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Weak hydrothermal carbonation of the Ongeluk volcanics: evidence for low CO_2 concentrations in seawater and atmosphere during the Paleoproterozoic global glaciation

Takazo Shibuya[1,2,3*], Tsuyoshi Komiya[4], Ken Takai[1,2,3], Shigenori Maruyama[5,7] and Michael J. Russell[6]

Abstract

It was previously revealed that the total CO_2 concentration in seawater decreased during the Late Archean. In this paper, to assess the secular change of total CO_2 concentration in seawater, we focused on the Paleoproterozoic era when the Earth experienced its first recorded global glaciation. The 2.4 Ga Ongeluk Formation outcrops in the Kaapvaal Craton, South Africa. The formation consists mainly of submarine volcanic rocks that have erupted during the global glaciation. The undeformed lavas are mostly carbonate-free but contain rare disseminated calcites. The carbon isotope ratio of the disseminated calcite ($\delta^{13}C_{cc}$ vs. VPDB) ranges from − 31.9 to − 13.2 ‰. The relatively low $\delta^{13}C_{cc}$ values clearly indicate that the carbonation was partially contributed by ^{13}C-depleted CO_2 derived from decomposition of organic matter beneath the seafloor. The absence of $\delta^{13}C_{cc}$ higher than − 13.2‰ is consistent with the exceptionally ^{13}C-depleted CO_2 in the Ongeluk seawater during glaciation. The results suggest that carbonation occurred during subseafloor hydrothermal circulation just after the eruption of the lavas. Previously, it was reported that the carbonate content in the uppermost subseafloor crust decreased from 3.2 to 2.6 Ga, indicating a decrease in total CO_2 concentration in seawater during that time. However, the average CO_2 (as carbonate) content in the Ongeluk lavas (< 0.001 wt%) is much lower than those of 2.6 Ga representatives and even of modern equivalents. This finding suggests that the total CO_2 concentration in seawater further decreased during the period between 2.6 and 2.4 Ga. Thus, the very low content of carbonate in the Ongeluk lavas is probable evidence for the extremely low CO_2 concentration in seawater during the global glaciation. Considering that the carbonate content of the subseafloor crusts also shows a good correlation with independently estimated atmospheric pCO_2 levels through the Earth history, it seem highly likely that the low carbonate content in the Ongeluk lavas reflects the low atmospheric pCO_2 at that time. We conclude that the continuous decrease in CO_2 concentration of seawater/atm. from 3.2 Ga was one of the contributing factors to the Paleoproterozoic global glaciation.

Keywords: Paleoproterozoic global glaciation, Ongeluk volcanics, Carbonation, Carbon and oxygen isotopes, Seawater/atmosphere CO_2 level

* Correspondence: takazos@jamstec.go.jp
[1]Department of Subsurface Geobiological Analysis and Research (D-SUGAR), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima-cho, Yokosuka 237-0061, Japan
[2]Research and Development Center for Submarine Resources, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima-cho, Yokosuka 237-0061, Japan
Full list of author information is available at the end of the article

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Introduction

Because the Sun was approximately 30% less luminous at 4.6 Ga (Gough 1981), the mean temperature of the Earth's surface would have been below the freezing point of seawater if the albedo and atmospheric composition of the early Earth had been the same as at the present (Sagan and Mullen 1972). However, the occurrence of pillow lavas and sedimentary rocks clearly indicate the presence of liquid water on the early Earth (Sagan and Mullen 1972). This "faint young Sun paradox" has been explained by positing a greenhouse effect to counteract the lower solar luminosity (e.g., Kasting 1987, 1993; Sleep and Zahnle 2001). Yet, at present, this paradox has not yet been entirely resolved because the geologic record suggests that CO_2 levels in the Archean atmosphere potentially exerted enough of a greenhouse effect to avoid Earth freezing for contemporary albedos, whereas the presence of other greenhouse gases such as CH_4 and OCS was also reported (e.g., Pavlov et al. 2003; Ueno et al. 2009). Furthermore, the changes in albedos of the early Earth also had the potential to compensate the faint young Sun (Rosing et al. 2010). However, comprehensive geological studies provide evidence suggesting that atmospheric CO_2 levels in the early Earth were substantially higher than at present: e.g., > 100 PAL at 3.8–1.8 Ga (Ohmoto et al. 2004), > 100 PAL at 3.5–3.2 Ga (Lowe and Tice 2004), at > 7 PAL bar (25 °C) at 3.2 Ga (Hessler et al. 2004), 23×/÷3 PAL at 2.2 Ga (Sheldon 2006), 30–190 PAL at 2.15 Ga, and various other estimates for 2.77–1.85 Ga (Kanzaki and Murakami 2015).

The putative CO_2-rich atmosphere in the early Earth would also have kept oceans acidic and CO_2- and metal-rich (Konhauser et al. 2007). Such CO_2-rich seawater provided seafloor hydrothermal vent environments that would sustain the emergence and early evolution of life (Takai et al. 2006; Russell et al. 2010, 2014; Shibuya et al. 2015, 2016). Furthermore, chemical exchange reactions would have had particular characteristics as the then CO_2-rich seawater interfaced oceanic lithosphere (e.g., intense CO_2 fixation into the crust) (Nakamura and Kato 2004; Rouchon and Orberger 2008) resulting in the generation of novel high-temperature hydrothermal fluids (e.g., alkaline, silica-rich, metal-poor fluid, and Mg-rich fluid) (Shibuya et al. 2010; Ueda et al. 2016). These processes would have played a significant role in controlling the chemistry of early oceans. Therefore, the secular change of CO_2 levels in the atmosphere and seawater is important for understanding the evolution of surface environments and life on Earth.

In this context, the degree of carbonation of greenstones has been considered to qualitatively reflect CO_2 concentrations in ancient seawater (Kitajima et al. 2001; Nakamura and Kato 2004; Hofmann and Harris 2008). The 3.5 and 3.2 Ga greenstones in extensional geological settings (mid-ocean ridge or rift basin) underwent strong carbonation caused by intense interaction with ambient CO_2-rich seawater (Nakamura and Kato 2004; Shibuya et al. 2007a, 2012). Furthermore, the lower carbonate content in the 2.6 Ga greenstones compared to those in the 3.5 and 3.2 Ga greenstones indicated that the CO_2 concentration in seawater decreased during Late Archean period—possibly caused by the formation and breakdown of the supercontinent at around 2.7 Ga (Shibuya et al. 2013a). However, there are no data for the carbonation of subseafloor crust after 2.6 Ga, although the data from the DSDP/ODP drill cores have been obtained from the Phanerozoic crusts (Alt and Teagle 1999; Gillis and Coogan 2011).

In this paper, we focus on the Paleoproterozoic era when global climate drastically cooled to produce an ice age, though it reverted thereafter (Evans et al. 1997; Kirschvink et al. 2000; Harada et al. 2015). In this era, the atmospheric CO_2 level was temporarily insufficient to keep the Earth's surface above the freezing point of water. Previously, a number of triggers for the Paleoproterozoic global glaciation have been proposed: (1) the collapse of a methane greenhouse caused by the global rise of oxygen over the period ~2.5–2.2 Ga (Kopp et al. 2005), (2) the removal of atmospheric CO_2 via increased silicate weathering of the amalgamated supercontinent at ~2.5 Ga (Young 2013) and/or of the newly created voluminous continental flood basalts at 2.45 Ga (Melezhik 2006), and (3) the shutdown of volcanic CO_2 emissions resulting from a global magmatic lull that lasted from 2.45 to 2.2 Ga (Condie et al. 2009). All these models are premised upon low atmospheric CO_2 levels. To test this supposed prerequisite and to reveal the secular change of CO_2 concentration in seawater after 2.6 Ga, we investigated the carbonation of the Paleoproterozoic submarine volcanics in the Ongeluk Formation, Transvaal Supergroup, South Africa. Based on the lines of geological evidence, the Ongeluk volcanics are considered to have erupted during the global glaciation (Kirschvink et al. 2000; Kopp et al. 2005). Therefore, it is expected that the degree of carbonation of the Ongeluk volcanics qualitatively reflects the CO_2 concentration in seawater and atmosphere during that glaciation.
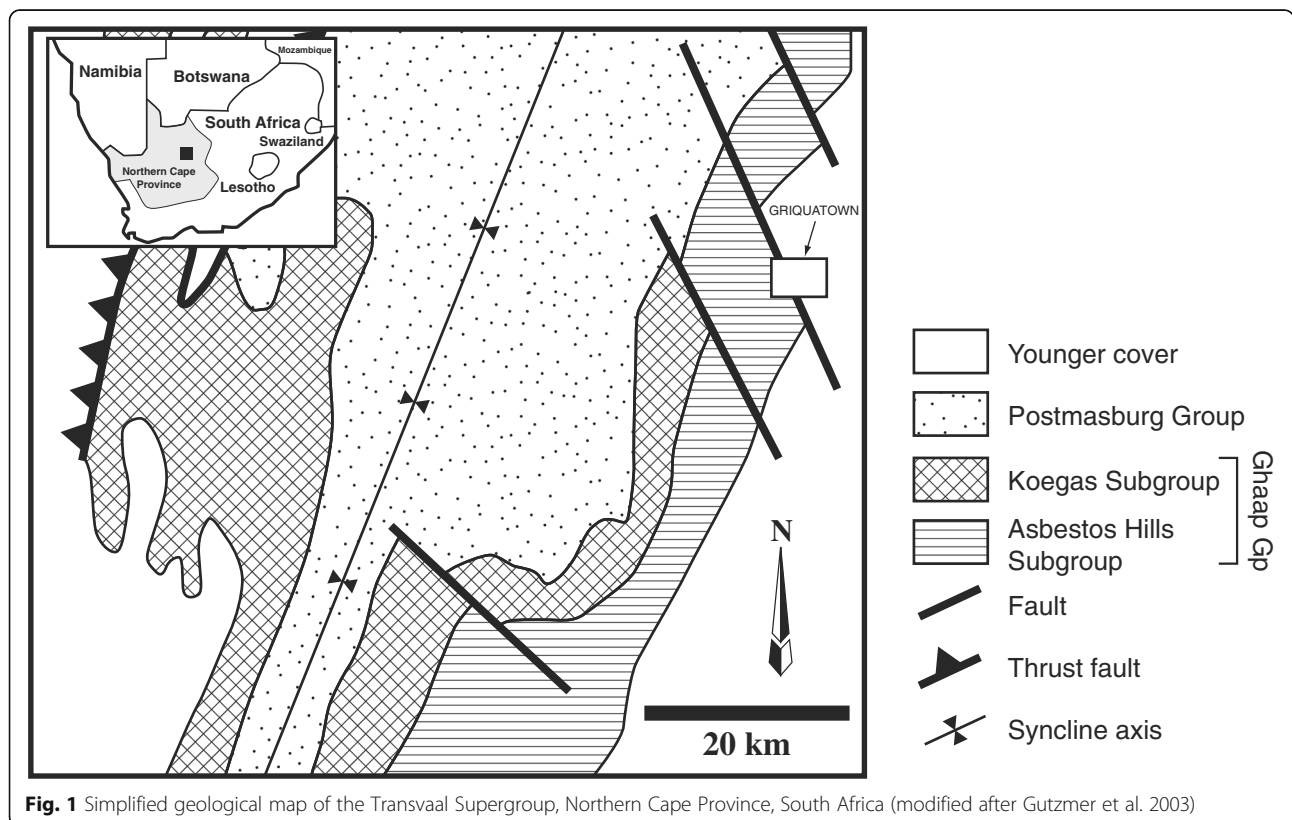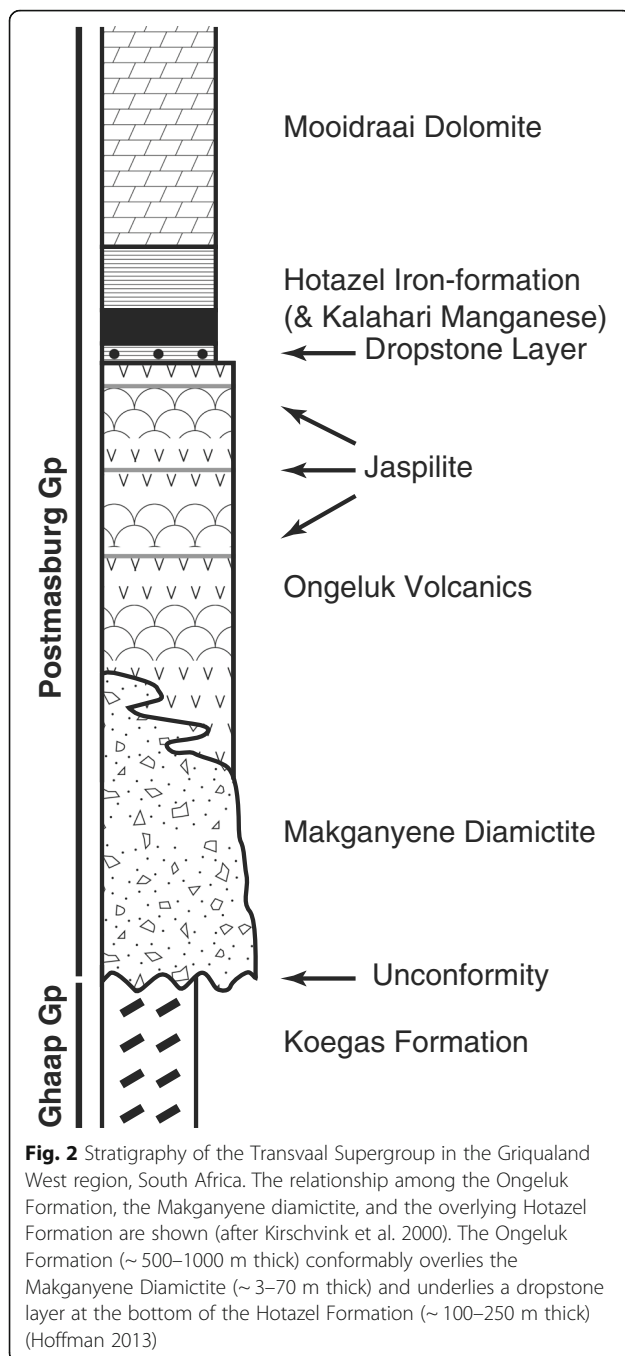
Methods

The Ongeluk formation

The Griqualand West Sequence in South Africa mainly comprises Late Archean to Paleoproterozoic sedimentary rocks and intercalating volcanic rocks deposited on the Kaapvaal Craton (Beukes and Smit 1987; Cornell et al. 1996). In the Griqualand West Sequence, the Transvaal Supergroup is subdivided into three groups by major unconformities; Ghaap Group, Postmasburg Group and Olifantshoek Group in stratigraclicly

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ascending order. The Paleoproterozoic Ongeluk Formation belongs to the Postmasburg Group that mainly consists of diamictite, volcanic rocks, terrigenous clastic rocks, banded iron formations, manganese formations, and shallow marine dolostones (Beukes and Smit 1987). The Postmasburg Group unconformably overlies the Ghaap Group, including Koegas and Asbestos Hill Subgroups composed of iron formation, shale, and quartzite (Fig. 1).

The Ongeluk Formation consists ~ 500–1000 m of basaltic-andesitic lavas comprising pillow lavas, massive sheet flows, and hyaloclastites, intercalated with jaspilite beds (Grobler and Botha 1976) (Fig. 2), indicating the subaqueous eruption of the Ongeluk lavas. The formation conformably overlies the glaciogenic deposits (Makganyene diamictite). The diamictite/lava contacts appear conformable without paleosols in borehole cores (de Villiers and Visser 1977; Evans et al. 1997). Additionally, volcanic shards and fragments are abundant in the upper part of the Makganyene Formation (de Villiers and Visser 1977; Evans et al. 1997), and the diamictite and the lava are interdigitated (Kirschvink et al. 2000; Polteau et al. 2006). These lines of geological evidence indicate that the Ongeluk volcanism and Makganyene glaciation overlapped in time. Therefore, the depositional paleolatitude of the Ongeluk Formation (11 ± 6°) provides strong evidence for low-latitude glaciation in a maritime setting

(Evans et al. 1997; Kirschvink et al. 2000; Hoffman 2013; Gumsley et al. 2017). Furthermore, the Hotazel Formation, consisting predominantly of manganese formation/banded iron formation which includes dropstones at its base (Kirschvink et al. 2000; Polteau et al. 2006), conformably overlies the Ongeluk Formation. The contact between these two formations is characterized by parallel bedding planes in both, ferruginous alteration at the top of the Ongeluk Formation, and the absence of a basal conglomerate. These relationships indicate that the Ongeluk lavas erupted during the global glacial period (Kirschvink et al. 2000; Kopp et al. 2005) (Fig. 2). Metamorphism of the Ongeluk Formation does not exceed prehnite-pumpellyite facies, so that the effects of ancient passive subseafloor hydrothermal alteration are still plain to see (Gutzmer et al. 2001). The age of the Ongeluk Formation had long been under debate because two possible depositional ages (2.2 and 2.4 Ga) were constrained by other formations stratigraphically close to the Ongeluk Formation (Bau et al. 1999; Cornell et al. 1996; Dorland 2004). However, a recent geochronogical work on the Ongeluk Formation itself strongly suggested that the exact age of the volcanism of the Ongeluk lavas was 2426 ± 3 Ma (Gumsley et al. 2017). Thus, 2.4 Ga is tentatively used here as the age of the Ongeluk Formation. The Ongeluk lavas are considered to have erupted in a shallow marine environment during the development of

Fig. 1 Simplified geological map of the Transvaal Supergroup, Northern Cape Province, South Africa (modified after Gutzmer et al. 2003)

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Fig. 2 Stratigraphy of the Transvaal Supergroup in the Griqualand West region, South Africa. The relationship among the Ongeluk Formation, the Makganyene diamictite, and the overlying Hotazel Formation are shown (after Kirschvink et al. 2000). The Ongeluk Formation (~ 500–1000 m thick) conformably overlies the Makganyene Diamictite (~ 3–70 m thick) and underlies a dropstone layer at the bottom of the Hotazel Formation (~ 100–250 m thick) (Hoffman 2013)

an extensional rifting basin on the Kaapvaal Craton (Cornell et al. 1996).

Lavas and hydrothermal jaspilites in the Ongeluk formation

The Ongeluk basaltic andesites are mostly undeformed, and igneous textures, such as intergranular, intersertal, and subophitic textures, are well preserved (Cornell et al. 1996; Gutzmer et al. 2001, 2003) (see also Fig. 3a). Igneous plagioclase and glass are mainly replaced by chlorite, albite, quartz, and minor pumpellyite and calcite, but igneous clinopyroxene survives. Although low-temperature clay minerals, often observed for modern altered seafloor rocks, are minor in the Ongeluk lavas, such textures are similar to those of modern hydrothermally altered seafloor volcanic rocks (e.g., Alt et al. 2010). The degree of carbonation of the Ongeluk basaltic andesites is weak; 17 of the 115 samples were identified to contain calcite under a microscope. These samples mainly contain disseminated calcites replacing igneous phases, but a few samples have vein-filling calcites (Fig. 3b, c).

The Ongeluk pillow lavas still retain open drainage cavities and interpillow voids. These are filled with quartz and/or jaspilite, which was likely precipitated penecontemporaneously with the interbedded jaspilite (Grobler and Botha 1976; Gutzmer et al. 2001, 2003). The precipitates in the drainage cavities have smooth, oval tubular shapes and are oriented parallel to the pillow tubes themselves or to the direction of lava flow. The cavities are isolated from one another and never cross-cut pillow rims nor do the precipitates in the voids ever cut the chilled margins of these rims. In the absence of such precipitates, the open spaces in volcanic rocks are obliterated by compaction during burial—strong evidence that these quartz precipitates formed relatively soon after eruption of the host volcanic rocks (Gutzmer et al. 2003). The jaspilite precipitates are composed mainly of microquartz and hematite and frequently form banded textures of red and white layers. The red layer consists of hematite and minor amounts of microquartz, magnetite, and pyrite, whereas the white layer comprises microquartz and larger subhedral andradite with subordinate hematite and disseminated calcite (Fig. 3d, e), as previously reported (Gutzmer et al. 2001). As observed for the lavas, minor jaspilite samples exhibit deformation textures such as brecciation and/or calcite veining (Fig. 3f). The formation temperature of these hydrothermal precipitates was estimated to be 64–160 °C from the homogenization temperature of fluid inclusions in the quartz (Gutzmer et al. 2001, 2003; Saito et al. 2016).

Analytical methods

Powdered samples were prepared with a tungsten mill from slab samples from which the weathered surface had been removed. In sealed vessels, CO_2 was extracted from the powder samples by using anhydrous phosphoric acid. The stable carbon and oxygen isotope ratios were analyzed using an isotope ratio mass spectrometer equipped with an automatic sampler (DELTA V plus and GasBench II at SI Science Co., Ltd., Japan) (Révész and Landwehr 2002). The isotopic ratios are presented in conventional δ notation. The carbon and oxygen isotope ratios were calibrated relative to the Vienna Pee Dee
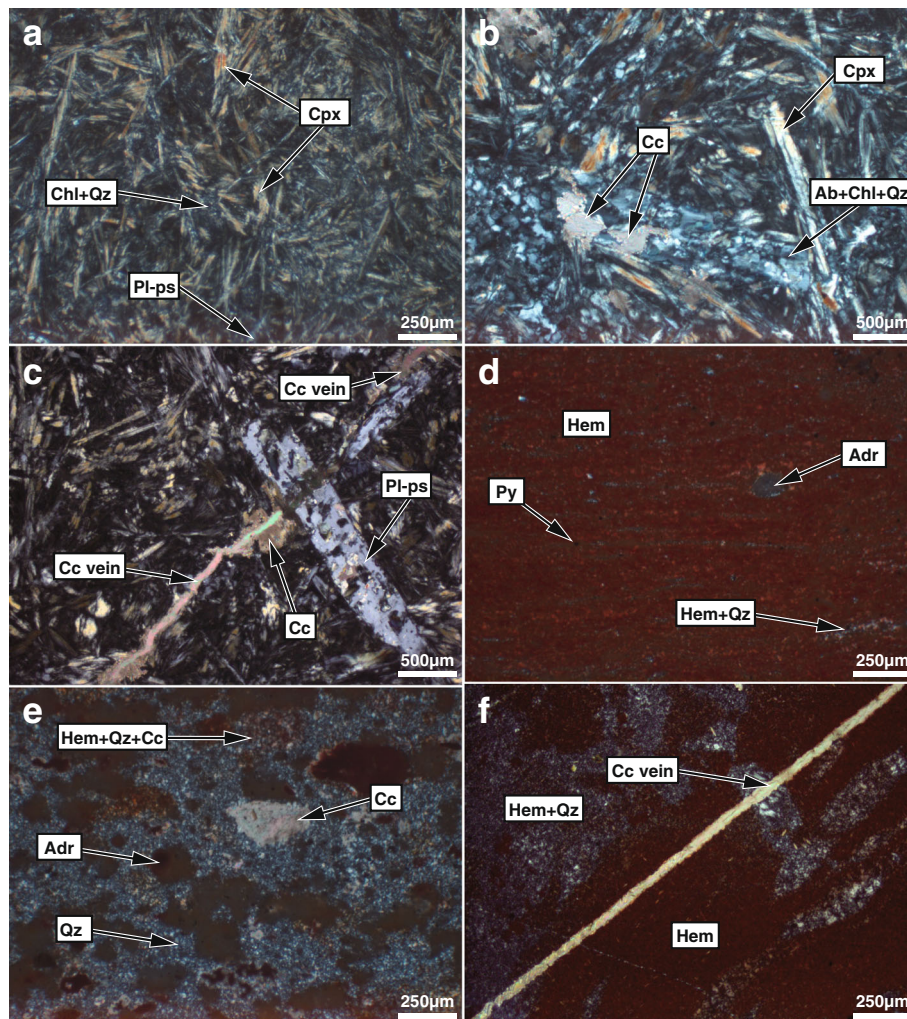
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Fig. 3 Photomicrographs of basaltic andesites and hydrothermal jaspilites in the Ongeluk Formation. **a** A typical basaltic andesite in which the igneous minerals and glass have been replaced by secondary minerals but the igneous texture is well preserved. **b** Disseminated calcite-bearing basaltic andesite in which igneous plagioclase has been replaced by secondary albite, chlorite, quartz, and calcite. **c** A calcite vein cutting all alteration minerals and igneous texture. **d** A hematite-rich layer of interpillow hydrothermal jaspilite. **e** A microquartz-rich layer of the interpillow hydrothermal jaspilite that includes calcite and andradite. **f** A calcite vein cutting jaspilite

Belemnite (VPDB). Based on replicate analyses of laboratory standard, the analytical reproducibility is estimated to be better than ± 0.2‰ for carbon and better than ± 0.5‰ for oxygen isotope ratios. In the analysis of the CO_2 content in the samples, the relative error is 5–10% of the reported values, depending on the amount of extracted CO_2.

Results and discussion

Based on the occurrence and mineral texture of the Ongeluk lavas and jaspilites, the disseminated calcites are considered to have formed during subseafloor hydrothermal circulation at that time, as previously reported (Gutzmer et al. 2001). In contrast, the calcite veins must have formed at least after the formation of the disseminated calcites, which might have occurred during a later stage of subseafloor hydrothermal circulation, though they could also relate to a later metamorphic or deformation event. The oxygen isotope ratios (δ^{18}O) of the disseminated calcites in the lavas and hydrothermal jaspilites range from − 17.9 to − 10.2 ‰ while their carbon isotope ratio (δ^{13}C) shows relatively low values ranging from − 31.9 to − 13.2 ‰ (Table 1 and Fig 4). Most of the calcites in hydrothermal jaspilites have lower δ^{18}O values than those in the Ongeluk lavas, but there is no obvious correlation to be made between the δ^{18}O and δ^{13}C values for all samples, indicating that the isotopic values have not been greatly modified since their formation. The CO_2

Table 1 Isotopic compositions of calcites and CO_2 content in the Ongeluk basaltic andesites and hydrothermal jaspilites

Sample no.	Rock type	Classification of calcite	CO_2 (wt%)	$\delta^{13}C$ (VPDB, ‰)	$\delta^{18}O$ (VPDB, ‰)	Temperature (°C)[a]
GU033	Basaltic andesite	Disseminated	0	− 14.2	− 15.2	123
GU034	Basaltic andesite	Disseminated	0	− 15.6	− 13.8	109
GU035	Basaltic andesite	Disseminated	0	− 13.2	− 14.6	117
GU036	Basaltic andesite	Disseminated	0.01	− 15.8	− 15.8	130
GU037	Basaltic andesite	Disseminated	0.01	− 16.1	− 14.3	114
GU038	Basaltic andesite	Disseminated	0	− 15.9	− 12.9	100
GU041	Basaltic andesite	Disseminated	0	− 18.9	− 14.1	112
GU045	Basaltic andesite	Disseminated	0	− 18.3	− 13.3	104
GU048	Basaltic andesite	Disseminated	0	− 15.7	− 13.2	103
GU049	Basaltic andesite	Disseminated	0	− 14.9	− 14.6	117
GU054	Basaltic andesite	Disseminated	0	− 23.5	− 14.3	114
GU055	Basaltic andesite	Disseminated	0.01	− 24.9	− 15	121
GU063	Basaltic andesite	Disseminated	0	− 22.3	− 12.3	94
GU110	Pillowed basaltic andesite (core)	Disseminated	0	− 15.6	− 10.2	77
GU172	Basaltic andesite	Disseminated	0	− 18.0	− 10.8	82
GU174	Basaltic andesite with calcite veins	Disseminated/vein	0.060	− 16.1	− 17.1	147
GU144	Interpillow jaspilite	–	0	− 17.0	− 17.6	153
GU149	Interpillow jaspilite	–	0	− 21.3	− 13.4	105
GU151	Interpillow jaspilite	–	0.01	− 31.9	− 17.9	158
GU150	Interpillow jaspilite with calcite/quartz veins	–	0.1	− 15.4	− 17.7	155
GU158	Brecciated interpillow jaspilite	–	0.05	− 12.5	− 17.8	156

[a]Formation temperature was estimated from the reported oxygen fractionation factor (O'Neil et al. 1969; Friedman and O'Neil 1977; Chacko et al. 2001) assuming a fluid with δ18O = 0‰ (SMOW)
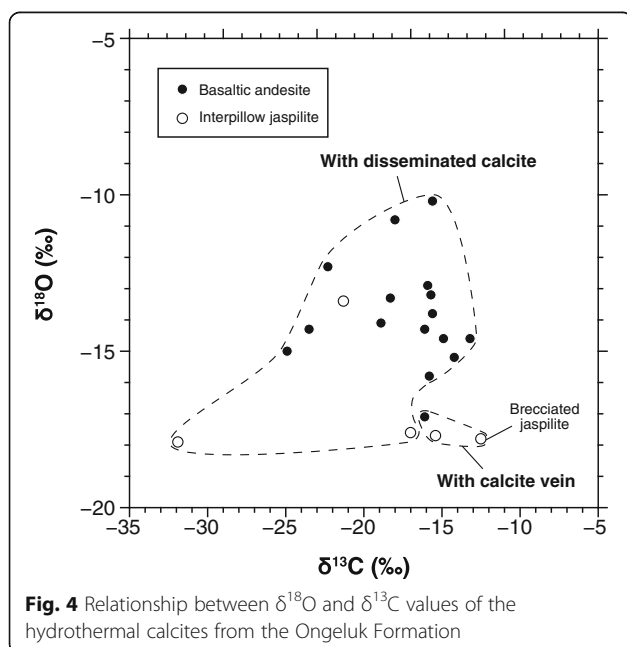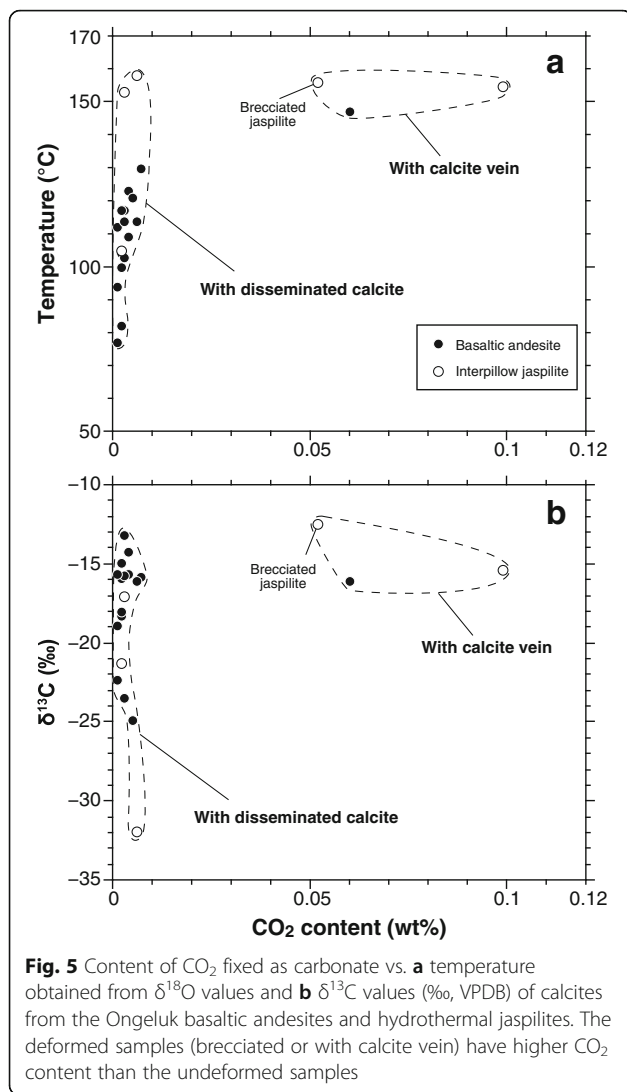

Fig. 4 Relationship between $\delta^{18}O$ and $\delta^{13}C$ values of the hydrothermal calcites from the Ongeluk Formation

contents of the undeformed samples (with disseminated calcites only) are lower than 0.007 wt% (almost equivalent to 0.016 wt% as $CaCO_3$) whereas those of the deformed samples (with calcite vein) have clearly higher CO_2 contents reaching 0.099 wt% (0.23 wt% as $CaCO_3$) (Table 1 and Fig 5). Based on these data, we discuss the carbonation of lavas and the formation temperature of jaspilites in the following sections.

Oxygen isotopes of the calcites in the Ongeluk lavas and jaspilites

The formation temperatures of calcites in the Ongeluk lavas and hydrothermal jaspilite should—if the calcites were formed due to the seafloor hydrothermal circulation—ideally be consistent with the temperatures of seafloor hydrothermal alteration independently estimated from fluid inclusions in the Ongeluk hydrothermal quartz (Gutzmer et al. 2003; Saito et al. 2016). To estimate the formation temperatures of calcites from their $\delta^{18}O$ values, a $\delta^{18}O$ value of seawater must be assumed. However, there have long been two different models on the evolution of the $\delta^{18}O$ value of seawater through the Earth's history; the one is a constant $\delta^{18}O$ value (e.g., Muehlenbachs and Clayton 1976; Blake et al.

Fig. 5 Content of CO_2 fixed as carbonate vs. **a** temperature obtained from $\delta^{18}O$ values and **b** $\delta^{13}C$ values (‰, VPDB) of calcites from the Ongeluk basaltic andesites and hydrothermal jaspilites. The deformed samples (brecciated or with calcite vein) have higher CO_2 content than the undeformed samples

2010; Tartèse et al. 2017) and the other is a gradually increasing $\delta^{18}O$ value (e.g., Kasting et al. 2006).

In the former case, using the oxygen isotope fractionation factors (O'Neil et al. 1969; Friedman and O'Neil 1977; Chacko et al. 2001), the formation temperatures of disseminated calcites in the lavas are calculated to be 77–130 °C (Table 1 and Fig. 5a). The $\delta^{18}O$ values of the calcites in the undeformed jaspilites provide a slightly higher formation temperature range (105–158 °C). The difference in the formation temperatures indicates that the disseminated calcites in the lavas were formed mainly as a result of interaction with relatively low-temperature downwelling seawater from the seafloor, whereas the precipitation of jaspilites took place with a larger contribution of high-temperature iron-rich hydrothermal fluids derived from the lower part of the hydrothermal circulation cell. Be that as it may, the temperatures obtained for both calcites in the undeformed lavas and the hydrothermal jaspilites fall

within the range of homogenization temperatures of the fluid inclusions (64–160 °C) in the Ongeluk hydrothermal quartz precipitates (Gutzmer et al. 2001, 2003; Saito et al. 2016). The consistency of the formation temperatures suggests that the generation of disseminated calcites in the lavas and jaspilites coincided with the precipitation of the hydrothermal quartz during subseafloor hydrothermal circulation. On the other hand, the calcites in the deformed samples show only high formation temperatures (147–156 °C), which are consistent with a metamorphic temperature not exceeding prehnite-pumpellyite facies (Gutzmer et al. 2001).

In the latter case that $\delta^{18}O$ value of seawater has increased from -9‰ (vs. SMOW) at 4.6 Ga to the present value (e.g., Kasting et al. 2006), and the $\delta^{18}O$ value of seawater is approximately -8‰ at 2.4 Ga. Using this value, the formation temperature of hydrothermal calcites and jaspilite was estimated to be 28–75 °C, which is clearly much lower than the formation temperature (64–160 °C) of hydrothermal quartz estimated from fluid inclusions therein (Gutzmer et al. 2003; Saito et al. 2016) and the alteration temperature estimated from the assemblage of secondary minerals in the lavas (Gutzmer et al. 2001). This discrepancy also forces the conclusion that the $\delta^{18}O$ value of seawater has remained almost constant through the Earth history (e.g., Holmden and Muehlenbachs 1993).

Carbon isotopes of the calcites in the Ongeluk lavas and jaspilites

Variation of calcite $\delta^{13}C$ values ($\delta^{13}C_{cc}$) in seafloor volcanic rocks tends to reflect the geological setting of hydrothermal alteration and the carbon sources (Fig. 6). In general, modern and Archean unsedimented ridge-derived oceanic crusts have $\delta^{13}C_{cc}$ values close to those of seawater (mostly -4 to 4‰), because subseafloor volcanic sequences are generally dominated by seawater-derived fluid due to their high permeability (Nakamura and Kato 2004; Gillis and Coogan 2011; Shibuya et al. 2012). On the other hand, the $\delta^{13}C_{cc}$ values of some rift lake volcanics in the Afar Rift (-7 to -1‰) are explained as a mixture of meteoric water (~ -15‰) and seawater, with a possible contribution of magmatic CO_2 (~ -5‰) (Fouillac et al. 1989), whereas hydrothermal calcite chimneys in Lake Abhé in the Afar Rift have $\delta^{13}C_{cc}$ values (~ 2 to 4‰) consistent with that of the alkaline lake water (0.6‰) equilibrated with atmospheric CO_2 (~ -7‰) (Dekov et al. 2014). In contrast, all sediment-related settings, such as modern sedimented ridge-derived oceanic crusts and modern/Archean oceanic rift basin basalts, bare relatively low $\delta^{13}C_{cc}$ values (< -15‰) as well as the values near the $\delta^{13}C$ of CO_2 ($\delta^{13}C_{CO2}$) in seawater which would represent a significant input of CO_2 derived from the decomposition of

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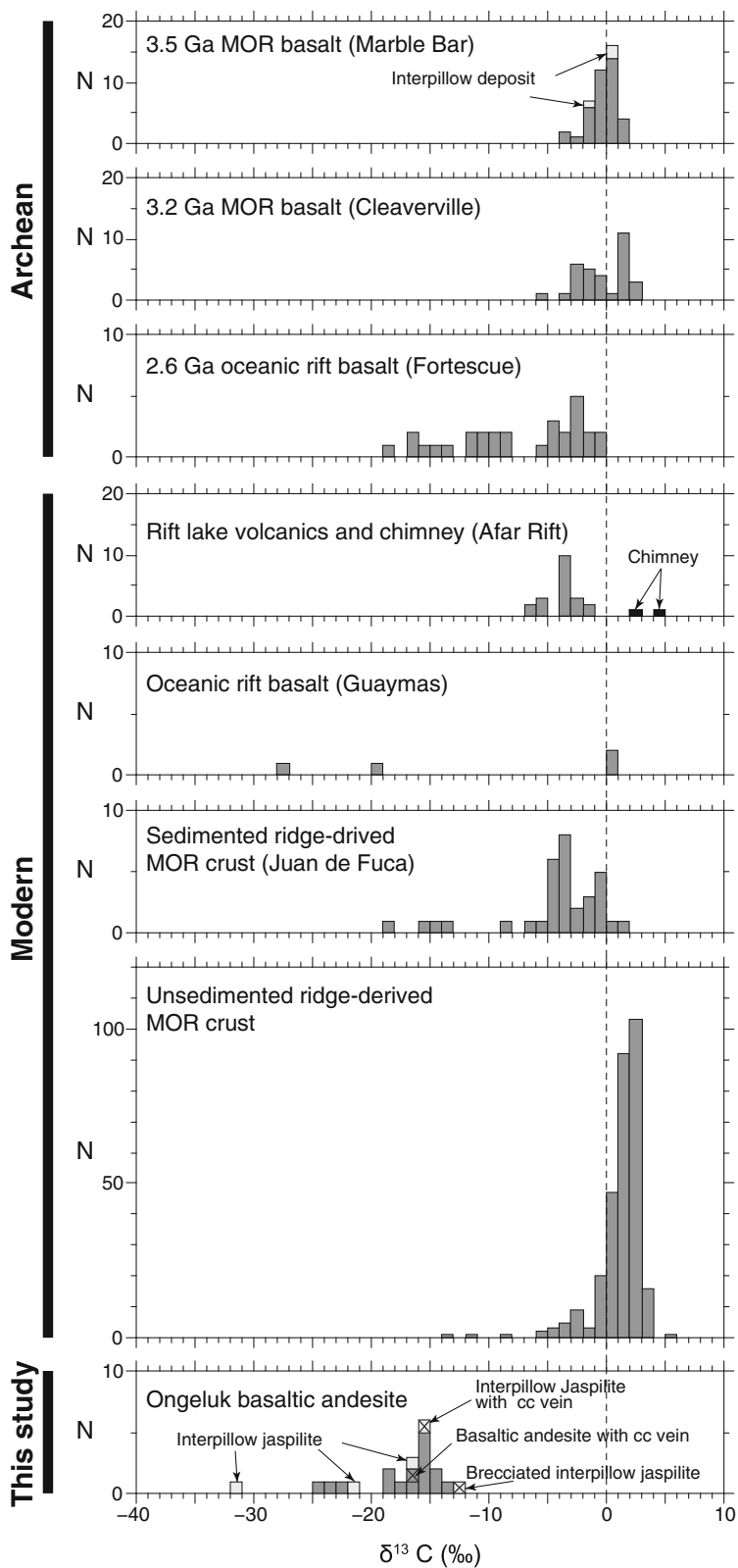
Fig. 6 (See legend on next page.)

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Fig. 6 $\delta^{13}C$ values (‰, VPDB) of hydrothermal calcites from the Ongeluk Formation. For comparison, data from modern unsedimented ridge-derived mid-ocean ridge (MOR) crusts (Gillis and Coogan 2011), sedimented ridge-derived MOR crusts (Coggon et al. 2004), rift-zone seafloor basalts (Gieskes et al. 1982), rift lake basement volcanics (Fouillac et al. 1989), and hydrothermal chimney (Dekov et al. 2014) from Afar Rift, Archean MOR basalts (Nakamura and Kato 2004; Shibuya et al. 2012), and rift-zone seafloor basalts (Shibuya et al. 2013a) are also shown

organic matter (Gieskes et al. 1982; Coggon et al. 2004; Shibuya et al. 2013a).

In this regard, the relatively low $\delta^{13}C_{cc}$ values down to –31.9‰ in the Ongeluk Formation is consistent with its geological setting (a sedimented rifting basin) where decomposition of organic matter in sedimentary rocks (e.g., underlying Makganyene Formation) could occur during the hydrothermal circulation. Another characteristic point is that $\delta^{13}C_{cc}$ values higher than – 13.2‰ were not identified in the undeformed lavas. This is consistent with the exceptionally $^{13}C-$ depleted CO_2 in the Ongeluk seawater at that time; the Paleoproterozoic long-term seawater $\delta^{13}C_{CO2}$ generally decreased and reached its lowest value (– 14 to – 8‰) at the time of the glaciation and then recovered thereafter (Polteau et al. 2006). Therefore, the wide variation of $\delta^{13}C_{cc}$ values of the Ongeluk lavas can be well explained by varying the mixing ratios between the CO_2 derived from the decomposition of subseafloor sedimentary organic matter and the ^{13}C-depleted CO_2 in seawater. For this reason, the measured CO_2 (as carbonate) content in the lavas likely corresponds to the upper limit of seawater-derived CO_2.

Secular change of carbonate content in the altered subseafloor crust

Because permeability decreases while temperature increases with increasing depth below the seafloor, carbonate minerals tend to become unstable, thereby leading to a decrease in fixed CO_2 in the basaltic crust and ophiolite (Gillis and Robinson 1988; Gillis and Coogan 2011; Alt and Teagle 1999; Shibuya et al. 2007a, 2007b, 2012). However, the carbonation of highly permeable, low- to moderate-temperature (<c. 200 °C) uppermost basaltic sequences presumably tends to reflect seawater CO_2 concentration. Furthermore, carbonation of seafloor basalts would be less significantly influenced by the seawater pH governing the speciation of CO_{2aq}, HCO_3^-, and CO_3^{2-}. Under constant pressure-temperature conditions, calcite precipitation from a solution is governed by activities of CO_3^{2-} and Ca^{2+} ions. In other words, the saturation state of calcite mainly depends on the total CO_2 concentration (CO_{2aq} + HCO_3^- + CO_3^{2-}) and pH value in seawater, at least when the activity of Ca^{2+} is constant. In seafloor hydrothermal systems, however, pH variations at low-moderate temperatures are much smaller than in solution because alteration minerals substantially buffer the pH of a coexisting fluid. For example, thermodynamic calculations indicated that fluid pH at 150 °C is potentially buffered to be 7.7 and 7.6 even after reactions with the Hadean weakly acidic, CO_2-rich seawater (total CO_2 = 200 mmol/kg) and with the present-day seawater (total CO_2 = 2 mmol/kg), respectively (Macleod et al. 1994). Such behavior of pH at low-moderate temperatures is also distinct from high-temperature fluids (> 300 °C) where pH values are influenced by an input of magmatic volatiles (e.g., Butterfield et al. 2003) and the presence or absence of carbonate minerals (Shibuya et al. 2010, 2013b). Accordingly, it is suggested that the content of fixed CO_2 as carbonate in the uppermost subseafloor crust qualitatively reflects total CO_2 concentration in seawater under a constant pressure-temperature condition. On the other hand, it was pointed out that high-temperature bottom seawater elevates temperature of subseafloor fluids and kinetically facilitates the formation reactions of carbonate minerals in the uppermost crust (Gillis and Coogan 2011), although carbonate minerals in altered mafic rocks become unstable with increasing temperature under equilibrium condition (e.g., Shibuya et al. 2013b). In this section, therefore, we discuss the secular change of total CO_2 concentration, pH, temperature, and partial pressure of CO_2 (pCO_2) in seawater based on the CO_2 content in the subseafloor uppermost crust (< 1 km deep from the seafloor) through geologic time.

In the Phanerozoic, the content of CO_2 as carbonate in the Jurassic/Cretaceous crusts is generally higher than that of younger crusts (Fig. 7a). This trend is more clearly evidenced in crusts with greater penetration depth. The CO_2 contents in the young crusts (< 13.6 Ma) with penetration depth of > 200 m (Holes 369B, 896A, and 504B) are lower than 1 wt% (Gillis and Coogan 2011; Alt and Teagle 1999) (Fig. 7a). These values probably reflect the total CO_2 concentration in seawater because the temperature of bottom seawater is presumably almost constant (e.g., 2 °C) and not high enough to effect carbonate formation in the uppermost crust during this period. In contrast, Jurassic and Cretaceous crusts with penetration depths of > 200 m (Holes 801C, 417A, 417D, and 418A) have higher CO_2 contents, up to 4.2 wt.%, than the younger crusts. It was previously suggested that the enhanced CO_2 uptake by the crust in the Cretaceous period can be explained only

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Fig. 7 Secular change of CO_2 (as carbonate) content in the altered subseafloor crust. **a** DSDP/ODP drill cores that penetrated basaltic basement (Alt and Teagle 1999; Gillis and Coogan 2011). The CO_2 content in the Jurassic/Cretaceous crusts is generally higher than that of younger crusts. Because the crusts with shallower penetration depth have large variation of CO_2 content, the crusts with penetration depth > 200 m is mainly discussed in the text. **b** The CO_2 content in Precambrian greenstones with geologically reconstructed depth > 1000 m from the ancient seafloor. Data from 3.5 Ga Apex Basalt in the Marble Bar area (Nakamura and Kato 2004), 3.5 Ga Mount Ada Basalt in the North Pole area (Kitajima et al. 2001; Terabayashi et al. 2003), 3.2 Ga Regal Formation in the Cleaverville area (Shibuya et al. 2012), 2.6 Ga Jeerinah and Bunjinah Formations in Beasley River area (Shibuya et al. 2013a) in the Pilbara Craton (Western Australia), and this study. Note that the CO_2 contents in the 3.5 Ga Mount Ada Basalt and the 3.2 Ga Regal Formation were calculated from the modal abundance of carbonate minerals in greenstones

by higher seawater temperatures (Brady and Gíslason 1997; Gillis and Coogan 2011). In this case, the high temperature of seawater was likely maintained by the strong greenhouse effect induced by high atmospheric pCO_2 in this era (Berner and Kothavala 2001), as suggested by other geologic records (e.g., paleosols; Ekart et al. 1999). High atmospheric pCO_2 might also elevate the total CO_2 concentration in seawater, in which case, the high total CO_2 concentration along with high temperature of seawater potentially accounts for the

high carbonate content in the Jurassic/Cretaceous uppermost crust.

In the Archean, the carbonate contents in the 3.5–3.2 Ga subseafloor crusts (5.7–7.9 wt% as CO_2) are obviously much higher than modern equivalents (Kitajima et al. 2001; Terabayashi et al. 2003; Nakamura and Kato 2004; Shibuya et al. 2012, 2013a) (Fig. 7b). Although the Archean seawater temperature has not been quantitatively constrained (Knauth and Lowe 2003; Robert and Chaussidon 2006; Blake et al. 2010), it is highly possible that the strong carbonation of Archean greenstones reflects high total CO_2 concentration in seawater. Furthermore, many geological and theoretical investigations indicate that the Early to Middle Archean atmosphere was extremely enriched in CO_2 to compensate the faint young Sun (Sagan and Mullen 1972; Kasting 1987; Ohmoto et al. 2004; Lowe and Tice 2004). Therefore, the high pCO_2 in the Early to Middle Archean seawater/atm. would be the primary factor elevating the total CO_2 concentration in seawater and the carbonate content in the subseafloor crust. In contrast, the 2.6 Ga subseafloor crust has relatively low CO_2 content (0.6 wt.%) that is comparable to modern equivalents, which suggests that total CO_2 concentration in seawater decreased during the period between 3.2 and 2.6 Ga (Shibuya et al. 2013a). The trigger for this decrease in seawater CO_2 is possibly the formation and breakdown of the supercontinent in the late Archean, the removal of precipitated sedimentary carbonate onto land during the amalgamation of continents, and the precipitation of platform carbonate on newly created passive margins during/after the continental breakdown (Shibuya et al. 2013a).

Compared with the contents of fixed CO_2 as carbonate of the Archean and Phanerozoic subseafloor uppermost crusts, the average CO_2 content in the Ongeluk lavas (< 0.001 wt% including calcite veins) is clearly lower than those of Late Archean and even the modern equivalents (e.g., 0.21 wt% in 504B), even though the CO_2 in the Ongeluk lavas includes organic matter-derived CO_2 in addition to the original seawater CO_2. These results carry the implication that total CO_2 concentration in seawater further decreased from Late Archean to the Paleoproterozoic because the temperature of the Ongeluk bottom seawater would not have been much lower than the modern temperature (e.g., 2 °C). Thus, the total CO_2 concentration in 2.4 Ga seawater may have been lower than the present level. Such decrease in the total CO_2 concentration in seawater from 3.2 to 2.4 Ga is also consistent with the decrease in atmospheric pCO_2 from the late Archean to Paleoproterozoic estimated from the paleosols (Kanzaki and Murakami 2015).

In principle, carbonate formation in the uppermost subseafloor crust should be influenced by not only temperature and total CO_2 concentration of seawater,

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but also other factors such as pressure dependence of carbonate stability. Nevertheless, as discussed above, the degree of hydrothermal carbonation of the uppermost subseafloor crust shows a good correlation with independently estimated atmospheric pCO_2 levels throughout Earth history. This overall trend implies that the secular change of atmospheric pCO_2 relates more closely to that of total CO_2 concentration in seawater rather than pH change. Thus, the exceptionally low CO_2 contents in the Ongeluk lavas would also reflect extremely low CO_2 levels in the seawater/atm. during the Paleoproterozoic global glaciation. Our conclusion supports the low atmospheric CO_2 levels at that time—a premise of the previously proposed hypotheses for the trigger of the Paleoproterozoic global glaciation (Kopp et al. 2005; Melezhik 2006; Condie et al. 2009; Young 2013).

Conclusions

The carbonate content in the Ongeluk lavas and its comparison with other equivalents of various ages revealed that the total CO_2 concentration in 2.4 Ga seawater was extremely low, which potentially accounts for the assumed low atmospheric CO_2 levels during the Paleoproterozoic global glaciation. More importantly, the present study indicates the possibility that the degree of carbonation of subseafloor crusts reflects the qualitative secular change of CO_2 concentration in seawater and atmosphere. Therefore, the carbonate content in post-2.4 Ga subseafloor crusts should be investigated to decode secular changes of CO_2 concentrations in seawater/atm., especially during the Proterozoic. Moreover, it is suggested that more quantitative compositions of ancient seawater can be estimated by analysis of subseafloor crust materials such as hydrothermally precipitated minerals and their fluid inclusions.

Abbreviations
Adr: Andradite; Cc: Calcite; Chl: Chlorite; Cpx: Clinopyroxene; Hem: Hematite; MOR: Mid-ocean ridge; PAL: Present atmospheric level; Pl-ps: Plagioclase pseudomorph; Py: Pyrite; Qz: Quartz; VPDB: Vienna Pee Dee Belemnite

Authors' contributions
TS and SM proposed the topic and conceived and designed the study. TK and TS carried out the geological investigation. TS conducted the petrological description and obtained the geochemical data. TK, KT, and MJR helped in their interpretation and collaborated with the corresponding author in the construction of the manuscript. All authors read and approved the final manuscript.

Author details
[1]Department of Subsurface Geobiological Analysis and Research (D-SUGAR), Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima-cho, Yokosuka 237-0061, Japan. [2]Research and Development Center for Submarine Resources, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima-cho, Yokosuka 237-0061, Japan. [3]Project Team for Development of New-Generation Research Protocol for Submarine Resources, Japan Agency for Marine-Earth Science and Technology (JAMSTEC), 2-15 Natsushima-cho, Yokosuka 237-0061, Japan. [4]Department of Earth Science and Astronomy, The University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153-8902, Japan. [5]Earth-Life Science Institute, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8551, Japan. [6]Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91108, USA. [7]Novosibirsk State University, Pirogova 1 630090, Russia.

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