

# Carbon fluxes from subducted carbonates revealed by uranium excess at Mount Vesuvius, Italy

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## ABSTRACT

The fate of carbonate-rich sediments recycled at destructive plate margins is a key issue for constraining the budget of deep CO<sub>2</sub> supplied to the atmosphere by volcanism. Experimental studies have demonstrated that metasomatic melts can be generated by partial melting of subducted carbonate-pelitic sediments, but signatures of the involvement of such components in erupted magmas are more elusive. We have made new U-Th disequilibria, Sr-Nd-Pb isotope, and high-precision δ<sup>238</sup>U analyses on lavas from Mount Vesuvius (Italy) and show that their measured <sup>238</sup>U excesses require a mantle source affected by the addition of U-rich carbonated melts, generated by partial melting of subducted calcareous sediments in the presence of residual epidote. Accordingly, we argue that the occurrence of <sup>238</sup>U excesses in “sediment-dominated” arc magmas represents diagnostic evidence of addition of carbonate sediments via subduction, hence providing constraints on deep carbon cycling within Earth. Our quantitative enrichment model, combined with published experimental results, allows us to estimate a resulting flux of 0.15–0.8 Mt/yr CO<sub>2</sub> from the subducted carbonates to the mantle source of Mount Vesuvius.

## INTRODUCTION

At destructive plate margins, the oceanic slab is subducted into the mantle, carrying both basaltic oceanic crust and overlying sediments. Part of this subducted material is then released at depth, affecting the mantle wedge above the slab, and it is eventually returned to the surface through volcanoes. This flux is a key part of element cycling on Earth (Kelemen and Manning, 2015).

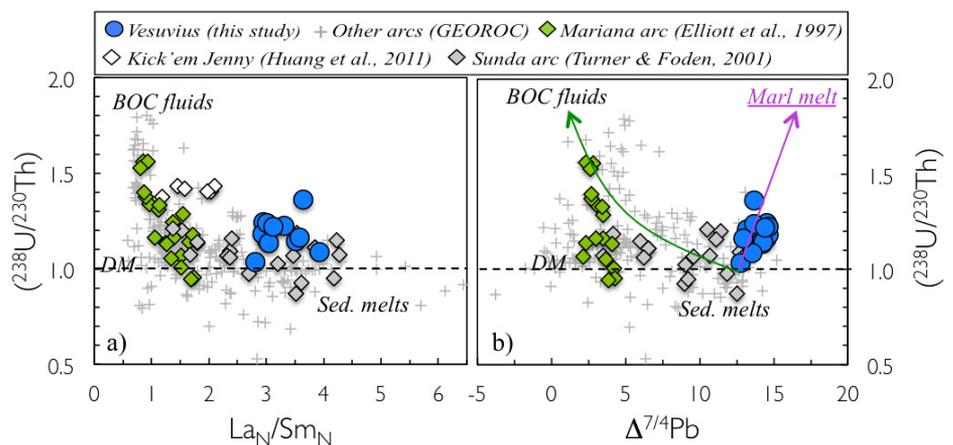
The evidence of this process can be found in the elemental and isotopic compositions of subduction-related magmas worldwide. Globally, the geochemistry of subduction-related volcanic rocks is dictated by the variable contribution of three main components (e.g., Elliott, 2003) (Fig. 1; Fig. DR1 in the GSA Data Repository<sup>1</sup>): (1) the depleted mantle (DM); (2) the slab-derived fluids, with isotope compositions similar to that of subducted basaltic oceanic crust (BOC); (3) the slab-derived melts, with crustal isotope signature, interpreted as deriving from the recycling of subducted sediments.

It can be difficult to deconvolve the contributions of these different components in arc magmas, not least for subducted carbonate-rich

sediments. Constraining their involvement is key to directly quantifying the origin of CO<sub>2</sub> emissions from volcanoes, with major consequences for atmospheric fluxes (Burton et al., 2013). Yet their contribution to subduction zone magmas is not necessarily distinctive in many traditionally used geochemical tracers.

Experimental studies (Poli, 2015; Skora et al., 2015) have shown that subducted carbonate-rich sediments (marls) may undergo partial melting if infiltrated by significant amounts of H<sub>2</sub>O. The involvement of subducted sedimentary carbonate in the genesis of some subduction-related volcanoes has been suggested on the basis of carbon isotope data on fumaroles and geothermal fluids (van Soest et al., 1998), of minor element contents in olivine (Ammannati et al., 2016), and of whole rock geochemical and isotope data (Conticelli et al., 2015). However, it is commonly difficult to constrain the nature of the recycled sediments from the isotopic compositions of erupted magmas.

Identifying the role of recycled carbonate sediments is further complicated by the possible occurrence of crustal limestone assimilation en route to the surface, which may modify the composition of the erupted magmas, overprinting some of the geochemical and isotopic signatures inherited from the mantle source (e.g., Iacono Marziano et al., 2009).



**Figure 1.** Plot of (<sup>238</sup>U/<sup>230</sup>Th) (parentheses denoting that the ratio is expressed as activities) versus chondrite-normalized La/Sm (A) and versus Δ<sup>74</sup>Pb (which represents the difference between the <sup>207</sup>Pb/<sup>204</sup>Pb of samples and that of Northern Hemisphere reference line (Hart, 1984) at the sample's <sup>206</sup>Pb/<sup>204</sup>Pb) (B). Samples from Mount Vesuvius (Italy; this study) are compared with other subduction-related volcanic rocks (data from GEOROC database, <http://georoc.mpch-mainz.gwdg.de/georoc/>). Samples from Mariana Islands (western North Pacific Ocean; Elliott et al., 1997; Avanzinelli et al., 2012) are representative of typical oceanic arc with variable contributions of sediment (sed.) melt relative to basaltic oceanic crust (BOC) fluids. Data for Kick'em Jenny (Caribbean; Huang et al., 2011) and Sunda arc (Indonesia; Turner and Foden, 2001) are representative of sediment-dominated arc lavas with possible contribution from carbonate-rich sediments. Depleted mantle is assumed to have (<sup>238</sup>U/<sup>230</sup>Th) = 1 and Δ<sup>74</sup>Pb = 0. Full data set for Mount Vesuvius samples is provided in the Data Repository (Tables DR1–DR4 [see footnote 1])

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<sup>1</sup>GSA Data Repository item 2018073, analytical methods, modeling description (including Figures DR1–DR4), and data tables (Tables DR1–DR7), is available online at <http://www.geosociety.org/datarepository/2018/> or on request from editing@geosociety.org.

In this study, we report the occurrence of marked  $^{238}\text{U}$  excesses at Mount Vesuvius (Italy), and coupling these  $^{230}\text{Th}$ - $^{238}\text{U}$  measurements with variations in  $\delta^{238}\text{U}$  (the parts-per-thousand difference in  $^{238}\text{U}/^{235}\text{U}$  relative to a reference solution standard, CRM145) and radiogenic isotope data (Sr, Nd, and Pb), we demonstrate the involvement of deep-recycled carbonate-rich lithologies in the mantle source of these magmas.

Uranium-series disequilibria in arc lavas have long been used to constrain the contribution of slab-derived liquids (fluids and/or melts), as well as the time scales of their transfer from the slab to the surface (e.g., Gill and Condomines, 1992; for further details, see the Data Repository). “Fluid-dominated” arcs are generally characterized by significant  $^{238}\text{U}$  excess over  $^{230}\text{Th}$ , that is,  $(^{238}\text{U}/^{230}\text{Th}) > 1$  (Fig. 1), a feature classically attributed either to the higher fluid mobility of U with respect to Th (e.g., Gill and Condomines, 1992), or to the presence of residual accessory phases preferentially retaining Th during melting of the subducting basaltic oceanic crust (Avanzinelli et al., 2012). Sediment melts, on the contrary, seem to impart either no disequilibrium (Condomines and Sigmarsson, 1993) or minor  $^{230}\text{Th}$  excesses (Avanzinelli et al., 2012) to the erupted lavas.

#### $^{238}\text{U}$ EXCESS AT MOUNT VESUVIUS AS TRACER FOR SUBDUCTION-DERIVED CARBONATE-RICH SEDIMENT MELTS

Mount Vesuvius lavas have significant  $^{238}\text{U}$  excesses (Voltaggio et al., 2004; Avanzinelli et al., 2008) (Fig. 1), which may suggest the involvement of BOC-derived fluids along the lines of the general processes proposed for arc magmas (Elliott, 2003).

Yet, when compared to the global arc database (Fig. 1), the observed  $^{238}\text{U}$  excesses in Vesuvius lavas are anomalous. Indeed, the geochemical and Sr-Nd-Pb isotopic compositions of Vesuvius lavas invariably lie at the “sediment-dominated” end of the global arc trend (Fig. 1; Fig. DR1), suggesting a mantle source strongly enriched by sediment-derived melts. In this scenario, the contribution from BOC-derived fluids should be obscured by the sediment-melt signal, due to the greater capacity of the latter as an incompatible trace-element carrier with respect to hydrous fluids.

Vesuvius lavas therefore are anomalous among subduction-related magmas. Yet, the occurrence of  $^{238}\text{U}$  excesses in sediment-dominated arc magmas is not a unique characteristic of Vesuvius (Fig. 1), but also occurs in a few other cases such as in the Lesser Antilles (e.g., Kick'em Jenny volcano; Huang et al., 2011), Nicaragua (Reagan et al., 1994), and part of the Sunda arc (e.g., Tabora and Sangeang Api volcanoes in Indonesia; Turner and Foden, 2001).

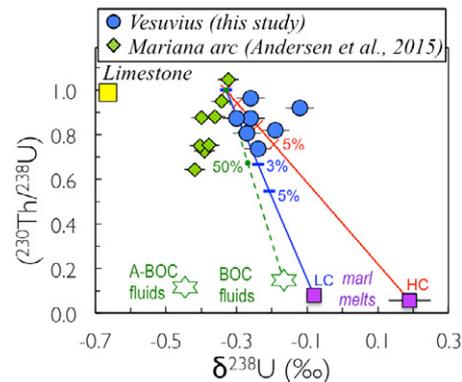
Given the sediment-derived trace element and long-lived isotope characteristics (i.e., Sr, Nd

and Pb; Fig. 1; Fig. DR1; Tables DR1–DR4 in the Data Repository) of Vesuvius lavas, the occurrence of large  $^{238}\text{U}$  excesses requires either extremely large amounts of BOC-derived fluids, to remain evident against the sediment contribution, or the addition of a sedimentary component recently enriched in U with respect to Th. When plotted against radiogenic isotope ratios such as  $^{87}\text{Sr}/^{86}\text{Sr}$  (Fig. DR3) and  $\Delta^{74}\text{Pb}$  (Hart, 1984; Fig. 1), Vesuvius lavas do not show a decrease of  $\Delta^{74}\text{Pb}$  with increasing  $(^{238}\text{U}/^{230}\text{Th})$  as would be expected if the  $^{238}\text{U}$  excess was due to BOC-derived fluids. Instead, the samples characterized by larger  $^{238}\text{U}$  excesses show similar or higher  $\Delta^{74}\text{Pb}$  (and  $^{87}\text{Sr}/^{86}\text{Sr}$ ) compared to samples close to secular equilibrium. Hence, the component responsible for the  $^{238}\text{U}$  excess at Mount Vesuvius also imparts a crustal signature to the magmas, indicating it must derive from subducted sediments.

To further constrain the origin of the U-rich component, we made high-precision  $\delta^{238}\text{U}$  measurements. Natural variations in  $^{238}\text{U}/^{235}\text{U}$  are linked to the partial reduction of hexavalent U(VI) to tetravalent U(IV) (see the review in Andersen et al., 2017) and are limited to the low-temperature environment of Earth's surface, so that the  $^{238}\text{U}/^{235}\text{U}$  signatures of magmas provide a robust tracer of near-surface-processed U. A recent study (Andersen et al., 2015) reported data for the Mariana arc, showing a clear trend from isotopically heavy U composition in sediment-dominated islands to isotopically light values in fluid-dominated ones. This feature, which is associated with the shift from  $^{230}\text{Th}$  to  $^{238}\text{U}$  excesses in erupted magmas (Fig. 2), has been interpreted to result from the isotopically light composition of U-rich fluids originating from the upper, most-altered portion of the BOC.

The Mount Vesuvius lavas measured in this study show instead an invariably heavy U isotopic composition, thus excluding a major role for fluids from the most altered portion of the BOC. Even considering the heavier  $\delta^{238}\text{U}$  reported for the bulk BOC (Andersen et al., 2015), exceedingly large amount of fluids would be required to generate the composition of Vesuvius lavas (Fig. 2). Coupled with the radiogenic isotope data (Fig. 1; Fig. DR3), these observations clearly indicate the need for a sediment-derived, isotopically heavy, U-rich component.

Thus, we analyzed the  $\delta^{238}\text{U}$  of a suite of Italian sediments that represent a likely analogue of the subducted sedimentary lithologies beneath Mount Vesuvius (Table DR4). This also includes a Mesozoic limestone of the type that forms the country rock hosting the magma chamber of Mount Vesuvius, which can be used to evaluate the effect of limestone assimilation that has been claimed to play a major role in controlling the magma compositions (Iacono Marziano et al., 2009). The Mesozoic limestone shows an extremely low  $\delta^{238}\text{U}$  (Fig. 2; Table DR4),



**Figure 2.** Plot of  $(^{230}\text{Th}/^{238}\text{U})$  versus  $\delta^{238}\text{U}$ . Averages between replicate analyses are plotted when available (Table DR4 in the Data Repository [see footnote 1]); error bars are based on reproducibility ( $2\sigma$ ) of international rock standards (Table DR4), and for  $(^{230}\text{Th}/^{238}\text{U})$  are smaller than symbol size; standard errors ( $2$  s.e.) for single measurements are reported in Table DR4. Data for Mariana Islands (western North Pacific Ocean; Andersen et al., 2015) are reported for comparison along with estimated composition of altered (A-BOC) and bulk basaltic oceanic crust (BOC) (Andersen et al., 2015). Mixing lines between mantle (assumed in secular equilibrium) and two possible sediment-melt components from high-carbonate (HC) and low-carbonate (LC) marls are reported. Mixing model with BOC-derived fluids is also shown. Mesozoic limestone sample (yellow square) is representative of wall-rock carbonate hosting Mount Vesuvius magma chamber. Details of model parameters are provided in Data Repository; compositions of all end members are reported in Table DR5.

indicating that the amount of U added to the magmas through limestone assimilation must be negligible. The same conclusion can be obtained from the subhorizontal alignment of the data on an U-Th isochron diagram. This does not exclude the occurrence of significant limestone assimilation at Mount Vesuvius ( $\sim 10\%$ ; Iacono Marziano et al., 2009) affecting some of the features of the magmas (e.g., major elements). In terms of U-Th disequilibria, however, this process may be responsible for some of the vertical scattering shown by the data on the U-Th isochron diagram (Fig. DR2), but not for the  $^{238}\text{U}$  excess (see details in the Data Repository).

On the contrary, the two carbonate-rich clays (i.e., marlstones) that we analyzed show high  $\delta^{238}\text{U}$ , making them suitable candidates to provide the distinctive signature of the studied magmas. The involvement of recycled carbonate-rich sediments as a “marl melt component” (MMC) can provide the solution to explain the  $^{238}\text{U}$  excess at Mount Vesuvius. A recent experimental study (Skora et al., 2015) showed that the abundances of some key trace elements in melts from calcareous sediments (i.e., marls) at sub-arc pressure-temperature ( $P$ - $T$ ) conditions are controlled by epidote, that it is stabilized during melting and can remain as a residual phase

until relatively high temperatures (900 °C). Epidote hosts limited amounts of U and Th, but it preferentially retains Th over U. Hence melts generated from carbonate-rich sediment in the presence of residual epidote have  $^{238}\text{U}$  excess, but at the same time they remain enriched in both Th and U. Natural evidence of the same process can be found in the composition of melt inclusions hosted in the deeply subducted carbonate rocks of the Kokchetav massif (northern Kazakhstan;  $P = 4.5\text{--}6.0$  GPa;  $T \sim 1000$  °C), which show extreme U/Th ratios ( $>2$ ; Korsakov and Hermann, 2006).

Therefore, melting of isotopically heavy, carbonate-rich pelitic sediments could produce suitable metasomatic agents to impart both the high  $\delta^{238}\text{U}$  and the  $^{238}\text{U}$  excess observed in Vesuvius lavas. In Figure 2, we modeled this process (see also Fig. DR3 and details in the Data Repository, and Table DR5), showing that  $<5\%$  of such a component is sufficient to impart U-series disequilibrium in a mantle source that had been previously strongly metasomatized, as evident from the radiogenic isotope composition of the samples with the smallest  $^{238}\text{U}$  excess (Fig. 1).

Evidence for such a process is not restricted to Mount Vesuvius. Other subduction-related magmas with sediment-dominated geochemical and radiogenic isotope signatures show significant  $^{238}\text{U}$  excess (e.g., Kick'em Jenny; Huang et al. 2011; Fig. 1). Therefore, we suggest that the presence of significant  $^{238}\text{U}$  excesses in enriched (i.e., sediment-dominated) subduction-related rocks may represent key evidence for the involvement of carbonate-rich subducted sediments.

This has important implications for constraining the carbon budget emissions at arcs. A recent study (Mason et al., 2017) suggested that shallow remobilization of crustal carbon (i.e., assimilation) may dominate the volcanic arc emissions over the deeper “subduction” carbon cycle, reporting Mount Vesuvius as one of the main locations where  $\text{CO}_2$  is mainly derived from interaction with the shallow crust (see also Iacono-Marziano et al., 2009). Our data indicate instead that subducted carbonate-rich sediment melts (MMC) have an important role in the chemical and isotopic composition of Vesuvius lavas, and Italian magmatism more generally (e.g., Avanzinelli et al., 2008; Conticelli et al., 2015), resulting in significant “subduction-derived”  $\text{CO}_2$  fluxes (see also Frezzotti et al., 2009).

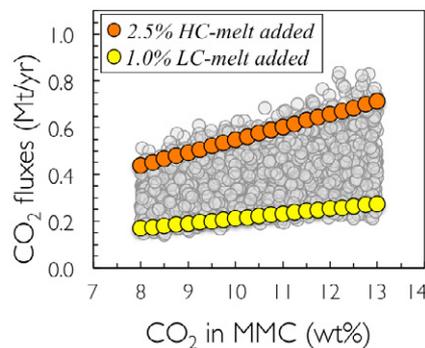
### MMC-DERIVED $\text{CO}_2$ FLUXES

We attempted to estimate the MMC-derived fluxes by combining the two-step mantle enrichment model used to explain the  $^{238}\text{U}$  excess of Vesuvius lavas with published parameters regarding the output rates of Mount Vesuvius and the amount of  $\text{CO}_2$  carried along with the MMC.

The rationale of our calculation is that, given the extreme incompatibility of U both during mantle melting and magma differentiation

(Blundy and Wood, 2003), it can be assumed that the total amount of U in Vesuvius magmatic products is the same as that hosted in their mantle source. Hence, knowing the magmatic output rates of Mount Vesuvius and the average U contents of the erupted products, it is possible to calculate the U flux from the mantle source. Combining this estimate with the U concentration calculated for the metasomatized mantle source in our two-step mantle enrichment model, we estimated the mass flux of mantle undergoing melting. Finally, we extrapolated the mass flux of MMC added to the mantle source of Mount Vesuvius from the proportion of MMC required to generate the observed average ( $^{230}\text{Th}/^{238}\text{U}$ ) of Vesuvius lavas (Table DR5). This can be converted to MMC-derived  $\text{CO}_2$  fluxes simply by estimating the amount of  $\text{CO}_2$  carried along with the MMC. Given the large uncertainties in several of the parameters used for the calculation—namely, (1) the U content of the erupted magmas, (2) the output rates, (3) the U and the  $\text{CO}_2$  content of the MMC, and (4) the amount of MMC required to produce the mean  $^{238}\text{U}$  excess observed in Vesuvius magmas—we performed Monte Carlo simulations, letting the four aforementioned parameters randomly vary between maximum and minimum values. Further details on the various parameters used are provided in the Data Repository and in Tables DR6 and DR7 therein. The results (Fig. 3) of our calculation yield average MMC-derived  $\text{CO}_2$  fluxes between  $\sim 0.15$  Mt/yr and  $\sim 0.8$  Mt/yr.

It is important to stress that the estimated fluxes presented in our study account only for the



**Figure 3. Calculated marl melt component (MMC)-derived  $\text{CO}_2$  fluxes plotted versus  $\text{CO}_2$  content of U-rich MMC used for each simulation (see text and Data Repository [see footnote 1] for further details). Gray circles represent all results of Monte Carlo simulations performed by letting main parameters used for calculation vary between minimum and maximum (see Table DR7); orange and yellow circles represent results obtained by keeping constant U concentration in erupted magmas ( $U_{\text{ves}} = 6.5$  ppm) and output rate (OR =  $3.5 \times 10^6$  m $^3$ /yr) in two case scenarios assuming 2.5% addition of high-carbonate (HC) and 1.0% addition of low-carbonate (LC) component (see Tables DR5 and DR6), respectively.**

$\text{CO}_2$  derived from the addition of the MMC and do not consider other possible sources of  $\text{CO}_2$  that contribute to the total  $\text{CO}_2$  fluxes released at Mount Vesuvius, such as those related to the shallow assimilation of limestone and those added from the subducted slab during the first step of mantle enrichment. Also, they represent an estimated  $\text{CO}_2$  flux averaged over the whole investigated period (A.D. 1697–1944), which would increase considerably (almost double) if considering only the active phases of the volcano (Scandone et al., 2008; see the Data Repository), and conversely decrease in low-activity phases. Therefore, it is difficult to compare our estimates with  $\text{CO}_2$  emissions from presently active volcanoes. Keeping this in mind, the range of MMC-derived  $\text{CO}_2$  fluxes calculated for Mount Vesuvius is comparable to fluxes calculated from present-day emission at arc volcanoes, such as Stromboli (southern Italy; 0.73 Mt/yr; Burton et al., 2013) and Montserrat (Lesser Antilles; 0.56 Mt/yr; Burton et al., 2013). This suggests that  $\text{CO}_2$  fluxes deriving from subducted carbonate-rich material are significant for the total carbon budget emitted at some arc volcanoes. Mount Vesuvius is not active at present, hence direct measurements of volcanic  $\text{CO}_2$  fluxes are not available, although estimates based on the isotopic composition of groundwater (Caliro et al., 2005) and diffuse soil degassing (Fronzoni et al., 2004) report values of  $\sim 0.1$  Mt/yr, which are lower than those indicated by our calculation. In addition, it must be taken into account that a significant portion of the present-day  $\text{CO}_2$  emitted around Mount Vesuvius has been linked to limestone assimilation (Iacono Marziano et al., 2009).

Yet, the  $^{238}\text{U}$  excesses of Vesuvius magmas, when combined with  $\delta^{238}\text{U}$  and Pb, Sr, and Nd isotope ratios, can only be explained by the addition in their source of carbonate-rich sediment melts that contributes significantly to the  $\text{CO}_2$  fluxes released at the surface, especially during the more-active phases of the volcano.

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