



# **Tracking the Serpentinite Feet of the Mediterranean Salt Giant**

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Received: 27 June 2018; Accepted: 12 September 2018; Published: 17 September 2018



Abstract: Interpretation of seismic profiles and results of scientific drillings in the Mediterranean subseafloor provided indication of gigantic salt deposits which rarely crop out on land, such as in Sicily. The salt giants were ascribed to the desiccation, driven by the solar energy, of the entire basin. Nevertheless, the evaporite model hardly explains deep-sea salt deposits. This paper considers a different hypothesis suggesting that seawater reached NaCl saturation during serpentinization of ultramafic rocks. Solid salts and brine pockets were buried within the serpentinite bodies being later (e.g., in the Messinian) released, due to serpentinite breakdown, and discharged at seafloor as hydrothermal heavy brines. Therefore, sea-bottom layers of brine at gypsum and halite saturation were formed. The model is applicable to the Mediterranean area since geophysical data revealed relicts of an aged (hence serpentinized) oceanic lithosphere, of Tethyan affinity, both in its western "Atlantic" extension (Gulf of Cádiz) and in eastern basins, and xenoliths from Hyblean diatremes (Sicily) provided evidence of buried serpentinites in the central area. In addition, the buoyant behavior of muddled serpentinite and salts (and hydrocarbons) gave rise to many composite diapirs throughout the Mediterranean area. Thus, the Mediterranean "salt giant" consists of several independent geobodies of serpentinite and salts.

Keywords: Mediterranean; marine salts; serpentinite; hydrothermal system; diapirism

# 1. Introduction

The Mediterranean is one of the most studied and less understood marine basins of the World, being too small to allow easy comparison with the oceans, too deep (up to 5267 m) to be compared with intracontinental basins [1]. The Mediterranean consists of several adjacent sub-basins, which are traditionally divided in eastern and western sectors by an ideal line extending through the Italian Peninsula, Sicily and the Pelagian Sea. The geodynamic evolution of the Mediterranean is still a hotly debated topic among geoscientists. There is a general agreement, however, that prior to the Alpine Orogeny, the Mediterranean area was occupied by part of a wide ocean, called "Tethys" [2].

The idea of a fully desiccated Mediterranean Basin in the Messinian age and the subsequent Zanclean flooding [3] still holds a wide audience (more details are given in Section 2). It is opportune to recall that the Mediterranean desiccation hypothesis is firmly based on the climate evaporite model. Although the latter is supported by natural (e.g., coastal Sabkhas, seashore desiccation ponds etc.) and experimental [4] evidence, it does not adequately explain the existence of gigantic salt deposits, largely exceeding the solute content of the putative basin seawater. Similarly, the sequential deposition and the relative amounts of different types of salts (mostly chlorides and sulfates), as inferred from field evidence, are generally quite different from those experimentally obtained [5,6]. Moreover, salt deposits in deep ocean subseafloor cannot be easily reconciled with the climate evaporite theory.

On the other hand, reasonable hypotheses to explain the origin of salt giants beyond the evaporite model exist. For example, Hovland et al. [7,8] suggested that salt deposits may be related to submarine hydrothermal activity, especially when the solution attains supercritical conditions. Similarly, Scribano et al. [9], approaching the problem from a petrologic perspective, suggested the salt giant origin in abyssal serpentinite systems. This paper is aimed at evaluating whether these challenging viewpoints are applicable to the Mediterranean salt deposits.

In this paper, we consider salt deposits with a secure primary marine origin only. In fact, some gypsum/anhydrite layers occurring in some Mediterranean mainland areas may be "terrestrial sulfates" (to mimic the term "terrestrial carbonates" by [10]) originated by the chemical reaction between sulfate groundwaters and in situ limestones, especially those affected by tectonic shearing, according to the following reactions [11]:

$$H_2S + 2O_2 \rightarrow (SO_4)^{2-} + 2H^+ (aq)$$
 (1)

$$CaCO_3 + (SO_4)^{2-} + 2H^+ + 2H_2O \rightarrow CaSO_4 2H_2O + CO_2 + H_2O$$
 (2)

Although the circulating sulfur probably derived from original marine sulfates, these occur at great depths, being therefore obvious the secondary origin of the sulfate produced by reaction (2).

One of the most important discoveries by modern marine geology expeditions regards oceanic areas, characterized by low spreading rate, where magmatic layers of "normal" oceanic crust are strongly reduced or absent [12–17]. Accordingly, seismic profiles and heat-flow data in these amagmatic areas are compatible with a "cold" and thick lithosphere, where an upper aseismic serpentinite layer overlies almost unaltered mantle ultramafics [18]. Another remarkable marine geology discovery is the common occurrence of active hydrothermal vents along (ultra)slow-spreading ridges, even in cases where igneous activity is low or absent. Scientific drilling enterprises into tectonically exhumed oceanic lower-crust also provided evidence of gabbroic rocks affected by recrystallization in presence of seawater-derived hydrothermal fluids (e.g., "hydrothermal metamorphism") [19,20].

Seafloor at slow-spreading oceanic crust generally displays a very rough morphology. For example, abyssal highs, called oceanic core complexes (OCCs) mostly consisting of serpentinized mantle peridotites and gabbroic rocks [21], have been interpreted as exhumed portions of the uppermost mantle along systems of low-angle detachment faults. Serpentinites, gabbros, and other rocks from OCCs are often sheared to different extends [22]. Furthermore, Chamot-Rooke et al. [23] noted that compressive deformation is distributed over a broad area in the slow-spreading oceanic lithosphere, reflecting an exceptionally high stress level even far away from plate boundaries. For instance, the authors calculated a 2.5–4.5% shortening of the sedimentary cover in the central Indian Ocean, due to both folding and thrusting. Similarly, seismic lines from the Transatlantic Angola-Brazil Geotraverse, performed by the Geological Institute of the Russian Academy of Sciences (GIN-RAS) in a tract 500–1000 km wide and ~4400 km in extent from the Brazilian Basin to the Angola Basin [24], evidenced plicative deformations of the sedimentary cover related to vertical motions of basement blocks, even far away from the spreading ridge. In fact, Sokolov [24,25] reports imbricate thrust structures in the eastern part of the Brazilian Basin, 600–1000 km away from the MAR, and hence in the Angola Basin. The author attributed these deformation to the stress field owing to volume increasing during serpentinization of the basement rocks and serpentinite diapirs upwelling throughout the sedimentary cover. Seismic profiles display several diapirs and other piercement structures protruding from the basement into their overburden. Slope-instability processes associated with development of diapiric structures have been observed in different basins the world over [26]. An intriguing consequence arising from aforementioned marine geology discoveries regards the possibility that during geological times wide portions of sediment-supporting ocean floor, already deformed by intraplate compressive tectonics, may be passively uplifted above sea level due to, for example, tilting of lithospheric blocks caused by lateral variations in density. These occurrences may lead investigators

to the apparently suitable, though erroneous, conclusion that such sedimentary units are genetically and spatially related to Mediterranean-type [27] thrust and fold orogenic belts.

The origin of the clayey fraction of the sedimentary cover in deeply serpentinized oceanic crust is also worth of discussing. Although part of marine clays are "normal" pelagic-type sediments, a (possibly large) part may derive from rock/seawater interaction in the oceanic crust, instead [28], being eventually associated with hydrothermal activity and seafloor mud-volcanism [29]. In fact, mud volcanoes are often set on the top of buried mud diapirs [30] and hence long-lived mud volcanoes can produce large dome-shaped edifices on seafloor. Moreover, clayey submarine ridges, sometimes exceeding hundreds km in length, can form in those cases where closely juxtaposed mud volcanoes were aligned along major fracture systems, as, for example, an extinct slow-spreading ridge [31]. Mud volcanoes often emit saline brines and hydrocarbons, possibly originating from buried serpentinites [9,32], and such fluids may be associated with other hydrothermal components [33,34]. Normal sediments (e.g., pelagic oozes, chalk) [35,36] and fragments of the wall rocks (likewise xenoliths in volcanic rocks) [37] are usually intercalated with the effusive hydrothermal clays which therefore may resemble a tectonic mélange. On these premises, it may be not a simple task (especially in submerged settings) to discriminate between dome-shaped bodies consisting of mélanges associated with accretionary wedge complexes, from those related to mud diapirs/volcanoes [38].

Even though the magmatic activity is starved at slow (and ultra-slow) spreading areas, it displays, when occurring, different petrologic and geochemical characteristics with respect to the typical MORB-type array [39]. Interestingly, plagiogranite veins often crosscut gabbroic rocks in OCCs [21]. More in general, igneous felsitic rocks are not rare in slow-spreading oceanic crust having been either interpreted as extreme differentiates from basaltic melts [40] or primary magmas after dehydration melting of hydrothermally altered gabbroic and ultramafic rocks [17,41,42]. Here it is opportune to mention that in the faulted scraps of two seamounts along the Mid Atlantic Ridge (45° N), granites, granodiorites, granite gneisses, diorites and amphibolites have been recovered from >2000 m water depth [43,44]. The authors remarked that the age and geochemical characteristics of these felsitic rocks strongly suggest that these occur in situ and are associated with basalts, metabasalts, altered gabbro and serpentinized peridotites.

Oceanic tectonics, as above depicted, implies the existence of an aged oceanic crust. In fact, serpentinization, formation of thick sedimentary covers and diapir upwelling are geological processes that require relatively long time to develop significantly. On the other hand, it is widely accepted that oceanic crust, formed in a fast-spreading regime, has a relatively short geological life being eventually subducted and consumed at the convergent side. Nevertheless, oceanic crust at (ultra)slow-spreading centers may experience stagnation and hence persisting in submarine conditions for periods >100 Ma [45]. Such a "cold", extensively fractured, almost stationary oceanic crust likely displays lateral variations in density due to different hydration degree of basement rocks, and different compactation of sedimentary layers. Thus, local pressure gradients, hence areas of tectonic instability, may originate "spontaneous" [46] or "self-sustaining" [47] episodes of intraoceanic subduction [48–50]. In other words, intraplate tectonic events, including subduction, having occurred in an old and stagnant oceanic lithospheric domain, will finally give rise to assemblages of igneous and metamorphic felsitic rocks more typical of continental than oceanic settings [49,51–53].

### 2. The Controversial Origin of the Mediterranean Salt Giant

Marine salt deposits in the Mediterranean area (Figure 1) are both exposed on land, such as in Sicily, and buried under a variously thick sedimentary cover, as imaged in seismic profiles or evidenced by scientific and commercial boreholes [54]. Both exposed and subsurface deposits are traditionally thought to be climate evaporites [55]. In particular, Hsü et al. [3] put forward the famous hypothesis that a tectonic barrier at the Gibraltar Strait hindered the communication between the Atlantic Ocean and the Mediterranean Sea, which fully evaporated, producing vast sabkha-like salty lowlands, 2–4 km below global sea level. This theory is merely postulated from the interpretation of seismic lines in

the western Mediterranean Basins [56] and puzzling results of the Leg 13 of the Deep Sea Drilling Program in the Balearic Basin. Although the idea of a Messinian salt giant spanning over the entire Mediterranean area is hitherto accepted by a considerable number of geologists, the hypothesis by Hsü et al. (1973) on the origin of the "salt giant" in a fully desiccated basin has been repeatedly challenged [57]. In fact, the estimated amount of buried and outcropping Mediterranean salts [58], would exceed by a factor ~50 the number of solutes normally contained in the Mediterranean seawater, which implies a series of desiccation and replenishment episodes inconsistent with the regional geodynamic evolution [59]. On the other hand, those hypotheses suggesting the evaporite deposition under persistent deep-water conditions must take into account that halite starts to precipitate when the remaining solution is reduced to 10% of the original seawater volume, implying a dramatic drop of the basin sea level.



**Figure 1.** The study area where the capital letters indicate the zones here considered from the salt-deposit perspective. A = Gulf of Cádiz; B = Alboran Sea; C = Algero Provençal Basin; D = Tyrrhenian Basin; E = Caltanissetta Trough (Sicily Mainland); F = northern Tunisia and Pelagian Sea; G = eastern Mediterranean Basins, including Ionian (G1), Herodotus (G2) and Levant (G3) basins. The colored circles indicate areas where there is geophysical inference or/and xenolith evidence of buried serpentinites, as in situ relicts of the Tethys Ocean lithosphere (More information is reported in the text).

On the above bases, it is opportune to mention that fossil archaeal lipids in cores of subseafloor salts drilled in the Sardino-Balearic and Ionian abyssal basins, strongly suggest the existence of surface waters with normal salinity (26–34 psus) and temperature of 25–28 °C, at the time of salt deposition [60]. Therefore, these authors inferred that such conditions point to a deep-water basin with normal salinity seawater floating on a higher-density, saturated in gypsum and halite, brine layer. The boundary between the layers ranged from 2000 to 2900 m b.s.l., vertical mixing across the extreme density gradients between brine and overlying seawater was, as usually, extremely slow [61]. A possible way to give rise to the aforementioned salt-saturated, near-bottom, brine layer is to add an adequate amount of solute (salt) to the solution (seawater). This fact would hint at a deep-seated source of salts adequately connected with seafloor by feeding fractures. This is not an odd conjecture, since marine geology expeditions in the central Red Sea [62,63] observed pools, several kilometers long and more than hundred meters deep, of highly saline brines in several axial topographic depressions, locally called "Deeps". Brine pools were related to the activity of "saline geysers" in the seafloor, intermittently erupting warm, salt-enriched, aqueous fluids overcoming the pressure exerted by a 2000 m seawater column [64,65]. Thus, salt bodies most probably occur in the Red Sea subseafloor feeding the saline volcanism on seafloor. Similar circumstances may have manifested in past marine basins, including Paleo Mediterranean Sea and Tethys Ocean. Therefore, this model rises the fundamental question on the origin of the postulated deep-seated "brine chambers" (to mimic "magma chambers" feeding igneous volcanism).

Anhydrous mafic silicate minerals from basalts and mantle rocks, cannot reach thermodynamic equilibrium with aqueous solutions in the range of pressures and temperatures compatible with a wide section of the oceanic crust. Thus, water dissolves some minerals yielding secondary products. Consequently, the water-rock system attains an "intrinsically inconsistent" [66] state, being contemporarily in disequilibrium with original minerals and in equilibrium with newly formed minerals. Since the system does not require external energy inputs, it can develop spontaneously and continuously for a very long geologic time. In other words, the hydration reactions persist as long as rocks and water coexist. For example, Mg-rich olivine and/or Mg-rich orthopyroxene will be transformed into serpentine group minerals ( $\pm$ different reaction by-products: [67]). In case the reactant is salty water, the salinity of the aqueous solution increases as the reaction proceeds, because the formation of serpentine consumes H<sub>2</sub>O from the solution, hence rejecting most of seawater solutes, according to the following reaction [68]:

$$Mg_2SiO_4 + MgSiO_3 + 2 H_2O + Na^+ + Cl^- \rightarrow Mg_3Si_2O_5(OH)_4 + NaCl$$
 (3)

Laboratory electromagnetic experiments [69] show that low-salinity aqueous fluids evolve towards high-salinity fluids during progressive serpentinization of Mg-rich olivine and pyroxenes.

In a closed system, the increase in salinity can be regarded as a proxy for the progress of the serpentinization reaction [70]. Moreover, these authors observed that the rate of serpentinization of olivine slows dramatically down as salinity increases and H<sub>2</sub>O activity decreases. This fact is obviously expected, because also in case of evaporation of seawater the rate of the process dramatically decreases as the salt concentration in the solution increases and H<sub>2</sub>O activity decreases [71]. Thus, the serpentinization of olivine-bearing rocks needs a further inflow of water to continue at full speed. In this respect, it is opportune to recall that serpentinization proceeds downwards in the oceanic crust throughout a network of braided fractures, which propagates to considerable depths according to a crack-and-seal mechanism [72,73]. Most salts separated from the reactant seawater, being deeply incorporated in the fractured host rock, will hardly be re-dissolved in the ocean (such a fate would have been inevitable, on the contrary, in case of exfoliation-type processes moving along flat reaction fronts). Salts and brines remain, therefore, indefinitely trapped in pores and fractures in the newly formed serpentinite as long as no perturbation events will occur [9]. Reasonable inference in such "hidden salts" [8] derives from the interpretation of geophysical data as, for instance, from electromagnetic records acquired in convergent geodynamic settings [69].

Scribano et al. [9], recalling that abyssal serpentinites contain about 13 wt % water, mentioned that in cases seawater is the reactant fluid, about 10.5 kg of seawater salts (hence about 8 kg NaCl) are left out during the formation of 1 m<sup>3</sup> serpentinite. Admitting that about 30 wt % of seawater chlorine is sequestered by insoluble minerals possibly occurring in the system, about 1 km<sup>3</sup> halite (density ~ 2.16 g/cm<sup>3</sup>) can be stored in a cubic volume with a 6.5 km side length of serpentinites (density  $\sim 2.5$  g/cm<sup>3</sup>). The accumulation of the previously dispersed salt particles in major fractures of the deep-seated country rocks is a crucial process, preliminary to the formation of shallow-seated deposits, even gigantic in size. Halite (as well as other marine chlorides) under geological conditions has negligible yield strength, and hence it deforms viscoplastically as a fluid [73]. In addition, the density of halite  $(2.16 \text{ g/cm}^3)$  is lower than serpentine group minerals  $(2.5-2.7 \text{ g/cm}^3)$ . Thus, salt particles, being in a gravitational disequilibrium, slowly move upwards through a network of fine fractures and micropores of the host serpentinite. Salts and heavy brines, en route to shallower levels, may accumulate into adequate spaces in coarsely fractured country rocks. An Otswald-ripening type mechanism [74] likely plays an important role in early stages of salt accumulation. The size of the final (shallow-seated) salt deposit is closely related to the effectiveness of such a deep-seated accumulation process and hence to the extent of the process through time.

Finally, the upwelling of salts to (or near) seafloor can develop as hydrothermal saline plumes or buoyant saline diapirs [8,9,65]. The hydrothermal plume mechanism (Figure 2a) needs a suitable heat source, such as an igneous intrusion. When the temperature of the system exceeds 400 °C, different dehydration reactions of hydrous serpentinite minerals take place releasing part, even the entire amount, of the formerly incorporated water [75]. Serpentinite dehydration by amorphization can also occur along fault planes and other tectonic discontinuities [76]. If the dehydrating serpentinite hosts marine salts, a hydrothermal aqueous hyperhaline solution is likely produced. Hovland et al. [7,65] put forward a theoretical model to explain the behavior of a hydrothermal saline brine in the subseafloor of a deep marine basin, and the formation of saline geysers as presently occurs in the Red Sea seafloor.



**Figure 2.** Cartoons qualitatively depicting two different mechanisms explaining the emplacement at seafloor of salts hosted in buried serpentinites, giving rise to a sea-bottom layer of heavy saline brines (full explanation is given in the text). (**a1**,**a2**): Two steps of the formation and upwelling of hydrothermal saline brines. (**b1**,**b2**): two steps of the upwelling to seafloor of nearby saline diapirs. Note the dissolution deeps formed at sites of diapirs exposition and the sea-bottom layer of high saline brines saturated in Halite and Gypsum.

In summary, Hovland et al. [65] recalled that at depths shallower than 2800 m (pressures below 30 MPa), or at temperatures lower than 430–374 °C, a given saline aqueous solutions is in a subcritical state and boiling may occur. Boiling combined with upward flow induces cooling and condensation. The latter releases latent heat and produces water, which will dissolve the surrounding salts. The highly soluble salts (e.g., K-bearing ones) are preferentially fractionated in the water-rich portion of the dense brine. This portion escapes first from the system, leaving the relatively less soluble halite to erupt to seafloor in "pure" form.

About the diapiric upwelling mechanism (Figure 2b) halite, contrarily to most seafloor sediments, does not attain compaction with depth, being therefore less dense than sedimentary overburden at depths >800 m [73]. Therefore, when salts reach the critical volume necessary to overcome the yield strength of the country rocks, they can rise vertically (Figure 2b) forming a dome-shaped geological body, called diapir (from the Greek meaning "to pierce through"). On a seismic profile, a salt diapir generally appears as an area with low amplitude, chaotic and unstructured reflections [77]. Areas of large reflections above this blank zone can depict the diapir shape, although processing of the input data may veil flank reflections [78]. Moreover, high amplitude reflections may appear inside a given diapir, being generally interpreted as signs of heterogeneous diapir composition [79]: Indeed, salt diapirs

often contain a variable amount of mud, which may consists of muddled serpentinites and retrograde clays after serpentine [80–83].

Several salt diapirs may coalesce forming vast salt "canopies". Salt diapirs rarely extrude both at seafloor and on land. Exposed chlorides have generally an ephemeral geological life, except where they are suddenly covered by impermeable sediments, protected by a sulfate or a saturated brine layer, or outcropping in regions characterized by extremely dry climate conditions, as the salt diapirs and glaciers of the Great Kavir and the salt extrusion at Kuh-e-Jahani, in Iran [84–86].

Here we consider, for conciseness, only halite among marine salts. Sulfate, it is known, is the third most abundant ionic species in seawater, after Na<sup>+</sup> and Cl<sup>-</sup>. Scribano et al. [9] highlighted the behavior of sulfates with respect to the halite deposits in serpentinite systems. Anhydrite and/or gypsum may form independent geobodies due to their retrograde solubility, often intercalated with halite deposits. In this respect, it is opportune to recall that gaseous and liquid hydrocarbons are one of the most intriguing by-products of the serpentinization reactions [87]. Upwelling methane and/or other hydrocarbons [32] may encounter sulfate horizons giving rise to a series of reactions [88] which produces, among others, limestone, H<sub>2</sub>S and elemental sulfur:

$$CaSO_4 + hydrocarbons \rightarrow CaCO_3 + H_2S + H_2O \pm S \pm CO_2$$
(4)

Thus, we put forward the hypothesis that reaction (4) may adequately explain the occurrence of irregular carbonate layers in exposed salt deposits, being such carbonates erroneously considered the first precipitate from evaporating seawater. The same reaction can be also accounted for sulfur deposits associated with Ca-sulfate and other marine salts.

Quantitative modeling on salt deposits related to seawater-induced serpentinization must consider that sedimentary criteria (e.g., assuming the lateral extension of a given vertical section of outcropping salt deposits as wide as the corresponding marine basin) are not applicable in this case, as well as in any geological processes which imply drainage, zonal accumulation and focused discharge of matter previously dispersed as small particles in its source rocks. In this respect, salt deposits, as geological bodies, can be more reliably compared with oil deposits and volcanic systems than sedimentary layers.

#### 3. Salt Occurrences in the Mediterranean Area: The Tethys Serpentinite Perspective

Eduard Suess (1831–1914), in the first volume of his work "Das Antlitz Der Erde" (1895) reported that the existing Mediterranean is the remnant of the Tethys Ocean, which extended parallel to the equator, and at one time, before the Atlantic came into existence, surrounded half the globe. In other words, the structural framework of the present Mediterranean area is the consequence of the Cenozoic closure of the Tethys Ocean [2]. Such a hypothesis has been later dismissed by almost all geoscientists, mostly based on the interpretation of both geophysical data and results of scientific and commercial seafloor drillings [89]. Nevertheless, it is known that the interpretation of seismic data is closely related to a given petrophysical model. If the model is significantly in error, then the conclusions may be misleading. For instance, experimental results show that partially serpentinized peridotites have seismic wave velocities similar, among others, to different igneous and metamorphic rocks typical of the lower continental crust [90].

Seismic data in some Mediterranean areas, such as in Sicily mainland and its offshore areas, may be either consistent with a thinned continental crust [91,92] or a serpentinized Tethyan basement [93,94]. The latter viewpoint has been plenty confirmed by the discovery of small (though abundant) fragments (i.e., xenoliths) of the buried Central Mediterranean basement entrained as xenoliths in volcanic rocks from Sicily [95–98]. Moreover, the general implications that can be drawn from the new concept of intraoceanic tectonics [23,24], above mentioned, may challenge widely accepted (dominant) viewpoints regarding the geological setting of many exposed and submerged Mediterranean areas.

On the above grounds, it becomes evident that the original idea by Suess [2,99], that Mediterranean is a Tethyan legacy, merits more consideration by modern geoscientists.

#### 3.1. Salts in the Gulf of Cádiz

Here, we first consider the marine area between southern Iberian and northern Moroccan Margins, extending from the Gibraltar Strait, to the east, to the Horseshow Abyssal Plain, to the west (zone "A" in Figure 1). Even though this zone is nominally part of the Atlantic Ocean, it displays physiographic characters and geological history also fitting in the Mediterranean domain [100]. Although we highlight essential geological aspects related to salt deposits only, it is worth mentioning that Duggen et al. [101] consider the geological setting of the Gulf of Cádiz area primarily related to the closure of the Rifean and Betic "corridors" (i.e., Atlantic-Mediterranean marine gateways) since late Miocene. The basement in the deep oceanic domains offshore SW Iberia, as in many Mediterranean areas, is buried under a thick layer of sediments, Mesozoic to recent in age [102]. Pioneering Deep-Sea Drilling expeditions on the Gorringe Bank [103], recovered serpentinized peridotite, gabbro, and volcanic rocks. The interpretation of seismic profiles has led some authors [104,105] to envisage relicts of an old oceanic lithosphere in the central part of Gulf of Cádiz. In particular, Sallares et al. [104] report that the fragment of oceanic crust identified in the velocity model consist of a layer of serpentinites, about 20 km in thickness, at the top of the unaltered section of the lithospheric mantle. The authors also comment that such an oceanic relict constitute the only remnant of the western Alpine-Tethys Ocean and one of the oldest oceanic crustal fragments currently preserved on Earth. Further studies on micro-seismicity in the Gulf of Cádiz area [106] confirm that the aforementioned oceanic "crust" consists of serpentinites, locally associated with décollements structures.

Thick (500–1400 m) marine salt deposits cover extensive parts of the basement in the Gulf of Cádiz [107]. Seismic profiles in the Gulf of Cádiz area also reveal an impressive array of diapiric structures, which in some places form elongated clusters, several tens of km in length and 1–14 km in width, called "diapiric ridges" [108,109]. Emplacement of these diapiric structures caused various deformations in the sedimentary overburden. Diapirs themselves appear sometimes deformed [110]. Gulf of Cádiz diapirs are widely considered salt bodies. Interestingly, Matias et al. [109] remarked that the Gulf of Cádiz salt unit is part of a much larger salt depositional system having existed prior to the opening of the central Atlantic, and hence forming conjugate salt basins in the Grand Banks-Lusitanian Basins, and Nova Scotia-Moroccan margins. On the contrary, some authors consider Gulf of Cádiz diapirs as mud-bodies, i.e., slowly upward-migrating mass of clay-rich sediment and fluid discharge [111]. Gaseous hydrocarbons play an important role in the mud-diapir formation, decreasing mud densities hence increasing buoyancy [112]. In fact, mud diapirs are often associated with extrusive geological structures called mud volcanoes [30]. The latter circumstance is consistent with the presence of active and extinct mud volcanoes in the culmination of some diapirs in the Gulf of Cádiz area [34]. On the other hand, some authors envisaged the multiple (e.g., mud diapirs and salt diapirs) or composite (e.g., mud-and-salt diapirs) nature of the Gulf of Cádiz buoyant geological bodies. In particular, Perez-Garcia et al. [79] report that marine geology expedition by RV Merian in May 2006 revealed the unequivocal evidence of strongly saline brines in mud volcano fluids in the Gulf of Cádiz. Hensen et al. [33] mention that nearly NaCl-saturated and strongly sulfate enriched fluids have been reported from Mercator mud volcano, in the same area.

### 3.2. Salts in the Alboran Basin

The Alboran Basin (Figure 1, zone B) extends about 400 km in length from east to west and 200 km in width from north to south, the maximum water depth being about 2 km [113]. This basin is partly surrounded by an east-west trending, U-shaped, mountain chain called the Betic-Gibraltair-Rif system [114,115]. A sedimentary sequence, up to 8 km in thickness, covers the Alboran Basin basement [105]. A submarine relief (Alboran Ridge), trending northeast-southwest extends across the basin [116]. The top of the ridge goes above sea level in northern segment giving rise to the Alboran Island. It consists of beds of andesitic pyroclastics which are cut by an altered tholeiitic sill, and are unconformably capped with Pleistocene sediments [117]. Seismic profiles imaged a submarine array of diapirs spread over a wide portion of the Alboran Basin, known as the "Alboran diapir

province". The overburden sediments display their maximum thickness between two diapiric highs, or at the border of the diapirs [113]. As usual, mud volcanoes occur above some diapirs, having been interpreted as due to overpressured fluids migrating from the inner parts of the diapiric bodies [118]. Alboran diapirs and mud volcanoes were sampled by core drills and studied by Sautkin et al. [118]. Though Alboran diapirs are generally thought to consist of mud, high-resolution seismic profiles imaged these diapirs as transparent to semitransparent seismic facies with a chaotic reflectors at their nuclei [113]. Thus, halite, gypsum and anhydrite may coexist with mud and hydrocarbons in these buried geological bodies. Comas et al. [119] report seismic inference that no important salt layers occur in many parts of the Alboran Basin, except in its southern part. Here, salt diapirs were imaged apparently issuing from the top of the oceanic basement [119].

A major structural feature of the Alboran area, as imaged by seismic profiles, is the relatively thin lithosphere and crust, the latter being less than 13 km in thickness [119]. Seismic profiles also evidence a basement section with a chaotic pattern [120]. Although these facts may be consistent with an exhumed, partially serpentinized oceanic mantle, close similar to the basement of the adjacent Gulf of Cádiz, scientific and commercial drillings on some buried structural highs in the western border areas of the Alboran Basin (e.g., ODP leg 161, site 976: [121]) recovered high-pressure (HP) metamorphic and igneous rocks compatible with a continental affinity [122]. More interestingly, these rocks display petrological characteristics broadly similar to those of the neighboring Paleozoic Alpujarride Complex of the Betic Cordillera (Southern Spain) and the corresponding Sebtides terrains (Northern Morocco: e.g., Puga et al., 1995). There are several geotectonic models regarding the geological significance of the Betic-Rif crustal domains. For example, Vergés and Fernàndez [115] consider this orogenic system due to the Tethys-Atlantic interaction along the Iberia-Africa plate boundary. It must be mentioned, however, that it is not yet proved that the entire Alboran Basin is paved with metamorphic rocks. In fact, dredging and diving data indicate that east of 4° W most of the basement highs consist of volcanic rocks only [119].

### 3.3. Salts in the Algerian-Provençal Basin

East of the Alboran Sea, several juxtaposed basins (namely: Balearic, Algerian, Provençal, Sardino and Ligurian) display the same geophysical and physiographic characteristics [56]. Therefore, we consider these basins as a whole, e.g., the "Algerian-Provençal Basin" (Figure 1, zone "C"). The basement of the aforementioned basin is widely considered oceanic, Neogene in age, the latter indication essentially deriving from speculative models [89,120]. It is worth noticing that the idea of giant salt deposits, Messinian in age, extending over a broad area of the Mediterranean subseafloor first arose from the interpretation of seismic profiles [56] and study of drill cores in a Deep Sea Drilling Program (DSDP) site in the Balearic section of the Algerian-Provençal Basin [2]. Auzende et al. [56] suggested that seismic profiles in the western Mediterranean Basins reveal a salt layer often affected by diapirism overlain by a sedimentary sequence. Auzende et al. [56] gave the aforementioned salt layer an Upper Miocene age. More precisely, the authors highlighted an upper reflector, which delineates the surface of several irregularly juxtaposing diapiric structures protruding in a sedimentary overburden. An intermediate group of reflectors also occurs, which is thought by the authors as the "mother bed" of the diapiric structures. This group wedges out against the basement, and when it is not warped it is 300 to 500 m thick, except north-east of the Balearic Islands where its thickness reaches 1000 m [56]. Inference on thickness, of course, are based on the occurrence of a clear bottom layer which, as reported by the Auzende et al. [56], is marked by a strong reflector (known as "M" reflector). Nevertheless, in the same paper the authors report that reflectors at the base of the salt layer are often poorly defined because of the screen effect of "domes". Broadening of the data-set through time has not given rise to significantly contrasting interpretation with respect to Auzende et al. [56], but some authors assert that an almost continuous series of reflectors is clearly imaged beneath diapirs [123].

The Algerian Basin section of the seismic line ESCI-Alb-2b-2c, interpreted by Medaouri et al. [120], clearly shows that bases of salt diapirs are located directly on the oceanic crust, their tops evidently piercing most part of the sedimentary overburden, including (supposed) Upper Miocene strata.

#### 3.4. Salts in the Tyrrhenian Basin

The Tyrrhenian Sea (Figure 1, zone "D") is a small, deep, triangular basin in the eastern part of the western Mediterranean, bordered by the Italian Peninsula to the north and to the east, by Sicily to the south, by Sardinia and Corsica Islands to the west.

Seismic profiles across the central part of the basin indicate a four-layers structure [1]: The uppermost layer displays  $V_P = 1.7-2.5 \text{ km} \cdot \text{s}^{-1}$ . The second layer is characterized by a steep velocity gradient, in which P-wave velocities increase from  $3.5 \text{ km} \cdot \text{s}^{-1}$  (top layer) to  $6.0 \text{ km} \cdot \text{s}^{-1}$  (bottom layer). The third layer displays a moderate velocity gradient, with  $V_P$  ranging from  $6.6 \text{ km} \cdot \text{s}^{-1}$  to approximately  $6.9 \text{ km} \cdot \text{s}^{-1}$  at 10 km below sea level. The bottom layer is located immediately above the Moho ( $V_P = 8.0 \text{ km} \cdot \text{s}^{-1}$ ). This seismic structure was related to an oceanic crust with a thickness, excluding the sedimentary cover, between 6 and 8 km [1]. The authors also report that some zones in the Tyrrhenian Basin are characterized by the absence of refracted arrivals, and  $V_P$  velocities increasing steadily from  $4.9 \text{ km} \cdot \text{s}^{-1}$  to  $7.5 \text{ km} \cdot \text{s}^{-1}$  at the base of the crust. This fact has led some authors [124] to relate these seismic features to continental crust, albeit its thickness never exceeds 10 km. It is, however, opportune to remark that aforementioned seismic structure is also compatible with a layer of ultramafic rocks with gradually decreasing serpentinization degree from top (about 90%) to bottom (about 50%) [94,125,126].

Refraction data suggest that salt deposits occur only in the western part of the Tyrrhenian Basin subseafloor, just off the coast of Sardinia [1]. Several contrasting hypotheses have been proposed on the geodynamic evolution of the Tyrrhenian Basin, including the one suggesting that this basin is a relict of the Tethys Ocean [127]. Although there is a general consensus that aforementioned hypothesis has lost all credibility [1,89,128], a Tethyan affinity may be consistent with results of scientific drilling in Central and Southern areas of the basin, suggesting that an exhumed serpentinized (hence aged) upper mantle here occurs beneath a cover of relatively young basalts [28].

#### 3.5. The "Giant" Crops Out: Salts in Central Sicily

Central Sicily (Figure 1, zone D and Figure 3) is classic ground for studies on Mediterranean salt deposits [129–131]. Gypsum and anhydrite crop out in various areas, whereas buried levels of halite and other soluble chlorides were intersected at different depths by mining tunnels during the period of sulfur exploitation, which lasted more than 100 years between XIX and XX Centuries. The prominent geological domain of Central Sicily consists of a northwestern-southeastern-trending tectonic depression known as "Caltanissetta trough" [132,133], which has been considered a deep marine basin throughout the Miocene, being now totally filled with clayey sediments and marine salts of the "Gessoso-Solfifera Group," Messinian in age [134]. Salts are discordantly covered by clayey mélanges and turbidites, traditionally thought to be terranes of the Apennine-Maghrebian Chain [135]. Although the present paper is not aimed at providing advances on regional geology, we would, however, suggest researchers presently studying this area to consider the possibility that the Caltanissetta Basin is a relict of the Tethys Ocean architecture, such as a nodal-basin [136]. In this respect, we recall that Finetti et al. [137] based on seismic reflection profiles, suggested that the lithosphere underneath the Ionian Basin, eastern Sicily offshore, is a relict of the Permian Tethys Ocean. Accordingly, the study of the distribution of deep-water Permian fauna in different Mediterranean areas led Vai [138,139] to infer that the buried roots of the entirety of Sicily is a relict of a branch of the Tethys Ocean, Early Permian in age, also known as the Oman-Iraq-Levantine-Sicily Texas seaway. Moreover, Polonia et al. [140] reported on serpentinite diapirs of probable Tethyan affinity in the western Ionian subseafloor, close to Sicily. In other words, Sicily and the adjacent Ionian Basin may have the same Tethyan lithospheric roots.

Nevertheless, the Ionian-Sicilian lithospheric continuity is hardly accepted by most geoscientists, since the eastern margin of Sicily (i.e., the Hybla-Malta escarpment) is commonly considered a "fossil" passive continental margin. In fact, Sicily is traditionally thought to be rooted on the Africa continental plate [141]. On the other hand, seismic profiles can give origin to debatable interpretations: a thin continental crust [91], or a strongly serpentinized oceanic lithosphere [93,94]. In this respect, the results of thirty-year study of deep-seated xenoliths coming from the Hyblean diatremes (southeastern Sicily) [95–98,142] provided strong lines of evidence that the unexposed basement of southeastern Sicily consists of a fossil oceanic core-complex of likely Tethyan affinity, and hence the Ionian margin of Sicily can be considered one of the deep slopes of the fossil Hyblean OCC.

Reasonably assuming that the Hyblean-Ionian foreland areas are rooted on the Tethyan lithosphere, what about the Central Sicily, where most Messinian salt deposits occur? Seismic tomographies [92,143] suggest that a low-velocity zone (4.40–5.16 km/s) beneath the Central Sicily occurs down to a depth of 5–15 km, corresponding to a thick sedimentary succession. Below, P-wave velocities (V<sub>P</sub>) vary in the range of  $5.30-5.80 \text{ km} \cdot \text{s}^{-1}$  down to a depth of 25 km, which were interpreted by Sgroi et al. [143] as metamorphic and igneous felsitic rocks constituting the postulated Africa continental plate. However, comparing these V<sub>P</sub> values with those reported by Giampiccolo et al. [94] for the Hyblean lithosphere, in the depth range of 10–12 km, we note that V<sub>P</sub> values beneath the Central Sicily are compatible with serpentinized peridotites having a degree of serpentinization of 70–80 vol %. The same inference could arise from the comparison of these V<sub>P</sub> values with abyssal peridotites [145] that are highly serpentinized (70–80 vol %). Finally, P-wave velocities estimated beneath the Central Sicily increase up to a value of 7.40–7.80 km·s<sup>-1</sup>, which does not change from the depth of 35 km downward, corresponding to unaltered mantle rocks as inferred by Sgroi et al. [143] and Calò et al. [92].

On the above premises, we suggest that the Central Sicily may be paved with serpentinized peridotites belonging to the Paleo Tethys Ocean, even though more detailed investigations will have to be carried out to better constraint this inference. Buried serpentinites, as already mentioned in this paper, can host "hidden" salts. How these hidden salts were emplaced in the Caltanissetta Basin seafloor in the Early Messinian time? Here we recall the mechanisms reported by Scribano et al. [9] for the upwelling of deep-seated salts. The hydrothermal advection mechanism (Section 2.1) implies the de-hydration of Tethyan serpentinites in the buried basement of the Caltanissetta Basin and hence a considerable input of heat is required, likely due to a shallow-seated igneous intrusion (e.g., a large mafic sill: Figure 2a). Nevertheless, the thick cover of Messinian salts and other sediments generally conceals evidence of past igneous activity, but isolated blocks of volcanic rocks, 5–20 m in thickness and up to 50 m in width, with alkali basalt composition and pillow structure, discontinuously outcrop in several parts of Central Sicily [146]. The authors also remarked that the volcanic rocks are interbedded within Cretaceous to Miocenic mud-breccias, the same that generally underlie Messinian salt deposits. In addition, foraminifera dating of the intrapillow clay indicates an Oligocene (Ruplelian) age [146]. These findings indicate that it is not an odd conjecture that one or more igneous intrusions there were emplaced at shallow depth in the Early Messinian in the Caltanissetta Basin, giving rise to deserpentinization episodes and the hydrothermal advective uprising of salts (Figure 2a).

Although the hydrothermal advection of deep-seated saline brines can be a reasonable mechanism to explain the formation of salt deposits in the Caltanissetta Basin [9], the possibility that some buoyant salt diapirs have jointly reached and pierced the seafloor of the basin in the Early Messinian can be put forward, too (e.g., Figure 2b). In fact, modern examples exist of large salt diapirs, which have pierced the entire overburden, and are partially exposed as salt glaciers either on land or at seafloor [85]. In this regard it is opportune to mention that salt diapirs, although dominantly consisting of halite, may also contain variable amounts of gypsum, anhydrite and clayey mud. Gypsum (or anhydrite) is the first material to be extruded at seafloor being usually located on flanks and at the top of a given diapir [73]. More interestingly, the mechanical stress for piercing the country rocks likely breaches the

gypsum accumulated on top of the diapir, giving rise to clastic deposits at seabed, as Perthuisot [147], evidenced in salt diapirs outcropping in northern Tunisia (see later). On the other hand, soluble salts extruded at seafloor may produce the brine layer at the basin bottom (Figure 2b) as invoked by Christeleit et al. [60] to explain salt deposits in Mediterranean deep basins.



**Figure 3.** Geological sketch-map of Sicily highlighting the area of the Caltanissetta Trough. simplified after [133].

3.5.1. Sicilian Salt Deposits: A Tentative Mass Balance

Here we consider a rectangular portion, with 75 km short side and 140 km long side, of the seafloor of the Caltanissetta Basin in the Early Messinian, coarsely corresponding to the surface area of the present Caltanissetta Trough (Central Sicily: Figure 3). Recalling the geological considerations on this area reported in Section 3.5, and the lithospheric model of the Southern Sicily area put forward by Manuella et al. [93] and Giampiccolo et al. [94], it is reasonable to hypothesize that the regional lithospheric column in the Middle Miocene consisted of about 3 km of pelagic sediments overlying an about 19 km thick section of serpentinized ultramafic rocks. The serpentinization degree of the considered portion of the lithospheric column presumably decreased with depth. In this respect, it is arbitrarily assumed that a 6 km section displayed 100% serpentinization, 7 km 65% and 6 km 35% serpentinization. Thus, a cumulative volume of 123,690 km<sup>3</sup> of 100% serpentinized

ultramafics (Figure 4) can be considered for mass balance calculation. Density of serpentinites is considered 2500 kg/m<sup>3</sup> [125], density of salts 2162 kg/m<sup>3</sup>. Recalling that a chrysotile-lizardite-bearing serpentinite contains about 13 wt % of water [148], a (seawater) volume of about 39,144 km<sup>3</sup> was consumed by the reaction, leaving apart about 741 km<sup>3</sup> of marine salts (Figure 4), variously disseminated in the entire volume of serpentinized ultramafic rocks. Such a serpentinization and consequent salt deposition probably occurred in an interval time from Late Paleozoic [98] to Miocene. According to the model described by Scribano et al. [9], part of the 741 km<sup>3</sup> of "hidden salts" [8] previously disseminated in the host serpentine, probably going together with gaseous and liquid hydrocarbons [32], slowly migrated through the fractured serpentinite geobody according to pressure gradients, hence accumulated in adequately large empty spaces, likely related to disjunctive tectonics. On Messinian time, an exceptional event (e.g., one or more igneous intrusions) produced local deserpentinization, advective upwelling and focused discharging at seafloor of hydrothermal heavy brines (e.g., Figure 2a).



**Figure 4.** Histogram depicting the estimated volumes (km<sup>3</sup>) of serpentinites, seawater and their salts in a 19 km deep lithospheric section tentatively corresponding to the Caltanissetta Basin (Central Sicily) in the Upper Miocene. (A) Cumulative volume of ~123,690 km<sup>3</sup> of 100% serpentinized ultramafic rocks; (B) Total volume of ultramafic rocks with different serpentinization degree (~199,500 km<sup>3</sup>); (C) Volume of seawater (38 psu) involved in the serpentinization process; (D) Volume of solid salts (~741 km<sup>3</sup>: note the scale change) extracted by the seawater volume as in (C) and dispersed in the volume of serpentinite as in (B). Full explanation is given in the text.

Estimating the quantity of salts out of the aforementioned 741 km<sup>3</sup> having been involved in the hydrothermal circulation, hence deposited in the Messinian seafloor of the Caltanissetta Basin, is a difficult task, since no compelling evidence of the volume of marine salt deposits in Central Sicily

occurs. In this respect, Francaviglia [149], based on a statistically significant number of drilling tests in two crucial areas, has proven the discontinuous distribution of marine salts over the Caltanissetta Trough. The aforementioned author also remarked the importance of the clayey component in the regional Messinian deposits. Based on our field observations through time and literature data [131], we cautiously suggest that no more than 300 km<sup>3</sup> marine salts were discontinuously deposited in the shallow levels of the Caltanissetta Trough. Some salt accumulations of several hundred meters in (apparent) thickness, as observed in a few partially outcropping deposits, can be tentatively ascribed to intercepted saline "stems" of previous hydrothermal vents [8]. Adding to the salts the volume of the hydrothermal clays [29] emplaced together with the salts, the aforementioned volume estimate would likely be increased by one order of magnitude or even more.

## 3.6. Salts in Central Part of the Mediterranean Margin of Africa and Pelagian Shelf

In northern Tunisia (zone F in Figure 1) there is an area elongated NE-SW, about 150 km in length, 40 km in width, where many salt diapirs occur (i.e., "zone des diapirs") [147]. The same author estimated a thickness of about 1000 m for the marine salt deposits associated with these diapirs. Where cropping out, the Tunisian diapirs display a mushroom-shaped top, hence consisting of strongly deformed, chaotic mass of gypsum, anhydrite, sandstones and carbonates. Saline springs indicates the presence of halite deposits at depth. Dolomite, black idiomorphic quartz crystals with anhydritic inclusions, scattered albite crystals, K-feldspars and "Mg-phyllites" are often associated with gypsum and anhydrite. These minerals are probably products of metasomatic reactions triggered by Si-, K-, and Mg-rich fluids circulating throughout the salt deposits [147]. K/Ar dating on metasomatic feldspars indicates that metasomatic processes may have occurred in a time lapse between 97 Ma and 18 Ma [150]. A Triassic age is generally suggested for Tunisian diapirs [151], although no geophysical data nor core drillings can substantiate such an assumption.

About salt deposits in the Mediterranean Margin of Libya, the interpretation of seismic profiles extending between both sides of the Gulf of Sirte display a strong, continuous reflector of the type that in other Mediterranean Basins is generally considered the Top of Messinian [152]. On the contrary Fiduk [153] remarks that additional seismic data clearly indicate that there is only a relatively thin, high amplitude and high velocity layer of non-halite evaporites (mainly anhydrite) which caps the Messinian section. Where this high amplitude and high velocity layer is absent, the entire Messinian interval displays a clear seismic continuity with no evidence of salty layers.

The interpretation of seismic lines across different areas of the Pelagian Shelf gives inference on halite deposits in deep subseafloor sections. In particular, Fiduk [153] reports on a series of tight, salt cored, "contractional folds" in the Pelagian offshore of Libya and Tunisia. In addition, the author remarks that basins adjacent to the "folds" display seismic geometries characteristic of salt withdrawal. Diapirs, whose composition has not yet clarified, also occur in the Central and Northern section of the Pelagian Shelf, offshore Sicily [137,154]. Salt occurrences in the Pelagian Shelf subseafloor are generally thought to be Mesozoic in age [155].

# 3.7. Salts in the Eastern Mediterranean Sea

The eastern Mediterranean Sea (zone "C" in Figure 1) is a deep basin, with a maximum depth of 5267 m b.s.l., extending from the submarine slopes of the Apulian and Pelagian shelves to western Asia. The eastern Mediterranean is traditionally divided into several sub-basins which, proceeding east-ward, include, among others, the Ionian (C1), Aegean, Herodotus (C2) and Levant (C3) basins. There is an ample consensus among geoscientists that many parts of, if not all, eastern Mediterranean Sea are set in an old oceanic lithosphere once belonging to the Tethys realm [156]. For example, the interpretation of geophysical data on the Ionian Basin (western section of the eastern Mediterranean Sea) led Finetti [137] to conclude that an 8–10 km thick oceanic crust there occurs overlain by 7–8 km thick sedimentary succession, Mesozoic to Tertiary in age. In addition, Catalano et al. [157] noticed that the heat flow of about 34 mW·m<sup>-2</sup> in the abyssal plain (-4000 m) is consistent with an old age

(Late Paleozoic?) of the crust. This fact conforms to a 90 km thick lithosphere, as estimated by Della Vedova and Pellis [158]. Polonia et al. [159] published pre-stacked depth-migrated seismic profiles in the Ionian Basin where salt deposits are described in the abyssal plain and within a thick mélange deposit which is interpreted by the authors as an accretionary wedge. Salt deposits were estimated up to 1000 m thick in the abyssal plain and up to 4 km thick within the "accretionary wedge" due to tectonic thickening. Seismic profiles in a nearby area also highlight a layer of possible marine salts, with a  $V_P$  value of 4.2 km s<sup>-1</sup>, about 500 m in thickness, intercalated in the sedimentary sequence [160]. In addition, time-migrated and pre-stack depth-migrated, northwestern-southeastern-oriented seismic lines allowed Polonia et al. [160] and Gallais et al. [160] to identify a large-scale set of reverse faults beneath the Ionian Abyssal Plain. Polonia et al. [159] related such features to a tectonic inversion of crustal blocks along inherited Mesozoic normal faults, highlighting that this is an example of intraplate shortening, since this area was far from the plate boundary when tectonic inversion took place. As previously mentioned, such an intraplate compressive deformation is not exclusive of the continental crust, occurring in several places of the central Indian Ocean [23] and in south Atlantic Ocean [24,25]. Most intriguingly, Sokolov [25] ascribed such compressive deformations to stress field associated with the upwelling of large serpentinite diapirs.

A belt of clayey seamounts, exceeding 1000 km in length, widely known as the "Mediterranean ridge", stretches from the Ionian Basin to the Levant Basin. The Mediterranean Ridge is punctuated along its entire length by mud volcanoes emitting massive mud flows, highly saline brines and hydrocarbons [35,36,161]. Brines also form seafloor saline ponds between contiguous mud volcanoes [162].

Granot [45], based on magnetic anomaly data, provided inference that Herodotus and Levant Basins are also paved with a very old oceanic crust, which is always buried under an exceptionally thick pile of sediments. Moreover, the author used the shape, or skewness, of aforementioned magnetic anomalies to constrain the timing of crustal formation, concluding that it formed about 340 million years ago, and hence belonging to the Paleozoic Tethys spreading system. Due to such an old age, the occurrence of serpentinites in the deep subseafloor of these basins is very probable, even though high-quality seismic imaging of the basement is here hampered by the thick sedimentary cover. In this respect, Schuiling [163] wisely suggested that the Troodos Ophiolite, on the Island of Cyprus, can be considered as a gigantic serpentinite diapir.

From the salt perspective, there is no compelling seismic evidence of important salt layers intercalated between the Herotodus and Levant sedimentary cover. The latter mostly consists of deep-water carbonate ooze, turbidites and clayey sediments [164]. In addition, diapiric structures, probably consisting of salt, are observed in the Latakia Basin, Herodotus Basin (C2 in Figure 1) and part of the Nile Cone [164–167]. Seismic indicators of focused fluid seepages in some of the eastern Mediterranean Basins, spanning the stratigraphic interval from late Miocene to Recent, were provided by [168]. The spectrum of the fluid flow features covers pockmarks, pipes, mud volcanoes, clastic mounds, gas chimneys and collapse structures. More interestingly, the authors report that some fluid seepages have certainly crosscut the entire package of Messinian layers, including salts. In other words, seismic data show evidence for continuous migration of fluids through the Messinian section and their discharge at the then-seafloor [169]. Bertoni et al. [168] highlight that the main pathways for fluid migration are represented by salt tectonics structures, including diapirs. The same authors also suggest that fluids consist of basin pore water, brines, hydrocarbons, diagenetic and deep crust/mantle fluids. On the contrary, Lazar et al. [169] pointed on gaseous and liquid hydrocarbons. About the provenance of these fluids, Lazar et al. [169] stated that seismic data clearly indicating pre-Miocenic horst structures with associated blanking and bright spots onlapping along the flanks and hence several chimney-like acoustic blankings occur above the top of this structure, as well as above its flanks.

The main goal of this review paper consists in evaluating whether the model of the origin of "salt giants" in abyssal serpentinite systems [9] is applicable to the Mediterranean case. The fundamental question regards the potential occurrence of serpentinites in different areas of the basin. Unfortunately, a very thick sedimentary cover conceals the basement all over the basin. Relevant geophysical data, as mentioned above, indicate that there is inference, even though compelling evidence is scarce, of an old oceanic lithosphere in different areas of the Mediterranean, from its Atlantic side (i.e., Gulf of Cádiz) to the Levant Basin. An oceanic lithosphere, especially if aged, may be

widely serpentinized, even containing alteration products after serpentine, such as clay minerals. Serpentinites would also host marine salts and abiogenic hydrocarbons [9,32]: Clayey mud, salts and hydrocarbons give eventually rise to buoyant geobodies, likewise diapirs.

Diapirs with any sizes form the structural leitmotif of seismic lines in different Mediterranean and Perimediterranean areas. Here, we recall the problem on getting reliable inference in the composition of a given diapir from its seismic image. As expected, salt, mud, and salt-and-mud mixtures may give rise to the same chaotic reflection patterns [77,170–173]. Moreover, inferring the geological significance of a layered seismic successions is not always a straightforward task. In fact, some seismic reflectors may be ambiguous, since they can be either due to salt layers, accumulation of fluids under an impermeable layer or varying degree of compaction and organic matter content of sediment layers [78,126,166,169,174]. Thus, we draw attention to the fact that no reliable information on size of a buried salt deposit can be obtained based on the interpretation of seismic profiles only. The interpretation of seismic data on the Gulf of Sirte, offshore Libya, is a clear example of such a seismic ambiguity. In fact, these data have been interpreted by several authors as indicating a layer of Messinian salts thickening basinward. On the contrary, more recent data have led Fiduk [153] to conclude that no remarkable halite layer occurs in the Messinian section in the aforementioned area. Thus, the Mediterranean "giant", despite the huge salt deposits outcropping in Sicily, may really display a significantly smaller size than previously thought.

#### 4.1. Problems with Numbers: Quantity and Age of Salts

A quantitative estimate of salt deposits in the entire Mediterranean area, as viewed from the serpentinite perspective, is hampered by the variability in rock properties and geological characteristics of the study area. Although previous studies propose general estimates of seawater consumption during the alteration of a dominantly basaltic oceanic crust [175], these data can fit hardly the case study, which considers abyssal-type serpentinites. Seawater-induced alteration of MOR-type basalts gives rise to the formation of numerous silicate minerals bearing significant amounts of alkalis and/or chlorine, therefore hampering the separation and accumulation of saline brines and salts from seawater. Provided the occurrence of buried (fossil) abyssal serpentinites in different places of the Mediterranean area [140,176], the available data on these geobodies are not enough to determine their volumes. An even more pronounced uncertainty occurs in estimating volumes of buried salts genetically and spatially related to serpentinites. Unlike the evaporite model, which predicts the lateral extension in thickness of salt deposits throughout the basin, serpentinite-related salt deposits likely display irregular geometric shapes with considerable variation in thickness. This fact is a logical consequence of the invoked process, which implies lateral and vertical migration, zonal accumulation and focused discharge of matter previously dispersed as small particles in its source serpentinites. In other words, if a mass balance is based on the assumption that a 750 m thick layer of "Messinian" salts occurs all over the bottom of the Mediterranean Basin, as indicated by some desiccation models [55], the serpentinite mechanism is not applicable, since an unconceivable large volume of serpentinites (e.g., a vertical section of serpentinites more than 100 km in thickness) is necessary to accumulate such an enormous quantity of salts. If, instead, the occurrence of subseafloor salt deposits is considered to be confined in space and discontinuous over time, as our model suggests, it can be sufficient to recall that one cubic kilometer of halite can be stored in a cubic volume of serpentinites with a 6.5 km side length [9]. Thus,

in cases of salt deposits cropping out on land, such as in Sicily, volume estimates can be cautiously put forward (Section 3.5.1).

Here no emphasis has been given to the geological age of the Mediterranean salt deposits, except for those cases, as in Central Sicily, in which a Messinian age is constrained by secure stratigraphic data. On the contrary, seismic stratigraphy, if not adequately supported by core-drill data, is generally affected by a wide error bar. Looking, for example, at the salt diapirs from northern Tunisia and those from the Gulf of Cádiz area, generally thought to be Triassic in age [107,151,177], we put forward the hypothesis that these buoyant geobodies have all the same Tethyan serpentinite roots as the Miocenic (?) salts occurring in subseafloor of different Mediterranean Basins.

Deep-seated xenoliths from diatremic structures in the Hyblean Plateau (Sicily), in the hearth of the Mediterranean, clearly indicate the Tethys affinity of the buried basement in this area [95,97,98,178]. This evidence, coupled with the aforementioned geophysical inference on Tethyan crust in other Mediterranean places, may provide clues to the idea put forward by Suess [2,99], that most of, if not all, the Mediterranean Basin is a relict of the (Paleozoic?) Tethys Ocean, having been scarcely affected by the deformation field related to the opening of the Atlantic Ocean and the closure of the Tethys.

## 4.2. Concluding Remark

Aforementioned discussion leads to conclude that there is not a single salt giant, Messinian in age, extending over the entire Mediterranean Basin. There are, instead, some/several independent salt deposits, with different shape and size, related to buried serpentinite geobodies of likely Tethyan affinity. We hope that the viewpoint put forward in the present paper may inspire future studies of marine geoscientists, particularly in setting up the research strategy to find, image and measure such, apparently elusive, salt giants, lying somewhere in subseafloor of the Mediterranean Basin.

**Author Contributions:** The paper was primarily conceived and written by V.S. with contribution and review of the co-authors. All authors contributed to the evaluation and discussion of the data.

Funding: This research was funded by University of Catania [Ricerca di Ateneo, 2017].

**Acknowledgments:** Some ideas expressed in this paper, especially those related to the hydrothermal process and mud volcanoes, were previously discussed with Martin Hovland, Håkon Rueslåtten and Hans Konrad Johnsen (Norwegian Hydrothermal Group). Constructive criticism by two anonymous reviewers is gratefully acknowledged. We dedicate this work to the memory of Fabio Lentini, University of Catania (1938–2017).

Conflicts of Interest: The authors declare no conflict of interest.

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