PROGRESSIVE DEVOLITIZATION OF GREYWACKE FROM SUB-CRITICAL TO SUPERCRITICAL CONDITIONS

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ABSTRACT

The source of volatiles such as Cl, S and CO_2 in geothermal systems is an object of frequent debate. Early experiments concluded that they could be derived solely from water-rock interaction. Others infer that some component of magmatic input is necessary. We have conducted experiments to measure the volatiles released during progressive heating of a greywacke typical of the basement rock of the Taupo Volcanic Zone.

The experiment was conducted using a high temperature and pressure fluid-rock interaction simulator. Temperature ranged from ambient to 400°C and pressure from 21 to 415 bar. The flow rate was maintained at 1 ml hr^{-1} throughout the experiment. A control experiment, using similar conditions, was conducted using crushed Brazilian quartz.

The results show that:

1) most Cl is released at lower temperature (<200°C) and cannot account for the amount of Cl in a geothermal system;
2) most SO_4 is released below 100°C and is derived from anhydrite;
3) 95% of the H_2S is released above 250°C, 65% of which is released at 300°C.

Several peaks in volatile concentration coincide with temperature changes suggesting that thermally-induced microfracturing provides enhanced access to the fluid. The results show good evidence that there is sufficient sulfide present in the basement rock of the TVZ to account for the sulfur present in the geothermal systems.

1. INTRODUCTION

The Taupo volcanic Zone (TVZ) geothermal fluids are characterised by variable amount of volatiles in addition to water. While the water is strongly dominated by a meteoric origin (with a variable proportion inferred from magmatic degassing; Giggenbach, 1995), the source of Cl, S, or CO_2 in the deep reservoir is a recurrent subject of discussion.

Ellis and Mahon (1964) proposed that Cl released from the volcanic rocks during hydrothermal alteration is more than sufficient to explain the concentrations in these elements in the geothermal waters. Henley and Ellis (1983) estimated using Ellis and Mahon (1964) leaching data that an extra magmatic source was necessary to provide enough Cl into Wairakei geothermal system. More than 2000 km^3 of rock would be required to be leached to provide sufficient Cl during the lifetime of the system. This value is unreasonable and not supported by the alteration halo around the system. Recent Cl isotope data suggests that the chlorine originates from andesitic or rhyolitic magmatism ($\delta^{37}Cl$ ranges -1.0 – 0.8 ‰, Bernal et al., 2014).

The sulfur source, however, is less constrained. Rare sulfur isotope studies report a narrow range of isotopic ratio for H_2S_{gas} (and sulfides) in the TVZ ($\sim\delta^{34}S_{H2S}$ 3 – 7 ‰; Browne, 1975; Robinson, 1987; Giggenbach, 1995). On the contrary, sulfate isotopic ratios vary strongly (-6 – 20 ‰) being dependant on oxidation processes such as quantitative oxidation of H_2S (Robinson, 1987; Simmons et al., 1994). The source of sulfur has been tentatively associated with deep magmatic degassing buffered by the basement greywacke (Robinson, 1987).

Recent work on melt inclusions is providing useful estimates of the composition of the magmatic fluids. Volatile content of melt inclusions trapped in quartz in rhyolite in the TVZ shows high Cl and H_2O content (up to 3000 ppm and 6.5 wt.% respectively) but low S (below detection limit or less than 80 mg kg^{-1} for Oruanui magmas) (Liu et al., 2005; Johnson et al., 2011; Bégué et al., 2014). Volatile saturation and phase separation are the dominant factors for this (Fig. 1).

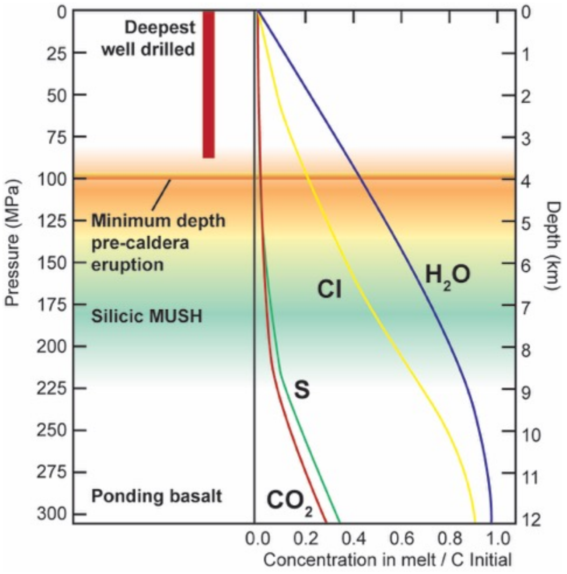

Figure 1: Schematic profile of the TVZ reporting the minimum magma emplacement depth and the MUSH zone compare to the saturation of volatile in a rhyolite melt (from Allan et al., 2013; Barker et al. 2015; Bégué et al., 2015; Brown et al. 1998; Deering et al., 2008; Shane et al, 2008; Wilson et al. 2006). The magmatic saturation is reported as the fraction of initial dissolved volatile contents remaining in the melt as a function of pressure for H_2O-rich rhyolitic magma (initial volatile concentrations are 5.5 wt% H_2O, 1000 ppm CO_2, 1000 ppm S, 100 ppm Cl; Wallace, 2003).

Magmas in the TVZ are estimated to pond between 100 and 200 MPa (4 - 8 km depth). At these depths most of the CO_2 and S is already strongly depleted in a silicic mush and have been exsolved. Although CO_2 will likely be transported to the surface and be incorporated in water at the deep geothermal discharge zone, the sulfur will react at depth and be fixed as sulfide in the deep crust, preventing its transport to the surface. Thus where does the abundant sulfur discharging in TVZ geothermal systems come from?

This preliminary work presents results from fluid-rock interaction experiments on greywacke from the TVZ basement (Fig. 2). It aims to test whether the greywacke can be the source for sulfur (and variable Cl) in the deep discharge of the geothermal systems. The flow-through experiments offer the possibility to revise the fluid-rock interactions leaching experiment results obtained by Ellis and Mahon (1964).

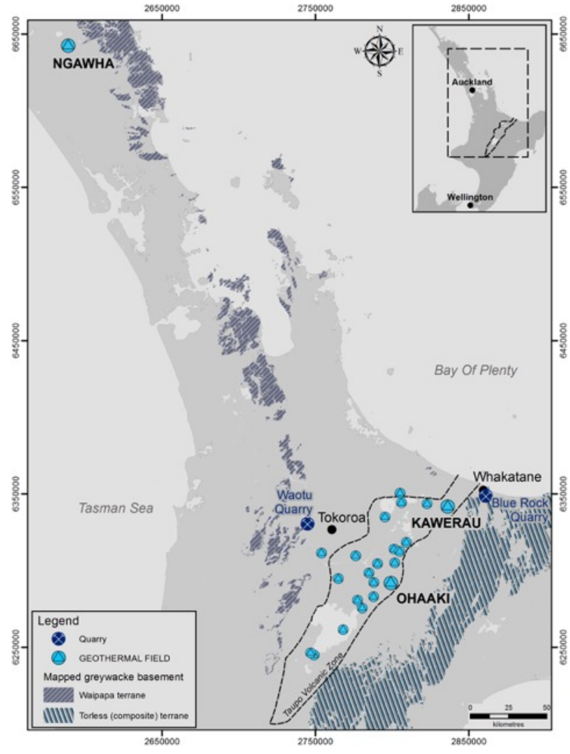

Figure 2: Map of the North Island, New Zealand, showing the extend of the two greywacke terranes Waipapa and Torlesse on both side of the Taupo Volcanic Zone.

2. METHOD

The greywacke was sourced from the Waotu Quarry, west of Tokoroa, New Zealand (Fig. 3). It is a Late Jurassic feldspathic litharenite of the Waipapa Terrane composed of quartz, plagioclase and lithic clasts in a matrix of quartz, albite, chlorite and illite clays (Fig. 3). Trace amounts of pyrite (<0.5%) and minor quartz-calcite veining are present. The ΣS and Cl content of the greywacke are 600 and <50 mg kg^{-1}, respectively. The rock was crushed and sieved to retain the 0.35 – 0.5 mm size fraction which was cleaned in an ultrasonic bath to remove fine material. A control experiment used crushed and cleaned inclusion-free Brazilian quartz in the 0.25 – 0.75 mm size fraction.

The experiment was conducted using a high temperature and pressure fluid-rock interaction simulator. The temperature ranged from ambient to 400°C and the pressure from 21 to 415 bar. Figure 4 shows the P-T path for the two experiments. The temperature in the quartz experiment was both prograde and retrograde. In the greywacke experiment, because more samples were collected at each temperature, it was only prograde due to the long length of the experiment. The fluid used was doubly-distilled water at a flow rate of 1 ml hr^{-1} in both experiments.

Fluid samples were analysed for major cations (Li, Na, K, Mg, Ca, Sr, Mn, Fe, As, Al, B, and SiO_2) by ICP-OES and anions (Cl^- and SO_4^{2-}) by IC. H_2S was determined by the methylene blue method/UV-Vis spectroscopy. The pH was measured using a standard pH meter. Samples from the control experiment were not analysed for H_2S as it was assumed that it would be below detection limit. Only the anion and H_2S results are reported here.

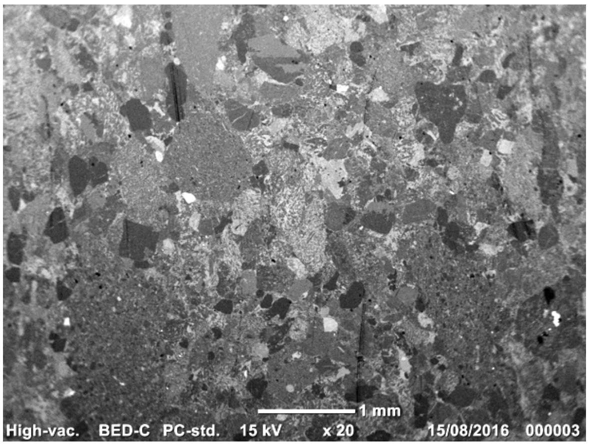

Figure 3: Scanning electron micrograph showing Waotu Quarry greywacke.

3. RESULTS

Figure 5 shows the chloride concentrations versus time for both experiments. The concentration of chloride in the entering fluid was <0.05 mg kg^{-1}, the detection limit. Most samples show measurable chloride. The origin of chloride in the quartz experiment (Fig. 5a) is uncertain but is probably a combination of chloride trapped in quartz, contamination from the apparatus and contamination during sampling and analysis, nevertheless, all control experiments samples measured below 0.5 mg kg^{-1}.

For the Waotu experiment, many samples contain concentrations above 0.5 mg kg^{-1} up to a maximum of 2.4 mg kg^{-1} at least up to about 250°C. After this temperature shift, almost all samples lie below 0.5 mg kg^{-1}. The cumulative flux curve (solid black line in Figure 5b) represents the integrated chloride concentration versus time normalised to 1 kg of rock. The curve shows a decrease in slope above about 250°C suggesting that the rate of chloride removal from the rock is slowing due to its overall decrease in abundance in the rock. The cumulative flux at the end of the experiment is about 38 mg kg^{-1} rock. This shows that most of the chloride has been removed from the greywacke as its original content was measured as <50 mg kg^{-1}.

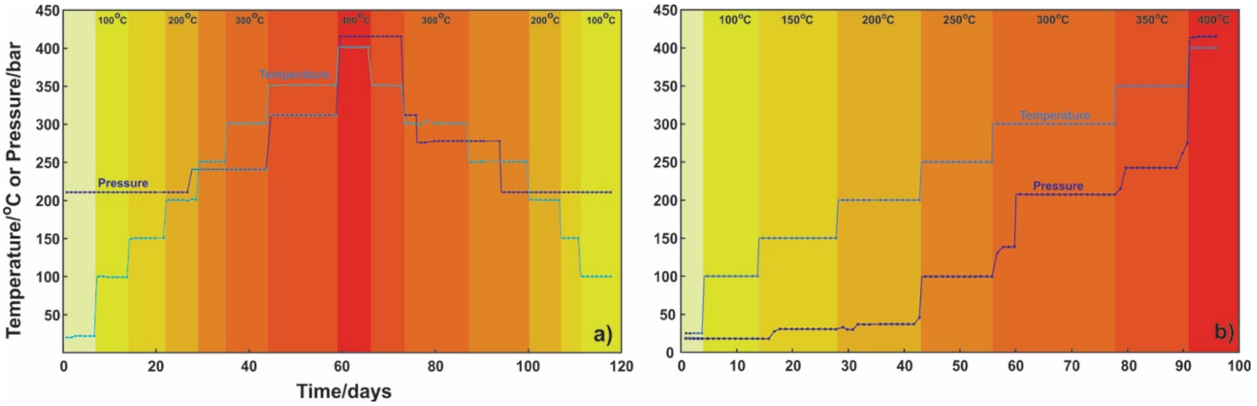

Figure 4: Pressure-Temperature path for a) the control experiment using inclusion-free Brazilian quartz and b) for the Waotu greywacke.

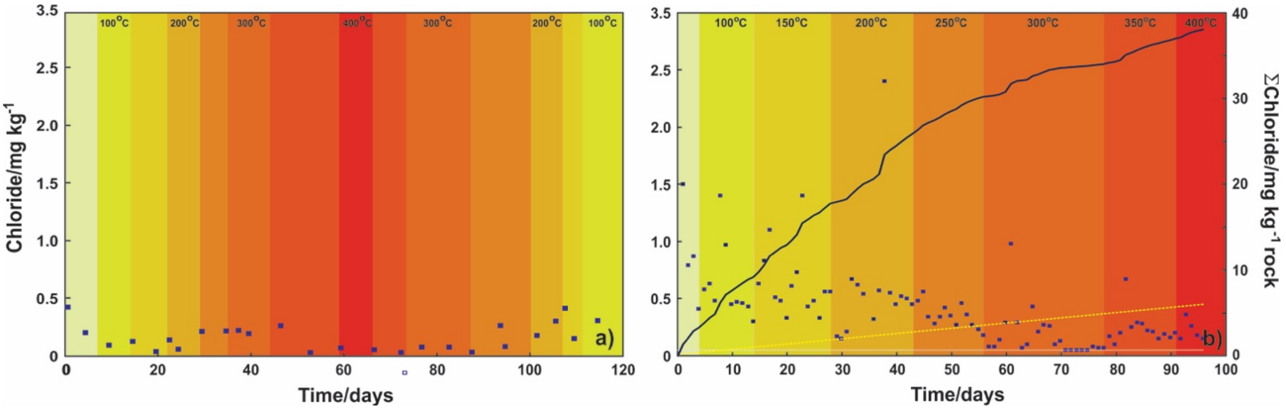

Figure 5: Chloride concentration in effluent samples a) from the Brazilian quartz experiment and b) the Waotu greywacke experiment. Solid white line is the detection limit for chloride. Dashed yellow line is the cumulative flux if all samples were at the detection limit. Solid black line is the cumulative chloride flux in mg kg^{-1} rock. The cumulative flux for the quartz experiments was not calculated because not all samples were analysed.

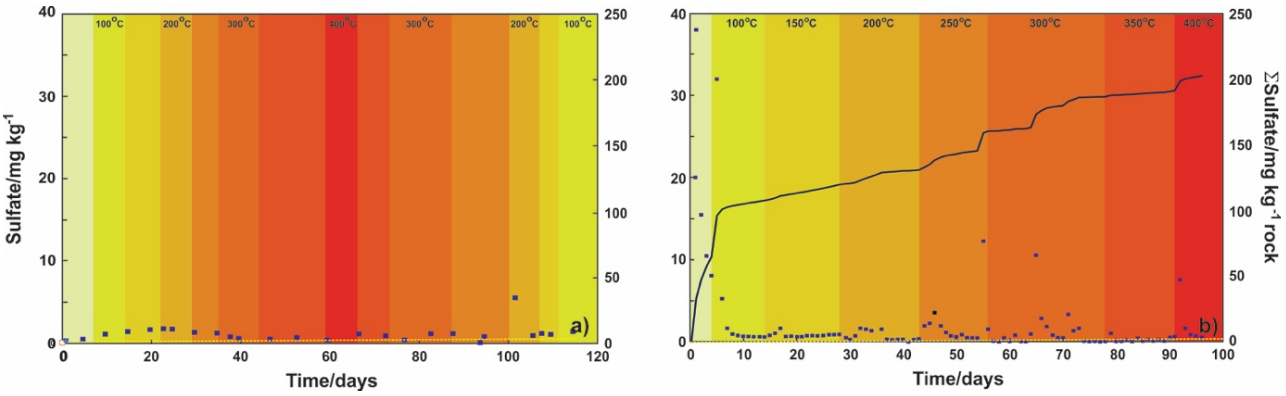

Figure 6. Sulfate concentration in effluent samples a) from the Brazilian quartz experiments and b) the Waotu greywacke experiment. Dashed yellow line is the cumulative flux if all samples were at the detection limit. Solid black line is the cumulative sulfate flux in mg kg^{-1} rock.

Figure 6 shows the sulfate concentration versus time for both experiments. The concentration of sulfate in the entering fluid was <0.03 mg kg^{-1}, the detection limit. All samples from both experiments show measureable sulfate concentrations usually ~1 mg kg^{-1}. In the control experiment sulfate was generally between 1 - 2 mg kg^{-1} throughout the experiment (Fig. 6a). This indicates that sulfate is not derived from quartz dissolution, as it would be expected to increase with temperature, but originates as background from the apparatus or during sampling.

In the greywacke experiment (Fig. 6b), the highest sulfate concentration is found in the first sample at room temperature (38 mg kg^{-1}). The concentration then decreases to 8 mg kg^{-1} before the temperature shift to 100^{o}C. After this temperature increase, the concentration rises to 32 mg kg^{-1} and then declines to values similar to the control experiment. This feature of sulfate concentration increase and then decrease is present after several temperature changes. The cumulative sulfate flux (solid line in Figure 6b) is about 200 mg kg^{-1} rock.

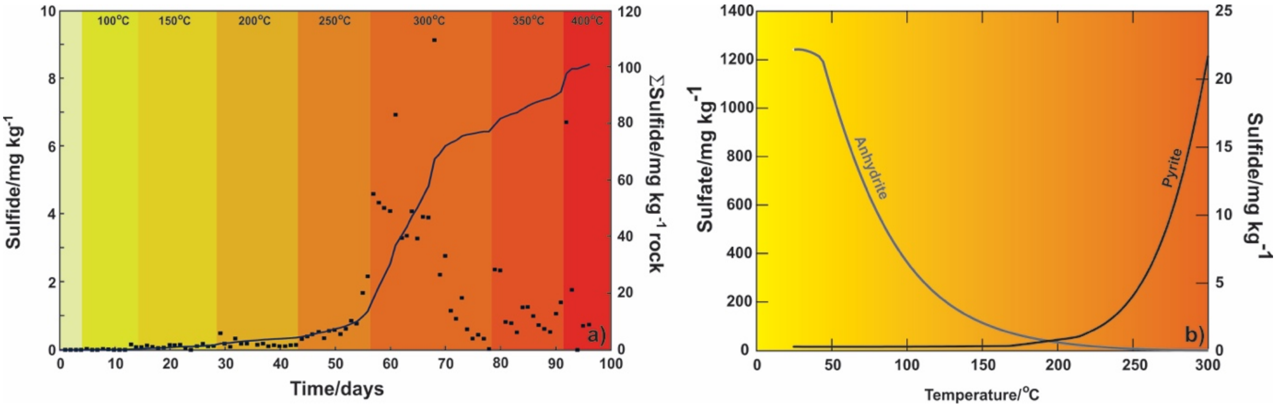

Figure 7: a) H_2S concentration in effluent samples from the Waotu greywacke experiment. Solid black line is the cumulative sulfide flux in mg kg^{-1} rock. Cumulative flux assuming all samples at detection is 1 mg kg^{-1} rock. Yellow dashed line not shown. b) the solubility of anhydrite and pyrite versus temperature at a fixed pH of 6.5.

Figure 7a shows the H_2S concentrations versus time for the Waotu experiment. Up until the temperature shift to 150^{o}C, the H_2S concentrations were below the detection limit of 0.01 mg kg^{-1}. At 150^{o}C, detectable H_2S concentrations are encountered. These increase slightly at 200^{o}C and then substantially after the temperature increase to 250^{o}C. The highest concentrations of H_2S are encountered at 300^{o}C and reach up to 9 mg kg^{-1} and then decrease back down to about 1 mg kg^{-1} before the shift to 350^{o}C. After each temperature shift from 300 to 350^{o}C and 350^{o}C to 400^{o}C, a spike in H_2S concentration which then declines is observed. The integrated H_2S flux (solid line in Figure 7a) shows a sharp increase during the 250°C period and demonstrates an inflection point at about 63 days.

4. DISCUSSION

The total chloride flux from the Waotu experiment was 38 mg kg^{-1} rock. It also appears that the fluid was capable of removing the majority of the chloride from the rock. Assuming 100% efficiency for chloride removal and a rock density of 2700 kg m^{-3}, 1 km^{3} of greywacke could provide 100,000 tonne of chloride. The volume of water that this would dissolve into over the lifetime of a geothermal system is difficult to assess. Using a conservative value of 1 km^{3} of fluid, this would result in an average concentration of about 100 mg kg^{-1} Cl, much lower than encountered in typical geothermal fluids of the TVZ (Giggenbach, 1995). If one takes into consideration the possibility of contamination from experimental artefacts, as demonstrated by the quartz experiment, the potential amount of chloride derived from the greywacke is even less.

Chloride flux from the experiment also showed that most was removed at lower temperatures. This would suggest that chloride would be released at the earlier stages of an evolving geothermal system and would not be available once circulating fluids reached temperatures above 200^{o}C.

The high flux of sulfate at room temperature can be attributed to the dissolution of trace amounts of sulfate minerals in the rock, with anhydrite the most likely candidate. The solubility of anhydrite in pure water at room temperature is about 1250 mg kg^{-1} SO_4 (Fig. 7b). Since the sulfate concentrations were well below this value and the fact that the concentration decreases over time at room temperature, means that it did not saturate and was mostly removed early in the experiment. As temperature was increased the sulfate concentrations decreased to levels similar to the control experiment so it is not possible to say anything definitive about sulfate flux at higher temperature. The spikes in sulfate concentration upon temperature shift are attributed to thermally-induced fracturing, allowing the fluid to access sulfate mineral grains inside the rock fragments (Siratovich *et al.*, 2015).

The total flux of sulfate during the first week of the experiment was 32 mg kg^{-1} rock. Assuming 100% removal of sulfate and a fluid:rock ratio of 1 km^{3}:1 km^{3}, this translates to a concentration in the fluid of 86 mg kg^{-1} SO_4. This sulfate would be removed at low temperature. If temperature increased, anhydrite would saturate and precipitate at about 150^{o}C, depending on the Ca concentration (Fig. 7b).

Sulfide concentration was not measured in the control experiment as there is no sulfur source either in the fluid or in the quartz, consequently, any sulfide produced during the Waotu greywacke experiment must be derived from the rock. Thus, the cumulative sulfide flux is the most reliable of the three anions measured. The two possible sources of sulfide are from the dissolution of metamorphic/diagenetic pyrite (Fig. 8) or reduction of sulfate derived from anhydrite.

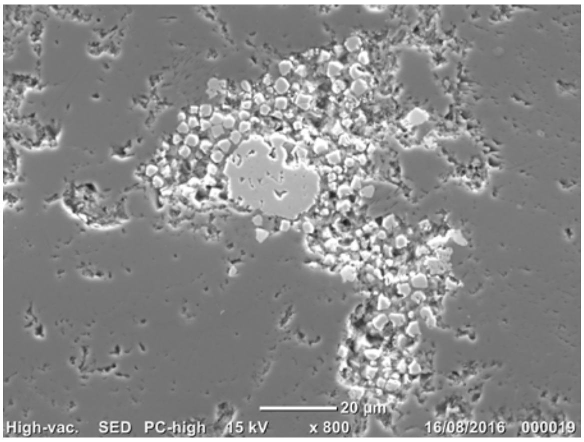

Figure 8: Framboidal metamorphic/diagenetic pyrite in unaltered Waotu greywacke.

Derivation from anhydrite is unlikely since most of this would have already been removed from the rock at an early stage. Also, the kinetics of sulfate reduction are highly inhibited at lower temperatures. This means that metamorphic/ diagenetic pyrite is the source of the reduced sulfur. Figure 7b shows the solubility of pyrite at a fixed pH of 6.5 versus temperature. At low temperature (<100ºC), low pyrite solubility and slow dissolution kinetics explain the lack of detectable sulfide in the effluent samples (Fig. 7b). As temperature increased up to 300ºC, progressively higher concentrations of sulfide are found. The solubility of pyrite in water between 175ºC and 300ºC should release between 1 – 22 mg kg^{-1} H_2S at pH 6.5. The effluent samples range between about 0.2 – 9 mg kg^{-1}. Taking into consideration that pH in the experiment could be slightly higher than the assumed 6.5 in the figure; it is likely that the solutions were close to equilibrium with pyrite, at least at 300ºC.

Figure 7a also shows that most of the sulfide was released between 250ºC and 300ºC as the concentration of sulfide produced decreases during the 300ºC interval and then is much less at 350 and 400ºC. The decrease in measured H_2S above 300°C reflects the almost total consumption of the pyrite. The sulfide concentrations also demonstrate the effect of thermally-induced fracturing at 350 and 400ºC.

The total flux of sulfide during the experiment was 102 mg kg^{-1} rock, therefore, 1 km^3 of rock is capable of producing 260,000 tonne of sulfur. Assuming 100% removal of sulfide and a fluid:rock ratio of 1 km^3:1 km^3, this translates to a concentration in the fluid of 275 mg kg^{-1} H_2S. It is important to note that unlike chloride and sulfate, 95% of the H_2S is released at temperatures >250ºC and 65% is released at 300ºC.

Combining sulfate and sulfide the ΣS released from the rock is about 107 mg kg^{-1} rock. Comparing this with chloride the ΣS:Cl ratio is approximately 2.85, much greater than found in any geothermal brine of the TVZ (0.001 – 0.03, Giggenbach, 1995). It follows that another source of chloride is required, i.e., a magmatic source.

The sequence of release also indicates that most Cl and SO_4 will be removed before any significant heating can be induced by an intruding magma body. In contrast, devolitization of the reduced sulfur by pyrite dissolution would require significant heating and thus only occur in the vicinity of an intrusive body at a relatively shallow depth.

5. CONCLUSION

Two experiments have been conducted to investigate the devolitization of Cl, SO_4 and H_2S from unaltered greywacke. The results show that:

4) most Cl is released at lower temperature (<200ºC) and cannot account for the amount of Cl in a geothermal system;
5) most SO_4 is released below 100ºC and is derived from anhydrite;
6) 95% of the H_2S is released above 250ºC, 65% of which is released at 300ºC.

The results show good evidence that there is sufficient sulfide present in the basement rock of the TVZ to account for the sulfur present in the geothermal systems. This could explain the homogeneous and heavy isotopic ratio of the sulfide in these systems.

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