Milos, the minerals island and its important asset: Bentonite

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Abstract. The island of Milos is an active mining site since the Antiquity. Exploitation began with the extraction of obsidian lumps and volcanic lavas and tuffs of specific type, that were used as millstones, sulphur and alum (alunite). Currently, the mining activity is focused on perlite and bentonite, even though some years ago, kaolin, silica, pozzolans and barite were also exploited. Milos bentonite is rather a specialty and not a commodity, as it has multifunctional properties, and therefore used in a wide range of industrial applications, such as foundry sand, drilling muds, lubricant oil, civil engineering structures (waterproofing and sealing, diaphragm wall construction, grouting, concrete workability additive, etc.), cat litter, iron ore pelletizing - Fe metallurgy in blast furnaces and also as “improver” for poor quality bentonites. The peculiar behaviour of Milos bentonites can be attributed to the combination of various geological and hydrogeological factors that occurred at the time of its formation from a glassy tuff precursor. Despite the continuous flourishing of tourism at the island, the mining activity does not face any threats to its existence, as both parties follow the specified regulations and environmental restrictions necessary to allow dual economic growth.

1 Introduction

Milos Island belongs to the Cyclades group of the Aegean islands, having an area of approximately 150 km^2. Milos, along with the neighboring island of Kimolos form the most important source of non-metallic raw materials among all the sites of the South Aegean Volcanic Arc (Fig. 1 and 2).

However, in Polyaigos Island, due to environmental restrictions, no mining is allowed. In Kimolos Island, there were several exploitable deposits of kaolin and bentonite in the south and north part of the island, but currently, the only commercial exploitation is at Prassa, in the NE part of the island, where snow-white bentonite of excellent quality is mined, along with the pumice tuff overburden and the underlying mixture of zeolite/ bentonite tuff (Fig. 3).

In Milos island, mining activities commenced as early as the Neolithic period with the extraction, processing and trading of obsidian, and millstones made from trachytic-andesitic lavas, alunite (alum) and sulphur at later times (Fig. 4 and 5) [1, 2, 3, 4, 5, 6, 7, 8, 9].

2 Geology and mineral resources

The substrate of the island is composed of metamorphic rocks of Mesozoic age [2]. Upon these rocks, a series of lavas were intruded, followed by the deposition of tuffaceous rocks, tuffites, and biogenic sediments of shallow marine origin, during the Upper Miocene through the Lower Pliocene to Pleistocene [2, 3, 10].

The ancient mining activity continued until early 20th century with the extraction of some metallic ores, such as mixed sulphides along with barite in the NE and the western part of the island, as well as manganese ores at the NW edge of the island [8, 11, 12, 13, 14, 15]. Efforts to investigate and exploit epithermal gold deposits located in Profitis Helias Mt in the late ‘90s were unsuccessful. Industrial minerals such as barite and kaolin were also exploited until the late 20th Century. Barite deposits were mainly located in the NE part of the island, close to IMERYS SA headquarters at Voudia. Besides barite, opal-CT and quartz accompanied the raw materials which were used for brake linings and rubbers [11].

The main kaolin deposits were located at the western part of the island (Rallaki) as well as at its eastern part (Lagada). Both deposits were owned by the cement company TITAN SA. Another significant deposit was located at the central part of the island, at Kastriani, owned by the S&B Industrial Minerals SA which was merged with IMERYS SA, as well as by Filis and Roussos family companies (Fig. 6). The initial exploitation of kaolin in the early 20th century was selective on the whitest and purest in kaolinite raw material using underground techniques and the material was used for ceramics. Later, the kaolin from all quarries was used only for the production of white cement, due to the increased Fe_2O_3, silica polymorphs and alunite content.

Glassy tuffs and tuffites, interbedded with diatomite beds were extracted from the SW part of the island, at Xylokeratia for uses as pozzolanic additive in cement

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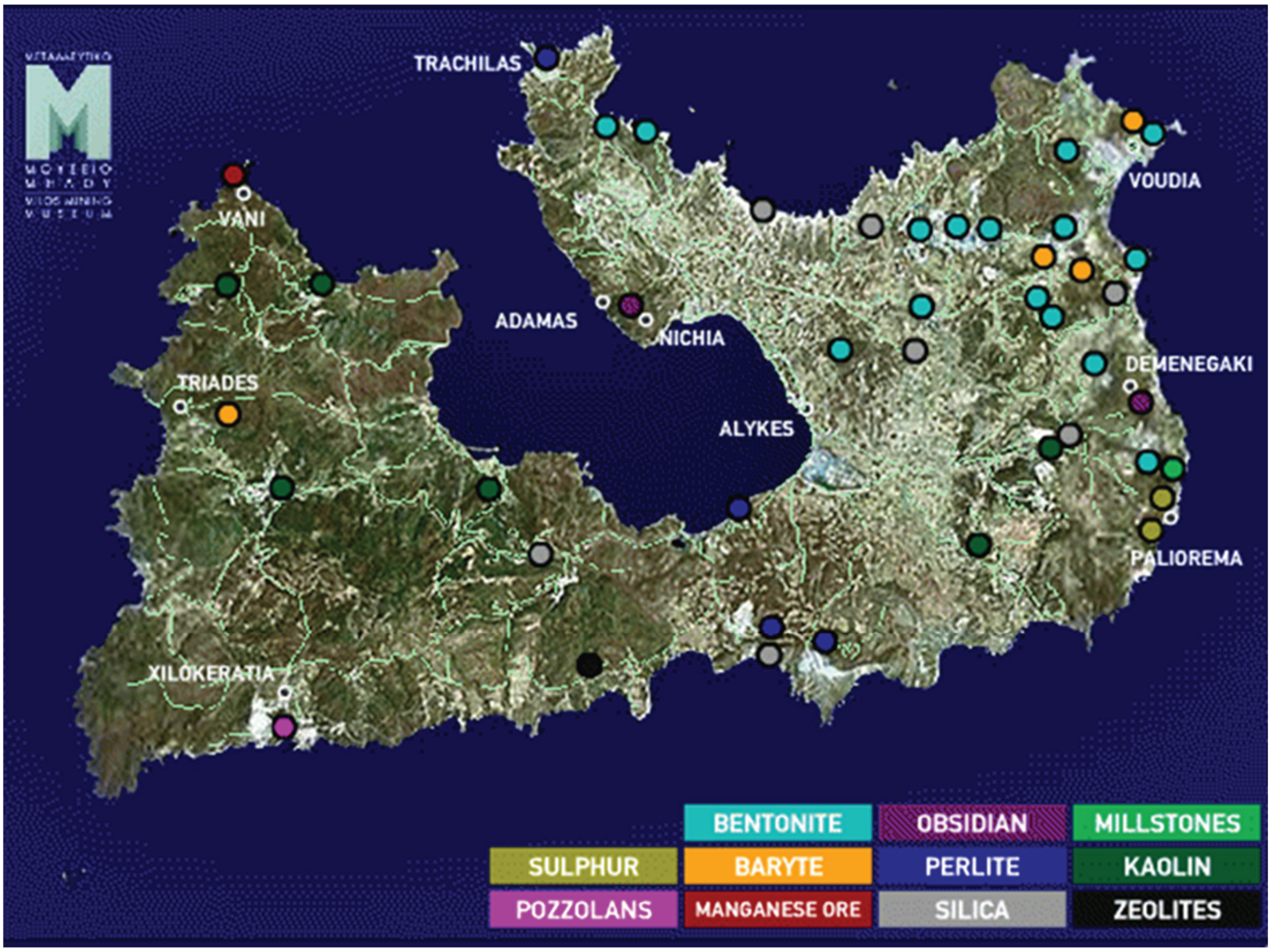

Fig. 1. The mineral wealth of Milos Island (source: Milos Mining Museum).

Fig. 2. Tectonic contacts of white kaolin/silica (right) with yellowish bentonite (center) and glassy tuff with artificial old caverns (left), Aggeria area, northeast Milos Island.

(Fig. 7). TITAN SA and Heracles SA, the two main cement companies activated in Greece have quarries adjacent to one another. Before 2011, the annual production exceeded 700.000 tons, recently falling to some tens of thousands per year. TITAN SA has closed its quarry and rehabilitates it, as perlite fines are currently used to replace pozzolanas.

Sandy deposits of silica polymorphs occur at various parts of the island, but the main deposits are at the east, center, and south part of it. The biggest deposits occur close to Kastriani and are genetically connected with the formation of the kaolin deposits. Besides quartz, cristobalite and opal-CT, they also host small patches of sulphur and alunite, depreciating the quality of the siliceous material which is currently used as a source of silica in the production of clinker in cement (Heracles SA). All these secondary minerals have been derived by the intense alteration of volcanic tuffs and lavas by H2S-rich acidic fluids (fumaroles), which are related to the post-volcanic activity in the island. The final authigenic mineral formed is sulphur which occurs with the form of massive crystal aggregates within kaolin and silica deposits (Fig. 5|). It is formed by the oxidation of the H2S in the atmosphere.

Milos hosts two of the major perlite deposits of Greece, a third one is located at the islet of Gyali in the

Fig. 3. The Roussos quarry of white bentonite, white pozzolanas (pumice tuff), and bentonite/zeolite mixtures, Prassa area, NE Kimolos Island.

Fig. 4. Black obsidian patches hosted in altered rhyolitic rock (Nychia area, close to Adamas port).

Fig. 5. Sulphur crystalline aggregates hosted in a white silica sandy deposit, used as silica additive in the clinker production of cement. Kastriani quarry of Heracles cement company (LAVA SA).

SE Aegean Sea. The two deposits of Milos are quite different in structure, as the north deposits at Trachilas represent hydrated massive lava bodies (Fig. 8, 9 and 10), whereas the southern deposit at Tsigrado represents hydrated reworked volcanic lava boulders and cobbles. The reserves amount to several million tons, while the annual production of perlite at both Milos and Gyali islands rank Greece as the second largest perlite producer worldwide, after the USA. The reason that perlite holds industrial uses is that its glassy phase is hydrated, due to the contact of the molten lava with seawater or groundwater during its movement to the surface. The level of H_2O in perlite ranges between 2-5% and according to some authors this derives from the hydration of obsidian. Obsidian is a less hydrated volcanic rock that has a H_2O content of less than 2% which is, however, enough to permit obsidian expansion by heating [16, 17]. Relatively recent research on New Zealand perlites revealed that water-rich magmas along with the presence of permeable structures in the subsurface due to hydrothermal brecciation may play an

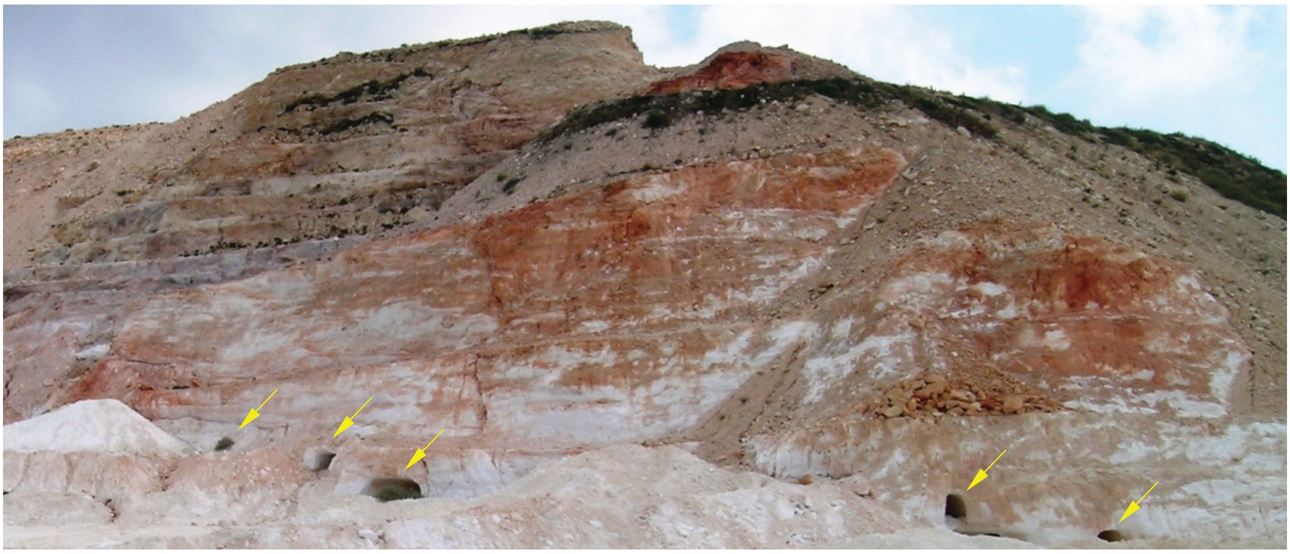

Fig. 6. The Kastriani kaolin S&B quarry in the late 90's. The old underground works can be seen (arrows). The specific quarry now accepts the perlite fines of IMERYS SA, as backfill.

Fig. 7. A quarry face at the Xylokeratia quarry of pozzolanas. Note the mixture of brown lapilli and grey fine-grained tuffs, with the white biogenic silica rich beds (diatomite). Faults are common in all quarries and outcrops across the island.

Fig. 8. The perlite quarry at Trachilas, north coast of Milos.

Fig. 9. Close up of a perlite outcrop at Trachilas.

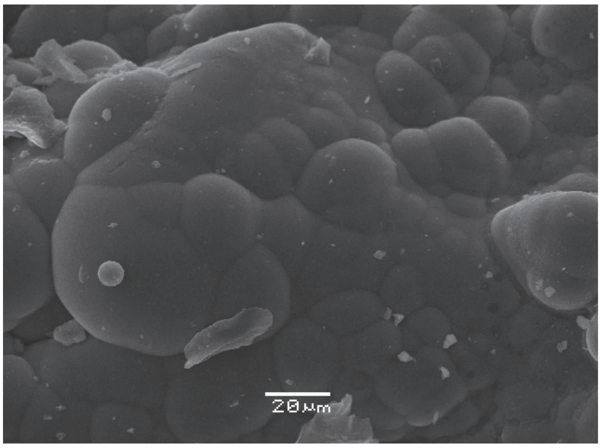

Fig. 10. The perlite of Trachilas under the Scanning Electron Microscope. Note the perlitic texture of the glassy material.

important role in the hydration of the original lava to form perlite [17]. Milos is a well-known geothermal field; therefore Milos perlites can have the same origin with that of New Zealand.

The perlitic material is crushed at proper grain-size and processed in a vertical furnace, heated to about 900-1100 ^{o}C. During their movement downwards the perlite particles expand as they violently lose their crystalline

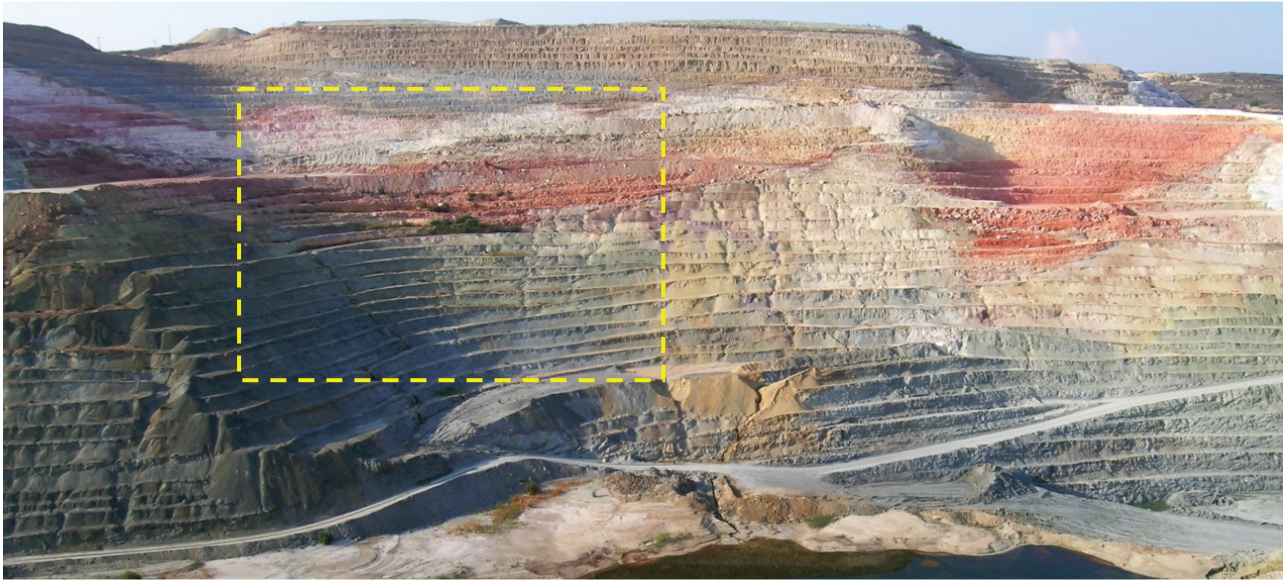

Fig. 11. Photo of the Aggeria bentonite mine in 2007 (dashed rectangle area shown in magnification in Fig. 12).

water, giving rise to a lightweight and soft angular grain. The expanded perlite is used in agriculture (hydroponics, gardening, etc) but also in the construction industry for insulation and lightweight constructions. The sorted perlite grains are shipped to port destinations across Europe and worldwide. Loading bridges are in Adamas bay and at Voudia. The domestic consumption represents only a minor amount of the total production at expansion facilities located in Ritsona, Boeotia, and elsewhere.

3 Bentonite

Bentonite is a multifunctional industrial mineral. Its main applications are listed below:

- In the foundry industry, as binding material in molds,
- In deep oil drilling,
- As a lubricant material,
- In civil engineering structures and especially geotechnical works (waterproofing and sealing, diaphragm wall construction, grouting, concrete workability additive, etc),
- As an insulating material,
- As cat litter,
- In animal feeding and as a food additive in general,
- In iron ore pelletizing - Fe metallurgy in blast furnaces. The valuable fine iron powder produced is collected with bentonite using the "snowdrift" method and thus recycled, and
- As miscellaneous and other unknown uses [18, 19, 20, 21, 22].

Bentonite has found its way in unsaturated soil mechanics applications as the basis of mixtures investigated over the past decades for nuclear waste repositories in various countries and research institutes around the world.

The key minerals in bentonite are smectite clays (mainly montmorillonite), a group of expansive clays which have a lattice sheet structure characterized as a 2:1 layer sheet silicate with one Al octahedral sheet sandwiched between two Si tetrahedral sheets [20, 22]. The flake faces are negatively charged, with the edges having a slightly positive charge. The negative charge that predominates is balanced by exchangeable Na+ that disperses away from the flakes, when mixed with water (Anon. 2002). Substitutions of Al and of Si by other elements, results in the adsorption of ions like Mg2+, Ca2+, Na+, Li+ between adjacent structural unit layers [20]. Smectites have a high specific surface area, high cation exchange capacity, interlayer surfaces that have unusual hydration characteristics, being able to produce thixotropic, pseudoplastic dispersions with an effective yield value [21, 22]. Regarding common soil mechanics properties, they exhibit very high liquid limit and plasticity index values, extremely high compressibility and very low angle of shearing resistance. Specifically in terms of unsaturated soil mechanics properties, smectite-rich soils exhibit much higher air-entry pressure values.

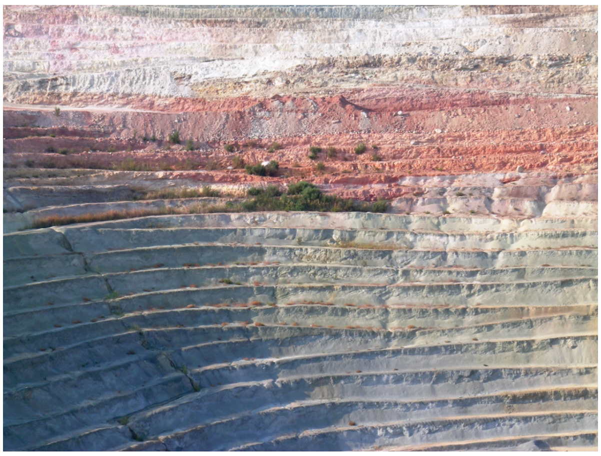

Fig. 12. Close up of dashed rectangle area shown in Fig. 11. Note the greenish-bluish soft clayey (bentonitic) material and the reddish and whitish barren overburden that represent calcareous beds rich in microfossils of shallow marine origin, stained by iron oxides, and partially altered glassy tuff, respectively.

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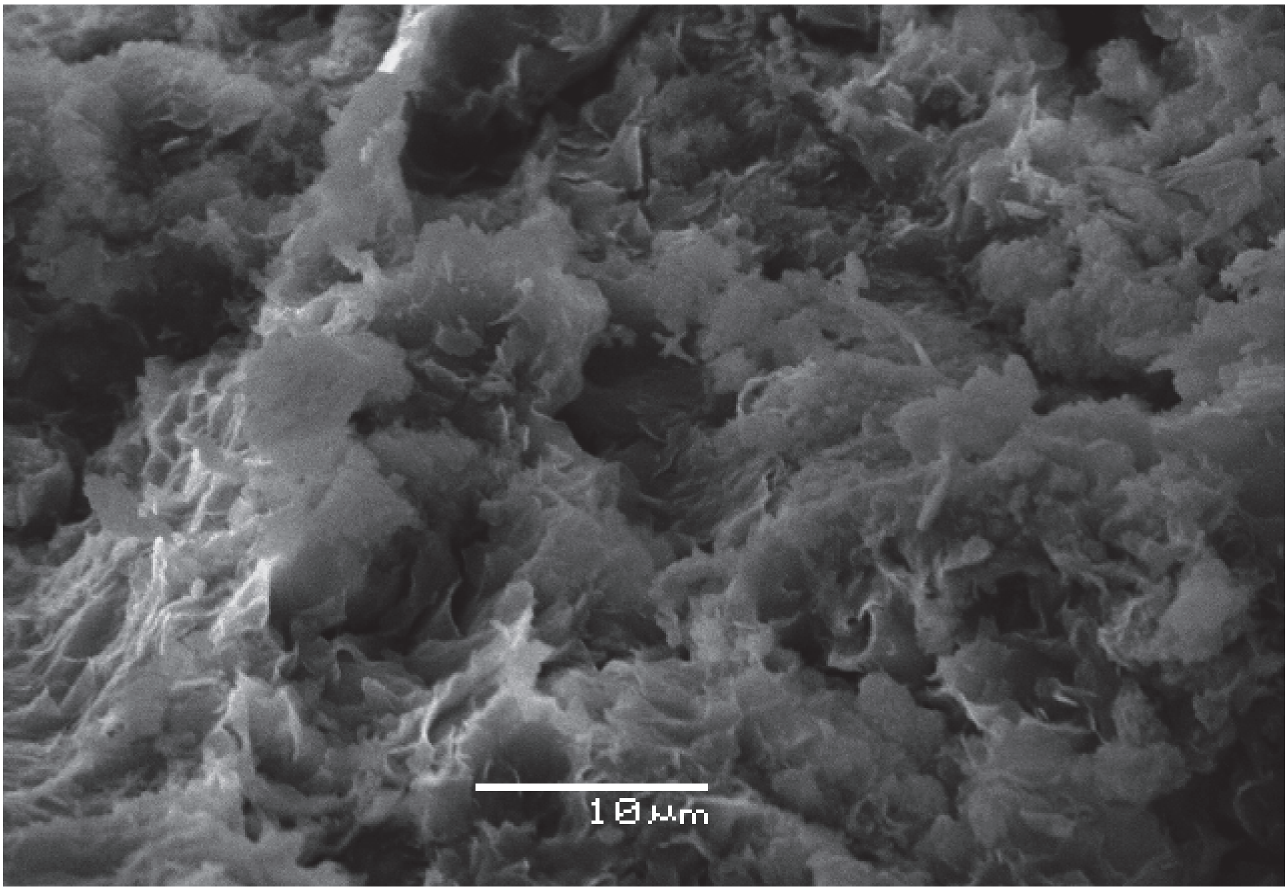

Fig. 13. SEM image of Aggeria bentonite. The montmorillonite sheet-like crystals predominate.

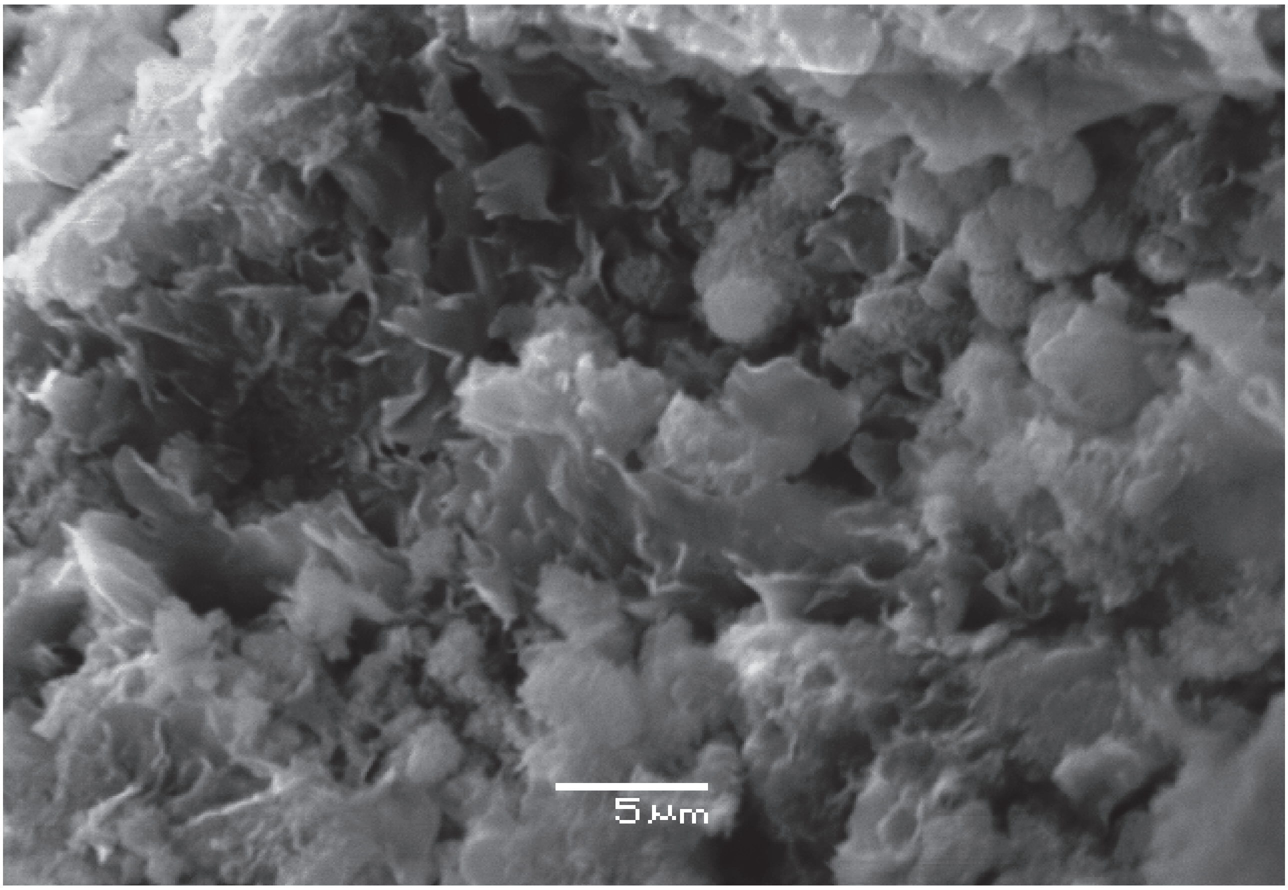

Fig. 14. SEM image of Aggeria bentonite. Opal-CT lepispheres are hosted in between the montmorillonite sheet-like crystals.

Greece is the world's second largest bentonite producer after the USA, with the overwhelming part of its production from Milos Island. Minor amounts, approximately 20.000 ton/yr belong to the exploitation of white bentonite from Kimolos Island (Bentomine SA). In 2021, the total bentonite production reached nearly 1.5 Mt. The bentonites of Milos consist mainly of dioctahedral (Ca–rich) smectite with minor amounts of illite, mixed layer illite, calcite and dolomite, silica polymorphs, potassium feldspars and plagioclase. There are also trace amounts of zeolites, alunite, kaolinite, anatase, barite, gypsum, pyrite, goethite, hematite and magnetite [23, 24].

The composition of Milos bentonites (mainly montmorillonite of several mineralogical types and traces of beidellite) is to some extent dependent on the composition of the volcanic parent rocks. In Voudia-Pollonia area, there are three neighboring bentonite quarries (Aggeria – the largest one-, Aghia Irini, and Koufi), all belonging to IMERYS S.A (Fig. 11, 12, 13 and 14). The company's target, over the next few years, is to integrate them in a development axis of an E - W direction, 1600 m long, for their full and efficient exploitation. A number of older bentonite mines in the area (Tsantili mine) have been filled with overburden materials from other mines and have been fully restored. Besides IMERYS SA, minor producers are also activated on the island, as well as on neighboring Kimolos Island, Mavrogiannis white bentonite quarry at Rema, SE Milos Island and Roussos snow-white bentonite, quarry at Prassa, NE Kimolos Island [24] respectively.

Milos bentonites originated from the alteration of volcanic tuffs in an alkaline environment. Even though older works proposed a diagenetic transformation of coarse- and fine-grained glassy tuffs successively deposited during the Plio-Pleistocene to bentonite in a shallow marine environment, recent measurements define a hydrothermal diagenetic origin of the volcanic glass to smectite clays at around 70 °C with the fluids originated from both, seawater and meteoric waters [25]. A subsequent steam heating event resulted in the formation of alunite-kaolinite-silica deposits which occur either in tectonic contact with the bentonite deposits, or as overburdens [25].

The physicochemical properties of Milos bentonites are unique, compared to bentonites from other locations, especially in civil engineering, having advantageous rheological properties (higher viscosity) in bentonite-cement slurries. Milos bentonite is rather a specialty and not a commodity, as it has multifunctional properties, and therefore used in a wide range of industrial applications and also as "improver" for poor quality bentonites. Recent work reports that one of the main reasons for that is that Milos bentonite contains poorly crystallized opal-CT, which dissolves during alkaline treatment with soda, yielding silica gel [26].

Quarry operations are divided into two periods, the winter period (November - April) and the summer period (May-October). During the winter period, bentonite deposits are stripped from overburden material, which is mainly used as backfill material at older mines, whereas for some time, glassy tuff overburden had been used as a pozzolanic cement additive. During the summer period, bentonite extraction is conducted at different degree levels (28m, 35m, 45m, 50m) using repels, depending on the deposit's forehead stability, and then processing inside factory facilities.

Bentonite as a clay material is impermeable when wet. However, in the quarry two inflows of groundwater occur. The first one is observed at the contact between overburden material (permeable) and bentonite (impermeable), where an almost freshwater spring discharges (Cl- ~900ppm) from the aquifer. The other one occurs at 4m altitude, providing 180cm^3/h of brackish water due to freshwater/seawater mixing, originating from faults. In order to avoid unwanted water, the company has built a small bentonite dam and, through an underground canal, water is poured into a pool and then into tanks for sprinkling the unpaved mine roads to control dust (2014 personal communications with S&B Industrial Minerals scientific staff).

Different colors observed in the deposit (Fig. 11 & 12) are the result of admixtures, i.e. blue - gray color due to sulfur compounds, such as FeS_x, whereas the purple color is attributed to Mn-oxides.

The typical procedure after bentonite mining is the following: material enters crusher Shredder having a breakage ability of about 6000 ton/day. Bentonite is impermeable and hence, only the upper 10cm are affected by rain. This material can be dried in order to be stored outside. Thus, bentonite is spread in drying fields- yards (Fig. 15) initially for the first natural drying (from about 25-30% water to 21%), but also for after mixing qualities (each field contains a similar bentonite quality).

Milos bentonite is of the Ca-rich type and not Na-rich smectite, which is more appropriate for the majority of applications, so the company converts it through an ion exchange treatment (activation) with sodium carbonate (3-5% depending on deposit's montmorillonite content) to Na-rich bentonite by admixing it in a wet process stage and exposing the mixture under atmospheric conditions (Fig. 16 & 17).

Further material drying is conducted in desiccators reducing humidity (from 15 to 9% depending on the rate required by the product produced). The company has the capability of 850.000 ton/year of industrial drying. Finally, the material is loaded onto ships using Voudia loading bridge, with a capacity of 600 ton/h. During every stage of bentonite industrial treatment, seven quality controls are conducted in order to ascertain certain properties, such as physical (moisture content, specific surface area), chemical (SO_4^{2-}, S^{2-}, SiO_2 content), physicochemical (viscosity and suspending ability, thixotropy, bonding properties), and plasticity [22].

Bentonite exports are almost constant to about 1.000.000 tons/year. Total area of bentonite mining (including Aspro Chorio in NE Milos and Zoulia) is 2.804 acres.

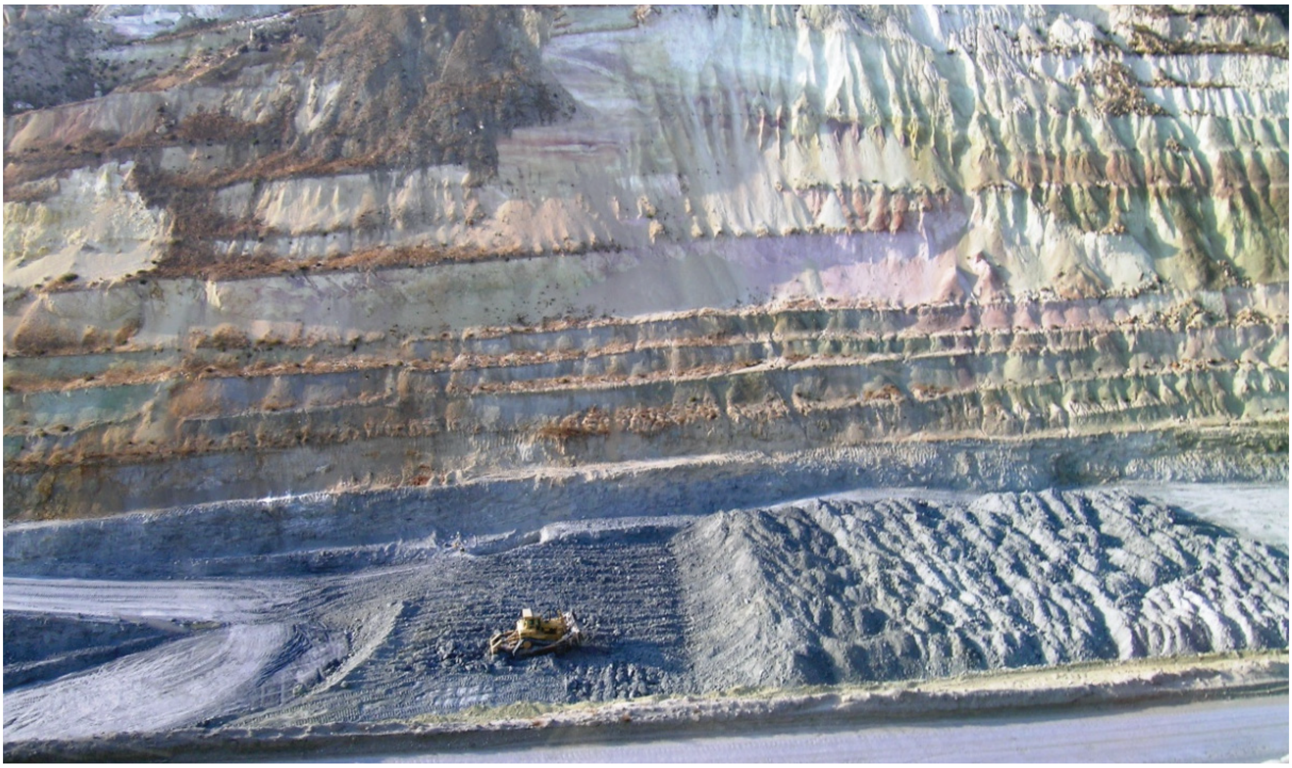

Fig. 15. Exposing the mined bentonite on the surface to homogenize and remove big boulders prior to sodification in yards.

Fig. 16. The soda-activated bentonite is ready to enter the processing plant for drying.

Fig. 17. Yard which hosts soda activated bentonite in successive beds of different qualities. The vertical extraction of the beds is beneficial allowing total homogenization of the bentonite to be achieved.

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4 Occurrences of other industrial minerals

In addition to the minerals and rocks described earlier, diatomite beds occur interbedded with pumice tuffs in the north, center, and NW part of the island (Fig. 18). They are of shallow marine origin and were partially extracted during the exploitation of pozzolanas at Xylokeratia. The other deposits occur close to the Adamas bay and at Sarakiniko, places where mining activity is not permitted.

Zeolitic tuffs composed mostly of mordenite and clinoptilolite occur at the south part of the island (Provatas), but also at the lowermost stratigraphic levels of the Aggeria bentonite deposit at the NE (Fig. 19). Their genesis is attributed to the action of alkaline fluids in areas of high heat flow rates (Provatas), whereas the Aggeria occurrences are typical of a diagenetic formation in an open hydrological system, where an initial glassy material was transformed to smectite clays and zeolites at lower stratigraphic levels. The Provatas occurrences are close to a church, so it is not possible to exploit them, whereas the Aggeria zeolites represent a small amount of the total mineral content, and these beds represent the floor of the bentonite extraction.

5 The future of mining in Milos

The island of Milos remains for many years the major producer of industrial minerals in Greece, counting for more than ¼ of the total volume, with perlite and bentonite exported to various consumers around the world [11]. Restoration-rehabilitations of mines are continuous throughout the island, and hence old mines and quarries such as those of Kastriani, Provatas, Gerakopetra, Xylokeratia, Rallaki and Ninos have already been restored. Cyclades islands but mainly Milos accommodate thousands of tourists every year with their numbers expected to increase considerably, especially after the COVID restrictions have passed away. It is therefore obvious that the economy of Milos is based on a dual basis, mining and tourism. All parts involved in such activities have to act according to the specified regulations, in order to avoid unnecessary conflicts and drawbacks.

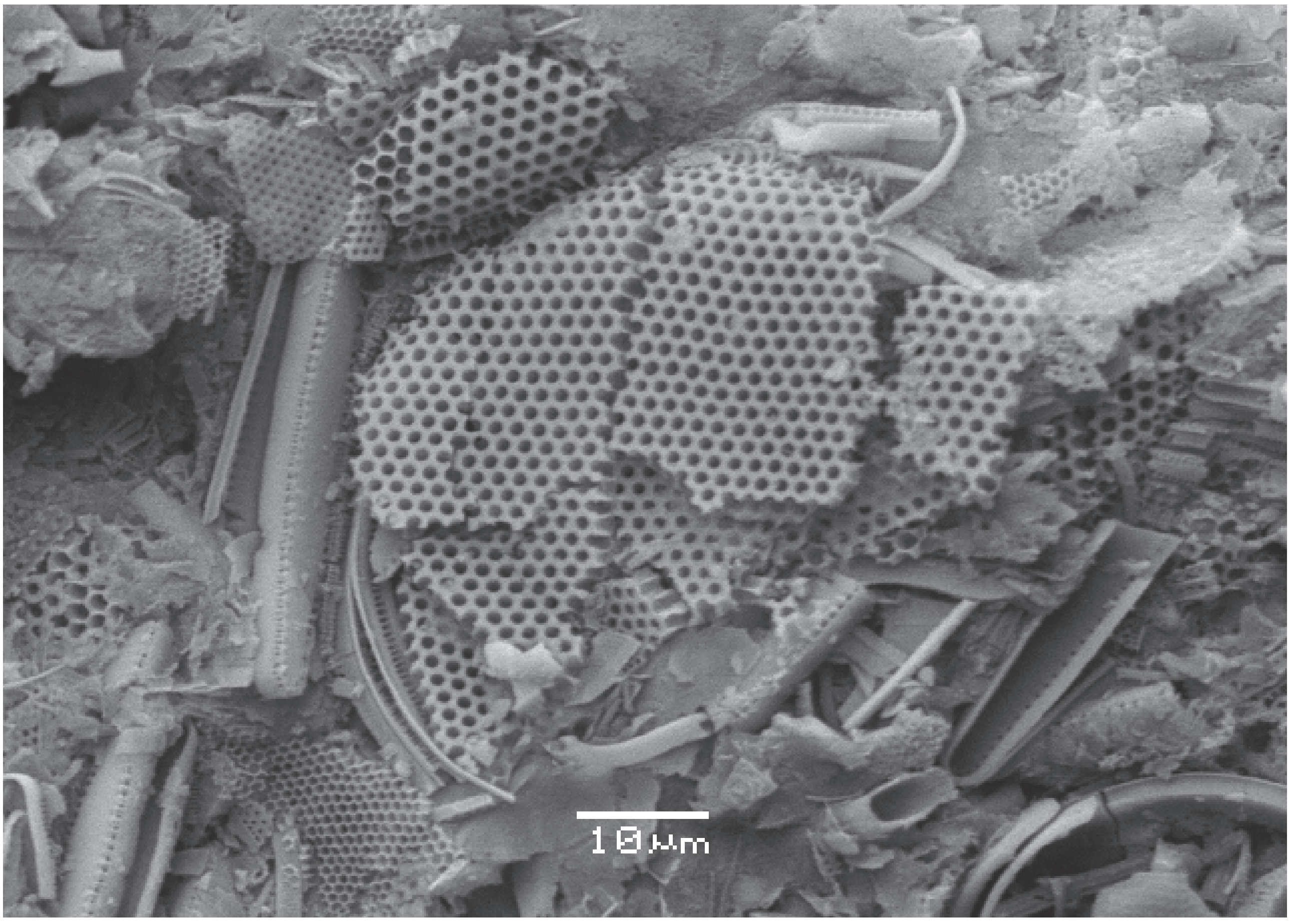

Fig. 18. SEM image of a diatomite bed (broken diatom frustules) hosted in between tuffs at the Xylokeratia quarry of pozzolanas.

Fig. 19. The fine-grained zeolitic tuff of Provatas, south Milos.

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