

Geochemistry of geothermal manifestations around Inielika volcano, central Flores, Indonesia

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Abstract: Surface water manifestations in the vicinity of the Inielika volcano complex have been investigated by the geochemical analysis of samples obtained from spring and river waters located on an almost straight line connecting the summit of the volcano, manifestations at lower altitudes in the Gou area and manifestations at still lower altitudes in the Mengeruda area with a maximum distance about 12 km east of the volcano. All water samples have been analyzed for major and trace elements.

The concentrations of major, trace and rare-earth elements of the water geothermal manifestations are temperature and pH dependences. They are also controlled by the nature of the complexation ligands, the patterns of the original primary minerals in rock that is subject to leaching or dissolution, glass and magmatic minerals, the dominant phases that control REE behaviour in volcanic areas, fractionation of secondary minerals during rock alteration, and a combination of mechanisms, which can be easily envisaged under natural conditions.

1. Introduction

Surface manifestations of volcanic-hydrothermal systems generally consist of steaming grounds, boiling mud pools or acid spring or gas emissions at the summit of volcano that are enriched in SO₂, H₂S, HCl and CO₂ (e.g., Giggenbach and Soto, 1992). Sometimes the manifestations appear as acid crater lakes fed by fumaroles, in the cases at Ijen volcano in East Java (Delmelle *et al.*, 2000) and Patuha volcano in West Java (Sriwana *et al.*, 2000). The composition of such waters is generally considered to be controlled by magmatic degassing of volatiles. Springs on the flanks of volcanoes often show a succession of water types, whereby acid water is discharged at higher altitudes and more neutral water at lower levels. In many cases, there are relations on the mixing of acid fluid with a magmatic component and neutral water of meteoric origin.

This report presents the results of the geochemical study of water manifestations around the Inielika volcano complex. The area shows a diversity of manifestations ranging from acid hot springs to neutral waters. Principal objectives of this work were to determine the chemical nature of the waters, identify their mutual relations and origin, and assess the extent to which a chemical equilibrium was reached with respect to major rock-forming

minerals. For this purpose, water samples were collected in June 2000 for the entire central part and eastern foothills of the volcano and analyzed for major and trace elements using various techniques.

2. Geological setting and history of volcanic activity

The study area comprises the Inielika volcano and its surroundings near Bajawa in the Ngada District, central Flores (Fig. 1). The area is situated at 120°58'00"E - 121°07'30"E and 08°40'09"S - 08°45'00"S covering approximately 190 km².

Inielika belongs to the row of active volcanoes in Flores, which are predominant in andesitic lava and pyroclastic flows affinity and eastern part of the Lesser Sunda Arc. Other Quaternary volcanoes in the vicinity of Inielika are Inierie and Ebulobo.

According to historical records, Inielika volcano has erupted three times, in 1905, 1908, and most recently in 2001. In November 1905, a sudden explosive eruption occurred. The eruption was probably a phreatic explosion. Akbar (1984 in Alzwar 1990) recognized mud and tephra deposits, which were supposedly generated by the phreatic character of the eruption. Kemmerling (1929) documented that a gas eruption occurred in 1908. Steam explosions have been observed in several places producing gas, ash and fragments of (altered) rocks, which damaged

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Keywords: geothermal manifestation; water type; major element; trace element; rare earth elements

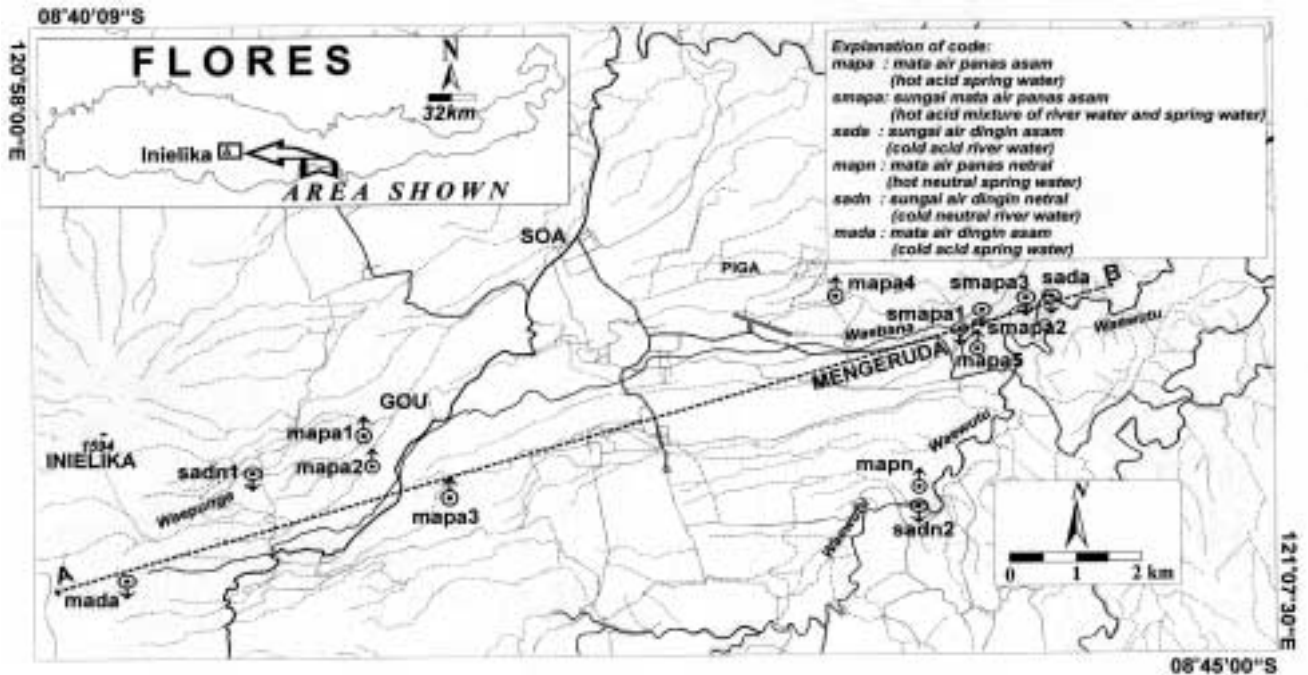


Fig. 1 Field setting and sample locations.

the vegetation in the vicinity. Trees around the crater were burnt.

Information on the most recent eruption of Inielika on January 11 - 16, 2001 has been given in VSI's weekly Report No. 599 (January 16 - 22, 2001). An ash explosion reached an altitude of 100 - 1000 m above the volcano. Two new craters trending SE-NW were formed. The SE crater has a 10 m deep hole with diameter of 50 m. The bottom of the crater is 25 m in diameter and closed. An ash plume appeared from the northern crater wall and was blown away to the south. The NW crater has a diameter of 20 m and depth of 1.10 m. The crater bottom is closed. An ash plume was ejected vertically.

The erupted material contains light-grey ash and lapilli. It fell as far as 500 m from the eruption point. The fumarolic temperature was 95 °C whereas the ground temperature near the fumarole location was 89 °C.

3. Analytical methods

3.1 Field methods

Field data on the manifestations of the Inielika volcano complex, which included observations in the Gou and Mengeruda areas on the eastern flank of the volcano, were compiled in June 2000.

Visual characteristics of the water manifestations were documented and some physical properties were directly measured in the field including water and air temperatures (by thermocouple EIRELEC, LTD, range -65 to 1150 °C), water flow rates and pH of the waters (by HANNA INSTRUMENT, type HI

8424 MICROCOMPUTER pH meter).

Water samples were collected and prepared for analysis following the procedures outlined in Mahon (1977). Each water sample consisted of three bottles. One 200 ml bottle of original untreated water was taken for the measurement of conductivity and the bicarbonate concentration. For other purposes, the water was directly filtered in the field through 0.45 µm millipore filters. One 100 ml bottle was kept for analysis of the major anions and one 100 ml bottle was acidified by HNO₃ conc. until a pH of 2 was reached, which was tested by universal pH paper. The bottles were marked with the location, name of the manifestation and information on the sample treatment.

3.2 Laboratory methods

Conductivity of the original water sample was measured with a conductivity meter (CHEMTRIX, TYPE 700, HILLSBORO OERE USA, range 0 - 20000 (µS/cm), and bicarbonate contents were determined by titration based on an acidic-basic solution method (pH 4.2 alkalinity). Both determinations were conducted in the VSI laboratory in Bandung.

Other chemical components were analyzed between January and April, 2001 using different techniques at the Laboratory of Chemical Analysis, Faculty of Earth Sciences, Utrecht University.

Concentrations of the major anions fluoride (F⁻), chloride (Cl⁻), bromide (Br⁻) and sulfate (SO₄²⁻) were determined by ion chromatography (IC) using a Dionex Dx-120 instrument.

The system was optimized for analyzing concen-

trations within the range of 0 - 8 mg/kg for F⁻, 0 - 200 mg/kg for Cl⁻, 0 - 25 mg/kg for Br⁻ and 0 - 500 mg/kg for SO₄²⁻.

Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) was used to determine the concentrations of major cations and some minor elements: Al, B, Ba, Co, Cu, Fe, K, Li, Mg, Mn, Na, Ni, S, Si, Sr, V and Zn.

Trace elements, in particular the rare earth elements (REE) were determined by ICP-MS because this instrument has lower detection limits and is more sensitive than the ICP-AES technique. The complete spectrum of REE was analyzed including the light rare earth elements (LREE) La, Ce, Pr, Nd, Sm, and Eu, and heavy rare earth elements (HREE) Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu.

ICP-MS analyses were performed after data on major cations, anions and conductivity were available for each sample, based on IC and ICP-AES analysis. The total concentration of all elements in a single sample could be around 100 - 200 mg/kg. If necessary, samples were diluted with a volume of distilled water up to 10 ml which was acidified with ultra-pure nitric acid.

4. Results

4.1 Sampling locations and field data

Thirteen water manifestations in the area of Inielika volcano, distributed between the volcano summit and the areas of Gou, Piga and Mengeruda to the east (Fig. 1) were investigated and water samples were collected from all these locations. Elevations range between 1405 m a.s.l. at the summit of Inielika to 275 m a.s.l. in the Mengeruda area.

The sampling sites are from high to low elevations as follows:

1. Inielika summit area: one sample of acid water from a cold spring (*mada*)
2. Gou area: three samples of acid water from hot springs (*mapa1, mapa2, mapa3*)
3. Gou area: one sample of neutral cold water from Waepunga river (*sadn1*)
4. Mengeruda area: two samples of acid water from hot springs (*mapa4, mapa5*)
5. Mengeruda area: three samples of hot water from the Waebana river, representing mixtures of hot-spring and river water (*smapa1, smapa2, smapa3*)
6. Mengeruda area: one sample of neutral water from a hot spring near Waewutu river (*mapn*)
7. Mengeruda area: one sample of neutral cold water from Waewutu river (*sadn2*)
8. Mengeruda area: one sample of acid cold water from Waewutu river after the confluence with Waebana river (*sada*)

Field data are compiled in Table 1. Maximum temperatures of 47.3 °C were observed in the acid springs of the Gou area, where pH values range between 2.7 and 3.7. The acid hot springs in the Mengeruda area have similar characteristics (T=41 - 44 °C and pH=3.2 - 3.4) as those of the Gou group. The pH of samples that represent mixtures of the Waebana river and hot springs is similar (3.4) to that of the acid hot springs in the area, whereas temperatures are somewhat lower (32.5 - 42.5 °C). The influence of the Waebana river water on the characteristics of the Waewutu river is clearly observed at the *sada* location after the confluence where the pH of the originally neutral Waewutu water (pH=6.6) dropped to a value of 4.5.

In terms of temperature and acidity, the water from the spring in the summit area of Inielika (*mada*) is an exception, as it is the only acid (pH=3.9) spring water that is not warm (T=19.1 °C).

4.2 Laboratory data

Major and trace element contents of all water samples are given in Table 1.

4.2.1 Major element contents

Only the neutral samples showed measurable bicarbonate contents (obtained in June 2000 in the Bandung Laboratory) whereas bicarbonate was not detected in the other samples.

Concentrations of the other anions F, Cl, Br, and SO₄ (Table 1) largely correlate with pH, as they are highest in the most acid waters, with maximum values being observed in one of the Gou springs (1737 mg/kg sulfate, 339 mg/kg chloride, 3.2 mg/kg fluoride and 0.54 mg/kg bromide). The acid Inielika spring is an exception because it only shows relatively high sulfate concentrations (653 mg/kg), whereas the other anions, including chloride, are low.

A plot of the concentrations in the Cl-SO₄-HCO₃ triangle diagram of Giggenbach (1988) shows that all hot spring waters can be classified as sulfate-type except for the only neutral hot spring (*mapn*) in the Mengeruda area, which has a typical bicarbonate nature (Fig. 2).

Plots of chloride and fluoride against sulfate (Figs. 3 and 4) show good correlations for the hot-spring and spring-fed river waters. Highest values are observed in two samples of the Gou springs. The S-Cl and S-F correlations suggest that trends in the direction of waters are influenced by magma-derived components.

The concentrations of major cations tend to correlate with pH and/or temperature. The SiO₂ contents (calculated from Si concentrations as produced by the ICP-AES technique) range between 93 and 150 mg/kg. As illustrated in Figs. 5 and 6, the highest

Table 1 Field data and composition of water samples. nd: not detected, <dl: below detection limit.

Sample Code	Ap1 mapa1	Ap2 mapa2	Ap3 mapa3	Ap4 mapa4	Ap5 mapa5	Ap6 mapa6	Ad1 mada	Ad2 sada1	Ad3 smapa1	Ad4 smapa2	Ad5 smapa3	Ad6 sada
Elev. (m)	740	750	718	400	325	350	1405	975	325	320	280	275
T (°C)	34.5	41.8	47.3	41.4	44.0	43.5	19.1	22.1	32.5	41.5	42.5	24.7
pH	3.7	3.0	2.7	3.2	3.4	7.1	3.9	6.6	3.4	3.4	3.4	4.5
EC (µmhos/cm)	1050	2600	4600	1700	1650	490	1100	300	1630	1660	1520	760
HCO ₃ (mg/kg)	nd	nd	nd	nd	nd	237	nd	100	nd	nd	nd	nd
IC (mg/kg) :												
F	1.0	1.5	3.2	1.0	0.9	<dl	<dl	<dl	1.1	1.0	1.0	1.5
Cl	26	131	339	90	99	3.0	1.6	1.4	90	91	90	39
Br	<dl	<dl	0.54	<dl	<dl	<dl	<dl	<dl	<dl	<dl	<dl	<dl
SO ₄	442	897	1737	600	597	23	653	61	572	571	577	222
ICP-AES : (mg/kg)												
Al	5.6	42	105	22	25	nd	64	nd	22	25	23	2.8
Ca	112	148	167	106	102	39	98	29	105	104	102	54
K	6.8	15	28	14	16	7.6	1.8	3.6	15	16	15	8.2
Mg	25	40	45	31	32	17	5.9	10	32	33	32	19
Na	27	51	64	39	47	29	13	11	43	46	45	25
S	153	299	539	200	198	8	219	20	188	190	189	79
SiO ₂	107	150	142	138	144	127	144	106	140	147	143	106
Sr	0.2	0.43	0.66	0.26	0.22	0.16	0.35	0.09	0.21	0.22	0.22	0.14
Fe	0.96	7.7	9.5	15.8	8	nd	nd	nd	9.5	13.5	12.5	2.3
As	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
ICP-MS : (µg/kg)												
Li	21	18	28	27	36	8.4	48	7.9	25	25	24	6.7
B	354	1257	2757	945	1230	125	128	46	974	1116	1123	423
Ti	78	123	210	103	109	50	99	45	97	101	101	60
Mn	540	1085	1560	736	760	0.3	170	0.1	1078	896	960	388
Co	0.20	0.07	0.16	0.17	0.15	nd	102	0.00	3.00	1.30	1.50	0.63
Ni	3.4	nd	nd	2.1	2.4	nd	184	0.94	2.6	0.9	2.1	nd
Cu	2.4	13	6.9	1.8	3.3	0.97	252	0.44	6.2	2.6	2.9	3
Zn	6.4	67	105	36	42	2.2	147	0.53	36	38	37	16
Rb	28	64	96	51	65	36	15	15	54	61	60	33
Sr	223	461	775	276	242	176	356	88	234	241	248	164
Zr	nd	nd	0.19	nd	nd	nd	nd	nd	0.48	nd	nd	nd
Nb	0.02	0.01	0.26	0.04	0.01	0	0.01	0	0.11	0.02	0.02	0.01
Mo	0.05	0.1	0.41	0.12	0.03	1.83	0.06	0.89	0.37	0.05	0.12	0.24
Cd	0.03	nd	0.07	nd	nd	0.01	1.6	nd	0.07	nd	nd	nd
Sn	nd	nd	0.1	nd	nd	0.01	nd	0	0	nd	0	0.03
Sb	0.0	0.0	0.1	0.0	nd	0.16	0.0	0.1	0.1	0.0	0.0	0.07
Ba	21	24	31	22	20	1.3	8.9	12	16	17	21	17
La	0.33	5.86	24.13	1.54	0.33	0.003	4.73	0.000	2.07	1.73	1.74	0.68
Ce	0.90	13.02	45.66	4.69	0.90	0.005	14.79	0.000	6.25	5.16	5.15	1.86
Pr	0.15	1.63	5.01	0.71	0.15	0.001	2.37	0.000	0.89	0.77	0.79	0.28
Nd	0.92	7.17	18.19	3.55	0.92	0.002	12.81	0.000	4.35	3.63	3.79	1.32
Sm	0.41	1.91	3.84	0.93	0.41	nd	3.75	nd	1.23	1.09	1.06	0.36
Eu	0.14	0.56	1.11	0.31	0.29	0.000	1.17	0.001	0.39	0.3	0.32	0.12
Gd	0.77	2.55	4.29	1.30	1.38	0.001	3.72	nd	1.56	1.39	1.42	0.52
Tb	0.15	0.43	0.72	0.25	0.24	0.000	0.59	nd	0.31	0.25	0.25	0.09
Dy	0.96	2.63	4.11	1.57	1.53	0.000	3.48	nd	1.7	1.55	1.61	0.53
Ho	0.2	0.53	0.8	0.3	0.3	nd	0.67	0.000	0.37	0.31	0.32	0.1
Er	0.47	1.36	2.08	0.82	0.81	0.000	1.73	0.000	0.97	0.88	0.88	0.3
Tm	0.05	0.16	0.32	0.1	0.1	nd	0.23	nd	0.15	0.11	0.12	0.04
Yb	0.29	0.98	1.6	0.61	0.64	0.002	1.5	0.000	0.78	0.68	0.72	0.21
Lu	0.04	0.13	0.27	0.09	0.10	0.000	0.21	nd	0.14	0.12	0.10	0.03
REE (µg/kg)	5.80	38.93	112.12	16.77	8.10	0.015	51.74	0.00177	21.16	17.99	18.26	6.43
Ta	0.012	0.015	0.122	0.02	0.017	0.003	0.017	0.004	0.051	0.015	0.02	0.008
Pb	0.32	1.09	0.98	1.82	2.88	0.14	0.44	0.012	1.43	2.12	2.08	0.51
Th	0.06	1.00	5.09	0.20	0.18	0.003	0.08	0.008	0.36	0.21	0.18	0.04
U	0.006	0.031	0.241	0.035	0.009	0.514	1.090	0.029	0.079	0.029	0.031	0.064
meq cat	9.7	18.5	27.8	13.3	13.5	4.8	13.1	2.9	13.1	13.8	13.4	6
meq an	10	22.5	45.9	15.1	15.3	4.5	13.6	2.9	14.5	14.5	14.6	5.7
IB (%)	-1.4	-9.7	-24.6	-6.4	-6.2	3.8	-2.2	-1	-5.1	-2.4	-4.3	2.2

Note : nd : not detected
<dl : below detection limit

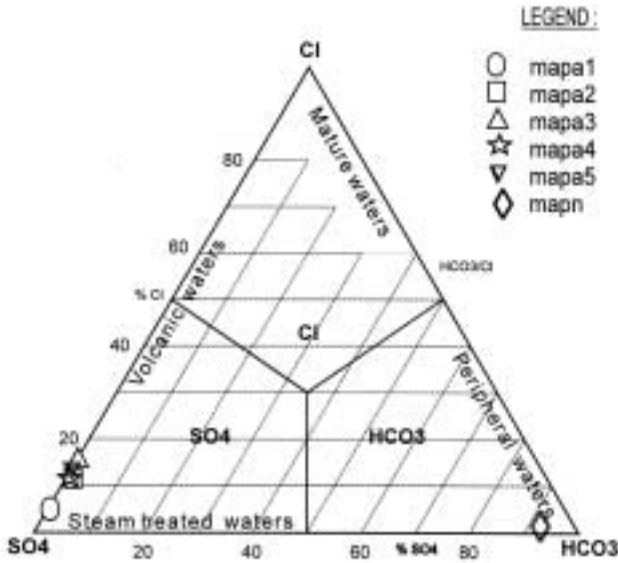


Fig. 2 Cl-SO₄-HCO₃ classification of hot springs.

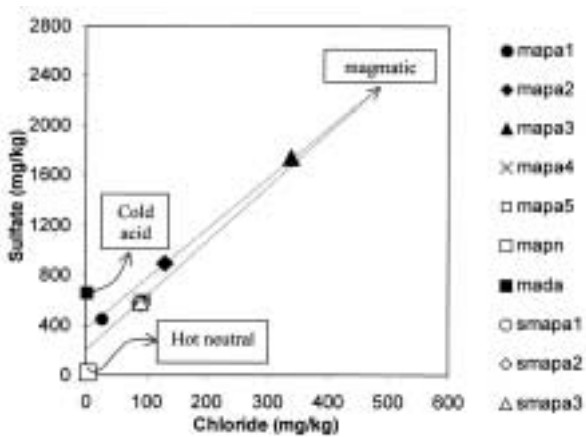


Fig. 3 Relationship of sulfate vs. chloride contents for spring waters and spring-fed river waters.

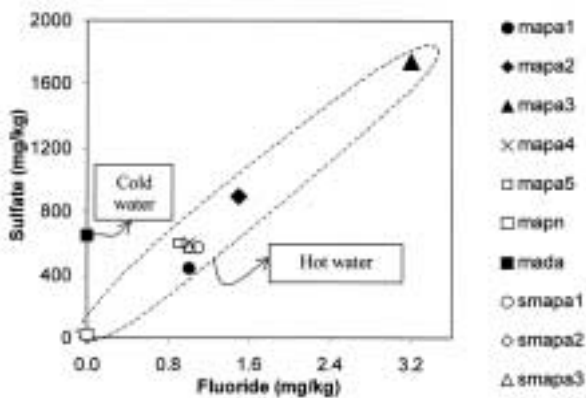


Fig. 4 Relationship of sulfate vs. fluoride contents for spring waters and spring-fed river waters.

values are found in waters with the lowest pH and highest temperatures, assuming the Inielika spring sample is ignored. The latter is relatively rich in SiO₂.

The Na-K-Mg diagram of Giggenbach (1988) shows that all waters plot in the lower right Mg-corner (Fig. 7), implying that they should be considered as immature waters.

Aluminum and iron concentrations strongly depend on pH, as can be expected (Figs. 8 and 9). Both elements were not detected in the neutral waters by ICP-AES. Interestingly, the acid Inielika spring contains a relatively high amount of Al (64 mg/kg), whereas Fe remained below the detection limit. With some exceptions, the Mengeruda and Gou waters tend to be higher in Fe and Al.

4.2.2 Trace element contents

Trace elements data, obtained by ICP-MS analysis include Li, B, Ti, Mn, Sr, Ti, Co, Ni, Cu, Zn, Rb, Zr, Nb, Mo, Cd, Sn, Sb, Ba, Pb, Th, U and the REE. Strontium was also analyzed by ICP-AES, and the results from both techniques are generally in agreement. Results are given in Table 1.

In most cases, the trace-element contents are lowest in the neutral waters (e.g. rivers and neutral hot spring *mapn*) and highest in the acid waters. Highest concentrations are generally observed in one of the acid hot springs in the Gou area (*mapa3*). Large variations exist for B (2757 µg/kg in *mapa3* against 40 µg/kg in *sadn2*), Ti (210 and 37 µg/kg), Mn (1560 and 4.9 µg/kg), Zn (105 and 14 µg/kg), Rb (96 and 13 µg/kg), Sr (775 and 90 µg/kg), Th (5.09 and 0.009 µg/kg), and the REEs. The neutral hot spring in the Mengeruda area (*mapn*) is characterized by very low concentrations of virtually all trace elements. In nearly all samples, Zr, Nb, Ta, Mo, Ni, Co, Cd, Sn and Sb show very low concentrations, often below detection limits.

In terms of trace elements, the Inielika spring (*mada*) is again an exception as it shows significantly deviating concentrations (Table 1). It has uncommonly high concentrations of Li, Co, Ni, Cu, Zn and U, which fall far outside the range observed in the other waters.

The abundances of total REEs vary between 112 µg/kg in the most acid hot spring of the Gou area (*mapa3*) and 0.002 µg/kg in the neutral Waepunga river on the flank of Inielika (*sadn1*). The neutral hot spring along Waewutu river has low REE concentrations of 0.02 µg/kg.

The REE abundances have been normalized to chondritic values and the resulting patterns are displayed in Figs. 10 and 11, where the REEs are plotted in order of increasing atomic number (LREE on the left and HREE on the right) against the logarithm of the ratio of the concentrations in sample

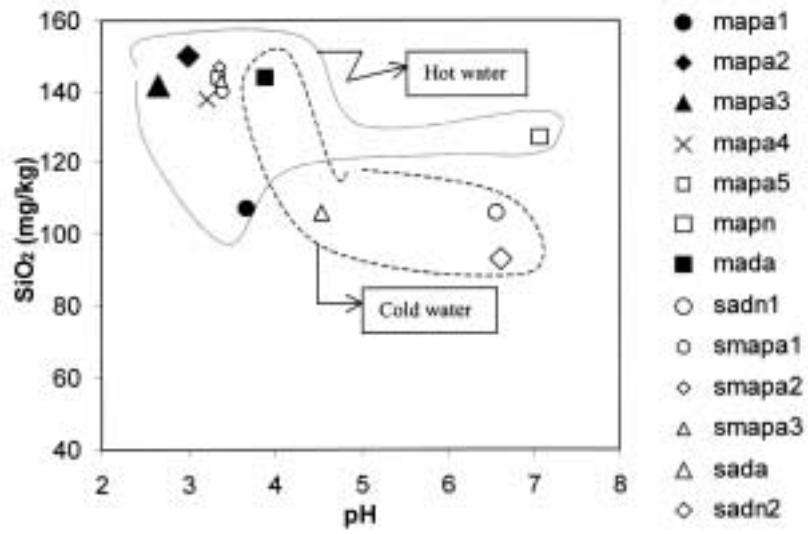


Fig. 5 Relationship of SiO₂ vs. pH for spring and river waters.

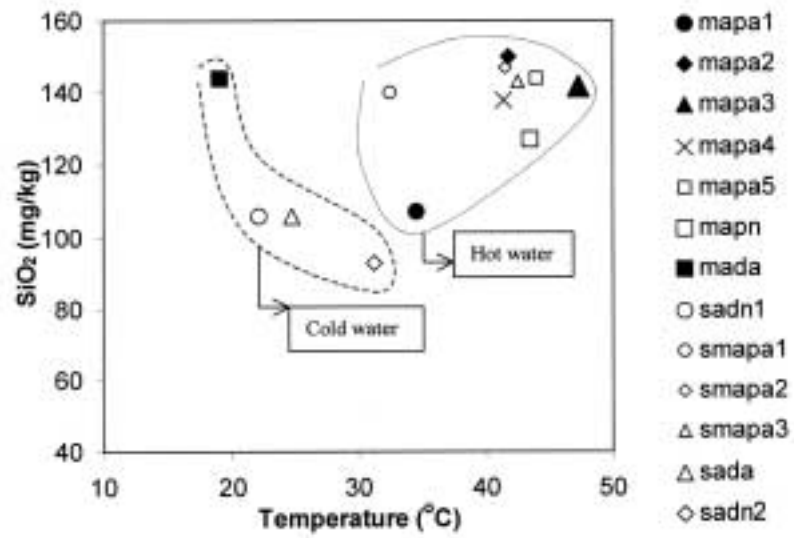


Fig. 6 Relationship of SiO₂ vs. temperature for spring and river waters.

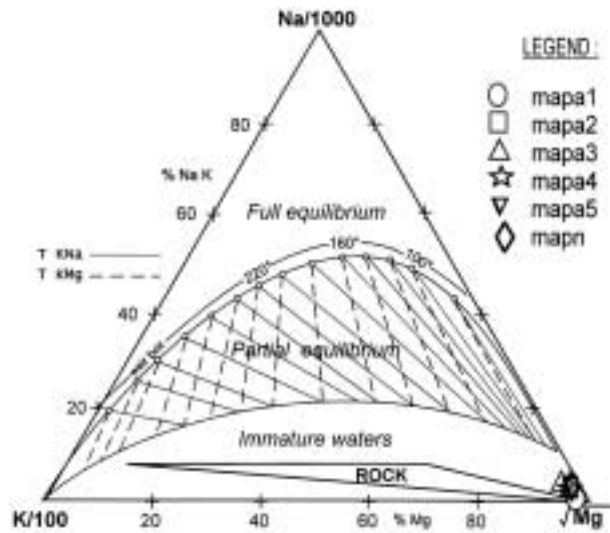


Fig. 7 Relative Na-K-Mg concentrations of hot springs.

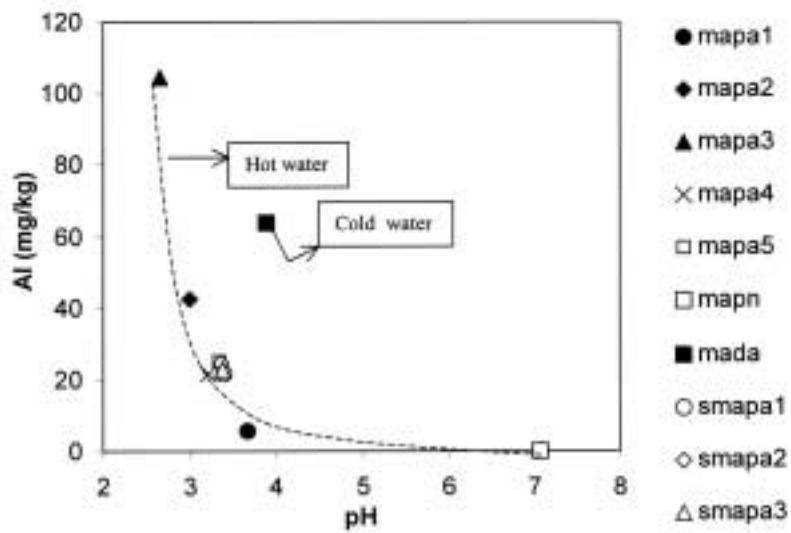


Fig. 8 Relationship of Al vs. pH for spring and spring-fed river waters.

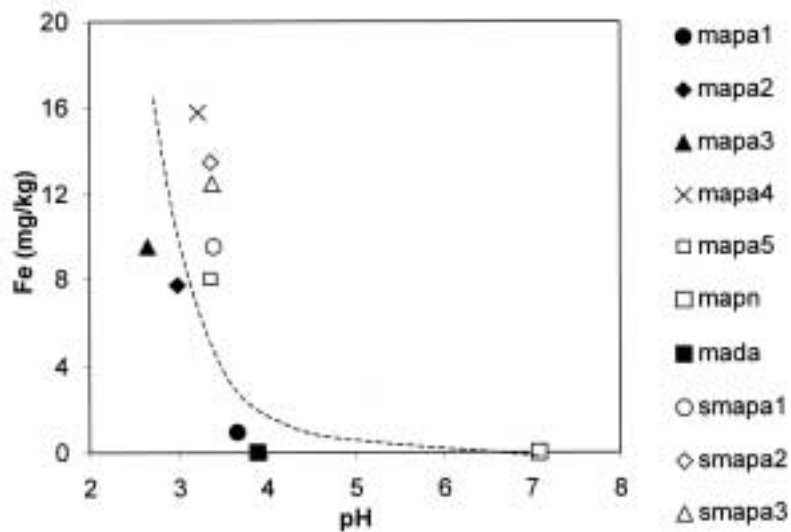


Fig. 9 Relationship of Fe vs. pH for spring and spring-fed river waters.

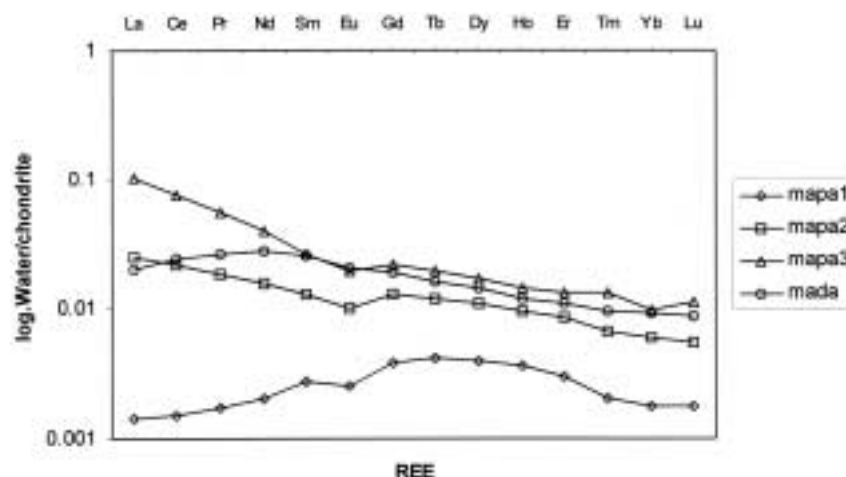


Fig. 10 REE patterns of hot and cold spring in the Gou area and from Inielika.

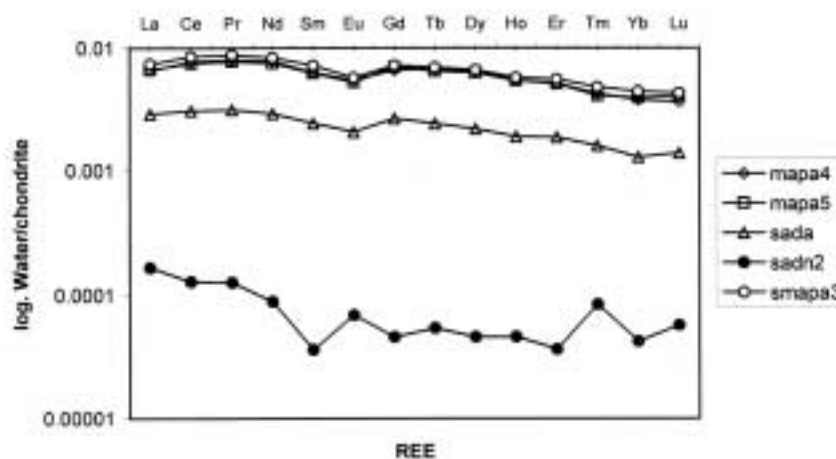


Fig. 11 REE patterns of hot spring and river waters in the Mengeruda area.

and chondrite. With the exception of the neutral sample *sadn2*, wherein REE concentrations are very low, all samples show smooth patterns proving the overall good quality of the REE data. Other neutral waters were not plotted, because the REE concentrations were too low.

The data quality was also tested by calculating the ion balance (IB), expressed in %, whereby negative values represent an excess in anions and positive values an excess in cations (Table 1). In general, deviations are smaller than 6 %.

5. Discussion

5.1 Neutral waters

The neutral waters (cold spring *sadn1*) and Waewutu river water (*sadn2*) show a very low concentration of the major element contents, except for bicarbonate (100 and 117 mg/kg) and silica (106 and

93 mg/kg). These values are common for subsurface waters that have interacted with rocks under near surface conditions.

The high bicarbonate concentration in the neutral hot spring (*mapn*), could be explained by the addition of CO₂ gas of magmatic origin (in absence of H₂S gas), oxidation of organic matter (the location is close to the rice fields) or supply of CO₂ from the air.

In other cases high bicarbonate contents can be produced by the dissolution of carbonates, but there is no evidence for the presence of carbonate rocks in the subsurface of the Inielika area.

5.2 Acid waters

All acid waters from hot springs and warm rivers in both the Gou and Mengeruda areas show similar characteristics. The acidity is largely due to sulfate but chloride and some fluoride are present as well.

Good correlations between sulfate and these halogens suggest that all these waters have a component in common. In many areas of active volcanism, S, Cl and F originate from the degassing magma at depth. Infiltration of magma-derived gas into the groundwater of meteoric origin produces acid water that sometimes occurs as acid crater lakes or acid springs. The correlations mentioned above suggest that the hot acid waters represent mixtures of acid fluids of magmatic origin with shallow neutral water of meteoric origin. The distances between the Gou and Mengeruda areas indicate that all the manifestations could be fed by one single (magmatic) hydrothermal system. The relatively low concentrations of S, Cl and F suggest that the manifestations are dominated by the meteoric component.

5.3 Inielika spring

The cold acid water of the Inielika spring near the summit (*mada*) is clearly different from other acid waters as high sulfate contents are accompanied by very low chloride and fluoride contents. This spring has the typical characteristics of steam-heated water, whereby H₂S-rich gas enters a small pond in the crater, but the low temperature suggests a prolonged cooling history or mixing with cool meteoric water.

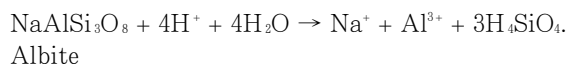
5.4 Cations

All the water samples in the Inielika complex are immature waters plotted in the Mg corner of the Na-Mg-K triangle (Fig. 7). This means the absence of an equilibrium with common Na-K minerals, which implies that the application of the cation geothermometers is not possible. The principal reason is the overall acidic nature of the waters, presumably caused by enrichment of sulfate (and to a lesser extent Cl and F) which probably has a magmatic origin. Due to the acidic conditions, cations may be released from minerals in the country rock.

The strong dependence of Al contents on the pH of the water sample in the Inielika volcano complex is consistent with many researches on natural waters in volcanic areas and elsewhere. According to Nordstrom (1982), the concentration of aluminum in neutral pH waters is commonly low because it is difficult to mobilize this element from aluminosilicate minerals. The transfer of aluminum from the rock-forming minerals to the water phase has been observed in acid mine waters, acid sulfate-bearing soil waters, acid geothermal waters, and poorly buffered lakes, streams and groundwater under relatively acidic conditions. In geothermal systems, the acidification is often produced by the oxidation of sulfur-bearing species (e.g., H₂S) producing SO₄²⁻.

Chen and Brantley (1997) studied the dissolution

rate of albite as a function of pH and temperature. At pH 1 to 4.5 (in the acid water solution), significant amounts of albite are dissolved at a temperature about 50 °C. The concentrations of Al and Na in the solution are controlled by the dissolution reaction:



In a solution of decreasing pH, the increasing abundance of hydrogen protons causes the reaction to shift to the right implying an increasing production of Na⁺, Al³⁺ and silicic acid.

As will be shown below, nearly all waters in the study area are unsaturated with respect to albite, kaolinite, and alunite ruling out the latter two reactions and those discussed by Martin *et al.* (2000). It is speculated that rock dissolution under acid conditions may be responsible for the observed Al concentrations, which would also be consistent with the REE patterns.

5.5 Rare Earth Element (REE) behavior

The REE patterns shown in Figs. 10 and 11 can be used to distinguish the origin of spring and river waters. The patterns of two of the acid hot springs in the Gou area (*mapa2* and *mapa3*) are similar in shape (Fig. 10) suggesting a common origin. In both cases, the LREE are enriched relative to the HREE. Overall higher concentrations in *mapa3* are correlated with a lower pH. Interestingly, the pattern of the third acid hot spring with the highest pH deviates not only in the overall abundances that are clearly lower but also in the LREE that are depleted. For comparison, the REE pattern of the nearby Inielika acid cold spring (*mada*) is shown as well. It is clearly different from the others with relatively low LREE abundances and only a minor LREE/HREE ratio. In all cases, minor negative Eu anomalies are present.

Figure 11 compares hot-spring and river waters in the Mengeruda area. In all cases, the patterns are relatively flat, implying little difference in the behavior of LREE and HREE. The acid hot-springs (*mapa4* and *mapa5*) and mixed acid water from hot-spring+Waebana river (*smapa3*) show an almost perfect overlap. These patterns are identical in shape with that of the acid Waewutu river water after the confluence with the Waebana river (*sada*). In all cases a minor Eu anomaly can be observed. These observations clearly show that the input from the acid hot springs is dominated in the Waebana river. The *sada* sample in the Waewutu river reflects the contribution from the Waebana river, but overall REE concentrations are lower because of the low REE concentrations upstream, represented by sample

sadn2.

In general, there are clear differences between the REE patterns of the western (Gou area) and eastern (Mengeruda area) manifestations. Only the Inielika spring shows similarities with the Mengeruda waters although the patterns are not fully identical.

Since the acid hot waters in the Gou and Mengeruda areas have quite similar water types and element concentrations, the differences in REE patterns are most likely to be explained by differences in rock types to which the fluids were exposed. Possibly, considering their higher LREE/HREE ratios in two of the Gou waters, these REE patterns are inherited from relatively acid (evolved) rocks (e.g., andesites). This interpretation may also be applied to the acid cold spring in the summit area of Inielika (*mada*). The deviating REE pattern of the *mapa1* sample in the Gou area suggests that the REE concentrations are influenced by local heterogeneities in rock types in the subsurface.

Because of the relatively low F concentrations and absence of bicarbonate, the mobility of the REE in the acid waters of the study area is possibly enhanced by complexation with sulfate. The small negative Eu anomalies that are observed in all the samples indicate that Eu is not preferentially mobilized relative to the other REE. Following the criteria of Lewis *et al.* (1997), none of the waters was exposed to high temperatures under reducing conditions. Instead, it is conceivable that the REE patterns largely reflect original patterns of the host rocks to which the fluids were exposed.

5.6 SOLVEQ modeling

In order to evaluate the saturation state of minerals from the water compositions, the SOLVEQ computer program (Spycher and Reed, 1989; Reed and Spycher, 1990) was applied on selected samples. Concentrations are the input values. A hypothetical (low) concentration of HS⁻ having a value of 0.01 ppm was adopted.

Results for the acid hot spring (*mapa3*) in the Gou area show that barite and silica phases (chalcedony, cristobalite, quartz, amorphous silica) are close to or somewhat above saturation, whereas all other minerals are undersaturated. Similar results were obtained for the acid hot spring (*mapa5*) in the Mengeruda area, where pyrite is also close to saturation. However it should be noted that the saturation state of the latter mineral is sensitive to the assumed input value for HS⁻. Mineral saturation states are also similar in the hot-spring Waebana river mixture (*smapa3*), where pyrophyllite is close to saturation as well. The acid cold spring of Inielika shows a different pattern. Not only are barite and the silica phases saturated, but also kaolinite and pyrophyllite. This observation agrees

with the field evidence because the spring is situated in an area of heavy rock alteration.

5.7 Hydrologic model

Figure 12 shows a hydrologic model for the study area by integrating the results from the Gou and Mengeruda areas. It is based on the hypothesis that S, Cl, and F-rich gas escapes from a magma source below the Inielika volcano. The ascending gases are incorporated into the groundwater, producing acid waters. These waters are thought to mix with meteoric recharge water in the upper part of the volcanic system. Afterward the mixture flows laterally away from the center and appears as acid hot-water manifestations in the Gou and Mengeruda areas. Transport at relatively shallow levels and limited buffering capacity of aquifers apparently precludes that an equilibrium with major rock-forming minerals is attained. Additional mixing at a greater distance could involve the addition of bicarbonate water from local sources.

6. Conclusions

Most of the manifestations produce acid-sulfate type waters with relatively small amounts of Cl and F. Bicarbonate type water represents a minority. Correlations between sulfate, chloride and fluoride suggest that the acid hot springs in the Gou and Mengeruda areas (including Waebana river water that is fed by hot springs) represent mixtures of a fluid with a magmatic component and water of largely meteoric origin. The latter mixing end member is rather dominant. In terms of Na-K-Mg relations, the waters are immature indicating a lack of an equilibrium with major rock-forming minerals.

Concentrations, which are particularly noticeable for Al and Fe, remain undetected by ICP-AES in neutral waters.

Chondrite-normalized REE abundances show smooth patterns with small negative Eu anomalies. Despite the overall chemical similarity of acid hot-spring waters in the Gou and Mengeruda areas, the REE patterns are distinct.

The chemical composition of an acid cold spring in the summit area of Inielika indicates that this water significantly deviates from the other manifestations and is clearly not genetically related.

The results of SOLVEQ modeling indicate that all the acid hot-spring waters are saturated with barite, chalcedony, cristobalite, quartz, amorphous silica, and sometimes possibly pyrite. Saturation of kaolinite and pyrophyllite was only observed in the acid cold water of the Inielika spring, which can form with the field evidence for rock alteration.

It is hypothesized that S, Cl and F-rich gases escape from a moving magma body below Inielika and

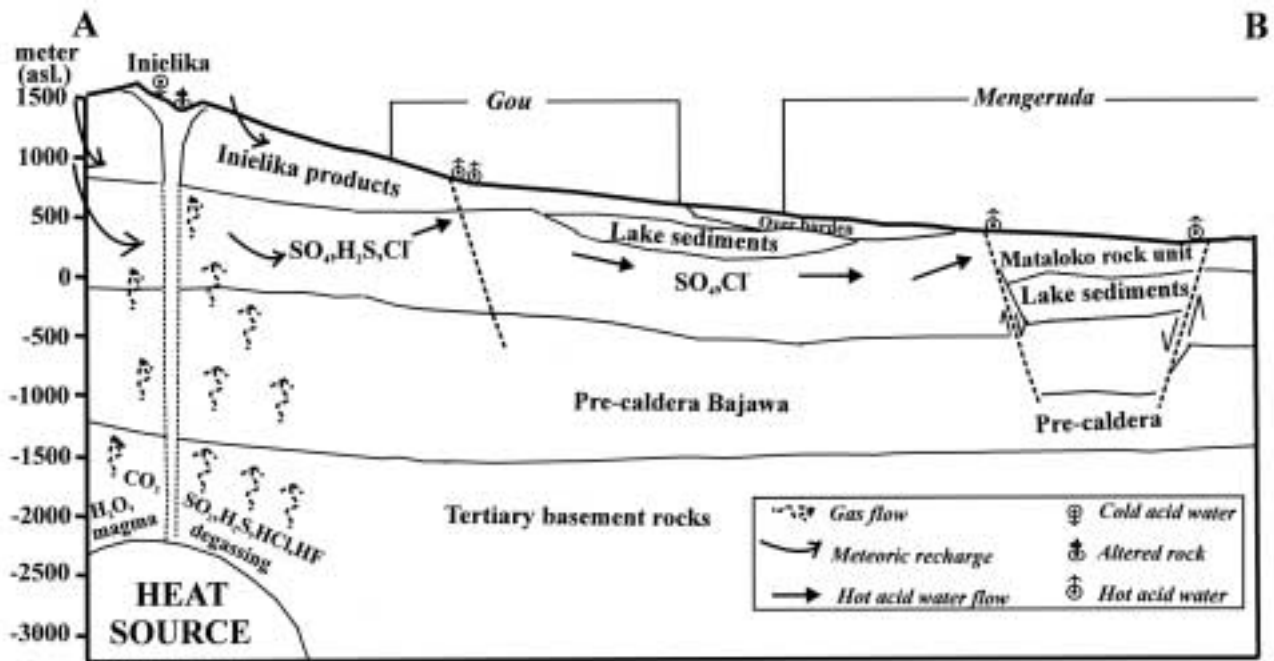


Fig. 12 Tentative hydrologic model Inielika volcano complex related to cross section A-B modified after Sundhoro (1999). Vertical scale has been exaggerated two times relative to the horizontal scale.

infiltrate water bodies in the summit region. After the resulting acid water mixes with a meteoric component, the mixture flows laterally towards the east and is discharged as acid hot-springs in the Gou and Mengeruda areas. Additional mixing with bicarbonate water from separate local systems may occur as well.

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References

- Alzwar, M. (1990) G. Inielika, Berita Berkala Vulkanologi Edisi Khusus, No. 150, Direktorat Vulkanologi, Bandung, Indonesia (in Indonesian).
- Arnorsson, S. (1985) The use of mixing models and chemical geothermometers for estimating underground temperatures in geothermal systems. *Journal of Volcanology and Geothermal Research*, **23**, 299-335.
- Arnorsson, S. (1975) Application of the Silica geothermometer in low temperature hydrothermal areas in Iceland. *American Journal of Sciences*, **275**, 763- 784.
- Bau, M., Usui, A., Pracejus, B., Mita, N., Kanai, Y., Irber, W. and Dulski, P. (1998) Geochemistry of low-temperature water-rock interaction: evidence from natural waters, andesite, and iron-oxyhydroxide precipitates at Nishiki-numa iron-spring, Hokkaido, Japan. *Chemical Geology*, **151**, 293-307.
- Bingqiu, Z. and Hui, Y. (1995) The use of geochemical indicator elements in the exploration for hot water sources within geothermal fields. *Journal of Geochemical Exploration*, **55**, 125-136.

- Chen, Y. and Brantley, S.L. (1997) Temperature- and pH-dependence of albite dissolution rate at acid pH. *Chemical Geology*, **135**, 275-290.
- Delmelle, P., Bernard, A., Kusakabe, M., Fisher, T. and Takano, B. (2000) Geochemistry of the magmatic-hydrothermal system of Kawah Ijen volcano, East Java, Indonesia. *Journal of Volcanology and Geothermal Research*, **97**, 31-53.
- Fournier, R. O., Sorey, M.L., Mariner, R.H. and Truesdell, A.H. (1979) Chemical and isotopic prediction of aquifer temperatures in the geothermal system at Long Valley, California. *Journal of Volcanology and Geothermal Research*, **5**, 17-34.
- Fulginiti, P., Gioncada, A. and Sbrana, A. (1999) Rare-earth element (REE) behaviour in the alteration facies of the active magmatic-hydrothermal system of Vulcano (Aeolian Islands, Italy). *Journal of Volcanology and Geothermal Research*, **88**, 325-342.
- Giggenbach, W.F. (1988) Geothermal solute equilibria. Derivation of Na-K-Mg-Ca geothermometers. *Geochimica et Cosmochimica Acta*, **52**, 2749-2765.
- Giggenbach, W.F. and Soto, R.C. (1992) Isotopic and chemical composition of water and steam discharges from volcanic-magmatic-hydrothermal systems of the Guanacaste geothermal Province, Costa Rica. *Applied Geochemistry*, **7**, 309-332.
- Giggenbach, W.F., Garcia, N.P., Londono, A.C., Rodriguez, V., Rojas, N.G. and Calvache, M.L.V. (1990) The chemistry of fumarolic vapor and thermal-spring discharges from the Nevado del Ruiz volcanic-magmatic-hydrothermal system, Columbia. *Journal of Volcanology and Geothermal Research*, **42**, 13-39.
- Goumas, M.G., Lygerou, V.A. and Papayannakis, L.E. (1999) Computational methods for planning and evaluating geothermal energy projects. *Energy Policy*, **27**, 147-154.
- Grasby, S.E., Hutcheon, I. and Krouse, H.R. (2000) The influence of water-rock interaction on the chemistry of thermal springs in western Canada. *Applied Geochemistry*, **15**, 439-454.
- Gulec, N. (1994) Geochemistry of thermal waters and its relation to the volcanism in the Kizilcahamam (Ankara) area, Turkey. *Journal of Volcanology and Geothermal Research*, **59**, 295-312.
- Johannesson, K.H., Zhou, X., Guo, C., Stetzenbach, K.J. and Hodge, V.F. (2000) Origin of rare earth element signatures in groundwaters of circumneutral pH from southern Nevada and eastern California, USA. *Chemical Geology*, **164**, 239-257.
- Johannesson, K.H., Stetzenbach, K.J. and Hodge, V.F. (1997) Rare earth elements as geochemical tracers of regional groundwater mixing. *Geochimica et Cosmochimica Acta*, **61**, 3605-3618.
- Kacandas, G.H. and Grandstaff, D.E. (1989) Differences between geothermal and experimentally derived fluids: how well do hydrothermal experiments model the composition of geothermal reservoir fluids? *Geochimica et Cosmochimica Acta*, **53**, 343-358.
- Kemmerling, G.L.L. (1929) *Vulcanen van Flores; Vulkanol. en. Seismolog.* Mededelingen, Dienst Mijnb. Ned. Indie.
- Kempton, K.A. and Rowe, G.L. (2000) Leakage of active crater lake brine through the north flank at Rincon de la Vieja volcano, northwest Costa Rica, and implications for crater collapse. *Journal of Volcanology and Geothermal Research*, **97**, 143-159.
- Land, L.S. and Macpherson, G.L. (1992) Geothermometry from brine analyses: Lessons from the Gulf Coast, U.S.A. *Applied Geochemistry*, **7**, 333-340.
- Lewis, A.J., Palmer, M.R., Sturchio, N.C. and Kemp, A.J. (1997) The rare earth element geochemistry of acid-sulphate and acid-sulphate-chloride geothermal systems from Yellowstone National Park, Wyoming, USA. *Geochimica et Cosmochimica Acta*, **61**, 695-706.
- Lewis, A.J., Komninou, A., Yardley, B.W.D. and Palmer, M.R. (1998) Rare earth element speciation in geothermal fluids from Yellowstone National Park, Wyoming, USA. *Geochimica et Cosmochimica Acta*, **62**, 657-663.
- Mahon, W.A.J. and Ellis, A.J. (1977) *Chemistry and Geothermal Systems*. New York San Francisco London.
- Mariner, R.H. and Willey, L.M. (1976) Geochemistry of thermal waters in Long Valley, Mono County, California. *Journal of Geophysical Research*, **81**, 792-800.
- Martin, R., Rodgers, K.A. and Browne, P.R.L. (2000) Aspects of the distribution and movement of aluminium in the surface of the Te Kopia geothermal field, Taupo Volcanic Zone, New Zealand. *Applied Geochemistry*, **15**, 1121-1136.
- Martinez, M., Fernadeze, E., Valdes, J., Barboza, V., Van der Laat, R., Duarte, E.,

- Malavassi, E., Sandoval, L., Barquero, J. and Marion, T. (2000) Chemical evolution and volcanic activity of the active crater lake of Poas volcano, Costa Rica, 1993-1997. *Journal of Volcanology and Geothermal Research*, **97**, 127-141.
- Michard, A. (1989) Rare earth element systematics in hydrothermal fluids. *Geochimica et Cosmochimica Acta*, **53**, 745-750.
- Michard, A. and Albarede, F. (1986) The Rare earth element content of hydrothermal fluids. *Chemical Geology*, **55**, 51-60.
- Mutlu, H. (1998) Chemical geothermometry and fluid-mineral equilibria for the Omer-Gecek thermal waters, Afyon area, Turkey. *Journal of Volcanology and Geothermal Research*, **80**, 303-321.
- Mutlu, H. and Gulec, N. (1998) Hydrogeochemical outline of thermal waters and geothermometry applications in Anatolia (Turkey). *Journal of Volcanology and Geothermal Research*, **85**, 495-515.
- Nordstrom, D.K. (1982) The effect of sulfate on Aluminum concentration in natural waters: some stability relations in the systems Al_2O_3 - SO_3 - H_2O at 298K. *Geochimica et Cosmochimica Acta*, **46**, 681- 692.
- Pang, Z.H. and Reed, M. (1998) Theoretical chemical thermometry on geothermal waters: Problems and methods. *Geochimica et Cosmochimica Acta*, **62**, 1083-1091.
- Reed, M.H. and Spycher, N.F. (1990) *Soltherm Data Base of Equilibrium Constants for Aqueous-Mineral-Gas Equilibria*. Department of Geological Sciences, University of Oregon, Eugene, Oregon.
- Rowe, G.L.J., Brantley, S.L., Fernandez, J.F. and Borgia, A. (1995) The chemical and hydrologic structure of Poas Volcano, Costa Rica. *Journal of Volcanology and Geothermal Research*, **64**, 233-267.
- Serrano, M.J.G., Sanz, L.F. and Nordstrom, D.K. (2000) REE speciation in low-temperature acidic waters and the competitive effects of aluminum. *Chemical Geology*, **165**, 167-180.
- Spycher N.F. and Reed M.H. (1989) *Solveq: A computer Program for Computing Aqueous-Mineral-Gas Equilibria*. Department of Geological Sciences, University of Oregon, Eugene, Oregon.
- Sundhoro, H. (1999) Penyelidikan Geologi dan Heat loss Daerah Panas bumi Gou, Kabupaten Ngada Nusa Tenggara Timur. Direktorat Vulkanologi, Bandung (in Indonesian).
- Sriwana, T., van Bergen, M.J., Varecamp, J.C., Sumarti, S., Takano, B., van Os, B.J.H. and Leng, M.J. (2000) Geochemistry of the acid Kawah Putih lake, Patuha Volcano, West Java, Indonesia. *Journal of Volcanology and Geothermal Research*, **97**, 77-104.
- Verma, S.P. and Santoyo, E. (1997) New improved equation for Na/K, Na/Li and SiO_2 geothermometers by outlier detection and reinjection. *Journal of Volcanology and Geothermal Research*, **79**, 9-23.
- Weiss, J. (1986) *Handbook of Ion Chromatography*. Dionex Corporation, Sunnyvale, California, 244 pp.
- White, D.E. (1957) Thermal waters of volcanic origin. *Geological Society American Bulletin*, **68**, 1637-1658.
- White, D.E. (1957) Magmatic, connate, and metamorphic waters. *Geological Society American Bulletin*, **68**, 1637-1658.

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インドネシア，フローレス島中央部イネリカ火山周辺の地熱徴候の地球化学

Dedi KUSNADI

要 旨

イネリカ火山コンプレックス付近の温泉および噴気調査として、イネリカ火山山頂から、これより低地のゴウ地域およびさらに低地のメンゲルダ地域までの、イネリカ火山から東へ最大 12 km におよぶほぼ直線上の湧水および河川水試料の地化学分析を実施した。全試料について主成分および微量成分を分析した。

温泉および噴気の主成分・微量成分および希土類の濃度は、温度と pH に依存する。すなわち、錯体を形成する配位子の性質、岩石の初期構成鉱物パターン（溶脱または溶解を受けている）、火山地域ではガラスとマグマ鉱物（希土類の挙動をコントロールする卓越相）、岩石の変質過程における 2 次鉱物の分別作用である。また複数のメカニズムが複合していることは、自然状態で容易に観察できる。

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