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Origin of salt giants in abyssal serpentinite systems

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Abstract Worldwide marine salt deposits ranging over the entire geological record are generally considered climate-related evaporites, derived from the precipitation of salts (mainly chlorides and sulfates) from saturated solutions driven by solar evaporation of seawater. This explanation may be realistic for a salt thickness ≤ 100 m, being therefore inadequate for thicker (>1 km) deposits. Moreover, sub-seafloor salt deposits in deep marine basins are difficult to reconcile with a surface evaporation model. Marine geology reports on abyssal serpentinite systems provide an alternative explanation for some salt deposits. Seawater-driven serpentinization consumes water and increases the salinity of the associated aqueous brines. Brines can be trapped in fractures and cavities in serpentinites and the surrounding 'country' rocks. Successive

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³ Independent Geology and Petroleum Engineering Consultant, 7041 Trondheim, Norway thermal dehydration of buried serpentinites can mobilize and accumulate the brines, forming highly saline hydrothermal solutions. These can migrate upwards and erupt onto the seafloor as saline geysers, which may form saltsaturated water pools, as are currently observed in numerous deeps in the Red Sea and elsewhere. The drainage of deep-seated saline brines to seafloor may be a long-lasting, effective process, mainly occurring in areas characterized by strong tectonic stresses and/or igneous intrusions. Alternatively, brines could be slowly expelled from fractured serpentinites by buoyancy gradients and, hence, separated salts/brines could intrude vertically into surrounding rocks, forming salt diapirs. Serpentinization is an ubiquitous, exothermic, long-lasting process which can modify large volumes of oceanic lithosphere over geological times. Therefore, buried salt deposits in many areas of the world can be reasonably related to serpentinites.

The elusive origin of giant salt deposits

One of the fundamental principles of geology is that the present is the key to the past. In this respect, worldwide marine salt deposits ranging over the entire geological record are generally considered climate-related evaporites, derived from the precipitation of salts (mainly chlorides and sulfates) from saturated solutions driven by solar evaporation of seawater (e.g., Warren 2006 and references therein). Several examples of present-day climate-related evaporite formations exist, such as supratidal lagoons (sab-khas) along the arid coastlines of the Persian Gulf. Sabkhas form subaerial, prograding and shoaling-upward evaporite

successions consisting of a basal layer of Ca(Mg)-carbonate overlaid by gypsum, halite, and a thin, topmost discontinuous layer of most soluble Mg- and K-bearing chlorides and sulfates (e.g., Butler 1969; Shearman 1963). This succession of minerals is consistent with traditional (e.g., Usiglio 1849; Van't Hoff 1909) and recent (e.g., Harvie et al. 1982) experimental data on mineral precipitation during seawater evaporation, and also is consistent with theoretical models on the ionic behavior during evaporation of electrolyte solutions (e.g., Pitzer 1991).

Similarly, marine salt deposits exposed on land, such as in Central Sicily (i.e., the "Gessoso Solfifera Group", Roveri et al. (2008) and references therein), are traditionally considered to be climate evaporites (Decima and Wezel 1971; Schreiber et al. 1976). In addition, seismic reflection profiles and deep-sea drilling studies provided lines of evidence of giant subseafloor salt deposits the world over, including some Mediterranean basins (e.g., Roveri et al. 2014; Cita 2006). The hypothesis that a tectonic barrier hindered the communication between the open sea and the given marine basin (e.g., the Mediterranean), which resulted in total desiccation, producing vast sabkha-like salty lowlands considerably below global sea level (e.g., Hsü et al. 1973), is widely acknowledged.

Could giant salt deposits have been formed in desiccated deep marine basins? To answer this question, we recall experimental data on seawater evaporation (Usiglio 1849) demonstrating that the complete evaporation of a 64.6 m column of seawater (38.4 psu) generates a 1 m layer of chlorides (mostly halite), and the complete evaporation of a 1000 m seawater (38.4 psu) column produces a 1 m layer of sulfates (mostly gypsum). Considering a salt thickness of about 1 km, results of Usiglio's experiment indicate that $a \ge 65$ km seawater column would have to be totally evaporated to produce those salt thicknesses. Even admitting several desiccation and replenishment episodes, such "geological taps" would be unrealistic scenarios on Earth.

In this respect, it is opportune to mention that models suggesting an evaporite deposition with no important changes in the basin sea-level (i.e., with a continuous, though limited, exchange of water with the open sea) have to consider that marine halides cannot precipitate from an undersaturated solution in the P-T range of terrestrial basins. For instance, recalling (e.g., Pitzer et al. 1984) that the ionic strength of pure NaCl solutions is never higher than 6 (mol/kg H₂O), halite starts to precipitate when the remaining solution is reduced to 10% of its original volume. Thus, if solute (salt) is not added to the solution, a dramatic decrease in the basin sea level inevitably occurs due to the evaporation of large parts of the solvent (water). In general, a few authors strongly dissented from the climate evaporite origin of giant salt deposits. For example, Sozansky (1973), recalling that no fossils and silicoclastic sediments occur in the 2-km thick halite deposits in the South Atlantic subseafloor, remarked that this absence is inconsistent with multiple desiccation-replenishment events, since skeletons and shells of marine organisms would have been present, testifying the replenishment of the evaporated basins with Atlantic seawater. Therefore, Sozansky (1973) tentatively suggested a deep-seated origin of salt deposits, albeit he did not provide further details on feasible halogenic processes at deep crustal (even mantle) depths. Besides, Momenzadeh (1990) suggested that worldwide giant salt deposits are related to the emplacement of alkaline basalts. Unfortunately, because of the lack of viable physical or physicochemical process, the above hypothesis cannot explain the salt occurrence in geological contexts where underlying alkaline basalts are lacking, or no igneous rocks occur.

Considering, for instance, the Mediterranean subseafloor salt deposits, organic geochemistry studies carried out by Christeleit et al. (2015) on fossil archaeal lipids 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. Therefore, these authors inferred that such conditions may be indicative of a deep-water basin, where normal salinity seawater floated on a higher-density brine layer, whose boundary ranged from 2000 to 2900 m b.s.l.-On these grounds, Christeleit et al. (2015) rule out the possibility that abyssal salts in the Mediterranean precipitated in a fully desiccated basin, since the connection with the Atlantic ocean was uninterrupted during Late Miocene. The authors conclude that their viewpoint would imply an unknown mechanism that created a deep marine basin with a shallow mixed layer (with normal salinity) and an underlying brine layer being saturated in gypsum and halite.

Here, we propose a mechanism to explain the formation of the brine layer.

Natural seawater salination processes: an overview

Evaporation

On the surface of a water basin, the phase transition from liquid to vapor may occur at temperatures below the boiling point, provided that the partial pressure of water vapor is lower than its equilibrium vapor pressure. When evaporation occurs far from equilibrium (e.g., long-lasting sunny and dry atmospheric conditions), it may happen that the basin will be deprived of huge volumes of water. Considering a marine basin, seawater progressively concentrates its solute fraction eventually giving rise to the precipitation of salts, such as carbonates, gypsum and halite, whose precipitation starts when the remaining water volume is of 50%, 20%, and 10%, respectively, whereas sylvite, carnallite, langbeinite, polyhalite, kainite and other highly soluble ("bitter") salts (e.g., Babel and Schreiber 2014) will form when the residual water is less than 2% of its original volume, according to the aforementioned Usiglio's experiment.

It is opportune to recall that evaporation is an endothermic process. Indeed, to convert 1 g of fresh water into a gaseous state at 20 °C, 2.6 MJ/kg of heat energy is needed (e.g., Slesarenko 2001). There is an extra 2% component of (solar) energy required from oceans to produce the same amount of water vapor, with respect to freshwater.

Cryogenic salination

Brine formation may occur during seawater freezing. During the crystallization of ice, ions from dissolved salts are rejected and hence concentration gradients form in the surrounding solution. The latter has a density decreasing linearly with distance from the interface with ice. Indeed, the convective exchange of dense brine with seawater is the dominant desalination process (gravity drainage) in sea ice (Griewank and Notz 2013). In addition, Jones et al. (2012) reported that seawater freezing produces salts concentrated in interstitial liquid brine inclusions, where solid salts may precipitate from the solution (carbonates first, followed by sulfates, and chlorides) in response to temperature gradients throughout the icy system.

Hydrothermal out-salting

Hydrothermal saline brines, with compositions comparable to the system NaCl-H₂O, are known in many natural occurrences. In fact, hypersaline fluid inclusions (FI), even bearing solid separates, are present in diverse mineral phases crystallized in the entire P-T range of the hydrothermal process (e.g., Bodnar and Vityk 1994; Bodnar 2003). In particular, there are considerable lines of evidence for the presence of saline, calcium-rich brines in rocks from mid-ocean ridge environments (e.g., Vanko and Stakes 1991), and the presence of high-Cl amphiboles in these rocks also supports the presence of saline brines (Vanko 1986). In this respect, we recall the complex, not yet fully understood, behavior of saline solutions in the temperature and pressure range round about the H₂O critical end point. In this respect, Bodnar (2003 and references therein) remarked that the H₂O-NaCl system is characterized by a large region of PTX (X = composition) space in which fluid immiscibility, represented by coexisting higher salinity liquid and lower salinity vapor, occurs (e.g., Fig. 1a).

The static dielectric constant of water is equal to 80 at standard conditions, but it dramatically drops when variations in T or T-P of the system give rise to changes in state (either gaseous or critical). For example, at 25 MPa and 450 °C the dielectric constant of H₂O is as low as 0.2



Fig. 1 a *P*–*T* phase diagram for the NaCl-H₂O system (modified after Becker et al. 2008) showing sub-vertical liquidus lines (representing the equilibrium between a liquid phase, with the indicated salinity in wt%, and halite), and the vapor-saturated halite solubility (vapor+liquid+halite—V+L+H) curve to 200 MPa. The *arrow* indicates the predicted salinity of aqueous solutions deriving from serpentinite dehydration, due to igneous intrusions, at a *P*=50 MPa, considering a 1-km thick serpentinite level starting from the seafloor, which is placed at a depth of 2000 m b.s.l. **b** Simplified *P*–*T* diagram of the Si–Mg–Fe–O system (modified after Seipold and Schilling 2003) illustrating the phase transitions, evidenced by the *arrow*, due to dehydration of a serpentinite into a peridotite and water. *r1* serpentinite = talc + forsterite + H₂O; *r2* talc + forsterite = enstatite + H₂O

(e.g., Hovland et al. 2006a and references therein), hence the hydrogen-bonded network deteriorates and becomes unable to shield effectively the salt ions; consequently, salts precipitate. Thus, the hydrothermal, or supercritical, precipitation of salts (called "shock-crystallization" by Tester et al. 1993, who first observed the phenomenon) occurs. In fact, Hovland et al. (2006a, b, 2014) first remarked that the aforementioned phenomenon has important implications in several geological processes, including seawater desalination and salt precipitation in abyssal hydrothermal systems, provided an effective source of heat, such as a shallow-seated igneous intrusion (Lewis and Lowell 2004a; Hovland et al. 2007; Gruen et al. 2014).

Hydration of anhydrous minerals

A number of rock-forming minerals are nominally anhydrous. Some of them can react with water, being therefore transformed into hydrous minerals. If the reactant is a complex electrolyte solution, such as seawater, it may undergo a partial, even total, desalination in a closed system with stoichiometric water/mineral ratio. Thus, in an open system the same process gives rise to the salination of the surroundings. According to Sanford (1981), we consider a monomineralic rock consisting of an anhydrous phase (A), at temperature and pressure within the stability field of a hydrous phase (H) with identical composition, having also seawater in pores or grain boundaries. The seawater in the rock tends to be depleted in H₂O and, hence, concentrated in dissolved components as the hydration reaction $(A + H_2O = H)$ proceeds. Once the trapped pore water is consumed, the reaction will cease. If high permeability allows additional (sea)water to permeate the rock, the hydration reaction continues, provided the availability of the anhydrous mineral (A) in the system. Eventually, after the almost complete consumption of H₂O, the remaining solution may become salt saturated. In this respect, Sanford (1981) suggests that succession of salt precipitates will be like those found in evaporite deposits.

Most importantly, hydration reactions related to geological processes are generally exothermic, that is, these proceed spontaneously without the input of external energy. In the next section, we focus our attention on the archetype of the hydration processes in submarine hydrothermal environments, the serpentinization of olivine and pyroxenes in ultramafic rocks.

Beyond the evaporite model: accumulation of seawater salts in abyssal serpentinites

During the past 30 years, marine geology expeditions at slow- and ultraslow-spreading centers discovered large areas of the seafloor paved with serpentinites (Fig. 2), locally hosting active hydrothermal systems (e.g., Kelley et al. 2001, 2007; Blackman et al. 2002; Dick et al. 2003; Früh-Green et al. 2004; Boschi et al. 2006; Snow and Edmond 2007; Ildefonse et al. 2007; Miranda and Dilek 2010; Silantyev et al. 2011). Serpentinite occurrences are generally ascribed to the tectonic uplift and exposure of mantle peridotites (mainly harzburgites) at or near the seafloor (e.g., Boschi et al. 2006). The interaction of Mg-rich



Fig. 2 Hand-specimen of an abyssal serpentinite, dredged during an IODP expedition in the Atlantis Massif (MAR), exhibiting fractures filled with calcium carbonate (image courtesy of G.L. Früh-*Green*: http://oceanexplorer.noaa.gov/explorations/05lostcity/background/serp/media/figure1.html)

olivine and orthopyroxene in peridotites with seawater generates serpentine (reaction 1) and minor amounts of additional reaction products (e.g., Palandri and Reed 2004; Evans 2004). Although there is considerable debate concerning the exact mechanisms and chemical reactions for the formation of serpentinites in submarine hydrothermal environments (Bach et al. 2004, 2006; Beard et al. 2009; Evans et al. 2013; Frost et al. 2013; Klein et al. 2013), we report a typical reaction (Evans 2004) describing the conversion of olivine and pyroxene to serpentine:

$$1.2 \text{ Mg}_{1.8}\text{Fe}_{0.2}\text{SiO}_4 + 0.76 \text{ Mg}_{0.9}\text{Fe}_{0.1}\text{SiO}_3 + 2.088 \text{ H}_2\text{O}$$

$$\rightarrow \text{Mg}_{2.85}\text{Fe}^{2+}_{0.11}\text{Fe}^{3+}_{0.08}\text{Si}_{1.96}\text{O}_5(\text{OH})_4 + 0.042 \text{ Fe}_3\text{O}_4$$

$$+ 0.176 \text{ H}_2$$
(1)

The strong exothermal behavior of reaction (1) (~35 kJ/ mol H_2O) is believed to represent the heat source responsible for non-volcanic, off-axis hydrothermal activity (Evans 2004).

As previously stated, during serpentinization in abyssal settings, olivine and Ca-poor pyroxene in mantle rocks (e.g., peridotite) is converted into serpentine minerals, with the uptake of OH groups from seawater. The latter contains about 3.5 wt% of dissolved salts. What is the fate of these salts during serpentinization?

Chloride is the most abundant ionic species in seawater $(Cl^- = 55 \text{ wt\%}; \text{ e.g.}, \text{Millero et al. 2008})$. An experimental study performed by Sharp and Barnes (2004) clarified the behavior of Cl and chlorides during seawater-driven peridotite serpentinization. The authors observed that abyssal serpentinites contain both chlorine related to water-soluble phases (hereafter mentioned as water 'soluble' chloride) and chlorine hosted in water insoluble minerals, such as iowaite (Bach et al. 2004 and references therein), amphiboles (Vanko 1986) and scapolite. Insoluble and soluble chlorine in oceanic serpentinites with isotopic signature

reflecting that of seawater and sediment pore-water has been also evidenced by Barnes and Sharps (2006), Bonifacie et al. (2008) and Kendrick et al. (2011). In fact, Silantyev et al. (2010) reported that a fluid with activity of $H_2O=0.9$ and approximately 28 wt% NaCl could be produced from seawater due to hydration reactions in the oceanic crust; this mechanism leads to the fluid saturation and the appearance of water-soluble chlorides in the intergranular space of highly serpentinized rocks.

More precisely, considering that the reactant seawater has a typical 2 wt% content of Cl, the incorporation of water 'insoluble' chloride in the serpentinite can be depicted by the following reaction (Sharp and Barnes 2004):

8
$$(Mg_{0.9}Fe_{0.1})_2SiO_4 + 14 H_2O + Cl^- \rightarrow 4 Mg_3Si_2O_5(OH)_4$$

+ $Mg_3Fe^{3+}(OH)_8Cl \times 2H_2O + e^-$ (2)

On the other hand, the 'soluble' chloride fraction produces halite (Sharp and Barnes 2004):

$$Mg_2SiO_4 + MgSiO_3 + 2 H_2O + Na^+ + Cl^-$$

$$\rightarrow Mg_3Si_2O_5(OH)_4 + NaCl$$
(3)

Owing to the complex composition of solutes in seawater (e.g., Babel and Schreiber 2014), a minor amount of chlorides other than NaCl can also forms.

Where are saline brines stored in serpentinites?

To answer this question, we consider some more detailed aspects of the process of hydration of abyssal peridotites. Sanford (1981) suggests that during serpentinization halides and other soluble salts may precipitate as submicroscopic grains along grain boundaries of relic and newly formed minerals of the serpentinite, salts being most concentrated where there is restricted outflow of fluid and where the hydration reaction has gone only partly to completion. Moreover, observations on serpentinites carried out by Tutolo et al. (2016) demonstrated that serpentine veins represent preferential pathways for fluids infiltration in abyssal peridotites. The authors reports that the inherent porosity of ultramafic rocks increases linearly with the degree of serpentinization, hence increasing the effective diffusion coefficients of water $(D_{\rm H2O}=10^{-7}-10^{-8} \text{ cm}^2 \cdot \text{s}^{-1})$, at 34 °C; MacDonald and Fyfe 1985) and salts $(D_{\text{NaCl}}=10^{-9})$ to 10^{-10} cm²·s⁻¹, at 34 °C; MacDonald and Fyfe 1985).

In addition to the aforementioned considerations, we recall that abyssal serpentinites mostly consist of chrysotile and lizardite polytypes, often coexisting, indicating temperature conditions ranging from that of deep-sea water up to 400 °C (normally \leq 300 °C; Evans 2004). In particular,

lizardite forms at low w/r, if water can access peridotites along tensile fractures and shear zones which allow water to penetrate deeper in peridotites. Detailed studies on the evolution of serpentinization were carried out by Sachan et al. (2007) and Schwarzenbach et al. (2016). At the outcrop scale, a crossing fracture pattern, known as "kernel pattern", can form and progressively branch during serpentinization. We put forward the hypothesis that saline brines are forced into the tensile fracture network and/or trapped in voids opened by deformation of the host lizardite.

Interestingly, Evans (2004) remarked that lizardite has an elevated force of crystallization delivering along the [001] crystallographic direction. On the contrary, chrysotile cannot exert a force of crystallization except possibly parallel to its cylinder axis and, hence, it often grows later, when olivine was mostly eliminated. Most typically, chrysotile grows as vein fillings of cross-fiber and slipfiber (Schwarzenbach et al. 2016), also occurring in serrate veinlets replacing lizardite. In other words, lizardite has the capacity to exert a force of crystallization, whereas chrysotile growth demands fluid-filled voids and isotropic stress. Indeed, Evans (2004) reported lizardite and chrysotile as a stress-antistress mineral pair.

Here, we consider a given volume of abyssal serpentinites consisting of lizardite with dispersed micrometric voids filled with saline brines. The subsequent crystallized chrysotile occupies the voids, expelling the brine from the serpentinite domain. Brine droplets, therefore, may coalesce and hence migrate throughout fracture systems in the serpentinite eventually accumulating in zones, particularly rich in empty spaces (Fig. 2; e.g., those affected by major tensile fracturing).

The lack of scientific reports of notable impregnation of marine salts in serpentinites may be due to their possible occurrence at abyssal depths, which are difficult to investigate with currently available instruments. Thus, samples dredged or drilled in serpentinite-paved seafloors may be unrepresentative of the whole serpentinized basement. Besides, the variable salinity of fluid venting from mid-ocean ridges is indicative of mixing between seawater and hydrothermal fluids that have undergone supercritical phase separation (Schoofs and Hansen 2000). In addition, serpentinites cropping out in ophiolite massifs would be likely deprived of their marine salts by dissolution and brecciation during the obduction events. On the other hand, microscopic fluid inclusions (FI) of saline brines are relatively common in serpentinized and hydrothermally altered ultramafic and mafic rocks from modern and ancient oceanic settings (e.g., Vanko et al 1992). Solid salt phase may be present when the FI were cooled to low temperature (Fig. 3).

Serpentinite salts, but how much?

Seafloor dredging and drilling at slow-spreading centers evidenced that 5-to-10% of this oceanic crust (i.e., millions km²) consists of serpentinites. In addition, the interpretation of geophysical data (e.g., residual gravity anomalies) indicates the occurrence of buried serpentinites, mainly along deep low-angle faults at slow spreading ridges (e.g., Alt and Shanks 2003 and references therein). Serpentinites, either exposed or buried, also occur on the continents, for instance in active and fossil suture zones (e.g., Sachan et al. 2007; Aziz et al. 2011).

Serpentinization of the oceanic lithosphere is a very effective and long-lasting hydration process, which can develop through geological times via crack-and-seal mechanism, producing large thicknesses of hydrous rocks. For example, on the basis of permeability experiments, Macdonald and Fyfe (1985) conclude that oceanic serpentinization is a relatively rapid process and they estimate that at 300 °C, a 1 km thick layer of serpentinite can form in approximately 1 Ma. In this respect, Li and Lee (2006) estimated a paleo-serpentinization depth of about 40 km for the Feather River Ophiolite in northern California, assuming that serpentinization is associated with infiltration of (sea)water through faults and fractures (Li and Lee 2006). To put forward a modern example, Qin and Singh (2015) provided seismic evidence of a present serpentinization depth of about 25 km in the Central Indian Basin (CIB), whereas the pristine lithospheric mantle is widely crosscut by an important system of faults, effective pathways for percolating seawater, down to a 45 km depth. On the basis of the regional distribution of the isotherms reported by the aforementioned authors, recalling the experimental results by Evans (2004) on the upper stability limits of serpentine



Fig. 3 Scanning electron microscope (SEM) image showing a saline brine inclusion with an aggregate of cubic halite crystals in a serpent-inite xenolith from Hyblean area (Sicily)

minerals, a 40 km future serpentinization depth can be estimated in this area.

Considering the salt perspective, a simplified quantitative approach to the chloride budget during serpentinization can arise from the assumption that abyssal serpentinizes contain about 13 wt% water. If seawater is the serpentinizing fluid, about 10.5 kg of seawater salts (hence about 8 kg NaCl) are left out during the formation of 1 m³ serpentinite. Recalling that a lizardite–chrysotile serpentinite has a density of about 2.5 g/cm³ (Christensen 2004), and the density of NaCl is ~2.16 g/cm³, 1 km³ halite can be stored in a cubic volume of serpentinites with a 6.5 km side length.

Although this fact alone might explain how salt giants can be formed, it must be remarked that thickness of serpentinite salt deposits is not a parameter closely related to thickness of the host serpentinites, nor in other geological processes which imply drainage, zonal accumulation and focused discharge of matter previously dispersed in its source rock (e.g., igneous intrusions, formation of hydrocarbon and ore deposits, etc.). In other words, it is not correct to state that the formation of 1 km of salts would imply a 275 km thick serpentinite body, because saline brine droplets can move upwards through the micro-fracture network of the serpentinite along directions with a strong lateral component, coalesce, eventually the brine drainage gives rise to large deposits in main fracture zones of the host rock.

In addition, several geochemical and isotopic parameters cannot discriminate between serpentinite and evaporite salts: for instance, $\delta^{37}Cl_{WSC}$ values in samples that underwent seawater-driven serpentinization are also consistent with isotopic fractionation between halite and aqueous solutions during evaporite formation (Barnes and Sharps 2006).

It is opportune to highlight that the migration of saline brines through the serpentinite fractures may have important effects even in their chemical composition. For example, recalling that salts that originate from brines generated in serpentinite systems cannot contain any Mg-bearing phases, since serpentinization removes most of the magnesium from seawater and incorporates the Mg into serpentine and brucite phases, phase changes in the serpentinites, such as carbonation, may result in abundant loss of magnesium (e.g., Früh-Green et al. 2004; Frost et al 2006), which can give rise to the formation of Mg-rich brines. In fact, Mg-bearing salts (bischofite-MgCl₂·6H₂O, kainite- $KMg(SO_4)Cl \cdot 3H_2O$ and carnallite— $KMgCl_3 \cdot 6H_2O$) were found in some serpentinites (Sharp and Barnes 2004). Thus, it may be not surprising to find Mg-bearing salts, though in scarce amounts, in worldwide salt deposits likely related to serpentinites. For example, in the Gessoso Solfifera Group in Central Sicily, kieserite-MgSO4·H2O, langbeinite- $K_2Mg_2(SO_4)_3$ and kaliborite— $KMg_2H[B_6O_8(OH)_5]_2(H_2O)_4$

were found in addition to bischofite, kainite and carnallite. This fact may also help to explain the occurrence of warm Mg-brine flow to the seafloor, as documented on the Mid-Mediterranean Ridge, where large brine-lakes occur on the seafloor (e.g., the Urania, Bannock, and Discovery basins; Wallmann et al 1997; Cita 2006).

Tracking the salt route from serpentinite source to deposits

About the mechanisms for brine aggregation and upward migration to form a salt deposit, here we qualitatively consider the hydrothermal-plume (a) and the buoyant-diapir (b) models. The former (a) ultimately depends on the available advective heat in the system and, hence, it requires dehydration reactions of hydrous serpentinite minerals at $T \ge 400$ °C. Deserpentinization is a well-known process in convergent settings, where serpentinites of the oceanic slab encounter increasing P-T conditions during subduction, releasing high saline, seawater related, aqueous fluids (e.g., Weiss et al. 2015). Serpentinite dehydration may occur also in intraplate settings with a suitable heat source, such as an igneous intrusion (e.g., Fig. 4). Serpentinite amorphization can also occur along fault planes and other tectonic discontinuities (Brantut et al. 2016).

The dehydration of serpentine minerals (i.e., antigorite, lizardite and chrysotile) can develop (Viti 2010) in the thermal range of 450–800 °C. The loss of structural water depends on the different interlayer bond strength of serpentine polytypes (weight loss ranging from 12.3 wt% in antigorite to 16.3 wt% in chrysotile). Thermodynamic calculations at a pressure range of 0.1–0.2 GPa show (Evans 2004; Seipold and Schilling 2003; Fig. 1b) that serpentine (Srp) breakdown develops at a temperature \geq 400 °C, producing forsterite (Fo), talc (Tlc) and water:

$$5Srp = 6Fo + Tlc + 9H_2O \tag{4}$$

At higher temperatures ($T > 600 \,^{\circ}$ C), forsterite reacts with talc generating anthophillite (Ath) and water (reaction 6; Evans 2004), whereas forsterite and anthophillite produce enstantite (En) and water at about 670 $^{\circ}$ C (reaction 7):

$$9Tlc + 4Fo = 5Ath + 2H_2O$$
(5)

$$Ath + Fo = 9En + H_2O$$
(6)

Normally, crustal aqueous fluids have lower density than country rocks, being therefore extremely buoyant and prone to move to shallower levels. More precisely, for the hydrothermal brine to migrate upwards, the brine overpressure must overcome the tensile strength of the country rocks and the normal stress on the brine-filled fractures. Quantifying the flow regime of the brines is applicable if



Fig. 4 Synoptic representation of the last stages of the serpentnitesalt model. Section (a) represents a hypothetical geological section of a subjacent serpentinite body hosting dispersed particles of seawater-brines and salts. The subsequent drainage of the brines and their venting at seafloor, as the consequence of local deserpentinization induced by an igneous intrusion, is outlined in **b**. The seafloor collapse, as indicated in the cartoon, is likely due to the volume decrease in the subjacent rock masses by deserpentinization reactions (full explanation is given in the text)

crucial petrophysical variables (porosity, water saturation, permeability etc.) are available. For instance, Becker and Fisher (2000), on the basis of results from ODP drilling in the Juan de Fuca area, estimated a regional oceanic crust porosity up to 25%. In general cases, it may occur that a low fracture density of the country rocks induces brines to attain a pervasive flow (e.g., no more than a few meters per year), which may be channelized (e.g., up to hundreds meters per year) in case of high fracture density.

The final stage of the aforementioned process consists in the brine eruption at seafloor. In this respect, the saline volcanism occurring in the Red Sea Deeps can be considered a modern analog. In fact, marine geology expeditions evidenced up to 5 km thick deposits of bedded salts on the flanks of the central Red Sea and brine pools in several axial topographic depressions (Deeps), more than 2000 m in depth, such as the "Atlantis II Deep" (e.g., Anschutz and Blanc 1996; Feldens and Mitchell 2015; Augustin et al. 2016). The brine pools were related to the activity of 'salt fountains' intermittently injecting warm, salt-enriched, aqueous fluids onto the seafloor (e.g., Ramboz et al. 1988).

Moreover, Hovland et al. (2007, 2015) reported a theoretical model to explain the mechanism of the seafloor saline volcanism suggesting that at depths shallower than 2800 m (pressures below 30 MPa), or at temperatures lower than 430–374 °C, the salt-bearing aqueous fluids (which may derive from deep-seated deserpentinization) are subcritical 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 more soluble salts (e.g., K-bearing ones) are preferentially fractionated in the water portion of the dense brine. This portion escapes first from the system, leaving the relatively less soluble halite to erupt later in "pure" form (Hovland et al. 2015).

A semi-quantitative approach to the serpentinite dehydration by magmatic heating at shallow crustal depth, hence useful for the case study, takes account of the theoretical model proposed by Manuella et al. (2016). In this respect, we assume that serpentinite dehydration occurred at a depth of 1000 m below seafloor, in a 2000 m deep marine basin, with a temperature difference (ΔT) between the serpentinite wall rocks and the igneous intrusion of 700 °C, and serpentinite specific gravity of 2500 kg/m³, in agreement with the mean value obtained by Christensen (2004). On these grounds, we estimate the heat Q necessary to dehydrate 1 m³ of serpentinite (2500 kg,) according to the equation (7):

$$Q = cp \cdot m \cdot \Delta T \tag{7}$$

where cp is the specific heat of serpentinites (700 $J \cdot kg^{-1} \cdot K^{-1}$; Waples and Waples 2004) at 2 °C, and 'm' is the mass (2500 kg). The resulting amount of heat equals to 1.23 GJ. This energy may be supplied by 1250 kg (~0.42 m³) of basaltic magma, considering that the specific heat of basalt at 1100 °C is of 1400 $J \cdot kg^{-1} \cdot K^{-1}$ (Waples and Waples 2004). Thus, about 350 kg of water (14 wt.%; Manuella et al. 2016) can be liberated from the complete dehydration of 1 m³ of serpentinite.

An alternative mechanism (b) of serpentinite salt migration and accumulation which requires no dramatic input of thermic energy can be related to buoyancy gradients in the serpentinite-brine system. Saline brines and their separated salts have lower densities than coherent host serpentinites and most rocks of the oceanic crust, including well-compacted sediment covers. Brines are first expelled from serpentinites through a network of micrometric to millimetric fractures (e.g., Fig. 2), then the brines converge towards more fractured and/or more porous zones of country rocks starting a slow, massive uprising finally producing longterm equilibrium shapes such as salt diapirs or "salt injectites" (Hovland et al. 2015).

It is opportune to mention that muddled serpentinite particles, and/or retrograde clays after serpentine, with interstitial seawater or brine (i.e., serpentinite or clayey muds) can also give rise to buoyant or geopressured diapirs (e.g., Boillot et al. 1988; Kido et al. 2002). Probably "composite" diapirs, consisting of both salt and mud, are more common than generally thought, particularly in subseafloor of marine basins paved with old oceanic crust. Albeit seismic wave velocities are lower in mud than salt (e.g., Sun et al. 1991), seismic reflection imaging hardly allows to discriminate between coexisting salt and mud in a given diapir (e.g., Graham and Pepper 2008; Perez-Garcia et al. 2011). Actually, salt acts as a barrier and scatters the seismic waves overshadowing possible mud volumes inside the diapir. Indeed, many velocity models can sharply image only the top (and external surfaces) of salt diapirs (e.g., Ratcliff et al. 1992; Farmer et al. 1993). This circumstance may bring into question inferences on sizes of buried salt deposits retrieved from the interpretation of seismic profiles only.

Salt deposits: an outlook on some problematic structures

As previously pointed out, venting brine fountains, like those observed in the Red Sea Deeps (Ramboz et al. 1988), may have probably occurred on the seafloor of different basins over the entire geological record. These fountains may have given rise to deep layers of warm, high-density saline brines overlain by a seawater layer with almost normal salinity. This scenery conforms to the conditions suggested by Christeleit et al. (2015) to explain the Messinian salt deposits in the Mediterranean areas. It appears, therefore, that salts separated from hydrothermal and evaporite brines can be ultimately deposited with about the same mechanisms, and hence producing geological bodies with similar primary structures. Thus, field evidence cannot be easily used as genetic indicator, also considering the potential effects of different post-depositional processes.

On the above grounds, we recall that salt deposits outcropping on land sometimes consist of alternating salt and clayey layers (Fig. 5), where the thickness of each layer ranges from a few millimeters to a few tens of centimeters, even more. The layers display either plane-parallel or undulate-parallel surfaces (e.g., isoclinal folding). Sometimes man-made cuts (due, for instance, to mining purposes) revealed more complex 3D patterns, such as "onion-type" concentric spheres. These rhythmically layered structures are generally considered a consequence of systematic variations in the external environment that generated the deposit (e.g., annual variations of the climate conditions). Folding is generally ascribed to subsequent tectonic events.

On the other hand, it is widely acknowledged that many rhythmic patterns, in various geological environments at different scales, can also result from self-organized processes in a non-equilibrium nonlinear geochemical system, not requiring fluctuating external events (e.g., L'Heureux 2013; Sadek and Sultan 2011). It is, therefore, worth to mention that a given volume of brine-bearing clayey mud can display diffusive and rheological properties similar to a gel containing electrolytes and, hence, capable of originating a Liesegang-type banding (Liesegang 1886). This phenomenon, or, more precisely, this class of phenomena, surely implies that the system is transiently out of



Fig. 5 Example of rhythmically alternating halite and clay layers in a salt deposit (Realmonte mine, Sicily). a *Large-scale view* emphasizing the complex 3D pattern of the layered sequence, **b** *detailed view* of a complex array of folds (photograph by Martin Hovland). Structures like these can be due to self-organized processes in non-equilibrium nonlinear geochemical systems. Full explanation is given in the text

equilibrium (l'Hereux 2013; Sultan et al. 2013). Although the chemical systems experimentally investigated often produce Liesegang-type patterns at microscopic scale, similar features can be observed in various geological bodies at different, even considerably large, scales (e.g., Jamtveit and Meakin 1999; Sultan et al. 2013).

Different theoretical approaches were put forward to explain Liesegang-type patterns (e.g., Hantz and Biró 2006). Here, we briefly mention the 100-years-old, though still effective, hypothesis of the supersaturation-nucleation-depletion cycle (Otswald 1900; Wagner 1950). The model is based on the observation that saturated solutions do not precipitate. The salt starts to precipitate when the solution attains a certain degree of supersaturation (i.e., the so-called nucleation threshold). The first layer forms away from the first precipitation region, delayed by diffusion over a zone initially depleted in the diffusing ions, until the ion product exceeds the supersaturation and nucleation thresholds. Then, this cycle is repeated and, hence, causes the formation of the next layer, periodically. Depending on the geometry and the dimensionality of the system, the observed patterns are layers, rings or spheres (Badr et al. 2011). More precisely, complex patterns occur when the reaction-diffusion front changes its direction, while the newly forming layers keep the orientation of previous layers. In the case of a front rotating with an appropriate speed, bent columnar structures build up, which develop into packet-type folds (Hantz and Biró 2006).

In simple systems, empirical laws were found to rule the spatial arrangement of the Liesegang bands and their formation timing: namely the time law (i); spacing law (ii) and width law (iii). Closely following Antal et al. (1998), the first law addresses the position X_n of the *n*th layer (n > 0) with respect to the time t_n of its formation, being strictly related to the velocity of diffusion of the reactant ions:

$$X_n \approx \sqrt{t_n}$$
 (8)

The spacing law (ii) indicates that for large n the ratio of the position of two consecutive layers approaches a constant value, called the "spacing coefficient" (P):

$$(X_n/X_n - 1) = 1 + P \tag{9}$$

with 0.05 < P < 0.4, in most cases. The width law (iii) states that the width W_n of a given layer is an increasing function of *n*. Accordingly, the space between consecutive layers in a Liesegang-type sequence generally increases through time (Hantz 2006).

Another self-organizing process, producing a Lieseganglike rhythmic banding, can be due to loss of water from a given hydrous mineral during diagenesis. For instance, closely alternating, fine-grained, sulfate and clayey levels which macroscopically resemble a varved texture are instead the result of load-pressure induced transformation of gypsum into anhydrite on sequential planar surfaces. This transformation locally produces water, which allows the intergranular hydrothermal-clay fraction to flush out, forming mm-thick, clay-rich layers (Fig. 6).

Serpentinite salts: the sulfates perspective

Sulfates, mostly gypsum and anhydrite, are known to be important components of the climate evaporite successions. **Fig. 6** Sample of a finely layered gypsum from Capodarso, Central Sicily $(37^{\circ}30'39.70''N;$ $14^{\circ}08'29.36''E)$; **b** SEM image of detail of same sample as indicated in the figure. Energydispersive X-ray spectra (EDS) of the main constituent minerals are reported. *G* gypsum, *A* Anhydrite: full explanation is given in the text



Sulfate is the third most abundant ionic species in seawater $(SO_4^{2-} = 7.72 \text{ wt\% on average})$ after Na⁺ (30.62 wt%) and Cl⁻ (55 wt%) (Millero et al. 2008). Although 1.74 g of gypsum may be formed from the complete evaporation of 1 l of seawater (38.4 psu), an estimate of the seawater sulfate budget during serpentinization is complicated. The reason is that sulfur may react with Ni-Fe oxides and alloy present in the serpentinite, to form Ni-Fe sulfides with different metal/sulfur ratios, depending on the redox conditions, water/rock ratio (w/r), pH and temperature of the system (Delacour et al. 2008). Moreover, part of the sulfide-sulfur mineral assemblage hosted in serpentinites will be converted to sulfate in the last stage of the serpentinization process, as a consequence of decreasing pH and increasing $f(O_2)$ and w/r in the system (Delacour et al. 2008; Palandri and Reed 2004; Frost and Beard 2007). Furthermore, the quantity per year $(0.4-6.0 \times 10^{12} \text{ g year}^1)$ of seawater sulfur entrapped as sulfide and sulfate in abyssal serpentinites is comparable to the quantity of sulfur annually exchanged in hydrothermal systems in mafic ocean crust at mid-ocean ridges and on ridge flanks (Alt and Schanks 2003).

Most importantly, seawater becomes supersaturated with respect to anhydrite when heated over $130 \,^{\circ}$ C, as this sulfate mineral has a retrograde solubility in water (Hovland et al. 2006a, b) and, hence, solubility decreases with increasing temperature. Thus, although part of the seawater sulfate is incorporated in the forming serpentinite at the early stage of the process, when the hydrothermal circulation is not fully developed and temperature in most parts of the system is <130 °C, as the temperature increases anhydrite may precipitate from the hot aqueous solution and accumulate at serpentinization front. In fact, the quantity of heat released by the serpentinization reaction is sufficient to produce convective circulation and temperatures ≥ 130 °C in different zones of the system in its mature stage (e.g., Rona et al. 2010 and references therein).

Moreover, the formation of Ca-sulfates requires the presence of Ca ions in the aqueous system. In this respect, we recall that numerous gabbroic bodies are generally intruded into mantle peridotites tectonically exposed at seafloor (e.g., Delacour et al. 2008; Silantyev et al. 2011). Therefore, the circulating saline brines, due to the serpentinization (see above), cause the spilitization of the gabbro (i.e., the albitization of plagioclase) releasing Ca into the fluid. So, this would prompt brines to become saturated in Ca-bearing phases, such as gypsum (and Cacarbonate). Fluid inclusion studies of altered submarine gabbros confirm that the fluids are Ca-rich (Vanko et al. 1988). In summary, the heat released by the serpentinization reactions may give rise to a hydrothermal circulation (Emmanuel and Berkowitz 2006) with seawater boiling and hence Ca-sulfate precipitation.

Conclusions and implications

On the above premises, it is reasonable to conclude that serpentinization and therein salt formation, migration, and accumulation are processes that can explain the formation of giant salt deposits in geological times. Salt deposits can be related to abyssal serpentinite systems, because seawater-driven hydration of ultramafic rocks consumes water, rejecting most solutes (salts). Serpentinizzation is an ubiquitous, long-lasting process throughout geological times with no demand for an external energy source. It is, therefore, reasonable to recognize the existence of buried, serpentinite-related salt deposits in many areas of the world, as well as in Martian serpentinites (Hovland et al. 2011).

In addition, we mention that alkali halide deposits at P-T conditions compatible with deep sedimentary basins behave like a semi-porous medium (e.g., Hovland et al. 2015; Ghanbarzadeh et al. 2015), being therefore potential loci for hydrocarbon deposits. Conversely, at shallower depths marine salts become a strongly impermeable fabric, forming adequate hydrocarbon "traps" (e.g., Dribus et al. 2008). Although this fact alone is generally accounted for the association of hydrocarbons with salt diapirs, in some cases such an association conjures up to a common serpentinite source. In fact, gaseous and liquid hydrocarbons can be originated by catalytic reduction of aqueous carbon dioxide and carbonate by dihydrogen produced by serpentinization reactions (e.g., Charlou et al. 1998; Konn et al. 2009; McCollom 2013; Etiope et al. 2011). Although the formation of hydrocarbons in serpentinite systems is out of question, the possibility that such abiotic hydrocarbons can give rise to exploitable deposits is still hotly debated among geoscientists (e.g., Hazen 2014).

About the possible use of abandoned salt mines as repositories of nuclear wastes, the suggested serpentinite model does not demand additional clues to existing risk evaluation templates done on the basis of the evaporite viewpoint.

More in general, due to the highly reactive properties of marine salts and their peculiar rheological behavior, deep-seated salt deposits reasonably play an important role in different geological processes, including those related to global tectonics and Wilson cycles (Hovland et al. 2016).

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