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# "Pieve Santo Stefano" is not a mud volcano: Comment on "Structural controls on a carbon dioxide-driven mud volcano field in the Northern Apennines" (by Bonini, 2009)

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## 1. Introduction

Bonini (2009) has recently written an interesting paper dealing with the structural setting and relationships to seismicity of a CO<sub>2</sub> (carbon dioxide)-driven mud volcano, called Pieve S. Stefano (PSS), located in the Northern Apennines of Italy. We outline here that PSS is not a mud volcano at all. The author erroneously attributes the term "mud volcano" (also featured in the title of the article) to a CO<sub>2</sub>-dominant gas manifestation, which should be considered as a "mofette" or more generally a dry CO<sub>2</sub>-vent (or "gas pool"; Minissale et al., 2000; Heinicke et al., 2006). Our comment does not dispute Bonini's data interpretations and conclusions (for which a first comment has already been made by Collettini, in press), but discusses why misuse of the term "mud volcano" may lead to misquotations in future mud volcano literature.

### 2. Definition of mud volcanoes

Mud volcanoes are well-known natural manifestations of the upward migration of fluids (gas, water) and solid phases (finegrained sediments, rocks) from deep sedimentary horizons (e.g., Kopf, 2002; Dimitrov, 2002). They are formed in sedimentary basins and involve mobilization of sedimentary rocks (=sedimentary volcanoes). A more constrained definition should include the requirement that gas and water must be related to hydrocarbon diagenetic and catagenetic production and accumulation processes: gas is predominantly composed of methane (CH<sub>4</sub>) and subordinately of other alkanes (mainly ethane and propane) and non-hydrocarbon gases such as CO<sub>2</sub>, nitrogen (N<sub>2</sub>), argon (Ar), helium (He). Water is "fossil", saline, is associated with hydrocarbon reservoirs and is often related to illitization of clay minerals. A global data-set shows that in 80% of terrestrial mud volcanoes, thermogenic methane is the main seeping gas; microbial CH<sub>4</sub> is less common (Etiope et al., 2009a). In few special cases, gas can be dominated by CO<sub>2</sub> or N<sub>2</sub>. Such mud volcanoes can occur in hydrocarbon systems close to subducting slabs and geothermal environments (e.g., Motyka et al., 1989) or are related to thermogenic reservoirs and final stages of natural gas generation (Baciu et al., 2007). However, they are always associated to what in petroleum geology literature is known as the "Total Petroleum System" (Magoon and Schmoker, 2000). Basically, a mud volcano is considered to represent a special type of "seep" occurring in petroliferous basins, often (but not always) linked to natural gas or oil reservoirs. Many large onshore hydrocarbon fields were discovered after drilling around mud volcanoes in Europe, the Caspian basin, Asia and the Caribbean (Etiope et al., 2009b). The development of faults, pressurised gas pool and compressional stress can be related to any surface gas manifestation, but the diagnostic and distinctive elements of a mud volcano should include: discharge of a threephase system (gas, water and sediments), diapirs or diatremes (see definitions in Kopf, 2002), the involvement of sedimentary rocks with gravitative instability resulting from rapid sedimentation, breccia in the discharged material, and the emission of natural gas related to a catagenetic hydrocarbon production system. So, the definition of "mud volcano" depends strictly on specific characteristics of the fluids discharged, subsurface structures and the regional geological framework.

### 3. Why "Pieve S. Stefano" is not a mud volcano

The gas manifestation of PSS lacks the essential features diagnostic of a mud volcano including the required geological

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framework of mud volcanism. There is no fossil saline water, no evidence of diapirs/diatremes, no breccia in the mud discharged. The amount of mud released is relatively low and the major gases are not related to a catagenetic hydrocarbon production system.

The surface vent is a sub-circular crater characterized by bubbling muddy water. Gas flow may reach hundreds of litres per minute (Bonini, 2009). Bonini (2009) writes that when extrusive mud gives rise to small conic edifices, vents can be referred to mud volcanoes, or "mud pie"-type mud volcanoes when the extrusive features exhibit low topographic relief. This is not correct; as discussed above, these morphological parameters are not sufficient to define a mud volcano.

Gas discharged from PSS vent is CO<sub>2</sub>-dominant (94.73%), with lower amounts of N<sub>2</sub> (4.8%), CH<sub>4</sub> (0.44%), H<sub>2</sub>S (0.04%) and other gases (Ar, CO, H<sub>2</sub>, He) at ppmv levels (Vaselli et al., 1997; Heinicke et al., 2006). The local gas reservoir at 3700 mb.s. has a similar composition (Heinicke et al., 2006). The isotopic ratios are consistent with a crustal origin for the sampled gases  $(\partial^{13}C_{CO_2} = -4.27\%$  PDB, helium isotope ratio R/Ra = 0.03-0.05). CO<sub>2</sub> is chiefly generated by thermo-metamorphic processes in the carbonate rocks, while N2 is mainly produced by the breakdown of NH<sub>4</sub>-rich K-feldspars and micas inside the Palaeozoic metamorphic basement rocks (Vaselli et al., 1997). Mofettes located a few km from PSS, show an organic hydrocarbon component related to thermogenesis, as indicated by the isotopic ratio of methane carbon  $(\partial^{13}C_{CH_4}\,=\,-38\%_{\!oo})$  and by the relatively high concentration of heavier hydrocarbons (ethane: 0.0062%, propane: 0.0012%; Minissale et al., 2000). This is common in central-north Apennines, but it is not peculiar to mud volcanism. Finally, H<sub>2</sub>S (0.04%) at PSS is likely related to geothermal processes (as in many other gas manifestations in Tuscany and along the Tyrrhenian volcanic belt) and not to hydrocarbon-related processes, such as thermochemical sulphate reduction (TSR; see for example Etiope et al., 2006). H<sub>2</sub>S is typically absent in mud volcanoes world wide (Etiope et al., 2009a).

In the PSS deep pool, deeply sourced water exists only as a minor component with a content of less than 0.5% in weight whilst surface water in the crater is primarily meteoric (rainwater; Heinicke et al., 2006). The PSS substratum is characterized by a sequence of continental Pleistocene alluvium (only 66 m), flysch, sandstones and carbonate rocks typical of the Appennine orogenic nappes. The basin is not characterized by long-lasting or rapid sedimentation or subsidence leading to horizons with gravitational instabilities, i.e. less dense sediment layers buried under denser units, as required in mud volcanism. Accordingly, the substratum does not have pierced structures, diapirs or diatremes. Fluid rising to the surface is basically only gas. There is no upwelling saline water, no solid fragments or breccia. Mud, released in small amounts, is of unknown origin: Bonini (2009) suggests it derives from Eocene shale units (located at about 1900 m depth) without providing analytical (micropalentological or mineralogical) proof, and that the presence of formation water in sandstones overlying the shales may have fluidized the mud during the passage of seismically induced fluid pressure pulses. This would imply a temporal (and dynamic) link between seismic events and the generation of low viscosity mud. Obviously, this is not the case, as the gas manifestation is continuously active, whilst enhanced fluid expulsions are also independent of earthquakes (Heinicke et al., 2006). In absence of specific analyses, we cannot exclude the possibility that mud may be derived from recent sediments of the Tiber Valley. It is in any case evident that the high CO<sub>2</sub> pressure in the deeper reservoir, as compared to the hydrostatic pressure, is solely responsible for the transport of gas to the surface (as suggested also by Heinicke et al., 2006).

#### 4. Conclusion

The term "mud volcano" cannot be used simply for any gas manifestation resembling a mud pool or where extrusive mud gives rise to small conic edifices. Many CO<sub>2</sub>-vents, related to geothermal or hydrothermal environments, may show such characteristics (for example the Yellowstone gas manifestations). It is not only a problem of terminology, because the attribution of "mud volcano" to a surface gas manifestation implies the existence of a series of specific geologic processes and features. Presently a lot of mud volcano research is being carried out, including numerous publications in planetary geology (for example mud volcanism on Mars; Skinner and Mazzini, in press). Erroneous attributions of terrestrial mud volcanoes, as for the PSS case, can lead to misinterpretations and misquotations. In Italy mud volcanism has been extensively studied in the last ten years: the origin, distribution, geodynamic environment and nature of released gas are well-known (Martinelli and Judd, 2004; Etiope et al., 2007). All hydrocarbon seeps are clearly related to tectonic and neotectonic faults along the external (eastern) margin of the Apennine chain and in the folded foredeep (Etiope et al., 2007). It is unfortunate that Bonini (2009), though a valuable paper for its structural and seismological discussion, contains such a mistake. We recommend that Bonini's article be used as reference for studies on the relationships between seismicity and surface gas manifestations in general, but absolutely not as an example of mud volcanism.

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