

# COMPARISON OF MAIN ION COMPOSITION OF WATER SAMPLES FROM LAVA CAVES ON HAWAII, USA, AND JEJU ISLAND, SOUTH KOREA

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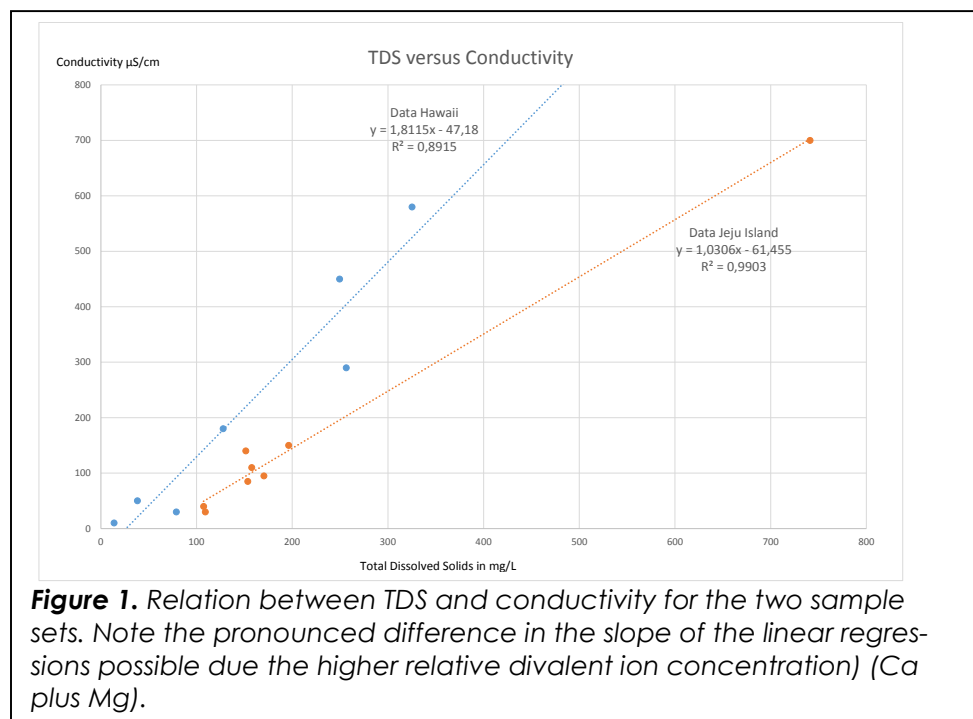
## Abstract

In spring 2015 we collected twelve water samples from various caves and three from the hydrothermal seawater pool of Ahalanui Park in Hawaii. An additional nine samples, including one from the island's tap water, were collected from caves on Jeju Island, South Korea, in August 2015 (see Kempe and Woo, 2016, this vol-

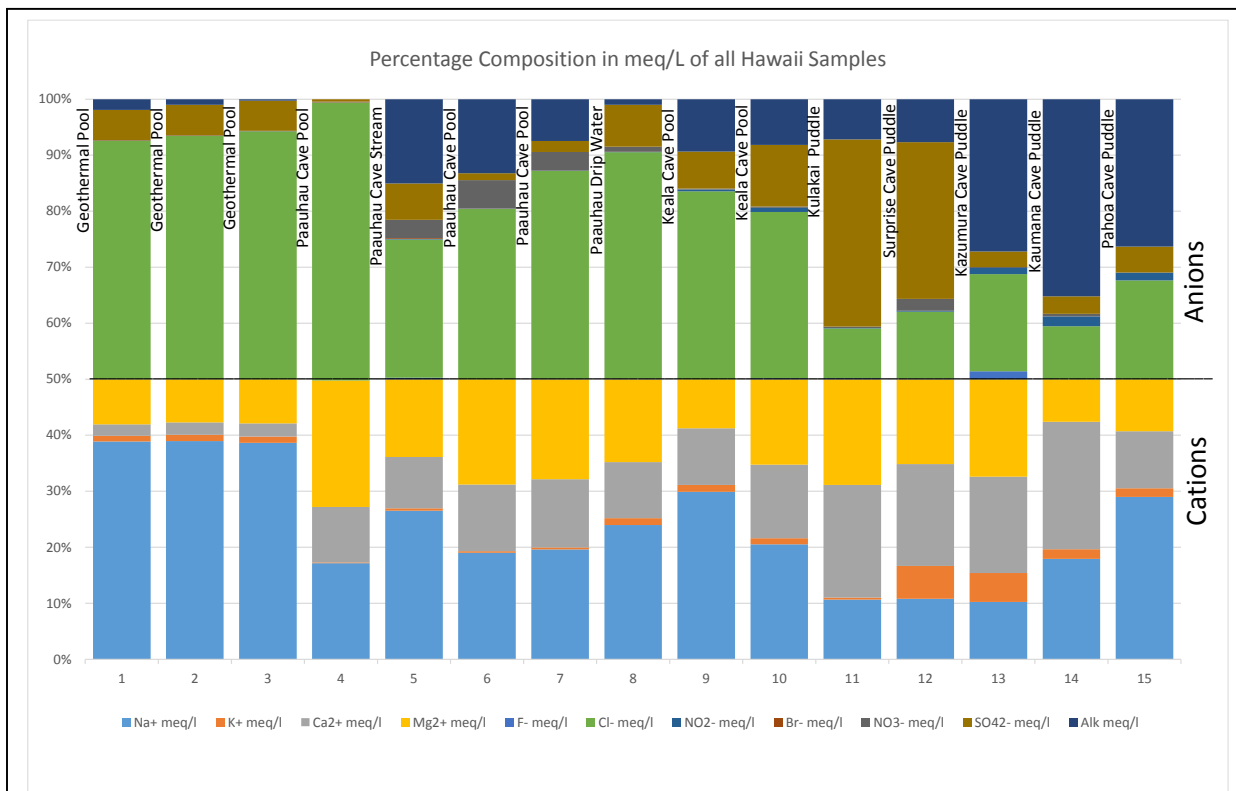
ume). Temperature, pH and conductivity were measured in the field on most of the samples and major cation and anion concentrations were determined by ion-chromatography at the University of Hamburg. Results were given in mg/L (ppm) and then recalculated for their equivalent concentrations (meq/L) by division of the individual equivalent weights. Total Alkalinity (TA = bicarbonate) was calculated by the equivalent charge balance between cations and anions:

TA = sum of cations – sum of anions.  
Only one sample (No.4, Pool Pa'auhau) showed a negative balance, suggesting a very low alkalinity. TA was therefore set to zero.

Results show a remarkable spread in the concentrations of Total Dissolved Solids (TDS in mg/L) (Fig. 1) as well as in relative composition (Figs. 2, 3). This came as a surprise since all samples (apart those from the thermal pool and the Jeju tap water) represent waters that



**Figure 1.** Relation between TDS and conductivity for the two sample sets. Note the pronounced difference in the slope of the linear regressions possible due the higher relative divalent ion concentration (Ca plus Mg).



**Figure 2.**  
Relative composition of water samples from Hawaii.

filtered through relatively thin cave roofs composed of basaltic lava. It was expected that they show a relatively similar composition and that only the total concentration (TDS) would vary due to different rates of evaporation. Figure 1 shows the correlation of TDS versus conductivity of the cave samples (where data are available).

The sample with the highest mineral load (2350 mg/L; No. 4 in Figure 2; not on Figure 1) from Hawaii is from a pool near the entrance in Pa'auhau Cave (Kempe et al., 2003). Its main anion is chloride. Its main cation is Mg followed by Na and Ca. From all cave waters these are also the absolutely highest Mg, Ca and Na concentrations (261, 375, 189 mg/L, respectively). This suggests that the pool (relatively near to the entrance of the cave) has been concentrated by evaporation and any alkalinity has been forced out of solution by precipitation of CaCO<sub>3</sub>. The high TDS suggest that possibly also gypsum saturation had been reached.

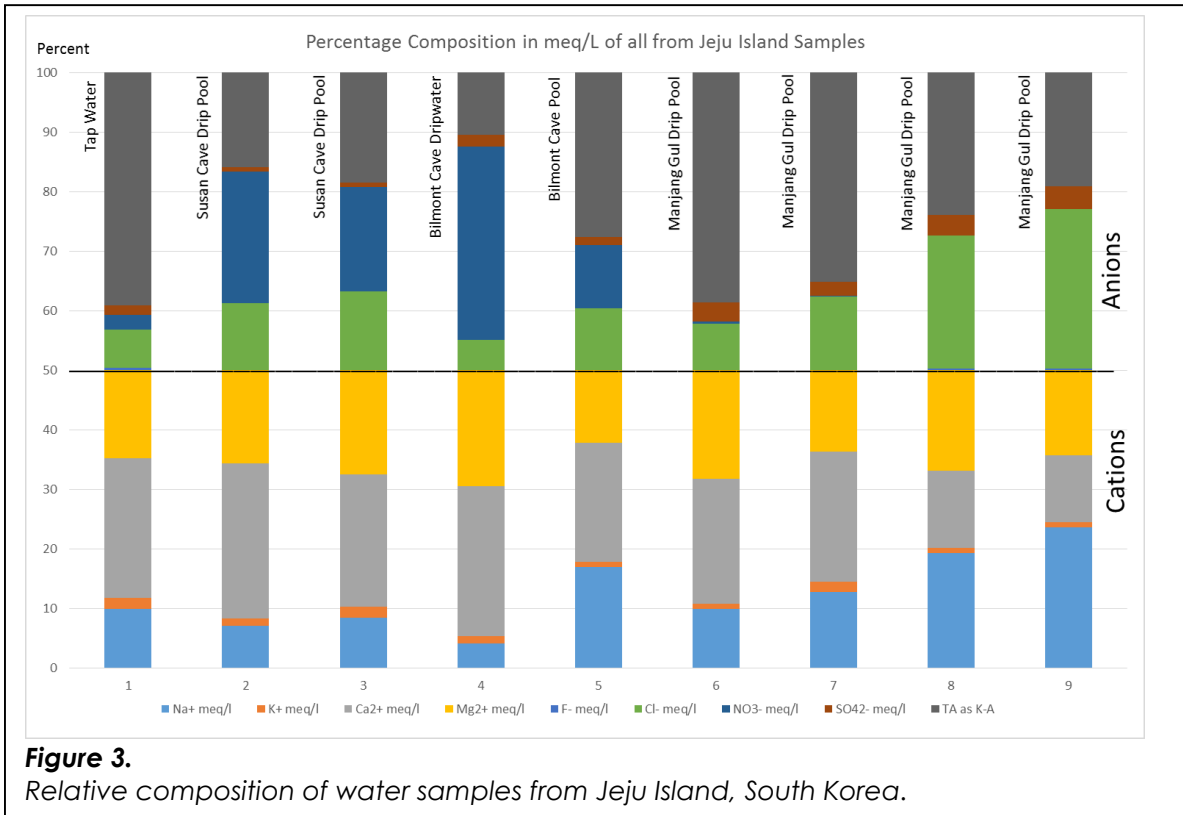
The second highest concentrated sample (740 mg/l and 700 μS/cm) is not from an stagnant cave puddle but from a ceiling seep in Bilemot Cave (Jeju) that is not concentrated by evaporation but is characterized by a very high nitrate concentration (390 mg/L) (Sample point upper right on Fig. 1; No 4 on Fig. 3). Thus its

mineral load must derive from agricultural drainage, not from the weathering of basalt.

The three hydrothermal pool samples show stable relative compositions similar to seawater. Their relative composition is clearly different for all other samples, showing that the cave waters are not derived from sea-spray.

Overall the Hawaii samples seem to have higher relative sodium and chloride concentrations but lower total alkalinities than the Jeju samples. Tentatively this may suggest a quicker seepage because of younger ages of the lavas involved. Also Hawaii has higher sulfate relative concentrations suggesting that the younger lavas still leach more sulfate than the older lavas on Jeju.

The five samples from Pa'auhau Cave (samples 4 to 8) are all very different in terms of alkalinity content. From all caves sampled on Hawaii this is the geologically oldest (Kempe et al., 2003) but also the one with the thickest roof (about 10 m). Its magnesium concentration varies the most and sulfate is relatively low, again suggesting longer weathering history that gave time to remove most of the sulfur contained in the lava. Remarkable is also the high nitrate concentration, suggesting contamination by sewage. Sample 8, Pa'auhau



Dripwater, has also a measurable ammonia concentration (ca. 4 mg/L), suggesting input of raw sewage from the village above. Thus some of the variance in the Pa‘auhau samples may be anthropogenic in origin.

It was difficult to find puddles in Kulakai and Surprise caves large enough to take samples. These two caves are situated in the dry area of the Ocean View Area and therefore show high sulfate and calcium values in accordance with the wide-spread occurrence of gypsum in the area.

The samples from Kaumana (see Kempe and Ketz-Kempe, 2016, this volume), Kazumura and Pahoia Caves seem to form one group of high similarity, all with high alkalinities, collected in the windward, moist area of Big Island. Keala Cave is in the same area and should therefore be similar, but it is not. Specifically it has very low alkalinities. The reason for these differences remains unclear.

The samples from Jeju seem to fall into two groups, one with significant and even very large nitrate concentrations (Bilemot and Susan Caves) and one that has only very small nitrate concentrations. The latter samples derive from Manjang Gul, a World Natural Heritage Site that has no agriculture above ground.

Overall there seem to be three significant sources for cave waters: Precipitation (sodium and chloride), agriculture and sewage (nitrate, ammonia), and the products of rock weathering by carbonic acid (the bulk of the remaining ions). Both total concentrations and relative concentrations vary significantly. A dependence on the climatic situation and on the age of the rock and duration of weathering can be hypothesized.

## References

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