

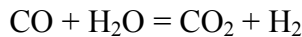
Carbon and oxygen isotopic equilibrium in fumarolic CO: Applications for remote temperature measurements

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The stable carbon and oxygen isotopic compositions ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) of CO were determined for high temperature fumarolic gases on Satsuma-Iwo-Jima volcano, Japan, as well as $\delta^{13}\text{C}$ and/or $\delta^{18}\text{O}$ of co-existing CO_2 and H_2O . It turns out that both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO reached to the isotope exchange equilibrium with CO_2 and H_2O , respectively, under the temperature of more than 800 °C (Fig. 1). We conclude that following chemical reactions is so rapid in both directions in the fumarolic gases at the temperature.



Besides, the results also suggest that the reactions fall into sufficiently slow at the sampling temperature (surrounding air temperature), because the isotopic compositions were quenched at the temperature just before the sampling. As a result, we anticipate similar quenched state for the components in volcanic plume, highly diluted fumarolic gas floating around volcano.

In principle, the chemical and/or isotope equilibrium in volcanic gases enables us to monitor remote temperature of volcanic fumaroles at a distant site, if we could deduce the chemical/isotopic compositions of every related components in fumaroles from a distant site using the chemical/isotopic compositions in volcanic plume. In practical, however, it is difficult to deduce chemical/isotopic compositions in fumaroles from those in volcanic

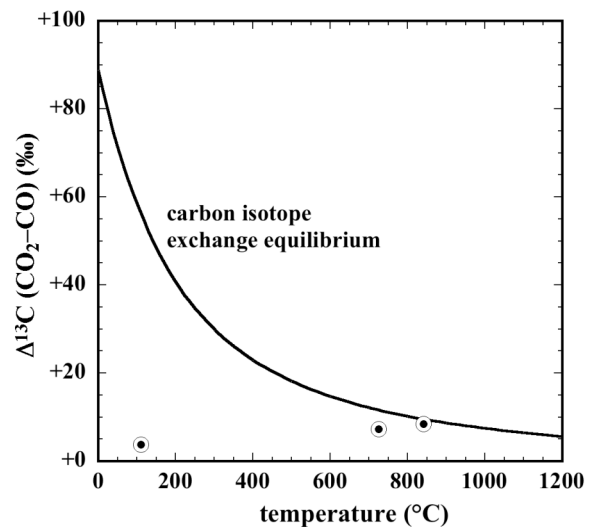


Fig.1 The $\delta^{13}\text{C}$ difference between CO_2 and CO ($\Delta^{13}\text{C}(\text{CO}_2\text{-CO})$) in fumarolic gases plotted against the fumarolic temperature, together with the $\Delta^{13}\text{C}(\text{CO}_2\text{-CO})$ under isotopic equilibrium condition (Richet et al., 1977).

plume, because most components in fumaroles are condensable (H_2O , SO_2 , and H_2S , etc.), and/or major in atmosphere (H_2O and CO_2 , etc.).

In case of the stable isotopic compositions of CO, however, it would be highly possible to deduce those in fumaroles using those in volcanic plume, because it is less condensable and minor in atmosphere (less than 0.3 ppmv). Besides, because both H_2O and CO_2 are major in volcanic fumaroles, their stable isotopic compositions can be regarded as constant irrespective to the temperature change. That is to say, the variation range in the stable isotopic compositions in fumarolic CO can be attributed to the total variation in the isotopic equilibrium state in fumaroles, which mostly corresponds to change in the fumarolic temperature.

To check this hypothesis, addition to fumarolic gases, we also determined $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO in volcanic plume emitted from Satsuma-Iwo-Jima volcano, as well as mixing ratios. By using the isotopic compositions of CO in volcanic plume sampled at a distant site from the fumaroles (several to several hundred meters), we verified the possibility that we could deduce the isotopic compositions in high temperature fumaroles or not. Recent advances in stable isotope measurements using CF-IRMS enable us such highly sensitive measurements of CO even in atmospheric level of several 100 ppbv (Tsunogai et al., 2002).

We found that the reciprocal of CO mixing ratio ($1/[\text{CO}]$) in the volcanic plume exhibited

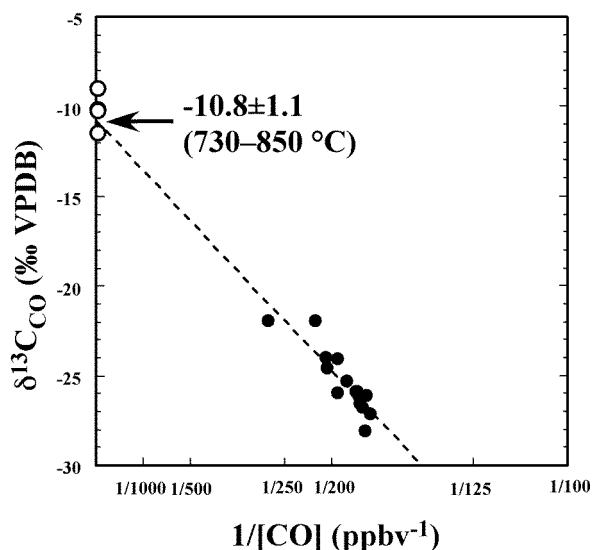


Fig.2 $\delta^{13}\text{C}_{\text{CO}}$ vs $1/(\text{mixing ratio})$ plot for CO in volcanic plume (●), together with those in fumarolic gases (○). The dotted line corresponds to the linear regression to the volcanic plume.

linear correlation with $\delta^{13}\text{C}$ of CO (Fig.2). The linear correlation suggests that both mixing ratio and $\delta^{13}\text{C}$ of CO in the plume were determined through simple mixing between two endmembers: CO in ambient atmosphere (high $1/[\text{CO}]$ endmember) and that in fumaroles (low $1/[\text{CO}]$ endmember). By extrapolating the linear correlation to $1/[\text{CO}] = 0$, we estimated the $\delta^{13}\text{C}$ of CO in high temperature fumaroles as -10.8 ± 1.1 , which coincide well with that actually emitted from the high temperature fumaroles. The present result suggest that determination of both mixing ratio and $\delta^{13}\text{C}$ of CO in volcanic plume, we can deduce the temperature of fumaroles, if the temperature exceed 800 °C.