Geophysical Research Abstracts Vol. 21, EGU2019-15389, 2019 EGU General Assembly 2019 © Author(s) 2019. CC Attribution 4.0 license.



## The role of the water-gas interaction in controlling the chemistry of volatiles emitted in a seismic region: the central Apennines case (Italy)

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In the past few decades, much attention has been posed on the natural degassing occurring far from volcanic systems, such as the Earth's regions affected by continental rifting and active tectonics (Irwin and Barnes, 1980; Chiodini et al. 2000). Indeed, seismic regions are today worldwide renowned for being sites of extensive emissions of deep fluids (e.g., Italiano et al. 2009; Di Luccio et al. 2018). Furthermore, it has been proposed that the coseismic release of crustal-trapped over-pressurized fluids may represent one of the main triggering mechanisms of the aftershocks of large earthquakes (Miller et al. 2004). However, the primary composition of uprising gases can be modified upon migration to the surface as a result of solubility-controlled fractionation due to gas-water interactions. In a seismic region such processes have to be investigated and quantified in order to constrain possible modifications of the emitted fluids due to seismicity.

Here we report the investigation of the chemical and isotope (He and C) signature of gas discharged in the earthquake-prone area of the Umbria region located in central Apennines (Italy). This region is strongly affected by widespread surface degassing (mainly CO<sub>2</sub>) and characterized by fluid over-pressure at depth (Chiodini et al. 2004). Taking into consideration the C isotope composition, we observe that the  $\delta 13CCO_2$  of the sampled gases tends to be more negative from south to north along with a gradual enrichment of the less soluble volatiles (He and N2) with respect to CO2 abundance. Our data also confirm a regional variation of the He isotopic signature in the outgassing volatiles. We show that fractionation processes affecting the carbon isotope composition of the investigated gases can be obtained through a Rayleigh-type condensation model to explain the measured carbon isotope values. This variability both in gas concentrations and isotopic values can be ascribed to fractionation effects due to difference in solubility of the gas components during water-gas interaction. Partial dissolution of uprising  $CO_2$  in circulating groundwaters can affect the primary  $\delta 13CCO_2$  of the gas phase leading to an increase of the He/CO2 and N2/CO2 vs.  $\delta 13$ CCO2 ratios in the residual gas phase. This study highlights the pristine sources of the emitted fluids and how water-gas interactions control their composition. The main goal of this investigation is to emphasize the physicochemical processes governing the concentrations and isotope signature of natural emissions in seismic regions. Moreover, this study is also aimed at the development of a hydrogeological model necessary to shed light on the possible relationship between crustal degassing, fluid flow-induced seismicity, tectonics and water-gas interaction at regional scale. Finally, we show that variations of the water-gas interaction can modify the gas chemistry furnishing new tools to understand the earthquake-related signals that fluids transport to the surface.

## References

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