

On the nature of carbonate-rich volcanic rocks in Central Italy. A reply to comments by Woolley et al.

ANGELO PECCERILLO*

Dipartimento di Scienze della Terra, Università di Perugia, Piazza Università, 06100, Perugia, Italy

ABSTRACT. — In an early paper (Peccerillo, 1998a) and in a more recent one (Peccerillo, 2004), I raised doubts about the hypothesis of Woolley and coworkers that the carbonate-rich pyroclastic rocks from the Intra-Appennine Province of central Italy (IAP) represent carbonatites. Eight years after publication of my 1998 paper, an answer finally arrives from Woolley and coworkers. Woolley *et al.* (2005) accept that mineralogical criteria and abundances of incompatible elements, including REE, are insufficient to establish a carbonatitic nature for IAP rocks, but they remain firmly convinced that carbonate-rich rocks from IAP are carbonatites, and that there is no significant interaction between magmas and carbonate wall rocks in the IAP. However, they do not provide an explanation for the high oxygen isotopic ratios of silicate phases, and do not account for the diluent effect of carbonates on silicate fraction observed in pairs of coexisting lavas and carbonate-rich rocks. Therefore, my key objections remain unanswered.

I believe that high oxygen isotope ratios of both carbonates ($\delta^{18}\text{O}\text{‰} = +20$ to $+25$) and, in particular, of silicate phases ($\delta^{18}\text{O}\text{‰} = +11$ to $+14$) of IAP rocks, together with the diluent effect of carbonate fraction observed in pairs of bulk carbonate-rich rocks and associated lavas at San Venanzo and Cupaello, cast doubts on a magmatic origin for carbonates. Whatever the opinion one may have on IAP carbonate-rich rocks, however, the alleged equivalence between

IAP and Vulture volcano is unfounded, since the two occurrences differ for major, trace element and isotopic compositions, as well as for volcanological characteristics and geodynamic setting. Even more so, is for African carbonatite-kamafugite association whose composition and geodynamic significance have little or nothing to do with IAP. Incompatible element distribution and radiogenic isotopes of IAP rocks are very similar or identical to those of mafic rocks from the Roman province, indicating a genesis in similar metasomatic mantle sources and the same geodynamic significance.

RIASSUNTO. — In due precedenti lavori (Peccerillo, 1998a; 2004) avevo sollevato dubbi sull'ipotesi avanzata da Woolley e collaboratori che le piroclastiti ricche in carbonato dei vulcani monogenici intra-appenninici dell'Italia centrale (IAP) potessero rappresentare delle carbonatiti, ipotizzando un'origine esterna della componente carbonatica, derivata probabilmente da interazione tra magmi kamafugitici e rocce carbonatiche incassanti. Nella loro risposta, Woolley *et al.* (2005) ammettono che alcuni dei criteri da loro stessi utilizzati in passato sono insufficienti per stabilire la natura carbonatitica di queste rocce, ma ribadiscono l'assenza di dubbi sull'origine magmatica del carbonato, riaffermando la assoluta certezza che l'interazione tra magma e rocce incassanti non ha avuto alcun ruolo nel vulcanismo intra-appenninico.

Tuttavia gli argomenti portati a supporto di questa loro affermazione sono piuttosto deboli e non risolvono i dubbi iniziali, specialmente per quanto

* E-mail: pecceang@unipg.it

riguarda la geochimica degli isotopi dell'ossigeno sia nella componente carbonatica sia, e soprattutto, in quella silicatica, e gli effetti di diluizione della frazione carbonatica su quella silicatica kamafugitica.

Nella mia risposta sostengo che gli elevati rapporti isotopici dell'ossigeno sia per la frazione carbonatica ($\delta^{18}\text{O}\text{‰} \sim +20$ to $+25$) che per quella silicatica ($\delta^{18}\text{O}\text{‰} \sim +11$ to $+14$), sono difficili da spiegare se non si ammette un'interazione tra magmi e sedimenti carbonatici. Inoltre sostengo che le vulcaniti del Vulture e meno ancora quelle dell'Africa Orientale, che Woolley e collaboratori ritengono analoghe alla IAP, non hanno alcuna relazione con il magmatismo intra-appenninico, data la forte diversità composizionale, vulcanologico-strutturale e di ambientazione geodinamica delle tre province magmatiche. I magmi della IAP hanno distribuzione degli elementi incompatibili e rapporti degli isotopi radiogenici (Sr-Nd-Pb) molto simili o identici a quelli delle rocce mafiche della Provincia Romana, indicando una genesi in sorgenti mantelliche simili, interessate dallo stesso tipo di processi metasomatici in uno stesso ambiente geodinamico.

KEY WORDS: *Italian magmatism, ultrapotassic magmatism, carbonate-rich rocks, carbonatites, mama contamination.*

INTRODUCTION

Woolley *et al.* (2005) finally answer to the objections I have raised in two papers (Peccerillo, 1998a; 2004) and at several international conferences, including the one on carbonatites organised in London on January 2001 by Woolley and coworkers. My objections had cast doubts on the widely accepted idea that the carbonate-rich rocks from the Intra-Apennine magmatic Province (IAP) of central Italy represent carbonatites, suggesting that the carbonate component is not magmatic in origin but may be originated by magma-wall rock interaction.

Before going through the comments of Woolley *et al.*, I wish to clarify a few points, which will help in the following discussion:

1. Although I was the first to report on a complete set of trace element and Sr isotopic data for IAP kamafugitic lavas (Peccerillo *et al.*, 1988), I do not share the opinion of Woolley and coworkers that the IAP rocks are of paramount

importance for understanding the genesis and geodynamic significance of magmatism in central Italy. All the available data clearly demonstrate that the IAP rocks have similar or identical trace element and radiogenic isotope signatures as the mafic rocks from the Roman Province. This is shown in the diagrams reported in Figs. 1 and 2. To me, these striking similarities (hope Woolley and coworkers will agree) strongly support that both the IAP and the Roman magmas have been formed in similar and anomalous upper mantle sources that have suffered the same type of compositional modification by metasomatic processes (see Peccerillo, 2005 for a review). However, the IAP rocks, especially carbonate-rich pyroclastics, are generally more altered than several Roman lavas and may have suffered interaction with carbonatic wall rocks. This leads me to conclusion that it is much wiser to rely upon Roman rocks rather than on the few monogenetic, altered (and probably contaminated) rocks from the IAP, if one wants to understand the many and complex petrogenetic and geodynamic aspects of central Italy magmatism. The unexceptional relevance I credit to IAP rocks was one of the reasons for my reluctance to write the 2004 paper on *Periodico di Mineralogia*. The other reason was the lack of reaction from Woolley and coworkers to my 1998 paper and to the numerous communications to national and international conferences (e.g. Peccerillo, 1998b), which I considered quite surprising.

2. I believe it unfounded to consider the Vulture magmatism as part of the IAP. As early stated by Washington (1906), Mt. Vulture (the so-called "Apulian Region") has different mineralogical and major element characteristics than any other Italian volcano. Recent studies on Mt. Vulture (De Fino *et al.*, 1986; Beccaluva *et al.*, 2002; De Astis *et al.*, 2006) demonstrated distinct compositions for trace element abundances and ratios as the IAP rocks (Figs. 1 and 2). Moreover, the Mt. Vulture stratovolcano is situated in a distinct structural setting as the IAP. The latter occurs in the axial zone of the Apennines, along extensional basins behind the Apennine compression front. Vulture is situated east of the Apennines, on the margin of the Apulia foreland, a promontory of the African plate, i.e. basically in an intraplate setting. The reasons why Woolley and coworkers carry on with

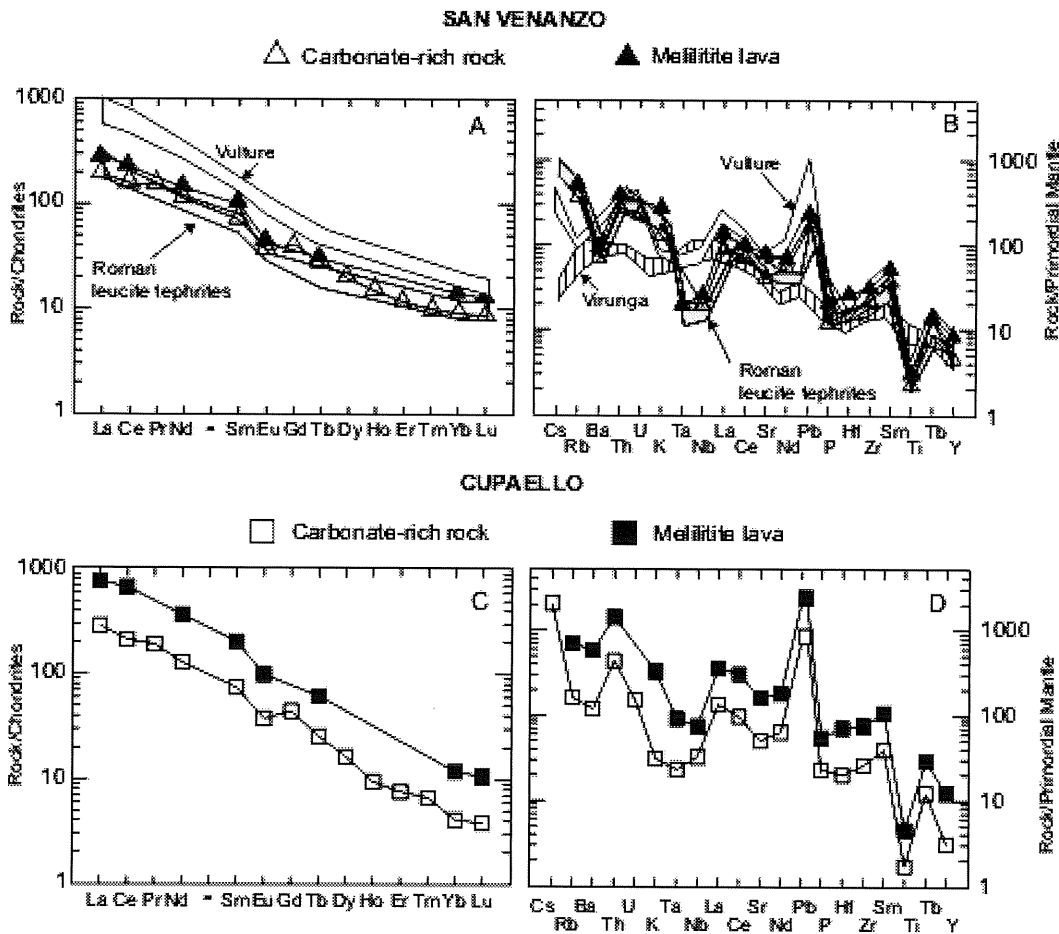


Fig. 1 – REE and incompatible element patterns of lavas and carbonate-rich rocks from San Venanzo and Cupaello. The fields of the Roman Province, Mt. Vulture and Virunga (East Africa) mafic rocks ($\text{MgO} > 5 \text{ wt}\%$) are reported for comparison. For source of data see Peccerillo (2005, Chapter 3 and attached CD-ROM).

putting everything together is hard to understand. Even more invalid, is the claimed relationship with East African volcanoes, which have totally different geochemical and isotopic signatures than IAP (Figs. 1 and 2). I did never write or believe that all kamafugites and carbonatites derive from assimilation processes. Therefore, any attempt to invoke the lack of carbonates in east Africa to exclude contamination in the Apennines seems to me out of place. More about this in my reply to Bailey's comments.

3. I did never believe (and I did never write) that the volcanic rocks from the IAP are skarns. Rocks from San Venanzo, Cupaello and Polino are certainly volcanic in origin, although I have suggested that there are numerous clues indicating interaction with wall carbonate rocks. I have cited skarns to underline how some of the mineralogical and geochemical features observed in IAP rocks are also found in skarns, whose origin by interaction between magmatic and carbonate sedimentary components is beyond discussion.

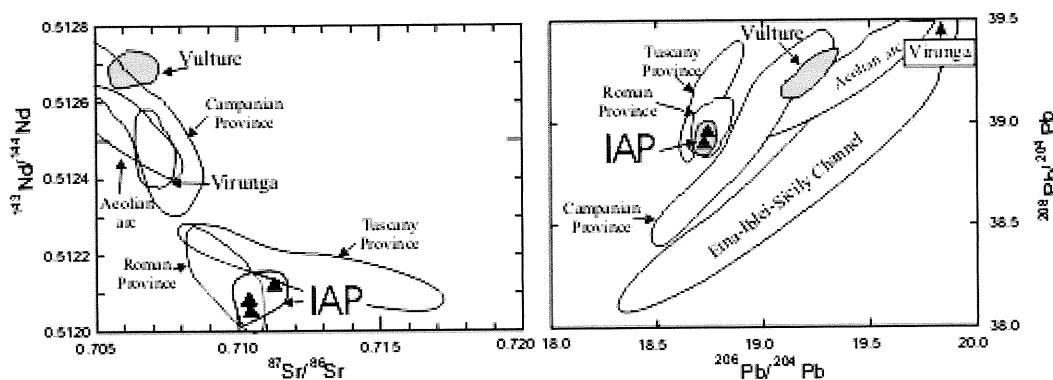


Fig. 2 – Sr-Nd-Pb isotope compositions of San Venanzo and Cupaello rocks (full triangles). The fields of mafic rocks from other volcanic provinces in Italy are reported for comparison. For source of data see Peccerillo (2005).

EVIDENCE FOR AND AGAINST CARBONATITIC ORIGIN

Let pass now to single comments of Woolley *et al.* (2005):

1. *High concentrations of LILE and REE.* Woolley and coworkers have repeatedly emphasised the importance of REE and incompatible element abundances and patterns to support carbonatitic nature for IAP rocks. Statements like “...chondrite normalised plot for REE display straight, steep patterns typical for carbonatites, as illustrated by plot of average sovite”, and “Mantle normalised HFSE for both lava and lapilli show typical extrusive carbonatite patterns” are so frequent (e.g., Stoppa and Woolley, 1997; Stoppa and Cundari, 1998), that is not the case to recall them any longer. Now, Woolley *et al.* (2005) admit that abundances of LILE and REE patterns by themselves do not prove or support a carbonatitic origin for the IAP carbonate rich-rocks and that REE patterns and negative Eu anomaly, first mentioned in Italian kamafugites by Peccerillo *et al.* (1988), parallel those of the Roman Province. I agree totally with this late but welcome conclusion. Fig. 1 clearly shows that IAP rocks resemble closely the nearby Roman Province. Such a close similarity cannot be observed with any kamafugite or carbonatite from Africa or elsewhere, as frequently suggested (e.g., Stoppa, 2003, Fig. 4).

2. *Trace element contents of calcite.* Incompatible element contents in calcite from the IAP rocks must be considered with care when drawing conclusions on origin of carbonates. If carbonates were incorporated in some way from wall rocks into the IAP magmas, their present trace element contents may have very little in common with original compositions. It is well known that various phases of magmas involved in a mixing or assimilation process undergo continuous compositional changes because of the tendency for the system to reequilibrate to the new physico-chemical conditions. Strongly variable diffusive fractionation affects various chemical elements at different rates, depending on diffusion coefficients, chemical potential gradients and on the efficiency of mixing dynamics (e.g., Nakamura and Kushiro, 1998; Appora *et al.*, 2003; Perugini and Poli, 2004; Perugini *et al.*, 2003; 2005 and references therein). Consequently, various phases modify more or less strongly their original elemental and isotopic signatures, making it incorrect considering their final composition as representative of the starting one. In contrast, the composition of the mixed system as a whole does not change with ongoing mixing and equilibration processes, unless there is loss of components, e.g. by degassing, fractional crystallisation or else. In any case, the whole rock analysis furnishes more reliable and direct information on mixing and assimilation processes than data on single phases.

I also have strong doubts that analyses of acid leached fractions as those reported by Stoppa and Woolley (1997; Table 3), do actually represent reliable compositions of the carbonate fraction. This is suggested to me by results of acid leaching on two very fresh carbonate-free rocks from Vulcini that have similar composition as the San Venanzo lava (Di Battistini *et al.*, 2001). Solutions obtained after rapid attack by diluted HCl at room temperature on one gram of powdered samples, were found to contain significant concentrations of trace elements. Conversely, a depletion was observed in the acid insoluble residue. Such a simple experiment, that everybody can replicate at home, clearly indicates that rapid acid leaching is able to scavenge quite a lot of elements out of silicates or other non-carbonate phases. This casts doubts on the assumption that acid leachates represent reliable compositions of the carbonate fraction. Such a problem, which was also pointed out by Stoppa and Woolley (1997), may be much more severe in altered, fine-grained pyroclastic rocks such as those from the IAP.

3. *Mineral unique or not unique to carbonatites.* Woolley *et al.* (2005) agree that minerals such as beddeleyite, Th-rich pyrochlore, Zr-rich-garnet etc. are not unique to carbonatite. Therefore, previous statements that the presence of these rare minerals are peculiar to carbonatitic rocks (e.g. Stoppa and Lupini, 1992) have to be considered as incorrect.

4. *Sr isotopes.* Castorina *et al.* (2000) report $^{87}\text{Sr}/^{86}\text{Sr}$ data for HCl-soluble (allegedly carbonate) and HCl-insoluble (silicate) fractions for nine samples from the IAP. They claimed that isotopic signatures of carbonate and silicate fraction from single rocks are virtually indistinguishable and that there is isotopic equilibrium between carbonatite and melilitite for single occurrences. This alleged isotopic equilibrium is used to exclude wall rock interaction and to suggest cogenetic origin for carbonate and silicates components, possibly by unmixing from a parental carbonate-silicate melt. In my 2004 paper, I reported on only two out of the nine samples analysed by Castorina *et al.* (Polino sample PO2-5: $^{87}\text{Sr}/^{86}\text{Sr}_{\text{silicate}} = 0.710793 \pm 9$, $^{87}\text{Sr}/^{86}\text{Sr}_{\text{calcite}} = 0.710343 \pm 30$; San Venanzo sample PPC-3d: $^{87}\text{Sr}/^{86}\text{Sr}_{\text{silicate}} = 0.712113 \pm 16$, $^{87}\text{Sr}/^{86}\text{Sr}_{\text{calcite}} = 0.710415 \pm 12$) and stated that these cannot be considered as equilibrium compositions. Woolley *et al.* (2005) argue that these represent exceptions

rather than a rule and, therefore, reaffirm isotopic equilibrium. I strongly disagree with such a statement. *First*, two samples over a total of nine can be hardly defined as an exception. *Second*, strong disequilibrium is also present for the Cupaello carbonate-rich sample COP-11, which shows isotopic variation between whole rock and separated silicate phases as high as one unit on the third decimal place ($^{87}\text{Sr}/^{86}\text{Sr}_{\text{whole rock}} = 0.710075 \pm 16$, $^{87}\text{Sr}/^{86}\text{Sr}_{\text{cpx}} = 0.711267 \pm 11$; $^{87}\text{Sr}/^{86}\text{Sr}_{\text{phlogopite}} = 0.711436 \pm 13$). Unfortunately, no values are reported for calcite (why?), but comparison between whole rock and host silicate minerals suggests that calcite is much less radiogenic than silicates. *Third*, some other samples among those reported by Castorina *et al.* (2000) for Polino and San Venanzo show Sr isotopic values for coexisting silicate and carbonate fractions that are well outside analytical error (see Table 2 of Castorina *et al.* 2000). To conclude, I do not see much reason for further discussion on this issue. It is obvious to me that isotopic disequilibrium is indeed present in a considerable number of IAP carbonate-rich rocks. Frankly, I believe that it would be much better for science to try to explain such a disequilibrium rather than saying it does not exist.

I do also feel that isotopic disequilibrium may be even higher than emerging from the data. Castorina *et al.* (2000) used acid leaching techniques to analyse carbonate fractions. The data on carbonate-free rocks from Vulcini discussed above strongly suggest that acid leaching may take significant amounts of Sr out of silicates. If so, Sr isotope analyses of acid leachates could yield $^{87}\text{Sr}/^{86}\text{Sr}$ values much closer to silicate phases than expected for pure carbonates.

The rest of the discussion by Woolley *et al.* (2005) on variation of Sr isotopes during carbonate assimilation is flawed by the several other oversimplification. For instance, they assume a single type of carbonate material as contaminant. However, the geological situation is much more complex, and the thousand meters of bedrock sequences crossed by IAP magmas include Permo-Triassic phillites and quartzites, Late Triassic to Oligocene marls, limestones and dolostones, Miocene terrigenous turbiditic rocks, and Plio-Quaternary sediments filling extensional basins (e.g. Barchi *et al.*, 2001). Any of these rocks may have potentially contributed to contamination, thus

making models of pure carbonate contamination unrealistic. The objection that rapid magma ascent prevents contamination is untenable, given, for instance, the evidence coming from the nearby Tuscany Province in which rapid ascending primitive melts containing mantle xenoliths, were able to dissolve as much as 30% crustal material (Conticelli, 1998).

5. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. It is well known that oxygen isotopic compositions of carbonates in extrusive carbonatites are affected heavily by secondary processes. I amply acknowledged this in my previous papers. However, the very high oxygen isotope ratios for calcite from inside San Venanzo lavas (17 analyses for calcite from the groundmass, cavities and from pegmatoid veins cutting the lava show $\delta^{18}\text{O} \sim +24\text{‰}$ to $+26\text{‰}$; Turi, 1969) is somewhat intriguing, since these carbonates are less exposed to secondary alteration than pyroclastic rocks. As for carbon isotopes, negative values of $\delta^{13}\text{C}$ are common in calcites whose origin from sedimentary carbonates is beyond discussion (i.e. skarns). This is not surprising, since fractionation of stable isotopes during geological processes is variable from one element to the other and for different physico-chemical processes (e.g., Valley, 1986). However, what is impressive with IAP rocks is that the silicate phases from the lavas have extremely high $\delta^{18}\text{O}$ (from +11 to +14 for whole rocks and separated olivine and clinopyroxene phenocrysts at San Venanzo and Cupaello; Turi *et al.*, 1986; Holm and Munksgaard 1982, 1986; author's unpublished data). I believe that these data deserve an explanation, but did not read any in the Woolley *et al.* (2005) comments. Are these mantle compositions? Or, instead, do they represent evidence or at least a clue that silicate magmas interacted with the very thick carbonate bedrock sequence during their ascent?

EVIDENCE FROM SAN VENANZO AND CUPAELLO

Woolley *et al.* (2005) report on trace element contents of calcite from Oricola rocks, and claim that these provide conclusive evidence in favour of a carbonatitic nature. I have discussed in the previous paragraphs how data on separated phases should be considered with care. For these reasons, most of the discussion in my previous papers

(Peccerillo, 1998a, 2004) was based on comparison between bulk compositions of associated lavas and carbonate-rich pyroclastics. I restricted my discussion to the San Venanzo and Cupaello centres because these are the only two places in the IAP where carbonate-rich pyroclastic rocks occur in association with lavas. It seems obvious to me that discussion on possible relationships between silicate lavas and carbonate-rich rocks should be restricted to pair of rocks coming from the same volcano. This would not need stressing, but I heard and read too many times drawing conclusions on assimilation, mixing and unmixing, equilibrium and disequilibrium, based on comparison between a carbonate-rich rock from a volcano and a silicate lava from another volcano, or on comparison between regional averages of carbonate-rich and silicate rocks. In my opinion, this is not acceptable and hope will not be reiterated in the future.

If whole rock compositions are considered, it is evident that the shape of REE and incompatible element patterns of silicate lavas and carbonate-rich rocks from the same volcano is very much the same. However, it is also evident that there is a decrease of incompatible element abundances from lavas to the associated carbonate-rich rocks, and such a decrease is roughly proportional to the calcite contents. In my previous papers (Peccerillo, 1998a, 2004), I used CaO as a proxy for increasing calcite, which may be questionable, but roughly the same result is obtained using the calcite modal composition as reported by Stoppa and Woolley (1987; about 10-20% in the San Venanzo and some 50-60% in the Cupaello carbonate-rich rocks). Element decrease also affects Sr and Ba that are present in high concentrations in some calcites (Stoppa and Woolley, 1997). Based on this comparison as well as on the statement of Woolley and coworkers that the carbonate-rich rocks are mixtures of carbonate and melilitite material (e.g., Stoppa and Woolley, 1997), I concluded that the carbonate fraction is a diluent of the silicate composition. Therefore, a barren composition for the bulk of carbonate fraction was inferred. This conflicts with a magmatic origin. The reasons of this diluent effect of the carbonate fraction is not explained by Woolley *et al.* (2005) in their comments to my papers.

Finally, I would briefly comment on isotopic effects of mixing between central Italy kamafugitic

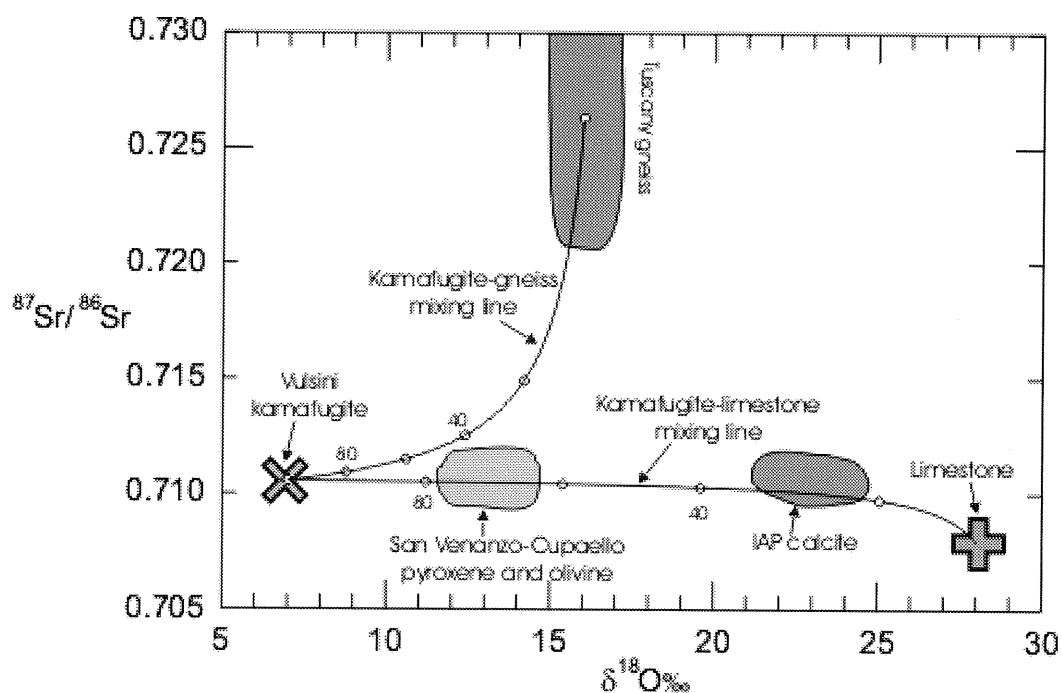


Fig. 3 – O-Sr isotope mixing models between a kamafugite magma from Vulsini, a carbonate rock from Apennines and Tuscany metasedimentary basement. The fields of the IAP calcite and of San Venanzo and Cupaello olivine and clinopyroxene are shown. For source of data see Peccerillo (2005, Chapter 3 and attached CD-ROM).

magma and crustal rocks. This has been discussed several times and will be only shortly recalled here. Fig. 3 shows a simple bulk mixing model between kamafugite from Vulsini (Barnekow, 2000; Di Battistini *et al.*, 2001) and crustal rocks. It is obvious that mixing between kamafugite and carbonates modifies much more strongly oxygen than Sr isotopic ratios of kamafugite. For instance, modification of one unit on the fourth decimal place (which has been considered as negligible by Castorina *et al.*, 2000) is obtained after some 30-40% addition of pure carbonate rocks ($Sr = 117$; $^{87}Sr/^{86}Sr = 0.708$; $\delta^{18}O = +30\text{‰}$; see Castorina *et al.*, 2000). This is due to buffering effects by high Sr contents of ultrapotassic magmas. The same degree of carbonate addition induces an increase of $\delta^{18}O$ by a factor of two! A similar, though less dramatic effect, is produced by assimilation of metasediments. It goes without saying that simple two-end member mixing is an oversimplification

of crust-magma interaction processes occurring in nature. In any case, oxygen isotope variations are by far the most dramatic isotopic modification observed on magmas rich in Sr (e.g., Taylor and Sheppard, 1986). I consider rather astonishing that the flood of studies on IAP rocks did never consider oxygen isotope ratios of silicate phases, in spite of the much more important information these could provide on possible assimilation processes. In contrast, statements like “poorly variable Sr isotopic ratios exclude magma contamination” or similar are commonly read in papers and heard at conferences, which is rather depressing.

CONCLUSIONS

In their comments, Woolley *et al.* (2005) agree that, contrary to their previous statements, mineralogical criteria and high concentrations of

incompatible elements and REE do not prove a carbonatitic nature for IAP carbonate-rich rocks. I add that IAP rocks have very similar incompatible element and REE patterns as well as radiogenic isotopic compositions (Sr-Nd-Pb) as the mafic rocks of the Roman province, suggesting a genesis in a common source, which was modified by the same type of metasomatic event. Therefore, they have the same geodynamic significance.

Woolley *et al.* (2005) report on incompatible element contents and isotopic compositions of carbonate fractions of IAP rocks to argue for a magmatic origin. I reply that analyses of phases from mixed rocks may not tell much about original compositions of end-members, since elemental and isotopic abundances are obliterated by diffusion that tends to eliminate chemical potential gradients. Much more informative is the study of whole rocks, whose composition, if not modified by other processes (e.g., loss of components by secondary alteration or else), only depend on compositions of end-members and on the proportions these participate into the mixing. These studies indicate that carbonate-rich rocks of the IAP show lower incompatible element concentration, but similar patterns, as the associated lavas, suggesting that the carbonate fraction is a diluent of kamafugite magma.

Finally, Woolley *et al.* (2005) use data on Vulture and East African rocks to support their ideas on petrogenesis and geodynamic significance of IAP rocks. I rebut such an approach, given the petrological, geochemical, isotopic, volcanological and geodynamic differences among the three volcanic provinces.

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REFERENCES

- APPORA I., EILER J.M., MATTHEWS A. and STOLPER E.M. (2003) — *Experimental determination of oxygen isotope fractionation between CO₂ vapor and soda-melilite melt*. *Geochim. Cosmochim. Acta*, **67**, 459-471.
- BARCHI M., LANDUZZI A., MINELLI G. and PIALLI G. (2001) — *Outhern Northern Apennines*. In: Vai G.B. and Martini P.I. (eds.) *Anatomy of an Orogen. The Apennines and the adjacent Mediterranean basins*. Kluwer, Dordrecht, pp. 215-254.
- BARNEKOW P. (2000) — *Volcanic rocks from central Italy: an Oxygen isotopic microanalytical and geochemical study*. PhD Thesis, University of Gottingen, 99 pp.
- BECCALUVA L., COLTORTI M., DI GIROLAMO P., MELLUSO L., MILANI L., MORRA V. and SIENA F. (2002) — *Petrogenesis and evolution of Mt. Vulture alkaline volcanism (Southern Italy)*. *Mineral. Petrol.* **74**, 277-297.
- CASTORINA F., STOPPA F., CUNDARI A. and BARBIERI M. (2000) — *An enriched mantle source for Italy's melilitite-carbonatite association as inferred by its Nd-Sr isotope signature*. *Mineral. Mag.*, **64**, 625-639.
- CONTICELLI S. (1998) — *The effect of crustal contamination on ultrapotassic magmas with lamproitic affinity: mineralogical, geochemical and isotope data from the Torre Alfina lavas and xenoliths, Central Italy*. *Chem. Geol.*, **149**, 51-81.
- DE ASTIS G., KEMPTON P.D., PECCERILLO A. and WU T.W. (2006) — *Trace element and isotopic variations from Mt. Vulture to Campanian volcanoes: constraints for slab detachment and mantle inflow beneath southern Italy*. *Contrib. Mineral. Petrol.*, in press.
- DE FINO M., LA VOLPE L., PECCERILLO A., PICCARRETA G. and POLI G. (1986) — *Petrogenesis of Monte Vulture volcano, Italy: inferences from mineral chemistry, major and trace element data*. *Contrib. Mineral. Petrol.*, **92**, 135-145.
- DI BATTISTINI G., MONTANINI A., VEMIA L., BARGOSI G.M. and CASTORINA F. (1998) — *Petrology and geochemistry of ultrapotassic rocks from the Montefiascone volcanic complex (Central Italy): magmatic evolution and petrogenesis*. *Lithos*, **43**, 169-195.
- HOLM P.M. and MUNKSGAARD N.C. (1982) — *Evidence for mantle metasomatism: an oxygen and strontium isotope study of the Vulsinian district, central Italy*. *Earth Planet. Sci. Lett.*, **60**, 376-388.
- HOLM P.M. and MUNKSGAARD N.C. (1986) — *Reply to: a criticism of the Holm-Munksgaard oxygen and strontium isotope study of the Vulsinian District, Central Italy*. *Earth Planet. Sci. Lett.*, **78**, 454-459.
- NAKAMURA E. and KUSHIRO I. (1998) — *Trace element diffusion in jadeite and diopside melts at high pressures and its geochemical implication*. *Geochim. Cosmochim. Acta*, **62**, 3151-3160.

- PECCERILLO A. (1998a) — *Relationships between ultrapotassic and carbonate-rich volcanic rocks in central Italy: petrogenetic implications and geodynamic significance*. *Lithos*, **43**, 267-279.
- PECCERILLO A. (1998b) — *Relationships between potassic and carbonate-rich volcanics in central Italy*. IAVCEI Intern. Volcanol. Congr., 11-16 July 1998, Cape Town, South Africa.
- PECCERILLO A. (1999) — *Multiple mantle metasomatism in central-southern Italy: geochemical effects, timing and geodynamic implications*. *Geology*, **27**, 315-318.
- PECCERILLO A. (2004) — *Carbonate-rich pyroclastic rocks from central Apennines: carbonatites or carbonated rocks? A commentary*. *Per. Mineral.*, **73**, 165-175.
- PECCERILLO A. (2005) — *Plio-Quaternary volcanism in Italy. Petrology, Geochemistry, Geodynamics*. Springer, Heidelberg, 365 pp.
- PECCERILLO A., POLI G. and SERRI G. (1988) — *Petrogenesis of orenditic and kamafugitic rocks from Central Italy*. *Canad. Mineral.*, **26**, 45-65.
- PERUGINI D. and POLI G. (2004) — *Analysis and numerical simulation of chaotic advection and chemical diffusion during magma mixing: petrological implications*. *Lithos*, **78**, 43-66.
- PERUGINI D., BUSÀ T., POLI G. and NAZZARENI S. (2003) — *The role of chaotic dynamics and flow fields in the development of disequilibrium textures in volcanic rocks*. *J. Petrol.*, **44**, 733-756.
- PERUGINI D., POLI G. and VALENTINI L. (2005) — *Strange attractors in plagioclase oscillatory zoning: petrological implications*. *Contrib. Mineral. Petrol.*, **149**, 482-497.
- STOPPA F. (2003) — *Consensus and open questions about Italian CO₂ driven magma from the mantle*. *Per. Mineral.*, **57**, 1-8.
- STOPPA F. and LUPINI L. (1993) — *Mineralogy and petrology of the Polino monticellite calciocarbonatite (Central Italy)*. *Mineral. Petrol.*, **49**, 213-231.
- STOPPA F. and WOOLLEY A.R. (1997) — *The Italian carbonatites: field occurrence, petrology and regional significance*. *Mineral. Petrol.*, **59**, 43-67.
- STOPPA F. and CUNDARI A. (1998) — *Origin and multiple crystallisation of the kamafugite-carbonatite association: the San Venanzo-Pian di Celle occurrence (Umbria, Italy)*. *Min. Mag.*, **62**, 273-289.
- TAYLOR H.P. and SHEPPARD S.M.F. (1986) — *Igneous rocks: I. Processes of isotopic fractionation and isotope systematics*. *Rev. Mineral.*, **16**, 227-271.
- TURI B., TAYLOR H.P. and FERRARA G. (1986) — *A criticism of the Holm-Munksgaard oxygen and strontium isotope study of the Vulsinian district, central Italy*. *Earth Planet. Sci. Lett.*, **78**, 447-453.
- TURI B. (1969) — *La composizione isotopica dell'ossigeno e del carbonio dei carbonati presenti nelle vulcaniti di S. Venanzo (Umbria)*. *Per. Mineral.*, **38**, 589-603.
- VALLEY J.W. (1986) — *Stable isotope geochemistry of metamorphic rocks*. *Rev. Miner.*, **16**, 445-481.
- WASHINGTON H.S. (1906) — *The Roman Comagmatic Region*. Carnegie Inst. Washington Publ. 57, 199 pp.
- WOOLLEY A.R., BAILEY D.K., CASTORINA F., ROSATELLI G., STOPPA F. and WALL F. (2005) — *Reply to "Carbonate-rich pyroclastic rock from central Apennines: carbonatites or carbonated rocks? A commentary" by A. Peccerillo*. *Per. Mineral.*, this issue.

