A New Study of the Lower Levels of the Los Frailes Caldera (Spain) for the Location and Characterisation of Pozzolans as Construction Materials

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Abstract: Over the last two decades, there was been intensive study of pozzolans on the surface of the Los Frailes Caldera (Spain) for possible use as construction materials; however, research into the deepest underlying horizons has not yet been done. The main object of this paper is to present the results of the research carried out at different levels of depth, down to 30 m, to locate and demonstrate the presence of pozzolans in the depths of the Los Frailes Caldera. To achieve this, a series of analyses were carried out to classify the samples extracted from the various levels of depth, starting at the surface and continuing down to 30 m, which consisted of XRD, XRF, and SEM. Other technological tests were also performed such as chemical analysis of pozzolanic quality (CAQP) and pozzolanicity (PT) tests, at 8 and 15 days. Lastly, a geophysical study using electrical resistivity tomography (ERT) was developed to define the thickness and physical properties of the horizons of pozzolanic materials at depth, as well as to establish the depth of the deposit. The results obtained by XRD, XRF, and SEM confirmed the presence of pozzolans consisting of strongly zeolitized and bentonitised tuffs (ZBVT) in the lower levels of the Los Frailes Caldera, indicating that these horizons continue uninterruptedly beyond 30 m deep. The results of the CAQP and PT established that the ZBVTs that lie in the depths have pozzolanic qualities. On the other hand, the ERT study showed that ZBVT levels continue into the depths, thus proving that the lower limit of the deposit is even deeper. The results obtained in this work could have a positive impact on an increase in the reserves of pozzolanic raw materials in the researched area and could be used in the manufacture of light aggregates for mortars, concretes, and pozzolanic cements, consistent with the environment and effective in reducing CO_2 emissions during the production process.

Keywords: pozzolans; zeolitized-bentonitised volcanic tuffs; construction materials; cement; electrical tomography

1. Introduction

Los Frailes Caldera has been investigated for several decades because it is considered an enclave of great interest, not only from a geological and geochemical point of view, but also because of the presence of volcanic materials, whose physical, chemical, and mineralogical characteristics provide it with properties that have attracted the attention of many researchers and technologists. Geological investigations have established that Los Frailes Caldera contains volcanic materials of medium basic chemism consisting of basaltic andesites and dacites of the Los Frailes Unit (FR-1), more acidic varieties such as dacites and rhyolites of the Rodalquilar Complex, and pyroxenic basaltic andesites of

the Los Frailes Unit (FR-2) [1–5] (Figure 1). According to Arribas [1] Los Frailes Caldera is a circular volcanic structure which is approximately 5 km in diameter, which was formed 14.4 ± 0.8 ma ago because of eruptive processes of several pyroclastic flows of dacitic and andesitic composition. At the same time, Benito et al. [6], Costafreda [7], Costafreda and Martin [8], Costafreda et al. [9], Presa et al. [10], and Stamatakis et al. [11] have recently investigated and described minerals and industrial rocks inside Los Frailes Caldera, consisting of strongly zeolitized and bentonitized cineritic tuffs (ZBT) and glassy volcanic tuffs (GVT), to be used in the production of pozzolanic cements, mortars, concretes, and as light aggregates for concrete. Other researchers [12–14] have focused their research on the bentonite deposits of the Los Frailes Caldera and surrounding distal areas. However, the studies carried out on the deposits of zeolite and bentonite inside the caldera have traditionally been developed on the surface, as the materials' physical, chemical, and mineral properties were unknown at the deeper horizons.
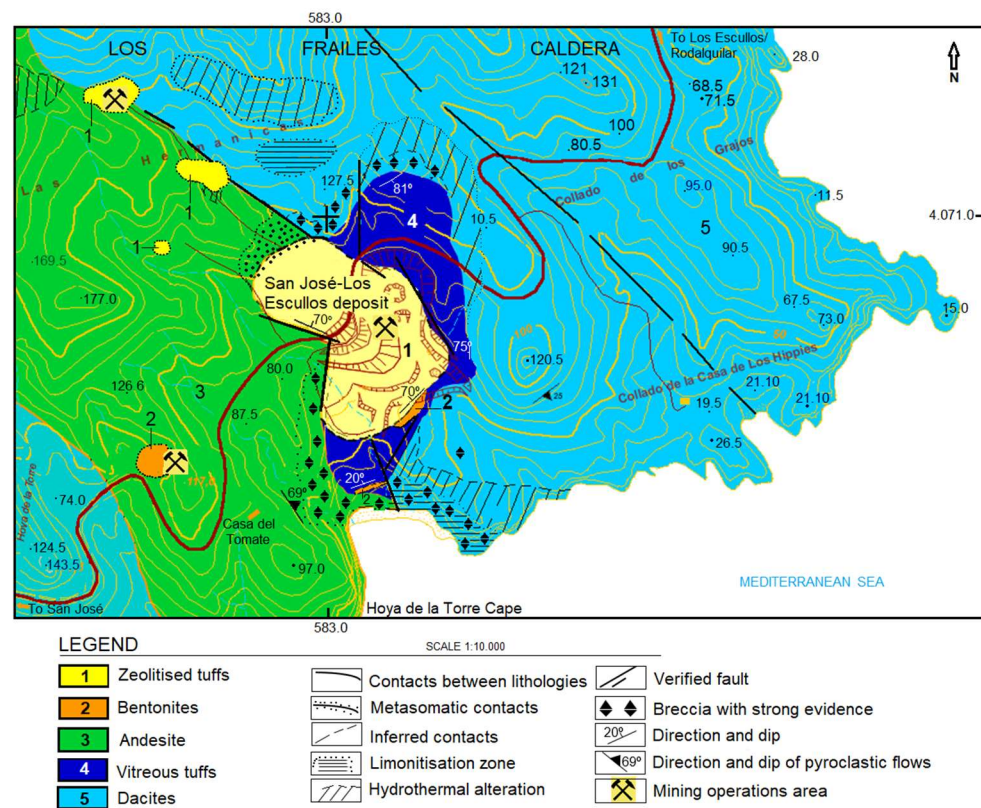

Figure 1. Geological map of the central part of the Los Frailes Caldera [15].

The intent of this study is to research, for the first time, the underlying horizons of de Los Frailes Caldera, from the ground surface to 30 m depth, with the use of exploration drilling and geophysical techniques consisting of electric resistivity tomography (ERT).

This work has been structured as follows: a lithogeochemical sampling of drilling cores was carried out at different depth intervals; a series of samples were characterized by chemical and mineralogical tests; and finally, a geophysical research campaign was carried out on the site to delimit the contours of the area investigated in depth (Figure 2).

Since in the previous investigations carried out in Los Frailes Caldera, no studies have taken place below the surface to establish the nature of the pozzolanic materials, therefore this research is considered new.

Figure 2. Location of the research area and details of the tomographic profiles. The location of the profiles is based on Google Earth data [16].

2. Materials and Methods

2.1. Materials

A series of core samples were obtained at various levels of depth (0.00–30.00 m) and were used in the study of the subsoil of the Los Frailes Caldera. The drill hole samples were obtained courtesy of Empresa Minera Sepiolsa (Spain). A sample of approximately 5 kg was taken from each level by lithogeochemical sampling of drill core fragments. The samples selected in this research are made up of vitreous, crystalline, lithic, and clastic tuffs with a cineritic texture; they are characterized by their strong alteration to zeolite and bentonite. Table 1 shows data on the number of samples, sampling depth, and a brief lithological description of each level.

2.2. Methods

2.2.1. X-ray Diffraction (XRD)

A study was carried out by X-ray diffraction (XRD) to determine the mineral phases present at the various levels of depth (0.0, 1.0, 5.20, 10.20, 15.0, 20.40, 27.30, and 30.0 m.) The equipment used was a Rigaku Miniflex-600, equipped with a 600 w, a goniometer with a Cu cathode X-ray tube, graphite monochromator, a standard scintillation counter, and a rotating charger for 6 samples. The power used in the analysis process was 1ø, 100–240 v,

and 50/60 Hz. The control of the equipment and the processing was carried out from a computer, by means of the PDXL software. To perform the test, 500 mg of sample were ground up and sieved to 74 μm to later prepare the test tablets in the standard moulds of the equipment's sample holders. The determination of the crystalline phases was recorded in a 2θ range from 4° to 60°, with a step of 0.01° and a step time of 5° per minute, with a voltage and current of 40 kV and 15 mA, respectively.

Table 1. Description data, depth, and type of samples investigated.

Sample	Description of the Sample *	Sampling Depth (m)	Type of Sample
LFCS-01	ZBT	0.00	Outcrop
LFCS-02	ZBT	1.00	Drill core
LFCS-03	ZBT	5.20	Drill core
LFCS-04	BZT	10.20	Drill core
LFCS-05	BZT	15.00	Drill core
LFCS-06	BZT	20.40	Drill core
LFCS-07	GVT	27.30	Drill core
LFCS-08	GVT	30.00	Drill core

* ZBT: Zeolitized-bentonitised tuff; BZT: Bentonitised-zeolitized tuff; GVT: Glassy volcanic tuff.

2.2.2. Scanning Electron Microscope (SEM)

The morphological characterization of the samples was carried out with a Hitachi S-570 scanning electron microscope from the Centralized Laboratory of the Escuela Técnica Superior de Ingenieros de Minas y Energía of the Universidad Politécnica de Madrid. The equipment has a Kevex-1728 analyser, a Polaron BIORAD, a power supply for evaporation, and a Polaron SEM coating system. The equipment reaches a resolution of 3.5 nm and an amplification of 200×103. Winshell and Printerface Programmes were used to manage the information obtained during the study of the analysed sample and take microphotographs. The samples were reduced to a diameter between 0.2 and 0.5 cm; previously pulverised, they were spread on an adhesive graphitized tape, which was fixed on the surface of the sample holder. The samples were then covered with a layer of graphite which was applied under vacuum, by means of the Polaron SEM Coating System.

2.2.3. X-ray Fluorescence (XRF)

X-ray fluorescence is an elementary technique that provides quantitative information on the chemical composition of the analysed material. The 8 study samples were analysed with a Philips WDXRF spectrometer (PW1404) equipped with a collimator to reduce the angle of divergence of the X-rays. The radiation intensity ranged from 10 to 100 kV, and the use of monochromator facilitated the isolation of the measured radiation, thus guaranteeing an adequate wavelength. To carry out the test, the samples were reduced to 200 mesh using an automatic agate mortar. An amount equivalent to 6–8 g of sample was mixed in 1.5 mL of elbaite (250 cc acetone and 12.5 g plastic), then left to dry at room temperature for 5 min. It was then pressed using the Herzog press to obtain a pill of 5 cm in diameter, which was finally placed inside the X-ray spectrometer for quantitative analysis by the XRF.

2.2.4. Chemical Analysis to Determine the Quality as Pozzolan (CAQP)

The chemical analysis to determine the quality as pozzolan (CAQP) was carried out under the indications of the Standard UNE-EN 196-2-2014 [17], to determine the amount of certain compounds necessary to classify the samples investigated as natural pozzolans and recommend their possible uses in the manufacture of pozzolanic cements. The compounds studied are total SiO_2 (TS), reactive SiO_2 (RS), total CaO (TC), reactive CaO (RC), in addition to MgO, Al_2O_3, and Fe_2O_3. The insoluble residue (IR) was also determined by a test with HCI.

2.2.5. Pozzolanicity Test (PT) at 8 and 15 Days

The 8 samples from different levels of depth of the deposit were tested to evaluate their pozzolanic properties. Pozzolanicity tells us about the ability of the materials to react with $Ca(OH)_2$ in dissolution, when they are finely ground up. The pozzolanicity test was performed on a mixture of 75% Portland cement (PC) and 25% natural sample at 8 and 15 days. In order to assess the pozzolanic properties of a material, the concentration of hydroxyl ions and the concentration of calcium ions, expressed as calcium oxide, must be calculated according to the European Standard UNE-EN 196-5:2011 [18] which specifies the procedure to be followed and the materials necessary to carry out the test.

The calculated concentrations of materials with pozzolanic properties are below the saturation concentration curve in calcium ions as a function of the concentration of hydroxyl ions at 40 °C [18].

2.2.6. Geophysical Study Using Electric Resistivity Tomography (ERT)

The geophysical study by means of electric resistivity tomography (ERT), carried out inside Los Frailes Caldera, aimed to determine the thicknesses of the horizon of the pozzolanic materials in its depths, based on its natural physical properties. Swedish Terrameter SAS geophysical equipment, from ABEM Instruments, was used for this work. The equipment is made up of a basic Terrameter SAS/4000, with SELECTOR ABEM ES 10-64C, and operates in three different modalities, including resistivity (R), induced polarization (IP), and spontaneous potential (SP). It includes an ABEM LUND system for developing tomographic resistivity profiles. The maximum voltage in electrodes is 400 v. The export, treatment, and processing of the data is carried out by an RS 232 connector. The equipment operates with two softwares: the SAS 1000/4000 Utility and the RES2DInv.

3. Results and Discussion

3.1. X-ray Diffraction (XRD)

The study of the mineralogical phases determined by XRD established that the samples investigated are made up of a main phase of zeolite, the main mineral being mordenite (Mor). The secondary phases correspond to smectite (Sme) of motmorillonite variety, illite (Ill), plagioclase (PI) halloysite (Hly), quartz (Qtz), gypsum (Gyp), muscovite (MS), as well as an amorphous phase (Am) represented by altered volcanic glass (Figure 3).

According to the X-ray diffraction patterns obtained by each sample from different depths, an uninterrupted proliferation of the mordenite phase is observed at all levels, which is evidenced in the discussion stated in Section 2.2. An increase in the amorphous phase is highlighted in all X-ray diffraction patterns, mainly in those representing the LFCS-07 and LFCS-08 samples; the latter could be interpreted as a remnant feature of the Neogene volcanic period in the southeast of the Iberian Peninsula, in which frequent horizons of pyroclastic material in the form of glass and cinerite could have been formed; this deduction is made due to the conclusions reached by previous researchers, including Seligman et al. [19] and Angelopoulos et al. [20]. Despite the mineralogical complexity of the samples investigated, it is established that this fact contributes to the manifestation of their pozzolanic properties [7].

3.2. Scanning Electron Microscopy (SEM)

Figure 4a–h shows eight microphotographs corresponding to the samples investigated (LFCS-01 to 08), obtained by SEM. According to these results, the predominant mineral phase is the mordenite variety zeolite, which is present throughout the stratigraphic column of the study area, from the surface to 30 m, which represents the lower limit of study. In addition to mordenite, the smectite (montmorillonite), muscovite, plagioclase, halloysite, gypsum, quartz, and devitrified volcanic glass representing the amorphous phase was detected. According to the information offered in Figure 4b,c,g, it follows that zeolitic mineralization occurred from the hydrothermal alteration of the amorphous phase; this reasoning is also reflected in the work of Presa et al. [10].
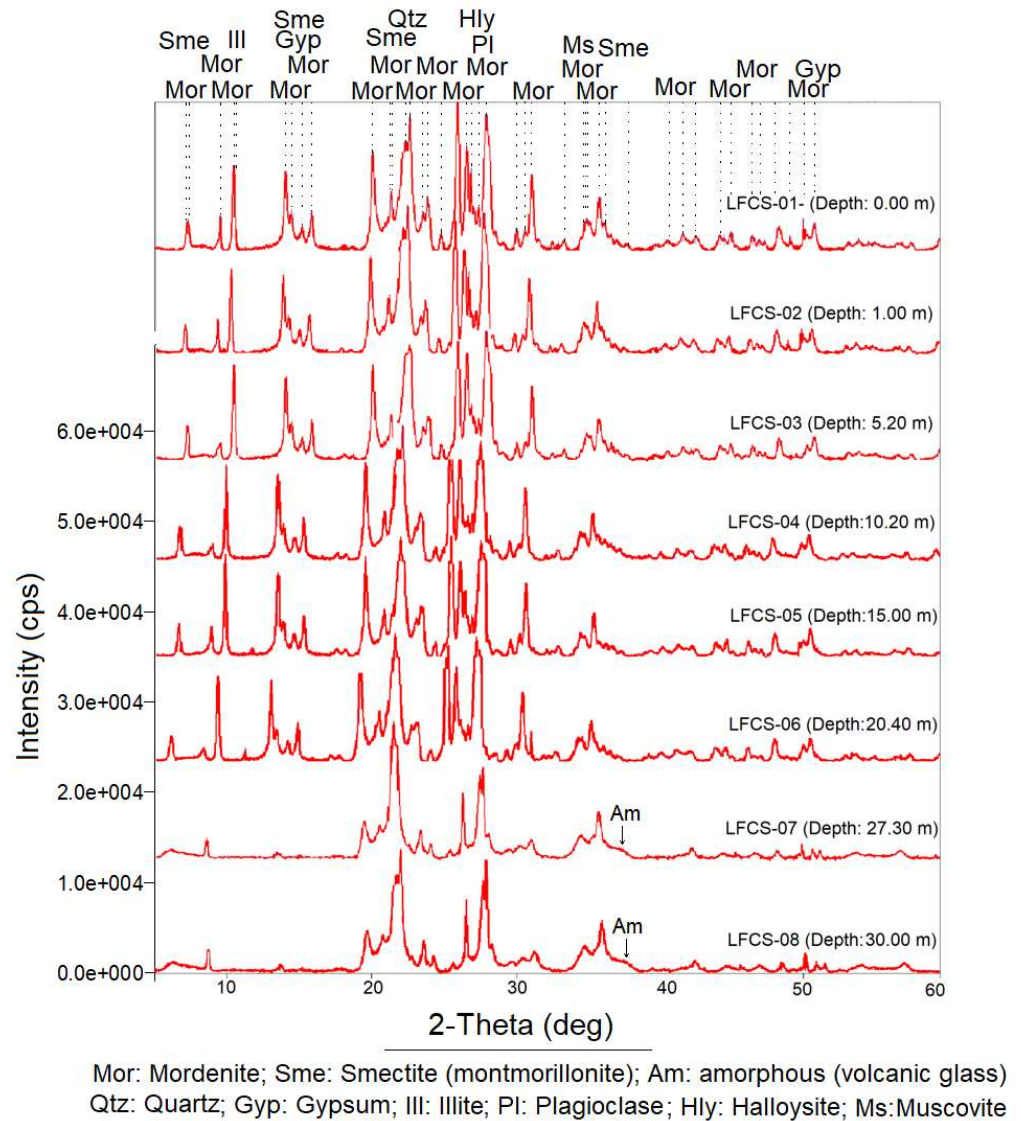
Figure 3. X-ray diffraction patterns of the investigated samples obtained by XRD.

A fact worth mentioning is the abundance of mordenite even at the deepest levels of the Los Frailes Caldera. The mordenite lies uninterrupted from the surface to the depths, a fact which positively affects the potential of zeolite reserves of this geological enclave. The frequent presence of the mordenite phase in the samples is of indisputable importance due to the influence of its most characteristic properties, such as its conformation as a porous solid, cation exchange capacity (CEC), proven pozzolanic reactivity, and chemical composition [21].

As can be seen, the results obtained by SEM confirm those presented and discussed in Section 2.1 of this work.

3.3. X-ray Fluorescence (XRF)

Table 2 shows the chemical composition of the samples investigated, obtained by XRF. The main aspect to highlight is the variation in the percentages of SiO_2 and Al_2O_3 within a relatively close range. For example, SiO_2 ranges from 60.91 to 68.65% (LFCS-06 and LFCS-04, respectively), while Al_2O_3 ranges from 11.20 to 12.61% (LFCS-02 and LFCS-05). Costafreda and Martin [8] have shown that the percentages of $SiO_2 \geq 15\%$ and $Al_2O_3 \geq 11\%$ positively influence the pozzolanic capacity of certain zeolites and dacitic tuffs.
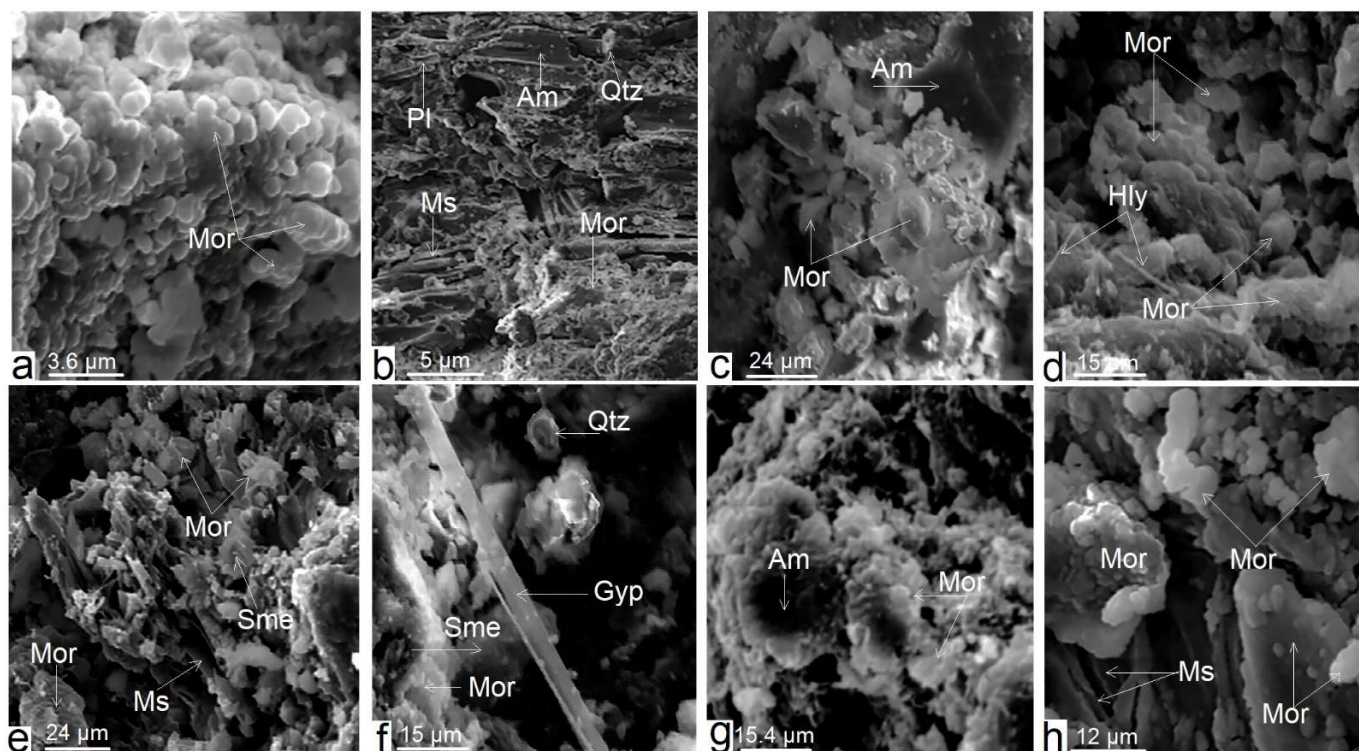
Figure 4. Microphotographs of the investigated samples obtained by SEM.

Fe_2O_3 contents range from 1.2% (LFCS-06) to 2.17% (LFCS-02); however, we must highlight ranges of values between 1.45% (LFCS-05) and 2.17% (LFCS-02), which are larger and comparable with those calculated by Costafreda et al. [9] in zones proximal to the research area. The higher contents of MgO (2.94–3.2%) may indicate the possible relationship that exists between the andesite host rock that lies in the study area, which has been affected by hydrothermal processes as stated by Arribas [1] and Costafreda et al. [9].

Table 2. Chemical composition (%) of the samples investigated determined by X-ray fluorescence (XRF).

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	Total Alkali Equivalent	LOI *	Si/Al
LFCS-01	65.17	11.57	1.40	0.96	3.20	1.36	1.93	0.8	12.60	4.3
LFCS-02	62.90	11.20	2.17	1.33	3.10	2.33	2.42	1.5	11.90	4.3
LFCS-03	67.25	12.07	1.63	1.56	2.21	1.78	1.57	1.1	10.50	4.4
LFCS-04	68.65	11.32	1.49	2.93	2.05	1.92	1.46	1.2	11.90	4.3
LFCS-05	66.47	12.61	1.45	1.56	2.94	1.52	1.11	1.0	12.30	4.6
LFCS-06	60.91	12.33	1.20	1.90	0.93	2.16	1.62	1.4	10.80	4.5
LFCS-07	66.08	11.37	1.60	1.57	1.55	2.64	2.11	1.7	12.30	4.3
LFCS-08	67.70	11.22	1.48	1.03	1.35	2.57	2.37	1.6	14.80	4.5

* Loss on ignition.

The values calculated for CaO, K_2O, and Na_2O are within the ranges of results presented and discussed by García-Romero et al. [14] for calc-alkaline environments of formation from zeolite and bentonite deposits. One aspect to highlight is the loss on ignition (LOI) of the samples analysed, which is visibly high in all cases, specifically in the samples LFCS-08, LFCS-01, LFCS-07, and LFCS-05. This fact can be interpreted as one of the main causes of the pozzolanic reactivity of the samples together with the significant presence of SiO_2 and Al_2O_3, which is in accordance with the conclusions of Rosell et al. [21]. The Loss on Ignition (LOI) values presented have been related in this research to the intrinsic properties of zeolites, such as the extremely large active surface, absorption capacity, and low sulphate contents [9], which are indispensable for their use as a pozzolan and as a possible construction material. In addition, the calculation of the ratio Si/Al:4.3–4.6 (Table 2) has allowed us to establish that the zeolite found in each of the samples investigated corresponds to the mordenite variety.

3.4. Chemical Analysis to Determine the Quality as Pozzolan (CAQP)

Table 3 shows the results of the chemical analysis (CAQP) carried out to determine the quality of the samples investigated as pozzolans. As discussed in Section 3.3, the percentage of SiO_2 and Al_2O_3 is the most remarkable fact in the chemical composition of these samples; beyond this, emphasis is placed on the results of reactive SiO_2, i.e., the portion of total SiO_2 capable of reacting against HCL [17]. This fact is considered of great relevance in this study, since it highlights one of the main effects produced by the pozzolanic reactivity of the investigated samples [22–25].

Table 3. Results of the quality chemical analysis as pozzolans of the samples investigated according to Standard UNE-EN 196-2:2014 [17].

Compounds (%)	Samples							
	LFCS-01	**LFCS-02**	**LFCS-03**	**LFCS-04**	**LFCS-05**	**LFCS-06**	**LFCS-07**	**LFCS-08**
Total SiO_2	65.5	63.2	67.9	69.3	68.81	60.77	66.29	67.62
Reactive SiO_2	58.7	59.0	59.4	58.8	58.76	58.0	59.3	58.93
MgO	0.73	0.78	0.75	0.51	1.12	0.91	0.82	0.75
Total CaO	1.55	1.59	1.93	1.45	1.77	1.63	1.60	1.80
Reactive CaO	1.32	1.37	1.33	0.21	1.64	1.39	1.30	1.41
Fe_2O_3	1.39	1.41	1.30	1.45	1.32	1.41	1.43	1.47
Al_2O_3	11.07	11.21	12.03	11.31	12.12	12.01	11.67	11.05
SO_3	0.04	0.03	0.05	0.04	0.1	0.03	0.21	0.06
I.R.*	2.22	3.71	2.18	2.20	2.17	2.47	2.34	2.43

* I.R. Insoluble residue.

Costafreda et al. [9] have established that 97–98.7% of the total SiO_2 contained in zeolitized tuffs can react against $Ca(OH)_2$. According to Table 3, the ratio of total CaO to reactive CaO is positive for pozzolanic reactivity, as is Al_2O_3. In all the samples investigated, practically negligible values of SO_3 show up; this fact is highly relevant for its use as a raw material in the manufacturing of pozzolanic cements [26].

Finally, emphasis is placed on the percentages calculated for insoluble residue (I.R.), which in any case does not reach 3%. Everything discussed above can be considered as the basis of the pozzolanic reactivity process that is extensively detailed in Section 3.5 of this paper.

3.5. Pozzolanicity Test (PT) at 8 and 15 Days

According to Figure 5a,b, all samples investigated, both at 8 and 15 days, show a remarkable pozzolanic reactivity. At eight days (Figure 5a), in the area under the isothermal

solubility curve at 40 °C, there is an evident tendency to the concentration of all samples, showing a similar behaviour, although the LFCS-08 sample can be clearly highlighted as the most pozzolanic.
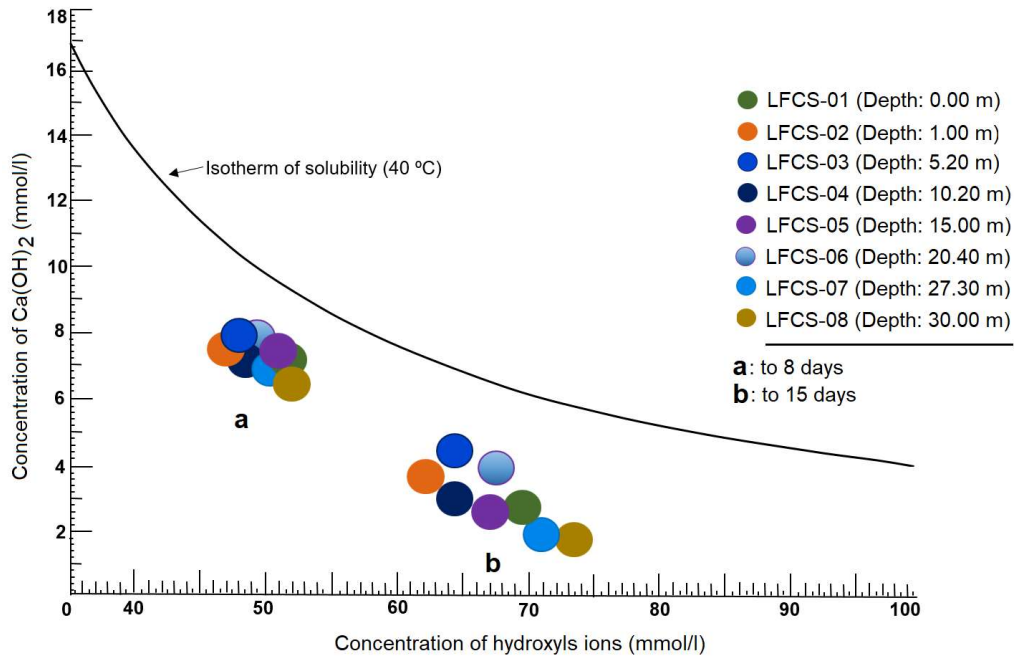

Figure 5. Variation in the time of pozzolanic reactivity of the investigated samples. (**a**) to 8 days; (**b**) to 15 days.

The analysis of Figure 5b at 15 days provides somewhat different criteria compared to what was observed at 8 days, consisting of a marked tendency to linearity of the samples under the solubility isotherm. In this case, the remarkable pozzolanic nature of the LFCS-08 sample can be verified in relation to the other samples. Comparatively, the degree of pozzolanicity of the samples investigated at 15 days can be established as follows: LFCS-08, LFCS-07, LFCS-01, LFCS-05, LFCS-04, LFCS-02, LFCS-06, and LFCS-03. The analysis made in this work establishes the nature of the pozzolanic materials by means of their tendency to react slowly with $Ca(OH)_2$ in the first reaction period, as shown in Figure 5a up to 8 days; however, as time passes a spontaneous reaction occurs (15 days). The pozzolanic behaviour of the investigated samples shows great similarities with the results obtained by Donatello et al. [27]. The results presented and discussed in this subsection confirm the suitability of the samples investigated for possible use as construction materials.

3.6. Geophysical Study Using Electric Resistivity Tomography (ERT)

According to Table 4, the values of electric resistivity (ERT) vary within a relatively wide range, the largest being >40 Ω·m, the intermediates between 15–40 Ω·m, and the minimums of <15 Ω·m. The first fact to highlight is the low value of ERT (<15 Ω·m) of the lithological horizons constituted by strongly zeolitized-bentonitised tuffs (ZBT); normally, these materials tend to have a markedly high resistivity, as Noor et al. [28] have established, however, very different behaviours have been reported in this study.

Table 4. Resistivity values vs. lithology values at different depths of study.

Resistivity [Ω·m]	Lithology
<15	Zeolitized-bentonitised tuff phase
15–40	Bentonitised-zeolitized tuff phase
>40	Glassy volcanic tuff phase

For the interpretation of the geoelectric levels, several isoresistivity intervals were unified (Table 4 and Figure 6a–c) and contrasted with the data of the surveys close to the ERT measurement profiles; in this way, a first geoelectric level was differentiated (Figure 6a) with resistivities less than 15 Ω·m coinciding with the horizon of ZBT. Below this level lies the BZT horizon with resistivity values of 15 to 40 Ω·m (Figure 6b). A horizon consisting of GVT lies even lower, in which resistivity values greater than 40 Ω·m were determined (Figure 6c).
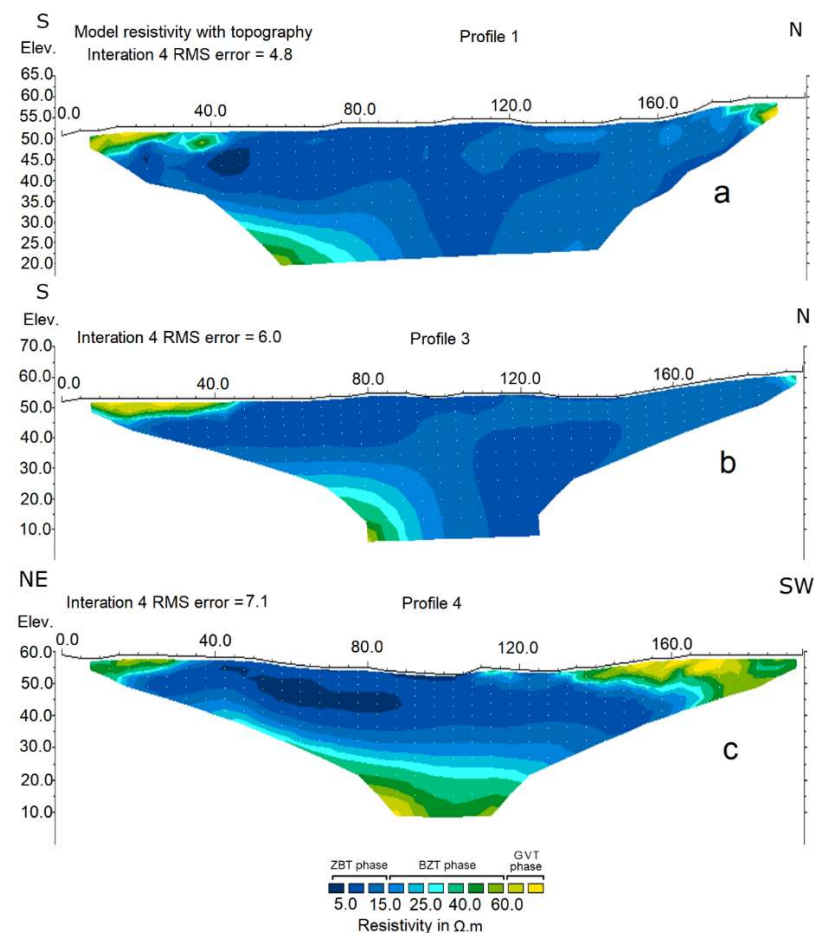

Figure 6. Tomographic profiles of resistivity according to the data obtained by the geophysical method of ERT. Profiles (**a**) (north-south direction), (**b**) (north-south direction) and (**c**) (north-east/south-west) show the behaviour of ERT values on lithological horizons at different depths.

According to the results of the work carried out in Los Frailes Caldera, some criteria were established that can explain the low values of the ERT, such as the effect of hydrothermal processes that form zeolitic and bentonitic mineralization, already mentioned by Costafreda [7] and Martinez et al. [29]; and proximity to the sea and the influence of saline compounds [7] as well as the pressure exerted by the overlying materials on the underlying ones [30], which causes the segregation and migration of fluids from the pores and inter-layers of zeolite and smectites, respectively, by diagenetic processes. As Costafreda [9]

states, these fluids can be located in the contacts between different lithologies. On the other hand, in this study it has been possible to establish a close relationship between the complex mineralogical constitution of the zeolitized and bentonitised tuffs of the Los Frailes Caldera (Figures 3 and 4) and the behaviour of the resistivity values (Table 4 and Figure 6). The abundance of the mordenite crystals described in Sections 3.1 and 3.2 seems to be one of the causes that explain the low values of electrical resistivity as the depth increases. The above can reasonably be supported by the conclusions established by Parthasarathy [30], Tagomori et al. [31], Hersir and Arnason [32], and Utami [33].

Finally, is the results discussed in this subsection can be well correlated with those interpreted in the previous subsections; this indicates that the choice of the different methods applied in this research is correct. In addition, it is necessary to mention that if the mineral composition is taken into account, the chemical composition and the pozzolanic properties of the samples analysed at different depths, added to the results of the ERT then there will be great interest in the greater depths of the Los Frailes Caldera, especially regarding increased geological reserves.

4. Conclusions

The results of the XRD, XRF, and SEM have established that the composition of the investigated samples represent several mineral phases such as mordenite, smectite (montmorillonite), illite, plagioclase, halloysite, quartz, gypsum, muscovite, and amorphous material, with mordenite being the main phase. According to these analyses, the lower levels of the Los Frailes Caldera are mineralized from the surface to the depth of the study, set at 30 m.

The results of the chemical analysis to determine the quality as pozzolans (CAQP) of the investigated samples have revealed a high content of SiO_2 and Al_2O_3 and very low contents of SO_3 and insoluble residue (I.R.), which is a basic condition that pozzolanic materials must meet.

The pozzolanicity test (PT) establishes that all the samples investigated are pozzolanic; however, the fact that this reactivity is most evident in the samples that come from the last two levels of study (LFCS-07 and LFCS-08) gives a new perspective to the lower horizons of the Los Frailes Caldera.

The geophysical study using ERT has demonstrated the presence of pozzolanic materials in depth, consisting of ZBT, BZT, and GVT, which are characterized by a marked pozzolanic reactivity; this fact is of great interest. However, these studies failed to establish the real depth of the aforementioned materials, which has to be considered as a positive factor, concluding that the deposit is even more extensive in depth.

All the results presented and discussed in this work could be used as direct criteria for new prospecting and exploration work of the study area aimed at the expansion of geological reserves. Similarly, these results could be considered when improving the quality of pozzolanic cements and reducing greenhouse gasses.

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