast is categorized as AG, although the presence of olivine was not reported in the AG clasts described by Valencia et al. (2019).

The FG group includes variable types of ferroan lithologies (described above; also see Fagan et al. 2014; Valencia et al. 2019). One clast of pyroxene gabbro (part of the FG group) in the PTS is approximately  $7.8 \times 5.2$  mm across in this PTS (Fig. 2c). The clast consists mostly of plagioclase and pyroxene, which are in subequal proportions. Plagioclase (red in Fig. 2c) occurs as both small and large crystals, ranging up to 1.6 mm across. The pyroxene crystals are up to 2.0 mm across and are zoned to Fe-rich compositions (from dark green to blue color in Fig. 2c), which are characteristic of the pyroxene gabbro lithology as defined by Fagan et al. (2014). No silica minerals were identified in the internal texture of this clast, although silica minerals (e.g., tridymite) were found along the boundary between the FG clast and the breccia matrix, and in veins that cut through the clast (Kayama et al. 2018). In addition to the large pyroxene gabbro clast, other FG lithologies are present as smaller clasts in the PTS and in other specimens of NWA 2727 (Bunch et al. 2006; Valencia et al. 2019).

One large basaltic clast, covering an area of  $5.6 \times 3.6$  mm is present in the PTS (Fig. 2d). Olivine phenocrysts (light blue in Fig. 2d) are surrounded by a fine-grained groundmass of pyroxene (dark blue in Fig. 2d) and plagioclase (red in Fig. 2d). The grain sizes of olivine phenocrysts are from  $0.3 \times 0.1$  mm to  $0.6 \times 0.3$  mm across. The presence of olivine phenocrysts and fine-grained groundmass consisting of pyroxene and plagioclase of this basaltic clast are similar to the olivine-phyric basalt (OPB) described by Valencia et al. (2019).

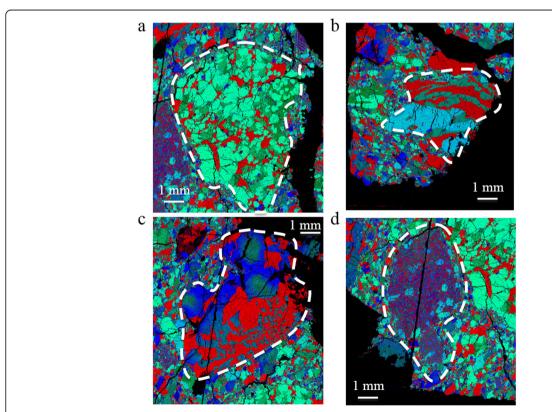
Plane-polarized light, BSE, and elemental RGB images of the silicic clast are presented in Fig. 3. The silicic clast consists mostly of plagioclase, alkali feldspar, and silica, which comprise > 80 vol% of the mode as exposed in our PTS (Table 1; Fig. 3). The silicic clast is  $2.2 \times 1.3$  mm in size in this PTS. Olivine and high-Ca pyroxene also occur in the clast, and Caphosphate, ilmenite, chromite, and troilite are present as minor minerals. All of the Ca-phosphate analyzed here by EPMA yielded apatite stoichiometry; merrillite was not identified.



**Fig. 1** False-color X-ray elemental image of NWA 2727 breccia modified after Kayama et al. (2018). Red, green, and blue (RGB) represent Al, Mg, and Fe, respectively. K $\alpha$  X-rays were used for all elements. Clast name abbreviations: *OG* olivine gabbro, *AG* anorthositic gabbro, *OPB* olivine-phyric basalt

Plagioclase is present in the center of the clast and tends to be in contact with silica (Fig. 3c, d). Silica occurs as (1) massive to elongate grains up to 550 µm in long diameter (labeled Si<sup>(1)</sup> in Fig. 3d); (2) narrow domains enveloping thin plagioclase feldspar laths ( $\sim 50 \ \mu m \ across$ ) (labeled Si<sup>(2)</sup> in Fig. 3d); and (3) elongate crystals intergrown with K-Ba-feldspar (labeled Si<sup>(3)</sup> in Fig. 3d). K-Ba-feldspar is not as abundant as plagioclase or silica, but comprises approximately 15 vol% of the mode in the clast and appears to have co-crystallized with silica. Most of the mafic minerals occur in a cluster of olivine (310  $\mu$ m × 260  $\mu$ m), pyroxene, and apatite near the left margin of the clast as shown in Fig. 3c, d. In this part of the clast, fine pyroxene crystals (< 100 µm; Px fine1 in Fig. 3c) occur adjacent to apatite. Pyroxene also occurs as fine clusters of crystals disseminated among silica and feldspar near the right margin of the clast (< 100 µm; Px fine2 in Fig. 3c), and one coarser crystal (210  $\mu m \times 140 \mu m$ ) occurs near the bottom of the clast (Px crs in Fig. 3c).

Silica is abundant in the clast, constituting nearly 40% of the mode (Table 1). Silica polymorphs were determined using micro-Raman spectroscopy in digital maps of three localities within the clast (Fig. 3e-h). Most spectra showed weak bands indicative of poor crystallinity,



**Fig. 2** False-color X-ray elemental images of mafic lithologies of NWA 2727. Detailed explanations of each figure are as follows: **a** olivine gabbro (OG); **b** anorthositic gabbro (AG); **c** pyroxene gabbro; **d** olivine-phyric basalt (OPB). RGB elemental map with R = Al, G = Mg, B = Fe

but some points yielded spectral patterns characteristic of tridymite, cristobalite, and quartz, all present within the clast (Fig. 4). Quartz was identified only where silica is intergrown with K-Ba-feldspar, whereas cristobalite and tridymite were found where the silica has a more massive texture (Fig. 3e–h).

Mafic mineral crystals in the silicic clast are much finer-grained (0.3 mm in maximum dimension) than those of three gabbros (OG, AG, FG), and similar in size to olivine phenocrysts in the OPB. The finer-grained texture of the silicic clast indicates more rapid cooling history than those of the three gabbros. Silica minerals with abundant plagioclase feldspar were not identified in OG, AG, and FG lithologies in this PTS. The silicic clast occurs isolated in breccia, and has no spatial or zoning relationships with those gabbros. Some of FG clasts (symplectite and ARFe) in other portions of NWA 773 clan include silica minerals (Fagan et al. 2014; Valencia et al. 2019), but the modal abundances of silica are less and grain sizes are smaller than silica of the silicic clast.

#### Mineral compositions in the silicic clast

Olivine and ilmenite in the silicic clast have Fe# (molar Fe/  $[Fe + Mg] \times 100$ ) of 99–100 (Table 2) corresponding to late-stage magmatic crystallization. All of the pyroxene analyses indicate hedenbergitic compositions with Fe# and Ti# both  $\geq$  99 (Ti# = molar Ti/[Ti + Cr]  $\times$  100) (Table 2; Figs. 5 and 6). Fine pyroxene crystals that are interwoven with apatite in the mafic cluster and the coarse pyroxene have essentially identical Wo-En-Fs compositions; the fine pyroxene near the upper right margin (Px fine2 in Fig. 3) has slightly lower Wo-content (Wo<sub>36–38</sub> in Fig. 5). All pyroxenes in the silicic clast are more ferroan than those in the ARFe clasts analyzed by Fagan et al. (2014) (Figs. 5 and 6). All analyzed pyroxenes from the silicic clast have a Ti/ Al ratio ranging from 0.4 to 0.6 with an average value of 0.5 as shown in Fig. 6a. In lunar basaltic rocks, low Ti/Al (~0.25) is associated with pyroxene that crystallized prior to feldspar, whereas higher Ti/Al (~0.5) indicates pyroxene that crystallized after feldspar crystallization had started (Bence et al. 1970; Fagan et al. 2014). Thus, it is likely that all of the pyroxene from the clast crystallized after the onset of feldspar crystallization. The high Fe# and Ti# are consistent with late-stage crystallization in an igneous system (Fig. 6b).

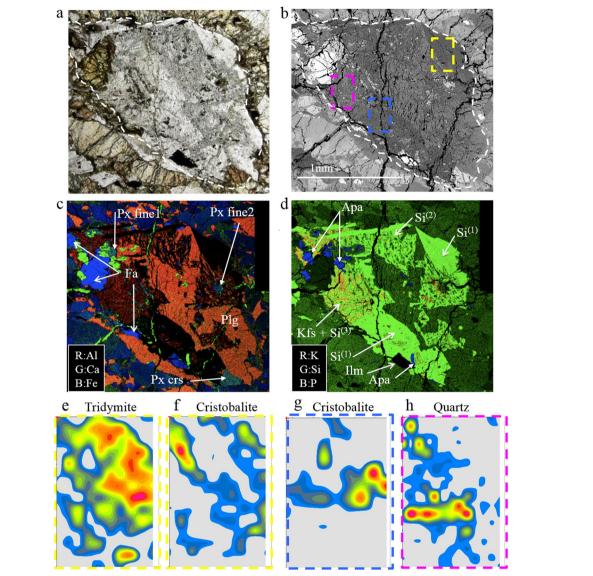
Plagioclase has chemical compositions near  $An_{87}$  with limited Ab-An zoning ( $An_{82-91}$ ; Table 3). The An value is higher than those of plagioclase in the Apollo granitic samples ( $An_{80-50}$ ; Wieczorek et al. 2006). The FeO content in plagioclase (1.15 wt%) is higher than those in the Apollo granite/felsite (0.06–0.79 wt%: Warren et al. 1983; Jolliff 1991; Seddio et al. 2013, 2015) and KREEP basalt (0.16–0.71 wt%: Simon et al. 1988; Papike et al.

1991), and the FeO content in plagioclase of the silicic clast is as high as those of the Apollo very-low-Ti mare basalt (0.90-1.34 wt% in Papike et al. 1991). Minor K<sub>2</sub>O (Or<sub>~2</sub>) was detected in all analyses of plagioclase and BaO was detected in some analyses, though only in minor concentrations (< 0.2 wt% BaO). Alkali feldspar is enriched in K, with minor Na, detectable Ca, and variable Ba (Ab<sub>3</sub>An<sub>2</sub>Or<sub>95</sub>Cn<sub>0</sub>-Ab<sub>4</sub>An<sub>2</sub>Or<sub>81</sub>Cn<sub>13</sub>). The BaO concentration in the K-Ba-feldspar is zoned (0.1-6.7 wt%). Analyses of silica are mostly  $SiO_2$ , with minor  $TiO_2$  (mostly 0.1 to 0.2 wt%); K2O and Al2O3 were detected during analyses, possibly due to beam overlap with adjacent feldspar. However, as noted by Seddio et al. (2015), the hightemperature polymorphs of silica have more open structures than quartz and thus, may accommodate elevated concentrations of minor elements. The silicic clast formed at or near the lunar surface at a cooling rate fast enough to preserve cristobalite and tridymite. Zoning of BaOconcentration in K-Ba-feldspar is consistent with a fast cooling rate, as are the fine grain sizes of mafic minerals in the silicic clast. These features indicate that this clast is not plutonic rock, but rather derived from volcanic or near-surface origin. On the IUGS classification of volcanic rocks based on modal abundances of silica, alkali feldspar, and plagioclase, this clast falls on the boundary between rhyolite and dacite (Fig. 7).

# Comparison of major element composition of the silicic clast with other lithologies in NWA 773 clan

The whole rock composition of the silicic clast was determined by modal recombination (Table 4) using modal abundances, densities of minerals, and their elemental concentrations. All Fe is calculated as  $Fe^{2+}$ . And the density of all  $SiO_2$  is used as 2.2 g cm<sup>-3</sup>, which is comparable to the density of cristobalite (Holland and Powell 2011). Based on bulk  $SiO_2$  and  $Na_2O + K_2O$  contents, the silicic clast falls along andesite-dacite boundary on the total alkali-silica (TAS) diagram of Le Bas et al. (1992); Fig. 8). This clast is characterized as a dacite on the basis of the low-pressure origin indicated by cristobalite and tridymite combined with the bulk composition.

The bulk composition of the dacite clast is compared with those of other clast lithologies (OG, AG, FG, OPB) in NWA 773 clan and the Apollo quartz monzodiorite (QMD), granite, and felsite in Table 4. The dacite clast is more enriched in  $SiO_2$  and alkali elements (Na, K, Ba) than other lithologies of NWA 773 clan. Furthermore, the bulk composition of the dacite (Mg# < 1) is much more ferroan than other NWA 773 clan lithologies that were analyzed by Valencia et al. (Mg# $_{51-70}$ , see Table 4). From the above results, the dacite clast appears to be a distinct lithology from the existing lithologies in the NWA 773 clan. On the other hand, the concentrations of  $SiO_2$  and



**Fig. 3** Images of silicic clast and Raman maps showing silica polymorphs. Detailed explanations of each figure are as follows: **a** photomicrograph in plane polarized light; **b** back-scattered electrons (BSE); **c** RGB elemental map with R = AI, G = Ca, B = Fe, **d** RGB image with R = K, G = Si, B = P. Silica occurs as: (1) massive to elongate grains; (2) narrow domains enveloping thin plagioclase feldspar laths; and (3) elongate crystals intercalated with K-Ba-feldspar. Areas where Raman peaks were mapped are color-coded in panel **b**, with maps **e**, **f** enclosed in the yellow box, map **g** in the blue box, and map **h** in the purple box. The Raman peak intensity maps show the following peaks: **e** peak intensity at 351 cm<sup>-1</sup> (tridymite); **f** peak intensity at 411 cm<sup>-1</sup> (cristobalite); **h** peak intensity at 464 cm<sup>-1</sup> (quartz). Warm colors (red) indicate high peak intensities and dark (blue) colors denote low intensities. Mineral abbreviations: *Apa* apatite, *Fa* fayalite, *Ilm* ilmenite, *Kfs* K-feldspar, *Plq* plagioclase, *Px* pyroxene, *Si* silica

alkali elements in the dacite are not as high as those in the Apollo granite and felsite. The bulk  $P_2O_5$  content (1.3 wt%) in the dacite clast is higher than those (0.086–0.34 wt%) of other lithologies in NWA 773 clan and Apollo granite/felsite (0.05–0.20 wt%: Quick et al. 1977; Seddio et al. 2013), but falls in the range of  $P_2O_5$  concentrations of QMD (0.25–1.72 wt%: Taylor et al. 1980; Ryder and Martinez 1991; Jolliff et al. 1993; Fagan et al. 2014).

## Discussion

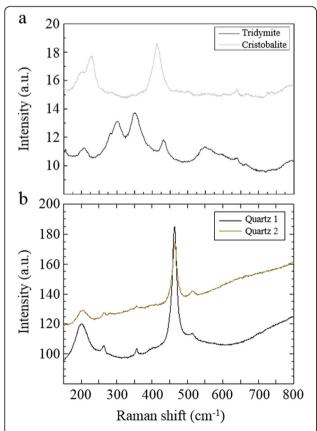
# Comparisons of the dacite clast with other lunar silicic rocks

The high Fe# of mafic silicates combined with the abundance of silica in the dacite clast can be explained by crystallization from a residual liquid after fractional crystallization. Some of the silica in the clast is intergrown with feldspars, suggesting co-crystallization of silica with plagioclase and alkali feldspars during stages of crystallization from liquid. The interlocking textures of

Table 1 Modal abundances (vol%) of minerals in the NWA 2727 silicic clast, Apollo granite, QMD

Sample name	NWA 2727	12033,634-34	12023,14-10	12032,366-19	15405,145
Clast	Silicic clast	Granite	Granite	Granite	QMD
Refer.	this work	Seddio et al. (2015)	Seddio et al. (2014)	Seddio et al. (2013)	Fagan et al. (2014)
Ol	4.9	7.1	0.8	2.8	-
LCP	-	8.7	2.2	5.5	12.1
HCP	5.9				13.7
Plg	31.4	30.3	14.2	6.3	20.2
Kfs	14.9	21.1	45.7	52.3	24.5
Si	39.4	24.0	36.7	32.0	23.8
Ox	<1	1.0	<1	<2	2.3
Ар	2.6	4.0	Tr	Tr	0.3
Mer	-	3.9	-	Tr	2.8

Ol olivine, LCP low-Ca pyroxene (pigeonite + orthopyroxene), HCP high-Ca pyroxene (augite), Plg plagioclase, Kfs K-feldspar, Si silica, Ox oxide phases, Ap apatite, Mer merrillite, Tr trace amount. The unit of modal abundances in Seddio et al. (2013, 2014) are converted into "vol%" from "wt%"



**Fig. 4** Representative Raman spectra of **a** tridymite and cristobalite and **b** quartz in the silicic clast. Raman bands of tridymite at 207, 301, 351, and 432 cm<sup>-1</sup>, cristobalite at 228 and 411 cm<sup>-1</sup>, and quartz at 199 and 464 cm<sup>-1</sup> (e.g., Etchepare et al. 1974; Ling et al. 2011; Seddio et al. 2015) were detected

the dacite clast are distinct from granulitic textures (mainly minerals having rounded shapes) associated with silicic rocks formed by impact, and no shock melt pockets were observed (Takeda 1986; Barrat et al. 2009; Takeda et al. 2015). Moganite, a monoclinic SiO<sub>2</sub> polymorph associated with carbonaceous chondrite-derived lunar alkaline fluid that becomes a source of subsurface ice deposits, has been identified along with the highpressure polymorphs coesite in matrix grains and stishovite in some shock veins elsewhere in NWA 2727 (Kayama et al. 2018). Some portions of cristobalite and tridymite also occur in silica micrograins in the shock veins, which apparently transformed from moganite during post-shock decompression. However, the coarse grain sizes and intergrown feldspar texture of the dacite clast are distinct from the shock-related occurrences of silica identified by Kayama et al. (2018). Therefore, the formation of tridymite and cristobalite in the dacite clast by unloading after shock impact can be excluded; a shock melt origin of the dacite clast is unlikely. We infer that this clast crystallized from silicic melt that formed by endogenic igneous processes on the Moon.

The occurrence of three low-pressure silica polymorphs indicates rapid, near-surface cooling, and disequilibrium. Cristobalite and tridymite observed in the clast are thought to have been quenched from conditions of low pressures (< 1 GPa) and high temperatures (~ 870 to ~ 1500 °C) (e.g., Presnall 1995; Koike et al. 2013). These silica polymorphs are also found in silicic volcanic settings in terrestrial settings (e.g., Baxter et al. 1999; Hamasaki 2002; Horwell et al. 2010), and the presence of tridymite on the surface of Mars has been interpreted as an indicator of silicic volcanism (Morris et al. 2016). The presence of cristobalite provides evidence of higher crystallization temperature (Koike et al. 2013)

**Table 2** Average compositions of olivine, pyroxene and ilmenite in the silicic clast

	Olivine 4		Pyroxene 10		Ilmenite 2	
n						
wt%	mean	s.d.	mean	s.d.	mean	s.d.
SiO <sub>2</sub>	30.53	0.27	46.48	0.71	0.06	0.04
TiO <sub>2</sub>	0.06	0.02	0.99	0.28	51.29	0.23
$Al_2O_3$	< 0.03		1.32	0.37	0.06	0.02
Cr <sub>2</sub> O <sub>3</sub>	< 0.04		< 0.04		< 0.04	
FeO .	68.91	0.58	32.87	2.16	47.32	0.70
MnO	0.81	0.11	0.34	0.04	0.43	0.15
MgO	0.15	0.03	0.12	0.06	0.04	0.04
CaO	0.63	0.11	18.54	1.75	0.07	0.02
Na <sub>2</sub> O	0.05	0.02	0.04	0.02	< 0.02	
< <sub>2</sub> O	< 0.01		<0.01		0.01	0.00
P <sub>2</sub> O <sub>5</sub>	0.06	0.03	< 0.03		< 0.03	
BaO	na		0.07	0.04	na	
Гotal	101.2		100.8		99.3	
at. per oxy at.	4		6		3	
ŝi	1.013	0.006	1.927	0.025	0.002	0.001
ī	0.001	0.001	0.031	0.009	0.985	0.001
Al	b.d.		0.065	0.018	0.002	0.001
<u> Îr</u>	b.d.		b.d.		b.d.	
e	1.912	0.015	1.140	0.077	1.011	0.010
Лn	0.023	0.003	0.012	0.001	0.009	0.003
Иg	0.007	0.001	0.008	0.003	0.002	0.002
	0.022	0.004	0.823	0.076	0.002	0.000
la	0.004	0.001	0.003	0.002	b.d.	
	b.d.		b.d.		0.000	0.000
)	0.002	0.001	b.d.		b.d.	
За	na		0.001	0.001	na	na
otal	2.984		4.010		2.013	
e#	99.8		99.3		99.8	
No			41.8			
Ēn			0.4			
-s			57.8			
Γi#			99.9			
Γi/Al			0.48			

Note: Our values in "s.d." column are the standard deviations (1 $\sigma$ ) of the individual mineral compositions and reflect the compositional variation of each mineral in the silicic clast. The word of "n" means number of analyses, "b.d." means below the detection limit, "n.a." means no analysis

than typical lunar granitic samples (T < 1000 °C) (Jolliff et al. 1999; Gullikson et al. 2016). The occurrence of three low-pressure silica polymorphs in the same rock is unusual; however, Seddio et al. (2015) observed hackle fracture patterns in quartz in Apollo samples of lunar granites, and inferred that the fractures formed by a volume reduction during recrystallization from cristobalite

or tridymite to quartz. The phase transition to quartz would depend on cooling rate. The dacite clast probably crystallized at a relatively fast cooling rate that resulted in incomplete transformation of the high-T polymorphs to quartz. The poor crystallinity of much of the silica in the clast is likely due to rapid cooling during crystallization.

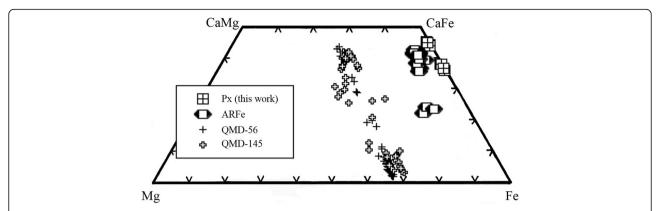
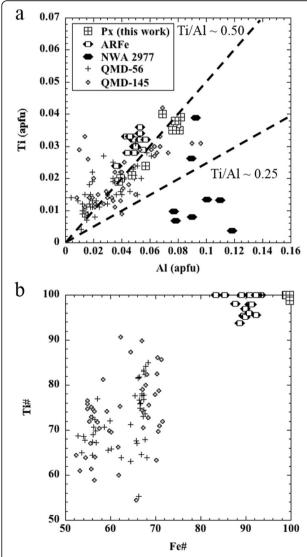


Fig. 5 Pyroxene quadrilateral compositions from the silicic clast (this work). Compositions reported by Fagan et al. (2014) for pyroxenes from NWA 773 ARFe clasts and 15405 QMD (56, 145), are also shown



**Fig. 6 a** Al versus Ti and **b** Fe# versus Ti# in pyroxenes from the silicic clast (this work). Compositions of ARFe clasts in NWA 773 (Fagan et al. 2014), NWA 2977 OG (Nagaoka et al. 2015), and 15405 QMD (56, 145) (Fagan et al. 2014) are also shown

Other silica-bearing igneous clasts in NWA 773 clan include clinopyroxene-phyric basalt (CPB) clasts, symplectite, and alkaline-phase-ferroan (ARFe) clasts (Fagan et al. 2014; Kayama et al. 2018). The symplectite and ARFe classifications of Fagan et al. (2014) are grouped together as variations within ferroan gabbro (FG) by Valencia et al. (2019), but both groups of workers (Fagan et al. 2014; Valencia et al. 2019) report similar textures and mineral compositions. The CPB clasts have anhedral quartz single crystals on the order of  $\leq 40 \, \mu m$  across and have abundant pyroxene + feldspar-rich groundmass, distinct from the dacite clast (Kayama et al. 2018). The symplectite (one variety of FG of Valencia et al. 2019) is composed of fayalite, silica, and hedenbergitic pyroxene with curved, fine intermingled textures (Fagan et al. 2003, 2014; Jolliff et al. 2003). Fayalite, silica, and hedenbergitic pyroxene also occur in the dacite clast, but feldspars also are abundant in the clast, and the textures and formation processes are distinct. Whereas the symplectites formed dominantly by pyroxferroite breakdown (Fagan et al. 2003, 2014; Jolliff et al. 2003; Valencia et al. 2019), textures in the dacite clast are consistent with formation by igneous crystallization from melt.

Igneous textures, such as elongate K-feldspar intergrown with silica, also occur in some ARFe clasts of NWA 773 (Fagan et al. 2014; approximately equivalent to silica-K-feldspar granophyre-bearing clasts of Jolliff et al. 2003, and grouped within the FG lithology of Valencia et al. 2019, see their Figs. 9–11 of FG-A, FG-B, FG-C, FG-D, FG-F, FG-I). The presence of ferroan mafic silicates, silica, feldspar, and Ca-phosphates are common to the FG/ARFe lithology (combining the classification schemes of Fagan et al. 2014 and Valencia et al. 2019) and the dacite clast, and textures in FG/ARFe rocks and dacite clast indicate igneous origin. In detail, however, the two lithologies are distinct. In the FG/ARFe clasts,

Table 3 Average compositions of plagioclase, K,Ba-feldspar and silica in the silicic clast

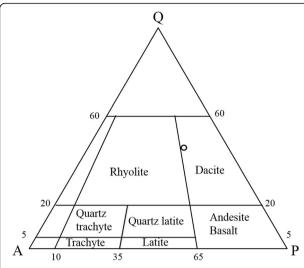
	Plagioclase 13		K,Ba-feldspar 6		Silica 11	
n						
wt%	mean	s.d.	mean	s.d.	mean	s.d.
SiO <sub>2</sub>	47.29	1.13	62.81	1.86	99.61	0.78
TiO <sub>2</sub>	< 0.05		0.18	0.12	0.16	0.03
$Al_2O_3$	31.91	1.14	19.57	0.60	0.55	0.18
$Cr_2O_3$	< 0.04		< 0.04		<0.04	
FeO	1.15	0.29	0.14	0.05	0.11	0.08
MnO	< 0.04		< 0.04		<0.04	
MgO	<0.02		< 0.02		<0.02	
CaO	18.14	0.79	0.31	0.12	0.05	0.03
Na <sub>2</sub> O	1.26	0.25	0.42	0.04	0.09	0.04
K <sub>2</sub> O	0.33	0.14	14.61	1.00	0.28	0.14
P <sub>2</sub> O <sub>5</sub>	< 0.03		< 0.03		<0.03	
BaO	0.09	0.05	3.45	2.30	0.03	0.02
Total	100.17		101.49		100.88	
atoms per oxy at.	8		8		2	
Si	2.187	0.051	2.919	0.050	0.992	0.002
Ti	b.d.		0.007	0.004	0.001	0.000
Al	1.740	0.058	1.073	0.046	0.006	0.002
Cr	b.d.		b.d.		b.d.	
Fe	0.045	0.011	0.005	0.002	0.001	0.001
Mn	b.d.		b.d.		b.d.	
Mg	b.d		b.d.		b.d.	
Ca	0.899	0.038	0.016	0.006	0.001	0.000
Na	0.113	0.023	0.038	0.004	0.002	0.001
K	0.020	0.008	0.866	0.049	0.003	0.002
Р	b.d		b.d.		b.d.	
Ва	0.002	0.001	0.063	0.043	0.000	0.000
total	5.006		4.987		1.006	
Ab	10.9		3.9			
An	87.0		1.6			
Or	1.9		88.1			
Cn	0.2		6.4			

Note: Our values in "s.d." column are the standard deviations ( $1\sigma$ ) of the individual mineral compositions and reflect the compositional variation of each mineral in the silicic clast. The number of analyses is indicated by "n", "b.d." means below the detection limit. The BaO content was determined in 11 of the 13 analyses of plagioclase feldspar

K-feldspar is more abundant than plagioclase, but the reverse is true for the dacite clast. The main Ca-phosphate in the FG/ARFe lithology is merrillite, whereas only apatite has been identified in the dacite clast. Finally, although K-feldspar and silica are characteristic of the FG/ARFe clasts, they typically occur in minor modal abundances compared to mafic silicates. In contrast, feldspars and silica are much more abundant than mafic phases in the dacite clast. The differences in mineral modes reflect

the high bulk  $SiO_2$  content of the dacite compared to the FG/ARFe clasts (Fagan et al. 2014; Valencia et al. 2019), suggesting differences in origin.

Therefore, although the dacite clast shares several features of the FG/ARFe lithology described by Fagan et al. (2014) and Valencia et al. (2019), the dacite clast appears to be a new lithology in the NWA 773 clan, which has not been described previously. While we cannot rule out the possibility that the dacite clast is an unusual variety



**Fig. 7** IUGS Classification of volcanic rocks (Streckeisen 1979). White circle plot represents the silicic clast (this work)

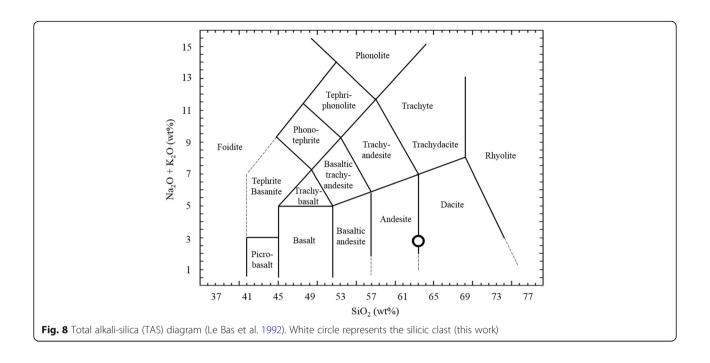
of the FG/ARFe lithology, the high  ${\rm SiO_2}$ -content, high ratio of plagioclase/K-feldspar and occurrence of apatite without merrillite all point toward a distinct origin for the dacite clast (see "Petrogenesis of the dacite clast" section for further discussion).

The whole-rock composition distinguishes the dacite clast from other lunar silicic rocks such as QMD and granite. In Fig. 9, the bulk composition of the dacite clast is compared with lunar evolved rocks returned by Apollo missions (KREEP basalt, QMD, granite/felsite, granitic breccia) (Hubbard et al. 1973; Rhodes and Hubbard 1973; Murali et al. 1977; Quick et al. 1977; Warren and Wasson 1978; Warren et al. 1978; Taylor et al. 1980; Warren et al. 1983; Salpas et al. 1987; Lindstrom et al. 1988; Simon et al. 1988; Morris et al. 1990; Jolliff et al. 1991; Marvin et al. 1991; Ryder and Martinez 1991; Snyder et al. 1992; Jolliff et al. 1993; Seddio et al. 2013; Fagan et al. 2014). Lunar sample return missions collected no dacite or andesite samples (that have yet been identified), so several analyses of terrestrial ferroan (Mg# < 50) andesite and dacite (Shimazu et al. 1985; Gust and Arculus 1986; Imai et al. 1995; Togashi et al. 2000; Sensarma and Palme 2013) are plotted in Fig. 9 for the comparison.

The dacite clast plots between QMD and lunar granitic rocks in terms of SiO2 versus MgO + FeO contents (Fig. 9a), and is distinct from the clusters of lunar KREEP basalts, QMD, and granitic rocks in terms of SiO<sub>2</sub> versus Al<sub>2</sub>O<sub>3</sub> (Fig. 9b). In both cases, the clast is similar to some of the terrestrial ferroan andesite/dacite samples. However, the dacite clast has lower Na2O + K<sub>2</sub>O contents at comparable SiO<sub>2</sub> and is more ferroan than both the terrestrial andesite/dacites and lunar granitic rocks (Fig. 9c, d). The difference in alkalis reflects the lower mode of K-feldspar and the low albite content (Ab<sub>11</sub>) of plagioclase in comparison with the Apollo granitic samples and in the terrestrial andesite/dacite. The reported whole-rock Na<sub>2</sub>O and K<sub>2</sub>O (and SiO<sub>2</sub>) concentrations of the dacite in NWA 773 clan depend of course on the mode of the clast, which is likely to vary

**Table 4** Major element abundances of the silicic clast (this work), other lithologies (OG, AG, FG, OPB) in NWA 773 clan, and Apollo evolved samples

	NWA 2727 Silicic clast This work	NWA 773 clan				15405,145	12032, 366-19	12013, light	
		OG	AG	FG	OPB	QMD	Granite	Felsite	
Oxide (wt%)		Valencia et al. 2019				Fagan et al. 2014	Seddio et al. 2013	Warren et al. 1983	
SiO <sub>2</sub>	63.0	43.47	47.3	47.52	45.39	60.3	70.1	73	
TiO <sub>2</sub>	0.89	0.36	0.17	1.07	0.85	2.15	1.07	0.6	
$Al_2O_3$	13.5	5.02	19.5	6.91	8.01	10.3	13.5	11.9	
Cr <sub>2</sub> O <sub>3</sub>	<0.1	0.42	0.28	0.44	0.52	0.08	-	-	
FeO	9.3	19.08	9.58	19.83	21.72	11.0	4.98	0.90	
MnO	<0.1	0.234	0.17	0.279	0.284	0.17	0.07	-	
MgO	<0.1	24.65	7.05	12.92	12.71	3.18	0.14	0.7	
CaO	9.2	7.04	15.1	10.83	9.59	7.6	3.04	1.4	
Na <sub>2</sub> O	0.51	0.122	0.38	0.157	0.163	0.76	2.47	1.40	
K <sub>2</sub> O	2.3	0.029	0.04	0.150	0.018	3.42	4.58	6.80	
$P_2O_5$	1.3	0.086	-	0.34	0.094	1.42	0.052	-	
BaO	0.54	0.01	< 0.07	0.03	0.01	-	0.68	0.65	
Total	100.5	100.5	99.6	100.5	99.4	100.4	100.7	97.4	
Mg#	<1	70	57	54	51	34	5	58	



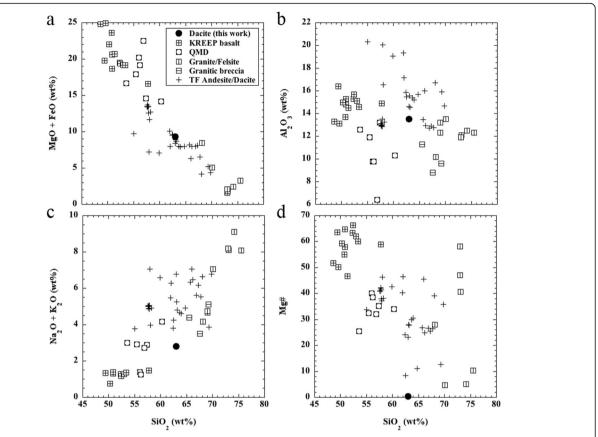
at least somewhat from the mode of the original lithology on the Moon. If the clast has disproportionately high modes of silica or low modes of feldspars, then the calculated  $Na_2O + K_2O$  vs.  $SiO_2$  content could fall along the lunar variation trend shown in Fig. 9c. However, the low Ab-content of plagioclase and high Fe# of mafic silicates of the dacite clast are distinct from the terrestrial and most of the lunar samples plotted in Fig. 9.

#### Petrogenesis of the dacite clast

Although there are mineralogical and compositional differences between the dacite and FG/ARFe lithology described by Fagan et al. (2014) and Valencia et al. (2019), the origin of the dacite clast is broadly similar to the origin of the FG/ ARFe lithology. Both lithologies crystallized from igneous liquids that were depleted in MgO and enriched in SiO<sub>2</sub> and alkalis. Composite clasts with zoned pyroxene ± feldspar attached to FG/ARFe domains indicate that the FG/ ARFe lithology formed after Fe-enrichment (Mg-depletion) by fractional crystallization (Fagan et al. 2014; Valencia et al. 2019). Rounded inclusions in fayalite in the FG/ARFe lithology contain igneous feldspathic glass or alkali feldspar + silica, and formed by immiscibility of alkali-silica-rich liquid from Fe-rich silicate liquid (see Rutherford et al. 1974, 1976). Spatial continuity of variations within the FG lithology (ARFe rocks, symplectites, and pyroxene gabbro), combined with mineral compositions in the OG lithology and similar U-Pb ages of baddeleyite are strong evidence that these gabbroic rocks-OG, AG, FG lithologiesformed from a co-magmatic sequence of crystallization (Fagan et al. 2014; Shaulis et al. 2017; Valencia et al. 2019).

Whether the dacite clast also formed as part of the same NWA 773 clan co-magmatic sequence that started with OG is problematic. As described above, the high Fe# of mafic silicates and the general mineral assemblage of the dacite are similar to the glass and feldspar + silica-bearing immiscible inclusions in FG/ARFe rocks. If the FG/ARFe immiscible inclusions coalesced, they might have formed a more coarse-grained rock similar to the dacite. However, the immiscible inclusions are dominated by alkali feldspar rather than plagioclase, and the main Caphosphate of the ARFe lithology is merrillite rather than apatite. Therefore, if the dacite formed from the alkalisilica-rich inclusions in the ARFe rocks, simple coalescence of inclusions alone is not a likely origin of the dacite. Some additional mixing with plagioclase materials or additional petrologic steps would be required to make the dacite from the ARFe inclusions. Based on the evidence currently available, we favor the interpretation that the dacite clast formed in a system independent of the olivine gabbro  $\rightarrow$  anorthositic gabbro  $\rightarrow$  ferroan gabbro (pyroxene gabbro + symplectite + ARFe) trend.

The presence of apatite without merrillite in the dacite clast is somewhat unusual because both Ca-phosphate minerals commonly occur together in felsic rocks from the Moon (Jolliff et al. 1993; Seddio et al. 2013, 2015; Fagan et al. 2014). However, apatite-bearing felsic rocks in which no merrillite was identified have been identified in lunar samples. Jolliff et al. (1993) reported apatite but no



**Fig. 9** Comparisons of bulk compositions between the silicic clast (Dacite; this work), Apollo evolved samples and several terrestrial andesite/dacites (see text): **a** SiO<sub>2</sub> vs. MgO + FeO, **b** SiO<sub>2</sub> vs. Al<sub>2</sub>O<sub>3</sub>, **c** SiO<sub>2</sub> vs. Na<sub>2</sub>O + K<sub>2</sub>O, **d** SiO<sub>2</sub> vs. Mg#. Rocks shown in the plot include: the silicic clast (dacite; this work); KREEP basalt (Hubbard et al. 1973; Rhodes and Hubbard 1973; Murali et al. 1977; Warren and Wasson 1978; Warren et al. 1978; Salpas et al. 1987; Simon et al. 1988); QMD (Taylor et al. 1980; Lindstrom et al. 1988; Marvin et al. 1991; Ryder and Martinez 1991; Jolliff et al. 1993; Fagan et al. 2014); granite/felsite (Quick et al. 1977; Warren et al. 1983; Morris et al. 1990; Jolliff et al. 1991; Snyder et al. 1992; Seddio et al. 2013); granitic breccia (Morris et al. 1990); terrestrial ferroan (TF) andesite/dacite (Shimazu et al. 1985; Gust and Arculus 1986; Imai et al. 1995; Togashi et al. 2000; Sensarma and Palme 2013)

merrillite in Apollo felsite 14161,7269, and likewise, Warren et al. (1983) identified apatite without merrillite in the granitic sample 14303,204. Factors controlling apatite vs. merrillite are in all likelihood connected to the relative abundances of volatile elements, which are concentrated in apatite, and of rare earth elements, which are concentrated in merrillite. Thus, the dacite clast, like other apatite-rich/merrillite-poor felsic rocks, probably formed in setting that was relatively volatile-rich on the Moon.

Another possible factor in the origin of the dacite is silicate liquid immiscibility (SLI). Immiscibility has been discussed as a possible explanation for the formation of lunar granites and the absence of intermediate lithologies (e.g., Jolliff 1991; Seddio et al. 2013). The occurrence of SLI has been found as micro-scale inclusions in a variety of lunar samples (e.g., Roedder and Weiblen 1970; Shearer et al. 2001) in addition to the evidence from the NWA 773 clan described above. SLI might have played a role in the origin of the dacite clast.

However, no direct textural evidence of SLI has been identified in the dacite. The dacite clast is isolated in breccia: there are no spatial or zoning relationships that show a genetic relationship with lithologies of the NWA 773 clan OG magmatic system. On the other hand, the possibility that the dacite might have formed by immiscibility of other magmatic system involving large-scale gravity separation of silica-rich melt from a parent melt remains plausible in view of the fact that the dacite composition plots on the edge of the miscibility gap of Roedder (1951) (see Appendix). The partitioning of Ba between Fe-rich and Si-alkali-rich immiscible liquids depends on the molar (Na<sub>2</sub>O + K<sub>2</sub>O + CaO + BaO)/Al<sub>2</sub>O<sub>3</sub> ratio in the granitic immiscible melt. If the ratio is below 1, Ba is partitioned into the granitic melt and if the ratio is over 1, Ba is partitioned into the basic melt (Neal and Taylor 1989). The "alkali"/Al<sub>2</sub>O<sub>3</sub> ratio of the dacite clast (1.5) is over 1, and the value is within the range of "alkali"/Al<sub>2</sub>O<sub>3</sub> values of most lunar granites/felsites (1.0-1.7 from Warren et al.

1983; Neal and Taylor 1989; Morris et al. 1990; Snyder et al. 1992; Seddio et al. 2013; except for 73255c, 0.84 from Warren et al. 1983). The presence of BaO in zoned alkali feldspar of the dacite clast shows that some BaO was present in the igneous melt at the time of crystallization. It is possible that BaO was rapidly depleted from the melt by alkali feldspar crystallization. A potential immiscible pair of the dacite clast has not been identified, so partitioning of BaO between immiscible liquids cannot be assessed in detail. However, similar values of "alkalis"/Al<sub>2</sub>O<sub>3</sub> of the dacite clast and several granitic samples from the Moon suggest general similarities in compositional evolution of BaO in lunar felsic rocks.

Previous work (Gullikson et al. 2016) supports the crustal melting model for the production of lunar granite from crustal protoliths by partial melting at temperatures below  $1000\,^{\circ}$ C. This model is consistent with the observation that quartz is the only  $SiO_2$  polymorph found in lunar granitic samples (Warren et al. 1983; Ling et al. 2011). However, this low-temperature crystallization model does not fit the dacite clast from NWA 2727 because the higher-temperature silica polymorphs cristobalite and tridymite occur along with quartz in the dacite.

The presence of a silica-rich feldspathic glass in the lunar meteorite Yamato 983885 (Y-983885) also requires silica-enrichment followed by rapid cooling (Arai et al. 2005). According to the model of Arai et al. (2005), the Si, Al, K-rich glass was derived from rapid cooling of an immiscible felsic liquid that separated from parent liquid before the crystallization of silica (Arai et al. 2005). The glass in Y-983885 apparently represents a case of silica-enrichment followed by rapid cooling distinct from the origin of the dacite clast in NWA 2727. No glass was identified in the dacite clast, suggesting that it cooled more slowly than the Y-983885 glass, but still fast enough to preserve the three low-pressure silica polymorphs.

The high Fe#<sub>99-100</sub> of mafic silicates in dacite clast can be explained by crystallization from residual liquid after Mg-depletion by fractional crystallization. The Apollo granite (12032,366-19) studied by Seddio et al. (2013) has a ferroan composition with fayalite and hedenbergite similar to the dacite clast and is interpreted as a product of extended fractional crystallization. Thus, it also has a ferroan composition like the dacite. The coexistence of multiple polymorphs of silica in the NWA 2727 dacite clast distinguishes the dacite from the Apollo 12032,366-19 granite, though the quartz in the Apollo 12 granite has a hackle pattern suggestive of contraction after crystallization and may have recrystallized from a higher-temperature silica polymorph (Seddio et al. 2013, 2015).

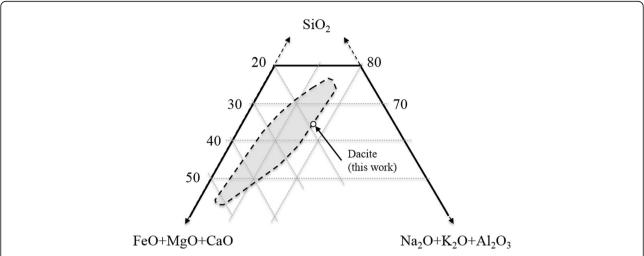
Calzada-Diaz et al. (2015) investigated the launch site of the NWA 773 using bulk composition, lunar global element maps (FeO, TiO<sub>2</sub>, and Th), and age constraints. They suggested that Mare Serenitatis, Crisium, or the west side of Oceanus Procellarum are plausible candidates of the launch site of NWA 773. Most proposed sites of silicic volcanism identified by remote sensing occur in the PKT, located on lunar nearside (Glotch et al. 2010). The presence of the dacite clast is, thus, consistent with a PKT origin for meteorites of the NWA 773 clan, as are the mafic composition, geochemical KREEP signature, and young crystallization age. Thus, among the possibilities discussed by Calzada-Diaz et al. (2015), we prefer the Procellarum and Serenitatis launch sites, as Crisium is farther from the PKT (also see Jolliff et al. 2003). In future work, we will investigate the launch site of NWA 773 clan by comparing the geochemical and petrological data with imaging data with higher spatial resolution.

#### **Conclusions**

NWA 773 clan of lunar meteorites includes a diversity of lithologies: olivine gabbro, anorthositic gabbro, ferroan gabbro (pyroxene gabbro, ferroan symplectite, alkaline-phase ferroan (FG/ARFe)), olivine- and pyroxene-phyric basalts, and, as shown in this study, at least one clast of a silicic lithology. Based on its petrological and geochemical composition, the silicic clast is a dacite. The dacite clast has silica polymorphs of cristobalite, tridymite, and quartz, indicating rapid cooling history of a silicic magma at or near the surface of the Moon. The high silica content, high Fe# and Ti# of pyroxene in the clast are consistent with formation at late-stages of magmatic differentiation. Its highly ferroan (Mg# < 1) and intermediate SiO<sub>2</sub> composition (63 wt%) distinguish the dacite clast from other evolved lunar rocks.

The dacite clast differs from the NWA 773 clan FG/ARFe clasts in the following: (1) plagioclase is more abundant than K-feldspar; (2) only apatite has been identified in the dacite clast, whereas the main Ca-phosphate in the ARFe lithology is merrillite; (3) feldspars and silica are much more abundant than mafic minerals in the dacite clast. The NWA 773 FG/ ARFe clasts formed in a co-magmatic system that also produced the OG and AG lithologies, pyroxene gabbro, and symplectite. The FG/ARFe clasts have curved inclusions of silica-rich feldspathic glass and/or silica + K-feldspar intergrowths. Both types of inclusions in the FG/ARFe clasts formed by silicate liquid immiscibility after Fe-enrichment. However, the dacite clast shows no direct textural evidence of immiscibility associated with the OG magmatic system. The highly ferroan and silica-rich composition of dacite clast formed at least in part by crystallization from residual liquid after Mg-depletion by fractional crystallization of a parental melt. It is possible that immiscibility followed fractional crystallization. The presence of the dacite clast, taken together with mafic composition, geochemical KREEPrich signature and young crystallization age, suggest an origin in or around PKT for meteorites of the NWA 773 clan.

# **Appendix**



**Fig. 10** Ternary diagram among  $SiO_2$ , FeO + MgO + CaO,  $Na_2O + K_2O + Al_2O_3$  (Seddio et al. 2013). Black dotted line encloses the field of SLI (Roedder 1951). White circle plot represents the dacite clast (this work)

#### Abbreviations

ARFe: Alkaline Ferroan; BSE: Back-Scattered Electron; EPMA: Electron probe micro-analyzer; KREEP: Potassium (K); OC: Olivine cumulate gabbro; P: Phosphorus; PKT: Procellarum KREEP Terrane; PTS: Polished thin section; QMD: Quartz monzodiorite; REE: Rare earth element; RGB: Red, Green, Blue; SEM: Scanning electron microscope; SLI: Silicate liquid immiscibility; TAS: Total alkali-silica

#### Acknowledgments

We are grateful for loans of thin section from NASA/JSC (R.A. Zeigler, curator) for Apollo 15405 QMD. We acknowledge the helpful comments from two anonymous reviewers and editorial handling by Noriko Kita.

#### Authors' contributions

HN proposed the topic, conceived and designed the study. HN and TF carried out the SEM and EPMA analyses. MK carried out Raman spectroscopy. HN, TF, and MK analyzed the data and helped in their interpretation. All authors discussed the manuscript. All authors read and approved the final manuscript.

#### Fundina

This work was supported in part by Research Fellowships for Young Scientists from the Japan Society for the Promotion of Science (JSPS) 18 J01786 (Pl: Hiroshi Nagaoka) and by JSPS KAKENHI Grant Number 18H01298 (Pl: Masahiro Kayama).

#### Availability of data and materials

Data sharing not applicable to this article as no datasets were generated or analyzed during the current study. Please contact author for data requests.

#### Competing interests

The authors declare that they have no competing interests.

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Received: 2 July 2019 Accepted: 5 February 2020 Published online: 02 March 2020

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