SERPENTINIZATION AND ABIOGENIC PRODUCTION OF HYDROCARBONS IN THE ULTRAMAFIC BASEMENT OF HYBLEAN PLATEAU: MINERALOGICAL AND PETROLOGICAL INFERENCES FROM XENOLITHS

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THE HYBLEAN XENOLITHS

A large number of xenoliths occur in Miocenic volcanoclastic deposits in the Hyblean Plateau (South-eatern Sicily, Italy; Fig. 1), represented by spinel peridotites, websterites, gabbros and various sedimentary and volcanic rocks belonging to the Meso-Cenozoic succession (Scribano, 1987). Surprisingly, no rocks typical of continental crust have been ever found, although the Hyblean area was traditionally considered part of the Pelagian Foreland, belonging to the African continental crust (Lentini *et al.*, 1996). It must be remarked this hypothesis is based only on the interpretation of few seismic data (*e.g.* Finetti *et al.*, 1996; Catalano *et al.*, 2000), in contrast to structural and geophysical anomalies which differ from those of the Nubian lithospheric block (Brancato *et al.*, 2009).

Fig. 1 - Miocenic diatremes in the Hyblean Plateau (south-eastern Sicily, Italy).

At this regard, the comparison between sheared-oxide gabbro xenoliths respect to the present-day knowledge on the slow and ultra-slow spreading ridges, particularly in the MAR and SWIR settings, supported the hypothesis of Scribano *et al.* (2006b) that Meso-Cenozoic succession lies upon an oceanic core-complex, tectonically exposed at the sea-floor of an early oceanic domain, probably the Permo-Thetys Ocean (Vai, 2003). Moreover, Scribano *et al.* (2006a) inferred the existence of a fossil abyssal-type hydrothermal system in the Hyblean basement, on the basis of a petrologic and mineralogical investigation on a set of hydrothermally altered gabbroic xenoliths. Among the numerous hydrothermal minerals, albite, aegirine-augite, titanite, sulfides, and even hydrothermal zircons are worth of notice. In particular, the latter enabled to date the early stage of the hydrothermal system, and hence serpentinization according to Dubińska *et al.* (2004), to the Middle Triassic (Sapienza *et al.*, 2007).

On this ground, Scribano & Ioppolo (2006) supposed that serpentinized ultramafic basement of the Hyblean Plateau could be considered a suitable place for the abiotic formation of hydrocarbons. In fact, fluids emitted by serpentinite-hosted hydrothermal system are enriched in hydrocarbons, whose origin is often associated to the abiogenic synthesis by Fischer-Tropsch-type reaction (*e.g.* Holm & Charlou, 2001). This exothermic process is triggered by the reduction of carbon oxides (mainly CO_2) with H_2, deriving from serpentinization reactions [see reactions (1) and (2); Schroeder *et al.*, 2002], which produced initially methane in presence of catalysts constituted of oxides or sulfides of group VIII metals (*e.g.* Fe, Ni, Co; Fu *et al.*, 2007), according to the reaction (3), and successively heavier hydrocarbons by progressive polymerization (*e.g.* Pikovskii *et al.*, 2004)

$$6\ (Mg,Fe)_2SiO_4 + 7\ H_2O \rightarrow 3\ (Mg,Fe)_3Si_2O_5(OH)_4 + Fe_3O_4 + H_2 \quad (1)$$

$$(Mg,Fe)_2SiO_4 + (Mg,Fe)SiO_3 + 2\ H_2O \rightarrow (Mg,Fe)_3Si_2O_5(OH)_4 + H_2 \quad (2)$$

$$n\ CO_2 + (3n+1)\ H_2 \rightarrow C_nH_{(2n+2)} + 2n\ H_2O \text{ (Konn } et\ al.\text{, 2009)} \quad (3)$$

Consequently, the present dissertation reports data deriving from mineralogical and petrological investigations carried out on some hydrothermally-modified xenoliths, in order to (a) study the physico-chemical conditions in the supposed hydrothermal system, and (b) to contribute to the multidisciplinary research on the possible presence of hydrocarbons in Hyblean xenoliths. In particular, serpentine veins and their cogenetic minerals were firstly studied in eight peridotite xenoliths, sampled in tuff-breccia deposits in Valle Guffari (Fig. 1; South-western side of Mt. Lauro, Hyblean Plateau).

SERPENTINE VEINS AND COGENETIC MINERALS

Peridotite xenoliths contain serpentine veins with a composite structure (Fig. 2; Cogulu & Laurent 1984), showing at crossed polarizers, an optically isotropic mesh rims, and a central ribbon with low birefringence and undulatory extinction. This particular structure could be produced by a crack-seal mechanism as proposed by Andreani *et al.* (2004). XRPD (X-ray Powder Diffraction) analyses on hand-picked fragments of veins revealed the presence of two serpentine polytypes, *i.e.* chrysotile $2M_{c1}$ and

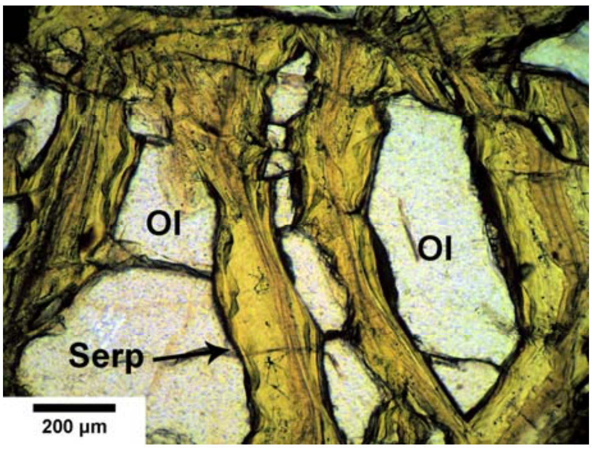

Fig. 2 - Composite structure of serpentine veins (Serp), inside olivine grains (Ol).

lizardite 1*T*. The absence of antigorite suggests that temperature of formation of serpentine minerals never exceed 350-400°C (Bach *et al.*, 2004, and references therein).

Serpentine veins contain several cogenetic minerals, mainly constituted of sulfides, which were analyzed by XRD on whole rock powders and contextually by microprobe (EDS mode). Structural and chemical investigations brought to identify predominant S-poor sulfides, *i.e.* godlevskite, millerite and heazlewoodite, and subordinately S-rich sulfides, *i.e.* polydymite and spionkopite.

Furthermore, aragonite veins occur in serpentine, often associated with veinlets of a fluorapatite enriched in Na and S (Fig. 3), whose crystallographic formula, $(Ca_{4.56}Na_{0.44})_{\Sigma 5.00}[(P_{2.30}S_{0.70})_{\Sigma 3.00}(O_4)_3]$-$(F_{0.62}Cl_{0.07}OH_{0.31})_{\Sigma 2.00}$, is akin to a mineral identified as (Na,S)-rich fluorapatite in a hydrothermal deposit in Japan by Shiga & Urashima (1987), successively renamed clinohydroxylapatite by Chakhmouradian & Medici (2006).

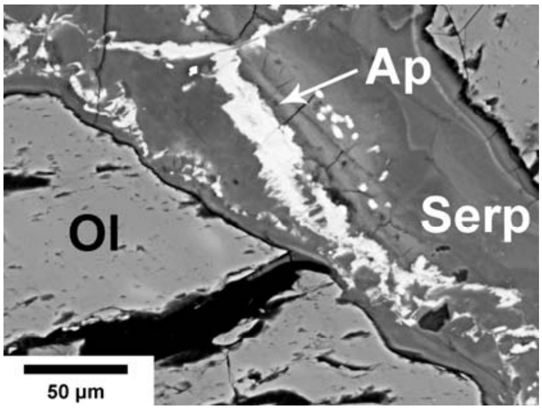

Fig. 3 - Back-scattering image showing a (Na,S)-rich fluorapatite (Ap) veinlet in serpentine (Serp).

At this regard, the presence of serpentine containing insidious alteration products of microscopic to sub-microscopic sizes, was neglected in studies devoted to find evidences for mantle metasomatism, especially the cryptic type (Menzies & Hawkesworth, 1987), since serpentinization is generally considered an isochemical process. In particular, the occurrence of apatite could explain the enrichment in LREE observed in several peridotite xenoliths (Menzies *et al.*, 1985) that was interpreted as a certain clue of mantle metasomatism, even if it is well known these elements can entry the crystal lattice of fluorapatite in substitution of Ca.

The evidence of reactions at an open system in the studied Hyblean xenoliths impose an appropriate remark on the origin of such contaminants, that is whether the origin of the analysed fluorapatite is linked to the supposed hydrothermal system, or to the eruptive context in which the xenolith was embedded. At this regard, juvenile nephelinite clasts contain up to 3 wt.% P_2O_5 (*e.g.* Suiting & Schminke, 2009), which could support the magmatic nature of P and hence of apatite in xenoliths. However, Tonarini *et al.* (1996) demonstrated that the enrichment of LREE and other incompatible elements in Hyblean peridotites is dated back to the Permo-Trias, in agreement with the age of hydrothermal system, therefore excluding any possible contaminations of magmatic nature. Additionally, apatite was reported both in oceanic serpentinites (Cannat *et al.*, 1992) and in some ophiolites (Mitsis & Economou-Eliopoulos, 2001), in which no magmatic contaminants were detected.

Serpentine veins enclose numerous fluid inclusions, containing chlorides constituted of dendritic aggregates of Na-rich sylvite (Fig. 4), which originate in the thermal range 200-380°C according to the values of NaCl molar fraction (X_{NaCl}) reported in the stability diagram NaCl-KCl proposed by Waldbaum (1969). Other inclusions contain rare grains of native metals, consisting of Fe and Ag.

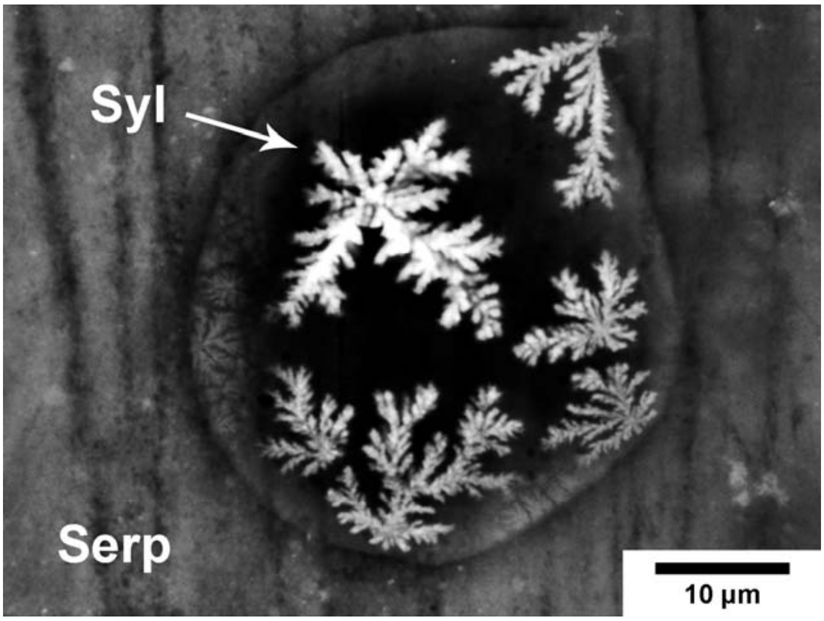

Fig. 4 - Back-scattering image of a dendritic aggregate of Na-sylvite (Syl) in a fluid inclusion in serpentine.

HYDROCARBONS IN MAFIC XENOLITHS

Some metasomazized gabbroic xenoliths were investigated by a team of researchers, from the Chemical Science and Geological Science Depts., Catania University, to find proofs supporting the hypothesis introduced by Scribano & Ioppolo (2006).

Chemical analyses were carried out by means of FT-IR (Fourier Transform-Infrared Spectroscopy) and EI-DPMS (Electron Impact-Direct Pyrolysis Mass Spectrometry), which confirmed the presence of aliphatic and aliphatic-aromatic hydrocarbons. Bulk rock analyses by XRPD revealed the presence of some crystalline organic minerals: idrialite $C_{22}H_{14}$, evenkite $(CH_3)_2(CH_2)_{22}$, karpatite $C_{24}H_{12}$, kratochvilite $(C_6H_4)_2CH_2$, and simonellite $C_{19}H_{24}$. These results were recently published by Ciliberto *et al.* (2009).

CONCLUSIONS

Mineralogical and petrological investigations in serpentine veins in some partially serpentinized peridotite xenoliths, support the following remarks:

1) Serpentine veins are formed by chrysotile $2M_{c1}$ and lizardite $1T$, which represent two common polytypes of oceanic serpentinites (*e.g.* Augustin *et al.*, 2008).

2) The presence in serpentine of chlorides in fluid inclusions and Cl in its structure, as revealed by WDS analyses, suggests the circulation of hypersaline hydrothermal solutions deriving from seawater, similarly to some oceanic serpentinites studied by Bonifacie *et al.* (2008).

3) The occurrence inside veins of two parageneses, respectively formed by oxidized and reduced phases, could suggest two different evolutive stages of the supposed hydrothermal system, as a consequence of the upraising of the Hyblean Plateau due to volume increase of serpentinized ultramafic rocks forming it, as hypothesized by Scribano *et al.* (2009). The first stage should be characterized by low fO_2 and high temperature, in which sulfides, native elements and hydrocarbons were produced, and successively a second stage marked by high fO_2 and low temperature, compatible with the formation of oxidized phases (*e.g.* carbonates, polydymite).

Finally, the comparison between petrological data on Hyblean mafic and ultramafic xenoliths with the present-day information on the active hydrothermal fields in Middle-Atlantic Ridge (MAR), suggest that Meso-Cenozoic successions lye upon ultramafic rocks affected by a variable, though generally elevated, degree of serpentinization, which could have important bearing on the structural and geophysical features of the South-eastern corner of Sicily and neighbouring areas.

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