Alkaline fluids in a volcanic-hydrothermal system – Savo, Solomon Islands

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ABSTRACT: Savo volcano, Solomon Islands, is host to an active hydrothermal system that is potentially analogous to high sulfidation epithermal Au deposits. Chemical and stable isotope data from fluids discharged at the surface indicate a relatively shallow condensate layer fed by magmatic volatiles including SO_2. Acidic condensates are buffered to high pH by wall rock reaction, leading to the precipitation of unusual carbonate-silica sinters at the surface, in an environment where low pH fluids and associated products would be expected.

KEYWORDS: High sulfidation; epithermal; volcanic-hydrothermal; Savo; Solomon Islands;

1 INTRODUCTION

Volcanic-hydrothermal systems are believed to be the environment of formation of high sulfidation epithermal Au deposits (Hedenquist et al. 1993). Current models for the genesis of high sulfidation deposits suggest a two-stage genesis, with a pre-ore alteration stage, when low pH magmatic vapor condensates attack the host rocks and generate the characteristic advanced argillic and "vuggy silica" alteration assemblages, followed by a later mineralization stage (see Cooke and Simmons 2000, and references therein).

Studies of active volcanic-hydrothermal systems typically identify acidic fluids and associated alteration at the surface (e.g. Delmelle et al. 2000), yet a significant number of high sulfidation deposits show evidence of higher pH fluids and alteration, and clear evidence of fluid neutralization by water-rock interaction (e.g. Hedenquist et al. 1994).

Hot springs at Savo volcano, Solomon Islands, are neutral to high pH, and produce unusual carbonate-silica-sulfate sinters at the surface, features not typically associated with active volcanic-hydrothermal systems.

2 GEOLOGICAL SETTING

Savo is an andesite to dacite stratovolcano related to the north-eastwards subduction of the Woodlark Basin at the South Solomon Trench System, which initiated in the Upper Miocene. Savo has been subaerial for less than 100,000 years and last erupted in the 1840s (Petterson et al. 2003). Partial melting of the young oceanic crust of the Woodlark slab exerts an important control on magma chemistry across the Solomon arc (e.g. Konig et al. 2007), and may be responsible for high sodium contents in the more evolved portions of the igneous suite at Savo (up 8 wt% Na_2O in dacites). Much of the island is covered by heavily vegetated pyroclastic deposits and dacite domes.

Savo's active hydrothermal system is expressed at the surface in the central crater by fumaroles and steaming ground, and by hot springs and steaming ground on the flanks. There are no springs in the crater.

3 METHODS

Water samples were collected from a number of different hot springs and cold wells. Samples were filtered to <0.45 μm, with fractions taken for cation determination by ICP-AES and anion determination by ion chromatography.

Sulfur isotope analysis on native sulfur from fumaroles and aqueous sulfate from hot springs (precipitated as $BaSO_4$) was performed using standard techniques.

Water was collected from hot springs and condensed from crater fumaroles for $\delta^{18}O$ and δD determination.

A range of altered samples and hot spring precipitates were taken from active thermal areas. Mineralogy was determined by XRD and SEM.

Table 1: Typical compositions of fluids discharged at Savo volcano. Units mg/l unless noted otherwise.		
	Alkaline Sulphate	Acid Sulphate
pH	8.23	2.54
Al (μg/l)	BDL	15790
Ca	119.6	57.6
Fe	BDL	24.1
Mg	9.96	15.5
Na	205.8	45.4
Si	176.3	62.8
Cl	41.5	4.4
SO_4^{2-}	692	549
HCO_3^-	87	70

4 RESULTS

Steaming ground and fumaroles in the crater were just above 100°C, i.e. slightly superheated steam. Areas of steaming ground are accompanied by advanced argillic assemblages (residual silica + kaolinite ± alunite ± native sulfur).

Fumarole native sulfur $\delta^{34}S$ ranges from -3.9 to -6.2 ‰ (Fig. 1). Stable isotopes of condensed steam plot on a trend showing relative depletion in the heavy isotopes compared to hot springs and local meteoric and ground water (Fig. 2).

Hot springs classified as acid sulfate have pH <7 and temperature 95-100°C. Acid sulfate springs are found in a number of locations on the flank, closely associated with areas of steaming ground. Springs are no more than 30 cm in diameter, and the water is rich in suspended solids. $\delta^{34}S_{SO4}$ ranges from 0.6 to -3.5 ‰ (Fig. 1). The springs have higher $\delta^{18}O$ and δD than cold groundwater (Fig. 2).

Alkaline sulfate springs are found in a number of locations on the upper flanks of the volcano (less than 1 km from the crater wall). In some
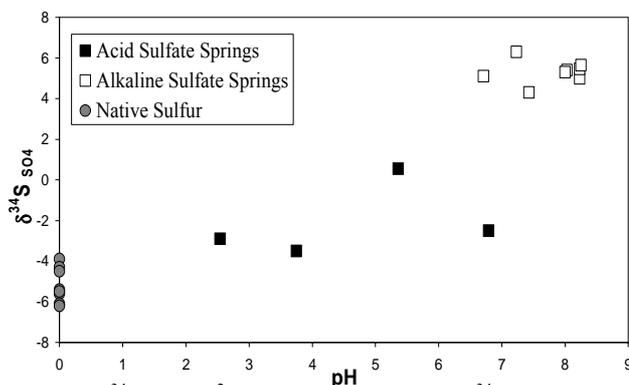

Fig. 1: $\delta^{34}S$ of $SO4^{2-}$ vs. pH for hot springs. $\delta^{34}S$ of native sulfur from fumaroles also shown.

locations they occur within a few meters of acid sulfate springs and steaming ground. The water in the springs is clear, and may be discharged under pressure forming "spouters". The temperature of these springs is 100°C, and many can be observed to boil at the surface. pH is near-neutral to alkaline (6.5 to 8.5). $\delta^{34}S_{SO4}$ ranges from 4.0 to 6.5 ‰ (Fig. 1). Alkaline sulfate waters have higher $\delta^{18}O$ and δD than the non-thermal groundwater samples from Savo (Fig. 2).

Alkaline sulfate hot springs are commonly surrounded by precipitates consisting of amorphous silica + calcite ± anhydrite. Textures are similar to those seen in silica sinters and geyserites from low sulfidation style geothermal systems.

In both spring types, sulfate is the dominant anion, and Cl⁻ is negligible (Table 1).
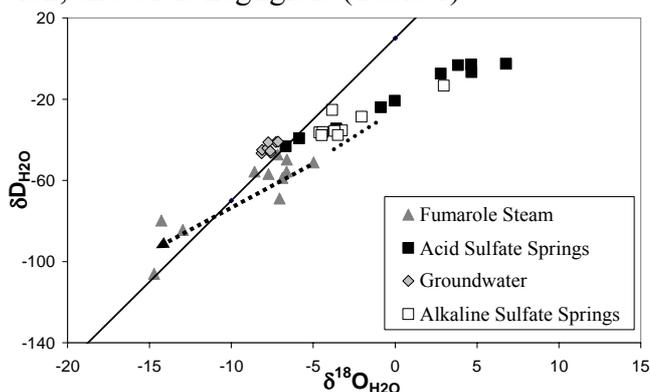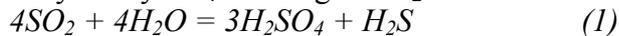

Fig. 2: Stable isotopes of water. Shows condensation trend from Equation 2 (dashed arrow), liquids produced by condensation (dotted line) and global meteoric water (solid line).

5 DISCUSSION

5.1 Sulfur Isotopes

The isotopically heavy $\delta^{34}S$ of the alkaline sulfate springs can be related to the low $\delta^{34}S$ values of the acid sulfate fluids and fumarole sul-

fur by the process of condensation of magmatic volatiles in the upper levels of the volcanic edifice and disproportionation of SO_2. At temperatures below 350°C this will produce isotopically heavy SO_4^{2-} and lighter H_2S:

$$4SO_2 + 4H_2O = 3H_2SO_4 + H_2S \qquad (1)$$

The isotopically heavy sulfate is carried in the alkaline sulfate waters. The H_2S produced is largely non-condensable until oxidation to sulfate and native sulfur with negative $\delta^{34}S$ values in the near-surface. Sulfate formed by H_2S oxidation is found in acid sulfate springs (Rye 2005).

5.2 Water isotopes

The trend in $\delta^{18}O$ and δD values of fumarole steam samples is consistent with a Rayleigh condensation process acting in the subsurface at ~150°C. The dashed arrow on Fig. 2 represents the equation:

$$(1000 + \delta_r) / (1000 + \delta_i) = f^{\alpha-1} \qquad (2)$$

where δ_r = the isotopic composition of steam after condensation, δ_i = composition before condensation (the isotopically heaviest steam sampled), f = fraction of steam condensed, and α = fractionation factor at 150°C.

The liquid produced by condensation of the steam in Equation 2 correlates closely to the alkaline sulfate waters (dotted line, Fig. 2), allowing for a small degree of mixing with meteoric water. Along with the sulphur isotopes, this suggests that alkaline sulphate waters are derived by condensation of magmatic volatiles in the upper edifice of the volcano.

Acid sulfate springs show strong enrichment in the heavier isotopes of water. This phenomenon has been reported for a number of steam-heated hot springs, and is due to kinetic fractionation by evaporation (Giggenbach and Stewart 1982). Alkaline sulfate springs are less prone to evaporative enrichment as they have a much higher recharge rate.

Boiling of the alkaline sulfate water will produce the steam that heats and supplies H_2S to the acid sulfate waters, and accounts for their close spatial association.

5.3 Chemistry and Alteration

The condensed magmatic volatiles would be initially low pH due to sulfuric and carbonic acid. The high sodium (as albite) content of the host rocks provides an effective neutralizing agent for the acidity. The core of the system would be dominated by low pH fluids, grading out to progressively higher pH as the fluids continue to react with the host rocks. Subsurface boiling provides a final increase in pH before surface discharge as alkaline sulfate springs. The chemistry of the acid sulfate springs is consistent with a steam-heated derivation, with H_2S oxidation producing low pH fluids. Cation chemistry is a result of non-equilibrium acid leaching, which produces advanced argillic alteration. H_2S oxidation around crater fumaroles produces alteration similar to that near acid sulfate springs.
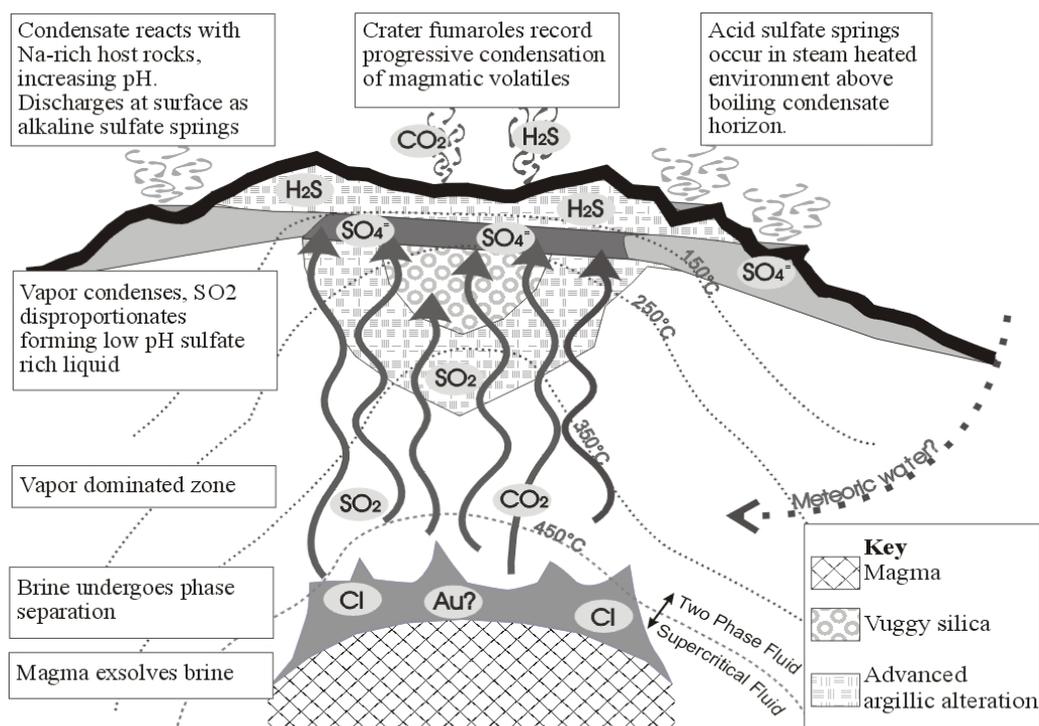

Fig. 3: Schematic model of hydrothermal system at Savo. Not to scale.

5.4 *Model for the Hydrothermal System of Savo*

The positive $\delta^{34}S$ in the alkaline sulfate waters suggests an origin from a magmatic-derived, SO_2 bearing vapor. The absence of significant amounts of chloride in the thermal waters discharged at the surface suggests that it is being retained in an aqueous phase at depth (Fig. 3). An aqueous phase at temperatures above 350°C would be capable of retaining Cl and allowing SO_2 to remain in the vapor phase. Thus the model involves aqueous brine separating from magma at depth and then boiling. A vapor dominated zone separates the brine from the shallow condensate layer. Such a brine is capable of introducing Au into the epithermal environment (Cooke and Simmons 2000).

The condensate is initially low pH, producing advanced argillic alteration. Wall rock reaction increases the pH, producing alkaline sulfate waters. Where these waters boil beneath the surface, steaming ground is formed above. Perched aquifers and surface waters may be heated by the steam, and H_2S carried with the steam is oxidized to produce acid sulfate springs.

6 CONCLUSIONS

Based on chemical and isotopic characteristics, we suggest the fluids discharged at Savo volcano are the surface expression of a volcanic-hydrothermal system that is potentially analogous to high sulfidation deposits.

Unusual carbonate-silica-sulfate sinters and alkaline sulfate fluids record neutralization of acidic condensates by wall rock interaction. Alkaline fluids and their products may be present in the lithocap of high sulfidation deposits and as such may represent important exploration pathfinders.

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