



Title	Geological background of the Kairei and Edmond hydrothermal fields along the Central Indian Ridge : Implications for the distinct chemistry between their vent fluids
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# Geological background of the Kairei and Edmond hydrothermal fields along the Central Indian Ridge: Implications of their vent fluids' distinct chemistry

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## ABSTRACT

Hydrogen-rich hydrothermal areas, such as those in the Indian Ocean, may have had an influence on early evolution of life on Earth and thus have attracted interest because they may be a proxy for ancient ecosystems. The Kairei and Edmond hydrothermal fields in the Indian Ocean are separated by 160 km, but exhibit distinct fluid chemistry: Kairei fluids are hydrogen-rich; Edmond fluids are hydrogen-poor. At this region, the Central Indian Ridge shows an intermediate spreading rate, 48 mm year<sup>-1</sup> as full rate, where the hydrothermal fields occur. Kairei field vent fluids show persistently high concentrations of H<sub>2</sub>. The Kairei field seems to be unique among hydrogen-enriched hydrothermal regions: most similar hydrogen-rich hydrothermal activity occurs along slowly spreading ridge, <40 mm year<sup>-1</sup>. The geological and tectonic aspects of the Kairei and Edmond hydrothermal fields were studied to try to elucidate geological constraints on hydrogen production. Visual observations of the seafloor near Kairei from a submersible revealed olivine-rich plutonic rocks with olivine gabbro-troctolite-dunite assemblages exposed within 15 km of the vent field, with serpentinized ultramafic mantle rocks on the Oceanic Core Complex (OCC). The OCC area might be a recharge zone of Kairei hydrothermal activity producing H<sub>2</sub>-rich vent fluids. The chaotic seafloor within 30 km of the Kairei field reflects a magma-starved condition persisting there for 1 Myr. Asymmetric geomagnetic and gravity anomalies near the Kairei field can be used to infer that patchy olivine-rich intrusions are scattered within mantle ultramafics, where infiltrated seawater reacts with magma and ultramafic rocks or olivine-rich rocks. The heterogeneous uppermost lithosphere containing shallow olivine-rich rock facies surrounding the Kairei field provides abundant H<sub>2</sub> into the vent fluid through serpentinization. The hydrogen-rich Kairei field is hosted by basalt, with mafic-ultramafic olivine-rich lithology; the ordinary, hydrogen-poor Edmond field is hosted by a normal basaltic lithology. The contrasting geochemical signatures of the two fields reported here can also be found in ancient rocks from a juvenile Earth. This suggests that lithology-controlled generation of hydrogen may have operated for a long time and be relevant to the origin of life on Earth.

Key words: hydrogen production, Kairei hydrothermal field, oceanic core complex, serpentinization, troctolite, Uraniwa Hills

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## INTRODUCTION

Seafloor hydrothermal fields have attracted great interest in many disciplines of Earth and biological sciences since their initial discovery in the late 1970s (Hessler & Kaharl 1995). A remarkable feature of the habitat around hydrothermal fields is that lithotrophic micro-organisms are independent of energy derived from sunlight (cf. Takai *et al.* 2006). Such an environment resembles early stages of the Earth's history: pre-photosynthetic worlds founded in the dark abyss. Consequently, some predominant ideas about the origin of life specifically relate to deep-sea hydrothermal systems.

Such postulated models of early Earth history have come to constitute part of an important field of science. Microbiologists have proposed various possibilities for establishment of microbial ecosystems in the very early stages of Earth history. Among the proposed scenarios, a modern proxy ecosystem for the earliest stages in our evolution favours hydrogen-rich fluids in abyssal hydrothermal systems (Takai *et al.* 2004). Therefore, understanding the mechanism that supplies hydrogen to the vent fluids will presumably help understand the earliest stages of evolution of life on Earth. This is one reason why such hydrothermal fields enriched in hydrogen have been investigated extensively in the last decade.

To date, most hydrogen-rich hydrothermal activity has been found along the slowly spreading, approximately 40 mm year<sup>-1</sup> or less, Mid Atlantic Ridge (MAR). Among them, the activities of the Rainbow, Lost City, and Logachev hydrothermal fields have been well documented (Charlou *et al.* 2002; Kelley *et al.* 2005). Recently, two more examples have been explored (Beltenev *et al.* 2007; Walter *et al.* 2008). With limited supply of magma near the slowly spreading ridges, deep lithologies of oceanic lithosphere, plutonic gabbros or mantle peridotites, become widely exposed on the seafloor. Frequently, such exposures form dome-shaped geologic bodies that designated Oceanic Core Complexes (OCCs). In fact, the Lost City field is located on one of the OCCs: the Atlantis Massif (Kelley *et al.* 2005). Among abiotic sources of hydrogen, serpentinization of mantle peridotites is favoured near OCCs because of the greater and more sustained production of hydrogen than that by other mechanisms, e.g. radiolysis, dyke-penetration into shallow crust, or silicate catalysis at fault areas (e.g. Bach 2007; Blair *et al.* 2007).

The Indian Ocean hydrothermal fields occupy a unique position to facilitate our understanding of the hydrogen production in the Mid-Oceanic Ridge (MOR) environment. Two active hydrothermal fields, Kairei and Edmond, exist along the Central Indian Ridge (CIR) showing an intermediate spreading rate (~48 mm year<sup>-1</sup>). These two hydrothermal fields show geochemically-distinct signatures in their vent fluids, despite being only 160 km apart. The Kairei field seems to be a unique case of hydrogen-rich hydrothermal activity outside of the slowly spreading ridge environment; it is located at 25.32°S, 70.04°E towards the northern end of the first segment of CIR (CIR-1), counted from the Rodriguez Triple Junction (25.5°S, 70°E; Fig. 1), which incidentally was the first hydrothermal field discovered in the Indian Ocean (Gamo *et al.* 2001). In contrast, the neighbouring Edmond field shows normal or lower hydrogen concentrations typical of a MOR environment (Gallant & Von Damm 2006). It is located at 23.88°S, 69.60°E, near the northern end of the third segment of the CIR, CIR-3 (Van Dover *et al.* 2001). A model was previously proposed to explain the unique characteristics of Kairei vent fluids in comparison to the Edmond fluids (Gallant & Von Damm 2006): sub seafloor precipitation of sulphide, generating H<sub>2</sub> as a by-product. This model excludes the possibility that alteration of ultramafic, olivine-rich mantle rocks provides abundant hydrogen to vent fluid, because they did not find such rocks in the vicinity. However, no exploration of the wider regional geological environment has been reported prior to our study.

In this paper, we report a comprehensive investigation of the linkage between the fluid chemistry and the tectono-geological environment of both the Kairei and Edmond hydrothermal fields. For this purpose, local geological observations coupled with regional geophysical surveys of the areas surrounding each hydrothermal field were performed using a manned JAMSTEC submersible (Shinkai6500) in January 2006 during the YK05-16 cruise.

## MATERIALS AND METHODS

### Fluid chemistry revisited

Hydrothermal fluids were sampled using gas-tight bottles (WHAT'S sampler; Tsunogai *et al.* 2003; Saegusa *et al.* 2006), which were attached to the Shinkai6500 manned

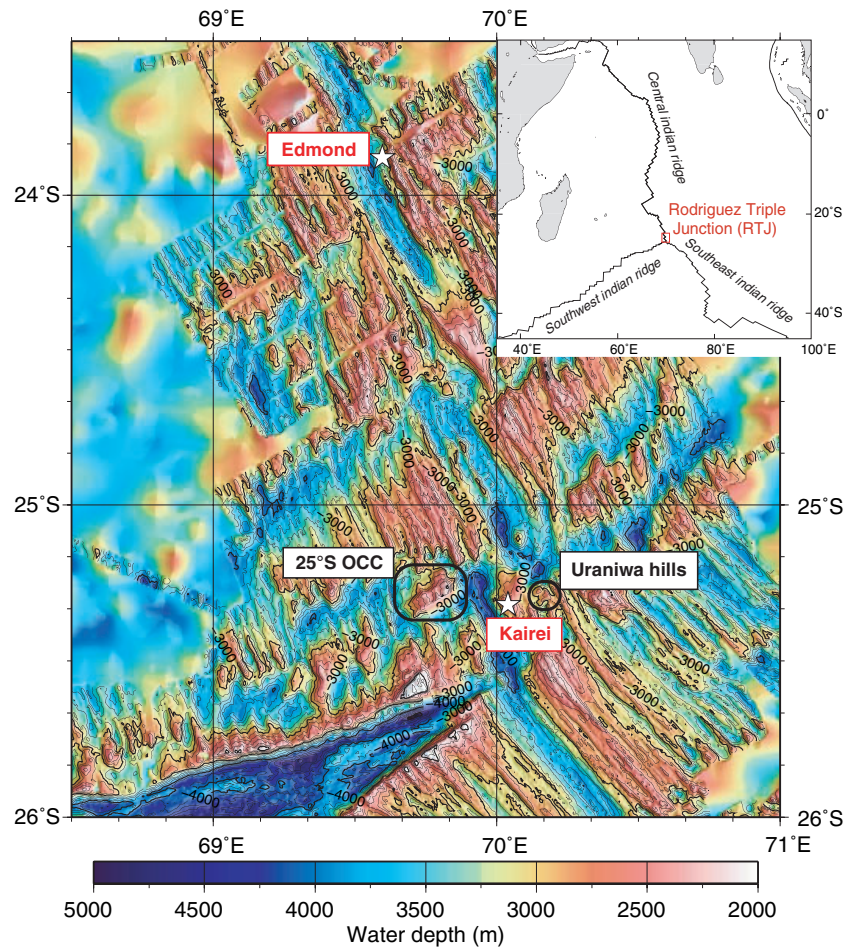


Fig. 1. Generalized bathymetry of the studied area. Data sources of multi narrow beam bathymetry: KH93-3, KR00-05, YK01-15, YK05-16 [<http://www.jamstec.go.jp/dsr/>] and the cruises using French vessels (Briais 1995).

submersible. Immediately after the dive was completed, sampled fluids for gas and water chemistry were processed onboard. All dissolved gases were separated from the fluid solution using a gas extractor (Konno *et al.* 2006). The extracted gases were stored in 50-ml metallic flasks and analysed onshore after the cruise. The residual fluids in the gas extractor were transferred to polyethylene flasks after filtration and were analysed for water chemistry. At Hokkaido University, the carbon isotopic compositions of  $\Sigma\text{CO}_2$  and  $\text{CH}_4$  with their contents were assessed using isotope-ratio-monitoring GC/MS. At the Ocean Research Institute of the University of Tokyo (ORI),  $\text{H}_2$  gas concentrations and isotope compositions of hydrogen were determined using a continuous flow isotope ratio mass spectrometer system (Kawagucci *et al.* 2007): the isotopic compositions will be reported elsewhere (Kawagucci *et al.*, in preparation). Elemental composition of the water samples were determined at Kyushu University. The concentrations chloride, potassium and sulfate were determined by Mohr method, by flame spectrophotometry and by ion chromatography, respectively. Other major (Na, Ca, Mg, Si) and minor (Mn, Sr, Ba, Fe) elements

were measured using ICP-AES after appropriate dilution of the samples. Alkalinity was determined by titration with hydrochloric acid with Gran plot estimation of the endpoint on board (Table 1). pH and  $\text{H}_2\text{S}$  were also measured on board.

#### Seafloor observation, bathymetry, and geophysics

During the YK05-16 research cruise, visual geological and volcanological observations from a manned submersible were guided using detailed bathymetric information obtained using a multi-narrow beam echo sounder (MNBES, SeaBEAM 2112) of the R/V Yokosuka. Such multi-beam bathymetry is the minimum requirement for geological study of the seafloor. It enables samples to be taken as precisely as those taken on land. In addition, a region-wide bathymetric survey with gravity and geomagnetic observations was conducted during the expedition. Linkages between the respective water chemistries of two hydrothermal fields and geological environments or microbial communities were also targeted. Through visual observation, lava fragments partially embedded in the sediments



were sampled using the Shinkai6500 submersible's manipulators.

### Rock chemistry

The rock samples used for this study were obtained using the submersible's manipulators under visual observation through the submersible's viewport with video recording of their occurrence. Fresh glass shards of lava fragments were selected for analyses from among a suite of rock samples obtained during the submersible dives in the cruise.

Major element compositions of hand-picked, glassy, lava fragments ( $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{FeO}$ ,  $\text{MnO}$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{P}_2\text{O}_5$ ; Table 2A) were assessed at Kanazawa University using an electron microprobe (JXA-8800; JEOL). The analyses were performed using an accelerating voltage of 15 kV and a beam current of 10 nA using a 10- $\mu\text{m}$ -diameter-beam. The X-ray peaks were counted for 10 s and backgrounds in both high-wavelength and low-wavelength sides were measured for 5 s. In addition, JEOL software using ZAF corrections was used. No loss of Na was observed during the analysis under analytical conditions.

Trace-element compositions of lava glasses (Table 2B) were determined using an ICP-MS (7500S; Agilent Technologies Inc.) equipped with an ArF excimer laser ablation system (193 nm, 5 Hz, GeoLas Q-plus; MicroLas Laser-system GmbH) at Kanazawa University (Ishida *et al.* 2004). Ablation of a 50- $\mu\text{m}$ -diameter area was necessary to avoid microcrystal ablation. The peak of  $^{43}\text{Ca}$  was monitored as an internal standard, as described in Longerich *et al.* (1996); the NIST SRM 612 glass was used as the calibration standard. A glass standard was analysed initially before each batch of analyses (each batch being eight analyses) with a linear drift correction of standard intensities applied between each calibration. The elemental concentrations of glasses were taken from Pearce *et al.* (1997). Detailed analytical procedures and the precision and accuracy of the data on NIST SRM 614 and BCR-2G reference standard glasses with identical analytical conditions appear in Morishita *et al.* (2005a,b).

## RESULTS

### Fluid chemistry

Plots of selected major elements and  $\text{H}_2$  concentrations versus Mg concentration in sampled fluids display linear relationships representing mixing between a single or a few hydrothermal end-member and ambient seawater in each hydrothermal field (Fig. 2 A–F). Estimated compositions of end-member fluids for each vent area are listed in Table 1. A remarkable feature of the Kairei hydrothermal fluid includes its much greater  $\text{H}_2$  concentration in the

end-member than in seawater: 2.5–3.7  $\text{mmol kg}^{-1}$  of  $\text{H}_2$  versus 1  $\text{mmol kg}^{-1}$  in seawater (Table 1; Fig. 2F; McLaughlin-West *et al.* 1999). This elevated  $\text{H}_2$  concentration range lies within the reported variation in the field: 2.5–8.5  $\text{mmol kg}^{-1}$  (Van Dover *et al.* 2001; Takai *et al.* 2004; Gallant & Von Damm 2006). On the other hand, the  $\text{H}_2$  concentrations in the Edmond fluids are markedly low: 0.055–0.111  $\text{mmol kg}^{-1}$ . This concentration range resembles that found elsewhere on the East Pacific Rise and Mid Atlantic Ridge hosted by mid-ocean ridge basalts (MORB).

Another stark difference between the fluid chemistries of the areas is that of the Na concentration and Na/Cl ratio. In Kairei, the Na/Cl ratio of the fluid end-member corresponds well to that of seawater, approximately 0.85 (Nozaki 2001), which is consistent with the phase separation of the infiltrated seawater beneath the seafloor. Slightly concentrated Na from the seawater of 480–520  $\text{mmol kg}^{-1}$  suggests that their origin is the brine part of the separated phases. Here, the Na concentration in seawater was 465  $\text{mmol kg}^{-1}$ . On the other hand, Na/Cl ratios of vent fluids in the Edmond field are much lower, <0.75, although their Na concentrations are much higher, 700–710  $\text{mmol kg}^{-1}$ , than those of seawater. This relates to the much more strongly enriched Cl concentration of the fluid end-member in the Edmond field, 930–970  $\text{mmol kg}^{-1}$  than the 542  $\text{mmol kg}^{-1}$  in seawater. Similar to Na, other alkaline and alkaline earth elements, e.g. K and Ba, are strongly enriched in Edmond fluids as a factor of two or more compared to those in Kairei fluids. Respective K concentrations in Kairei and Edmond are 12.5–13.8  $\text{mmol kg}^{-1}$  and 39–42  $\text{mmol kg}^{-1}$ ; Ba concentrations in fluid are upto 43  $\mu\text{mol kg}^{-1}$  for Kairei and upto 120  $\mu\text{mol kg}^{-1}$  for Edmond.

### Visual sea floor observation and regional bathymetry in a segment scale

Local geological conditions near Kairei and Edmond are broadly similar, with respect to their volcanic features, for about the 1–2 km distance over which the areas were explored using the submersible (Fig. 3). However, the immediate vicinities of the vent areas were covered with hydrothermal precipitates and collapsed dead chimneys. The Kairei hydrothermal field developed on the shoulder of the west-facing slope of a recently formed abyssal hill of CIR-1, designated as Hakuho Knoll. It comprises piles of flat or lobate sheet flows (Fig. 3A). Similarly, the Edmond field developed on another abyssal hill of CIR-3. The vicinity of the Edmond field is a flat surface with partly wrinkled lava flows, largely covered by a layer of sediment <30 cm in thickness, as measured using a carry-on sub bottom sound profiler (Strata Box; SyQwest Inc., Warwick, RI, USA). In addition to hydrothermal precipitates, the

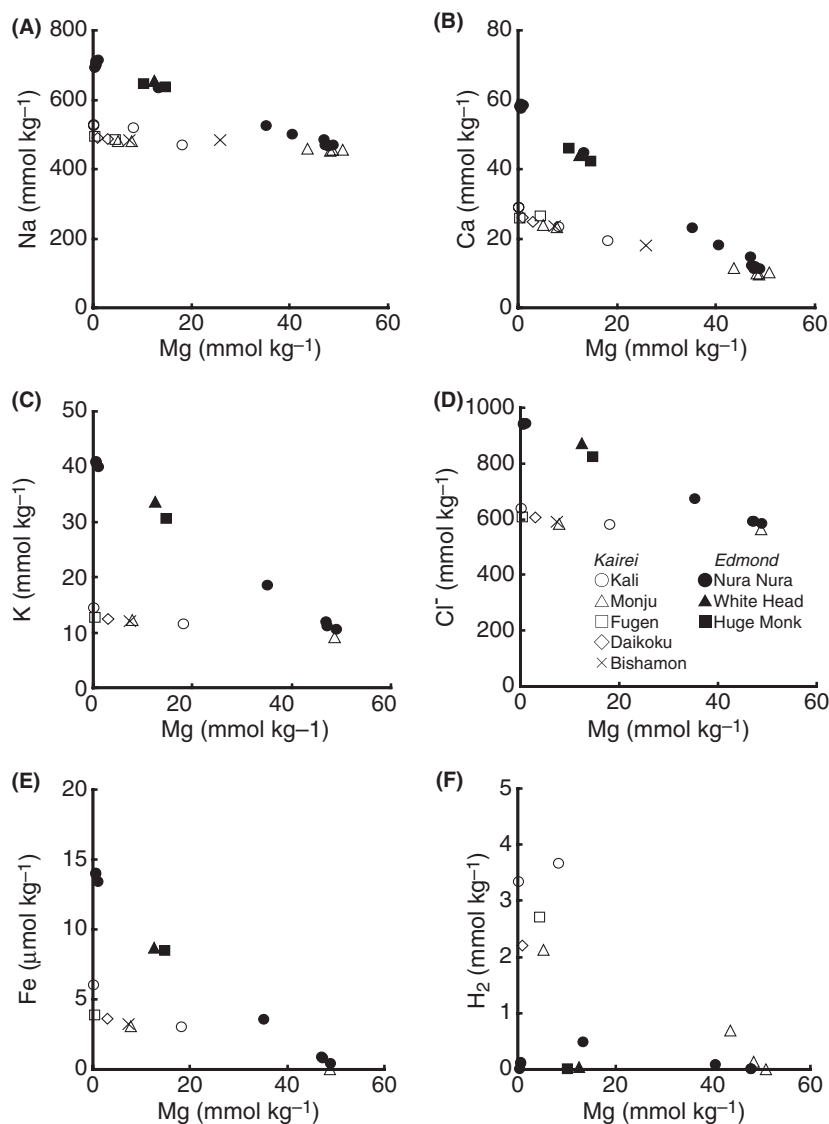


Fig. 2. Relationships of selected major elements and H<sub>2</sub> concentrations versus Mg concentration in sampled fluids. Symbols are shown in sub-panel (D).

seafloor comprises basaltic pillows and massive flows (Fig. 3B). The flow surface partly showed a flat, lobate sheet shape or a smooth or slightly wrinkled surface, indicating a higher flow rate than those observed as pillow piles.

In terms of tectonics at the segment-scale of CIR, the environments of Kairei and Edmond differ greatly. The morphological contrast between the vicinities of the two hydrothermal fields might influence on the geological pathway of the recharged vent fluid.

Near the Kairei field, the regional seafloor morphology is distinctly heterogeneous within 30 km from the current ridge axis, roughly reflecting the most recent 1 Myr of local seafloor spreading. Abyssal hills, which normally develop parallel to the present day ridge axis, are widely disorganized away from CIR-1 (Fig. 4A). For example, a deep linear shape is visible at 70°12'E, 25°16'S (Fig. 4A)

associated with partly symmetric abyssal hills on both sides, which might be an abandoned ridge axis. This might, in turn, have originated from the unstable nature of seafloor spreading in the area accompanied with a ridge jump.

In contrast, in the area off CIR-3 around the Edmond field, regular ridge-parallel abyssal hills extending to ca. 60 km away from the ridge axis were not disorganized (Fig. 4B). Almost at the western edge of the survey area off CIR-3, a corrugated seafloor was mapped with a partly ridge-perpendicular alignment. Apparently, CIR-3 has maintained its robust magmatism for approximately 2 Myr.

CIR-1 is also characterized by two well-defined Oceanic Core Complex (OCC) structures found within 20 km of the Kairei field. One is located 20 km west of the Kairei field, currently across the ridge axis (25°S OCC; Mitchell *et al.* 1998). The other is located 15 km east of the Kairei field, hereinafter designated as Uraniwa Hills, that was

**Table 1** Estimated end member compositions of hydrothermal fluids sampled from Kairei and Edmond fields. -: not analysed.

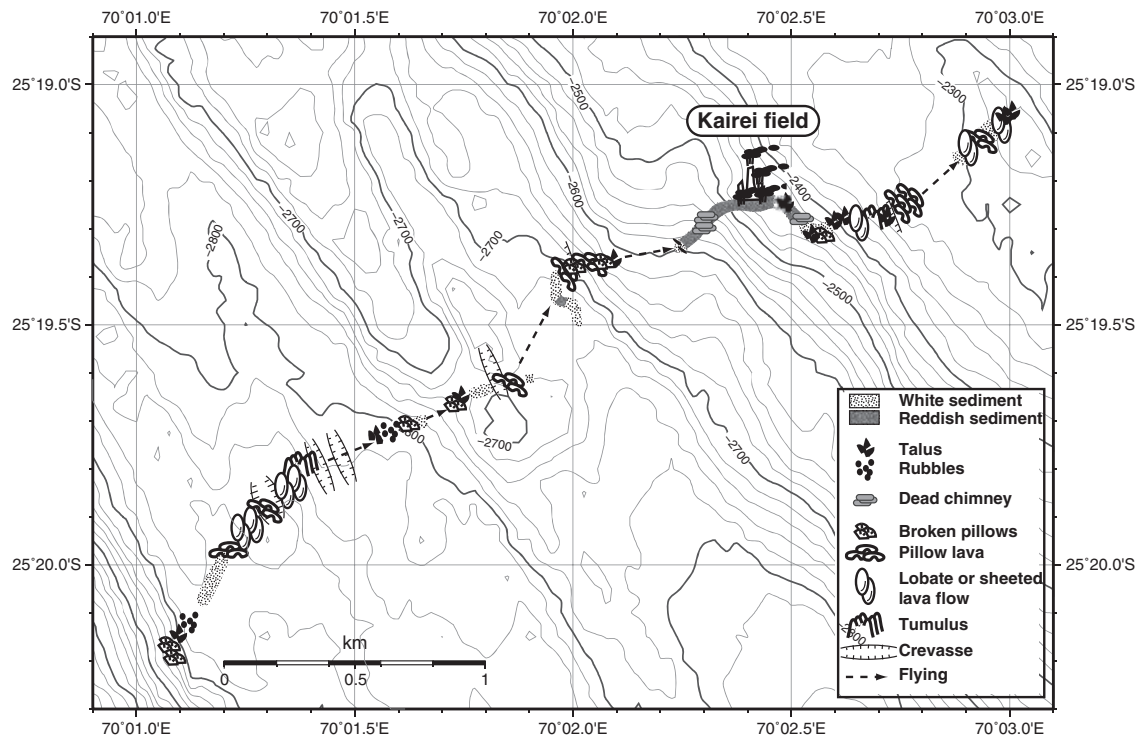
Area	Vent name	Depth (m)	Na mmol kg <sup>-1</sup>	Ca mmol kg <sup>-1</sup>	K mmol kg <sup>-1</sup>	Si mmol kg <sup>-1</sup>	Cl <sup>-</sup> mmol kg <sup>-1</sup>	SO <sub>4</sub> <sup>2-</sup> mmol kg <sup>-1</sup>
Kairei Field	Kali	2450	518 ± 15	27.2 ± 0.8	13.8 ± 0.6	16.0 ± 0.7	623 ± 6	-0.17 ± 0.02
	Monju	2420	484 ± 20	25.6 ± 1.0	12.8 ± 0.8	16.7 ± 0.9	589 ± 7	0.93 ± 0.48
	Fugen	2420	489 ± 19	26.7 ± 1.0	12.7 ± 0.7	16.8 ± 0.9	606 ± 7	-0.06 ± 0.02
	Daikoku	2443	489 ± 18	25.9 ± 1.0	12.7 ± 0.7	16.8 ± 0.9	611 ± 7	6.93 ± 0.45
	Bishamon	2432	490 ± 26	25.9 ± 1.2	12.5 ± 0.8	16.9 ± 0.9	595 ± 7	-0.63 ± 0.39
Edmond Field	Nura Nura	3280	704 ± 14	58.5 ± 1.2	40.8 ± 1.2	20.2 ± 0.6	946 ± 6	-0.30 ± 0.02
	White Head	3290	713 ± 32	54.9 ± 2.3	41.5 ± 2.4	19.6 ± 1.1	973 ± 15	-8.30 ± 0.80
	Huge Monk	3290	697 ± 32	55.3 ± 2.3	39.1 ± 2.3	18.2 ± 1.1	928 ± 15	-2.19 ± 0.99

Area	Vent name	Depth (m)	pH	Alkalinity mmol kg <sup>-1</sup>	Mn μmol kg <sup>-1</sup>	Sr μmol kg <sup>-1</sup>	Ba μmol kg <sup>-1</sup>	Fe μmol kg <sup>-1</sup>
Kairei Field	Kali	2450	3.4	-0.456 ± 0.006	828 ± 35	74.2 ± 3.3	42.5 ± 2.3	5.40 ± 0.25
	Monju	2420	3.6	-1.24 ± 0.04	848 ± 44	66.5 ± 4.2	10.6 ± 0.6	3.67 ± 0.19
	Fugen	2420	3.4	-0.288 ± 0.004	840 ± 43	68.2 ± 3.5	14.8 ± 0.8	3.86 ± 0.20
	Daikoku	2443	3.4	-0.788 ± 0.015	828 ± 42	66.7 ± 3.7	9.54 ± 0.48	3.86 ± 0.20
	Bishamon	2432	3.4	-1.09 ± 0.04	828 ± 48	66.6 ± 0.3	5.51 ± 0.29	3.73 ± 0.20
Edmond Field	Nura Nura	3280	3.3	-0.397 ± 0.006	1360 ± 40	181 ± 6	102 ± 3	13.9 ± 0.4
	White Head	3290	3.1	-1.34 ± 0.08	1420 ± 80	175 ± 11	49.7 ± 2.7	11.5 ± 0.7
	Huge Monk	3290	3.2	-1.55 ± 0.10	1360 ± 80	177 ± 11	119 ± 7	11.8 ± 0.7

Area	Vent name	Depth (m)	H <sub>2</sub> S mmol kg <sup>-1</sup>	ΣCO <sub>2</sub> mmol kg <sup>-1</sup>	H <sub>2</sub> mmol kg <sup>-1</sup>	CH <sub>4</sub> μmol kg <sup>-1</sup>	δ <sup>13</sup> C <sub>CO2</sub> ‰ PDB	δ <sup>13</sup> C <sub>CH4</sub> ‰ PDB
Kairei Field	Kali	2450	4.81 ± 0.17	9.47 ± 0.47	3.71 ± 0.14	123 ± 6	-5.3 ± 0.3	-9.8 ± 0.3
	Monju	2420	-	8.57 ± 0.58	2.48 ± 0.12	163 ± 11	-5.1 ± 0.3	-17.6 ± 0.3
	Fugen	2420	6.40 ± 0.07	10.1 ± 0.7	2.97 ± 0.15	202 ± 14	-5.1 ± 0.3	-18.0 ± 0.3
	Daikoku	2443	5.90 ± 0.07	-	-	-	-	-
	Bishamon	2432	6.06 ± 0.09	-	-	-	-	-
Edmond Field	Nura Nura	3280	3.98 ± 0.03	13.7 ± 0.5	0.1116 ± 0.0037	314 ± 12	-5.4 ± 0.3	-13.5 ± 0.3
	White Head	3290	1.83 ± 0.04	9.95 ± 0.71	0.0556 ± 0.0031	283 ± 20	-5.0 ± 0.3	-12.5 ± 0.3
	Huge Monk	3290	1.15 ± 0.03	15.8 ± 1.1	-	233 ± 16	-5.8 ± 0.3	-13.0 ± 0.3

**Fig. 3.** Route maps of submersible dives. Data source of multi narrow beam bathymetry: YK05-16 [http://www.jamstec.go.jp/dsr/]. (A) Route map of the Shinkai6500 submersible dive #918 (dive observer: H. Kumagai). (B) Route map of the Shinkai6500 submersible dive #923 (dive observer: T. Shibuya).

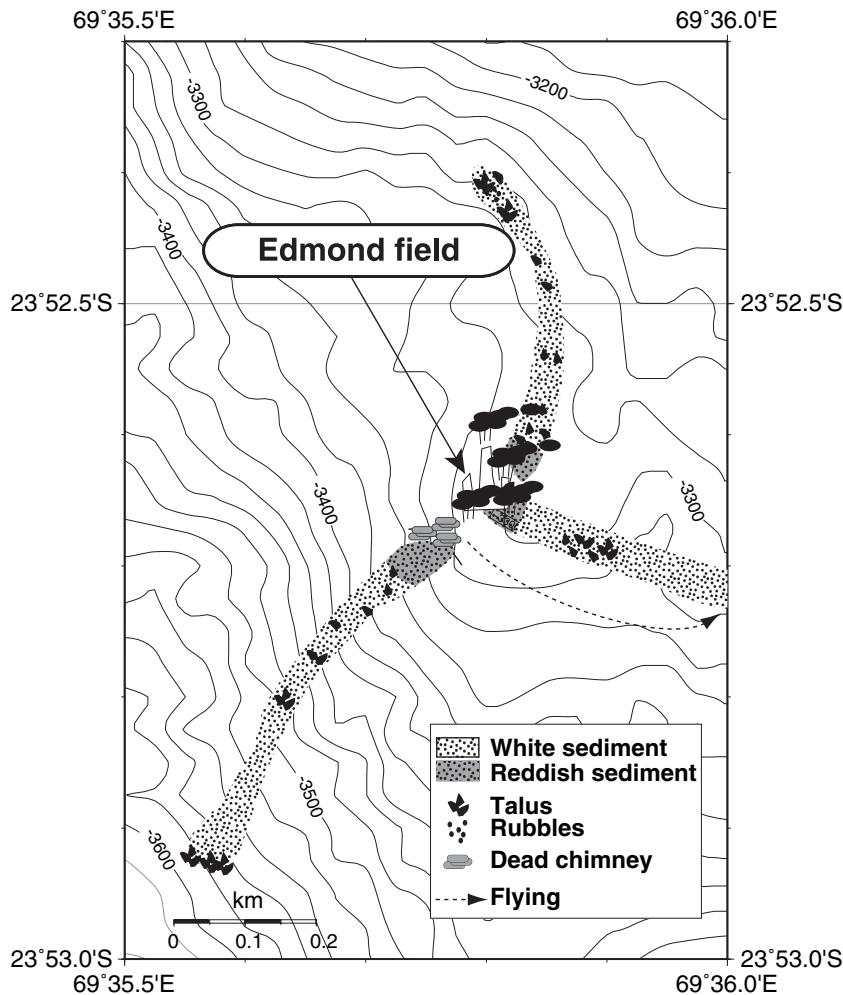


Fig. 3B. Continued

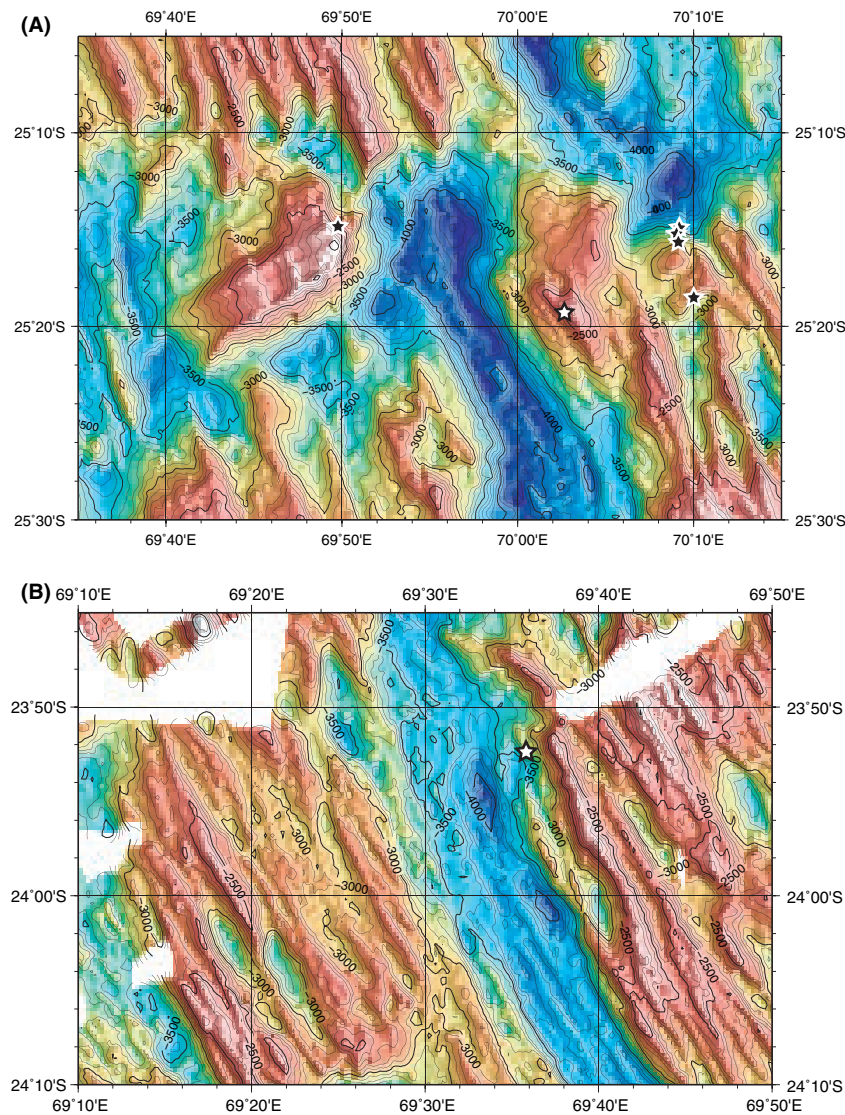
newly recognized in our expedition. Such OCCs are mainly found under magma-starved conditions near slowly-spreading ridges, although the Central Indian Ridge (CIR) has been classified as having an intermediate rate of seafloor spreading. Actually, two weathered peridotites, of which possible protoliths are lherzolite and harzburgite, were sampled among the basalt- to gabbro-dominated rock suites on the 25°S OCC (Fig 4A). At Uraniwa Hills, olivine-abundant mafic plutonic rocks including troctolites and olivine gabbros were also sampled in addition to a dunite (Fig.4A; Morishita *et al.*, in preparation; Nakamura and Bach, submitted to EPSL). In addition, Hellebrand *et al.* (2002) reported that an ultramafic rock had also been obtained on the top of an obliquely elongated hill, 30° oblique in an anti-clockwise direction from the current ridge axis. Consequently, a substantial fraction of shallow crust near the Kairei field, where basaltic volcanic rocks were previously anticipated, actually consists of ultramafic mantle material and olivine-rich plutonic rocks.

#### Rock chemistry

All lava samples near the two hydrothermal fields are basaltic. Most of the compatible element contents of the lava samples near hydrothermal fields both overlap with a rather primitive nature: the Kairei field lava has 50.6–51.5 wt% SiO<sub>2</sub>, 8.4–8.9 wt% MgO and 7.9–8.6 wt% FeO, whereas the lava of the Edmond field contains 50.8–51.2 wt% SiO<sub>2</sub>, 7.6–8.0 wt% MgO, and 8.2–8.6 wt% FeO. Because of this similarity, the differences of Mg#, defined as  $Mg^{2+}/(Mg^{2+} + Fe^{2+})$  in molar proportions, in both areas are of a similar range: 0.66–0.64 for Kairei and 0.63–0.62 for Edmond, respectively.

In contrast, such similarity is not the case for incompatible elements. The concentrations of incompatible elements are high in the Edmond lava but low in the Kairei lava. This is readily apparent from their K<sub>2</sub>O, Na<sub>2</sub>O and TiO<sub>2</sub> concentrations. Kairei lava has <0.06 wt% of K<sub>2</sub>O, 2.65–3.10 wt% of Na<sub>2</sub>O and 1.04–1.24 wt% of TiO<sub>2</sub>; Edmond lava has 0.11–0.15 wt% of K<sub>2</sub>O, 3.08–3.22 wt% of Na<sub>2</sub>O





**Fig. 4.** Regional bathymetry around each hydrothermal field indicating as an open star. The closed stars in panel A (Kairei field) indicated the locality where either serpentinitized peridotites or troctolites were sampled. Data source of multi narrow beam bathymetry: YK05-16 [<http://www.jamstec.go.jp/dsr/>]. (A) Kairei. (B) Edmond.

and 1.26–1.42 wt% of  $\text{TiO}_2$ . All lava samples fall in the area of tholeiite in an alkaline diagram (Macdonald & Kat-sura 1964).

Such a depleted nature of Kairei lava can be clarified by observation of its trace elements. Although all lava samples from both areas show as depleted a nature in trace elements as do other MORB, the lava samples near the Kairei field are greatly depleted compared to those of the Edmond field. The La/Sm normalized to CI chondrite, expressed as  $(\text{La}/\text{Sm})_n$ , of both Kairei and Edmond areas are 0.41–0.5 and 0.72–0.80 respectively. Another normalization can be applied to emphasize this contrast. The Edmond lavas are less depleted in trace

elements than ‘Normal MORB’ (Sun & McDonough 1989), of which  $(\text{La}/\text{Sm})_n$  is 0.61. In contrast, the Kairei lavas are more depleted than those in the normal MORB. Therefore, in a trace element diagram, where the elements are ordered by their incompatibility, the Edmond lava is expressed by curves elevated from the horizontal line on the left, highly incompatible trace element side, but Kairei lavas form valleys on that side (Fig. 5). Interestingly, the Th/Nb values of Kairei lava vary widely, 0.046–0.109, contrasted with the narrow range of Edmond lava: 0.070–0.085. This Th/Nb range results from the variable concentrations of Nb in Kairei lavas: 0.4–0.9 ppm.



**Table 2** (A) Major element composition and trace element concentration for lava samples from vent vicinity.

wt%	Kairei						Edmond				Standard	
	918R02	<i>n</i> = 19	918R03	<i>n</i> = 13	918R10	<i>n</i> = 12	923R07	<i>n</i> = 18	923R08	<i>n</i> = 11	BCR-2G	<i>n</i> = 16
SiO <sub>2</sub>	50.9	0.3	51.5	0.2	50.9	0.2	51.1	0.2	51.0	0.3	54.6	0.4
TiO <sub>2</sub>	1.11	0.07	1.19	0.06	1.06	0.05	1.37	0.07	1.30	0.08	2.33	0.07
Al <sub>2</sub> O <sub>3</sub>	16.3	0.2	16.0	0.1	16.1	0.1	15.8	0.2	15.8	0.1	13.6	0.2
FeO	8.2	0.2	8.4	0.3	8.1	0.2	8.5	0.2	8.6	0.3	12.5	0.3
MnO	0.16	0.04	0.17	0.04	0.15	0.03	0.15	0.04	0.16	0.03	0.19	0.05
MgO	8.7	0.2	8.4	0.1	8.7	0.1	7.8	0.1	8.0	0.1	3.7	0.1
CaO	11.8	0.2	11.5	0.2	11.9	0.1	11.2	0.2	11.1	0.1	7.2	0.2
Na <sub>2</sub> O	2.7	0.1	3.0	0.1	2.8	0.1	3.2	0.1	3.1	0.1	3.3	0.1
K <sub>2</sub> O	0.03	0.02	0.05	0.02	0.04	0.02	0.12	0.02	0.12	0.03	1.73	0.08
P <sub>2</sub> O <sub>5</sub>	< 0.1		0.11	0.07	0.07	0.06	0.13	0.06	0.13	0.05	0.39	0.08
Total	99.8	0.5	100.4	0.5	99.9	0.3	99.3	0.5	99.2	0.5	99.5	0.7

ppm	Kairei						Edmond				Standard	
	918R02	<i>n</i> = 5	918R03	<i>n</i> = 4	918R10	<i>n</i> = 4	923R07	<i>n</i> = 5	923R08	<i>n</i> = 3	BCR-2G	<i>n</i> = 9
Li	6.8	0.2	7.3	0.1	6.6	0.2	6.8	0.2	7.0	0.1	11.5	0.3
B	2.2	0.4	2.5	0.4	1.9	0.5	2.4	0.2	2.2	0.7	7.0	0.6
Sc	33	0.5	34	0.4	34	0.5	35	0.4	35	0.4	32.1	0.7
V	260	5	266	6	252	6	266	6	269	5	485	9.7
Cr	425	6	413	7	435	6	367	9	376	10	19	1
Co	48	1.0	48	0.5	48	0.8	43	1.1	45	0.9	44	1.0
Ni	142	4	133	2	131	5	112	3	125	2	21	2
Rb	< 0.2		0.51	0.10	< 0.2		2.07	0.09	2.09	0.05	59	1.3
Sr	86.6	1.0	102.4	1.0	93.5	1.2	125.6	0.8	125.7	0.5	319	3
Y	22.5	0.2	23.0	0.4	21.4	0.2	24.6	0.2	23.9	0.3	28.6	0.4
Zr	49.8	0.4	56.7	0.8	47.1	0.8	72.5	0.6	70.2	0.6	146	2
Nb	0.50	0.03	0.92	0.03	0.44	0.03	2.62	0.06	2.56	0.08	12.4	0.2
Cs	< 0.1		< 0.1		< 0.1		< 0.1		< 0.1		1.4	0.0
Ba	2.74	0.08	6.37	0.30	1.90	0.02	19.9	0.4	20.1	0.4	660	7
La	1.67	0.05	2.15	0.02	1.63	0.06	3.55	0.05	3.48	0.06	23.0	0.4
Ce	6.68	0.07	8.09	0.08	6.42	0.14	11.33	0.06	11.23	0.16	53.8	0.9
Pr	1.14	0.05	1.39	0.02	1.09	0.01	1.71	0.04	1.69	0.03	6.27	0.14
Nd	6.82	0.10	7.78	0.16	6.40	0.17	9.19	0.18	9.06	0.21	26.43	0.61
Sm	2.51	0.12	2.61	0.10	2.29	0.07	3.03	0.10	2.93	0.08	5.84	0.09
Eu	0.97	0.04	1.03	0.02	0.92	0.04	1.11	0.03	1.12	0.04	1.82	0.06
Gd	3.28	0.06	3.39	0.10	3.13	0.09	3.71	0.07	3.66	0.06	5.61	0.13
Tb	0.58	0.03	0.59	0.03	0.55	0.02	0.65	0.02	0.63	0.04	0.86	0.03
Dy	4.18	0.13	4.28	0.15	3.93	0.07	4.55	0.09	4.39	0.11	5.45	0.14
Ho	0.89	0.01	0.88	0.04	0.84	0.02	0.97	0.01	0.93	0.03	1.08	0.04
Er	2.50	0.08	2.49	0.03	2.38	0.04	2.70	0.06	2.61	0.06	2.98	0.08
Tm	0.36	0.01	0.35	0.00	0.36	0.01	0.38	0.02	0.35	0.01	0.45	0.01
Yb	2.60	0.11	2.57	0.03	2.41	0.07	2.73	0.02	2.71	0.04	3.02	0.09
Lu	0.35	0.01	0.37	0.02	0.33	0.02	0.38	0.01	0.36	0.02	0.42	0.02
Hf	1.52	0.11	1.61	0.04	1.37	0.02	1.95	0.03	1.83	0.06	3.87	0.11
Ta	0.04	0.01	0.06	0.01	0.03	0.01	0.16	0.01	0.16	0.00	0.70	0.02
Pb	0.50	0.05	0.65	0.02	0.54	0.05	0.67	0.06	0.75	0.06	14.3	0.3
Th	0.04	0.01	0.07	0.01	0.04	0.01	0.20	0.01	0.21	0.02	5.20	0.12
U	0.02	0.00	0.02	0.01	0.01	0.00	0.07	0.01	0.07	0.00	1.88	0.06

in the crust underlying the vent site, although this is not the case for the Kairei vent site, as previously suggested by Gallant & Von Damm (2006).

Fe concentrations in hydrothermal fluids in MOR environment are controlled by phase equilibria for Fe-bearing minerals (e.g., magnetite, hematite, pyrite, pyrrhotite, chlorite) and by the solubility of Fe in the hydrothermal fluids (Ding & Seyfried 1992; Saccocia & Seyfried 1994). Solubility of Fe is, in turn, controlled by temperature, chloride

content and pH (Ding & Seyfried 1992). Although Fe/Cl ratios of both Kairei and Edmond fluids are well within the ranges reported for MOR hydrothermal fluids (Gallant & Von Damm 2006), Fe concentrations of Edmond fluids are more than two times higher than those of Kairei fluids, despite the temperatures of end-member fluids being similar: Kairei 369°C, Edmond 381°C. The difference of the Fe concentrations are partly explainable by the somewhat higher Cl concentrations in the Edmond fluid relative to

the Kairei hydrothermal fluids. In addition, Edmond fluids have lower pH values than Kairei fluids. Even a small decrease of pH in hydrothermal fluids could drastically increase Fe concentration (Ding & Seyfried 1992). Therefore, the difference of pH between Kairei and Edmond fluids appears to be responsible for that of Fe concentrations. It should also be noted that supercritical phase separation of hydrothermal fluids drastically increases the Fe/Cl ratio in the brine phase (Seyfried & Ding 1995). This could also play an important role, explaining the high Fe/Cl ratio of the brine-rich Edmond fluids.

In a typical MOR hydrothermal system, concentrations of  $H_2$  are known to be controlled primarily by redox reactions involving Fe-oxides and Fe-sulphides such as hematite-magnetite and pyrite-pyrrhotite-magnetite. These buffer reactions result in less than approximately  $1 \text{ mmol kg}^{-1} H_2$  in the hydrothermal fluids at typical hydrothermal conditions of 350–400°C and 500 bar (e.g., Seyfried & Ding 1995; Wetzell & Shock 2000). The Kairei vent field is on a typical basaltic abyssal hill designated as Hakuho knoll. However,  $H_2$  concentrations of the hydrothermal fluids are surprisingly high, up to one order of magnitude higher than typical MOR hydrothermal fluids. To account for the unusually high concentration of  $H_2$ , Gallant & Von Damm (2006) proposed a model whereby  $H_2$  was generated by precipitation reactions of metal sulphide minerals, which relies on reactions of (non-sulphide) iron minerals with  $H_2S$  in the hydrothermal fluid. However, to generate the observed concentration of  $H_2$  (approximately  $8 \text{ mmol kg}^{-1}$ ) by metal sulphide-precipitation reactions, very high concentrations of Fe (ca. 13–20  $\text{mmol kg}^{-1}$ ) in the original fluids are required. This appears to be impossible for the Kairei hydrothermal fluids having seawater-like Cl contents of approximately  $600 \text{ mmol kg}^{-1}$ . Moreover, despite the fact that such metal sulphide precipitation can plausibly occur in typical MOR hydrothermal systems, almost all known basalt-hosted hydrothermal fluids exhibit much lower  $H_2$  concentrations (approximately one order of magnitude lower) than Kairei fluids (e.g. Wetzell & Shock 2000; Charlou *et al.* 2002).

The discovery, reported here, of the presence of serpentinized olivine-rich rocks exposed near the Kairei vent field suggests an alternative mechanism for generating elevated  $H_2$ . The serpentinization of olivine-rich ultramafics such as abyssal peridotite is well-known to generate considerably  $H_2$ -enriched hydrothermal fluids (e.g. Wetzell & Shock 2000; Allen & Seyfried 2003). This process might supply  $H_2$  to the Kairei fluids as well as in the other  $H_2$ -enriched hydrothermal vent fields along Mid Atlantic Ridge (Charlou *et al.* 2002; Douville *et al.* 2002). Although the dunite, troctolite and olivine gabbro from the Uraniwa-Hills are not typical mantle peridotites, it is noteworthy that these rocks contain substantial amounts of olivine, and have great potential for  $H_2$ -production. Indeed, the oliv-

ine-rich gabbroic rocks were affected pervasively by serpentinization (Morishita *et al.* 2008), directly indicating the generation of abundant  $H_2$  into the Kairei hydrothermal fluids during hydrothermal alteration.

## CONCLUDING REMARKS

The heterogeneous structure of the shallow lithosphere seems to have led to large chemical variations in vent fluids. From this perspective, the distinct chemical fluid compositions of two hydrothermal fields, Kairei and Edmond in the Indian Ocean, are attributable to the different rock facies associated with the pathway of discharged hydrothermal vent fluids. The unique geochemical character of the Kairei vent fluid, which had been explained by unusual geochemical reactions beneath the seafloor by Gallant & Von Damm (2006), can also be explained using the occurrence of unique olivine-rich rock facies in the recharge zone of vent fluid. Rocks of this type are not in the group of the mantle-derived ultramafic rocks, but in the group of the deepest part of the mafic crust and reaction zone between upwelling magma and the surrounding residual mantle rocks at the MOHO transition zone. In contrast, the geochemical characteristics of the Edmond vent fluid are fully explained using the reaction within normal mafic crustal materials with a geochemically-enriched trace element nature. The difference in lithology is largely attributable to the tectonic history in each region. In essence, the limited contribution of the unique rock facies to the Kairei vent fluid is related to its heterogeneous structure, reflecting the complex history of seafloor spreading around the triple junction area. The geophysical and morphological observations described herein support the occurrence of the heterogeneous shallow lithosphere around the Kairei hydrothermal field.

The discovery of olivine-rich troctolites at the Uraniwa Hills leads us to propose its important geological role in the oldest ancestral biological community on the ancient Earth. Probably, only minor exposure of ultramafic mantle rocks occurred during the early stages of Earth's history because of frequent and vigorous volcanism driven by mantle convection. However, certain ultramafic volcanic rocks, designated as komatiites, are widely found in Archaean lithological units (>2.5 Ga). Their geochemical character broadly resembles that of the troctolites found in this expedition: hydrothermal fluid associated with komatiites might have fostered hydrogen-favouring progenitors on ancient Earth.

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