



# Editorial Gas Hydrate: Environmental and Climate Impacts

Umberta Tinivella <sup>1,\*</sup>, Michela Giustiniani <sup>1</sup>, Ivan de la Cruz Vargas Cordero <sup>2</sup> and Atanas Vasilev <sup>3</sup>

- Geophysical Department, OGS (Istituto Nazionale di Oceanografia e di Geofisica Sperimentale), Borgo Grotta Gigante 42/C, 34010 Sgonico, Italy; mgiustiniani@inogs.it
- <sup>2</sup> Facultad de Ingeniería, Universidad Andrés Bello, Quillota 980, Viña del Mar 2531015, Chile; ivan.vargas@unab.cl
- <sup>3</sup> Institute of Oceanology, Bulgarian Academy of Sciences, 9000 Varna, Bulgaria; gasberg@io-bas.bg
- \* Correspondence: utinivella@inogs.it; Tel.: +39-040-2140-219

Received: 10 October 2019; Accepted: 14 October 2019; Published: 18 October 2019



**Abstract:** This Special Issue reports research spanning from the analysis of indirect data, modelling, laboratory and geological data confirming the intrinsic multidisciplinarity of the gas hydrate studies. The study areas are (1) Arctic, (2) Brazil, (3) Chile and (4) the Mediterranean region. The results furnished an important tessera of the knowledge about the relationship of a gas hydrate system with other complex natural phenomena such as climate change, slope stability and earthquakes, and human activities.

**Keywords:** natural gas hydrate; methane cycle; global change; ecosystem; geohazards; risk assessment; environmental impact; multidisciplinary; blue growth

## 1. Introduction

In recent decades, gas hydrates have been considered a possible reservoir of natural gas, even if the actual global estimate is very rough [1–4]. The growing interest in gas hydrate of the scientific and industrial communities is focused on: (1) the assessment of methane hydrate as a new "clean" energy source, (2) the relationship between gas hydrate and global climate change, (3) the geological hazards connected to the gas hydrate, and, recently, (4) a wide range of industrial applications based on the specifics of the processes of gas hydrates formation and dissociation. Gas hydrates can be related to environmental risks because their dissociation could affect seafloor stability and release methane (and associated gases) into the water column. Also well known, methane is an important greenhouse gas and any release of it into the atmosphere would have an impact on climate change [1,4–9].

Gas hydrates could have an influence on geopolitics. In fact, the biggest natural gas importers as China, India and Japan have significant hydrate reserves and started challenging and generous funded programs for marine gas hydrate production, i.e., [10–14]. On the other hand, other countries, such as Europe, have reduced financial resources dedicated to this topic.

Generally, gas hydrate deposits are investigated using geophysical methods, i.e., [15,16]. A significant progress/improvement in the twenty-first century of the deep water high resolution geophysical tools and technology is due mainly to acceleration of gas hydrate studies. The seismic technique, which is used mostly for gas hydrate investigation, allows for detecting a clear indicator of the boundary between hydrate and free gas accumulation, known as bottom simulating reflector (BSR), i.e., [17]. Moreover, the seismic data provide information about the geometry of the main geological structures, allowing for possible explanations of the presence/absence of gas hydrate [18,19]. In the last few years, the integration of geophysical (mainly seismic and electromagnetic data), geochemical, and heat-flow data have allowed for detecting and characterizing gas hydrate and free gas volumes and their distribution in the sediments, i.e., [20–23]. Thus, reviews of extensive geophysical surveys and

This Special Issue has offered to the scientific community an opportunity to illustrate multidisciplinary research developed in part of the word, such as Arctic and offshore Chile, where the interest about gas hydrate is from an energy and environmental point of view.

#### 2. An Overview of the Special Issue

The Special Issue is composed by 9 scientific articles and 1 review paper, spanning from analysis of indirect data, modelling, laboratory and geological data confirming the intrinsic multidisciplinarity of the gas hydrate studies. The papers are grouped based on the study areas that are (1) Arctic, (2) Brazil, (3) Chile and (4) Mediterranean region.

#### 2.1. Arctic

Natural gas hydrates are discovered for the first time in a permafrost region in Russia in 1976 [30]. Then, the number of studies was increased year by year, mainly due to the rapid increase of the surface temperature in this region in order to understand the relationship between gas hydrate stability and global warming, i.e., [31–34].

Chuvilin et al. [35,36] modeled the role of salt migration and warming in the destabilization of intra permafrost hydrates in order to understand if the destabilization of intrapermafrost gas hydrate could be related to methane emission on the Arctic shelf. The intrapermafrost hydrate could be present at a shallow depth and transform into a relict state. In the paper [35], the authors' studies of the interaction of frozen sandy sediments containing relict methane hydrates with salt solutions of different concentrations at negative temperatures to assess the conditions of intrapermafrost gas hydrates dissociation. The results of the experiments are that the migration of salts into frozen hydrate-containing sediments activates the decomposition of pore gas hydrates and increases the methane emission. Moreover, in the paper [36], the authors analyzed the effect of temperature increase on frozen sand and silt containing metastable pore methane hydrate in order to reconstruct the conditions for intrapermafrost gas hydrate dissociation. The experiments showed that the dissociation process in hydrate-bearing frozen sediments exposed to warming begins and ends before the onset of pore ice melting. The critical temperature sufficient for gas hydrate dissociation varies from -3.0 °C to -0.3 °C and depends on lithology (particle size) and salinity of the host frozen sediments. Considering an almost gradientless temperature distribution during degradation of subsea permafrost, even minor temperature increases can be expected to trigger large-scale dissociation of intrapermafrost hydrates. So, References [35,36] have furnished an important piece of the knowledge about the mechanism of massive methane release from bottom sediments of the East Siberian Arctic shelf.

Many studies have demonstrated the coexistence of subaqueous permafrost, gas hydrate and the effect of the subaqueous on their formation/dissociation, i.e., [37]. Nevertheless, before Reference [38], an empirical method, which allows for an easy initial estimation of the conditions sufficient to have the stability of hydrate below subaqueous permafrost in absence of direct geological or geophysical data, was missed. In this Special Issue, for the first time a quick-look method that allows estimating the steady-state conditions for gas hydrate stability in the presence of subaqueous permafrost is presented. Different thermodynamic conditions typical of subaqueous permafrost in shallow waters both in marine and lacustrine environments are considered. The approach is derived for pressure, temperature, and salinity conditions typical of subaqueous permafrost in marine (brine) and lacustrine (freshwater) environments and it can be easily and reliably applied to assess if the sufficient conditions to have hydrate stability are satisfied.

## 2.2. Brazil

In this area the gas hydrate is explored only recently. This Special Issue reported the review of the evidences of venting from gas hydrate provinces along Brazil's continental margin in [39]. In literature, only indirect indications of the presence of gas hydrate were reported analyzing seismic data in two deep-water depocenters: the Rio Grande cone in the Pelotas Basin and the Amazon deep-sea fan in the Foz do Amazonas basin. Recently, direct data, such as seafloor sampling of gas venting, confirmed gas hydrate presence. The modeling of the hydrate stability zone confirmed that the hydrate is stable for water depth greater than about 500–700 m. Moreover, the identified gas venting is located along the feather edge of the stability zone, suggesting gas hydrate dissociation or upward fluid flow through the stability zone facilitated by tectonic structures recording the gravitational collapse of depocenters.

Reference [40] focused their attention on the Amazon deep-sea fan and adjacent continental slope, investigating the molecular stable isotope compositions of hydrate bound and dissolved gases in sediments. A dominant microbial origin of methane via carbon dioxide reduction was detected; however, a possible mixture of thermogenic and microbial gases are recovered in sites located in the adjacent continental slope.

Finally, Reference [41] analyzed the deep structures related to the high concentrations of  $CO_2$  detected along the southeastern Brazilian Margin by using a multidisciplinary approach. Gravimetric and magnetic potential methods were used to identify major intrusive bodies, crustal thinning and other geotectonic elements of the southeastern Brazilian Margin. Modeling based on magnetic, gravity and seismic data suggests a major intrusive magmatic body just below the reservoir where a high  $CO_2$  accumulation was found. Small faults connecting this magmatic body with the sedimentary section could be the fairway for the magmatic sourced gas rise to reservoirs, confirming that mapping and understanding the crustal structure of sedimentary basins are important steps for "de-risking" in the exploration process.

To conclude, these three papers indicated that it is important to model the quantities of gas that may be transferred from sediments to the oceans offshore Brazil. Considering the possible existence of gas hydrate provinces in other basins along the Brazilian margin, further investigations are necessary.

## 2.3. Chile

In the last decade, the studies about gas hydrate presence along the Chilean Margin are increased rapidly, furnishing information about distribution and quantification of gas hydrate and free gas from seismic data analysis in several zones of the Chilean Margin, i.e., [42,43]. Here, Reference [44] presented an analysis of the spatial distribution, concentration, estimate of gas-phases (gas hydrate and free gas) and geothermal gradients in the accretionary prism, and forearc sediments offshore Taitao at the Chile Triple Junction. Seismic data analysis indicated high gas hydrate concentration and extremely high geothermal gradients. The large amount of hydrate and free gas estimated, the high seismicity, the mechanically unstable nature of the sediments, and the anomalous conditions of the geothermal gradient set the stage for potentially massive releases of methane to the ocean, mainly through hydrate dissociation and/or migration directly to the seabed through faults. So, the Chile Triple Junction is an important methane seepage area and should be the focus of novel geological, oceanographic, and ecological research.

In order to extrapolate information about potential hydrate distribution along the whole Chilean margin, Reference [45] modeled the gas hydrate stability zone using a steady state approach to evaluate the effects of climate change on gas hydrate stability. Present day conditions were modelled using published literature and compared with available measurements. Then, the effects of climate change on gas hydrate stability in 50 and 100 years on the basis of Intergovernmental Panel on Climate Change and National Aeronautics and Space Administration forecasts are modeled. An increase in temperature might cause the dissociation of gas hydrate that could strongly affect gas hydrate stability. Moreover, it is important to consider that the high seismicity of this area could have a strong effect on gas hydrate stability.

The results of these two papers confirm that the Chilean margin should be considered as a natural laboratory for understanding the relationship between gas hydrate systems and complex natural phenomena, such as climate change, slope stability and earthquakes.

#### 2.4. Mediterranean Region

In the Mediterranean Sea, evidences of the hydrate presence are unclear from indirect data analysis. Nerveless, the Eastern Mediterranean Sea is expected to host a significant amount of hydrate because large areas of the seabed are located within the hydrate stability zone [46]. Multiple observations indicate the availability of gas, required for the formation of hydrate, across the seafloor. In particular, numerous mud volcanoes are present, primarily along the accretionary complex and to a lesser degree in the Nile fan [47]. The scope of known seepage is continuously expanding as new data become available, providing further evidence for the potential for hydrate formation. To date, hydrate has been sampled only in several mud volcanoes of the accretionary complex, starting in the Anaximander Seamount region, i.e., [48,49]. In addition, a recent 3D dataset acquired in the Levan Basin, southeastern Mediterranean Sea, suggested that this region could be promising in regards to gas hydrate [50]. Reference [50] estimated the potential inventory of natural gas hydrate in the Levant Basin correlating the gas hydrate stability zone with seismic indicators of gas and providing a potentiality of carbon in this area.

Another key point to understand is whether or not the Mediterranean region hosted hydrate in the past. Compared to the abundant literature on present-day gas hydrates, only few studies deal with their past occurrence or with fossil seep-carbonates recording the dissociation of gas hydrates, i.e., [51]. In fossil sediments, the paleo-occurrence of gas hydrate is particularly challenging to assess, due to the lack of well-established proxies and to the uncertainties on the reconstruction of paleoenvironmental conditions (pressure, temperature, depth) controlling the hydrate stability field. Clathrate-like structures have been reported in fossil deposits and can be used as an indication of past gas hydrate destabilization, i.e., [52]. Additional evidences can be yielded by geochemical signatures, the large dimensions of seep-carbonate deposits (several hundred meters in lateral extent and tens of meters in thickness) and the association with sedimentary instability (soft-sediment deformations) in hosting sediments [53]. Reference [54] could be considered pioneer in this background. In fact, they combined multiple field and geochemical indicators for paleo-gas hydrate occurrence based on present-day analogues to investigate fossil seeps located in the northern Apennines. They recognized clathrate-like structures, such as thin-layered, spongy and muggy textures and microbreccias. Non-gravitational cementation fabrics and pinch-out terminations in cavities within the seep-carbonate deposits are ascribed to irregularly oriented dissociation of gas hydrates. Additional evidences for paleo-gas hydrates are provided by the large dimensions of seep-carbonate masses and by the association with sedimentary instability in the host sediments. Moreover, heavy oxygen isotopic values in the examined seep-carbonates indicated a contribution of isotopically heavier fluids released by gas hydrate decomposition. Their result agrees with the calculation of the stability field of methane hydrates for the northern Apennine wedge-foredeep system during the Miocene indicating the potential occurrence of shallow gas hydrates in the upper few tens of meters of sedimentary column.

So, References [50,54] suggest that the Mediterranean region should be investigated in order to understand the reason of the past-presence and the quite-absence of gas hydrate by using a multidisciplinary approach spanning from field data to modeling.

#### 3. Key Message for Future Research

This Special Issue points out that more studies are necessary to better understand the complexity of the natural gas hydrate system around the world. More efforts should be devoted to correctly quantify the global amount of carbon stored in hydrate form and their relationship with other complex natural phenomena, such as climate change, slope stability and earthquakes, and human activities. Therefore, we hope that new research will be started in order to acquire new data by using innovative

technologies to refine the existing theories or define new theoretical models that cover all aspects of this complex phenomena.

**Author Contributions:** This Editorial is the result of the collaboration of all authors. U.T. and M.G. created the main text; I.d.I.C.V.C. and A.V. made a minor edition and added a part of the Introduction.

Funding: A.V. contribution is in the frame of the Project KP-06-OPR04/7 GEOHydrate (Bulgarian Science Fund).

**Acknowledgments:** The Guest Editors thank all the authors, Geosciences' editors, and reviewers for their great contributions and commitment to this Special Issue. A special thank goes to Richard Li, Geosciences' Managing Editor, for his dedication to this project and his valuable collaboration in the design and setup of the Special Issue.

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

## References

- Kvenvolden, K.A. Gas hydrates—Geological perspective and global change. *Rev. Geophys.* 1993, 31, 173–187.
  [CrossRef]
- Milkov, A.; Sassen, R. Economic Geology of offshore gas hydrate accumulations and provinces. *Mar. Pet. Geol.* 2002, 19, 1–11. [CrossRef]
- 3. Makagon, Y.F. Natural gas hydrate—A promising source of energy. J. Nat. Gas Sci. Eng. 2010, 2, 49–59. [CrossRef]
- 4. Boswell, R.; Collett, T.S. Current perspectives on gas hydrate resources. *Energy Environ. Sci.* **2011**, *4*, 1206–1215. [CrossRef]
- 5. Henriet, J.-P.; Mienert, J. (Eds.) *Gas Hydrates. Relevance to World Margin Stability and Climatic Change;* Geological Society Special Publication No. 137; Geological Society of London: London, UK, 1998; 338p.
- 6. Kvenvolden, K.A. Potential effects of gas hydrate on human welfare. *Proc. Natl. Acad. Sci. USA* **1999**, *96*, 3420–3426. [CrossRef]
- de Garidel-Thoron, T.; Beafort, L.; Bassinot, F.; Hensy, P. Evidence for large methane releases to the atmosphere from deep-sea gas-hydrate dissociation during the last glacial episode. *Proc. Natl. Acad. Sci. USA* 2004, 101, 9187–9192. [CrossRef]
- Waite, W.F.; Santamarina, J.C.; Cortes, D.D.; Dugan, B.; Espinoza, D.N.; Germaine, J.; Jang, J.; Jung, J.W.; Kneafsey, T.J.; Shin, H.; et al. Physical properties of hydrate-bearing sediments. *Rev. Geophys.* 2009, 47. [CrossRef]
- 9. Ruppel, C.D.; Kessler, J.D. The interaction of climate change and methane hydrates. *Rev. Geophys.* 2017, 55, 126–168. [CrossRef]
- Dallimore, S.R.; Wright, J.F.; Nixon, F.M.; Kurihara, M.; Yamamoto, K.; Fujii, T.; Fujii, K.; Numasawa, M.; Yasuda, M.; Imasato, Y. Geologic and porous media factors affecting the 2007 production response characteristics of the JOGMEC/NRCAN/AURORA Mallik gas hydrate production research well. In Proceedings of the 6th International Conference on Gas Hydrates, Vancouver, BC, Canada, 6–10 July 2008; p. 10.
- 11. Dallimore, S.R.; Wright, J.F.; Yamamoto, K. Appendix D: Update on Mallik. In *Energy from Gas Hydrates: Assessing the Opportunities and Challenges for Canada;* Council of Canadian Academies: Ottawa, ON, Canada, 2008; pp. 196–200.
- 12. Gabitto, J.F.; Tsouris, C. Physical properties of gas hydrates: A review. J. Thermodyn. 2010, 2010, 271291. [CrossRef]
- 13. Song, Y.; Yang, L.; Zhao, J.; Liu, W.; Yang, M.; Li, Y.; Liu, Y.; Li, Q. The status of natural gas hydrate research in China: A review. *Renew. Sustain. Energy Rev.* **2014**, *31*, 778–791. [CrossRef]
- 14. Yamamoto, K.; Kanno, T.; Wang, X.-X.; Tamaki, M.; Fujii, T.; Chee, S.-S.; Wang, X.-W.; Pimenov, V.; Shako, V. Thermal responses of a gas hydrate-bearing sediment to a depressurization operation. *R. Soc. Chem.* **2017**, *7*, 5554–5577. [CrossRef]
- 15. Tinivella, U.; Accaino, F.; Della Vedova, B. Gas hydrates and active mud volcanism on the South Shetland continental margin, Antarctic Peninsula. *Geo-Mar. Lett.* **2008**, *28*, 97–106. [CrossRef]
- 16. Vargas-Cordero, I.; Tinivella, U.; Accaino, F.; Loreto, M.F.; Fanucci, F. Thermal state and concentration of gas hydrate and free gas of Coyhaique, Chilean Margin (44 30' S). *Mar. Pet. Geol.* **2010**, *27*, 1148–1156. [CrossRef]

- 17. Vargas-Cordero, I.; Tinivella, U.; Accaino, F.; Loreto, M.F.; Fanucci, F.; Reichert, C. Analyses of bottom simulating reflections offshore Arauco and Coyhaique (Chile). *Geo-Mar. Lett.* **2010**, *30*, 271–281. [CrossRef]
- 18. Villar-Muñoz, L.; Bento, J.P.; Klaeschen, D.; Tinivella, U.; Vargas-Cordero, I.; Behrmann, J.H. A first estimation of gas hydrates offshore Patagonia (Chile). *Mar. Pet. Geol.* **2018**, *96*, 232–239. [CrossRef]
- 19. Song, S.; Tinivella, U.; Giustiniani, M.; Singhroha, S.; Bünz, S.; Cassiani, G. OBS data analysis to quantify gas hydrate and free gas in the South Shetland margin (Antarctica). *Energies* **2018**, *11*, 3290. [CrossRef]
- 20. Coren, F.; Volpi, V.; Tinivella, U. Gas hydrate physical properties imaging by multi-attribute analysis—Blake Ridge BSR case history. *Mar. Geol.* **2001**, *178*, 197–210. [CrossRef]
- 21. Loreto, M.F.; Tinivella, U.; Accaino, F.; Giustiniani, M. Offshore Antarctic Peninsula gas hydrate reservoir characterization by geophysical data analysis. *Energies* **2011**, *4*, 39–56. [CrossRef]
- 22. Loreto, M.F.; Tinivella, U. Gas hydrate versus geological features: The South Shetland case study. *Mar. Pet. Geol.* **2012**, *36*, 164–171. [CrossRef]
- 23. Tinivella, U.; Giustiniani, M. Numerical simulation of coupled waves in borehole drilling through a BSR. *Mar. Pet. Geol.* **2013**, *44*, 34–40. [CrossRef]
- 24. Tinivella, U. A method for estimating gas hydrate and free gas concentrations in marine sediments. *Boll. Geofis. Teor. Appl.* **1999**, *40*, 19–30.
- 25. Tinivella, U. The seismic response to overpressure versus gas hydrate and free gas concentration. *J. Seism. Explor.* **2002**, *11*, 283–305.
- 26. Chand, S.; Minshull, T.A.; Gei, D.; Carcione, J.M. Elastic velocity models for gas-hydrate-bearing sediments—A comparison. *Geophys. J. Int.* 2004, 159, 573–590. [CrossRef]
- 27. Kumar, D.; Sen, M.K.; Bangs, N.L. Gas hydrate concentration and characteristics within Hydrate Ridge inferred from multicomponent seismic reflection data. *J. Geophys. Res. Solid Earth* 2007, 112. [CrossRef]
- 28. Vargas-Cordero, I.; Tinivella, U.; Villar-Muñoz, L.; Giustiniani, M. Gas hydrate and free gas estimation from seismic analysis offshore Chiloé island (Chile). *Andean Geol.* **2016**, *43*, 263–274. [CrossRef]
- 29. Vargas-Cordero, I.; Tinivella, U.; Villar-Muñoz, L.; Bento, J.P. High Gas Hydrate and Free Gas Concentrations: An Explanation for Seeps Offshore South Mocha Island. *Energies* **2018**, *11*, 3062. [CrossRef]
- 30. Makogon, Y. Hydrates of Hydrocarbon; Penn Well Publisher: Tulsa, OK, USA, 1997.
- 31. Tinivella, U.; Giustiniani, M. Variations in BSR depth due to gas hydrate stability versus pore pressure. *Glob. Planet. Chang.* **2013**, *100*, 119–128. [CrossRef]
- 32. Marin-Moreno, H.; Giustiniani, M.; Tinivella, U. The Potential Response of the Hydrate Reservoir in the South Shetland Margin, Antarctic Peninsula, to Ocean Warming over the 21st Century. *Polar Res.* **2015**, *34*, 27443. [CrossRef]
- 33. Marín-Moreno, H.; Giustiniani, M.; Tinivella, U.; Piñero, E. The challenges of quantifying the carbon stored in Arctic marine gas hydrate. *Mar. Pet. Geol.* **2016**, *71*, 76–82. [CrossRef]
- 34. Giustiniani, M.; Tinivella, U.; Sauli, C.; Della Vedova, B. Distribution of the gas hydrate stability zone in the Ross Sea, Antarctica [Distribución de la zona de estabilidad de hidratos de metano en el mar de Ross, Antártica]. *Andean Geol.* **2018**, *45*, 78–86. [CrossRef]
- Chuvilin, E.; Ekimova, V.; Bukhanov, B.; Grebenkin, S.; Shakhova, N.; Semiletov, I. Role of Salt Migration in Destabilization of Intra Permafrost Hydrates in the Arctic Shelf: Experimental Modeling. *Geosciences* 2019, 9, 188. [CrossRef]
- Chuvilin, E.; Davletshina, D.; Ekimova, V.; Bukhanov, B.; Shakhova, N.; Semiletov, I. Role of Warming in Destabilization of Intrapermafrost Gas Hydrates in the Arctic Shelf: Experimental Modeling. *Geosciences* 2019, 9, 407. [CrossRef]
- 37. Tinivella, U.; Giustiniani, M. Gas hydrate stability zone in shallow Arctic Ocean in presence of sub-sea permafrost. *Rend. Lincei* 2016, 27, 163–171. [CrossRef]
- 38. Tinivella, U.; Giustiniani, M.; MarĂ-n-Moreno, H. A Quick-Look Method for Initial Evaluation of Gas Hydrate Stability below Subaqueous Permafrost. *Geosciences* **2019**, *9*, 329. [CrossRef]
- 39. Ketzer, M.; Praeg, D.; Pivel, M.; Augustin, A.; Rodrigues, L.; Viana, A.; Cupertino, J. Gas Seeps at the Edge of the Gas Hydrate Stability Zone on Brazilia's Continental Margin. *Geosciences* **2019**, *9*, 193. [CrossRef]
- 40. Rodrigues, L.; Ketzer, J.; Oliveira, R.; dos Santos, V.; Augustin, A.; Cupertino, J.; Viana, A.; Leonel, B.; Dorle, W. Molecular and Isotopic Composition of Hydrate-Bound, Dissolved and Free Gases in the Amazon Deep-Sea Fan and Slope Sediments, Brazil. *Geosciences* **2019**, *9*, 73. [CrossRef]

- 41. Gamboa, L.; Ferraz, A.; Baptista, R.; Neto, E. Geotectonic Controls on CO2 Formation and Distribution Processes in the Brazilian Pre-Salt Basins. *Geosciences* **2019**, *9*, 252. [CrossRef]
- 42. Vargas-Cordero, I.; Tinivella, U.; Accaino, F.; Fanucci, F.; Loreto, M.F.; Lascano, M.E.; Reichert, C. Basal and frontal accretion processes versus BSR characteristics along the Chilean margin. *J. Geol. Res.* **2011**, 2011, 846101. [CrossRef]
- 43. Vargas-Cordero, I.; Tinivella, U.; Villar-Muñoz, L. Gas Hydrate and Free Gas Concentrations in Two Sites inside the Chilean Margin (Itata and Valdivia Offshores). *Energies* **2017**, *10*, 2154. [CrossRef]
- 44. Villar-Munoz, L.; Vargas-Cordero, I.; Bento, J.; Tinivella, U.; Fernandoy, F.; Giustiniani, M.; Behrmann, J.; Calderon-Diaz, S. Gas Hydrate Estimate in an Area of Deformation and High Heat Flow at the Chile Triple Junction. *Geosciences* **2019**, *9*, 28. [CrossRef]
- 45. Alessandrini, G.; Tinivella, U.; Giustiniani, M.; de la Cruz Vargas-Cordero, I.; Castellaro, S. Potential Instability of Gas Hydrates along the Chilean Margin Due to Ocean Warming. *Geosciences* **2019**, *9*, 234. [CrossRef]
- 46. Merey, S.; Longinos, S.N. Does the Mediterranean Sea have potential for producing gas hydrates? *J. Nat. Gas Sci. Eng.* **2018**, *55*, 113–134. [CrossRef]
- Minshull, T.A.; Marín-Moreno, H.; Betlem, P.; Bialas, J.; Bünz, S.; Burwicz, E.; Cameselle, A.L.; Cifci, G.; Giustiniani, M.; Hillman, J.I.T.; et al. Hydrate occurrence in Europe: A review of available evidence. *Mar. Pet. Geol.* 2020, 111, 735–764. [CrossRef]
- Zitter, T.A.C.; Huguen, C.; Woodside, J.M. Geology of mud volcanoes in the eastern Mediterranean from combined sidescan sonar and submersible surveys. Deep-Sea Res. Part I. Oceanogr. Res. 2005, 52, 457–475. [CrossRef]
- 49. Mascle, J.; Mary, F.; Praeg, D.; Brosolo, L.; Camera, L.; Ceramicola, S.; Dupre, S. Distribution and geological control of mud volcanoes and other fluid/free gas seepage features in the Mediterranean Sea and nearby Gulf of Cadiz. *Geo Mar. Lett.* **2014**, *34*, 89–110. [CrossRef]
- 50. Tayber, Z.; Meilijson, A.; Ben-Avraham, Z.; Makovsky, Y. Methane Hydrate Stability and Potential Resource in the Levant Basin, Southeastern Mediterranean Sea. *Geosciences* **2019**, *9*, 306. [CrossRef]
- 51. Accaino, F.; Bratus, A.; Conti, S.; Fontana, D.; Tinivella, U. Fluid seepage in mud volcanoes of the northern Apennines: An integrated geophysical and geological study. *J. Appl. Geophys.* 2007, 63, 90–101. [CrossRef]
- 52. Dela Pierre, F.; Martire, L.; Natalicchio, M.; Clari, P.; Petrea, C. Authigenic carbonates in Upper Miocene sediments of the Tertiary Piedmont Basin (NW Italy): Vestiges of an ancient gas hydrate stability zone? *GSA Bull.* **2010**, *122*, 994–1010. [CrossRef]
- 53. Conti, S.; Fontana, D.; Lucente, C.C.; Pini, G.A. Relationships between seep-carbonates, mud volcanism and basin geometry in the Late Miocene of the northern Apennines of Italy: The Montardone mélange. *Int. J. Earth Sci.* **2014**, *103*, 281–295. [CrossRef]
- 54. Argentino, C.; Conti, S.; Fioroni, C.; Fontana, D. Evidences for Paleo-Gas Hydrate Occurrence: What We Can Infer for the Miocene of the Northern Apennines (Italy). *Geosciences* **2019**, *9*, 134. [CrossRef]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).