Concrete with high-purity volcanic glass fine powder manufactured from pyroclastic deposit

A. Tomoyose¹ · T. Noguchi¹ · K. Sodeyama² · K. Higashi³

Received: 13 October 2019 / Accepted: 26 March 2020 © The Author(s) 2020 OPEN

Abstract
Volcanic deposits, which are pozzolanically reactive, have long been known to improve the durability of concrete. Nevertheless, it has also been pointed out that the use of a natural pozzolan as a supplementary cementitious material (SCM) can pose problems of low workability and slow strength development. Also, in addition, its composition and physical properties have large variety and variability. We have been conducting studies on the total utilization of volcanic deposits for applications suitable for respective properties by classifying them by floating speed difference and particle diameter. It is reported that sorting out particles less than 2.4 g/cm³ by dry gravity classification and removal of smaller clay fraction by dust collector is technically effective to recover high purity volcanic glass from pyroclastic flow deposits called “Ito-Shirasu”, which is a local name for pyroclastic flow deposits in Japan. In this study, concrete containing high-purity volcanic glass powders with different finenesses are investigated regarding fresh properties, strength development, chloride ion penetration and CO₂ reduction. As a result, it was found that volcanic glass powders made an excellent contribution to the improvement of flowability comparable to fly ash, the enhancement of strength comparable to silica fume, and the restraint of chloride ion penetration. Volcanic glass powders can also contribute to the reduction of CO₂ emission because the content of Portland cement can be significantly reduced to obtain the same strength compared to concrete with 100% Portland cement. This study provides a possibility to produce high performance SCMs in volcanic regions worldwide from volcanic ejecta by sorting out a high purity volcanic glass by the same method.

Keywords Volcanic glass · Natural pozzolan · Supplementary cementitious material · Dry gravity classification

1 Introduction
A quest for supplementary cementitious materials (SCMs) with a reactivity allowing them to be used as a replacement for Portland cement has been underway worldwide, with industrial byproducts including ground-granulated blast-furnace slag and fly ash being globally applied to actual construction. However, an expected reduction in the output of such materials, particularly fly ash, which is a byproduct of coal-fired power generation, was pointed out already in 2007 [1], amid the trend to cope with the environmental problems.

Though the term “pozzolan” is widely used today to describe a reactive material for concrete regardless of whether it is natural or artificial, it is derived from “pozzolana”, natural volcanic ejecta, which was used as a material for concrete in the Roman era. Volcanic ejecta and deposits, which are pozzolanically reactive, have long been known to improve the durability of concrete. No standard has been available for these materials due to them not being industrial products, with their physical

---

* A. Tomoyose, tomoyose@bme.arch.t.u-tokyo.ac.jp | ¹Department of Architecture, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, Japan. ²Kagoshima Prefectural Institute of Industrial Technology, 1445-1 Oda, Hayato-cho, Kirishima-shi, Kagoshima, Japan. ³Princple Co., Ltd, 1-17-8 Kamoike, Kagoshima-shi, Kagoshima, Japan.
properties widely varying. Volcanic ejecta and deposits have therefore not been actively employed for construction under the circumstances where laws and regulations require engineers to refer to standards. However, with a shift from specification codes to performance-based codes in sight, active use of natural resources in the future of North America has been highlighted [2].

Nevertheless, it has also been pointed out that the use of a natural pozzolan as a supplementary cementitious material can pose problems of low workability and slow strength development [3]. Also, in addition to the low performance as a natural SCM, its composition and physical properties are widely variable [4] and significantly scattered [5] when compared with industrial byproducts.

The wide variety of natural pozzolans are classified by their origins as shown in Fig. 1. They are broadly divided into two categories: primary volcanic and sedimentary. Diatomaceous earth, hydrothermal siliceous sinters, and detrital sediments belonging to the sedimentary category. The volcanic category includes zeolitized tuff, or volcanic tuff, which are also altered by diagenetic processes. Excepting the group of diatomaceous earth, all natural pozzolans are derived from volcanic rock and volcanic minerals [6]. In many cases these are studied and used as they are, through the processes of pulverization and classification (mostly into particles smaller than 45 μm) [6]. However, most of these natural pozzolans contain such inert minerals as quartz and feldspar, along with amorphous silicate (volcanic glass, VG), which causes reactivity.

Pyroclastic flow deposits referred to as “shirasu” cover a wide area, forming extensive pyroclastic plateaus with a layer about 10–200 m thick in the southern regions of Kyushu, Japan. The greatest amount of shirasu sediment, which is estimated to have a volume of 75 billion m³, is the Ito pyroclastic flow (A-Ito) that erupted out 29,000 years ago. This “Ito-shirasu” covers an area of about 3427 km², and it contains non-welded pyroclastic flow sediment, which includes crystalline minerals, VG, and clay fractions. It is said that utilizing Ito-shirasu as an industrial resource is very difficult for these impurities [7]. According to an origin-based classification, Ito-shirasu is included in the group of unaltered pyroclastic materials. There have been few practical trials to use Ito-shirasu as fine aggregate, but a house built with Ito-shirasu concrete won the 2017 American Concrete Institute overall “Excellence” award [8]. Despite their environmental advantage, significant barriers remain to widespread adoption of Ito-shirasu in place of natural sand and crushed sand. A major barrier is related to the typical properties of natural pozzolans; low fluidity due to high fineness and angular particles. It was also reported that Ito-shirasu concrete causes higher shrinkage than controls [9]. In addition, its low density (2.0–2.2 g/cm³) and high water absorption (2.5–9.2%) for fine aggregate are other barriers by laws and standards (JIS).

![Fig. 1](general_classification_scheme_of_natural_supplementary_materials.png)

Fig. 1 General classification scheme of natural supplementary materials. Processing usually involves crushing, grinding, and size separation mostly under 45μm. Modified after [4]
We have been conducting studies [10–14] on full utilization of Ito-shirasu by classifying it into various physical properties for various applications as construction materials. Equipment referred to as an air table is used for this classification. Figure 2 shows its mechanism. Its winnowing with the action of the vibration fluid bed can classify particles by their floating speed difference and particle diameter with low energy consumption.

We have previously blended the heavy particle and heavy dust fractions dry-classified by the air table from Ito-Shirasu, and found that the blend exhibited normal workability as fine aggregate equivalent to that of crushed sand [10]. Through this method using an air table, the amorphous content of the sorted light dust increased to 88% when that of raw material is about 60%. Furthermore, based on the analysis of the mineral composition and amorphous content of sorted light dust by Rietveld analysis, sorting out particles lighter than 2.4 g/cm³ by the air table and removal of the smaller clay fraction by a bag filter is technically effective to recover high-purity VG from the raw material [11]. The authors demonstrated that, by pulverizing this high-purity VG to powders (VGP) with a mean particle size of around 1 μm, a slump flow and 7-day and later strength equal to or greater than silica fume can be obtained when used for concrete at a water to binder ratio (W/B) = 0.2, even with smaller dosages of chemical admixtures. When used at W/B = 0.6, the concrete demonstrated excellent strength development from an age of 7 days even when up to 20% of normal Portland cement was replaced with VGP. That concrete also showed no reduction in the carbonation rate coefficient, indicating extremely high resistance to chloride ion penetration [10]. However, how the characteristics of VGP such as particle size, influence its behavior in a concrete mixture was overlooked, and whether or not dry classification by this method is effective only for Ito-shirau was unclear in the previous study.

First, this study aims to verify whether the effect of dry classification of volcanic deposits by an air table is limited only to Ito-Shirasu, which spreads over Southern Kyushu of Japan, or whether it is more universal, by analyzing powder properties. Second, concrete containing VGP with different fineness is investigated from a more practical aspect.

2 Test materials and experimental program

2.1 Raw material and manufacturing process of VGP

Ito-shirasu used in this investigation was delivered from Kanoya-city, Kagoshima Prefecture in Japan by a mine operator without any pretreatment as shown in Fig. 3. The mineral compositions of the particle size fractions and the chemical composition of the raw material reported
in the previous research [10–14] are presented in Fig. 4. According to previous studies from resource engineering [15], Ito-shirasu is perfectly divided into crystalline minerals and amorphous phase through heavy liquid separation using zinc bromide ($\rho = 2.4 \text{ g/cm}^3$). Therefore, as to mineral components in this figure, the fractions over and under 2.4 g/cm$^3$ are defined as crystalline and amorphous, respectively. The fraction under 1.5 g/cm$^3$ in particular is defined as pumice based on the definition of lightweight aggregate by JIS A 5002.

Similarly to a former report [12], the test material was prepared by drying the part passing a 5 mm sieve to a water content of 1% or less. Figure 5 shows details of the classifier used. This equipment consisting of an air table along with a cyclone and dust collector classifies the material into five components. The classifying conditions include the material feed, pore size of the sieve, concavo-convex shape, inclination angle, rotation frequency, vibration amplitude, and air flow. The density and size of each component can be adjusted by setting these conditions [9]. The particles are classified according to the density and mean size as listed in Table 1 along with the recovery rate. Most crystal minerals are recovered as heavy particles

1 mm or more in diameter and heavy dust less than 1 mm in diameter, while pumice is recovered as light particles. Among the light dust, fine particles recovered by the cyclone include high purity VG. The super fine part not recovered at the cyclone is recovered by the dust collector as the clay fraction (CF).

Figure 6 shows the size distributions of high-purity VG recovered by the cyclone and CF recovered by the dust collector measured by a laser diffractometer. The mean size of the fraction recovered by the dust collector is 4 μm, representing the fine particle fraction slightly contained in the ore, though the two curves partly overlap due to dry classification.

The sorted high-purity VG and CF were crushed and classified as shown in Fig. 7. High-purity VG primary-crushed by a roller mill into a powder (VGR) is pulverized and classified using three devices: a jet mill to recover RJF
and RJC by the dust collector and cyclone, respectively; an air classifier to recover RXF and RXC; and a cyclone to recover RF and RC. The fractions recovered by the dust collector (RJF, RXF, and RF) are referred to as fine powder. The fractions recovered by the cyclone (RJC, RXC, and RC) are referred to as coarse powder. These fractions, including the primary-crushed VGR, are referred to as VGP. Also, the CF, including its crushing, are collectively referred to as clay powder.

2.2 Chemical composition, ignition loss

Calibration curves of the standard minerals were prepared by the glass bead method for VGP and clay powder using lithium tetraborate as the flux, and their chemical compositions were measured by XRF. The ignition loss was calculated from the loss values obtained from samples dried for more than 12 h at 105 °C and then ignited at 1000 °C for 1 h.

2.3 Thermogravimetric analysis, water vapor adsorption, BET specific surface

Prior to heating, measurement samples for thermogravimetric analysis 20–30 mg in mass were vacuum-dried for more than 12 h to eliminate the effect of adsorption water in the atmosphere. These were then heated from the room temperature (approximately 20 °C) to 1100 °C at a rate of 10 °C/min with measurement intervals of 30 s.

The water vapor adsorption isotherm was measured at 25 °C using an automatic vapor adsorption meter. The specific surface was then determined by the BET method N2-adsorption. The measurement cell containing the sample was vacuumed and dried for 3 h at 105 °C to eliminate the effect of adsorption water.

2.4 MB adsorption

Adsorption of methylene blue (MB) was determined in accordance with JCAS I-61: 2008 (Test method for methylene blue adsorption of fly ash). Based on the preliminary test results, a MB solution was added to samples weighed to between 0.05 and 0.10 g, and the absorbance was measured by suction filtration. The MB adsorption of samples was calculated by preparing calibration curves from the absorbance by blank tests. Six types of VGP and three types of clay powder were used as the materials.

2.5 Mix proportion of concrete and test method

The experimental program for VGP was divided into four series, and tests were conducted on concrete mixtures. A forced-action double-axis mixer was used for mixing. Referring to the JIS test method for the activity index for silica fume (SF) and fly ash (FA), the W/B and replacement ratio were set at 0.2 and 10%, respectively, in Series I, whereas they were set at 0.5 and 25% in Series I, respectively. The materials and mixture proportions are listed in Tables 2 and 3, respectively. The reference SCM for Series I (W/B = 0.2) was SF. Its target air content and slump flow were 2.0 ± 1.0% and 65 ± 10 cm, respectively. The reference SCM for Series I (W/B = 0.5) was FA. Its target air content and slump were 5.0 ± 1.5% and 18 ± 2.5 cm, respectively. The chemical admixture dosage was adjusted to achieve the target air content and slump. Compression specimens (ϕ100 × 200 mm cylinders) were fabricated after testing the fresh properties, namely, the slump (only for Series II), slump flow, air content, concrete temperature, time to 50 cm flow, and time to end-of-flow (only for Series I). Compression tests were conducted at standard curing ages of 1, 4, 13, 26, and 52 weeks.

In Series III, the influence of VGP on the chloride diffusion of concrete was experimentally examined. Tests were performed on concrete specimens (W/B = 0.6) of three different sizes of VGP (RF, RC and VGR) with a replacement ratio of 20% and OPC for reference, according to the JSCE standard “Test method for apparent diffusion coefficient of chloride ion in concrete by submersion in salt water”. After cutting off 25 mm slices from the top and bottom ends of each cylinder, concrete specimens were cured in a water bath at 20 °C. The curing period was 28 days. Specimens were coated with epoxy except the circular placing surface and immersed in a 10% NaCl solution at 20 °C for 42 weeks. The total chloride ion profile was determined by cutting four 10 mm slices from each cylinder so that the centers of the slices would be the points at depths of 5, 20, 35, 50 and 65 mm from the uncoated surface. These were crushed to less than 150 μm and subjected to ion chromatography to quantify chloride ions in accordance with JIS A 1154 (Method of test for chloride ion content in hardened concrete).
In Series IV, the relational expressions between the binder-water ratio (B/W) and the 28-day compressive strength were experimentally determined to evaluate the environmental performance of concrete containing VGP on a practical basis. Tests were conducted at a ready-mixed concrete plant with actual shipping experience. All materials excepting VGP were the same as those normally shipped from the plant. Trial mixtures of RF, RC, and VGR were prepared with a fixed replacement ratio and three levels of W/Bs. Table 4 tabulates the test levels, proportioning factors, and fresh test results. The replacement ratio was 20% for RF, RC and VGR. RF was also tested with replacement ratios of 5% and 10%. The target slump and air content were 18 ± 3 cm and 4.5 ± 1.5%, respectively, for all mixtures. Compression tests were conducted at 28 days after standard curing.

### 3 Results

#### 3.1 Chemical composition and ignition loss

Table 5 tabulates the results of chemical composition and ignition loss measurements. As shown in Fig. 8, the SiO₂ content of both VGP and clay powder negatively correlate with both the ignition loss and Al₂O₃. The SiO₂ content and ignition loss of VGP are greater than 72% and lower than 3%, respectively, but after pulverization and classification, the SiO₂ content tends to slightly decrease in the fine powder fraction and slightly increase in the coarse powder fraction, with the difference being around 2%. As for clay powder, the SiO₂ content and ignition loss of CF are 65% and 4.5%, respectively, but the difference between those of the fine powder fraction (CFJF) and coarse powder fraction (CFJC) after pulverization and recovery are greater than those of VGP, being around 10% for SiO₂ content and around 3% for ignition loss. The Al₂O₃ content shows a similar trend.

VG is subjected to weathering action of water, undergoing hydration and elution, and follows a weathering sequence shown in Fig. 9, ultimately being modified to a clay mineral (halloysite, kaolinite and so on) [16]. SiO₂ is prone to elution through chemical changes, leaving compositions rich in Al₂O₃. Clay powder can therefore be regarded as being in a later stage of weathering in terms of chemical composition than VGP. In either case, fine powder shows a composition at a later stage of

---

**Table 2 Materials used**

| Material   | Properties                                      | Marks |
|------------|-------------------------------------------------|-------|
| Binder     |                                                 |       |
| Cement     | Normal portland cement, density: 3.24 g/cm³     | N, NPC|
|            | Low-heat portland cement, density: 3.24 g/cm³   | L, LPC|
| SCM        | VGP, SF, FA                                     | SCM   |
| Fine aggregate | Crushed lime, density: 2.67 g/cm³               | S1    |
|            | Crushed tight sand, density: 2.62 g/cm³         | S2    |
| Coarse aggregate  | Crushed tight sand, density: 2.64 g/cm³        | G1    |
|            | Crushed lime, density: 2.70 g/cm³               | G2    |
| Chemical admixture | High-range water-reducing admixture             | SP1   |
|            | Air-entraining and high-range water-reducing admixture | SP2   |
|            | Air-entraining and water reducing admixture     | SP3   |
|            | Air-entraining admixture                        | AE    |

| Table 3 Factors and level, mixing proportions |
|-----------------------------------------------|
| Series | W/B   | Cement | W (kg/m³) | SCM/B (%) | S1:S2 | S/a (%) | SCM used | Chemical admixture used | Target air content (%) | Target slump (cm) |
|--------|-------|--------|-----------|-----------|-------|---------|----------|------------------------|---------------------|-------------------|
| I      | 0.20  | L      | 160       | 10        | 4:6   | 45.2    | SF + 6 VGP | SP1                    | 2.0 ± 1.0            | Slump flow 65 ± 10  |
| II     | 0.50  | N      | 167       | 25        | 2.5:7.5| 42.8    | FA + 6 VGP | SP2 + AE              | 5.0 ± 1.0            | Slump 18 ± 2.5      |
| III    | 0.60  | N      | 183       | 5         | 2.5:7.5| 50.8    | RF       | SP3 + AE              | 5.0 ± 1.5            | Slump 18 ± 2.5      |

---
Table 4  Test levels, proportioning factors and fresh test results

| SCM-replacement | W/B (%) | W (kg/m³) | SP dosage (B * wt%) | AE dosage (B * wt%) | Slump (cm) | Air (%) |
|-----------------|---------|-----------|----------------------|----------------------|------------|---------|
| RF-20%          | 60      | 172       | 0.80                 | 0.3                  | 19.0       | 5.9     |
|                 | 50      | 170       | 0.90                 | 0.0                  | 19.0       | 5.7     |
|                 | 35      | 174       | 0.90                 | 0.0                  | 19.0       | 5.9     |
| VGR-20%         | 60      | 172       | 0.65                 | 0.2                  | 19.0       | 5.9     |
|                 | 50      | 170       | 0.65                 | 0.1                  | 19.0       | 4.6     |
|                 | 35      | 174       | 0.80                 | 0.0                  | 20.0       | 3.4     |
| RC-20%          | 60      | 172       | 0.65                 | 0.0                  | 20.0       | 5.4     |
|                 | 50      | 170       | 0.60                 | 0.1                  | 20.0       | 4.9     |
|                 | 35      | 174       | 0.95                 | 0.1                  | 20.0       | 3.7     |
| RF-5%           | 60      | 172       | 0.70                 | 0.0                  | 18.5       | 5.8     |
|                 | 50      | 170       | 0.90                 | 0.0                  | 20.5       | 4.8     |
|                 | 40      | 172       | 0.70                 | 0.0                  | 19.0       | 3.5     |
| RF-10%          | 60      | 172       | 0.70                 | 0.0                  | 18.0       | 5.2     |
|                 | 50      | 170       | 0.90                 | 0.0                  | 20.0       | 5.4     |
|                 | 40      | 172       | 0.85                 | 0.0                  | 21.0       | 4.0     |

Table 5  Chemical composition and LOI of the materials

| Sample | VGR | RJF | RJC | RXF | RXC | RF | RC | CF | CFJF | CFJC |
|--------|-----|-----|-----|-----|-----|----|----|----|------|------|
| SiO₂   | 73.9| 72.4| 74.3| 72.6| 74.2| 73.0| 74.3| 64.4| 60.5  | 69.2 |
| TiO₂   | 0.20| 0.21| 0.20| 0.21| 0.20| 0.21| 0.19| 0.30| 0.33  | 0.24 |
| Al₂O₃  | 12.8| 13.3| 12.6| 13.2| 12.7| 13.1| 12.6| 16.0| 16.9  | 13.7 |
| Fe₂O₃  | 1.89| 2.33| 1.76| 2.26| 1.83| 2.38| 1.78| 7.03| 8.26  | 5.07 |
| MnO    | 0.05| 0.06| 0.05| 0.06| 0.06| 0.05| 0.06| 0.05| 0.07  | 0.06 |
| MgO    | 0.30| 0.37| 0.26| 0.34| 0.29| 0.32| 0.28| 0.75| 1.09  | 0.52 |
| CaO    | 1.44| 1.56| 1.40| 1.55| 1.42| 1.51| 1.39| 1.47| 1.62  | 1.45 |
| Na₂O   | 3.78| 3.57| 3.91| 3.60| 3.71| 3.59| 3.75| 2.22| 1.75  | 2.59 |
| K₂O    | 3.34| 3.36| 3.38| 3.30| 3.37| 3.32| 3.35| 3.21| 3.05  | 3.76 |
| P₂O₅   | 0.03| 0.04| 0.03| 0.04| 0.03| 0.04| 0.03| 0.03| 0.04  | 0.03 |
| LOI    | 2.25| 2.81| 2.02| 2.84| 2.14| 2.47| 2.25| 4.47| 6.37  | 3.44 |
| Total  | 99.98|100.01|99.91|100.00|99.94|100.00|99.97|99.95|99.99  |100.06|

Fig. 8  Relation between SiO₂ and LOI (left), SiO₂ and Al₂O₃ (right)
Weathering than coarse powder, with the difference between fine and coarse powders of clay powder being greater.

### 3.2 Properties of adsorbed water

Figure 10 shows the thermogravimetric curves of three types of clay powder and three types of VGP from among the results of thermogravimetric analysis tests. The mass losses of CFJF and CF are significant, being 8% and 6%, respectively. Those of CFJC and RJF are similar at around 4%, but their ignition losses differed at 3.4% and 2.8%, respectively. This is presumably because the mass loss of RJF during drying at 105 °C for pretreatment before ignition loss measurement is greater as shown in the different low temperature ranges of their TG curves. The mass losses of RJC and VGR are both below 3%, demonstrating similar trends to the ignition loss results. Since VG derived from magma is reported to contain absorbed water, undegassed water, structural water equivalent to ignition loss whereas in a lot of cases ignition loss includes CO₂ as well [17], the losses in the TG curves are considered to be attributable to reduction in the moisture content, but the differential thermogravimetric curves shown in Fig. 11 demonstrate different trends of the peak temperatures of dehydration. One peak is found at around 250 °C for VGP including those not shown in the figure. This is a typical peak of VG [18]. The shift of this temperature toward a lower temperature as the sample is crushed to smaller particles [18] was also confirmed in the tests. For clay powder, peaks are found at less than 100 °C, around 250 °C, and 450 °C. The large peak at less than 100 °C is a tendency observed in allophane, an amorphous clay of weathered VG, indicating the presence of physical adsorbed water or interlayer water, which result from weathering-induced hydration and are not dehydrated by vacuum drying. Similar water is also found to be present in CF and CFJF.

At the peaks of 450 °C, slight endothermic shoulders are observed in all clay powders and in DTA as well. These are considered to be the dehydration of water bound by further hydration or of structural water (hydroxyl), suggesting an indication of clay mineralization [16].

Figure 12 shows part of the obtained water vapor adsorption isotherms. The adsorption and desorption
curves of RJF are separated, being hysteretic similar to Type II or Type H4 that suggest the presence of slit-shaped pores and micropores according to the classification by IUPAC [19]. CF shows hysteretic curves close to Type III or Type V, with adsorption being small in low pressure ranges less than 0.1, which demonstrates that adsorption does not occur while the interaction between vapors is greater. The total adsorption of CF is high, though its hydrophily can be low, with the difference between adsorption and desorption being large. Therefore, once water is adsorbed, it tends to be hard to be desorbed. Regarding TG curves for which the pretreatment is vacuum drying, CF shows a dehydration peak of $\Delta$TG at less than 100 °C. Therefore, the adsorbed water is mostly not desorbed at normal temperatures and low pressure, demonstrating properties close to allophane, which is used as a desiccant-adsorbent. Table 6 shows the BET specific surface determined from the water vapor adsorption at a pretreatment temperature of 105 °C and the nitrogen gas adsorption at a pretreatment temperature of 300 °C. CF was incalculable, as no linearity in the plots was found in the relative pressure range of 0.05–0.35. In contrast to SF, VGP and FA show BET specific surfaces by water vapor adsorption greater than that by nitrogen adsorption. In vapor adsorption, water is adsorbed selectively by hydrophilic sites, whereas nitrogen is an adsorbate that covers the entire powder surfaces uniformly. The surface physical properties can therefore be discussed by using different adsorbates. Since the BET specific surface is calculated in the relative pressure range of 0.05–0.35, the amount of water vapor adsorption of VGP in the low pressure range turned out to be great due to its high hydrophily.

### 3.3 BET specific surface area and adsorption

Figure 13 shows the relationship between the mean particle size and the BET specific surface. The BET specific surface of VGP increases as the mean size decreases. On the other hand, clay powder shows no particular trend between the mean particle size and the BET specific surface. The BET specific surfaces of CF and CFJF are particularly large, being twice as large as that of VGP with similar mean size. The state of particle surfaces can differ from that of VGP.

Figure 14 shows the relationship between the BET specific surface and the MB adsorption. The BET specific surface and MB adsorption of VGP are closely correlated, with all sizes meeting the requirement to be not more than 1.20 g/100 g (12.0 mg/g) by EN 197-1: 2000 for the MB adsorption of limestone as a cement component. On the other hand, clay powders exceed this limit, with the

![Fig. 12 Thermogravimetric curves of VGP and clay powder](image)

**Table 6** BET surface area determined from water and nitrogen

| Sample | VGR | RJF | RJC | RXF | RXC | RF | RC | CF | SF | FA |
|--------|-----|-----|-----|-----|-----|----|----|----|----|----|
| Water adsorption BET (m$^2$/g) | 10.0 | 41.9 | 11.2 | 23.6 | 8.4 | 18.6 | 6.4 | –  | 14.4 | 7.1 |
| Nitrogen adsorption BET (m$^2$/g) | 7.1  | 16.1 | 4.2  | 12.4 | 5.1  | 10.7 | 3.7 | 31.4 | 20.2 | 1.5 |

![Fig. 13 Relationship between mean particle size and BET surface area of VGP and Clay powder](image)
adsorption tending to be above the approximate line for VGP.

Focusing on the fact that silica is lost during the process of weathering, leaving alumina, the ratio of SiO₂ to Al₂O₃ (silica-alumina ratio) has been proposed as a most simple index to the degree of weathering, when the parent rock is the same [20]. Figure 15 shows the relationship between the silica-alumina ratio and the MB adsorption per unit BET specific surface. The chemical compositions of CFJF and CF represent particularly high degrees of weathering among the clay powders. Their MB adsorption is also 30% greater than that of VGP. When compared with CFJF and CF, the degree of weathering of CFJC is closer to that of VGP, but the value of adsorption is nearly twice as large as that of VGP. As for VGP, the degree of weathering of fine powder is slightly higher than coarse powder in terms of chemical composition, but their MB adsorptions can be regarded as being on the same level from their respective mean values and standard deviations. The adsorption of a polycarboxylate-based dispersant per unit area of powders of the same types (i.e., powders with the same compositions) is reported to be constant [21]. If this applies to MB, then fine and coarse powders of VGP can be regarded as the same powder from the aspect of dispersant adsorption, but clay powder cannot be regarded as the same type as VGPs. Also, the unit adsorption of CFJC is the largest, though its degree of weathering is not as high as CF and CFJF.

### 3.4 Fresh properties of concrete

Table 7 gives the fresh properties immediately after mixing and chemical admixture dosage of Series I. All VGPs are found to provide slump flows equal to or greater than SF with smaller chemical admixture dosages. In comparison with SF with a mean diameter of 0.1 μm, the size of VGP is large. It is therefore presumed that agglomerations are prone to be dispersed due to the small van der Waals forces, requiring a small chemical admixture dosage. The time to 50-cm flow of the coarse powders is longer than that of fine powders, with substantial viscosity and dilatancy to cause resistance to shoveling with

| Type pf SCM/BET surface area (m²/g) | Slump flow (cm) | Air (%) | Time to 500 mm flow (s) | Time to end-of-flow (s) | SP1 dosage (B * wt%) |
|-------------------------------------|-----------------|---------|------------------------|------------------------|---------------------|
| R16.1                               | 74.0×74.8       | 2.1     | 5.3                    | 97                     | 1.40                |
| RXF/15.2                            | 73.2×75.0       | 2.1     | 5.8                    | 118                    | 1.40                |
| RF/12.0                             | 73.8×72.2       | 1.8     | 5.5                    | 92                     | 1.40                |
| RC/4.2                              | 74.0×73.8       | 1.8     | 6.3                    | 95                     | 1.30                |
| RCX/5.1                             | 72.4×71.1       | 1.9     | 6.8                    | 102                    | 1.20                |
| RC/3.6                              | 69.8×68.2       | 1.9     | 8.3                    | 103                    | 1.20                |
| SF/17.7                             | 69.0×68.0       | 2.9     | 4.3                    | 79                     | 1.60                |
a cement shovel. Though the time to 50-cm flow with the three fine powders is longer than that with SF, the consistency was sufficiently practicable. Powders with a BET specific surface of 12 m²/g or greater contain sufficient amounts of fine particles to fill the spaces between cement particles, increasing the packing factor of the binder. This presumably achieves a microfiller effect comparable to SF. Based on these results, it is judged that, in fresh concrete with a W/B of around 0.2, fine powders with a BET specific surface of 12 m²/g or more provide a flowability-improving effect, while the effect is less evident with coarse powders with a BET specific surface of 5 m²/g or less.

However, it can be said that VGP is a supplementary cementitious material that is expected to produce a sufficient effect of improving the workability of low W/B mixtures as demonstrated in the present results, provided that its physical properties including grading are rectified during the process of crushing and classification and that impurities including clay minerals are removed.

Table 8 gives the fresh properties and chemical admixture dosage of Series II. The mixing time was the same for all VGPs. The dosage of the high-performance air-entraining and water-reducing admixture for fine powders to achieve the target slump is higher than FA, whereas the admixture dosage to achieve the target slump and air content with coarse powders was the same as SF. The use of VGP reduces the slump flow by 15%, leading to fresh concrete with a high yield value. This is presumably due to the effect of the angular shape of crushed VGP particles in contrast to spherical FA particles. However, coarse powders with a BET specific surface of 5 m²/g or less show sufficiently practicable viscosity comparable to FA. It can therefore be said, from these results, that the target slump and air content were achievable in fresh concrete with a W/B of around 0.5 by using the same dosage of a chemical admixture as FA, which is effective in improving the concrete flowability.

### Table 8 Fresh properties and chemical admixture dosage of Series II

| Type of SCM/BET surface area (m²/g) | Slump (cm) | Air (%) | SP2 dosage (B* wt%) | AE dosage (B* wt%) |
|------------------------------------|------------|---------|---------------------|--------------------|
| R1F/16.1                           | 18.5       | 5.8     | 1.10                | 0.40               |
| RXF/15.2                           | 19.5       | 5.8     | 1.10                | 0.40               |
| RF/12.0                            | 19.0       | 5.6     | 1.10                | 0.40               |
| RJC/4.2                            | 19.5       | 5.8     | 0.83                | 0.40               |
| RXC/5.1                            | 19.0       | 5.7     | 0.83                | 0.40               |
| RC/3.6                             | 18.0       | 5.5     | 0.83                | 0.40               |
| FA/1.4                             | 20.0       | 5.9     | 0.83                | 0.40               |

3.5 Strength development

Figure 16 shows the compressive strength with a W/B of 0.2. At an age of 4 weeks, the strength with VGPs is equal to or higher than with SF. At 13 weeks, the strength is equal to or lower than SF. It has been reported that, if the W/B is constant, then a 1% increase in the air content reduces the strength by 4–6%. The air content with SF is higher than that with VGP by around 1% in a fresh state. It follows that, even if the strength with VGP is reduced by 5%, it can be regarded as roughly comparable to SF up to 4 weeks. Figure 17 shows the compressive strength with W/B = 0.5. The strength with fine powders is approximately 20% higher than with FA, while that with coarse powders is equivalent to that with FA, at all ages.

Figure 18 shows the strength development. With W/B = 0.2, the strength gains with SF from 4 to 13 weeks are greater than with any of the VGPs, but the slopes from 7 to 28 days are similar for all specimens. With W/B = 0.5, similar tendencies are found in the strength development over time in both cases of FA and VGP.
of VGP correlate well with the BET specific surface at 1 week and delayed reaction of particles with smaller BET specific surfaces proceeds thereafter. However, the results that strength ratio to SF is 100% or higher up to 4 weeks but is less than SF at 13 weeks imply the effects of factors other than reactions, such as void percentage. Elucidation of strength development related to age remains a subject for future research.

Figure 20 shows the relative strength ratio to FA with W/B = 0.5. A closer correlation than 0.2 W/B is observed between VGP’s BET specific surface and strength ratio to FA, though with a slight scatter at 13 weeks. According to a former research on pastes with a replacement ratio of 20% and a W/B of 0.4, the reaction ratio of Type II fly ash specified in JIS A 6201 is around 10% at 7 days and 42–53% at 555 days, being affected by the amount, chemical composition, and fineness of the glass phase [23]. Since the only difference among the six types of VGPs in the present study is fineness, the obtained strength development presumably corresponds with the BET specific surface, which is closely related to fineness. However, the slightly low strength ratio to FA at 13 weeks requires further observation of long-term strength to elucidate the strength development mechanism.

3.6 Resistance to chloride ion penetration

Figure 21 shows the results of immersion tests on concrete specimens in 10% saltwater for 42 weeks after 4-week water curing. The concretes with W/B = 0.6 were OPC and concretes containing RF, VGR, and RC in place of 20% of cement. The chloride contents in the surfaces and deeper inward of concrete containing VGPs are significantly lower than those of OPC. Concrete containing RF or VGR not only
shields the penetration of chlorides at a depth of 20 mm but also inhibits its penetration at 10 mm. Even concrete containing RC with the smallest BET specific surface is found to shield chloride ion penetration at 35 mm. Though the shielding effect of RC is weaker than those of RF and VGR, it significantly improves the chloride ion resistance of concrete when compared with OPC. The apparent diffusion coefficients of OPC, RF, VGR, and RC regarding all chloride ions are 4.00, 0.16, 0.20, and 0.60 cm²/year, respectively. VGPs with a larger BET specific surface show a smaller apparent diffusion coefficient of chloride ions. In the case of a replacement ratio of 20%, even the apparent diffusion coefficient of RC with a BET specific surface of approximately 3 m²/g is less than 20% of that of OPC. The diffusion coefficients of VGR and RF with BET specific surfaces of approximately 7 m²/g and 11 m²/g, respectively, are less than 20% and less than 10%, respectively, of that of OPC.

3.7 W/B-strength relation and contribution to CO₂ reduction

Figure 22 shows the approximate lines calculated from the compression test results and the B/W-strength relational expressions. The relational expression for OPC in the figure is the expression adopted for the actual ready-mixed concrete made of the same materials and shipped by the plant. Due to approximation of trial mixtures with three levels by n = 1, the scatter of the results of 20%-replaced RF is wider than that of OPC approximated by n = 4. RF with a BET specific surface of 11 m²/g shows a higher strength than OPC with the same B/W even with a replacement ratio of 5%, and the effect remains up to a replacement ratio of 20%. The strength of VGR with a BET specific surface of 7 m²/g is slightly higher than OPC. That of RC with a BET specific surface of 3 m²/g is slightly lower than OPC. In Series II, the strength development is comparable to fly ash with a W/B of 50% and replacement ratio of 25%. It can therefore be regarded as equivalent to general fly ash of JIS Type II, which is available on the market in Japan. A higher strength at 91 days is therefore expected.

Figure 23 shows the unit cement reduction determined from calculation by the relational expression for proportioning to achieve compressive strengths of 30, 40, and 50 MPa. The unit water content of OPC proportioning for general slump control is assumed to be 180 kg/m³, whereas the unit water content in the flow control using VGP is assumed to be 170 kg/m³. By assuming the proportioning control strength as 50 MPa, the cement content can be reduced by more than 100 kg even with a replacement ratio of 10% at which the carbonation rate coefficient decreases. With a 20% replacement, the cement content can be reduced by 150 kg. Also, with RC, the B/W–strength relational expression of which is lower than cement, the cement demand to obtain the same strength becomes smaller, as the replacement ratio is 20%. Reductions of more than 50 kg are therefore achieved at all strength levels.
4 Discussion and conclusion

In the field of natural disaster science, the refractive index of VG is used as an index to the progress of weathering of a cliff, as it increases under the effect of hydration. Also, the particle structure of a glass shard is explained as a structure consisting of a non-hydrated core surrounded by a hydrated rim, since the refractive index of crushed glass shards is widened toward the lower side [24]. VG is a most weatherable material, and the smaller the particle, the faster the weathering proceeds, changing to a different soft material under chemical weathering action [25]. In view of these findings and the results of the present study, Fig. 24 shows the particle properties and process of crushing/classification.

Both VG and CF have a structure with a hydrated rim on the surfaces, and layers closer to the surface are softer and more prone to be pulverized during the crushing process, tending to be recovered by a dust collector. This agrees with the fact that fine and coarse powders have different chemical compositions and ignition losses. Based on the adsorption per unit area and the results of thermoanalysis of CFJC, it is considered hydration proceeds more to the cores of smaller-size CF particles than VG particles. In particular, CFJF has a concentrate of highly weathered surface layer. In other words, crushing after removing heavily weathered fine particles is effective in manufacturing unweathered high purity VGP, which is a high performance SCM, from volcanic deposits.

Whereas basaltic magma with low viscosity causes moderate volcanic activity, rhyolitic magma is generally said to cause violent and explosive eruption [4]. In other words, magma with a large SiO2 content is said to cause explosive eruption. The deposits of volcanic materials excepting gasses are classified into three types: pyroclastic fall deposit, pyroclastic flow deposit, and lava. Pyroclastic fall deposit results from a Plinian eruption shown in Fig. 25, whereas pyroclastic flow deposit results from a pyroclastic flow.

A Plinian eruption, an explosive one represented by the eruption of Mount Vesuvius in 79 AD, forms an eruptive column made of gases, magma and rocks crushed to pieces, and fragments of minerals directly above the crater for half an hour to several days. The temperatures of this column higher than the surrounding atmosphere cause convection. The top of the eruptive column is formed where the density of the column equals the surroundings and spreads horizontally. Low-density particles including volcanic ash and pumice are horizontally blown by the wind and begin to fall when their speed decreases to the point of equilibrium between air resistance and gravity; ‘terminal speed’. Since smaller particles are carried farther away due to their lower terminal speed, they are subjected to fractionation while flying. The material deposited near the crater is referred to as fall pumice. The material 2 mm or less in size is referred to as volcanic ash. Both are uniform in size and contain little crystal minerals or lithic fragments. There can be a case where weathered materials subjected to hydration are included, but high purity VG can be sorted out by the cyclone and dust collector of the present device for air classification.

On the other hand, collapse of an eruptive column leads to a so-called pyroclastic flow. A large-scale flow is formed by gravitational collapse of an eruptive column, which is regarded as a phenomenon of a rapid outflow of unclassified pumice, volcanic ash, and rock fragments with volcanic gases as shown in Fig. 26. Coarse particles tend to
be entrapped among fine particles due to the weak classifying action.

Though such ejecta, which is also referred to as tephra, is derived from magma, it also includes ‘accessory’ materials derived from the old volcanic body near the magma reservoir and conduit and ‘accidental’ materials, which are fragments of the basement rock. Their quantitative ratios vary depending on the scale and pattern of eruption and distance from the eruption source. After deposition, extraneous materials from the surrounding ground can be normally included during various stages of turning into soil. In view of the use as a SCM in the field of concrete, pyroclastic deposits resulting from explosive eruption of magma with a high SiO₂ content are advantageous from the aspect of the amount of resources, but they simultaneously entail abundant impurities other than pozzolantically reactive VG.

Ito-Shirasu presently under study is a large-scale pyroclastic flow sedimentation with an estimated reserve of 75 billion m³, but amorphous materials including pumice were reported to account for around 60% based on heavy liquid separation, while crystal minerals were approximately 40%. Also, the fine fraction of CF with a recovery ratio of 2% showed indications of weathering. According to the results of research into VG and other minerals contained in volcanic ejecta from Cascade Range in North America [26], the densities of pumice, glass shards, and lithic fragments were 0.7–1.2 g/cm³, 2.35–2.45 g/cm³, and 2.7–3.2 g/cm³, respectively. That of crystalline materials and crystal fragments was 2.6–5.2 g/cm³. Therefore, our findings from volcanic deposits in Japan that VG can be perfectly sorted out both with a density limit of 2.4 g/cm³ and with a diameter limit of around 5 μm can be applicable to volcanic ejecta from Cascade Range. Physical densities of particles should fall in constant ranges when considering the mechanisms acting on volcanic ejecta—eruption of liquid magma onto the ground and rapid cooling thereafter, crystallization within the underground magma, rocks present on the ground, weathering after deposition, and so on. In that sense, this study provides a possibility to produce high performance SCMs in volcanic regions worldwide from volcanic ejecta, which have been regarded as a low performance material, by sorting out a high purity VG by the same method using an air table.

The findings regarding concrete made using VGP obtained in this study include the following:

1. Fresh properties

With a W/B of around 0.2, VGP powder with a BET specific surface of 12 m²/g or more has a flowability-improving effect, while such an effect is judged as being weak with a BET specific surface of 5 m²/g or less. With a W/B of around 0.5 or more, a replacement ratio exceeding 10% of VGP with a BET specific surface of 12 m²/g or more increases the chemical admixture demand for achieving the target slump increases. With a BET specific surface of 5 m²/g or less, however, the target slump and air content can be achieved with a chemical admixture dosage equivalent to JIS Type II fly ash with a replacement ratio of 25%.

2. Strength properties

With a W/B of around 0.2, the BET specific surface of VGP correlates with the strength, demonstrating the strength-developing performance equivalent to SF with a BET specific surface of around 5 m²/g, and that equal to or higher than SF with a BET specific surface of 12 m²/g. At four weeks, the correlation between the BET specific surface and strength becomes weak, demonstrating a strength-developing performance equivalent to SF. At an age of 13 weeks, the correlation becomes even weaker, with the strength being equivalent or lower than SF. With a W/B of around 0.5 or more, a strength equivalent to JIS Type II fly ash with a replacement ratio of 25%.
If fly ash is obtained with a BET specific surface of around 3 m²/g. The strength becomes 20% higher than fly ash with a BET specific surface of 12 m²/g or more, with correlation between the BET specific surface and the strength being observed up to 91 days.

3. Durability and CO₂ reduction

The use of VGP with a BET specific surface of around 3 m²/g at a replacement ratio of 20% provides sufficient resistance to chloride ion penetration, being sufficiently effective in reducing the amount of Portland cement consumption.

Acknowledgements This research is supported by JSPS Grant-in-Aid for Scientific Research (A) with No. 18H03803 entitled “Carbon-minus Recyclable High-performance Concrete”.

Compliance with ethical standards
Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit http://creativecommons.org/licenses/by/4.0/. 

References
1. Scrivener KL, Kirkpatrick RJ (2008) Innovation in use and research on cementitious material. Cem Concr Res 38:128–136. https://doi.org/10.1016/j.cemconres.2007.09.025
2. Hooton RD (2008) Bridging the gap between research and standard. Cem Concr Res 38:247–258. https://doi.org/10.1016/j.cemconres.2007.09.012
3. Damtoft JS, Lukasik J, Herfort D, Sorrentino D, Gartner EM (2008) Sustainable development and climate change initiatives. Cem Concr Res 38:115–127. https://doi.org/10.1016/j.cemconres.2007.09.008
4. Snellings R, Mertens G, Olsen J (2012) Supplementary cemen-
titious materials. Rev Miner Geochem 74(1):211–278. https://doi.org/10.1016/j.cemconres.2012.09.008
5. Snellings R (2016) Assessing, understanding and unlocking supplementary cementitious materials. RILEM Tech Lett 1:50–55. https://doi.org/10.21809/rilemtel16.26
6. Mehta PK, Monteiro PJM (2006) Concrete microstructure, properties, and materials, 3rd edn. McGraw-Hill Companies, New York, pp 295–315
7. Oki K (2011) What is the “Shirasu” pyroclastic flow deposit and how to use it? Nat Kagoshima 37:153–159 (in Japanese)
8. Winners of the 2017 ACI Excellence in Concrete Construction Awards. Conc International (2017) 39(11):18–24
9. Choi H, Noguchi T, Tomoyose A, Ito T (2015) Experimental study on application of Ito-shirasu concrete to buildings. Proc Jpn Concr Ins 37(1):73–78 (in Japanese)
10. Tomoyose A, Noguchi T, Sodeyama K, Higashi K (2018) Total utilization of pyroclastic flow deposits as construction materials through dry gravity classification and pulverization. RILEM Tech Lett 7:36–74. https://doi.org/10.21809/rilemtellett.2018.66
11. Tomoyose A, Tomoyose T, Noguchi T, Higashi K (2018) Utilization of volcanic ejecta as a high-performance supplementary cementitious material by dry gravity classification and pulverization, RILEM Tech Lett 7:36–74. https://doi.org/10.21809/rilemtellett.2018.66
12. Sodeyama K, Tomoyose A, Noguchi T, Higashi K (2017) Total utilization of shirasu as construction materials through dry gravity classification and pulverization. J Soc Mater Sci Jpn 66(8):574–581. https://doi.org/10.2472/jsms.66.574
13. Tomoyose A, Noguchi T, Sodeyama K, Higashi K (2017) Stability of volcanic silicate powder for concrete manufactured from shirasu through gravity classification and pulverization. CAJ Proc Cem Concr 71(1):674–681. https://doi.org/10.14250/cement71.674
14. Tomoyose A, Noguchi T, Sodeyama K, Higashi K (2017) Fundamental study about volcanic glass classified from Ito-shirasu by gravity classification. Proc Jpn Concr Ins 38(1):151–156 (in Japanese)
15. Jinnai K, Kimura K, Isayama Y, Koga Y (1972) Studies on the beneficiation of the “Shirasu” as a mineral resource (III) on the magnetic separation tests of the “Shirasu”. Flotation 1972(48):33–42. https://doi.org/10.4144/rpsj1954.1972.33 (in Japanese)
16. Iwao S (1985) Nendo no Jiten. Asakura Publishing Co. Ltd, Shinjuku (in Japanese), ISBN: 4254162286
17. Taniguchi H (1972) Studies on Si⁴⁺ ion, Al³⁺ ion and H₂O(+) in volcanic glasses by means of infrared absorption and other methods. J Jpn Assoc Mineral Petroil Econ Geol 67(9):291–300. https://doi.org/10.2465/ganko1941.67.291 (in Japanese)
18. Tateyama H, Kimura K, Jinnai K, Tsunematsu K (1982) Changes on bloating properties of volcanic glass by weathering. J Clay Soc Jpn 22(1):1–10. https://doi.org/10.11362/jcssj nendo kagak menstru (in Japanese)
19. Sing KSW, Everett DH, Haul RAW, Moscou L, Pierotti RA, Rouquerol J, Siemieniewska T (1985) Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. Pure Appl Chem 57(4):603–619. https://doi.org/10.1351/pac198557040603
20. Ruxton BP (1968) Measures of the degree of chemical weathering of rocks. J Geol 76(5):518–527. https://doi.org/10.1086/627357
21. Ohta A, Uomoto T (1999) A study of the dispersing effects of polycarboxylate-based dispersant on fine particles. Conc Res Technol 10(2):131–140. https://doi.org/10.3151/crt19910.2_131
22. Sato M, Umemura Y, Koizumi K (2012) Effects of heat curing history on silicate structures and hydration of ultra high strength hardened cement. Cem Sci Concr Technol 66(1):522–523. https://doi.org/10.14250/cement66.515 (in Japanese)
23. Otsuka T, Mori S, Ishikawa M, Sakai E (2009) Relation between mineral compositions of fly ash and its pozzolanic reaction. Cem Sci Concr Technol 63(1):16–21. https://doi.org/10.14250/cement63.16 (in Japanese)
24. Yamashita T, Danhara T (1995) Problem in measuring refractive index of older tephra glass shards: effect of thin hydration layer. In: The geological society of Japan the 102nd
25. Tsukamoto H, Mizutani S (1988) Clay minerals in weathering process and their transformation. J Jpn Soc Eng Geol 29(3):231–241. https://doi.org/10.5110/jjseg.29.231 (in Japanese)

26. Shipley S, Sama-Wojcicki AM (1983) Maps showing distribution, thickness, and mass of late pleistocene and holocene tephra from major volcanoes in the Pacific northwest of the United States; a preliminary assessment of hazards from volcanic ejecta to nuclear reactors in the Pacific northwest, USGS, MF-1435. https://doi.org/10.3133/mf1435

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.