



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Journal of Volcanology and Geothermal Research 139 (2005) 211–226

Journal of volcanology
and geothermal research

www.elsevier.com/locate/jvolgeores

Stable and radiogenic isotopes as tracers for the origin, mixing and subsurface history of fluids in submarine shallow-water hydrothermal systems

Thomas Pichler

Department of Geology, University of South Florida, 4202 E. Fowler Avenue, Tampa, FL 33615, USA

Received 4 July 2003; accepted 20 August 2004

Abstract

The shallow-water hydrothermal system in Tutum Bay on the west side of Ambitle Island, Papua New Guinea provides us with an exceptional opportunity to study isotope systematics in a near shore setting. Compared to seawater, the hydrothermal fluids in Tutum Bay have lower values for δD , $\delta^{18}O$, $\delta^{13}C$, and ^{87}Sr and higher values for 3H , $\delta^{34}S(SO_4)$ and $\delta^{18}O(SO_4)$. The $\delta^{18}O$ and δD records for vents 1 and 4 indicate that fluid compositions remained stable over an extended period. Interpretation of isotope data clearly demonstrates the predominantly meteoric origin of Tutum Bay hydrothermal fluids, despite their location in a marine environment. $\delta^{18}O$ and δD values are identical to mean average annual precipitation in eastern Papua New Guinea. The hypothesis that these fluids are a simple product of mixing between seawater and onshore hydrothermal fluids from the Waramung (W-1) and Kapkai (W-2) thermal areas has been rejected, because the observed $\delta^{37}Cl$, 3H , $\delta^{34}S(SO_4)$ and $\delta^{18}O(SO_4)$ values cannot be explained by a simple mixing model. The application of $\delta^{18}O(SO_4)$ and $\delta^{13}C$ thermometers in combination with 3H values corroborates the three-step model of Pichler et al. [Pichler, T., Veizer, J., Hall, G.E.M., 1999. The chemical composition of shallow-water hydrothermal fluids in Tutum Bay, Ambitle Island, Papua New Guinea and their effect on ambient seawater. *Marine Chemistry* 64 (3) 229–252], where (1) phase separation in the deep reservoir beneath Ambitle Island produces a high temperature vapor that rises upward and subsequently reacts with cooler ground water to form a low pH, CO_2 -rich water of approximately 150–160 °C, (2) caused by the steep topography, this CO_2 -rich fluid moves laterally towards the margin of the hydrothermal system where it mixes with the marginal upflow of the deep reservoir fluid. This produces a dilute chloride water of approximately 165 °C, and (3) possibly the entrainment of minor amounts of ground or seawater during its final ascent.

© 2004 Elsevier B.V. All rights reserved.

Keywords: stable isotope; radiogenic isotope; shallow-water; hydrothermal system; venting

1. Introduction

Traditionally the research of hydrothermal systems has been divided into two groups, one working on deep-sea hydrothermal systems and the other on

E-mail address: pichler@chuma.cas.usf.edu.

sub-aerial hydrothermal or geothermal systems. Only recently we did start to appreciate the potential importance of a third type of hydrothermal system found in marine shallow-water near-shore environments or on the tops of seamounts (e.g., Pichler et al., 1999; Sedwick and Stüben, 1996). The known shallow-water hydrothermal systems, although submarine, have many of the attributes of their on-land counterparts and can be transitional in character between deep-sea hydrothermal vents and terrestrial hot springs. While the determination of fluid sources is relatively straightforward in deep marine and inland settings, the subject becomes more complex in coastal regions (offshore and on-shore) where marine and terrestrial sources may both be involved. A fluid in a hydrothermal system may be derived from any, or any combination, of the following sources: meteoric water, seawater, connate water, magmatic water and juvenile water. Mixing of waters from different sources affects many aspects of the geochemistry of a hydrothermal system, such as its chemical composition, isotopic composition, temperature profile or gas content. Deep-sea hydrothermal systems active along mid-oceanic ridges, in back-arc basins and on the flanks of seamounts most likely derive all their fluid from seawater, although a minor magmatic contribution cannot be completely ruled out. In contrast, on-land hydrothermal areas derive most of their fluid from meteoric sources, but a significant magmatic contribution is likely (e.g., Giggenbach, 1992).

The purpose of this paper is to test and evaluate several standard isotope techniques to address the complex mixing and subsurface history of the near-shore shallow-water hydrothermal system in Tutum Bay, Ambitle Island, Papua New Guinea. The main focus is on oxygen ($\delta^{18}\text{O}$), hydrogen (δD) and strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) isotopes, for which there is data from 1994 to 2000. In addition, some data are presented for sulfur and oxygen in sulfate, chlorine ($\delta^{37}\text{Cl}$) and tritium (^3H). The Tutum Bay hydrothermal system is ideal for this study because (1) results based on the interpretation of isotopic data can be compared to a previous physico-chemical model that was based solely on major, minor and trace element data (Pichler et al., 1999) and (2) the isotopic composition of Tutum Bay hydrothermal fluids can be directly compared to those of the deep reservoir fluid, as represented by sample

W-2 (Pichler et al., 1999). Considering the difficulties of working in a near-shore environment, a combination of elemental and isotopic techniques should provide us with a better model and a higher degree of confidence.

2. Location and geological setting

The study area lies along the southwest margin of Ambitle Island, one of the Feni islands in the southernmost island group of the Tabar-Feni chain, Papua New Guinea (Fig. 1). The islands of the Tabar-Feni chain are composed of Pliocene-to-Holocene alkaline volcanoes that occur in the fore-arc region of the former New Hanover–New Ireland–Bougainville island arc (Fig. 1). Ambitle Island is part of a Quaternary stratovolcano with a central eroded caldera built on poorly exposed Oligocene marine limestone (Wallace et al., 1983). Volcanic strata (interbedded lava flows, lahar deposits, tuffs, and scoriae) dip radially from the island, presumably extending beneath the shelf. Several geothermal areas are located primarily along the western coast and in the western part of the caldera near breaches in the caldera wall (Fig. 1).

Submarine hydrothermal venting occurs at Tutum Bay (Fig. 1) in shallow (5–10 m) water. Two types of venting are observed. (1) Focused discharge of a clear, hydrothermal fluid occurs at discrete ports, 10–15 cm in diameter. Fluid temperatures at vent orifices are between 89 and 98 °C and discharge rates are as high as 400 L/min. (2) Dispersed or diffuse discharge consists of streams of gas bubbles emerging directly through the sandy to pebbly unconsolidated sediment and through fractures in volcanic rocks. Based on their geographic location in Tutum Bay, the vents were divided into two groups, A (Vents 1, 2 and 3) and B (Vent 4). A more detailed description of Tutum Bay has been provided elsewhere (Pichler and Dix, 1996; Pichler et al., 1999) and color images can be found at <http://chuma.cas.usf.edu/~pichler>. A summary of the chemical compositions presented in Pichler et al. (1999) is given in Table 1.

3. Sampling and analytical procedures

Vent water samples were collected in 1994, 1996, 1997 and 2000, either by inserting a Teflon[®] tube as

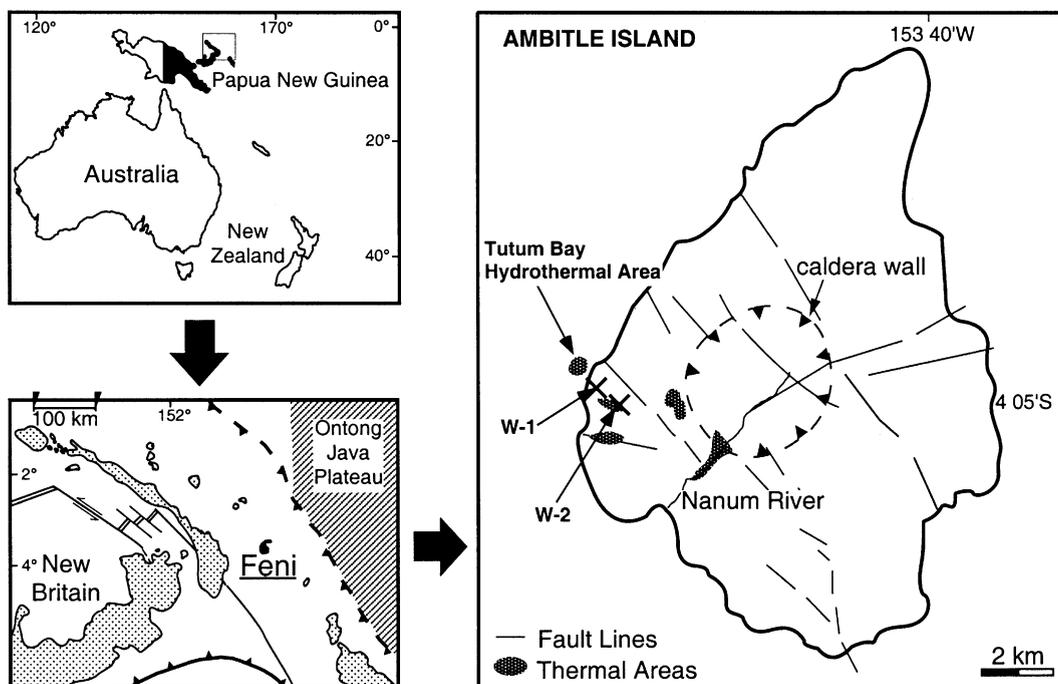


Fig. 1. Location of Ambitle Island, one of the Feni islands in eastern Papua New Guinea (modified after [Licence et al., 1987](#)). Geothermal areas indicated in dark are primarily along the western side of the island. W-1 and W-2 indicate locations where on-land hot springs were sampled.

far as possible into the vent orifice or covering the vent orifice with a Teflon[®] funnel. Medical syringes (60 mL) were connected to the Teflon tube or funnel via three-way stopcock. Using this setup, generally 15 syringes were filled at a time and brought to the surface and filtered together to assure homogenization of the sample. Samples for $\delta^{13}\text{C}$ analyses were filled into brown glass bottles (118 mL), poisoned with HgCl_2 and capped with phenolic screw caps with Polyseal[®] liners to avoid headspace. Duplicate samples are indicated by a capital letter following the sample number, i.e., 1B. Two of the three orifices at vent 3 were sampled; the two orifices 3-1 and 3-2 are approximately 2 m apart. At vent 4, three samples were taken from three different orifices within a single mound, i.e., 4a, 4b, 4c. A sample of ambient seawater (SW) from the center of Tutum Bay and the samples W-1 and W-2 from the on-shore hot springs (Fig. 1) were obtained by submerging a 1 L high-density polyethylene bottle. These samples were treated exactly as the Tutum Bay vent waters. Sample numbers correspond to those used in [Pichler et al. \(1999\)](#).

Two samples of gas bubbles (TB-1 and TB-2) were collected into 600 mL bottles through an inverted Teflon[®] funnel that was placed over the vent. The isotopic composition was analyzed at the Institute of Geological and Nuclear Sciences in Lower Hutt, New Zealand following [Giggenbach and Goguel \(1989\)](#).

Oxygen and hydrogen isotope ratios were determined at the G.G. Hatch Isotope Laboratory, University of Ottawa and are reported in delta notation (δ) relative to VSMOW. Oxygen was analyzed following CO_2 equilibration at 25 °C on a triple collector VG SIRA 12 mass spectrometer. The CO_2 –water fractionation factor used is 1.0412 ([Friedman and O'Neil, 1977](#)). The routine precision (2σ) on the analyses is 0.10‰. Hydrogen isotopes were determined on H_2 generated by zinc reduction in an automated double collector VG 602D mass spectrometer. The routine precision (2σ) for these analyses is 1.5‰. The isotopic composition of dissolved inorganic carbon (DIC) was determined on a triple collector VG SIRA 12 mass spectrometer by analysis of CO_2 generated by reaction with H_3PO_4 . The routine precision (2σ) on the analyses is 0.10‰. Tritium was analyzed by liquid

Table 1

Average chemical end member^a compositions of Tutum Bay hydrothermal fluids for area A and area B, compared to seawater and the two on-land hot springs W-1 and W-2 (modified from Pichler et al., 1999)

Sample	Unit	Vents Area A	Vents Area B	W-1	W-2	Seawater
pH		6.1	6.3	8.9	8.4	8.0
Cl	ppm	295	357	11,994	13,894	19,520
Br	ppm	6.8	10.7	29.6	21.8	45
SO ₄	ppm	930	880	6318	7075	2748
HCO ₃ ⁻	ppm	840	865	559	667	154
B	ppm	8.4	8.6	44.3	54.7	4.1
Si	ppm	108	105	84.6	103.0	0.2
Na	ppm	650	665	9700	11,250	10,450
K	ppm	76	94	1400	1560	354
Ca	ppm	201	180	7.4	4.7	405
Mg	ppm	0 ^a	0 ^a	0.3	0.1	1235
Li	ppb	1020	990	4272	5052	136
Mn	ppb	495	380	2.2	1.8	1.6
Fe	ppb	1720	1060	25	25	15
Rb	ppb	350	360	2768	3345	104
Sr	ppb	6790	6240	2125	2617	7990
Sb	ppb	8.2	9.1	156	31.2	0.6
Cs	ppb	59	63	448.4	550.0	0.5
Tl	ppb	4.5	5.2	20.2	16.5	0.25
As	ppb	820	955	1551	2907	3.7

^a End member compositions were extrapolated assuming a zero-Mg hydrothermal fluid.

scintillation counting (LSC) at the University of Waterloo following Taylor (1977). The seawater and on-land sample, W-2, were enriched approximately 15 times by electrolysis and then counted and values were decay-corrected to 01/01/81. Analytical uncertainty for these samples is approximately ± 0.8 TU. Tutum Bay samples were transferred from the syringes into argon flushed bottles and enriched 100 times prior to counting. The approximate analytical uncertainty for these samples is ± 0.1 TU. Chlorine 37 was determined on CH₃Cl that was synthesized by reaction of CH₃I with AgCl (e.g., Long et al., 1993). Analytical precision is $\sim 0.2\%$.

Sulfate $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ were determined on BaSO₄ at the University of Calgary (e.g., Mayer et al., 1995). BaSO₄ was precipitated with BaCl₂ and collected on a 0.45- μm filter. The pH was lowered to approximately 4 to 5 to prevent precipitation of BaCO₃. The on-land sample, W-2, contained significant amounts of sulfide, which was removed as CdS using CdAc prior to the precipitation of BaSO₄. The precision for $\delta^{34}\text{S}$ and for

$\delta^{18}\text{O}$ is better than 0.25‰ and 0.5‰ 2σ , respectively (B. Mayer, personal communication).

Strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) were measured on a five collector Finnigan MAT 262 solid source mass spectrometer at the Institut für Geologie, Mineralogie und Geophysik, Ruhr Universität, Bochum following Buhl et al. (1991). The average of 100 repeat measurements for the NBS 987 standard was 0.710224 ± 0.000008 .

4. End member calculations

Due to the inherent difficulty of sampling water underwater, the samples collected from the submarine vents in Tutum Bay are mixtures of hydrothermal fluid and seawater, because of entrainment of ambient cool seawater during sampling. Thus, prior to the interpretation of chemical data in a hydrothermal context, it is important to evaluate the amount of seawater entrained and to subtract this amount from the sample analysis (Bishoff and Dickson, 1975; Edmond et al., 1979). Assuming conservative behavior, several chemical species can be used to trace the mixing process if the concentration difference between seawater and hydrothermal fluid is sufficient. Pichler et al. (1999) investigated the use of Mg and Si as possible mixing tracers and concluded that Mg is the better choice to calculate end member concentrations for Tutum Bay vents. Here I adopted the same approach.

The end member values for tritium and for oxygen and hydrogen isotopes were calculated according to the following formula:

$$X_{\text{HF}} = (X_{\text{M}} - X_{\text{SW}}(\text{Mg}_{\text{M}}/\text{Mg}_{\text{SW}})) / (1 - (\text{Mg}_{\text{M}}/\text{Mg}_{\text{SW}})) \quad (1)$$

where X_{HF} is the calculated isotopic end member, X_{M} is the measured concentration, X_{SW} is the concentration in seawater. No correction of chemical composition for phase separation was attempted. In order to account for phase separation, the sampling pressure, steam composition and/or reservoir conditions have to be known (Henley et al., 1984). This information can generally be obtained when sampling in explored on-land geothermal systems, but not when sampling underwater hot-springs. The effect of phase

separation on the isotopic composition for Tutum Bay vent waters, however, seems to be negligible. Only minor amounts of steam were observed while sampling.

End member determinations for $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and for oxygen and sulfur isotopes in sulfate are more complex, because they depend not only on the isotopic ratios in the two end members, but also on their respective elemental concentrations. Thus end member correction for these isotopes is a three-step process. The first step is to calculate end member concentrations of Sr and SO_4^{2-} using Eq. (1). This is followed by the determination of the degree of mixing (x) using the Mg mass balance approach:

$$\text{Mg}_M = x \cdot \text{Mg}_{\text{HF}} + y \cdot \text{Mg}_{\text{SW}} \quad (2)$$

where Mg_M is the concentration of Mg in a mixture of hydrothermal fluid (HF) and seawater (SW), and x and y are the respective fractions ($x+y=1$). Under the assumption of a zero-Mg hydrothermal end member, Eq. (2) reduces to:

$$x = (\text{Mg}_{\text{SW}} - \text{Mg}_M) / \text{Mg}_{\text{SW}} \quad (3)$$

The hydrothermal end members can now be calculated by solving the following weighted mass balance equations:

$$\begin{aligned} (^{87}\text{Sr}/^{86}\text{Sr})_M &= (^{87}\text{Sr}/^{86}\text{Sr})_{\text{HF}}^* \cdot \text{Sr}_{\text{HF}} / \text{Sr}_M^* \cdot x \\ &+ (^{87}\text{Sr}/^{86}\text{Sr})_{\text{SW}}^* \cdot \text{Sr}_{\text{SW}} / \text{Sr}_M^* \cdot (1-x) \end{aligned} \quad (4)$$

$$\begin{aligned} \delta^{34}\text{S}_M &= \delta^{34}\text{S}_{\text{HF}}^* \cdot \text{SO}_4^{2-}_{\text{HF}} / \text{SO}_4^{2-}_M \cdot x \\ &+ \delta^{34}\text{S}_{\text{SW}}^* \cdot \text{SO}_4^{2-}_{\text{SW}} / \text{SO}_4^{2-}_M \cdot (1-x) \end{aligned} \quad (5)$$

$$\begin{aligned} \delta^{18}\text{O}_M &= \delta^{18}\text{O}_{\text{HF}}^* \cdot \text{SO}_4^{2-}_{\text{HF}} / \text{SO}_4^{2-}_M \cdot x \\ &+ \delta^{18}\text{O}_{\text{SW}}^* \cdot \text{SO}_4^{2-}_{\text{SW}} / \text{SO}_4^{2-}_M \cdot (1-x) \end{aligned} \quad (6)$$

for their respective hydrothermal end members.

5. Results

The $\delta^{13}\text{C}$ values of Tutum Bay vent waters are isotopically lighter than seawater. End member calculations were omitted because $\delta^{13}\text{C}$ values scatter significantly and there is only limited correlation with

Mg (Fig. 2a). This is somewhat surprising, but could be caused by post-sampling activity of HgCl_2 -resistant microbial organisms (Ian Clark, personal communication). Another factor could be the pH-dependent geochemistry of CO_2 and its dissolved species. Mixing with seawater will increase the pH and thus increase the abundance of HCO_3^- relative to H_2CO_3 , which in turn has an effect on CO_2 -degassing once the sample reaches the surface. Those samples with the lowest pH or least entrainment of seawater will degas more readily, causing the sample to become isotopically heavier. Thus $\delta^{13}\text{C}$ is the isotope value most susceptible to seawater contamination during sampling. Nevertheless, within limits, the mean of all samples ($\delta^{13}\text{C} - 1.9\text{‰}$) should be a reasonable estimate of the $\delta^{13}\text{C}$ composition. A detailed investigation of the $\delta^{13}\text{C}$ variation will be part of future fieldwork at this site.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of vent waters are considerably lower than local seawater (Table 2). Values for the whole data set (including seawater) are positively correlated with Mg^{2+} ($r^2 > 0.99$) and the degree of correlation remains high even after exclusion of the seawater value ($r^2 > 0.98$) (Fig. 2b). After end member determination all $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are identical within their analytical uncertainty of ± 0.000009 (Table 2). Their mean (0.70394) is almost identical to the Y -axis intercept of the linear regression, i.e., end member ratio (0.703933). Both ratios (mean and Y -axis intercept) are in very good agreement with the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of on-land samples (W-1 and W-2, Table 2) and those of subsurface rocks at Ambitle Island (0.703813, M. Perfit, personal communication) and, therefore, strengthen the assumption of a zero-Mg hydrothermal end member and the use of Mg^{2+} as a tracer of seawater mixing. The use of Mg is also corroborated by the virtual absence of Mg in W-1 and W-2 (Table 1).

$\delta^{18}\text{O}$ and δD are relatively lower compared to local seawater (Table 2). $\delta^{18}\text{O}$ is positively correlated with Mg^{2+} ($r^2 > 0.99$) and the degree of correlation remains high ($r^2 > 0.96$) after exclusion of the seawater value (Fig. 2c). δD values show no correlation with Mg^{2+} once the seawater point is removed (Fig. 2d). The relatively larger analytical error (when compared to $\delta^{18}\text{O}$) and the smaller relative range of observed values could be a possible cause. Of all samples only three deviated beyond their analytical error (Fig. 2d). Another factor could be the salinity variation between samples (TDS varies by more than 250%), which has

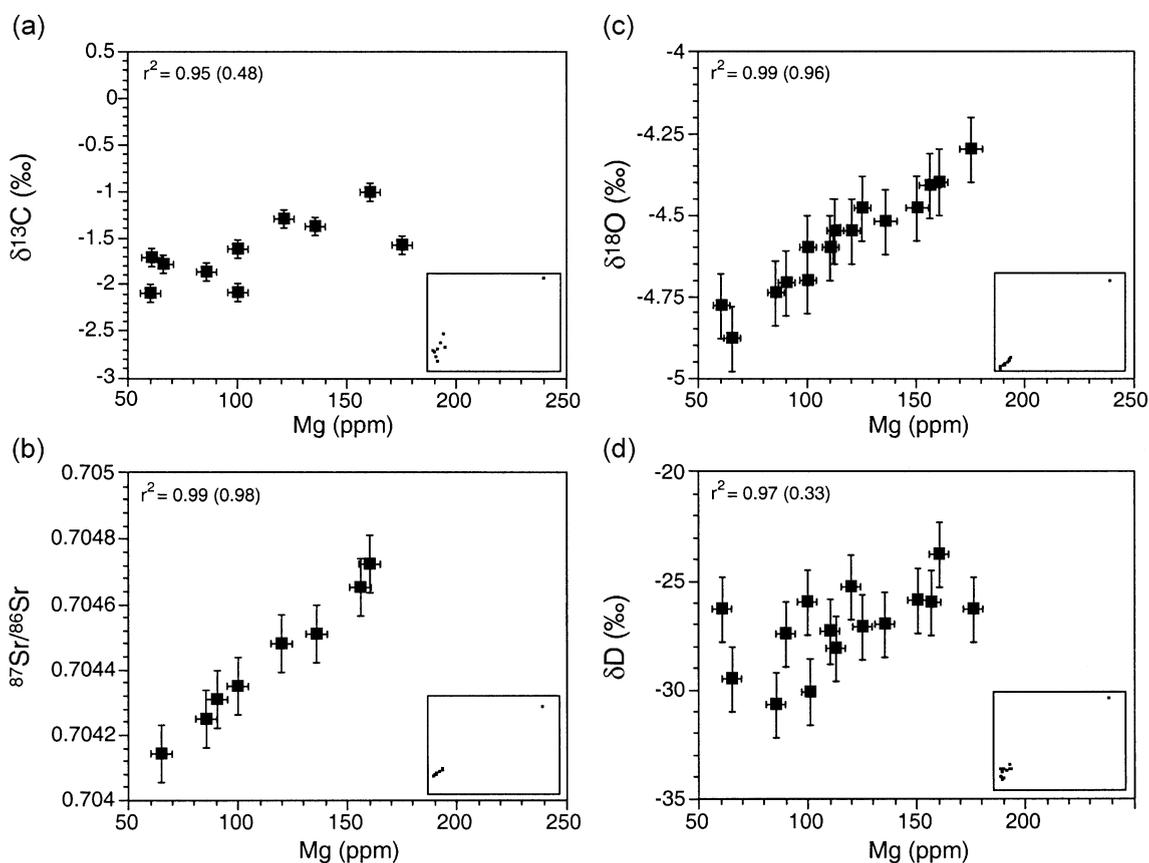


Fig. 2. $\delta^{13}\text{C}$, $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{18}\text{O}$ and δD vs. Mg vs. Mg in Tutum Bay vent waters and seawater. The small inset in the lower right corners show the whole data set including seawater (Mg=1235 ppm). r^2 is the correlation coefficient for the linear regression taking into account the whole data set including seawater and r^2 in brackets is the correlation coefficient for the linear regression excluding seawater. See text for more detail.

been shown to compromise the analyses of δD much more than $\delta^{18}\text{O}$. Although the merit of the δD values is unclear at this time, I decided to use the mean of Mg-corrected values for comparative purposes. This approach is supported by the similarity of the average Mg-corrected δD values for Tutum Bay vents and the weighted mean annual precipitation in the region (see below). After Mg-correction for seawater contamination, all values for $\delta^{18}\text{O}$ are identical within their analytical uncertainty (Table 2), although, they do not plot on the LMWL, because of the spread in δD values. The means of $\delta^{18}\text{O}$ (-5.1‰) and δD (-30.7‰) of Mg-corrected Tutum Bay vent water, however, are identical to the means of $\delta^{18}\text{O}$ (-5.2‰) and δD (-30.7‰) of local precipitation and thus plot exactly on the LMWL (Fig. 3). Vents 1 and 4 were sampled in 1994, 1996, 1997 and 2000 and end

member values did not deviate beyond their analytical uncertainty (Table 2), indicating that the isotopic composition of the vent fluids remained stable for that period of time.

Tritium levels in Tutum Bay vent fluids are higher than those in seawater and W-2. They are much closer to ^3H values for local precipitation (~ 2.8 TU) that were estimated based on IAEA precipitation data for 1978 to 1991 (IAEA/WMO, 1998). Mg-corrected end member values for vents 1 and 4 are identical within their analytical uncertainty, but there is a clear difference between the two vents. The ^3H concentration for vent 1 is higher than vent 4. The values for seawater and W-2 are reported as <0.8 TU, although a much lower value of <0.1 TU would be more representative for these types of waters (e.g., Ellis and Mahon, 1977).

Table 2
Isotopic composition of Tutum Bay hydrothermal fluids, onshore hot springs and local seawater

Sample location	Year	Mg (ppm)	$\delta^{13}\text{C}$ (‰) VPDB	$\delta^8\text{O}$ (‰) VSMOW	$\delta^8\text{O}(\text{e})^{\text{a}}$ (‰)	δD (‰) VSMOW	$\delta\text{D}(\text{e})$ (‰) VSMOW	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}(\text{e})$
1 ^b	1994	108	–	–4.7	–5.2	–25.9	–29.9	–	–
1	1996	57	–1.1	–4.8	–5.1	–26.3	–27.9	0.70414 (6700)	0.70386
1B	1996	60	–	–4.9	–5.2	–29.5	–31.3	–	–
1	1997	60	–1.7	–4.8	–5.1	–29.7	–31.7	–	–
1B	1997	65	–1.8	–4.7	–5.1	–24.6	–28.6	–	–
1	2000	138	–1.3	–4.5	–5.1	–27.5	–27.5	0.70449 (6700) ^c	0.70391
1B	2000	110	–	–4.6	–5.1	–28.1	–31.5	–	–
2	1996	140	–1.4	–4.5	–5.1	–27.0	–31.1	0.70451 (6900)	0.70394
2B	1996	163	–1.2	–4.4	–5.1	–26.0	–30.9	0.70465 (6900)	0.70398
3-1	1996	175	–1.6	–4.3	–5.1	–26.3	–31.7	–	–
3-1B	1996	92	–	–4.7	–5.1	–27.4	–30.1	0.70431 (7000)	0.70393
3-2	1996	100	–1.6	–4.6	–5.0	–30.1	–33.3	–	–
4a	1994	136	–	–4.3	–5.2	–28.6	–33.1	–	–
4a	1996	94	–1.8	–4.7	–5.1	–30.7	–33.8	0.70425 (6400)	0.70388
4a	1997	120	–1.9	–4.4	–5.1	–27.2	–32.2	–	–
4a	2000	124	–1.8	–4.4	–5.2	–28.1	–32.5	0.70431 (6700)	0.70399
4b	1996	100	–2.1	–4.7	–5.2	–26.0	–28.9	0.70435 (6300)	0.70393
4b	1997	100	–2.1	–4.5	–5.1	–27.5	–31.6	–	–
4c	1996	161	–	–4.4	–5.1	–23.8	–28.4	0.70472 (6700)	0.70406
W-1	1996	0.3	–0.9	–0.3	–	–14.8	–	0.70409	–
W-2	1996	0.1	–0.7	0.2	–	–17.7	–	0.70394	–
W-2	1997	0.2	–	–0.1	–	–16.7	–	–	–
SW	1996	1235	1.3	0.4	–	–6.6	–	0.70918 (7900)	–
SW	1997	1240	–	0.3	–	3.7	–	–	–

–, not determined; maximum error for strontium isotope values is ± 0.00009 .

^a These are end member values that were calculated assuming zero-Mg. Mg values for endmember calculations are from Pichler et al. (1999) and Pichler (unpublished data).

^b Sample numbers are as follows: 1–4c are Tutum Bay hydrothermal fluids, W-1 and W-2 are onland hydrothermal fluids and SW is seawater.

^c Sr values that were used for the end member calculations in ppb.

The $\delta^{34}\text{S}$ of vent fluid sulfate (SO_4^{2-}) is lower compared to local seawater, but very similar to the value for W-2 (Table 3). The average of all four $\delta^{34}\text{S}$ measurements for Tutum Bay vent fluids is 7.3‰ vs. 7.8‰ for W-2. With the exception of sample 4b, Mg-corrected end member values for vents 1 and 4 do not deviate beyond their analytical uncertainty. The sample W-2, from the Kapkai thermal area also contained dissolved sulfide with a $\delta^{34}\text{S}$ of –8.9‰.

The $\delta^{37}\text{Cl}$ values for Tutum Bay are very close to local seawater and W-2 (Table 3). Because of their relatively high predicted analytical uncertainty of $\sim \pm 0.2\text{‰}$ end member calculations were omitted. Considering the analytical uncertainty, the deviation from seawater ($\delta^{37}\text{Cl} = -0.2\text{‰}$) and from W-2

($\delta^{37}\text{Cl} = 0.3\text{‰}$) is only 0.03 and 0.07‰, respectively. Nevertheless, they possess limited significance because they fall intermediate between seawater and W-2 hydrothermal fluid.

The isotopic compositions of non-condensable gases collected from submarine vents in Tutum Bay are as follows: TB-1 $\delta^{13}\text{C}(\text{CO}_2) = -2.2\text{‰}$, $\delta^{13}\text{C}(\text{CH}_4) = -17.1\text{‰}$, $\delta\text{D}(\text{CH}_4) = -112\text{‰}$ and TB-4 $\delta^{13}\text{C}(\text{CO}_2) = -2.5\text{‰}$.

6. Discussion

The discharge composition of thermal springs is controlled by two sets of processes: (1) deep reservoir conditions, and (2) secondary processes

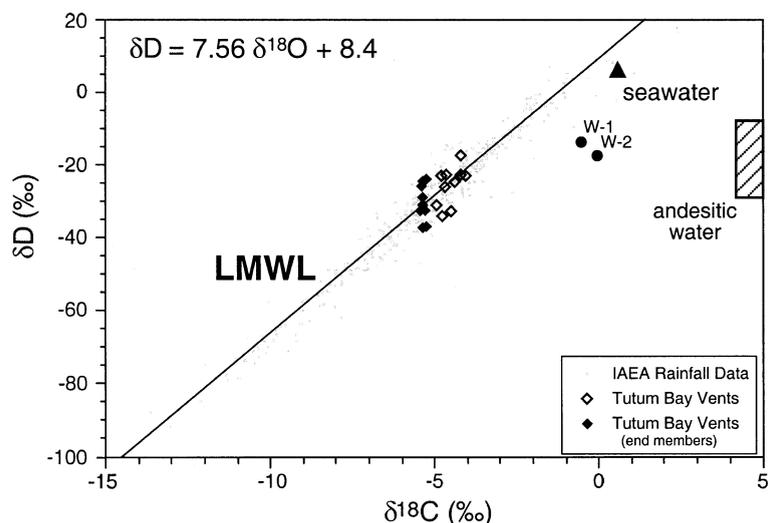


Fig. 3. Local Meteoric Water Line (LMWL) for Tutum Bay. Rainfall data are from the Global Network for Isotopes in Precipitation (GNIP) database (IAEA/WMO, 1998) and represent the four closest monitoring stations to Ambitle Island whose elevations are at sea level. The box for “andesitic water” is from Giggenbach (1992). The samples W-1 and W-2 plot slightly higher than the field for andesitic water, but are still within the range on hydrothermal fluids that were presented in Giggenbach (1992).

during ascent. In the deep reservoir, origin, host rock composition, temperature, direct magmatic contributions and residence time are the controlling factors. During ascent, a drop in pressure and temperature can initiate phase separation and mineral precipitation, causing a dramatic change in fluid composition. Mixing with other hydrothermal fluids and/or groundwater is possible at any depth. In near-shore and submarine environments mixing with seawater cannot be ruled out. The chemical composition of a hydrothermal fluid, sampled at the surface, contains an imprint of its subsurface history. Chemically inert

constituents (tracers) provide information about their source, whereas chemically reactive species (geoindicators) record physico-chemical changes (e.g., Ellis and Mahon, 1977; Giggenbach, 1991; Nicholson, 1992). Examples of widely used isotopic tracers are $\delta^{18}\text{O}$, δD , ^3H and $\delta^{37}\text{Cl}$, while $\delta^{13}\text{C}$, $\delta^{34}\text{S}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ are examples of prominent isotopic geoindicators. The boundary between the two groups, however, is not rigid and depending on the physico-chemical conditions of the hydrothermal system tracers may participate in chemical reactions and geoindicators can behave inertly.

Table 3
Sulfur, chloride and tritium isotopic composition of Tutum Bay hydrothermal fluids, on land hot springs and local seawater

Sample location	Year	Mg (ppm)	SO ₄ (ppm)	$\delta^{34}\text{S}$	$\delta^{34}\text{S}(\text{e})^{\text{a}}$	$\delta^{18}\text{O}$	$\delta^{18}\text{O}(\text{e})$	$\delta^{37}\text{Cl}$	^3H	$^3\text{H}(\text{e})$
				(‰)	(‰)	(‰)	(‰)	(‰)	(‰)	TU
				CDT	CDT	VSMOW	VSMOW	SMOC		
1 ^b	1997	60	1180	9.1	7.8	6.6	6.3	0.04	1.3	1.4
1B	1997	65	1090	8.9	7.2	6.6	6.2	–	–	–
4a	1997	120	1140	10.7	8.1	7.9	7.6	0.03	0.9	1.0
4b	1997	100	1070	8.7	5.9	7.0	6.5	–	–	–
W-2	1997	0.1	7075	7.8	–	3.1	–	0.3	<0.8	–
SW	1997	1235	2700	19.8	–	8.8	–	–0.2	<0.8	–

^a These are end member values that were calculated assuming zero-Mg. Mg and SO₄ values for endmember calculations are from Pichler et al. (1999) and Pichler (unpublished data).

^b Sample numbers are as in Table 2.

6.1. Origin of the hydrothermal fluid and probable mixing trends

Determination of the fluid origin is an important step in order to constrain subsurface processes and reservoir conditions. While the source determination is relatively straightforward in deep marine and inland settings, the subject becomes more complex in coastal regions (off-shore and on-shore) where seawater incursion can significantly alter the fluid composition in a hydrothermal system. For example, seawater mixing is present in the Savusava (Fiji), Puna (Hawaii) and Reykjanes (Iceland) hydrothermal systems (Nicholson, 1992). Similarly, meteoric water may be the source for submarine hydrothermal systems in coastal areas where a steep topography and ample supply of rainwater can force the Ghyben-Herzberg boundary substantially offshore (Chuck, 1967; Nahm, 1966). Tropical and subtropical island-arc volcanoes are good examples for these conditions. Subsurface sealing of a hydrothermal system, as argued for White Island, New Zealand (Giggenbach et al., 1989), can be another mechanism to prevent seawater from entering the near shore environment, thus allowing for a meteoric water dominated submarine hydrothermal system.

The deuterium and oxygen isotopic composition of water is generally a good indicator of its origin (Craig, 1961). All Tutum Bay vent waters plot very close to the local meteoric water line (LMWL) whose equation is (Fig. 3):

$$\delta D = 7.56 * \delta^{18}O + 8.4 \quad (7)$$

and their mean δD and $\delta^{18}O$ is almost identical to mean local precipitation (IAEA/WMO, 1998), thus indicating that they are of a local meteoric origin, although discharging in a submarine environment. Hydrothermal fluids normally plot to the right (higher $\delta^{18}O$) of the LMWL due to exchange of ^{18}O with rock that came into contact with the fluid (e.g., Craig, 1966) or caused by subsurface mixing with an “andesitic water” as defined by Giggenbach (1992). Tutum Bay vent waters did not shift to the right of the LMWL indicating that they have undergone only little water-rock isotope exchange or mixing with an “andesitic water”. Neither process, however, can be completely ruled out because an initial ^{18}O -shift to the right may have been later reversed by a subsequent

isotope exchange between CO_2 and H_2O . Isotope shifts to the left have been observed in several CO_2 -rich aquifers and hydrothermal waters (e.g., Vuataz and Goff, 1986). The two on-land hot springs, Waramung and Kapkai, show a significant diagonal shift to the right, which is caused by a change in both, $\delta^{18}O$ and δD (Fig. 3), which is in support of the “andesitic water” model by Giggenbach (1992), but contrary to the “horizontal only” shift of isotope exchange model by Craig (1966). The model of Craig (1966) assumes no exchange of hydrogen isotopes, thus the “horizontal only” shift, whereas Giggenbach (1992) demonstrated a significant change in δD , causing the diagonal shift to the right of the LMWL.

The $^{87}Sr/^{86}Sr$ ratios of Tutum Bay vent waters are quite different from local seawater, although their Sr concentrations are similar (Pichler et al., 1999). In contrast to the absolute Sr concentration, which in a hydrothermal fluid is controlled by host rock composition, pH (CO_2 content) and temperature, the $^{87}Sr/^{86}Sr$ ratios are independent of physico-chemical effects and similar or identical to those of the host rocks at isotopic equilibrium (e.g., Barnes et al., 1981). Based on their work at the Valles caldera, New Mexico, Vuataz et al. (1988) found that isotopic equilibrium for $^{87}Sr/^{86}Sr$ between a hydrothermal fluid and its host rock is rapidly attained. The same authors also noted that low Sr concentrations are generally characteristic of high temperature volcanic hosted hydrothermal systems, while high Sr concentrations are characteristic of low temperature and/or a Paleozoic sedimentary aquifer/reservoir. Thus a marine source for the Sr present in the Tutum Bay hydrothermal fluids can be excluded.

Subsequent to the early work of Eastoe et al. (1989) and Eastoe and Guilbert (1992) stable chlorine isotopes have not drawn much attention in studies of hydrothermal systems. The mass difference between the two stable chlorine isotopes, ^{35}Cl and ^{37}Cl , is relatively minor, thus mass-based fractionation, in particular at high temperatures, should be small. Chlorine isotopes, nevertheless, have proven to be valuable tracers for the origin of Cl^- in ground waters, sedimentary basin and crystalline shield brines (e.g., Clark and Fritz, 1997). This holds true despite the limited range of $\delta^{37}Cl$ in nature, where most values are between -1‰ and 1‰ (Eggenkamp, 1994), because chloride generally behaves inert with respect

to biological and inorganic reactions. As a result, variations in nature are largely due to mixing. The $\delta^{37}\text{Cl}$ of Tutum Bay hydrothermal fluids lies intermediate between values for seawater and sample W-2 (Table 3), thus indicating the possibility of mixing. Based on a mass-balance and mixing calculation, however, subsurface mixing between seawater and deep reservoir fluid (W-2) can be ruled out as a process for the formation of Tutum Bay hydrothermal fluids. Under the assumption that Cl^- behaves inertly, seawater ($\text{Cl}^- = 19,500$ ppm) and W-2 ($\text{Cl}^- = 13,900$ ppm) would have to mix at a ratio of approximately 0.42:0.58, which would correspond to a Cl^- concentration in the mixture of $\sim 16,300$ ppm. This concentration deviates by more than an order of magnitude from the actual values in Tutum Bay hydrothermal fluids (223–419 ppm), thus rejecting the seawater-W-2 mixing hypothesis. The likely scenario is a small addition of seawater and W-2 to the Tutum Bay vents in the form of marginal upward flow that is commonly seen in hydrothermal systems (e.g., Hedenquist, 1990).

To determine the source of sulfur in Tutum Bay vent fluids is complicated, because several processes have to be considered, such as: (1) mixing with seawater; (2) mixing with lateral outflow of deep reservoir fluid; (3) contribution from oxidation of magmatic H_2S ; and SO_2 and (4) leaching and oxidation of sulfide minerals. The $\delta^{34}\text{S}$ of vent fluid SO_4^{2-} , however, is distinctly different from seawater to rule out a significant seawater contribution (Table 3). If the sulfur source for Tutum Bay vent fluids is considered to be a mixture of local seawater and the deep reservoir fluid, then approximately 96% of the sulfur would be of hydrothermal origin. The similarity of the $\delta^{34}\text{S}$ between W-2 and the Tutum Bay vent fluids suggests a similar source for both fluids, which could be the disproportionation of volcanic SO_2 . Unfortunately it was not possible to measure the sulfide concentration in W-2, which would have allowed to calculate the total isotopic composition of sulfur, which in turn could have been used to further constrain the sulfur source.

The radiogenic hydrogen isotope ^3H (tritium) has been successfully employed to date modern ground waters and to evaluate subsurface mixing (e.g., Clark and Fritz, 1997). In hydrothermal systems its use as a dating tool is limited, because hydrothermal fluids

usually have residence times longer than 50 years (e.g., Nicholson, 1992). Nevertheless, ^3H is a good tracer to evaluate subsurface mixing between hydrothermal and meteoric waters (e.g., Kiryukhin et al., 1998; Pauwels et al., 1997). As expected, the concentration of ^3H in the on-land sample (W-2) is less than 0.8 (Table 3), indicating a recharge prior to 1953. The concentrations of ^3H in Tutum Bay vent waters are higher than those for W-2, but remain very close to their detection limits. Therefore, no attempt has been made for a quantitative age determination. Despite the increased analytical uncertainty they are of good use for a qualitative assessment of fluid age and subsurface mixing. Tritium measurements by the International Atomic Energy Association at their nearby Djajapura station, which is located on the main island of Papua, are 2.8 ± 1.1 for the period from 1971 to 1991 (IAEA/WMO, 1998). Tutum Bay vent fluids have 1 and 1.4 TU, indicating a mixture of sub modern and recent recharge (Clark and Fritz, 1997). The values seem to be too low to be exclusively caused by radioactive decay. Values are intermediate between local meteoric recharge (2.8 ± 1.1) and those for seawater and W-2 hydrothermal fluids (< 0.8). Low ^3H is added to the Tutum Bay hydrothermal fluids three times, once during formation of the bicarbonate-chloride water when the vapor phase that separated from the deep reservoir fluid condensed into shallow groundwater and secondly when the bicarbonate-chloride water mixed with the lateral upflow of deep reservoir fluid and the third time during mixing with seawater. During the lateral flow of the bicarbonate-chloride water decay of ^3H to ^2H will further lower the ^3H concentration.

The significant difference in ^3H concentration between vents 1 and 4 (Tables 3 and 4) is in accordance to the findings of Pichler et al. (1999), who divided Tutum Bay into area A and B, based on geographic location and chemical composition. They concluded that subsurface mixing is the responsible mechanism for the chemical difference, because compared to A, area B has a slightly higher concentration of elements that are present in samples W-1 and W-2. Thus the lower ^3H concentration of area B vent waters may be attributed to a larger subsurface addition of a hydrothermal fluid similar in composition to the on-land hot spring W-2.

Table 4
Average isotopic compositions for Tutum Bay hydrothermal end member vent fluids

Sample standard	$\delta^{18}\text{O}$ VSMOW	δD VSMOW	$^{87}\text{Sr}/^{86}\text{Sr}$	$\delta^{34}\text{S}_{\text{sulfate}}$ CDT	$\delta^{18}\text{O}_{\text{sulfate}}$ VSMOW	$\delta^{37}\text{Cl}$ SMOC	^3H TU
Vent 1	−5.1	−29.8	0.70389	8.2	6.4	0.05	1.4
Vent 2	−5.1	−31.0	0.70396	–	–	–	–
Vent 3	−5.1	−31.7	0.70393	–	–	–	–
Vent 4	−5.1	−30.2	0.70396	8.4	7.2	0.04	1.0

–, not determined.

Additional insight into potential processes controlling the fluid composition and subsurface processes may be provided by the isotopic composition of the gases. The $\delta^{13}\text{C}$ isotopic composition of the CO_2 could be reconciled with a predominantly mantle/magmatic origin, but could also point to the addition of carbon from marine carbonates. The $\delta^{13}\text{C}$ value of approximately -2.4‰ lies intermediate between the known range for marine carbonate derived (Welhan, 1988) and mantle derived CO_2 (Hoefs, 1997). At Ambitle, which is located on top of the Manus-Kilinailau trench, the mantle-derived CO_2 may be as heavy as -3‰ due to a possible contribution from subducted sediments. Poorter et al. (1991), reported CO_2 isotopic compositions of -3‰ for volcanic gases from the East Sunda and Banda arcs, Indonesia, which are in similar tectonic settings

on the west side of Papua New Guinea. The $\delta^{13}\text{C}$ composition as a stand-alone indicator of CO_2 origin remains ambiguous. However, with the support from chemical data, such as the relative concentrations of N_2 , He and CO_2 , (Pichler et al., 1999, Fig. 17) the predominantly mantle/magmatic origin can be further substantiated.

The carbon and hydrogen isotopic compositions of methane (CH_4) are similar to values reported for abiogenic CH_4 (Fig. 4). Due to the very steep geothermal gradient in Tutum Bay, subsurface temperatures are immediately above 100 °C , which should exclude bacterial fractionation. In particular, the distinct enrichment of heavy carbon isotopes leads to the conclusion that inorganic process such as the Fischer-Tropsch reaction are responsible for the CH_4 formation (e.g., Botz et al., 1996; Lyon and Hulston, 1984).

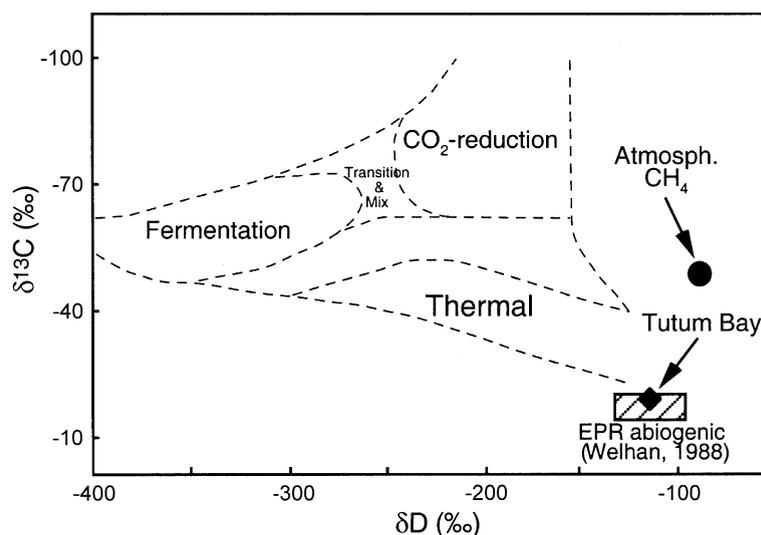


Fig. 4. Characteristic isotope fields for CH_4 formed by different processes (after Botz et al., 1996). The compositional field for East Pacific Rise (EPR) abiogenic CH_4 is from Welhan (1988).

6.2. Geothermometry

Isotope and solute geothermometers can help to estimate subsurface conditions. Their successful application has been extensively discussed in the geothermal literature and relies on five basic assumptions: (1) exclusively temperature dependent mineral–fluid reaction; (2) abundance of the mineral and/or solute; (3) chemical/isotopic equilibrium; (4) no re-equilibration; and (5) no mixing or dilution (Nicholson, 1992).

Perhaps the most widely used isotope thermometer is the fractionation of oxygen ($\delta^{18}\text{O}$) between SO_4^{2-} and liquid water. This thermometer is based on experimental data and has been successfully applied to many high temperature hydrothermal systems (Nicholson, 1992). In Tutum Bay temperatures calculated with the thermometer of Mizutani and Rafter (1969) are 156 and 146 °C for the vents 1 and 4, respectively. Calculated $\delta^{13}\text{C}$ equilibrium temperatures for the system $\text{CO}_{2(\text{g})}$ – HCO_3^- (Friedman and O'Neil, 1977) are in good agreement with those obtained from the sulfate thermometer. For the $\delta^{13}\text{C}$ range of CO_2 gas in Tutum Bay (–2.5 to –2.2‰) and HCO_3^- (–1.5 to –2.1‰) temperatures are between 145 and 170 °C. Let us consider one more time the process that leads to the formation of a CO_2 or bicarbonate water. Isenthalpic expansion of steam, separated from a deeper liquid phase close to atmospheric pressure, is accompanied by a drop in temperature to about 160 °C (Giggenbach, 1997). Bicarbonate waters formed due to interaction between groundwater and this 160 °C steam, have generally temperatures in the vicinity of 150 °C (e.g., Cioni and D'Amore, 1984; Hedenquist, 1990), which is similar to the temperature range indicated by the $\delta^{18}\text{O}(\text{SO}_4)$ and $\delta^{13}\text{C}$ thermometers.

In addition to those thermometers that are applied to the liquid phase, gas thermometers can also provide valuable information about the subsurface history of a hydrothermal fluid. Assuming equilibration of CO_2 and CH_4 in a liquid phase and preservation of equilibrium CH_4/CO_2 ratios (Giggenbach and Matsuo, 1991), the CH_4 – CO_2 equilibrium temperatures are between 257 and 291 °C (Pichler et al., 1999). These CH_4 – CO_2 equilibrium temperatures are in good agreement with reservoir fluid estimates of the solute and isotope geothermometers. While there is apparent

chemical equilibrium between CO_2 and CH_4 (as indicated by the temperature agreement), carbon isotopic equilibrium is not attained. A temperature calculated with the carbon isotope thermometer of Lyon and Hulston (1984) of 488 °C is too high to represent reservoir conditions. This is not surprising considering that isotopic equilibration time may be as long as 20,000 years at a temperature of 400 °C and 10^7 years at 300 °C (Giggenbach, 1982). This temperature most likely represents an earlier equilibrium at greater depth (e.g., Botz et al., 1996; Lyon and Hulston, 1984).

6.3. Relation to previous work at Tutum Bay

Pichler et al. (1999), concluded that the final physico-chemical vent compositions are the outcome of a two- or possibly three-step process, where: (1) phase separation in the deep reservoir beneath Ambitle Island produces a high temperature vapor that rises upward and subsequently reacts with cooler ground water to form a low pH, CO_2 -rich water of approximately 150–160 °C; (2) due to the steep topography, this CO_2 -rich fluid moves laterally towards the margin of the hydrothermal system where it mixes with the marginal upflow of the deep reservoir fluid; and (3) the entrainment of minor amounts of ground or seawater occurs during the final ascent and prior to discharge (Fig. 5). Step one produces a fluid that is highly reactive, causing the enrichment of pH-Eh sensitive elements such as Fe, Mn, Ca and Sr due to water–rock interaction in the shallow subsurface. The lateral movement combined with mixing of steps two and three produce a dilute chloride water of approximately 165 °C.

Pichler et al. (1999) developed this model based on field observations, elemental/chemical vent water composition, geothermometry applications and mixing calculations. They applied several solute thermometers and found that calculated temperatures differed quite drastically from thermometer to thermometer and fell into three groups (Pichler et al., 1999; Table 4): (1) the temperatures obtained with the chalcedony thermometer (Fournier, 1977) were between 98 and 100 °C; (2) the temperatures obtained with the Na/Li thermometer (Kharaka and Lico, 1982) were between 166 to 172 °C; and (3) the temperatures obtained with the Na/K thermometer

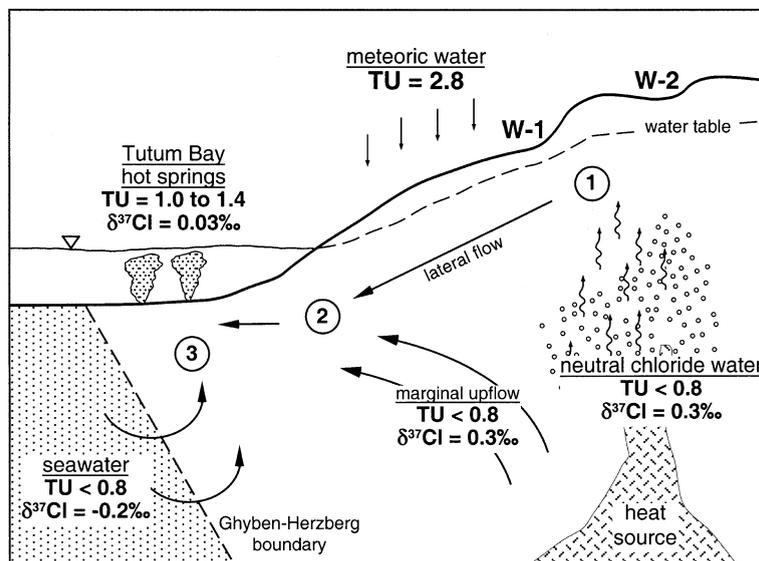


Fig. 5. Hypothetical cross-section through the Tutum Bay hydrothermal system, based on ^3H and $\delta^{37}\text{Cl}$. TU stands for tritium units. The circled numbers (1, 2 and 3) indicate the approximate location of subsurface reaction zones: (1) Formation of a steam heated bicarbonate water, (2) gravity driven lateral flow and mixing with marginal upflow from deep reservoir neutral chloride water, and (3) possible mixing with seawater near the Ghyben-Herzberg boundary. Similar flow patterns are common in most hydrothermal systems (e.g., Figs. 1 and 2 in Henley and Ellis, 1983).

(Fournier, 1979; Giggenbach, 1988) were between 246 and 273 °C. This overall range in temperatures is not surprising considering that most problems in the use of geothermometers arise from application to unsuitable samples. Different geothermometers, however, record different equilibria and disagreement does not immediately eliminate the use of one or the other. Careful application and evaluation of calculated temperatures can provide important clues to the overall hydrology of the hydrothermal system. In Tutum Bay the calculated temperatures represent three different stages of the hydrothermal system. The chalcedony temperatures represent discharge conditions, the Na/Li temperatures represent formation of a CO_2 -rich water and the Na/K temperatures represent the conditions in the deep reservoir (Pichler et al., 1999). The reservoir temperatures obtained in this study by use of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ thermometers are in good agreement with those of the Na/Li thermometer and support the formation of a bicarbonate water at a temperature of approximately 150–160 °C.

Oxygen and deuterium isotopes in combination with oxygen and sulfur isotopes of sulfate helped to further strengthen the assumption that the on-land

samples W-1 and W-2 represent the deep reservoir hydrothermal fluid. Initially these samples were classified as deep reservoir based on a combination of thermometry calculations and their position in the $\text{HCO}_3\text{--Cl--SO}_4$ ternary diagram (Pichler et al., 1999, Fig. 15). Oxygen and deuterium isotopes show a shift from the weighted annual mean of meteoric water towards the field of andesitic water (Fig. 3), which is as expected for deep reservoir hydrothermal fluid (Giggenbach, 1992). Temperatures calculated for W-2 with the oxygen (Mizutani and Rafter, 1969) and sulfur (D'Amore and Panichi, 1987) isotope thermometers indicate reservoir temperatures of 355 °C and 368 °C, respectively. It is particularly reassuring that both thermometers give approximately the same temperature, which would indicate that equilibrium has been reached. These temperatures although about 30–40 °C higher than those calculated by the element ratio thermometers (Pichler et al., 1999) most likely indicate the true reservoir temperature, because re-equilibration is slow.

The intermediate ^3H values (between local meteoric precipitation and deep reservoir hydrothermal fluid) of Tutum Bay hydrothermal is consistent with

the previous conclusion that there is a component of marginal upflow of deep reservoir hydrothermal fluid in the Tutum Bay hydrothermal fluid (Fig. 5). Chloride isotopes show a similar behavior, but due to the relatively large analytical error $\delta^{37}\text{Cl}$ is not as useful as ^3H .

The analyses of strontium isotopes proved extremely valuable in support of the zero-Mg end member approach taken by Pichler et al. (1999). The end member strontium isotopes were virtually identical to those of local volcanic rocks, which clearly supports the assumption of a zero-Mg hydrothermal end member.

Although the chemical and isotopic composition of all Tutum Bay vents is quite alike, compared to area A, area B vents have higher K, Rb, Sb, Cs, Tl, and As and lower Ca, Li, Mn, Fe, and Sr concentrations (Table 1). This seems to be directly related to the composition of samples W-1 and W-2 that also have elevated concentrations of K, Rb, Sb, Cs, Tl, and As and lower Ca, Li, Mn, Fe, and Sr concentrations (Table 1). Thus the slight chemical difference in area A and B vents may be attributed to a larger subsurface addition of a deep reservoir hydrothermal fluid similar in composition to W-1 and W-2. This can also be seen in the ^3H data. Tritium is slightly lower in the vent from Area B (V-4a) (Table 3), which would indicate a larger amount of deep reservoir hydrothermal fluid relative to Area A vent (V-1).

7. Summary and conclusions

Compared to seawater, the hydrothermal fluids in Tutum Bay have lower values for δD , $\delta^{18}\text{O}$, $\delta^{13}\text{C}$, ^{87}Sr , $\delta^{34}\text{S}(\text{SO}_4)$ and $\delta^{18}\text{O}(\text{SO}_4)$ and higher values for ^3H and $\delta^{37}\text{Cl}$. The $\delta^{18}\text{O}$ and δD records for vents 1 and 4, sampled over a 6-year period, indicate that isotopic fluid compositions remained stable for that period of time. Interpretation of isotope data clearly demonstrates the predominantly meteoric origin of Tutum Bay hydrothermal fluids, despite their location in a marine environment. $\delta^{18}\text{O}$ and δD values are identical to mean average annual precipitation in eastern Papua New Guinea. The hypothesis that these fluids are a simple product of mixing between seawater and onshore hydrothermal fluids from the Waramung (W-1) and Kapkai (W-2) thermal areas has

been rejected, because $\delta^{37}\text{Cl}$, ^3H , $\delta^{34}\text{S}(\text{SO}_4)$ and $\delta^{18}\text{O}(\text{SO}_4)$ values cannot be explained by a simple mixing model. The application of $\delta^{18}\text{O}(\text{SO}_4)$ and $\delta^{13}\text{C}$ thermometers in combination with ^3H and $\delta^{37}\text{Cl}$ values is consistent with the three-step model of Pichler et al. (1999), where (1) phase separation in the deep reservoir beneath Ambitle Island produces a high temperature vapor that rises upward and subsequently reacts with cooler ground water to form a low pH, CO_2 -rich water of approximately 150–160 °C, (2) caused by the steep topography, this CO_2 -rich fluid moves laterally towards the margin of the hydrothermal system where it mixes with the marginal upflow of the deep reservoir fluid. This produces a dilute chloride/bicarbonate water of approximately 165 °C, and (3) the entrainment of minor amounts of ground or seawater during its final ascent.

The actual end member isotopic composition of Tutum Bay vent fluids may be slightly different from the values reported in Tables 2 and 3, because of phase separation during ascent from the shallow reservoir and the Mg-correction for seawater contamination. Single-step phase separation during flashing of a liquid from 160 to 100 °C produces approximately 12% vapor, which would represent the maximum error for those isotopes that preferentially remain in the liquid phase.

The gas phase present in Tutum Bay is predominantly of magmatic/mantle origin with a minor contribution from subducted sediments. Carbon dioxide and methane are apparently in chemical equilibrium with a liquid phase in the deep reservoir, although $\delta^{13}\text{C}$ isotopic equilibrium has not been attained.

The division into area A and B, based initially on geographic location, was reinforced by ^3H and to a lesser degree by $\delta^{37}\text{Cl}$ composition. Although the isotopic composition of all Tutum Bay vent waters is quite alike, compared to area A, area B has lower ^3H and higher $\delta^{37}\text{Cl}$ values (Tables 2 and 3). This seems to be directly related to the composition of sample W-2 that has lower ^3H and higher $\delta^{37}\text{Cl}$ concentrations (Tables 2 and 3). This slight, but significant, chemical difference between area A and B may be attributed to a varying subsurface addition of deep reservoir fluid.

Overall the analyses of oxygen ($\delta^{18}\text{O}$), hydrogen (δD) and strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) isotopes proved extremely useful and helped to confirm previous

work at Tutum Bay. Based on observations at Tutum Bay it emerges that the combination of elemental and isotopic data is a necessary approach to study submarine hot springs in a near-shore environment. The use of sulfur ($\delta^{34}\text{S}$) and oxygen ($\delta^{18}\text{O}$) in sulfate, chlorine ($\delta^{37}\text{Cl}$), carbon ($\delta^{13}\text{C}$) and tritium (^3H) was limited to qualitative interpretations. This was caused by a combination of several factors, such as, analytical precision and inadequate sampling (e.g., not to measure sulfide in the field). On a qualitative level, however, they were useful to unravel the subsurface and mixing history of the Tutum Bay hydrothermal fluids. Thus future studies of shallow-water hydrothermal systems should include their analysis. For example, if $\delta^{37}\text{Cl}$ varies by more than 1–2‰ between mixing partners then this isotope would be an excellent candidate for mixing calculations.

Acknowledgments

I am grateful to Donna Switzer and Yannick Beaudoin for help underwater, to Dieter Buhl for the strontium isotope analyses and to Bernhard Mayer for the isotopic analyses of sulfate. Thanks to Philip Tolain and all the friendly people of Ambitle Island for their hospitality. Thanks for two excellent reviews by Ray Binns and Johan Varekamp.

References

- Barnes, I., Kistler, R.W., Mariner, R.H., Presser, T.S., 1981. Geochemical evidence on the nature of the basement rocks of the Sierra Nevada, California. U.S. Geological Survey Professional Paper 2181, 13 pp.
- Bishoff, J.L., Dickson, F.W., 1975. Seawater basalt interaction at 200 °C and 500 bars: implications for the origin of seafloor heavy metal deposits and the regulations of seawater chemistry. *Earth and Planetary Science Letters* 25, 385–397.
- Botz, R., et al., 1996. Hydrothermal gases offshore Milos Island, Greece. *Chemical Geology* 130, 161–173.
- Buhl, D., et al., 1991. Nature and nurture: environmental isotope story of the river Rhine. *Naturwissenschaften* 78, 337–346.
- Chuck, R.T., 1967. Groundwater resources development on tropical islands of volcanic origin. *Int. Conf. Water for Peace*, Washington, D.C., pp. 963–970.
- Cioni, R., D'Amore, F., 1984. A genetic model for the crater fumaroles of Vulcano Island (Sicily, Italy). *Geothermics* 13 (4), 375–384.
- Clark, I.D., Fritz, P., 1997. *Environmental Isotopes in Hydrogeology*. Lewis Publishers, Boca Raton, 328 pp.
- Craig, H., 1961. Isotopic variations in meteoric waters. *Science* 133, 1702–1703.
- Craig, H., 1966. Isotopic composition and origin of the Red Sea and Salton Sea geothermal brines. *Science* 154, 1544–1548.
- D'Amore, F., Panichi, C., 1987. Geochemistry in geothermal exploration. In: Economides, M., Ungemach, P. (Eds.), *Applied Geothermics*. Wiley and Sons, New York, pp. 69–89.
- Eastoe, C.J., Guilbert, J.M., 1992. Stable chlorine isotopes in hydrothermal processes. *Geochimica et Cosmochimica Acta* 56 (12), 4247–4255.
- Eastoe, C.J., Guilbert, J.M., Kaufmann, R.S., 1989. Preliminary evidence for fractionation of stable chlorine isotopes in ore-forming hydrothermal systems. *Geology* 17 (3), 285–288.
- Edmond, J.M., et al., 1979. Ridge crest hydrothermal activity and the balances of the major and minor elements in the ocean: the Galapagos data. *Earth and Planetary Science Letters* 46, 1–18.
- EGGENKAMP, H.G.M., 1994. The geochemistry of chlorine isotopes. PhD Thesis. Universiteit Utrecht, Utrecht, 150 pp.
- Ellis, A.J., Mahon, W.A.J., 1977. *Chemistry and Geothermal Systems*. Academic Press, New York, 392 pp.
- Fournier, R.O., 1977. Chemical geothermometers and mixing models for geothermal systems. *Geothermics* 5, 41–50.
- Fournier, R.O., 1979. A revised equation for the Na/K geothermometer. *Geothermal Research Council Transactions* 3, 221–224.
- Friedman, I., O'Neil, J.R. (Eds.), 1977. *Compilation of stable isotope fractionation factors of geochemical interest*. Data of Geochemistry, vol. 440-KK. U.S. Geological Survey Professional Paper, Washington, 12 pp.
- Giggenbach, W.F., 1982. Carbon-13 exchange between CO_2 and CH_4 under geothermal conditions. *Geochimica et Cosmochimica Acta* 46, 159–165.
- Giggenbach, W., 1988. Geothermal solute equilibria. Derivation of Na–K–Mg–Ca geoindicators. *Geochimica et Cosmochimica Acta* 52, 2749–2765.
- Giggenbach, W.F., 1991. Chemical techniques in geothermal exploration. In: D'Amore, F. (Ed.), *Application of Geochemistry in Geothermal Reservoir Development*. UNITAR/UNDP, Rome, pp. 252–270.
- Giggenbach, W.F., 1992. Isotopic shifts in waters from geothermal and volcanic systems along convergent plate boundaries and their origin. *Earth and Planetary Science Letters* 113, 495–510.
- Giggenbach, W.F., 1997. The origin and evolution of fluids in magmatic-hydrothermal systems. In: Barnes, H.L. (Ed.), *Geochemistry of Hydrothermal Ore Deposits*. Wiley, New York, pp. 737–796.
- Giggenbach, W.F., Goguel, R.L., 1989. *Collection and Analysis of Geothermal and Volcanic Water and Gas Discharges*, 2401. Institute of Nuclear and Geological Sciences, New Zealand.
- Giggenbach, W.F., Matsuo, S., 1991. Evaluation of results from second and third IAVCEI Field Workshops on Volcanic Gases, Mt. Usu, Japan, and White Island, New Zealand. *Applied Geochemistry* 6, 125–141.

- Giggenbach, W.F., Hedenquist, J.W., Houghton, B.F., Otway, P.M., Allis, R.G., 1989. Research drilling into the volcanic hydrothermal system on White Island, New Zealand. EOS (Transactions-American Geophysical Union) 70, 98–109.
- Hedenquist, J.W., 1990. The thermal and geochemical structure of the Broadlands-Ohaaki geothermal system, New Zealand. *Geothermics* 19, 151–185.
- Henley, R.W., Ellis, A.J., 1983. Geothermal systems ancient and modern: a geothermical review. *Earth-Science Reviews* 19, 1–50.
- Henley, R.W., Truesdell, A.H., Barton, P.B.J., 1984. Fluid-mineral equilibria in hydrothermal systems. *Reviews in Economic Geology*, vol. 1. Society of Economic Geologists, 267 pp.
- Hoefs, J., 1997. *Stable Isotope Geochemistry*. Springer, Berlin, 202 pp.
- IAEA/WMO, 1998. Global Network for Isotopes in Precipitation. The GNP Database. Release 3, October 1999. URL: <http://isohis.iaea.org>.
- Kharaka, Y.K., Lico, M.S., 1982. Chemical geothermometers applied to formation waters, Gulf of Mexico and California basins. *American Association of Petroleum Geologists Bulletin* 66, 588–598.
- Kiryukhin, A.V., Takahashi, M., Polyakov, A.Y., Lesnykh, M.D., 1998. Investigation of recharge of Mutnovsky geothermal field with use the isotope oxygen (O^{18}), hydrogen (D) and tritium (T) data. 23RD Stanford Geothermal Conference, Stanford, California, pp. 226–233.
- Licence, P.S., Terrill, J.E., Fergusson, L.J., 1987. Epithermal gold mineralization. Ambitle Island, Papua New Guinea, Pacific Rim Congress 87. Australasian Institute of Mining and Metallurgy, Gold Coast, Queensland, pp. 273–278.
- Long, A., et al., 1993. High-precision measurement of chlorine stable isotope ratios. *Geochimica et Cosmochimica Acta* 57 (12), 2907–2912.
- Lyon, G.L., Hulston, J.R., 1984. Carbon and hydrogen isotopic compositions of New Zealand geothermal gases. *Geochimica et Cosmochimica Acta* 48 (6), 1161–1171.
- Mayer, B., Fritz, P., Prietzel, J., Krouse, H.R., 1995. The use of stable sulfur and oxygen isotope ratios for interpreting the mobility of sulfate in aerobic forest soils. *Applied Geochemistry* 10 (2), 161–173.
- Mizutani, Y., Rafer, T.A., 1969. Oxygen isotopic fractionation in the bisulfate ion-water system. *New Zealand Journal of Science*, 54–59.
- Nahm, G.-Y., 1966. Geology and groundwater resources of volcanic island, Cheju-do. *Geology and Ground-Water Resources* 3, 109–133.
- Nicholson, K., 1992. *Geothermal Fluids*. Springer Verlag, 266 pp.
- Pauwels, H., Fouillac, C., Goff, F., Vuataz, F.-D., 1997. The isotopic and chemical composition of CO_2 -rich thermal waters in the Mont-Dore region (Massif-Central, France). *Applied Geochemistry* 12 (4), 411–427.
- Pichler, T., Dix, G.R., 1996. Hydrothermal venting within a coral reef ecosystem, Ambitle Island, Papua New Guinea. *Geology* 24 (5), 435–438.
- Pichler, T., Veizer, J., Hall, G.E.M., 1999. The chemical composition of shallow-water hydrothermal fluids in Tutum Bay, Ambitle Island, Papua New Guinea and their effect on ambient seawater. *Marine Chemistry* 64 (3), 229–252.
- Poorter, R.P.E., Varekamp, J.C., Poreda, R.J., van, B.M.J., Kreulen, R., 1991. Chemical and isotopic compositions of volcanic gases from the East Sunda and Banda arcs, Indonesia. *Geochimica et Cosmochimica Acta* 55 (12), 3795–3807.
- Sedwick, P., Stüben, D., 1996. Chemistry of shallow submarine warm springs in an arc-volcanic setting: vulcano Island, Aeolian Archipelago, Italy. *Marine Chemistry* 53, 146–161.
- Taylor, C.B., 1977. Tritium enrichment of environmental waters by electrolysis: development of cathodes exhibiting high isotopic separation and precise measurement of tritium enrichment factors. *International Conference of Low-Radioactivity Measurements and Applications, Slovenski Pedagogicke Nakladatelstvo, Bratislava*, pp. 131–140.
- Vuataz, F.-D., Goff, F., 1986. Isotope geochemistry of thermal and non-thermal waters in the Valles Caldera, Jemez Mountains, Northern New Mexico. *Journal of Geophysical Research* 91 (B2), 1835–1853.
- Vuataz, F.-D., Goff, F., Fouillac, C., Calvez, J.-Y., 1988. A strontium isotope study of the VC-1 core hole and associated hydrothermal fluids and rocks from Valles Caldera, Jemez Mountains, New Mexico. *Journal of Geophysical Research* 93 (B6), 6059–6067.
- Wallace, D.A., et al., 1983. Cainozoic volcanism of the Tabar, Lihir, Tanga, and Feni islands. Papua New Guinea: geology, whole-rock analyses, and rock-forming mineral compositions, vol. 243. Bureau of Mineral Resources Geology and Geophysics, Canberra.
- Welhan, J.A., 1988. Origins of methane in hydrothermal systems. *Chemical Geology* 71, 183–198.