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Carbonatites vs. carbonated rocks in central Italy. A reply to comments by Bell and Kjarsgaard

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Abstract. — In two previous papers (Peccerillo, 1998, 2004), I raised doubts about the widely accepted idea that the carbonate-rich pyroclastic rocks from the Intra-Apennine Province (IAP) are carbonatites. This provoked a late but considerable reaction from carbonatite scholars, including people unfamiliar with the subject and with the complex magmatic setting of central-southern Italy. Bell and Kjarsgaard do not give an answer to my questions, show a lack of knowledge of the subject in hand, and reveal scarce consideration for results of previous work. In my reply, I briefly discuss the scientific aspects raised by Bell and Kjarsgaard that are worthy of note, and highlight some philosophical and ethical aspects of their writing. I reiterate my objections, which remain unanswered, and conclude that further discussion on IAP rocks will have my consideration only if future comments, if any, will provide an answer to my questions and will lead to an advancement in our understanding of central Italy magmatism and its geodynamic significance.

Riassunto. — I miei dubbi sulla natura carbonatitica di alcune rocce piroclastiche delle zone interne dell'Appennino centrale, hanno prodotto, dopo quasi un decennio di afasia, un'improvvisa manifestazione di interesse concretizzatasi nell'invio di tre lavori di commento da parte di un nutrito gruppo di petrologi, molti dei quali non direttamente coinvolti nelle ricerche e nella discussione sulle rocce vulcaniche intra-appenniniche. Tutti questi commenti hanno in comune la caratteristica di evitare accuratamente la sostanza delle mie obiezioni, fornendo un esempio di discussione improduttiva che lascia irrisolti i problemi e inalterati i dubbi. Il lavoro di Bell e Kjarsgaard, oltre a non portare alcun elemento di novità e di originalità alla discussione, contiene un notevole numero di affermazioni inesatte, attribuisce scarso riconoscimento ai lavori precedenti, ed è contraddittorio dal punto di vista epistemologico. Nella mia risposta, fornisco brevemente, *currenti calamo*, un commento ai pochi argomenti di Bell e Kjarsgaard degni di nota, puntualizzo, mediante precisi riferimenti alla bibliografia, la paternità di certe idee e chiarisco alcuni miei punti di vista sull'approccio filosofico alla discussione in atto e alle problematiche geologiche nella loro generalità. Nelle conclusioni, riformulo le mie domande e i ripropongo i dubbi che non sono stati affatto risolti dalla discussione in atto. Esprimo, infine, l'auspicio che, per il futuro, gli eventuali nuovi commenti affrontino in maniera più precisa e pertinente le mie obiezioni. In assenza di tali requisiti minimi, ogni ulteriore discussione sarà considerata sterile e non meritevole di considerazione.

Introduction

Some years ago (Peccerillo, 1998) I raised doubts about the hypothesis that carbonate-rich pyroclastic rocks from central Italy may represent carbonatites. The same objections were reiterated at several national and international meetings and

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in a more recent paper published by the Italian journal Periodico di Mineralogia (Peccerillo, 2004).

After eight years of unawareness of my objections, there has been a sudden surge of interest and three separate comments have been submitted to Periodico di Mineralogia almost simultaneously (Bailey, 2005; Woolley *et al.*, 2005; Bell and Kjarsgaard, 2006). Whatever the reason of this unprecedented surge of interest among carbonatite scholars, it is welcome providing it addresses properly the questions I raised, offers new insight into the problem, and correctly reports on previous work and objections.

Unfortunately, this is not so in the case of the Bell and Kjarsgaard (hereafter BK) contribution, which adds nothing new to the problem, is replete with incorrect statements, and gives little consideration to previous work. For these reasons, I briefly address the few points made by BK that are worthy of note, I comment on ethical and philosophical aspects of the discussion, and reiterate questions that I asked earlier and still have not been answered.

REPLY

1) It is obvious that BK did not understand my critical approach to the idea of a carbonatitic nature of carbonate-rich rocks from IAP. My objective was not that of giving any model but rather the one of highlighting some peculiarities of the rocks that evidently contradict the carbonatite hypothesis. I clearly stated this in my papers (e.g., see appendix of Peccerillo, 2004; see also comments on Popperian falsificationism in the next paragraphs). Yet, I am not surprised that such an approach has difficulties to get through, knowing how unfamiliar many scientists are with the most basic elements of philosophy of science, something which does not seem to be restricted to Earth Sciences (see Howard, 2006). Coming back to our rocks, the objection I made is that the available data (Stoppa and Woolley, 1997) clearly indicate that IAP carbonate-rich pyroclastic rocks are poorer in almost all chemical species (except CaO and CO_2) than the associated lavas (Peccerillo, 1998, 2004, 2005a,b,c). The dilution is proportional to the amount of carbonate present in the pyroclastics rocks. Based on this observation, and accepting that the carbonate-rich pyroclastic rocks are a mixture of kamafugitic silicate magma and carbonates, as has clearly and repeatedly been stated by Stoppa and Woolley (1997), it was concluded that the carbonates were geochemically barren and acted as diluent of silicate kamafugitic fraction (Peccerillo, 1998, 2004, 2005a,b). This is at odds with the idea that the IAP carbonate-rich pyroclastics are carbonatitic in nature, since igneous carbonates are rich in incompatible elements. I suggested that barren carbonates likely originated from the bedrocks, which consist of abundant limestones and marls (e.g., Barchi *et al.*, 2001). BK select an incomplete list of possible processes whereby carbonate rocks could be incorporated into the magma, state that none work, and conclude that interaction between carbonates and kamafugite magma is not a viable mechanism to explain element dilution in IAP carbonate-rich pyroclastics. It is obvious, however, that they do not explain the element depletion in carbonate-rich pyroclastic rocks and, therefore, DO NOT ANSWER my question. I recently realised that this problem was first noticed by Stoppa and Woolley (1997) but had been largely ignored by the flood of papers appeared on IAP rocks in the last decade.

2) BK use volcanological and textural data to argue for a carbonatite nature for the carbonate-rich pyroclastic rocks from the IAP. I rebut this approach. Geochemical data should be used to classify volcanic rocks, as recommended by the Subcommision on the Nomenclature of Igneous Rocks of the IUGS (La Maitre, 1989). En passing, exsolution of CO_2 is not the only process that generates explosive eruptions, and new investigation suggests that magma-water interaction is the cause of explosive activity at San Venanzo (Zanon, 2005).

3) Castorina *et al.* (2000) state that there is isotopic equilibrium between carbonate and the silicate fraction in IAP carbonate-rich rocks, a view that was reiterated by Woolley *et al.* (2005). This was suggested to represent an evidence for carbonate-silicate unmixing. Based on the original Sr-isotope data of Castorina *et al.* (2000), that differ by up to three units in the third decimal place, I rebutted such a statement (Peccerillo, 2005a). BK finally recognise that there is isotopic disequilibrium. I welcome this assertion.

4) The IAP rocks have very high oxygen isotope ratios for both whole rocks and separated phenocrysts ($\delta^{18}O$ = +12 to +14‰; Holm and Munksgaard, 1982, 1986; Turi *et al.*, 1986; Peccerillo, unpublished data). The carbonate fraction has even higher values (around $\delta^{18}O$ = +20 to +25‰; Turi, 1969; Stoppa and Woolley, 1997). BK recognise this is an anomaly for mantle-derived rocks and attribute it to the source. However, this amounts only to ignoring rather than solving the problem, unless one can also explain why the source should be so enriched in heavy oxygen. BK mention that all the rocks from the Roman Province have high $\delta^{18}O$‰, thus suggesting that such a feature is a regional characteristic of mantle sources. Regrettably, they omit reporting numbers. A complete, accurate and updated scrutiny of published data clearly shows that oxygen isotopic ratios of Roman rocks, though variable, are much lower than those of the IAP (e.g., Turi and Taylor, 1976; Holm and Munksgaard, 1982; Ferrara *et al.*, 1985; Turi *et al.*, 1986). The phenocryst compositions of the most primitive Roman rocks fall very close to or within the mantle array. Values of $\delta^{18}O_{SMOW}$ around +6.0‰ were found by Dallai *et al.* (2004) for pyroxenes from the Alban Hills. These values correspond to the base-level of $\delta^{18}O$‰ of subduction-related rocks, as recognised by Harmon and Hoefs (1995). It is beyond doubt that IAP volcanics are very anomalous for their high $\delta^{18}O$‰, also when compared with Roman rocks. In contrast, IAP rocks have similar incompatible element abundances and patterns as well as radiogenic isotope signatures (Sr, Nd, Pb, Hf) to the most mafic Roman rocks (Peccerillo, 2005a,b,c). The simplest, and therefore the most likely, explanation for these peculiarities is that, whereas both the Roman and IAP rocks come from geochemically similar sources, the IAP monogenetic volcanoes underwent stronger interaction with wall carbonate rocks then the Roman mafic magmas. Such an interaction process dramatically modified the oxygen isotope composition but did not affect significantly the trace element ratios and radiogenic isotope signatures, due to the buffering effect of the high concentrations of trace elements in ultrapotassic magmas and to the low abundances of these elements in sedimentary carbonates.

5) I agree that comparing pyroclastic rocks with intrusive rocks may be meaningless, as I comment further in the next paragraph. I used the composition of average world carbonatite (Peccerillo, 1998, 2004) simply to highlight the high concentrations of incompatible trace elements in carbonatitic magmas. By the way, comparison of IAP rocks with sovites has been amply used by practised carbonatite petrologists (e.g., Stoppa and Woolley, 1997).

6) BK use quantitative tests for kamafugite lava and bulk pyroclastic rock compositions to exclude the interaction of kamafugitic magma with carbonate wall rocks. As I have clearly stated in previous papers (see Peccerillo, 2005b), this approach is badly flawed. Pyroclastic rocks have complex compositions that do not only depend on the nature and amounts of juvenile fragments, but also on several other factors including clast selection during transport, incorporation of external material and post-depositional alteration of fine ashes to mention just a few. It is obvious, therefore, that quantitative comparison between compositions of lavas and BULK pyroclastic rocks, is a nonsense. For the case under discussion, Cupaello pyroclastic rocks contain phases such as alkali feldspar (Stoppa and Cundari, 1995) that are not present in the melilite-bearing kamafugitic lavas. They are also more altered than lavas, as indicated by their low K_2O contents (less than 1 wt% in the bulk pyroclastic rock as compared with 8-10 wt% in the associated lavas; e.g. Peccerillo *et al.*, 1988; Stoppa and Woolley, 1997). Because of these problems, I used a broadly qualitative approach in comparing lavas and associated carbonate-rich pyroclastics (Peccerillo, 2005a,b). In conclusion, mass balance calculations as those of BK are easy to do but useless mathematical exercises. I discussed this issue earlier (Peccerillo, 2005b) and am a bit embarrassed to have to recall it to allegedly expert petrologists. In any case, these models do not answer to the dilution problem I mention in point (1).

Additional remarks

I conclude by pointing out where BK make untrue statements, do not give appropriate recognition to the findings of others, and are contradictory in their philosophical approach to discussion.

For example, BK state that I never considered the possibility of subduction-related mantle contamination by marls. This is false. I suggested and modelled this process in several papers (e.g., Peccerillo *et al.*, 1988; Conticelli and Peccerillo, 1992; Peccerillo, 2005c).

BK state that I have advocated a role for limestone in the genesis of magmatism in central Italy. This is untrue. Following other authors (e.g., Cox *et al.*, 1976), I have stated in many papers that the first order petrological and geochemical characteristics of central Italy magmatism reflect anomalous mantle sources that were contaminated by various types of upper crustal material, including marls (e.g., Peccerillo *et al.*, 1988; Peccerillo, 2005c and references therein). However, some magmas, in particular those from the IAP, have interacted with various types of wall rocks, as demonstrated by many studies (e.g., Turi *et al.*, 1986; Conticelli, 1998; Peccerillo, 1998; Dallai *et al.*, 2004).

BK state that the upper mantle beneath Tuscany and Western Alps resembles pelagic sediments/upper crust. They do not quote any paper in support of this statement, giving the impression that this is their original finding. However, it has already been stated repeatedly that the mafic rocks from Tuscany and Western Alps, but also from SE Spain, resemble upper crustal rocks, in particular pelitic sediments or granites, for their incompatible element patterns and radiogenic isotope signatures (Peccerillo *et al.*, 1988; Conticelli and Peccerillo, 1992; Peccerillo, 1999, 2002, 2005c; Peccerillo and Martinotti, 2006 and references therein). Based on this observation, it was long ago concluded that the mantle source beneath these regions has an upper-crustal-like trace element and radiogenic isotope composition, attributed to contamination by subducted silicic sediments (e.g., Peccerillo *et al.*, 1988; Peccerillo, 2005c; Peccerillo and Martinotti, 2006). I brought such a finding to the attention of the senior author of BK in several personal communications, and suggested this theme as a subject for doctoral thesis. BK ignore this work, but instead invent a new name for this anomalous upper mantle (ITEM: Italian Enriched Mantle), thereby giving the impression of a new finding. Whereas I am glad that BK accept my idea of a crustal-like composition for upper mantle beneath central Italy and Western Alps, I would also have appreciated some acknowledgements for primary authorship of this finding. Also, I believe that the name ITEM may be misleading, since this type of mantle composition is not restricted to Italy but occurs in several other places, including SE Spain, Serbia, and Tibet (Peccerillo and Martinotti, 2006).

Finally, BK criticise my statement that Popperian falsificationism is not always applicable to Earth Sciences and conclude that if something is not falsifiable it is not science. Nevertheless, many leading philosophers of science including Imre Lakatos, Dudley Shapere, Hilary Putnam, Thomas Kuhn, disagree that falsification is the boundary between science and non-science. Personally, I find huge merit in the rigour of Popperian falsificationism and have tried to apply it to the present discussion, something which has been missed by BK. Following the majority of science philosophers, I believe, however, that falsificationism is hardly applicable to many theories in Earth science. As an example, consider one of the most popular paradigms in modern geology: the plume theory. Does this theory admit falsification? Is there any datum or key experiment that could falsify the theory? I doubt it (see also discussion in Glen, 2005). Shall we then conclude that plumes are not science but “witchcraft”, to use wording of BK? I believe that mantle plume theory IS science. However, when I read about plumes suggested to be stalled for tens of million years at several hundreds km depth, stiff instead of soft, and so powerful they can open remotely the whole Mediterranean Sea between two huge converging continental blocks (Bell *et al.*, 2004), I start having serious doubts that the plume theory is always science.

CONCLUSIONS

The many comments (Woolley *et al.*, 2005; Bailey, 2005; Bell and Kjarsgaard, 2006) related to my doubts regarding the nature of carbonate-rich rocks from the IAP have added little to our understanding of these rocks, leaving the main problems still unsolved. Woolley *et al.* (2005) accepted that, contrary to their previous statements, the exotic mineralogy and incompatible trace element enrichment of IAP carbonate-rich rocks have little power to establish their carbonatitic nature. BK accept that there is isotopic disequilibrium in the IAP rocks. Except for this small advance, none of the other key questions has been answered:

1. Why the carbonate-rich rocks have depleted compositions (except for CaO and CO_2) with respect to the associated lavas? Why is the degree of element depletion related to the amount of calcite present in the rocks? These key questions were ignored by Wooley *et al.* (2005) and have not been answered by Bailey (2005) or Bell and Kjarsgaard (2006), as discussed earlier. Since no answer has been given to these questions, any Popperian falsificationist, as BK appear to be, would probably conclude that this unexplained feature of IAP rocks falsifies the carbonatite hypothesis.

2. Why do clinopyroxene and olivine phenocrysts from the lavas of IAP volcanoes have very high oxygen isotope ratios ($\delta^{18}O$ = +12 to +14‰)? If this is a regional feature of the source, as assumed by BK, why it is not observed in the rocks of the Roman Province, which have similar to identical trace element abundances and ratios as well as radiogenic isotope signatures (Sr, Nd, Pb, Hf) to the IAP products? My answer is that the high heavy oxygen contents derive from interaction between magma and carbonate wall rocks, a process that is likely in IAP monogenetic volcanoes formed by ascent of small pulses of magmas that cross thousands of meters of carbonate sediments. If this conclusion is thought wrong, an alternative explanation should be provided. Since no alternative has been given, any Popperian falsificationist should probably conclude that oxygen isotope data falsify the hypothesis of lack of interaction of magma and wall rocks.

I conclude by reaffirming my belief that, whatever the nature of the IAP rocks, the very similar trace-element and radiogenic-isotope composition to the voluminous mafic lavas of the Roman Province clearly suggests that all these magmas come from the same anomalous source that has had a similar evolution history in the same geodynamic context. The much fresher and more abundant rocks of the Roman Province provide more reliable data than the monogenetic, often altered and probably contaminated volcanoes of IAP, and in my view should be used preferentially to clarify the petrological and geodynamic problems of central Italy magmatism.

My doubts on the carbonatitic nature of the IAP rocks have raised fierce opposition by some members of the carbonatite community. This is positive, since discussion is a *sine qua non* of scientific research. However, debate is useless if it does not provide any new insight into the problem in hand. Therefore, I will consider future comments, if any, only in the case they will give an answer to my objections, or will add something new to the genesis of central Italy magmatism. Since an answer to my objections is still lacking, I believe that the hypothesis of a carbonatitic nature of IAP carbonate-rich rocks has to be considered at best as unfounded.

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