## **Data Repository Item DR2009083**

## 1. Petrological variations due to carbonate assimilation (after Iacono Marziano et al., 2008):

The trend depicted by the melt inclusions in Figure 2 is characterized by a continuous decrease in SiO<sub>2</sub> as MgO decreases from the magmatic end member (SiO<sub>2</sub>>51 wt%) to the skarn end member (SiO<sub>2</sub><44 wt%), accompanied by an increase in alkalis and Al<sub>2</sub>O<sub>3</sub>. Such trends cannot be explained by crystal fractionation alone, because they would require the massive crystallization of a strongly silica-rich phase which does not exist at Mount Vesuvius. Instead, the experimental results show that such variations are consistent with the effect of carbonate assimilation by basaltic magmas in the upper crust. SiO<sub>2</sub> is consumed by both reactions (1) and (2) in the text, leading to the silica depletion of the residual melt, as recognized in Mount Vesuvius eruptive products. Na<sub>2</sub>O, K<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> are passively enriched in the melt by clinopyroxene crystallization. MgO and CaO are consumed by clinopyroxene crystallization but are also variably supplied by carbonate assimilation depending on the type of assimilated rock (dolomite or calcite). Minor differences between the experimental and the natural melt chemistries depend on the starting composition of the uncontaminated magma (e.g. see  $Al_2O_3$  in Fig. 2) and on the type of assimilated carbonate (i.e. calcite assimilation increases more the CaO content of the melt than dolomite).

Marianelli et al., 2005 estimated entrapment pressures of 200-400 MPa for the inclusions in Figure 2, on the basis of their  $CO_2$ -H<sub>2</sub>O contents, implying that the assimilation process should occur at depths of ca. 7.5-15 km. However, the solubility laws that they used refer to MORB compositions and most likely underestimate  $CO_2$  solubility in Mount Vesuvius alkaline compositions (see CO<sub>2</sub> solubility data at 200 MPa in Iacono Marziano et al., 2008), and therefore probably overestimate entrapment depths.

## 2. Methods: Details of mass balance calculations

- Components (*i*): SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO, FeO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, H<sub>2</sub>O, CO<sub>2</sub>
- Known parameters:

 $i^{shoshonite}$ : component concentrations (wt%) in the uncontaminated melt (after Marianelli et al. 2005).

 $i^{calcite}$ ,  $i^{dolomite}$ : component concentrations (wt%) in the carbonates (CaCO<sub>3</sub>, CaMg(CO<sub>3</sub>)<sub>2</sub>).

 $i^{cpx}$ ,  $i^{olivine}$ ,  $i^{leucite}$ ,  $i^{oxide}$ : average component concentrations (wt%) in the minerals (after Fulignati et al. 2004; Marianelli et al. 2005).

*i* <sup>*fluid*</sup>: component concentrations (wt%) in the fluid phase. For H<sub>2</sub>O, solubility laws in molten silicate (Newman and Lowenstern 2002) were used to relate H<sub>2</sub>O concentration in the magma (H<sub>2</sub>O wt%<sup>melt</sup>) to its molar fraction in the gas ( $X_{H2O}^{fluid}$ ):

 $\left[H_2 O \text{ wt\%}\right]^{melt} = 0.0976^* (X_{H2O} * P_{total})^{\frac{1}{2}}$ 

where  $P_{total}$  is the total pressure, here assumed to be 2000 bar (200 MPa), on the basis of the storage conditions estimated in Marianelli et al., 2005. CO<sub>2</sub> molar fraction in the gas was (1- $X_{H20}^{fluid}$ ).

• Unknown parameters:

%<sup>calcite</sup>, %<sup>dolomite</sup>: amounts of assimilated carbonates %<sup>cpx</sup>, %<sup>olivine</sup>, %<sup>leucite</sup>, %<sup>oxide</sup>: mineral proportions %<sup>fluid</sup>: fluid proportion

• Three assimilation/crystallization steps were considered:

$$\begin{array}{c} \text{SHOSHONITE} \\ \text{+DOLOMITE} \\ \text{+CALCITE} \\ \text{+ CRYSTALLIZATION} \end{array} \rightarrow \overrightarrow{\text{TEPHRITE I}} \\ \overrightarrow{\text{HOOLOMITE}} \\ \text{+CALCITE} \\ \text{+ CRYSTALLIZATION} \end{array} \rightarrow \overrightarrow{\text{TEPHRITE II}} \\ \overrightarrow{\text{HOOLOMITE}} \\ \text{+CALCITE} \\ \text{+CALCITE} \\ \text{+CALCITE} \\ \text{+CALCITE} \\ \text{+CALCITE} \\ \text{+CRYSTALLIZATION} \end{array} \rightarrow \overrightarrow{\text{FOIDITE}} \end{array}$$

In each step of the calculation, only the residual melt resulting from the previous step is considered to undergo assimilation + crystallization (i.e. batch crystallization: both solid and gaseous fractions from the previous step are not taken into account).

• Equations solved for each component:

 $i^{tephriteI} = [(100 - \%^{\text{calcite}} - \%^{\text{dolomite}}) \bullet i^{shoshonite} + (\%^{\text{calcite}} \bullet i^{calcite}) + (\%^{\text{dolomite}} \bullet i^{dolomite}) - (\%^{\text{cpx}} \bullet i^{cpx}) - (\%^{\text{dolomite}}) - (\%^{\text{cpx}} \bullet i^{leucite}) - (\%^{\text{oxide}} \bullet i^{oxide}) - (\%^{\text{fluid}} \bullet i^{fluid})] / (100 - \%^{\text{cpx}} - \%^{\text{olivine}} - \%^{\text{olivine}}) - (\%^{\text{oxide}} \bullet i^{leucite}) - (\%^{\text{fluid}} \bullet i^{fluid})] / (100 - \%^{\text{cpx}} - \%^{\text{olivine}} - \%^{\text{olivine}})$   $i^{tephriteII} = [(100 - \%^{\text{calcite}} - \%^{\text{dolomite}}) \bullet i^{tephriteI} + (\%^{\text{calcite}} \bullet i^{calcite}) + (\%^{\text{dolomite}} \bullet i^{dolomite}) - (\%^{\text{cpx}} \bullet i^{cpx}) - (\%^{\text{olivine}} \bullet i^{olivine}) - (\%^{\text{cpx}} \bullet i^{leucite}) - (\%^{\text{oxide}} \bullet i^{oxide}) - (\%^{\text{fluid}} \bullet i^{fluid})] / (100 - \%^{\text{cpx}} - \%^{\text{olivine}}) - (\%^{\text{cpx}} \bullet i^{cpx}) - (\%^{\text{oxide}} \bullet i^{oxide}) - (\%^{\text{fluid}} \bullet i^{fluid})] / (100 - \%^{\text{cpx}} - \%^{\text{olivine}} - \%^{\text{olivine}}) - (\%^{\text{olivine}} \bullet i^{oxide}) - (\%^{\text{oxide}} \bullet i^{oxide}) - (\%^{\text{fluid}} \bullet i^{fluid})] / (100 - \%^{\text{cpx}} - \%^{\text{olivine}} - \%^{\text{olivine}} - \%^{\text{olivine}} - \%^{\text{olivine}}) - (\%^{\text{olivine}} \bullet i^{oxide}) - (\%^{\text{olivine}} \bullet i^{fluid})] - (100 - \%^{\text{cpx}} - \%^{\text{olivine}} - \%^{\text{olivine}} - \%^{\text{olivine}} - \%^{\text{olivine}}) - (\%^{\text{olivine}} \bullet i^{oxide}) - (\%^{\text{olivine}} \bullet i^{fluid})] - (100 - \%^{\text{cpx}} - \%^{\text{olivine}} -$ 

 $i^{foidite} = [(100 - \%^{\text{calcite}} - \%^{\text{dolomite}}) \bullet i^{tephriteII} + (\%^{\text{calcite}} \bullet i^{calcite}) + (\%^{\text{dolomite}} \bullet i^{dolomite}) - (\%^{\text{cpx}} \bullet i^{cpx}) - (\%^{\text{olvine}} \bullet i^{olvine}) - (\%^{\text{cpx}} \bullet i^{cpx}) - (\%^{\text{fluid}} \bullet i^{olvine}) - (\%^{\text{fluid}} \bullet i^{olvine})] / (100 - \%^{\text{cpx}} - \%^{\text{olvine}} - \%^{\text{olvine}} - \%^{\text{olvine}}) - (\%^{\text{fluid}} \bullet i^{olvine})] / (100 - \%^{\text{cpx}} - \%^{\text{olvine}} - \%^{\text{olvine}}) - (\%^{\text{fluid}} \bullet i^{olvine})] / (100 - \%^{\text{cpx}} - \%^{\text{olvine}} - \%^{\text{olvine}})$ 

where  $i^{tephriteI}$ ,  $i^{tephriteII}$ ,  $i^{foidite}$  are the component abundances in the contaminated melts. The unknown parameters were computed by minimizing the difference between  $i^{tephriteI}$ ,  $i^{tephriteII}$ ,  $i^{foidite}$  and the average abundances in natural melt inclusions determined after Fulignati et al. 2004; Marianelli et al. 2005.

## **3. Additional References**

- Del Moro, A., Fulignati, P., Marianelli, P., and Sbrana, A. (2001), Magma contamination by direct wall rock interaction: constraints from xenoliths from the walls of a carbonate-hosted magma chamber (Vesuvius 1944 eruption), *J. Volcanol. Geotherm. Res.*, *112*, 15-24.
- Newman, S., Lowenstern, J.B. (2002), VolatileCalc: a silicate melt-H2O-CO2 solution model written in Visual Basic for Excel, *Comput. Geosci.*, 28, 597.

balance calculations.					
Rock name	Shoshonite <sup>c</sup>	Trachybasalt	Tephrite	Foidite	Tephrite avg.
Petrological	Uncontaminated	Contaminated	Contaminated	Contaminated	Contaminated
signification	magma	magma	magma	magma	magma
wt% dolomite <sup>a</sup>	0	4.39	12.44	13.95	8.07-9.45
wt% calcite <sup>a</sup>	0	1.74	1.74	6.34	1.74-1.80
wt% total carbonate <sup>a</sup>	0	6.13	14.15	21.99	9.81-11.19
wt% $\operatorname{CO}_2^{b}$	0	2.89	6.76	10.30	4.67-5.33
Melt composition (wt%)					
SiO <sub>2</sub>	51.26	49.09	46.20	43.33	47.91
TiO <sub>2</sub>	0.94	1.07	1.17	1.57	0.93
$Al_2O_3$	12.39	13.95	17.30	18.10	16.50
MgO	8.63	7.88	5.95	3.58	6.74
FeO	7.29	8.04	8.79	10.34	7.35
CaO	12.23	12.31	11.06	11.10	11.62
Na <sub>2</sub> O	1.58	1.69	2.19	3.50	2.36
K <sub>2</sub> O	4.86	5.09	6.20	7.25	5.78
$P_2O_5$	0.82	0.89	1.15	1.23	0.82
Total	100	100	100	100	100
Na+K	6.44	6.77	8.38	10.75	8.14
H <sub>2</sub> O	3.88	3.50	1.88	1.93	2.00
CO <sub>2</sub>	0.20	0.20	0.20	0.20	0.20
Phase proportions (%)					
Fluid $(H_2O + CO_2)$	0	3.43	5.76	6.55	6.69-7.66
Melt	100	80.37	66.45	51.87	54.55-72.76
Olivine	0	0.50	2.24	0	1.68-2.76
Clinopyroxene	0	15.70	25.56	36.17	18.88-36.02
Leucite	0	0	0	2.88	0
Oxide	0	0	0	2.53	0
<b>Cpx composition</b> (wt%) <sup>d</sup>					
SiO <sub>2</sub>		51.90	49.70	46.60	49.70
TiO <sub>2</sub>		0.48	0.94	0.75	0.94
$Al_2O_3$		2.50	4.90	9.60	4.90
$Cr_2O_3$		0.10	0.05	0.00	0.05
MgO		16.70	13.92	13.50	13.92
FeO		4.00	6.75	3.90	6.75
MnO		0.06	0.09	0.09	0.09
CaO		24.70	23.40	25.40	23.40
Na <sub>2</sub> O		0.15	0.23	0.11	0.23
<b>Olivine composition</b> (wt%) <sup>d</sup>					
SiO <sub>2</sub>		41	41		41
TiO <sub>2</sub>		0	0		0
Al <sub>2</sub> O <sub>3</sub>		0	0		0
$Cr_2O_3$		0	0		0
MgO		48	48		48
FeO		48	11		48
MnO		0.2	0.2		0.2
CaO		0.2	0.2		0.2
Na <sub>2</sub> O		0.3	0.5		0.3
11020		U	U		0

Table DR1: Melt compositions, amounts of assimilated carbonates and phase proportions resulting from mass balance calculations.

<sup>*a*</sup> *Cumulative amounts of assimilated carbonates calculated for each composition.* 

<sup>b</sup> Cumulative amounts of  $CO_2$  liberated by the assimilation of both carbonates.

<sup>c</sup> Composition after Marianelli et al. 2005 assumed to represent the uncontaminated magma.

<sup>d</sup> Compositions of clinopyroxene and olivine crystallizing at each assimilation step. These are average compositions representative of each rock type (Joron et al. 1987; Del Moro et al. 2001; Fulignati et al. 2004; Marianelli et al. 2005), in agreement with the experimental data of Iacono Marziano et al. 2008.