



## **Distinguishing CO<sub>2</sub>, CO, H<sub>2</sub>, H<sub>2</sub>S and CH<sub>4</sub> of shallow and deep hydrothermal origin by diffuse degassing multi-sensor mapping**

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Hydrothermal gas-phase reactions such as the catalytic hydrogenation of CO<sub>2</sub> (Sabatier-Process) and of CO (Fischer-Tropsch-Process) can occur within the shallow parts of hydrothermal systems. These two reactions lead to elevated methane concentrations as well as CH<sub>4</sub>/CO and CH<sub>4</sub>/CO<sub>2</sub> ratios. Exsolving magmatic CO<sub>2</sub> and H<sub>2</sub> mix into these gases from below, before they are detected at the surface, and lead to a dampening or even reversal of such elevated CH<sub>4</sub>/CO<sub>2</sub> ratios. Condensation phenomena in shallow vapor-dominated parts of a hydrothermal system, as well as degassing of hot springs, create their own gas compositions. In complex surface expressions of hydrothermal systems, all four of these processes can be responsible for seemingly homogenous but actually mixed gas chemical signatures, which are emitted through discrete structures (fractures and fumaroles), pool surfaces, and diffuse degassing structures. Whereas the measurement of discrete degassing structures and pool gases has been performed for nearly 150 years (Bunsen, 1857), assessing diffuse degassing structures is a relatively young field of study.

In-situ single-sensor detection and mapping of diffuse degassing phenomena in hydrothermal and volcanic areas can be used to elucidate subsurface tectonic structures, assess emission rates, and monitor emission variability (Williams 1985; Chiodini et al. 1996, Werner et al., 2003). More than one technique has been deployed to measure several gas species simultaneously (e.g., Crenshaw et al. 1982), and correlations of one gas species (usually CO<sub>2</sub>) with physical parameters like heat flux (Brombach et al., 2001), or with another gas species (Rn, He) have been demonstrated (Barberi & Carapezza 1994; Williams-Jones et al., 2000).

Recently, correlations of multiple gas species with one another were reported (Schwandner et al., 2004), leading to the possibility of quantitative mapping of sub-surface hydrothermal chemical processes by simultaneous measurement of reaction partners and products that continuously and diffusely degas. In the present study, we joined a fully-quantitative multi-sensor instrument (Draeger Multiwarn II) to a modified accumulation-chamber sensing method (Chiodini et al., 1996) and measured diffuse degassing of CH<sub>4</sub>, H<sub>2</sub>, CO<sub>2</sub>, CO, and H<sub>2</sub>S. In this approach, each batch of gas that is recirculated through the detector is simultaneously analyzed by all sensors.

We investigated the diffuse degassing characteristics of CO<sub>2</sub>, CO, H<sub>2</sub>, H<sub>2</sub>S and CH<sub>4</sub> in two magmatic-hydrothermal areas at Yellowstone National Park (USA): Sylvan Springs and the Greater Obsidian Pool Area. Diffuse degassing of CO<sub>2</sub> in the Greater Obsidian Pool Area near Goose Lake (Mud Volcano area, Yellowstone NP) was assessed by Werner & Brantley (2000). The site is characterized by SW-NE trending faults and residual rhyolitic extrusives which are thought to be related to the Sour Creek resurgent dome activity. Hydrothermal activity in the Mud Volcano area is vapor-dominated, with a seasonal and diurnal varying influence of both meteoric runoff waters and vapor condensation phenomena at the surface. Hydrothermal alteration is abundant, and many pools dot the area (Werner & Brantley, 2000).

At Obsidian Pool, the spatial distribution of carbon dioxide flux shows strong point sources, and weak linearly arranged degassing areas (diffuse degassing structures). The spatial flux distribution of reduced gases appears entirely unrelated to the carbon dioxide flux, indicating that a different process is responsible. As an example, CO<sub>2</sub> most strongly degasses along linear features and point sources, whereas the areal flux distribution of hydrogen is elevated near hot springs. The H<sub>2</sub>/CO<sub>2</sub> ratio, accordingly, neither correlates nor anticorrelates with CO<sub>2</sub>, but appears to be related to areas near pools that show physical signs of vapor condensation.

At Sylvan Springs, a discrepancy between the spatial distribution of carbon dioxide flux and that of reduced gases, similar to that in the Greater Obsidian Pool area, is also observed. The same distinction between the underlying processes is suspected. At least two populations of degassing regimes are observed within each of the data sets for degassing species (as displayed by flux vs. probability characteristics). In addition, a ENE-WSW striking lineament separates a CO<sub>2</sub> dominated area to the NNW from a region dominated by reduced gases.

Inspection of all the data in a flux vs. cumulative probability diagram reveals at least two distinct degassing populations for CO<sub>2</sub>, H<sub>2</sub> and CO fluxes at both sites. Inflection points in the probability percentile - flux correlation denote population boundaries, which in the case of reduced gases are slightly different in the two areas, while they

appear to be similar for CO<sub>2</sub>. At both sites, these are approximately 1-10 and >12 mol m<sup>-2</sup> d<sup>-1</sup> CO<sub>2</sub>, <0.1 and 0.1-1 and >1 mol m<sup>-2</sup> d<sup>-1</sup> H<sub>2</sub>, as well as <0.02 and >0.02 mol m<sup>-2</sup> d<sup>-1</sup> CO. At Sylvan Springs, two populations are observed for H<sub>2</sub>S data (not enough data at Obsidian Pool).

Our results show that elevated reduced gas emissions appear to be most prominent near hot springs and in zones where vapor condensation is apparent, whereas CO<sub>2</sub>-dominated degassing is most abundant over vapor-dominated areas of the hydrothermal system and is probably oriented along subsurface tectonic structures. The multimodal distribution allows us to distinguish deep degassing sources (CO<sub>2</sub> anomalies) from mostly shallow localized hydrothermal processes (reduced gas anomalies).

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