EGU21-15484
https://doi.org/10.5194/egusphere-egu21-15484
EGU General Assembly 2021

Noble gases and carbon isotopes in natural gas samples from seismic active areas of southern Apennines (Italy)

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In seismic active areas, the primary composition of natural gas emissions can be modified upon migration to the surface and storage in crustal reservoirs as the result of secondary chemical processes at shallow levels that can change the pristine composition of the fluids creating misunderstanding in the evaluation of the contributions due to different sources. Noble gases are among the most powerful indicators of such natural processes. In particular, Helium (hereafter He) is a reliable geochemical tracer for discriminating the crustal and mantle components in the outgassing gases due to the different origin of its two isotopes (^{3}He has a primordial origin, whereas ^{4}He is continuously produced by radioactive α-decay of ^{235,238}U and ^{232}Th). Therefore, the ^{3}He/^{4}He ratio is considered one of the most efficient geochemical tracers, whose variations can be directly ascribed to magmatic/crustal dynamics and therefore it is of primary importance in volcanic and seismic forecasting. In this study, we report chemical and isotopic (helium and carbon) data of gases and water emitted from three areas characterized by a high seismic hazard and located within the southern Apennines seismogenic belt. Through two fieldwork campaigns in 2019-2020, about 15 sites were inspected. Carbon dioxide is the main component in most of investigated sites (> 90 vol.%), except for Pozzo Tramutola, that is CH_4-dominated. He and N_2 concentrations are significantly variable (from 6 to 260 ppm and from 0.22 to 12.78 vol%, respectively). In agreement to previous investigations (Italiano et al., 2001; Caracausi and Paternoster, 2015), the sites in the Matese area are characterised by typical metamorphic [MOU1] N_2 values and low content of He and Ar and seem to be the result of mixing processes between crustal and/or metamorphic and atmospheric or ASW end-member. The sampled fluids have ^{3}He/^{4}He ratios from 0.02 to 2.92 Ra with corresponding He/Ne ratios in the range of 0.353-508.10. These ^{4}He/^{20}Ne ratios are much higher than the same ratio in the atmosphere (He/Ne=0.318; Ozima-Podosek, 2002) supporting that atmospheric He component in the sampled fluids is negligible for most sites. In general, we recognized that ^{3}He/^{4}He ratios indicate mixing between radiogenic and mantle end-members and Mefite site has highest mantle values that are close to the ratio at Mt Vesuvio and Pleghreian volcanic systems (< 60 from the study area). The ^{40}Ar/^{36}Ar ratios show a small range from values close to atmosphere up to ^{40}Ar/^{36}Ar = 325. We also investigated the carbon species and their isotopes. To investigate the genetic origins of the methane we have used web-based machine learning tool that determines the origin of natural gases (Snodgrass-Milkov, 2020) and the results shown that methane is mainly thermogenic even if

we also recognized an abiotic component in a few of sites. This study will provide data for the reconstruction of a basic model for interpreting the relationships between outgassing and tectonics, and further for interpreting possible seismic-induced variation

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