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Sustainable exploitation of mafic rock quarry waste for carbon sequestration following ball milling

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ABSTRACT

Mineral carbonation has been proposed as a safe method for carbon capture and storage (CCS). Mafic lithologies are among the most promising rocks for mineral carbonation due to their high content in Ca, Fe and Mg-bearing silicate minerals, which react with CO₂ to form stable carbonate phases. Here, we discuss the potential of using waste material from mafic rock quarries for CCS, following the ball milling process. In contrast with other mineral carbonation strategies, the proposed use of quarry fines (< 75 µm) could eliminate some of the cost associated with the extraction and grinding of the source material, making the whole methodology more economically and technologically viable. Potential applications include the use of ball-milled mafic rock quarry fines (i) as feedstock for *ex situ* mineral carbonation, and (ii) as nano-additives in replacement to the binder, for the production of environmentally-friendly building materials with potential ability to sequester CO₂. Both applications could substantially contribute to the mitigation of atmospheric CO₂ concentrations over the next few decades, as well as to the upturn of the quarrying industry in many European countries that have abundant mafic lithologies, such as in Cyprus and Hungary.

1. Introduction

The dramatic increase in atmospheric CO₂ concentration due to the widespread use of fossil fuels is one of the greatest challenges of this century. This anthropogenic impact on the global carbon cycle is considered to be the main reason for the observed climate change over the past decades (IPCC, 2005), which seems to be largely irreversible on human time scales (Solomon et al., 2009). Thus, many researchers have proposed a variety of technologies for carbon capture and storage (CCS) in order to stem the ongoing climate problem. This has stimulated research on the potential use of waste materials for carbon sequestration (Araizi et al., 2016; Assima et al., 2013; Bodénan et al., 2014; Contreras et al., 2015; Gadikota and Park, 2014; Ghacham et al., 2015; Gunning et al., 2010; Kaliyavaradhan and Ling, 2017; Kuwahara and Yamashita, 2013; Lechat et al., 2016; Li and Hitch, 2016a, 2016b, 2017a, 2017b; Noack et al., 2014; Ukwattage et al., 2015).

Mineral carbonation is a CCS technology that was initially proposed by Seifritz (1990) and includes the reaction of CO₂ with rocks

containing Ca- and/or Mg-silicate minerals to form stable carbonate minerals, such as calcite (CaCO₃), dolomite (CaMg(CO₃)₂) and magnesite (MgCO₃) (Lackner et al., 1995; Oelkers et al., 2008; Olajire, 2013; Power et al., 2013; Sanna et al., 2014). These minerals provide a long-lasting, thermodynamically stable and environmentally benign CO₂ storage option (Oelkers et al., 2008). Thus, the aforementioned CCS method minimizes the risk of leakage and facilitates the safe storage of human CO₂ emissions (e.g., Gislason and Oelkers, 2014; Matter et al., 2016; Seifritz, 1990).

The reactions of mineral carbonation are thermodynamically favoured under natural conditions but proceed slowly. Therefore, by hastening these reactions, a substantial contribution to the strategies for mitigating the atmospheric accumulation of CO₂ in much shorter time scales can be achieved. An overview of the fundamental processes of CO₂ sequestration strategies via carbon mineralization is given by Power et al. (2013). The main carbonation reactions of mafic and ultramafic rocks, which are considered as the most promising lithologies for the mineralization of CO₂, are given below:

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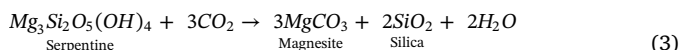
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The strategies that include the conversion of CO₂ into carbonate minerals are divided into (i) *in situ* processes, involving transport and injection of CO₂ into mafic or ultramafic rocks (e.g., Matter and Kelemen, 2009; Matter et al., 2016), and (ii) *ex situ* processes, involving carbonation in industrial reactors, after mining, crushing, grinding and/or milling the rock material (e.g., Bodéan et al., 2014; Gerdemann et al., 2007). Although *ex situ* carbonation is not sufficient to offset the anthropogenic CO₂ emissions alone (Power et al., 2013), it could provide a potential solution to sequester CO₂ from smaller emitters, where geological storage is not a viable option (Sanna et al., 2014). However, one of the major challenges of *ex situ* mineral carbonation is the scale of mining the feed material, which is unambiguously an important economic and environmental problem. This barrier could partially be overcome by using suitable quarry waste materials (fines) as a feedstock for *ex situ* carbonation. Quarry fines are unavoidable by-products of the extraction and processing of aggregates, comprising a significant proportion of the current quarry output. Contrary to many other wastes, quarry fines are usually inert and non-hazardous.

Substantial quantities of industrial waste materials that are suitable feedstock for mineral carbonation exist worldwide (Renforth et al., 2011). Here, we discuss the potential of exploiting waste material (quarry fines) from mafic rock quarries for the safe storage of CO₂, following enhancement of their reactivity via ball milling. Mafic rocks are mainly composed of Mg, Fe and Ca-silicate minerals; thus, they are good candidates for mineral carbonation. In addition, the potential benefits of using these waste materials in the building industry is discussed. The goal of this paper is to highlight the advantages, as well as the uncertainties related to this approach, emphasizing on its potential application in Cyprus and Hungary.

2. Production of ultrafine rock materials via ball milling

2.1. The ball milling process

Ball milling has been used successfully for many years to produce a variety of ultrafine powders (Suryanarayana, 2001). It is considered a great technique for modifying the intrinsic properties of rocks and producing nanoscale materials (Kleiv and Thornhill, 2016; Li and Hitch, 2016c; Rigopoulos et al., 2015a; Turianicová et al., 2013). For scientific and engineering reasons, the term “nanoscale” signifies the size range of approximately 1–100 nm (Hochella, 2008).

An advantage of using the ball milling process is that, with simple equipment, which includes a mill, a vial and a number of balls, novel nanomaterials with tailored properties and predictable performance can be obtained. A popular mill is the planetary ball mill (Fig. 1a), the name of which is attributed to the planet-like movement of the vial. The latter is arranged on a rotating disk and a mechanism causes its rotation around its own axis. As shown in Fig. 1b, the vial and the supporting disk rotate in opposite directions; the combination of these movements produces forces between the balls and the material in the vial that result in the reduction of particle size to the nanoscale range. This type of mill has been used by many researchers for the production of nanoscale materials based on certain minerals or rocks (e.g., Munz et al., 2012; Rigopoulos et al., 2015b). An example of rock material after a few hours of wet ball milling can be seen in Fig. 1c.

Mechanical activation through milling can notably improve the

reaction kinetics of rocks (e.g., Haug et al., 2010; Li and Hitch, 2016a). The ball-milled rock materials have noticeably different properties compared to the unmilled ones. Specifically, the milling process strongly affects the physicochemical properties of rocks, mainly their surface area and adsorption properties.

The study of the physical and chemical processes between nanoparticles and CO₂ is a research field that is increasingly gaining attention as a method to reduce atmospheric CO₂ concentrations. In general, an increase of specific surface area is accompanied by an increase of CO₂ uptake; however, in most cases there is not a continuous positive trend (e.g., Rigopoulos et al., 2015a). Milling techniques have been applied to olivine (e.g., Kleiv and Thornhill, 2006; Li and Hitch, 2016c; Sandvik et al., 2011) in order to improve its CO₂ adsorption properties. Rigopoulos et al. (2015a, 2015b, 2016a, 2018a, 2018b) proved that ball milling substantially increases the specific surface area and CO₂ uptake of mafic and ultramafic rocks (see Table 1). More recently, Li and Hitch (2016a, 2016b, 2017a, 2017b) and Rigopoulos et al. (2016b) showed that milling can also substantially enhance the CO₂-storage capacity of ultramafic and mafic rock waste materials; thus, the latter could potentially be used for carbon sequestration purposes.

Due to the simplicity of the ball milling method, industrial ball mills are already used for the production of ultrafine materials (e.g. in the cement industry) and could therefore be used for the development of nano-sized geomaterials with enhanced CO₂ uptake based on quarry wastes. However, the optimum milling parameters in terms of CO₂ uptake are usually different for each rock material (e.g., see Rigopoulos et al., 2015a, 2015b). In addition, prolonged milling may be required in some cases to increase the CO₂ adsorption capacity of certain waste materials. This can considerably increase the energy consumption and thus reduce the efficiency of the overall method.

2.2. Energy requirements

The energy requirements of *ex situ* mineral carbonation are high and the scale of the whole approach could make this CCS method impractical (Gerdemann et al., 2007). The major challenge is the scale of mining the source material, which is an important economic and environmental issue. According to O'Connor et al. (2005), the energy required for the initial crushing step is estimated to be 2 kWh/ton. Grinding down to 75 μm adds another 11 kWh/ton, while further grinding down to 38 μm using ball mills adds ~70 kWh/ton (Gerdemann et al., 2007). Additionally, the potential intense wear of the milling equipment can increase the cost and further reduce the efficiency of the whole approach (Haug et al., 2010). The aforementioned indicate that the application of the ball milling process for the reduction of the rock particle size to the nanoscale range could notably increase the energy consumption. As such, the high cost and CO₂ emissions associated with the production and transportation of nanoscale rock materials may limit the large-scale implementation of this *ex situ* carbonation method.

Subsequently, although mafic lithotypes are among the most promising materials for the *ex situ* mineralization of CO₂, the main drawback of using these rocks is the necessity of mining, crushing and grinding, which will substantially reduce the carbon sequestration efficiency of the entire approach. On the other hand, the use of mafic rock quarry fines (< 75 μm) for carbon sequestration could eliminate some of the cost and energy associated with the extraction and grinding of the starting rock material (Sanna et al., 2014; Rigopoulos et al., 2016b), making the whole methodology more economically viable. Furthermore, the final nano-sized quarry waste materials could be used to sequester the CO₂ emissions of the quarry from which they are produced. This can substantially reduce the costs associated with the transportation of the rock material, thereby facilitating the extensive application of this approach by the quarrying industry. In addition, if mechanical activation is implemented by the quarrying industry as an integrated part of the total milling process and not as an isolated step, the

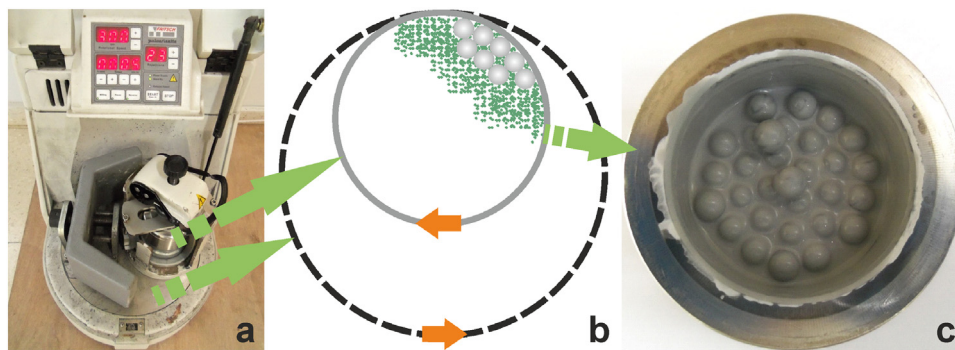


Fig. 1. (a) Planetary ball mill, (b) scheme showing the planet-like movement of the vial, and (c) an ultramafic rock material after a few hours of wet ball milling.

Table 1

Specific surface areas (BET) and amounts of adsorbed CO_2 ($\mu\text{mol g}^{-1}$) estimated through CO_2 chemisorption followed by temperature-programmed desorption (CO_2 -TPD) experiments, for various mafic and ultramafic unmilled and ball-milled samples. The initial (unmilled) rock materials were prepared using a stainless steel pulverizer and then sieved to obtain the 104–150 μm size fraction. The ball-milled samples with the highest CO_2 uptakes are given (data from Rigopoulos et al., 2015a, 2016a, 2016b, 2018b).

Lithotype	Milling duration	BET ($\text{m}^2 \text{g}^{-1}$)	CO_2 uptake ($\mu\text{mol CO}_2 \text{g}^{-1}$)
Basalt	unmilled	9.0	56.3
	4 h	58.9	222.1
Dunite	unmilled	6.8	40.1
	12 h	51.9	278.1
Harzburgite	unmilled	2.2	22.8
	16 h	53.1	103.4
Dolerite (quarry waste)	unmilled	8.4	0.8
	20 h	32.9	96.9

operational energy consumption could be reduced to practical levels (Haug et al., 2010).

3. Potential applications of ball-milled mafic rock quarry waste

The main purpose of this paper is to illustrate how the sustainable exploitation of mafic rock quarry waste materials could contribute to the European and International strategies for the mitigation of climate change. The general concept is based on the use of ball-milled mafic rock quarry fines (i) as feedstock for *ex situ* mineral carbonation, and (ii) as nano-additives in the building materials industry. These two applications are analysed and discussed below, emphasizing on their interrelationship.

Several studies have been performed to propose effective *ex situ* mineral carbonation methods using industrial waste materials (e.g., Harrison et al., 2013; Power et al., 2010; Pronost et al., 2011; Renforth et al., 2011; Rigopoulos et al., 2016b; Wilson et al., 2010). Although the latter are typically fine-grained with high reactive surface areas, their reactivity needs to be further enhanced in order to promote the sequestration of CO_2 within shorter time scales. This can be achieved by further reducing their grain size to the nanoscale range using various milling techniques.

It is worth pointing out that mafic lithotypes (e.g., dolerites, basalts) are considered as high-quality aggregate materials for the construction industry (e.g., Korkanç and Tuğrul, 2004; Rigopoulos et al., 2010, 2015c) and that they exist in significant quantities throughout the world. Therefore, the aggregate and construction industries could possibly use the fine-grained material produced during mafic rock quarrying in order to sequester at least part of their own CO_2 emissions. This could comprise a great financial advantage for the industry and would result in substantial environmental benefits.

Additionally, special emphasis should be placed on the fact that carbonation of mafic rock quarry wastes may also decrease the hazardous nature of certain materials, such as asbestos mine tailings (Bobicki et al., 2012). Significant quantities of asbestos minerals (e.g., actinolite and/or tremolite) may exist in mafic rock quarry fines. The crystals of asbestos minerals are considered dangerous for public health, provided that their length is $> 5 \mu\text{m}$, their diameter is $< 3 \mu\text{m}$, and their aspect ratio is > 3 (e.g., Rigopoulos et al., 2014). The carbonation process could destroy the asbestiform nature of these minerals, thereby eliminating any adverse health effects.

Subsequently, the end-products of such an *ex situ* mineral carbonation route could be used by the construction industry as a raw material (Huntzinger et al., 2009; Oelkers and Cole, 2008). Due to the potential hydraulicity of the final carbonated material, this could be used as additive for the production of composite building materials (mortars and/or concretes), thus rendering the whole approach even more economically attractive.

An alternative option could be the use of ball-milled mafic rock quarry wastes, before carbonation, as nano-additives in composite building materials (e.g., mortars/renders). Although many researchers have investigated the effect of specific nano-additives on the performance of a variety of building materials (e.g., Korpa et al., 2008; Norhasri et al., 2017; Theodoridou et al., 2016; Zyganitidis et al., 2011), only a limited number of studies have focused on the performance of composites modified by the addition of ball-milled wastes (Al-Jabri and Shoukry, 2014; Hamzaoui et al., 2016). For example, nanoscale mafic rock quarry waste materials could be added in mortars/renders as a replacement to the lime or cement binder. It is worth pointing out that huge quantities of CO_2 are released into the atmosphere during the production of lime and cement (IPCC, 2006). Therefore, the potential addition of nanoscale quarry waste materials, as a replacement of the aforementioned binders, could provide an innovative and sustainable option to the building industry, with great economic and environmental advantages. Such an approach could notably contribute to the reduction of anthropogenic CO_2 emissions. Furthermore, the cement and lime industries could potentially integrate the development of nano-sized quarry waste materials into their production lines, which already utilize ball mills; this would considerably reduce the energy consumption and cost of the whole approach.

The nanoscale mafic rock quarry waste materials, which are characterized by enhanced CO_2 adsorption capacities (Table 1; Rigopoulos et al., 2016b), could potentially improve the physico-mechanical performance of the hardened composites by speeding-up and boosting the carbonation reaction kinetics. A further improvement of the engineering properties of the composite building materials can also be achieved due to the filler effect of the nano-additives, which results in composites with increased cohesiveness (Duran et al., 2014; Quercia et al., 2012). Therefore, the ability of the nano-modified building materials to sequester CO_2 via in situ mineral carbonation, in combination with any potential improvement of their physico-mechanical

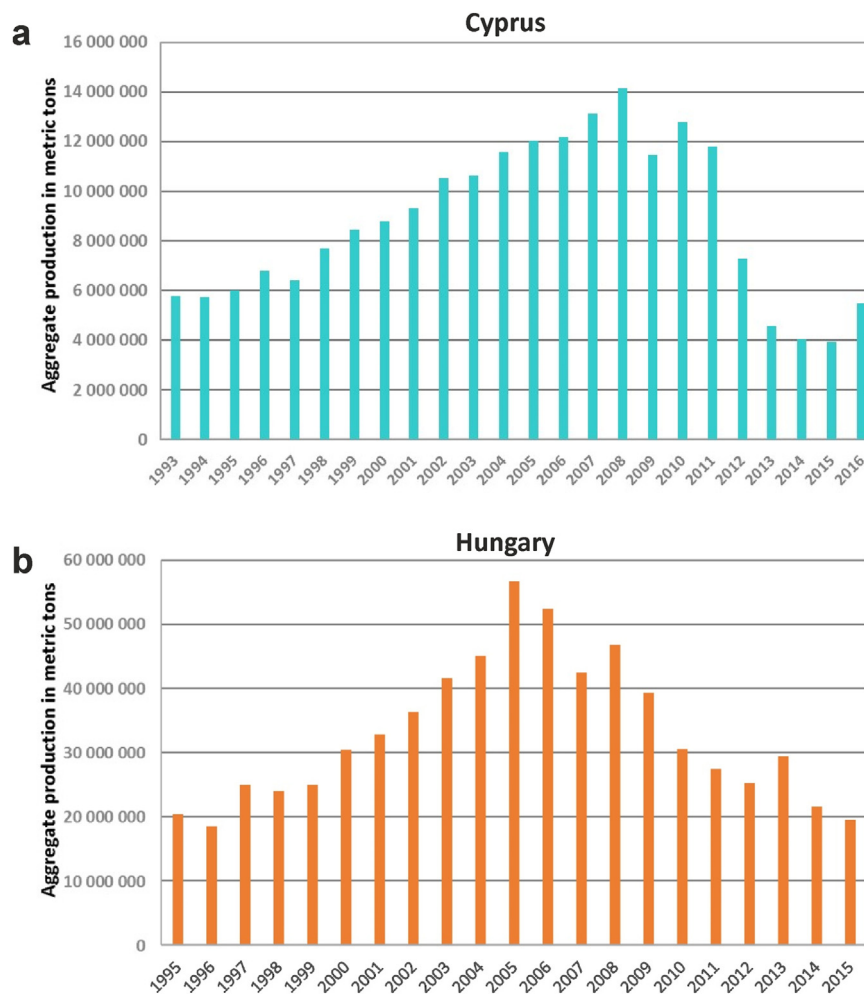


Fig. 2. Aggregate sales in (a) Cyprus from 1993 to 2016 (data from The Mines Service of Cyprus), and (b) Hungary from 1995 to 2015 (data from Hungarian Office for Mining and Geology).

properties, could result in huge economic benefits for the construction industry, which is considered as one of the major CO₂ emitters, contributing at the same time to the mitigation of its CO₂ emissions.

Based on the applications discussed above, it becomes evident that mineral carbonation of ball-milled mafic rock quarry waste materials could take place either in industrial reactors, thereby applying the classic scheme of *ex situ* mineral carbonation, or in situ within the structure of a variety of building materials. Both applications could contribute to the reduction of atmospheric CO₂ concentrations over the next few decades.

4. The case of Cyprus and Hungary

4.1. Promising lithologies for mineral carbonation

The quarrying industry in Europe, and particularly in Cyprus and Hungary, has been hit by the recent economic recession due to socio-economic and political reasons. The aggregate sales in these countries show a dramatic reduction (Fig. 2a,b). It is worth noting that in 2012 the mining sector of Cyprus had only a limited effect on the national economy, as opposed to previous years (Newman, 2012). At the same time, the production by the mining and quarrying sector in Hungary continued to show a dramatic decrease (Anderson, 2012). The sustainable exploitation of existing quarry waste materials for

environmental purposes could notably contribute to the upturn of this industrial sector in the aforementioned countries. Special emphasis should be placed on the fact that such an approach would support the European/International strategic policy targets in terms of greenhouse gas emission reduction and would contribute to the mitigation of global climate change. Specifically, the use of quarry wastes for carbon sequestration purposes is in line with the recent COP21 Paris Agreement. The latter, which has been signed by both Cyprus and Hungary, sets out a global action plan to put the world on track to avoid future dangerous climate change by limiting global warming to well below 2 °C above pre-industrial levels (UNFCCC, 2016).

In 2014, the total amount of waste from quarrying and mining activities in 28 European countries reached ca. 705 million tons, while 155,399 and 82,576 t were produced in Cyprus and Hungary, respectively (Eurostat, 2017). A significant number of aggregate quarries in Cyprus are located in the wider area of the Late Cretaceous Troodos ophiolite complex, which constitutes the geological core of the island. These quarries mainly extract dolerites, which could be used for carbon sequestration. The waste materials produced in dolerite quarries usually exhibit a very fine-grained character, containing a significant proportion of material with grain size < 75 µm. The area of the whole ophiolite is about 3200 km², covering approximately 1/3 of the total area of Cyprus (Fig. 3). It is worth mentioning that the dolerite exposures, which constitute the sheeted dyke complex of the Troodos

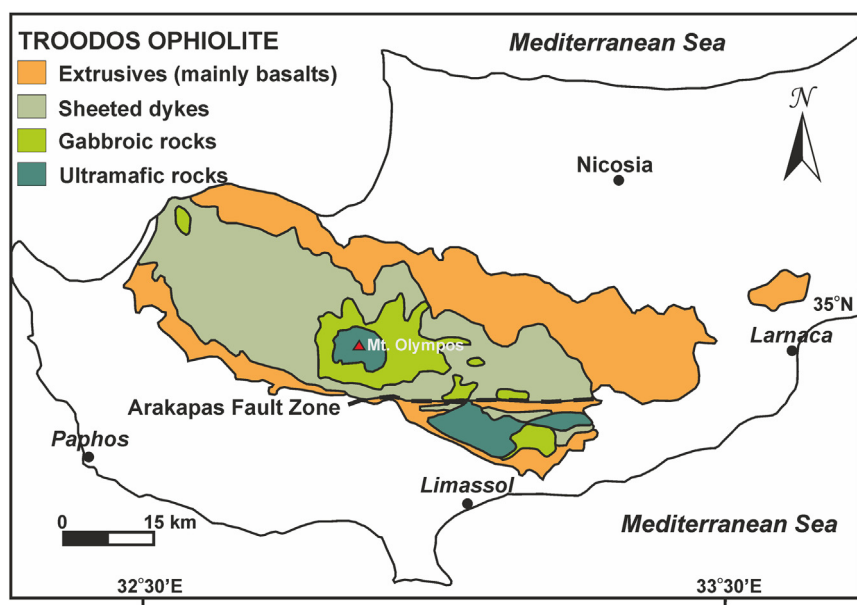


Fig. 3. Simplified geological map of the Troodos ophiolite, modified after Pearce and Robinson (2010).

ophiolite, cover an area of about 1/3 of the total area of the ophiolite complex. The overlying pillow lavas, which are traditionally divided into the “Lower” and “Upper” Pillow Lava units (LPL and UPL) (Gass and Smewing, 1973), comprise a significant part of the ophiolite (Fig. 3). The younger UPL are composed of basaltic andesites and basalts with common picritic lava flows and dykes (e.g., Schmincke et al., 1983), while the older LPL are mainly andesitic, resembling evolved island-arc tholeiites (e.g., Robinson et al., 1983). The UPL unit also involves Mg-rich lavas ($\text{MgO} > 30 \text{ wt\%}$; e.g., see Cameron, 1985), which contain significant proportions of forsteritic olivine phenocrysts. The high reactivity of these lithologies make them very promising rocks for carbon sequestration via mineral carbonation. Although there are no quarries extracting exclusively basalts, small outcrops of the latter usually exist in some dolerite quarries. Nevertheless, it is important to note that both mafic lithotypes contain Mg, Fe and Ca-silicate minerals that are promising for mineral carbonation.

In Hungary, basaltic rocks were formed during the Miocene-Pliocene volcanic activity of the Pannonian Basin, in an intracontinental setting. They represent the latest stage of volcanic activity of the Carpathian system (Németh and Martin, 1999). The alkaline basaltic rocks occur in two very distinct volcanic fields. The largest one is found north of Lake Balaton (Bakony–Balaton Upland), while the smallest one is located in NE Hungary, close to the boarder with Slovakia (Fig. 4). This latter one forms an integral part of the Nógrád–Gemer volcanic field (Harangi et al., 2015). According to Balogh and Németh (2005), the volcanic activity in both areas began in Late Miocene ($\sim 7.8\text{--}8.0 \text{ Ma}$ ago) and terminated $\sim 6 \text{ Ma}$ later. The basaltic volcanism covers $\sim 3500 \text{ km}^2$ in Balaton Highland (Németh and Martin, 1999), while it appears in a much smaller area in NE Hungary (Fig. 4). The volcanic activity produced a wide range of volcanic landforms, such as maars, tuff rings, scoria cones and lava flows. However, erosion has removed a significant amount ($\sim 100\text{--}300 \text{ m}$) of the overlying volcanic rocks, often exposing vents and massive basalts (Németh et al., 2003). The basaltic lavas and vent filling basalts are the ones that have been widely used for aggregate production in Hungary (Török, 2015). The composition of basaltic rocks shows some differences in the two aforementioned areas. The exposures of Balaton Highland are mostly olivine basalts, while those existing in Nógrád area are mainly pyroxene

basalts (Harangi et al., 2015). Regarding their chemical composition, both types of basalts are considered alkaline, with MgO contents $> 8 \text{ wt\%}$. Those of NE Hungary (Nógrád area) are slightly more enriched in Mg, often reaching MgO contents of $\sim 10 \text{ wt\%}$ (Harangi et al., 2015).

The quarrying activity in Hungary has been terminated at several sites, leaving significant amounts of waste in the Balaton Highland area. The waste materials of both abandoned and active quarries show a wide range of grain size fractions, from coarse aggregates to fine materials, with the latter comprising the most abundant fraction.

4.2. Experimental results

Recent experimental results in a variety of rock types from Cyprus show that the specific surface area and CO_2 uptake of dunites, harzburgites, basalts and waste materials from dolerite quarries can be substantially increased by ball milling (Fig. 5; Table 1). The dunite and the basalt show the highest increase of specific surface area and CO_2 uptake after ball milling (Fig. 5; Table 1). The specific surface area of the basalt, however, shows an abrupt decrease after 8 h of milling due to the agglomeration of nanoparticles (Rigopoulos et al., 2015a); thus, further milling beyond the 8 h reported was not performed in that case. A similar behavior was observed for the harzburgite after 20 h of milling (Fig. 5).

The higher carbon sequestration efficiency of the dunite and basalt is attributed to a large extent to their higher specific surface areas, compared to the other rock types tested (Fig. 5). This is also in agreement with measurements of nanoparticles in representative transmission electron microscopy (TEM) images, which revealed that the ball-milled dunite and basalt are composed of smaller nanoparticles compared to the other lithologies. Specifically, the majority of the particle sizes in the milled dunite, basalt, harzburgite and dolerite with the highest CO_2 uptakes (see Table 1) ranged between 15 and 20 nm, 20–35 nm, 15–60 nm, and 30–50 nm, respectively.

The higher CO_2 uptake values of the dunite and basalt are nevertheless also attributed to their high contents in forsteritic olivine, which is among the most promising minerals for the mineralization of CO_2 . On the other hand, the lower CO_2 uptake of the harzburgite is attributed to the fact that a significant amount of its olivine has been converted into

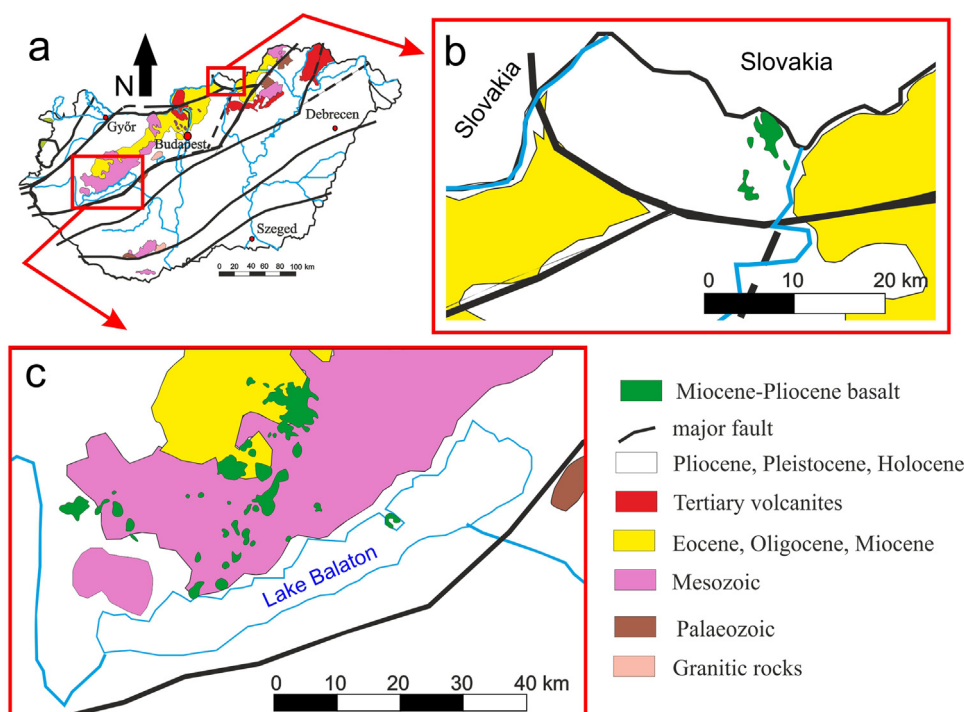


Fig. 4. Simplified geological map of Hungary (a) showing the two largest basaltic volcanic fields of NE Hungary in Nógrád area (b) and Bakony-Balaton Highland (c) (modified after Haas, 2013 and Török, 2015).

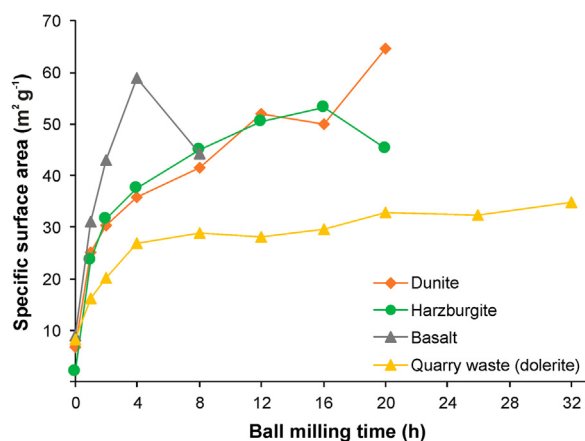


Fig. 5. (a) BET ($\text{m}^2 \text{g}^{-1}$) specific surface area plotted versus the ball milling time (h) for a dunite, harzburgite, basalt, and quarry waste (dolerite) (data from Rigopoulos et al., 2015a, 2016a, 2016b, 2018b).

serpentine, as well as to the presence of a significant amount of enstatite, which is a less promising mineral for the sequestration of CO_2 compared to olivine.

The dolerite quarry waste material showed the smallest increase of specific surface area (Fig. 5), as well as the smallest CO_2 uptake after ball milling compared to the other rock materials. The latter is primarily attributed to the higher degree of hydrothermal alteration of the dolerite; this has resulted in the development of a notable amount of hydrous minerals (mainly chlorite and actinolite), which reduced its reactivity with CO_2 . However, the CO_2 -storage capacity of the ball-milled dolerite quarry waste was increased by a factor of ~ 120 after 20 h of ball milling (Table 1). This is mainly attributed to the notable reduction of its particle size to the nanoscale, as well as to the structural disordering of the constituent Ca, Fe and Mg-silicate minerals (mainly augite and anorthite). The significant reduction of the dolerite quarry waste particle size after ball milling can be seen in Fig. 6. The existence of nanoparticles in the milled dolerite quarry waste has been confirmed based on TEM observations (Fig. 7).

The ball-milled dolerite quarry waste material has been used as an

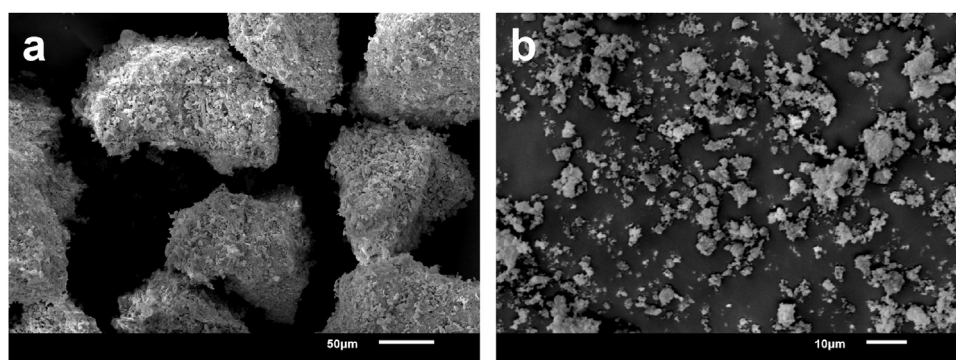


Fig. 6. SEM images showing the significant reduction of particle size after ball milling: (a) non-ball-milled (fraction: 104–150 μm), and (b) ball-milled waste material from a dolerite quarry located in the Troodos ophiolite (Cyprus). The magnification in (a) is significantly lower compared to (b).

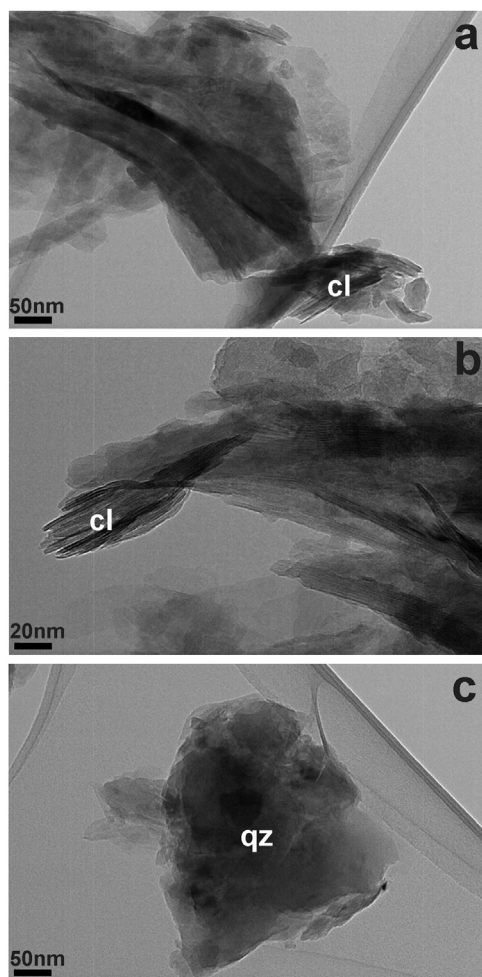


Fig. 7. TEM images of a ball-milled waste material from a dolerite quarry located in the Troodos ophiolite, showing nanoscale crystals of (a, b) clinochlore (cl), and (c) quartz (qz).

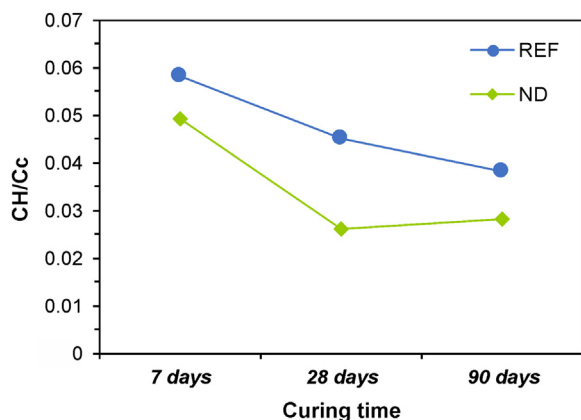


Fig. 8. Quantification of the carbonation process using the ratio of calcium hydroxide (CH) to calcite (Cc), estimated via thermal analyses. The data correspond to material from the surface of lime-based composites (REF: reference composite, ND: composite with 5% w/w ball-milled dolerite quarry waste as a replacement of the lime binder).

additive in lime-based mortars, in replacement to the binder, at a mere 5% w/w. The results clearly showed an enhancement of the carbonation process of the composite end-product. This was quantified using

the ratio of calcium hydroxide ($\text{Ca}(\text{OH})_2$) to calcite (CaCO_3), estimated via thermal analyses (Fig. 8). The aforementioned ratio was also calculated for a reference composite (i.e., without nano-additives), revealing a significant enhancement of carbonation in the composite with nanoscale dolerite, especially between 7 and 28 curing days (Fig. 8).

Besides the enhancement of the carbonation reaction kinetics, the addition of the ball-milled dolerite quarry waste material to the lime composite also led to a notably denser and more homogeneous microstructure (Fig. 9a) compared to the reference material (Fig. 9b). This was confirmed based on scanning electron microscopy observations.

The results presented above suggest that the use of similar mafic rock quarry wastes as nano-additives in replacement to the binder in composite building materials, which rely on carbonation for hardening, could be a great advantage for the building industry. Taking into account that a substantial quantity of waste materials around the globe comes from the operation of mafic rock quarries, it becomes evident that the use of these materials for carbon sequestration purposes could comprise a great step for the development of policies regarding the sustainable exploitation of quarry waste worldwide. Nevertheless, it should be underlined that the dolerite quarry waste material used here showed the highest increase in its CO_2 uptake after 20 h of ball milling (Table 1). Prolonged milling could dramatically increase the energy consumption and cost of the overall carbon sequestration approach. Despite the fact that, in the case of waste materials (original particle size $< 75 \mu\text{m}$), the mining and grinding steps are avoided, thereby offsetting to some degree the increased energy consumption due to prolonged milling, the ultimate goal of all CCS approaches should be to achieve a high carbon sequestration efficiency in relation to the cost/energy required. For mafic rock quarry wastes, this could be achieved by using a feedstock that is less altered compared to the studied dolerite. Such a rock type could be the studied basalt, in which the highest values of specific surface area and CO_2 uptake were acquired after a significantly shorter duration of ball milling compared to the dolerite (see Fig. 5 and Table 1).

5. Conclusions

The long-term goal of EU waste management policies is to reduce the amount of waste materials generated, and when this is unavoidable to promote wastes as a resource in order to achieve higher levels of recycling and safe disposal. In line with this goal, this paper highlighted how the sustainable exploitation of mafic rock quarry waste could contribute to the strategy for the mitigation of climate change, as well as to the upturn of the quarrying industry in Europe, focusing on the examples of Cyprus and Hungary.

Experimental results revealed that the CO_2 -storage capacity of waste material from mafic rock quarries can be strongly enhanced via ball milling and that the ball-milled end-product may be used by the construction industry as additive, in replacement to the binder, for the production of environmentally-friendly composite building materials. The enhancement of the carbonation reactions in the latter could contribute to the sequestration of CO_2 via in situ mineral carbonation, as well as to the development of building materials with improved engineering properties.

It is important to note that mafic rocks are not only abundant in Cyprus and Hungary, but also worldwide. In addition, it should be underlined that similar applications could be proposed for quarry fines generated from ultramafic rock quarries, which contain even higher contents of Mg-silicate minerals and also show global abundance. Hence, the proposed approach for the sustainable management of solid wastes generated from quarrying processes could have a considerable positive economic impact on the quarrying and building industries worldwide.

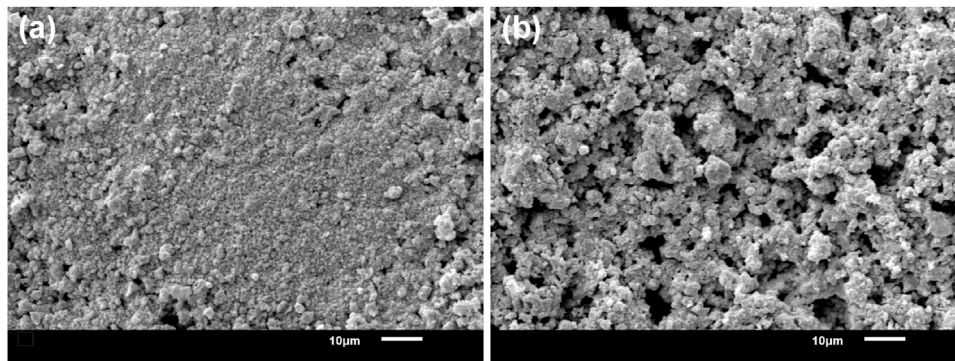


Fig. 9. Scanning electron microscopy (SEM) images from the surface of (a) a nano-modified lime-based composite (with 5% w/w ball-milled dolerite quarry waste as a replacement of the lime binder), and (b) a reference lime-based composite (without nano-additives) after 28 curing days.

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