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In situ determination of the carbon isotopologues of the CO_2 emitted by soils

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The stable carbon isotopes of CO_2 provide constraints about the sources and the fluxes between different carbon reservoirs and sinks such as the atmosphere, the biosphere, the carbon dioxide of deep origin, and the oceans. From a volcanological standpoint, the amount of CO_2 emitted by soils during unrests equals or exceeds the carbon dioxide released from the craters of the volcanoes. Among the techniques of volcano surveillance, the stable isotope composition of carbon of the CO_2 emitted from the ground is a proxy for magmatic activity. Since decades, the carbon isotope composition has been analyzed in the laboratory by mass spectrometer on the gas samples collected in field. Since a few years ago, the development of new optical class of isotope analyzer based on the infrared laser allowed to determine in situ the isotope composition of the atmospheric CO_2.

This study focuses on the measurement in situ of $\delta^{13}C$ of the CO_2 emitted by soils and shows the results of the tests carried out in the laboratory and in field. A special gas sampling method has been fine tuned to collect the gas at a constant flux rate from a depth of 50 cm in the soils, and to identify the isotopologues of the CO_2. The method has been tested in the laboratory and in field with a Delta Ray™ Isotope Ratio Infrared Spectrometer of the ThermoFisher Scientific, field-able to analyze the $\delta^{13}C$ and $\delta^{18}O$ of CO_2. The gases were collected by a pumping system, and addressed online to the analyzer through a precision valve. This tailor-made device was added to the standard equipment of the instrument in order to adjust the gas flow in input to the analyzer. In this way, the CO_2 concentration in the cell fulfills the concentration range of the analyzer (200 - 3500 ppm vol) in spite of the CO_2 concentration in the ground gases.

The spatial survey of carbon isotopologues of CO_2 emitted by soils were performed at Vulcano (Aeolian Islands) on a sampling grid that consists of 20 measurement points on a 2.2 km^2 area at the base of the La Fossa cone. The measurement of the soil CO_2 flux was also performed in the same sampling grid according to the dynamic concentration method.

The results indicate that the sampling system allows the measurement of $\delta^{13}C$ in the ground gases with CO_2 concentration in the range from < 1000 ppm vol to 100% vol. During the spatial survey we measured $\delta^{13}C$ of CO_2 values in the range -22‰ (organic source) to 0‰, that represents the signature of deep source of CO_2 at Vulcano. Furthermore, the measurement of the $\delta^{13}C$ allowed to differentiate the sources (volcanic, biogenic, atmospheric) involved in the CO_2 emissions from the soils, and identify two areas of degassing with isotopic signature of deep origin at Faraglione and Grotta dei Palizzi. Furthermore, the results of the extensive investigation of both the spatial distribution of the carbon isotopologues and the CO_2 flux from soils allowed to assess the budget of CO_2 of deep origin emitted from the degassing areas.