



## Mediterranean basin basalts as potential materials for thermal energy storage in concentrated solar plants



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### ABSTRACT

Nowadays there is an intense research for developing alternative thermal energies storage materials, able to work at the 800–1000 °C temperature range, for concentrated solar plants. The challenge is wide and extends from different ceramics to natural rocks. In the present work, the aim is first to select representative basaltic rocks from different localities over the Mediterranean basin and close volcanic sites, these going from Tenerife Island up to Egypt. Second, to evaluate the effect of mineralogy, composition and texture of such natural materials on thermal properties during heating process (up to 1000 °C). All analyzed basalts are stable over a wide range of temperatures and especially those containing high amounts of MgO and FeO\*, since they present valuable physical and chemical potential as being used as thermal storage material in concentrated solar plant operating until 1000 °C.

### 1. Introduction

Currently, the continuous increase of the petroleum price requires finding new energetic alternatives to this source. Renewable energies resources as bio-power, geothermal power, wind and solar energy seem to be the most accomplished alternatives to replace conventional energy source based on oil, coal or natural gas [1,2]. Among them, solar power technologies have been adequately developed to be considered as a key technology for electricity generation. Specifically, concentrated solar plant (CSP) has drawn the attention during the last decades. In CSP, solar radiation from heliostats field is transmitted and concentrated on a solar receiver. Heat transfer fluids are widely used to bring heat from the solar receiver to a power block for producing electricity. One of the main challenges for solar energy technologies is to avoid fluctuations due to sunlight (night and day, seasons, cloud and dust) so that an efficient storage of solar energy is needed to guarantee a constant or controlled electricity production. At present, this technology mainly uses molten salts as thermal storage material (TSM) but several drawbacks have been detected. One of them is the huge amount of molten salts necessary for few hours of heat storage. For example, considering both the direct and the indirect absorber, up to 28,000 t of

molten salts are required on the Andasol solar plant (Spain) [3]. This circumstance causes unavoidable production problems of molten nitrates salts besides the fact they are mostly exploited in Chili, which increases the price after importation [4]. Another problem is the corrosion of tubes and turbines induced by molten salts [5]. Moreover, this storage technology can be only used in the particular case of medium-temperature CSP using a solar trough or linear-Fresnel concentrating systems. In the case of higher concentrating systems using heliostats and central receivers at the top of solar towers, no storage technology is currently available for future high temperature technologies, which are expected to work at the 800–1000 °C temperature range.

In order to overcome the problems presented by molten salts, several alternative solutions have been proposed [6–8]. Some recent works have been focused on cements and some ceramics obtained from the treatment of waste such as asbestos or slags from steel industry [9–11]. Treatment of asbestos is performed by an original process based on torch plasma treatment at high temperature. After melting, the inertized waste is cooled down at room temperature and a partially crystallized glass is obtained. An extensive study has been performed on this option and it has been shown that this low-cost alternative material was well adapted for this application [11]. However, despite of the high

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potential of this material as a TSM substitute, there are some disadvantages that should be overcome such as a high-energy consumer process to produce a homogeneous glass [12]. In addition, the possible compositional fluctuation of collected wastes could lead to important variations on the final glass composition, and hence on the heat capacities of the final product.

Natural rocks have also been proposed as alternative materials forming an air rock packed bed, due to their abundance, stability, and ability to store thermal energy [13–16]. A large variety of rocks can be found in the Earth's crust but they have a large variety of compositions which strongly depends on their origin. They are broadly classified as sedimentary CaO-MgO based rocks (i.e., limestones) or SiO<sub>2</sub>-based rocks (sandstones and greywackes), magmatic and metamorphic rocks. Several studies have been already performed on sedimentary natural rocks, such as silex or limestones, although the use of these rocks as TSM requires making important pretreatment processes to avoid their fracturing during the heating/cooling cycles [13,17]. Thus, over the different types of rocks, those having a magmatic/metamorphic origin can be considered as good candidates for being used as heat storage material in CSP, because of their composition, inner structure and formation conditions (> 700 °C and high pressures), which provide to the rock a high stability under severe thermal conditions.

In the present work, we focused mainly on magmatic stones and more particularly on those having a basaltic composition. To our knowledge, only few studies were focused on the potential of basaltic rocks as heat storage materials for solar energy applications (i.e., Gunerhan et al. [18]). However, experiments were mostly performed at room temperature, conditions which are far away from the working temperatures of concentrated solar plants. Analysis of the thermo-physical behavior at high temperature was performed by Mostafa et al. [19] and Grirate et al. [16]. The former studied the temperature dependence of the thermal properties of some basalts collected from different regions in the eastern desert of Egypt at the RT–900 °C temperature range, while the latter found that basalts from Morocco exhibit high heat capacities compared with other Morocco rocks such as Granite, Quartzite, Marble or Hornfels.

In order to shed light to this issue, several basaltic rocks were picked from different countries located very close to the Mediterranean basin (see Fig. 1). The chemical composition of the samples was first determined by X-ray fluorescence spectrometry (XRF) to identify chemical variations between them. Then, the chemical stability of the samples was evaluated through differential scanning calorimetry and in-situ X-ray diffraction recorded until 1000 °C. Once known the stability of the samples, heat capacity, thermal emissivity, thermal diffusivity, thermal conductivity and thermal expansion behavior have been investigated

from room temperature up to 1000 °C.

## 2. Materials and methods

### 2.1. Samples localization

Basaltic rocks selected for this study are from different countries: Spain, France, Greece and Egypt (Fig. 1) and cover the range of basaltic compositions characteristic of the different Mediterranean volcanic regions allowing an accuracy study of properties fluctuations depending on the basalt localization. Several samples from Spain, were selected: one from Tenerife (TEN) in Canary Islands [20–22] and two from the Garrotxa volcanic complex in Catalunya region (from “Pomareda” (POM) and “Banya del Boc” (BAN)). [23] In France, two basaltic rocks from the Auvergne (from “Mont-Dore” (MON) and “Pranal” (PRA)) were selected. For the others locations, one sample is from Santorini (SAN) in Greece [24–26] and the other one, from the southern border of Egypt (EGY). It should be noted that All samples were selected considering that these were already the focus of previous petrological studies which characterized their petrography (mineralogy, texture and matrix composition) or in contrast the rocks had a composition similar to such ones. This information is crucial to understand and to anticipate possible changes in mineralogy or matrix characteristic that could affect the thermal response of the rocks during the heating up/ cooling down of the sample.

### 2.2. Sample preparation

Due to the heterogeneity of these rocks, for each specimen, different pieces were selected, ground in agate mortar and milled together. This step allowed a homogeneous distribution of the different phases presented in the samples, which limited the impact of big crystal pieces on the XRF, DSC and XRD analysis. Moreover, samples were milled in a planetary miller using a tungsten bowl, with 3 tungsten balls of 30 mm diameter. At least 20 rotations of 30 s, with a speed of 300 rpm, were applied on the bowl containing balls and pieces of basaltic stone bloc. At the end of the cycle, if big pieces of materials were still present, they were grounded in an alumina mortar by manual crushing. Scanning electronic microscopy (SEM) images were acquired on a FEI ESEM XL 40 apparatus. The surfaces of the samples were previously polished mechanically. For emittance and thermal diffusivity measurements, basaltic rocks were cut using a diamond saw for obtaining square shape. Samples for emittance had a side of 8 mm and a thickness of 3 mm, while for thermal diffusivity measurements, they had a side of 10 mm and a thickness of 2 mm. For heat capacity measurements, three cylindrical polished samples (same mass) with a diameter of 2.5 mm were made using a core drill and diamond drill. The thickness of the cylinders has to be inferior to 5 mm to be placed into the sample chamber. Last, density ( $\rho$ ) measurements were carried out at room temperature using the Archimedes method with absolute ethanol as the immersion fluid. The accuracy of the density measurement is  $\pm 0.05 \text{ g cm}^{-3}$ .

### 2.3. X-Rays Fluorescence (XRF)

Chemical compositions of basaltic rocks were determined on fused pellets using 1 g of the basaltic stone powder for analysis, 5 g of melter Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> (PpexCertiPrep) with purity of 100% and 3 drops of LiBr (SpexSamplePrep). The analyses were performed on a Shimadzu EDS720 X-ray fluorescence spectrometer. Qualitative and quantitative analysis are made by the EDX software developed by Shimadzu.

### 2.4. XRD

The mineral assemblage of each sample was first identified with SEM analyses, performed on thin sections of the different samples and second (for being consistent with the next section below) confirmed by

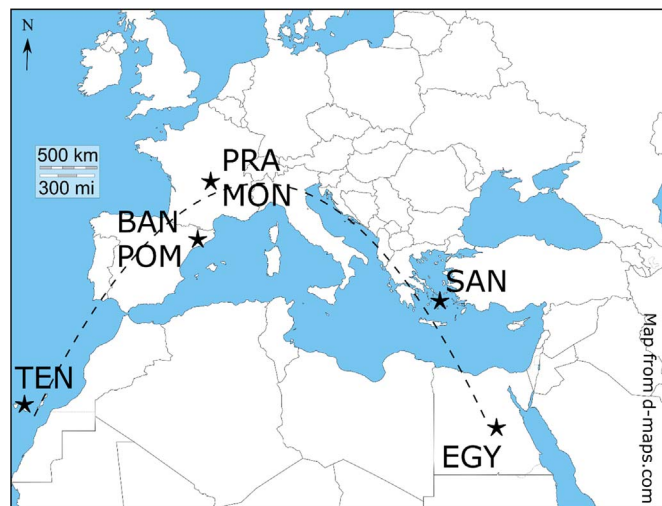


Fig. 1. Mediterranean basin map with samples localizations of this work.

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