Geophysical and geochemical data used to infer origin and evolution of natural CO_2 in Italy

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CO_2-degassing is well documented throughout the whole Italian peninsula and previous studies based on geochemistry of gases have already shown the existence of different CO_2 sources, (Minissale *et al*., 1997) ranging from deep mantle-derived CO_2 related to volcanism, to more "crustal" sources", that are less documented. Italian Peninsula is characterized by a high R/Ra gradient increasing from the North to the South. Geochemical ratios (R/Ra and $CO_2/^3He$) fit quite closely to a mixing curve between a mantle-derived end member (in the south) and a crustal end member in the North.

The high R/Ra ratio recorded in Southern Italy is easily related to Calabria slab mantle wedge processes.
Concerning the central Italian volcanism, the R/Ra ratio reaches 4, indicating a strong influence of mantle-derived helium, with an important continental/ crustal contribution.

Geochemical (elemental and isotopic ratios) and seismological (P-wave tomography and SKS splitting) data support the existence of a large window in the Adrian plate underneath the southern Apennines. The influence of the slab mantle wedge is not observed here. However, window appears at the northern lateral Calabria slab edges allowing mantle inflow induced by the Calabria retrograde motion (Gasparini *et al*.,2002; Faccenna *et al*., 2005; 2007).

In the North-Central part of Apennines, the reported helium isotopic ratios point to a general prevalence of crustal influence (typical crustal values estimated around 0,02 and 0,05 Ra). A significant component of mantle-derived helium is only found in the geothermal areas of Larderello (Northern Italy) where a large thermal anomaly is present at depth. (Cloetingh *et al*., 2010). By combining geophysical and geological observations we propose to explain this local anomalous ratio by a local asthenospheric upwelling, probably associated with lithospheric delamination, or slab break off processes.

Using this approach, we provide a new insight on the origin of CO_2, and we propose a strong relationship between diagenesis and/or metamorphic processes associated with subduction dynamics, rather than thermal decomposition of carbonates.

Mussel shells as archives of geogenic and anthropogenic dissolved REE

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Mussel shells may be used to evaluate trace element bioavailability, as the carbonate shell precipitates from the mussel's internal extrapallial fluid and not from external ambient water. We determined the REE distribution in shells of marine hydrothermal *Bathymodiolus* and littoral *Mytilus edulis* and of freshwater *Corbicula fluminea* mussels, and in the respective ambient river or seawater. Marine *Bathymodiolus* and *Mytilus edulis* shells reflect the presence and absence, resp, of positive Eu anomalies in their ambient waters, suggesting that positive Eu anomalies in mussel shells might be used to detect hidden or fossil high-temperature hydrothermal vent sites, thus helping exploration of VMS deposits [1]. Water from the Weser and Rhine rivers both display anthropogenic positive Gd anomalies that result from input of Gd used in MRI contrast agents, and the lower reaches of the Rhine River also show large an-thropogenic positive La anomalies [2]. While this La anomaly also occurs in *Corbicula* shells from the Rhine River, neither shells from the Rhine nor from the Weser River show a Gd anomaly. This demonstrates that in contrast to anthropogenic La, the Gd complexes used as MRI contrast agents are not bioavailable, which is further evidence of their conservative behaviour.

[1] Bau, M., Balan, S., Schmidt, K., Koschinsky, A. (2010) *Earth Planet. Sci. Lett.*, **299**, 310–316. [2] Kulaksiz, S. & Bau, M. (2011) *Environment International*, **37**, 973-979