温泉科学（J. Hot Spring Sci.），60，410-417（2011）

原　　著

Dissolved Inorganic Carbon Rich in Mantle Component of Hot Spring Waters from the Hitoyoshi Basin in a Non-volcanic Region of Central Kyushu, Japan

Shinji Ohsawa[1)], Takuya Sakai[2)], Makoto Yamada[1)], Taketoshi Mishima[1)], Shin Yoshikawa[3)] and Tsuneomi Kagiyama[3)]

(Received Oct. 4, 2010, Accepted Dec. 20, 2010)

九州中部の非火山地域に位置する人吉盆地のマントル成分に富んだ温泉水の溶存無機炭素

大沢信二[1)]，酒井拓哉[2)]，山田　誠[1)]，三島壮智[1)]，吉川　慎[3)]，鍵山恒臣[3)]

要　　旨

九州地方の阿蘇火山と霧島火山の間に位置する非火山地域の地下に深部流体を検出するために，地球化学的な広域温泉調査を実施した．調査した温泉の内8ヶ所において，全溶存無機炭素（DIC）を含めた主要溶存化学成分の濃度を測定し、水の同位体組成（δDとδ^{18}O）およびDICの炭素安定同位体比（δ^{13}C）を得ることができたが，同時に溶存希ガス成分（HeとNe）の化学・同位体データも取得することができた．希ガスデータの同位体システマティックスを検討した他，C/^{3}H比とδ^{13}Cの関係からDICの炭素の起源推定を行ったところ，霧島火山の北方数十kmにある人吉盆地内において，沈み込み帯の火山性CO_2とは異なるマントル由来のヘリウムを伴ったマントル成分に富むDICを含む温泉の湧出があることを認めた．

キーワード：温泉，ヘリウム，全溶存無機炭素，同位体，起源，人吉盆地

Abstract

To detect deep-seated aqueous fluid in the non-volcanic region between Aso and

[1)] Beppu Geothermal Research Laboratory, Institute for Geothermal Sciences, Graduate School of Science, Kyoto University, Noguchibaru, Beppu, Oita 874-0903, Japan. [1)] 京都大学大学院理学研究科附属地球熱学研究施設　〒874-0903　大分県別府市野口原.

[2)] Graduate School of Education, Oita University, 700 Dannoharu, Oita 870-1192, Japan. [2)] 大分大学大学院教育学研究科教科教育専攻理科教育専修　〒870-1192　大分県大分市大字旦野原700.

[3)] Aso Volcanological Laboratory, Institute for Geothermal Sciences, Graduate School of Science, Kyoto University, Minami-Aso, Aso, Kumamoto 869-1404, Japan. [3)] 京都大学大学院理学研究科附属地球熱学研究施設火山研究センター　〒869-1404　熊本県阿蘇郡南阿蘇村河陽5280.

Kirishima volcanoes of Kyushu District, we conducted a geochemical investigation of hot springs over a wide area. Although the main geochemical data obtained were major chemical components, dissolved inorganic carbon (DIC), water isotope compositions (δD and δ^{18}O), and δ^{13}C of DIC, we also obtained chemical and isotopic data of rare gases (He and Ne), from eight sites of the hot springs in this area. From isotope systematics of the rare gas data and consideration of source carbon of DIC based on the relation between C/^{3}He ratio and δ^{13}C, we concluded that hot spring waters bearing DIC extremely rich in mantle component with mantle-derived He, which differ from subduction-related volcanic CO_2, are discharged from the Hitoyoshi Basin located several tens of kilometers north of Kirishima volcano.

Key words : Hot spring, Helium, Dissolved inorganic carbon, Isotope, Origin, Hitoyoshi Basin

1. Introduction

Kyushu District in Japan is crowded with active Quaternary volcanoes, but it includes an extensive non-volcanic area between Aso and Kirishima volcanoes (Fig. 1). This area mainly comprises Mesozoic formations aligned mainly southwest-northeast, although Miocene igneous rocks are scattered, as presented in Fig. 1. Many people have investigated the problem of why no active volcano exists in this area. Some suppositions have been presented (e.g., Horikoshi, 1979 ; Kobayashi, 1986 ; Yoshida and Seno, 1992). However, the problem has not been resolved.

Recently, a high crustal conductive zone was reportedly found in this area (Kagiyama and Munekane, 2006). Referring to a distribution map of isopleths of the Curie point depth (Okubo *et al.,* 1989), it can be thought that no igneous body with temperature greater than 500℃ lies to a

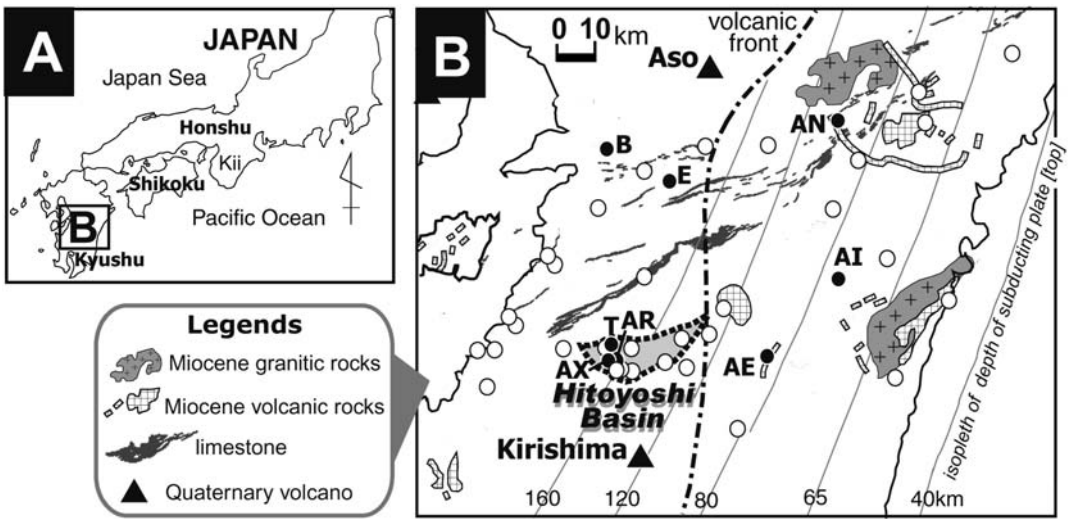

Fig. 1　Localities of hot springs investigated in this study (●) with related geologic information. Open circles (○) denote other hot springs examined simultaneously in this study. Distribution of limestone masses is cited from the seamless digital geological map of Japan 1 : 200,000 produced by Geological Survey of Japan, AIST (Feb 1, 2010 version). Distributions of Miocene granitic and volcanic rocks are traced from Fig. 3. 25 in Regional Geology of Japan Part 9 Kyushu (Editorial Committee of Kyushu, 1992). The isopleths of depth of subducting plate [top] are cited from Ishihara and Yoshida (1992).

depth of around 10 km under this area ; it will be considered alternatively that aqueous fluid is seated latently. Accordingly, we investigated many hot springs in this area seeking deep-seated aqueous fluid and obtained a stable carbon isotope ratio ($\delta^{13}C$) of dissolved inorganic carbon ($DIC=CO_2(aq)+HCO_3^-+CO_3^{2-}$), together with concentrations of major chemical components including DIC and water isotope composition (δD and $\delta^{18}O$). We also collected water samples to obtain geochemical data of dissolved rare gases (He and Ne), in cases where atmospheric-air contact to hot spring water was avoidable at sampling. Eventually, eight samples were obtained.

Examining the relation between the $\delta^{13}C$ and $C/^3He$ ratio on the samples in conformity to previous reports (Sano and Marty, 1995 ; Sano *et al.,* 1997 ; Nishio *et al.,* 1998 ; Sato *et al.,* 1999 ; Ohsawa and Yusa, 2001 ; Yamamoto *et al.,* 2001 ; Deines, 2002 ; Sumino *et al.,* 2004 ; Doğan *et al.,* 2006 ; Mao *et al.,* 2009 ; Ohba *et al.,* 2010), we found DIC extremely rich in mantle component accompanied with mantle-derived He in hot spring waters discharged from the Hitoyoshi Basin. Therefore, we expressly report this result herein before the presentation of other geochemical data.

2. Sampling and analyses

Hot spring waters, for analyses of dissolved inorganic carbon (DIC) and dissolved rare gases (He and Ne) and also for their isotope measurements, were collected from wells at eight hot spring sites (solid circles T, AR, AX, AI, AE, AN, B, and E in Fig. 1). Samples for DIC were stored in a CO_2 gas-tight plastic bottle (Barex®, Nikko Hansen & Co., Ltd., Japan), following the example of Ohsawa *et al.* (2002). Hot spring waters for rare gases were introduced directly in a soft copper pipe (outside diameter, 9.5 mm ; inside diameter, 7.9 mm ; length, 30 cm ; capacity, about 40 mL) avoiding air-contamination ; they were sealed using special clamps, following the example of Morikawa *et al.* (2008).

Concentrations of DIC were determined using a CO_2-gas electrode with an ion meter after all carbonate species in the sample water were converted into CO_2 (aq) by addition of sulfuric acid. Stable carbon isotope ratios ($\delta^{13}C$) of DIC were obtained by transferring the generated CO_2 gas through addition of phosphoric acid to $SrCO_3$ precipitated from the sample water to a mass spectrometer at the Stable Isotope Laboratory of IGNS, New Zealand. Concentrations of dissolved He, Ne, and ^3He were analyzed using mass spectrometry at the Geo-Science Laboratory, Japan after extracting dissolved gases from the water samples in the copper pipe. Maximum errors of the analyses were roughly estimated as [He] ± 1.0%, [Ne] ± 2%, [^3He] ± 1.5%, [DIC] ± 3% (at ca. 50 mg/L), and $\delta^{13}C \pm 0.2‰$.

3. Results and discussion

Chemical and isotopic data obtained from the samples are presented in Table 1 with information showing the well depth and water temperature. The $^3He/^4He$ value is calculated from concentrations of ^3He and He considering ^4He to be the greater part of He. The measured $^3He/^4He$ ratios normalized by the atmospheric value (1.39×10^{-6}) are shown in Fig. 2 against $^4He/^{20}Ne$ ratios, which are substituted from He/Ne ratios. All samples in this diagram are

Table 1　Chemical and isotopic data of dissolved inorganic carbon (DIC) and dissolved noble gases of hot spring waters investigated in this study.

No.	Latitude (N)	Longitude (E)	Depth of well (m)	Water temp. (℃)	DIC (mg/L)	δ^{13}C-DIC (‰)	He (ccSTP/g)	Ne (ccSTP/g)	^{3}He/^{4}He
T	32°14′57″	130°44′48	1000	38.2	520	−10.0	3.53×10^{-5}	1.13×10^{-6}	4.92×10^{-6}
AR	32°12′34″	130°45′47″	?	49.6	360	−13.9	9.43×10^{-6}	2.15×10^{-7}	1.02×10^{-5}
AX	32°13′33″	130°43′2″	400	42.3	560	−9.0	3.34×10^{-4}	6.00×10^{-7}	1.97×10^{-6}
AI	32°23′22″	131°19′52″	1500	37.1	435	−3.7	9.39×10^{-7}	2.90×10^{-8}	9.98×10^{-7}
AE	32°13′25″	131°9′49″	1400	36.5	740	−4.5	2.80×10^{-6}	1.01×10^{-7}	9.04×10^{-7}
AN	32°43′30″	131°20′48″	1000	27.8	105	−13.3	2.73×10^{-7}	2.29×10^{-7}	3.67×10^{-7}
B	32°40′1″	130°44′1″	996	35.5	109	−13.5	6.82×10^{-8}	1.78×10^{-7}	9.60×10^{-7}
E	32°36′32″	130°53′0″	1000	29.6	45	−16.3	6.14×10^{-7}	3.98×10^{-7}	3.68×10^{-7}

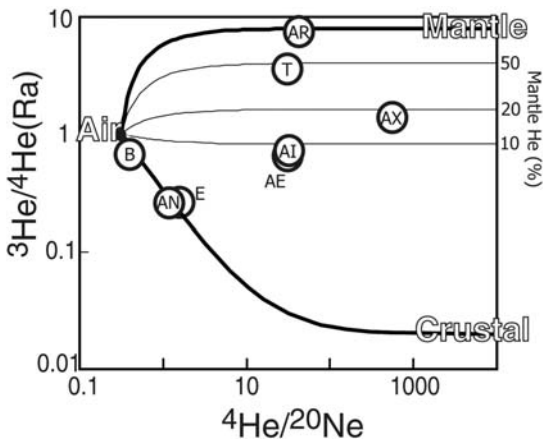

Fig. 2　Plot of ^{3}He/^{4}He versus ^{4}He/^{20}Ne ratios for water samples obtained for this study. The upper line represents the mixing line between air and upper mantle components ; the lower one is a mixing line for air and crust components. The medium thickness lines show trajectories for mixing between air and deep-originated gas for various mantle helium components of 10, 20 and 50%.

distributed in a region that is explainable in terms of a mixing model with three end-member components : upper mantle gas, crustal gas containing a large amount of radiogenic ^{4}He, and atmospheric air. Two thick lines connecting atmospheric air to mantle gas and to crustal gas in Fig. 2 are the mixing lines. Sample AR is close to the upper mixing line to the mantle end member. Samples B, AN, and E are on the lower mixing line from atmospheric air to crustal gas. Samples T, AX, AE, and AI contain all the components, but mixing proportions of atmospheric air component are almost zero, as determined using a calculation method of contribution of the three end members presented by Shimizu *et al.* (2005). By this calculation, contributions of mantle He on sample AR, T, AX, AE, and AI are estimated as 91%, 44%, 18%, 8%, and 9%, respectively. Those of atmospheric He on samples B, AN, and E are shown as 83%, 27%, and 21%, respectively.

Figure 3 portrays a diagram showing the C/^{3}He ratio as a function of δ^{13}C value presented by Sano and Marty (1995). It is used to be applied to obtain a rigid constraint on the origin of DIC for hot spring water samples. This figure shows data of eight water samples (T, AR, AX, AI, AE, AN, B, and E) together with mantle, sedimentary organic carbon and marine carbonate (Sano and Marty, 1995 ; Nishio *et al.,* 1998 ; Deines, 2002), and subduction-related fumarolic gases from Kirishima and Aso volcanoes (Sato *et al.,* 1999 ; NEDO, 1989). All samples show mixing features of mantle, sedimentary organic carbon and marine carbonate components. However, contributions of the components vary and can be divided roughly into three groups. Samples B,

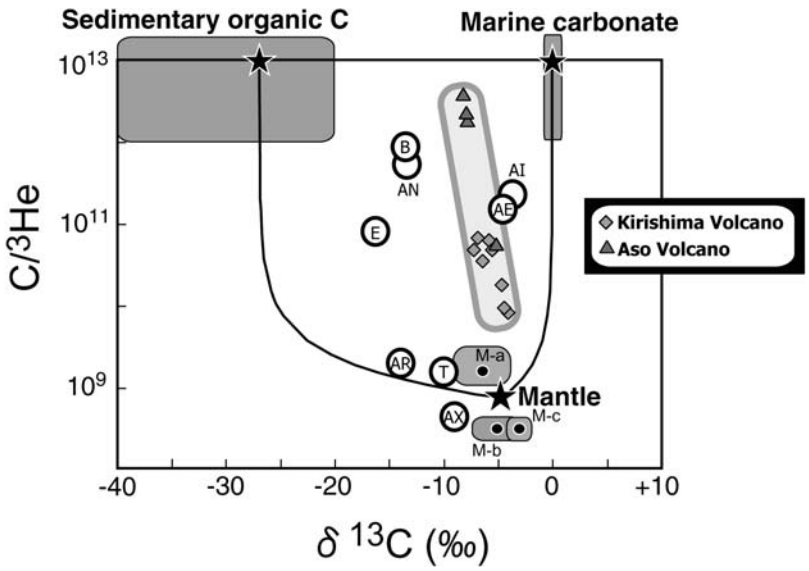

Fig. 3　Correlation between C/^{3}He ratio and δ^{13}C of DIC for water samples in this study. In addition, model end members for mantle (M-a : Sano and Marty, 1995 ; M-b : Deines, 2002 ; M-c : Nishio et al., 1998), marine carbonate (Sano and Marty, 1995) and sedimentary organic carbon [mean value of Sano and Marty (1995), Deines (2002) and Nishio *et al.* (1998)] are shown in this figure. The tie lines of the model end members are mixing lines.

AN, and E are rich in the sedimentary organic carbon component. These samples contain remarkable amounts of atmospheric He as presented above, showing that the organic carbon is probably be derived from soil. Samples AR, T, and AX are rich in the mantle component, whereas samples AE and AI are not rich in the mantle component but rich in the marine carbonate component. This distinction on the C/^{3}He—δ^{13}C diagram is approximately consistent with the He isotope systematics described above. Moreover, samples AE and AI have features similar to those of subduction-related volcanic CO_2.

We examined the geographical distribution of geochemically differentiated hot springs. Hot springs B, AN, and E are located in the northwestern part of the studied area occupied by old geologic bodes accompanied with many limestone areas shown in Fig. 1 (Sambagawa and Chichibu Belts). The contributions of the marine carbonate component on DIC of these hot spring waters are not negligible, perhaps because of the small limestone bodies. Hot springs AI and AE, whose DIC are rich in the marine carbonate component more than hot springs B, AN, and E, are located in the southeastern part of the studied area. Because the surface distribution of limestone is scarce in this area, the DIC rich in the marine carbonate component of these hot spring waters (AI and AE) is originated in greater depths, probably derived from dehydrated fluid from the subducting Philippine-Sea Plate such as Umeda *et al.* (2006) assumed at the Kii Peninsula of SW Japan. Because hot spring AE is situated along a distribution of Miocene volcanic rocks, the possibility exists that such a DIC is residual magmatic CO_2 in old igneous body, but if so, the same feature ought to appear on hot spring AN. Hot springs AR, T, and AX,

whose DIC are rich in the mantle component, are situated in the Hitoyoshi Basin, which is thought to be a tectonic basin (e.g., Chida, 2000). The southern part of Kyushu, including this basin area from Pliocene to Pleistocene, was on a regional stress field by extensional or transtensional tectonics of NW—SE or NNE—SSW direction (Yamaji *et al.*, 2003). The high contributions of the mantle component to DIC and He of hot spring waters in the Hitoyoshi Basin suggest that a fluid channel for uprising of mantle-derived CO_2 and He must be formed in the crust under this basin area.

Acknowledgments

Owners of hot springs at all sampling sites are acknowledged for permitting sample collection. We also thank workers of the Geo-Science Laboratory, Japan, and the Stable Isotope Laboratory of IGNS, New Zealand, for their technical assistance. This research was partially supported by a Ministry of Education, Culture, Sports, Science and Technology, Grant-in-Aid for Scientific Research (B) 19310116. Anonymous referees provided useful comments that led to considerable improvements in this manuscript.

References

Chida, N. (2000) : Active fault along the southern margin of the Hitoyoshi Basin, Kumamoto Prefecture, southwest Japan. Active Fault Research, **19**, 87–90 (in Japanese with English abstract).

Deines, P. (2002) : The carbon isotope geochemistry of mantle xenoliths. Earth-Science Reviews, **58**, 247–278.

Doğan, T., Sumino, H., Nagao, K. and Notsu, N. (2006) : Release of mantle helium from forearc region of the Southwest Japan arc. Chem. Geol., **233**, 235–248.

Editorial Committee of Kyushu (1992) : Regional Geology of Japan Part 9 Kyushu, Kyoritsu Shuppan CO., LTD, Tokyo (in Japanese).

Geological Survey of Japan, AIST (ed., 2010) : Seamless digital geological map of Japan 1 : 200,000. Feb 1, 2010 version. Research Information Database DB084, Geological Survey of Japan, National Institute of Advanced Industrial Science and Technology.

Horikoshi, E. (1979) : Downward extension of the Kurosegawa tectonic zone based on the distribution of Quaternary volcanoes. J. Geological Soc. Japan, **85**, 427–434 (in Japanese with English abstract).

Ishihara, K. and Yoshida, A. (1992) : Configuration of the Philippine sea slab and seismic activity in and around Kyushu. J. Seismological Society of Japan (Zisin), **45**, 45–51 (in Japanese with English abstract).

Kagiyama, T. and Munekane, H. (2006) : Resistivity structure of volcanic and non-volcanic areas in Kyushu, Japan. Gekkan Chikyu, **28**, 110–114 (in Japanese).

Kobayashi, Y. (1986) : Quaternary arc volcanism and its bearing on tectonics. J. Volcanol. Soc. Japan, **30**, S137–S152 (in Japanese with English abstract).

Mao, X., Wang, Y., Chudaev, O.V. and Wang, X. (2009) : Geochemical Evidence of Gas Sources of CO_2-Rich Cold Springs from Wudalianchi, Northeast China. J. Earth Science, **20**, 959–970.

Morikawa, N., Kazahaya, K., Fourre, E., Takahashi, H.A., Jean-Baptiste, P., Ohwada, M., LeGuern, F.J. and Nakama, A. (2008) : Magmatic He distribution around Unzen volcano inferred from intensive investigation of helium isotopes in groundwater. J. Volcanol. Geotherm. Res., **175**, 218–230.

New Energy Development Organization (NEDO) (1989) : Regional exploration of geothermal fluid circulation system, Aso area. National Geothermal Resources Exploration Project (3rd phase), Prepared for the Ministry of International Trade and Industry by the New Energy Development Organization, 108 p. (in Japanese).

Nishio, Y., Sasaki, S., Gamo, T., Hiyagon, H. and Sano, Y. (1998) : Carbon and helium isotope systematics of North Fiji Basin basalt glasses : carbon geochemical cycle in the subduction zone. Earth Planet. Sci. Lett. **154**, 127–138.

Ohba, T., Sawa, T., Taira, N., Yang, T.F., Lee, H.F., Lan, T.F., Ohwada, M., Morikawa, N. and Kazahaya, K. (2010) : Magmatic fluids of Tatun volcanic group, Taiwan. Applied Geochemistry, **25**, 513–523.

Okubo, Y., Tsu, H. and Ogawa, K. (1989) : Estimation of Curie point temperature and geothermal structure of island arcs of Japan. Tectonophysics, **159**, 279–290.

Ohsawa, S. and Yusa, Y. (2001) : High $\delta^{13}C$ fumarolic CO_2 discharged from Ogasawara—Iwojima, an active volcanic island in the Izu-Bonin Arc. J. Geotherm. Res. Soc. Jpn. **23**, 197–205.

Ohsawa, S., Kazahaya, K., Yasuhara, M., Kono, T., Kitaoka, K., Yusa, Y. and Yamaguchi, Y. (2002) : Escape of volcanic gas into shallow groundwater systems at Unzen volcano (Japan) : evidence from chemical and stable carbon isotope compositions of dissolved inorganic carbon. Limnology, **3**, 169–173.

Sano, Y. and Marty, B. (1995) : Origin of carbon in fumarolic gas from island arcs. Chem. Geol., **119**, 265–274.

Sano, Y., Gamo, Y. and Williams, S.N. (1997) : Secular variations of helium and carbon isotopes at Galeras volcano, Colombia. J. Volcanol. Geotherm. Res., **77**, 255–265.

Sato, M., Mori, T., Notsu, K. and Wakita, H. (1999) : Carbon and helium isotopic composition of fumarolic and hot spring gases from Kirishima Volcanic area. Bull. Volcanol. Soc. Jpn, **44**, 279–283 (in Japanese with English abstract).

Shimizu, A., Sumino, H., Nagao, K., Notsu, K. and Mitropoulos, P. (2005) : Variation in noble gas isotopic composition of gas samples from the Aegean arc, Greece. J. Volcanol. Geotherm. Res., **140**, 321–339.

Sumino, H., Notsua, K., Nakai, S., Sato, M., Nagao, K., Hosoe, M. and Wakita, H. (2004) : Noble gas and carbon isotopes of fumarolic gas from Iwojima volcano, Izu—Ogasawara arc, Japan : implications for the origin of unusual arc magmatism. Chem. Geol., **209**, 153–173.

Umeda, K., Ogawa, Y., Asamori, K. and Oikawa, T. (2006) : Aqueous fluids derived from a subducting slab : Observed high ^{3}He emanation and conductive anomaly in a non-volcanic region, Kii Peninsula southwest Japan. J. Volcanol. Geothermal. Res., **149**, 47–61.

Yamaji, A., Hase, Y. and Torii, M. (2003) : Paleostresses inferred from mesoscale faults in the Late Pliocene Hitoyoshi Formation : implications for the formation of vein-type ore deposits in southern Kyushu, Japan. Shigen Chishitsu, **53**, 217–225 (in Japanese with English abstract).

Yamamoto, J., Watanabe, M., Nozaki, Y. and Sano, Y. (2001) : Helium and carbon isotopes in

fluorites : implications for mantle carbon contribution in an ancient subduction zone. J. Volcanol. Geotherm. Res., **107**, 19–26.

Yoshida, A. and Seno, T. (1992) : Tectonic origin of the Aso volcano. Bull. Volcanol. Soc. Japan. **37**, 297–301 (in Japanese).