

## Carbonate volcanics in Italy: numerical tests for the hypothesis of lava-sedimentary limestone mixing

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**ABSTRACT.** — Simple mixing of fragmented silicate lava with high level sedimentary limestone has been advocated for the formation of the carbonate-rich volcanic rocks of Italy. This is tested on the classic San Venanzo volcanics, using major element analyses. The limiting composition that would need to be added to San Venanzo lava (containing 41% SiO<sub>2</sub>) to produce the carbonate rich volcanic (with 39% SiO<sub>2</sub>) is not calcite, but silicate (with 38% SiO<sub>2</sub>). Alternatively, subtraction of calcite from the carbonate rich volcanic yields a limiting composition (with 53% SiO<sub>2</sub>) quite unlike the lava. Simple mixing cannot be reconciled with the major element chemistry of the rocks.

**RIASSUNTO.** — La genesi delle rocce vulcaniche italiane ricche di carbonato è stata ricondotta ad un semplice miscelamento a bassa profondità di porzioni di lava silicatica con calcari sedimentari. Questa interpretazione è basata sullo studio della chimica degli elementi maggiori delle vulcaniti di San Venanzo. Per produrre rocce vulcaniche ricche di carbonato (con 39% di SiO<sub>2</sub>) si dovrebbe aggiungere alle lave di San Venanzo (contenenti il 41% di SiO<sub>2</sub>) non calcite ma silicato (con 38% di SiO<sub>2</sub>). Alternativamente la sottrazione di calcite da una roccia vulcanica ricca di carbonato produrrebbe una composizione (con 53% di SiO<sub>2</sub>) molto diversa da quella della lava. La chimica degli elementi maggiori delle rocce non può essere spiegata tramite semplici processi di miscelamento.

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### COMMENTARY

Recently, in this journal, Peccerillo (2004) reiterated his hypothesis (Peccerillo, 1998) that the carbonate-rich volcanic rocks of central Italy were products of mixing silicate lavas with high level sedimentary limestone. This re-statement was at the exhortation of the Editor, because the earlier paper had evoked no comment. There may be as many reasons for lack of comment as there were readers: my own view was that it was an alternative hypothesis to that of Stoppa and Woolley (1997) using existing evidence (with the critical analyses derived from that source) and if comment were needed it was best left to others more directly involved. Now, a specific call for comments has been made, and should be answered, lest it be thought that silence signifies tacit approval.

My own experience of carbonate volcanism dates from 1956 (by coincidence the same year that Smith (1956) first pointed out the links between melilitite and carbonatite). My interest has not waned, and in the case of the Italian rocks I have yet to see any evidence that they should be considered uniquely different from the melilitite-carbonatite association elsewhere in the world (Peccerillo, 2004). In Uganda, for instance, limestones of sedimentary origin are so rare that the major quarries for the cement industry are in carbonatite, yet the type kamafugite volcanism in SW Uganda also has carbonate volcanism, just like that since

recognised in central Italy. These points have been made before (Bailey and Collier, 2000) and that contribution also passed without comment, so at least one experience is shared: however, the aim here is not to extend comparisons between these two classic kamafugite provinces, but solely to test the mixing hypothesis as proposed for Italy.

In the natural sciences, as Popper (1959) points out, many hypotheses are not susceptible to falsification, but simple mixing is not in this category because the basic assumption (mixing) is quantified (and can be tested) as soon as the end members are specified. In this case, the mixing is prescribed in terms of "fragmented silicate rocks into which calcite has been incorporated during their passage through the sedimentary rocks which they have intruded," and "element depletion is proportional to their carbonate content" (Peccerillo, 2004, pp. 167 and 172). To illustrate this, Peccerillo (1998, Fig. 4) uses chemical variation diagrams for selected variables (from four separate complexes) plotted against CaO. Some of these might be taken

as indicating broad negative correlations with CaO, as would be required by such mixing, but, of course, this could not constitute proof, nor even a stringent test of the hypothesis. In fact, the poor correlations revealed in some of the diagrams only serve to raise questions, because closer scrutiny shows that for any individual complex none of the tie lines between silicate lava and carbonate volcanics is colinear with sedimentary limestone. To apply a rigorous test, the complete sets of major elements in the end members must be compared first, because the arithmetic of mixing is completely constrained by the requirements of constant sum.

Addition/subtraction variation diagrams can be used to summarise the array (providing simple graphical solutions, Bowen, 1928), or the limiting numerical compositions of the required additive or residue (after extraction) can be calculated precisely. Results for the two San Venanzo samples used by Peccerillo are given in Fig.1 and Table 1. If the carbonate volcanic (CV) were the product of mixing lava (L) with calcite (as proposed)

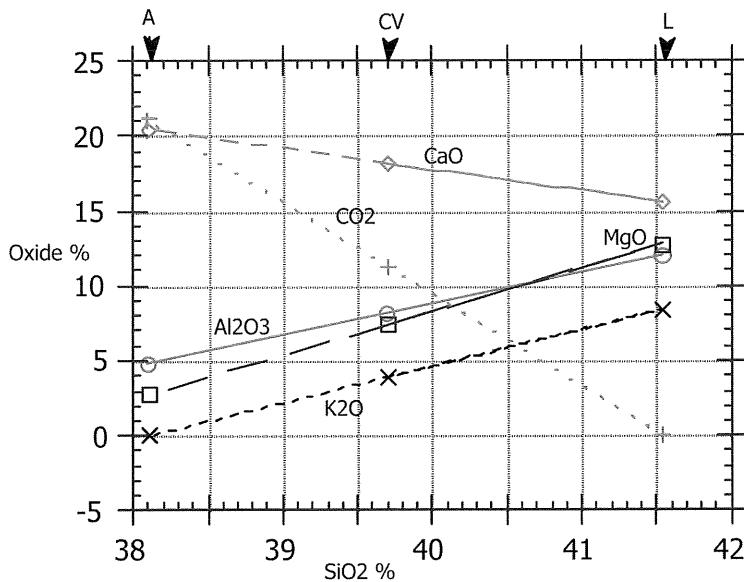


Fig. 1 – Addition diagram for San Venanzo, illustrating the requirements for generating carbonate volcanic (CV) by mixing silicate volcanic (L) with material from another source. The limiting composition (A) is defined by the first component running to zero (in this case, K<sub>2</sub>O). If CV were a mix, the proportions of A and L would be given by the lever rule: 53.5% A with 46.5% L.

TABLE 1  
 Addition and subtraction analyses data for San Venanzo.  
 Carbonate volcanic: CV (PC9-1, Table 2, Stoppa and Woolley, 1997).  
 Silicate volcanic: L (Anal. 1, Table 1, Peccerillo, 2004).  
 A; limiting composition of material needed to mix with L to produce CV.  
 CV, L and A are shown in the addition diagram, Figure 1.  
 Residue: composition of residue after extraction of calcite from CV.

| Oxide Wt %                     | CV    | L     | A     | Residue |
|--------------------------------|-------|-------|-------|---------|
| SiO <sub>2</sub>               | 39.70 | 41.54 | 38.12 | 53.48   |
| TiO <sub>2</sub>               | 0.56  | 0.69  | 0.45  | 0.75    |
| Al <sub>2</sub> O <sub>3</sub> | 8.16  | 12.00 | 4.86  | 10.99   |
| FeO <sup>T</sup>               | 5.16  | 6.49  | 4.02  | 6.95    |
| MnO                            | 0.10  | 0.11  | 0.09  | 0.13    |
| MgO                            | 7.39  | 12.77 | 2.77  | 9.96    |
| CaO                            | 18.20 | 15.60 | 20.43 | 5.15    |
| Na <sub>2</sub> O              | 0.56  | 1.14  | 0.06  | 0.75    |
| K <sub>2</sub> O               | 3.89  | 8.40  | 0.02  | 5.24    |
| P <sub>2</sub> O <sub>5</sub>  | 0.23  | 0.42  | 0.07  | 0.31    |
| LOI                            | 3.95  | 0.00  | 7.34  | 5.32    |
| CO <sub>2</sub>                | 11.30 | 0.00  | 21.00 | 0.00    |
| Sum                            | 99.50 | 99.16 | 99.23 | 99.04   |

FeO<sup>T</sup>: Total iron as FeO.

then, in the variation diagram based on SiO<sub>2</sub>, all oxide tie lines between L and CV (except CaO and CO<sub>2</sub>) must extrapolate to zero at the origin (zero SiO<sub>2</sub>). Fig.1 shows this is not so, and the limiting composition for the material (A) that would be required for mixing is found at 38.12% SiO<sub>2</sub> (defined by the first oxide extrapolated to zero, in this case K<sub>2</sub>O). Numerical values for composition A are given in Table 1.

In the Peccerillo tables of analyses (Table 1, 1998 and 2004) LOI and CO<sub>2</sub> are not provided, but full analyses of the carbonate volcanics are given in Stoppa and Woolley (1997, Table 2) including LOI and CO<sub>2</sub>. These analyses permit an alternative, completely precise test of the mixing hypothesis, because the normative calcite (cc) in CV can be calculated from the CO<sub>2</sub> value. Deduction of cc from the whole rock analysis for CV then gives the composition of the non-carbonate residue.

According to the mixing hypothesis this residue should match the composition of the associated lava (L), and the result for San Venanzo is given in Table 1, showing that the lava (L) and the residue (Residue) are completely different.

These two tests, showing the limit of any addition to L, and the residue after subtraction of calcite from CV, show that simple mixing will not work for San Venanzo, and the same applies to Cupaello. Major element tests thus disqualify the mixing hypothesis, and it follows that any manipulations of the trace element data from L and CV (even though they may offer other insights) can never be cogent to the mixing hypothesis.

For Polino no lava is reported, and the non-carbonate residue is largely mantle debris (olivine/monticellite + phlogopite; Stoppa and Lupini, 1993); hence the carbonatitic chemistry of the

eruptive would be left unexplained (unless, of course, it were carbonatite!).

#### CONCLUSION

Sedimentary limestone from country rocks, when incorporated in a carbonate eruptive, is usually readily distinguished (Riley et al., 1999; Stoppa and Woolley, 1997). Once this has been done, the volcanic carbonate has much to tell about the physical and chemical state of the underlying mantle, and surely this should be the critical focus for trying to unravel the geodynamics of the Italian province. Every effort should now be devoted to deciphering the vital information lodged in the mantle carbonate.

San Venanzo is a classic volcano in petrology, and any new interpretation must be expected to arouse questioning from Italian colleagues: it is to be hoped that others with alternative views will follow Peccerillo's lead in stimulating the wider debate. Only then will Italian geodynamics be integrated in the global picture. My comments are directed to this end, with the hope that they will be accepted in a spirit of scientific exchange in the international forum.

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