Geographical variations in Sr and Nd isotopic ratios of cryoconite on Asian glaciers

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Received 9 October 2013, revised 3 March 2014
Accepted for publication 18 March 2014
Published 11 April 2014

Abstract
Cryoconite is a dark-coloured surface dust deposited on glaciers that consists of wind-blown mineral particles, as well as organic matter derived from microbes living on glaciers. In this paper, we analyse the Sr and Nd isotopic ratios of four mineral fractions (i.e., the saline, carbonate, phosphate, and silicate mineral fractions), as well as the organic fraction, of cryoconite samples obtained from six Asian glaciers (the Altai, Pamir, Tien Shan, Qillian Shan, and Himalayan regions), and discuss their geographical variations in terms of the geological origins of the mineral particles and the biogeochemical processes on the glaciers. The silicate mineral fraction showed lower Sr and higher Nd ratios for the glaciers located to the north (Altai, $^{87}\text{Sr} / ^{86}\text{Sr}$: 0.713 490–0.715 284, $\varepsilon_{\text{Nd}}(0)$: $-6.4$ to $-5.6$), while higher Sr and lower Nd ratios for the glaciers located to the south (Himalayas, $^{87}\text{Sr} / ^{86}\text{Sr}$: 0.740 121–0.742 088, $\varepsilon_{\text{Nd}}(0)$: $-16.4$ to $-15.7$); the ratios were similar to those of desert sand, loess, and river sediments in the respective regions of the glaciers. This result suggests that the silicate minerals within the cryoconites were derived from different sources depending on the geographical locations of the glaciers. The isotopic ratios of the saline, carbonate, and phosphate mineral fractions were distinct from those of the silicate fraction, and were similar to those of evaporites and apatite deposits from the Asian deserts, but also varied geographically, indicating that they are likely to reflect their geological origin. The Sr isotopic ratios of the organic fraction were similar to those of the saline and carbonate fractions from glaciers in the central area (Tien Shan and Qillian Shan), but were higher than those of the saline and carbonate fractions, and lower than the phosphate mineral fraction, in the northern and southern areas. The ratios of organic fraction may be determined from the mixing ratio of calcium sources incorporated by microbes on the glaciers.

Keywords: cryoconite, Sr isotope ratios, Nd isotope ratios, glacier, Asia

Online supplementary data available from stacks.iop.org/ERL/9/045007/mmedia

1. Introduction

Cryoconite is a dark-coloured surface dust deposited on glacial ice, and is commonly found on glaciers worldwide. It usually consists of mineral particles, which originate from basal till
and/or wind-blown dust, as well as organic matter derived mainly from photosynthetic microbes living on the glaciers (e.g., Takeuchi et al. 2001). The dark colouration of cryoconite acts to reduce the surface albedo of glaciers and so accelerates their melting in many parts of the world. Oerlemans et al. (2009) reported that the accumulation of mineral and biogenic dust (cryoconite) has substantially darkened a glacier in Switzerland since 2003, which is likely to cause surface albedo reduction and removal of ice from the glacier. Large amounts of cryoconite have also resulted in a darkening of the western ablation zone of Greenland ice sheet and decreased the surface albedo (Wientjes et al. 2011). Furthermore, the melting rate of the intact surface was reported to be three times larger than that of the surface without cryoconite on a Himalayan glacier (Kohshima et al. 1993). The mass balance of Asian glaciers could therefore be greatly affected by the quantity and quality of cryoconite. Thus, it is important to study the formation process of cryoconite to understand the variations in the recent change in glacial mass balance.

Although cryoconite has been well studied biologically (e.g. Takeuchi et al. 2001, Margesin et al. 2002, Anesio et al. 2009), mineralogical information of cryoconite is still limited. Mineral particles deposited on glaciers significantly affect the abundance and composition of cryoconite. For example, enormous amounts of mineral dust are provided on glaciers in central Asia, such as in the Tien Shan and Qillian Shan Mountains, from surrounding vast arid areas (e.g. Wake et al. 1992, Wu et al. 2010, Xu et al. 2012). The mineral dust inputs on glaciers may depend on the sources and transportation processes of eolian dust in the vicinity of the glaciers. Furthermore, minerals in cryoconite possibly affect microbial production and community structure on glacier surfaces. Previous studies report that filamentous cyanobacteria are dominant on glaciers in central Asia, and they could promote formation of cryoconite on the glacier surface (Takeuchi and Li 2008), while green algae are dominant on glaciers in northern Asia and the Arctic regions (Takeuchi et al. 2001, 2006). As the glacial microbes are likely to incorporate nutrient from mineral particles as well as dissolved components in snow and ice (e.g. Fjerdingstad 1973, Wientjes et al. 2011), minerals on glaciers could have an effect on their biomass and species of the microbes via nutrient condition. Thus, mineral particles on glaciers play an important role in the formation of cryoconite. Some studies have analysed minerals in cryoconite to reveal the nutrient source for microbes (e.g. Stibal et al. 2008, Hodson et al. 2010). However, the geographical variations in the sources of mineral particles on glaciers and their effect on the microbial community and biogeochemical processes that contribute to cryoconite formation remain unclear.

Analysis of the stable isotopic ratios of strontium \(^{87}\text{Sr}/^{86}\text{Sr}\) and neodymium \((\Delta^{143}\text{Nd})/^{144}\text{Nd}\) or \(\varepsilon\text{Nd}(0)\) can assist our understanding of the transportation processes and dynamics of the mineral components of cryoconite. Sr and Nd are commonly contained in natural substances such as rocks, water and organisms, although they are present at trace levels. These isotopic ratios vary significantly depending on their geological origins. In particular, the Sr isotopic ratio is closely correlated with abundance of K and Rb as \(^{87}\text{Rb}\) is the parent nuclide of \(^{87}\text{Sr}\). Since they rarely change during transportation in the atmosphere or after deposition as sediments (e.g. Biscaye et al. 1997, Capo et al. 1998) the Sr and Nd isotopic ratios have been commonly used in loess or sediment studies to determine the geological sources of the minerals, and have revealed that there are large geographical variations in the ratios of sediments, such as desert sand, soil, loess, and volcanic ash collected in the world, and even within Asia (e.g. Goldstein et al. 1984, Nakano et al. 2004). Therefore, the Sr and Nd isotopic ratios of cryoconite can be used to identify the sources of mineral dust on glaciers. Nagatsuka et al. (2010) first showed the isotopic ratios of minerals in cryoconite on a glacier in the Tien Shan Mountains in China. The isotope ratios did not correspond to those of soil or moraine around the glacier, but to those of the Taklamakan desert, which is located further south of the glacier, suggesting that the desert is the main source of mineral dust on the glacier. However, it is still not clear whether source areas of mineral dust vary among glaciers in different geographical locations or not. The Sr isotopic ratio can also be used to investigate the effect of mineral particles on the biotic community in cryoconite. As the chemical characteristics of Sr are similar to those of Ca, which is one of the elements essential for living organisms, its isotopic ratio has been used as a tracer for Ca in biogeochemical studies (e.g. Miller et al. 1993, Åberg 1995, Bailey et al. 1996, Yokoo and Nakano 2001, Oliver et al. 2003, Cartwright et al. 2006). Thus, the Sr isotopic ratio in organic matter in cryoconite can reflect mineral sources incorporated into the microbes as nutrients. Nutrient conditions on glaciers are thought to be important for cryoconite formation. Thus, the Sr isotopic ratio in the organic matter could provide a means of revealing biogeochemical processes in cryoconite.

In this study, we aim to describe the geographical variations in origins of minerals in cryoconite and nutrient sources incorporated into microbes on glaciers in Asia. As previous studies have shown that Sr and Nd isotopic ratios of minerals from Asian desert significantly varied among their geographical locations (e.g. Nakano et al. 2004, Chen et al. 2007), this regional variation may also be shown in those of minerals in cryoconites on Asian glaciers, which is assumed to affect the nutrient condition for microbes. Sr and Nd isotopic ratios, and the mineral and major element (Na, Mg, Al, P, K, Ca, and Fe) compositions of cryoconites collected from six mountain glaciers in geographically different regions of Asia (Altai, Pamir, Tien Shan, Qillian Shan, and Himalayan regions) were analysed. The cryoconites were chemically separated into five fractions, four mineral fractions (i.e., saline, carbonate, phosphate, and silicate minerals), as well as the organic fraction, and the isotopic ratios of each fraction were measured. Variations in the isotopic ratios are discussed in terms of sources of each mineral and their effect on biogeochemical processes on the glaciers.

2. Samples and analytical method

We analysed cryoconites collected from six mountain glaciers in Asia: the Akkem Glacier in the Altai, Russia (AK); the Fedchenko Glacier in the Pamir, Tajikistan (FD); the
Figure 1. Location map showing cryoconite sample sites on Asian glaciers and the possible sources of minerals found in the cryoconites: AK: Akkem Glacier, FD: Fedchenko Glacier, GG: Grigoriev Icecap, UM: Urumqi Glacier no. 1, MG: Miaoergou Glacier, QY: Qiyi Glacier, YL: Yala Glacier, A: Balkhash (loess), B: Junggar Basin (loess), C: North China (loess and sand), D: Taklamakan desert (loess and sand), E: Southern Gobi desert and the Loess Plateau (loess and sand), F: Himalayas (river sediment), G: Thar desert (sand), H: Qaidam desert (sand).

Grigoriev Ice Cap and the Miaoergou Glacier in the Tien Shan, Kyrgyzstan and China (GG and MG, respectively); the Qiyi Glacier in the Qillian Shan, China (QY); and the Yala Glacier in the Himalayas, Nepal (YL, figure 1, supplementary table 1 available at stacks.iop.org/ERL/9/045007/mmedia). We also used data from the Urumqi Glacier no. 1 in the Tien Shan, China (UM) published in Nagatsuka et al (2010). Five samples of cryoconite were randomly collected on each site of the glaciers with a stainless-steel scoop and stored in clean 30 ml polyethylene bottles. All the cryoconite samples were collected from the ice surface of the glaciers in the ablation area and were most likely to be composed of mineral particles and organic matter that had accumulated on the surface for decades to hundreds of years.

The cryoconite was observed with optical microscopes (Olympus BX51 and Leica MZ-12). The size of the cryoconite and the constituent (mineral particles) were manually measured on digital photographs with an image-processing application (Image J, National Institutes of Health, USA). 200 particles of cryoconite and mineral particles were randomly chosen from the photographs and their longest diameter was measured, respectively.

The mineralogical composition of the cryoconite was determined by x-ray diffraction analysis (XRD) using a RIGAKU Geigerflex RAD 11-B at Chiba University, Japan. The x-ray target was Cu Kα, the tube voltage was 40 kV, and the tube current was 25 mA. Scans were performed from 2.0° to 40° (2θ) at a rate of 2° (2θ) per minute. Our analysis followed the method of Nagatsuka et al (2010). The major element concentrations (Na, Mg, Al, P, K, Ca, and Fe) of the cryoconite were determined by inductively coupled plasma–mass spectrometer (ICP–MS; Agilent 7500cx) at the Research Institute for Humanity and Nature (RIHN), Kyoto, Japan. The cryoconite samples were digested in 38% hydrofluoric acid (HF), 70% perchloric acid (HClO₄), and 68% nitric acid (HNO₃), and were then further dissolved with 1N HNO₃ prior to analysis. Bulk cryoconite samples were used for both the mineralogical and elemental composition analyses.

To measure the Sr and Nd isotopic ratios of the mineral and organic fractions in the cryoconite, the samples were chemically separated into five fractions using four different acid solutions: (1) ultra-pure water (H₂O), (2) hydrogen peroxide solution (H₂O₂), (3) acetic acid (HOAc), (4) hydrochloric acid (HCl), and (5) HCl residual fraction. Fractions (1), (2), (3), and (4) were extracted in the following sequence: for 5 min with H₂O at room temperature, for 24 h with 10% H₂O₂ at 70°C, for 2 h with 5% HOAc at 75°C, and for 45 min with 20% hydrochloric acid HCl at 100°C, respectively. All extractions were conducted in a Teflon air-proof system. The residual of HCl was digested with 38% hydrofluoric acid (HF), 70% perchloric acid (HClO₄), and 68% nitric acid (HNO₃) at 200°C, and the (5) HCl residual fraction was then obtained. In this paper, we assumed that these fractions (1)–(5) corresponded to (1) saline minerals, (2) organic matter, (3) carbonate minerals, (4) phosphate minerals, and (5) silicate minerals, respectively, based on the study of the same extractions of Chinese desert sand and soil by Yokoo (2000). These extractions were performed in a class 100 clean laboratory at RIHN. For details of the extraction method, see Nagatsuka et al (2010).
The Sr and Nd ratios were determined with a TRITON thermal ionization mass spectrometer (Thermo Fisher Scientific K.K.) at RIHN, following the analytical method of Nagatsuka et al. (2010). Sr isotope samples were measured for all five fractions, and Nd isotopes were measured for the HCl extracted and residual fractions. However, because of limited machine time, we were only able to measure one sample from each glacier, with the exception of the Fedchenko Glacier, for all fractions, while other samples were measured for only the HCl residual fraction (silicate mineral fraction, see supplementary table 2 available at stacks.iop.org/ERL/9/045007/mmedia). According to previous work on a glacier in the Tien Shan (Nagatsuka et al. 2010), spatial variations in the isotopic ratios of cryoconite on a single glacier surface are sufficiently small to allow discussion of geographical variations in this study (standard deviations (SD): H$_2$O extracted fraction = 0.003 431, H$_2$O$_2$ extracted fraction = 0.005 879, HOAc extracted fraction = 0.003 640, HCl extracted fraction = 0.007 048, and HCl residual fraction = 0.008 227). These small spatial variations are likely due to homogenized composition of cryoconite that repeatedly grew and disintegrated over a cycle of several years on the glacier (Takeuchi et al. 2010). The measured $^{87}$Sr/$^{86}$Sr and $^{143}$Nd/$^{144}$Nd values were normalized to a $^{86}$Sr/$^{88}$Sr value of 0.1194 and a $^{146}$Nd/$^{144}$Nd value of 0.7219, respectively. The mean $^{87}$Sr/$^{86}$Sr ratio of NIST-SRM987 and the mean $^{143}$Nd/$^{144}$Nd ratio of JNdI-1 (the international standard specimens for Sr and Nd isotopes determined during this study) were 0.710 252 ± 0.000 004 (mean ± SD, n = 45) and 0.512 105 ± 0.000 004 (mean ± SD, n = 23), respectively. The measured Sr and Nd isotopic ratios of each standard specimen and sample were determined by repeated measurements (100 and 140 times, respectively). The internal precision of the Sr and Nd isotope ratios were better than 0.000 005 during the course of this study. For convenience, the $^{143}$Nd/$^{144}$Nd ratios were normalized and denoted as $\varepsilon$Nd(0) = [(143Nd/144Nd)/0.512 636–1] × 10^4.

3. Results

3.1. Cryoconite composition

Microscopic observations showed that the cryoconite deposits on the glaciers analysed here consisted mainly of mineral particles and organic matter, including dark-coloured amorphous particles, snow algae, and cyanobacteria cells (figure 2). These constituents were aggregated to form spherical granules, as described by Takeuchi et al. (2001), on all of the glaciers sampled. The size of the granules ranged from 500 to 1400 µm (mean for each sample). The mineral particles in the cryoconites were larger in the Altai and Himalayas (mean = 42.4–63.5 µm) than in the other glaciers (mean = 10.5–32.5 µm, supplementary table 2 available at stacks.iop.org/ERL/9/045007/mmedia).

The chemical extractions of the cryoconites showed that the major mass fraction (dry weight) was the HCl residual fraction (silicates) in all samples (70.3%–92.2%), and the second largest was the HCl extracted fraction (6.3%–25.7%). The other three fractions (extracted using H$_2$O, H$_2$O$_2$, and HOAc) were generally smaller (0.2%–2.7%, 0.8%–2.7%, and 0.1%–1.7%, respectively, supplementary table 3 available at stacks.iop.org/ERL/9/045007/mmedia).

3.2. Mineralogical composition of cryoconite

The XRD spectra of the cryoconite samples were generally similar among the glaciers, and showed peaks for several silicate minerals (figure 3). The observed peaks in all samples

Figure 2. Photograph of components in cryoconite on the Urumqi Glacier no. 1, (A) mineral particles (B) dark-coloured amorphous particles, (C) microbes (cyanobacteria).
Figure 3. X-ray diffraction (XRD) spectra of minerals contained in cryoconite samples from Asian glaciers.

were identified as quartz (26.7°), potassium feldspar (27.5°), plagioclase (28.2°), and clay minerals such as chlorite (18.6°), illite (8.9°), and kaolinite (12.5°, 25.2°). However, the peak intensity of potassium feldspar was significantly low except in the Himalayan sample (YL). The peaks for saline, carbonate, and phosphate minerals were not detected, probably owing to the low concentration of these minerals in the samples.

3.3. Elemental composition of cryoconite

The major element composition (Na, Mg, Al, P, K, Ca, and Fe) was also generally similar among the glaciers. The highest element concentration was Al, and the lowest was P, in all of the samples. In addition, Fe and K were relatively high (supplementary table 4 available at stacks.iop.org/ERL/9/045007/mmedia). This compositional trend is similar to that of Chinese loess reported by Yokoo et al (2004). However, the cryoconite from the Himalayas (YL) showed a different composition to that of the other glaciers, with relatively high K levels and low Mg and Fe contents compared with the other elements.

The ratios of these elemental compositions showed some distinctive features among the glaciers (figure 4, supplementary table 4 available at stacks.iop.org/ERL/9/045007/mmedia). For example, according to eolian dust studies in northern China (e.g., Zhang et al 1997, Sun et al 2005, Wu et al 2010), the ratios of the dust-derived elements, such as Fe and Ca to Al can show regional variations, and can also be used to identify dust source areas. The Fe/Al ratios of the Altai and Pamir (AK and FD) samples were relatively high

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4. Discussion

4.1. Sources of silicate minerals in cryoconite on Asian glaciers

The dominant fraction in the cryoconites on the glaciers was the HCl residual fraction, which corresponds to silicate minerals. The Sr and Nd isotopic ratios of this fraction showed regional variation among the glaciers, and could be classified into three groups: north, central, and south Asia (figure 6). The isotopic ratios from the northern area (Altai) showed lower Sr and higher Nd values, while those from the southern area (Himalayas) showed higher Sr and lower Nd values. The Sr and Nd isotopic ratios of the cryoconites deposited on glaciers located in the central area (Pamir, Tien Shan, and Qillian Shan) showed intermediate values between those of the northern and southern samples. This regional trend in the isotopic ratios is consistent with the analysis of wind-blown dust collected from snow on glaciers in western China (Xu et al. 2012). Moreover, the latitudinal trend of the Nd isotopic ratios is consistent with those of Chinese desert sand and moraine (Honda et al. 2004), which show higher Nd values at higher latitudes. This suggests that the origin of the silicate minerals in the cryoconite deposits differs substantially according to the geographical location of the glaciers.

Compared with the Sr and Nd isotopic ratios of silicate minerals in desert sand, loess, and river sediments reported over Asia, those of the cryoconite on each glacier were similar to those in such sediments from the areas surrounding the glaciers (figure 6). The isotopic ratios in the northern area (AK) were similar to the values of North China, Junggar, and Balkhash (Honda et al. 2004, Nakano et al. 2004, Nagatsuka 2012); those of the central area (FD, GG, UM, MG, and QY) were similar to the values recorded in the Taklamakan desert, southern Gobi desert, and on the Loess Plateau (Honda et al. 2004, Nakano et al. 2004); and those of the southern area (YL) were similar to those from the Himalayas and Thar desert (Singh and France-Lanord 2002, Tripathi et al. 2004). This indicates that the isotopic ratios of the cryoconite deposits reflect the geology of the area surrounding the glaciers. The silicate minerals in the cryoconites are likely to be derived from the area surrounding the glaciers as shown in figure 7. These source areas are consistent with the dust sources suggested by air mass back trajectories over Asian mountain glaciers (Xu et al. 2012).

Although the Nd isotopic ratios from the central area (FD, GG, UM, MG, and QY) were similar to each other, the Sr isotopic ratios varied among the glaciers. This variation in the Sr isotopic ratios may reflect not only their origins, but also their particle size. Previous studies have demonstrated that the Sr isotopic ratio of minerals increases with a decrease in the size of mineral particles (e.g., Biscaye et al. 1997) since the small size particles consist mainly of clay minerals, which is enriched in K and also Rb (Kanayama et al. 2005). In contrast, the Nd isotopic ratios showed similar trends for all cryoconite samples, which were higher in the HCl extracted fraction than in the HCl residual fraction.

Figure 5. Sr isotopic ratios of the five fractions extracted from the cryoconites deposited on Asian glaciers. The isotopic ratios of UM are the mean values of cryoconite on the glaciers.

Figure 6. Sr and Nd isotopic ratios of the HCl residual fractions (silicate minerals) in the cryoconites. Coloured triangles show the ratios of loess, sand, and stream sediments from Asia.
Figure 7. Location map showing the trajectories of mineral particles in cryoconites on Asian glaciers. Coloured circles show possible source areas of minerals on glaciers in north, central, and south Asia (A: Balkhash, B: Junggar, C: North China, D: Taklamakan, E: Southern Gobi & Loess Plateau, F: Himalaya, G: Thar, H: Qaidam, Blue coloured: northern area includes Altai, Pink coloured: central area includes Pamir, Tien Shan, and Qillian Shan, Green coloured: southern area includes Himalaya).

is westerly, mineral dust on the glaciers is transported from west to east and gradually decreases in size as a result of the eolian sorting. Thus, the higher Sr isotopic ratios of QY located in the east are likely due to finer particle size than those on the other three glaciers, although other factors such as clay mineral composition also possibly cause the variations in the Sr isotopic ratios in the central area.

The elemental composition of the cryoconites also supports the notion of a difference in silicate mineral origins among the glaciers. The Fe/Al ratios of the cryoconites varied among the glaciers from north to south (0.37–0.62, figure 4, supplementary table 4 available at stacks.iop.org/ERL/9/045007/mmedia) as did the Sr and Nd isotopic ratios. The Fe/Al ratios were also similar to those of the upper continental crust (UCC; mean = 0.62). As the Fe/Al ratio is not expected to change during transport, and any differences in this ratio result mainly from changes in clay mineral composition (Schutz and Rahn 1982), it is likely to highlight differences in the source of silicate minerals for each glacier. In contrast, the Ca/Al ratios of the cryoconites showed smaller variations (0.08–0.12) and were lower than those of the UCC (mean = 0.37, Taylor and McLennan 1985). The Ca/Al ratio might be subjected to precipitation scavenging and dissolution during transport (e.g. Ma et al 2004). The cryoconites on the ice surface of the glaciers were deposited over long periods (probably several to hundreds of years), as the surface is in an ablation area and thus exposed to every melting season. Therefore, the low and stable Ca concentration in the cryoconites is likely to have been due to dissolution by meltwater and homogenization during deposition on the glacial surface.

Although the XRD spectra showed mineralogical composition was almost similar among the glaciers, the relative abundance of each mineral also possibly cause the regional variations in the Sr and Nd isotopic ratios and in elemental composition. The XRD analysis revealed that all cryoconite samples contained five main silicate minerals: quartz, potassium feldspar, plagioclase, chlorite, illite, and kaolinite (figure 3). These minerals are generally contained in desert sand and loess from central Asia (e.g. Chang et al 2000, Svensson et al 2000, Yokoo et al 2004). XRD results also showed that the peak intensities of each mineral varied among the cryoconite samples. For example, higher peak intensity of potassium feldspar was observed in cryoconite on the Himalayas (YL), indicating relatively higher abundance of the mineral. These variations probably also affect the Sr and Nd isotopic ratios of each region.

4.2. Comparison of the Sr and Nd isotopic ratios of saline, carbonate, and phosphate minerals in cryoconites

Lower or higher Sr and Nd isotopic ratios in the H2O, HOAc, and HCl extracted fractions (saline, carbonate, and phosphate minerals, respectively), compared with those in the HCl residual fraction (silicate minerals), indicate that these minerals have different isotopic features from the silicate minerals. Yokoo et al (2004) revealed that the isotopic ratios in the H2O extracted fraction from Chinese desert sand were similar to those of evaporites, such as halite and gypsum formed during evaporation of water in arid soils, and those in HOAc extracted fraction were similar to those of carbonates (mainly calcite), respectively. Furthermore, the isotopic ratios
in the HCl extracted fraction were similar to those of apatite formed in arid areas. Thus, the isotopic ratios of each fraction are likely to reflect those of source areas of each mineral.

The variations in the Sr and Nd isotopic ratios of the H$_2$O, HOAc, and HCl extracted fractions are likely to reflect the geological origins of the saline, carbonate, and phosphate minerals deposited on each glacier. When the Sr isotopic ratios of the saline and carbonate minerals in cryoconite samples from the three regions were plotted with data from various other regions in Asia (Nakano et al. 2004, Yokoo et al. 2004), the isotopic ratios of the northern (AK) and central areas (GG, UM, MG, and QY) were similar to those of north China, the southern Gobi desert, the Loess Plateau, and the Taklamakan desert (figure 8). This suggests that the saline and carbonate minerals deposited on the glaciers in the north and central areas were derived from evaporites in these Asian deserts. On the other hand, the Sr isotopic ratios of the southern area (YL) showed significantly higher values than those of the Asian deserts, suggesting that saline and carbonate minerals in the southern cryoconites were derived from other source areas.

The Sr and Nd isotopic ratio of the HCl extracted fraction were higher than those of the H$_2$O and HOAc extracted fractions (saline and carbonate minerals, figure 8, supplementary table 5 available at stacks.iop.org/ERL/9/045007/mmedia). They are also likely to show regional characteristics related to the source areas of the phosphate minerals. The Sr isotopic ratios of the central area (GG, UM, MG, and QY) were lower than those from the northern (AK) and southern areas (YL), and were similar to those of the Chinese desert sand reported by Yokoo et al. (2004). This indicates that phosphate minerals deposited in the central area were derived mainly from apatite formed in arid regions around the glaciers. The higher Sr values in the north and south may reflect other geological properties for the phosphate minerals or relative abundance of other minerals, such as chloride and dolomite, which are also soluble in HCl (Yokoo et al. 2004).

The Sr and Nd isotopic ratios in all the mineral fractions corresponded with those of certainly similar source areas to each other although the isotopic ratios in some fractions might be homogenized through dissolution and precipitation in the cryoconites. This indicates that the saline, carbonate, and phosphate minerals as well as the silicate minerals in the cryoconites were likely to be derived from the same origins.

### 4.3. Isotopic ratios in organic matter as an indicator of microbial nutrient sources

The Sr isotopic ratios of the H$_2$O$_2$ extracted fraction, which correspond to organic matter, are likely to reflect the biological processes associated with the formation of the organic matter as well as the ratios of the minerals providing the Ca for the process. The organic fraction in the cryoconites analysed in this study ranged from 2.9 to 9.4% in dry weight (Takeuchi et al. 2001, 2005, 2006, Takeuchi and Li 2008, Takeuchi et al. 2008). Possible sources of organic matter in the cryoconite may have been wind-blown soil organic matter from the ground surface surrounding the glacier, and/or organic matter derived from microbes living on the glacier (Sibat et al. 2008). However, most of the organics are mainly composed of in situ production by microbes on the glaciers because the organic matter content in wind-blown material is much less than those in cryoconite and microscopy showed abundant cyanobacteria in all of the cryoconite (Takeuchi et al. 2001). Furthermore, a previous study showed that the Sr isotopic ratios of organic fraction in cryoconite on a glacier in Asia (Urumqi Glacier no. 1) were distinctively lower than those in soil around the glacier, suggesting that the organic matter was unlikely to be derived from allochthonous (Nagatsuka et al. 2010). Therefore, most of the organic matter in the cryoconites seems to be mainly derived from the microbes living on the glaciers.

The glacial microbes are likely to grow photosynthetically and reproduce by incorporating nutrients from mineral particles and dissolved components in snow and ice on glaciers. Fjerdingstad (1973) analysed heavy metals contents in microbes and surface snow on glacier in Greenland that revealed higher biological concentration factor of elements essential for living organisms, such as Si, Fe and K. This study also reported that the factor of Sr (600) was significantly higher than that of three essential minerals (200–250) although Sr is of little significance itself as a nutrient. As Sr has geochemical characteristics similar to that of Ca because of similar atomic radius, it can readily substitute for Ca (e.g. Capo et al. 1998). Lower biological concentration factor of Ca as shown in Fjerdingstad (1973) may also be supported that Ca incorporated into the microbes on the glacier can be partly substituted by Sr. Therefore, the Sr isotopic ratios in organisms show values similar to the source of Ca entrained within them. As the Sr isotopic fractionation is very small in physical, chemical, and biological processes in sediments, hydrosphere, and food chain (e.g. Faure 1986, Miller et al. 1993, Capo et al. 1998, Halicz et al. 2008), the isotopic ratio measured from an organism can reflect the isotope ratios of its nutriment. Thus, the Sr isotopic ratios of organic matter in the cryoconite are likely to reflect the values of the minerals that are the source of Ca incorporated into it.
The Sr isotopic ratios of organic matter differed significantly among the glaciers (figure 5, supplementary table 5 available at stacks.iop.org/ERL/9/045007/mmedia). The ratios from the central area (GG, UM, MG, and QY) were lower than those to the north and south (AK and YL, respectively). This is likely to reflect the geological origins of the minerals providing the microbial nutrient (Ca) sources. Compared with the Sr isotopic ratios of the mineral fractions, those of the organic matter in the central area were similar to those of the saline and carbonate minerals, suggesting that microbes on the glaciers incorporated Ca from these two minerals, which were easily dissolved in the glacial meltwater. In contrast, the ratios of the organic matter in the north and south were higher than the saline and carbonate minerals. This indicates that the microbes on these two glaciers (i.e., AK and YL) incorporated Ca not only from saline and carbonate minerals, but also from other sources. As the Sr isotopic ratios of AK and YL showed intermediate values that were higher than the saline and carbonate minerals but lower than the phosphate and silicate minerals, they may have also incorporated Ca from phosphate or silicate minerals. However, the microbes on the Asian glaciers are unlikely to have incorporated Ca from silicate minerals alone. This suggests that microbes on the glaciers incorporated Ca not only from saline and carbonate minerals, but rather from phosphate mineral because the solubility of silicate minerals in water is low when the pH is below 9.0 and the temperature is near 0°C (e.g. Krauskopf 1956), and the pH on the glaciers ranged from 2.9 to 7.8 (Takeuchi et al 2006, Dong et al 2009, Takeuchi 2005, 2006, 2007, 2008). Therefore, the isotopic values were likely to be determined by the mixing ratio of Ca sources incorporated by microbes on the glaciers. On the glaciers in the central area, only the saline and carbonate minerals seem to be used as Ca sources by microbes. This is probably due to the plentiful supply of saline and carbonate minerals from nearby deserts, such as the Taklamakan and Gobi (e.g. Zhang et al 1995, Honda and Shimizu 1998). On the other hand, microbes on the glaciers in the northern and southern areas (AK and YL) seem to incorporate Ca not only from saline and carbonate minerals, but also from phosphate minerals. As shown in supplementary table 3 (available at stacks.iop.org/ERL/9/045007/mmedia), the amounts of saline and carbonate minerals (H₂O and HOAc extracted fractions) on the two glaciers in the north and south (0.001–0.006 g) are relatively lower than those on the glaciers in the central area (0.001–0.019 g). On these glaciers, Ca from saline and carbonate minerals alone may be insufficient for the microbes. Furthermore, the phosphorus demand of microbes may affect incorporation of Ca from the phosphate minerals. The cryoconite ecosystem is known for being phosphorus limited (e.g. Mindl et al 2007, Stibal and Tranter 2007). The wind-blown phosphate minerals may therefore fertilize the ecosystem on the glacier, in which case the isotopic ratios of the organic matter would be similar to those of the phosphate minerals. Thus, the isotopic ratios suggest that the microbes in the north (AK) and south (YL) might incorporate phosphate, together with Ca, from the minerals. However, there are still some uncertainties in identifying the nutrient sources for the microbes based on the Sr isotopic ratios alone since elemental concentration in the organic fraction was not measured in this study, which can show the nutrient cycles more clearly and has also used in biological studies on glaciers (e.g. Stibal et al 2008, Wientjes et al 2011). Furthermore, HCl is a strong acid and as such can leach 87Sr from crystal lattices especially from mica and clays, and this can increase Sr isotope ratios in water and saline, carbonate, and phosphate minerals above those of silicate minerals (Anderson et al 1997, Bullen et al 1997). Therefore, the elemental composition analysis of each extraction would be necessary to verify which mineral provides the nutrients to the microbes on the glaciers. Although further analysis of nutrient cycles is necessary on each glacier as mentioned above, the Sr isotopic ratios of the organic fraction suggest that nutrient cycles in the glacier ecosystems differ between glaciers located in the central, northern, and southern regions of Asia.

5. Conclusions

The Sr and Nd isotopic ratios of the mineral and organic fractions of cryoconite deposits from six Asian glaciers show geographic variations. The isotopic ratios of the silicate mineral fractions (HCl residual fraction) in the cryoconites showed significant regional variations among the northern (Altai), central (Pamir, Tien Shan, and Qillian Shan), and southern (Himalayas) areas. The isotopic ratios were similar to the values from loess, desert sand, and river sediments in the areas surrounding each glacier. This suggests that the origin of the silicate minerals in these cryoconites is substantially different among the three regions, and that the source of the silicate minerals is the area surrounding each glacier.

The Sr and Nd isotopic ratios of saline, carbonate, and phosphate mineral fractions (H₂O, HOAc, and HCl extracted fractions, respectively) in the cryoconites also showed regional characteristics. The isotopic ratios of the central area (Tien Shan and Qillian Shan) were similar to those of evaporites and apatite in Chinese desert sand, while those to the north (Altai) and south (Himalayas) showed significantly different values from those of the Asian deserts. They are likely to reflect the geological properties of source areas.

The Sr isotopic ratios of the organic fraction (H₂O₂ extracted fraction) in the cryoconites also varied according to geographical location. The isotopic ratio of the organic fraction was similar to that of the saline and carbonate fractions in the central area, while it was higher than those of these two mineral fractions, but lower than the phosphate fraction, in the northern and southern areas. These values may be controlled by the mixing ratio of minerals that are the sources of Ca incorporated into the microbes on the glaciers. This indicates that the microbes in the central area incorporated Ca mainly from the saline and carbonate minerals, and those in the northern and southern areas from the phosphate minerals in addition to these two minerals.

Our study shows that the sources of mineral particles in cryoconites on Asian glaciers vary according to the geographical location of the glaciers and that the composition of the mineral particles could affect microbes on the glaciers via nutrient condition. Mineral particles on the glaciers in central area are supplied from large deserts such as Taklimakan in this area, while those in northern and southern areas are from

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local deserts or ground surface in each region. The difference may also affect the variation in the microbial community (cyanobacteria and green algae) between the glaciers. These results suggest that regional geology could affect the formation of cryoconite. A proper understanding of the spatial variations in the cryoconite formation process is essential when evaluating the mass balance of glaciers in Asia. The Sr and Nd isotopic ratios of the fractions extracted from the cryoconite samples could be a useful tool in analysing the relationship between cryoconite and the geology around glaciers. Although further analysis is required, such as determining the elemental compositions of each fraction and measuring the isotopic ratios of fine minerals (<5 μm fraction) to identify also long distance transportation, regional geology appears to be an important element in cryoconite formation on glaciers.

Acknowledgments

We thank the staff of the Research Institute of Humanity and Nature (RIHN) for their generous support, Toshinori Kobayashi and Dr Yu Saitou of RIHN for their valuable assistance in the isotopic analysis, and Drs Atsuyuki Inoue and Noboru Furukawa of Chiba University for helping with XRD analysis. We also thank two anonymous reviewers for many helpful suggestions, which greatly improved this manuscript. This study was financially supported by a Grant-in-Aid for JSPS Fellows, by JSPS KAKENHI Grant Numbers 21681003, 23221004, and 22241005, and by the IIi Project and the Isotopes Environmental Study funded by the Research Institute for Humanity and Nature, Japan.

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