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Sr immobilization in irradiated Portland cement paste exposed to carbonation

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Abstract

Cement based materials are widely used as binding matrices for radionuclides in low and intermediate level waste management applications. We studied the effect of irradiation and carbonation under atmospheric condition on the leaching of Sr from Portland cement paste. Samples were exposed to gamma irradiation or subjected to thermal treatment under either inert or atmospheric conditions. Leaching tests were performed and supplemented by post-leaching characterization including local chemical analysis (LA-ICPMS) crystallographic analysis (XRD), and EPMA imaging. The combination of these methods enabled us to link between the crystallography, texture and composition of the treated samples and their ability to retain Sr ions. Results show that carbonation was the main factor determining the retention of Sr ions, whereas irradiation did not have a significant effect. Moreover, carbonation has a positive effect on the retention of Sr ions in the matrix with the formation of a carbonated zone.

Keywords:

cement paste (D), carbonation (C), radioactive waste (E), leaching, characterization (B)

1. Introduction

Cement based materials are widely used in the nuclear industry for low and intermediate level waste management applications due to their availability, low cost, good chemical compatibility with waste ions and mechanical stability. The prediction of the long-term behavior of cementitious waste packages requires the identification and the understanding of degradation mechanisms that might affect the structure. One of these degradation mechanisms is water radiolysis, resulting from the immobilized radioactive waste elements, which leads to dehydration and release of H_2 gas, and thus carries potential impacts on the safety of the wasteform [1,2]. Cement carbonation occurring at atmospheric conditions (in presence of CO_2), is an additional degradation mechanism that could affect the waste-form stability [2,3]. The temperature increase induced by the irradiation could produce favorable conditions for enhanced carbonation. The extent of carbonation depends on CO_2 partial pressure [4-6], moisture content in the sample pores [4,7-9] and temperature [10-12]. Although the carbonation reaction occurs in the aqueous phase and therefore slows down as water activity decreases, at highly saturated conditions the diffusion of carbon dioxide is reduced and even inhibited by water filling the pores. Therefore, carbonation occurs most rapidly at intermediate saturation of the cement paste.

There are few published data on the effect of irradiation on the immobilization of radioactive waste in cement based materials. One of the studies [2] concluded that the enhanced carbonation associated with irradiation, leads to crystallographic, textural and chemical modifications and thus affects the immobilization of radionuclides in the matrix. The effect of carbonation on the leaching resistance of cementitious pastes has been extensively studied [13-16], but contradictory results were reported. These contradictions originate from the fact that in some cases carbonation might improve waste retention either by precipitation as insoluble carbonates, or due to the reduced

porosity of the carbonated matrix, while in other cases retention was reduced, possibly as a result of micro-cracking due to shrinkage during carbonation or rearrangement in pore connectivity [15-19].

The objective of this study is to gain understanding concerning the combined effect of irradiation and carbonation on Sr retention in cement paste. The experimental approach included the exposure of cement samples to different degradation mechanisms (irradiation and thermal treatment under either inert or atmospheric conditions) followed by leaching tests. The samples were studied using XRD, to obtain their crystalline phase composition before and after treatment and leaching. LA-ICP-MS and EPMA were applied to explore the local changes in the chemical composition due to the various treatments, allowing the evaluation of the different treatments on the durability and leaching resistivity of cementitious pastes.

2. Experimental

2.1. Sample preparation

The cement used for this study is a CEM I Val d'Azergues cement from Lafarge Company (France). It is composed of 96% of clinker, 1% of filler and 3% of gypsum. The chemical composition of the cement is presented in Table 1. Cementitious samples were prepared with a water to cement ratio (w/c) of 0.4. A non-radioactive Sr solution, using the nitrate salt, $\text{Sr}(\text{NO}_3)_2$ (Aldrich chemicals), has been added to the cement to prepare a Sr-spiked-cementitious paste, in order to simulate a waste stream to be cemented, with a target Sr concentration of 3.66 mg Sr/g paste. Non-spiked (blank) samples were prepared in order to assess the effect of the Sr addition on the on the crystallography, texture and composition of the paste.

All specimens were cast in plastic molds (diameter of 40 mm and height of 100 mm) and sealed. After setting, the samples were de-molded, inserted into polypropylene bags, sealed again and allowed to self-cure at room temperature for 28 days. The cured specimens were sliced using a diamond saw into 15 mm thick disc shaped samples. The list of samples is presented in Table 2.

2.2 Degradation procedures

2.2.1 Gamma irradiation

Sample irradiation was performed using a ^{60}Co source in a commercial irradiation facility (Sorvan Ltd, Israel). The irradiation has been performed at a dose rate of 24 Gy/min, over a period of 6 months, to reach a total dose of 5.0×10^6 Gy.

Samples were irradiated either under inert conditions or exposed to the ambient atmospheric conditions of the irradiation cell. Samples irradiated under inert conditions were placed in Pyrex® ampoules and sealed at sub-atmospheric pressure (500 torr) and under an Ar atmosphere. As the irradiation cell lacks climate control, fluctuations in the atmospheric conditions are expected during the irradiation period. The average operating temperature and the relative humidity in the irradiation chamber were $\sim 40^\circ\text{C}$ and $\sim 30\%$, respectively.

2.2.2 Thermal degradation

Samples exposed to thermal degradation were polished before the treatment in order to remove any possible surface alteration prior to the experiment.

Samples were placed inside a climatic chamber at 40°C, 32% RH at atmospheric conditions for 6 months. Samples treated under inert conditions were placed in a reactor filled with N₂ at 32% RH, fixed by a MgCl₂ saturated solution [20], inside the same climatic chamber.

2.3 Characterization methods

2.3.1 XRD analysis

Crystallographic characterization was performed using X-Ray diffraction (XRD). Measurements were carried out using a PANalytical X'Pert diffractometer (Cu K α , λ = 1.54 Å), on the angular range of 5° - 65°, in increments of 0.017° or 0.033°.

XRD analyses were performed on bulk samples. Analysis of bulk samples eliminates a preliminary grinding and avoids possible effects of preferential orientation encountered in the powder method.

In order to obtain XRD profiles, the polished surface was analyzed, consequently a thin layer of the sample (from 30 to 150 μ m of thickness) was removed by polishing and the newly exposed surface was then analyzed. This method allowed us to obtain a series of diffractograms as a function of the depth of the sample. Prior to the XRD characterization, five points were marked on the bottom of the sample and the sample thickness at each of the points was measured using a micrometer screw gauge. The samples were then manually polished using 120 grit silicon carbide paper. After each polishing step, the sample thickness was measured again at each of the 5 points using the micrometer screw gauge. For each of the 5 measured points the difference between the initial thickness and the measured thickness (which refers to the measured depth) was calculated. The average of all 5 points was denoted as the sample depth analysed. Grinding was performed up

to a depth of approximately 3500 μm in the sample, until reaching the non-altered part of the sample.

XRD results were analyzed using the Reference Intensity Ratio (RIR) method [21](Johnson and Zhou, 2000) which scales all diffraction data to a Corundum (Al_2O_3) standard. The RIR factors were obtained from ICSD using POWD-12++ and are presented in Table 3. The scale factors are determined from the strongest intensity lines of both the analyte and corundum. In cases where the calculation was performed using a different diffraction line, an additional correction factor was applied, proportional to the relative intensity of the chosen diffraction line as compared to the strongest diffraction line, denoted here as peak fraction.

Due to the presence of non-crystalline phases in the cementitious matrix, the RIR approach was used as a semi-quantitative method, allowing us to normalize the diffraction intensities, and thus making qualitative comparison only between the different crystalline phases in a specific sample. Therefore the results are presented as intensity normalized by RIR factor and the peak fraction (Table 3).

2.3.2 LA-ICPMS analysis

Cement samples were cleaved, exposing a cross-section extending from the surface into the sample core. Each sample was placed in a cell equipped with an inlet nozzle of 0.5 mm diameter. Laser ablation was conducted using an ArF-excimer laser (New Wave) emitting 15 ns long pulses at a wavelength of 193 nm, with repetition rate of 10 Hz, at a power of 7 J/cm², with fluence of 5.05 J/cm². The cell was flushed with 0.5 L/min helium, washing the vaporized sample into the mass spectrometer. SRM NIST610 glass was used as standard. Ablation of the standard was conducted at the beginning and the end of each ablation session, at a spot size of 50 μm .

The analyzed spot size varied across the cement samples in order to attain maximal resolution near the surface where leaching and precipitation are expected to have the strongest effect, and a lower resolution but higher signal at inner sample areas. A spot size of 10 μm was used at the outermost 120 μm of the sample, then a spot size of 50 μm was applied for the next 900 μm , and finally a spot size of 100 μm was used for the innermost 3000-4000 μm .

The ICP-MS analysis was conducted by AGILENT (7500 CX) ORS quadrupole mass spectrometer with a RF power of 1500W, injection tube diameter of 2.0 mm, nebulizer and auxiliary gas flows of 0.9 L/min Ar .

Table 4 lists the analyzed isotopes, the average limit of detection for the different isotopes at different spot sizes and the average analytical error for the various isotopes as a function of the spot size used.

For all three spot sizes the average error is generally lower than 3% (except for Ba in the 10 μm spot size) An average error lower than 1% is obtained for all isotopes at 100 μm spot size. For ^{88}Sr and ^{42}Ca , the most important analytes in this paper, the analytical error is $\leq 1\%$.

SiO_2 was used as an internal standard, at a concentration of 20.6% (the concentration measured in the original cement powder).

SiO_2 was used as its concentration is relatively high, thus, it is easily detected using the ICP-MS.

Furthermore, Si concentration is not expected to decrease significantly due to leaching effects.

In order to obtain coherent concentration display between all the samples, the different element concentrations (C) are presented relative to the concentration of the innermost spot analyzed (C_0), assuming that this point resides within the undisturbed inner sample volume.

Figure 1 shows the normalized ^{25}Mg and ^{42}Ca signals obtained as a function of distance from the surface of a leached sample, together with the analyzed spot size used. These results demonstrate

that in spite of the higher limit of detection and larger error for the smaller spot size, spot size has no effect on the calculated concentration of Mg, representing an element with minimal leaching. Additionally, no correlation was found between the spot size used and the concentration calculated for Ca, confirming that concentration changes are not an artifact of the spot size.

2.3.3. EPMA (Electron Probe Micro-Analysis)

Samples were impregnated in epoxy (Epofix by Struers) using a Citovac device (by Struers) for 10 min at a pressure of 0.73 bar. The impregnated samples were polished parallel to the sample surface using a Saphir 250 polishing machine manufactured by ATM. The samples were initially polished using SiC polishing paper with 320, 600 and 1200 grid, and finally using a diamond suspension of 3 and 1 μm . Samples were then carbon coated and mounted on the EPMA stand. EPMA imaging and analyses were conducted using a JEOL 8230 superprobe EPMA with EDS (Energy-Dispersive X-ray Spectroscopy) and four wavelength-dispersive spectrometers (WDS) for microanalysis. Beam conditions were set to 15 keV and 15 nA. Silicate and oxide standards were used for EDS analyses. Data was processed with a PRZ correction procedure. Back-scattered electron (BSE) and secondary (SEC) electron imaging were applied.

2.4 Leaching experiments

The leaching tests were performed according to the standard ANS-16.1 procedure [22], using deionized water as the leachant. According to this procedure, the leachant volume (cm^3) equals 10 times the surface area of the tested sample (cm^2). Samples were immersed for 90 days, with leachant replacement at predetermined leaching intervals of 2, 7, 24, 48, 72, 96, 120, 456, 1128,

177 and 2136 hours. Following the standard procedure, the leaching tests were performed in closed
178 vessels under static, atmospheric conditions.

179 Leaching tests have been performed for samples treated under the different conditions and for
180 untreated reference samples. Duplicate samples containing Sr were tested except for the sample
181 irradiated at inert conditions, for which a single sample was available.

182 To assess the effect of initial Sr concentration on the leachability, an additional blank sample
183 prepared with no Sr doping was tested.

184 The concentrations of Sr and Ca in the leachate were determined using Inductive Coupled Plasma
185 Optical Emission Spectroscopy (SPECTRO ARCOS ICP-OES) for each leaching interval.

186 3. Results

187 3.1 Crystallographic characterization of untreated HPC (hydrated Portland cement) samples

188 The powder diffraction pattern of a crushed non-treated sample (not presented) displays the typical
189 crystallographic composition for a CEM I cementitious paste: portlandite (Ca(OH)_2), ettringite
190 ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$) and C-S-H (calcium silicate hydrate phases) as hydrated phases and
191 possible presence of a small amount of calcite (CaCO_3) and some residual anhydrous phases (C_4AF
192 for $(\text{CaO})_4\text{Al}_2\text{O}_3\text{Fe}_2\text{O}_3$, C_2S for $(\text{CaO})_2\text{SiO}_2$ and C_3S for $(\text{CaO})_3\text{SiO}_2$). As expected, no Sr bearing
193 phases have been identified by XRD analysis.

3.2 Characterization of treated HPC samples

3.2.1 Characterization of samples aged under inert conditions

Surface XRD analysis of samples treated under inert conditions (not presented) showed the full disappearance of ettringite. Additionally, in the irradiated samples calcite was detected at the surface, with a corresponding depletion of portlandite. This superficial precipitation had probably occurred during sample preparation. Calcite was not found at the surface of the sample treated in the climatic chamber which was polished prior to the thermal treatment (section 2.2.2).

EPMA imaging of a sample irradiated under inert conditions and the corresponding relative concentrations of Ca, Ba and Sr as obtained by LA-ICPMS are presented in Figures 2 and 3, respectively. The EPMA BSE image of the sample shows a very thin uneven front (10-100 μm) at the sample surface, with a denser but brighter appearance (Fig. 2), while the rest of the sample remains virtually unchanged.

The concentration profiles of Sr, Ca, and Ba along a cross-section in the same sample (Fig. 3) indicate a constant concentration for these three elements throughout most of the sample, except for the 80-100 μm outer surface, where the concentration of all three elements shows significant scatter. This scatter might reflect the uneven precipitation of a carbonate phases near the surface. The precipitation of such phases is probably due to exposure to atmospheric conditions during sample preparation. These results are in agreement with the formation of a thin calcite layer at the sample surface as observed by XRD, and with the EPMA-BSE image showing a thin dense layer at the sample surface.

3.2.2 Characterization of samples treated under atmospheric conditions

216 Samples aged under atmospheric conditions, either in the climatic chamber or during the
217 irradiation process, present similar crystallographic patterns.

218 The crystallographic composition of both samples consists of calcite near the surface of the sample
219 with corresponding disappearance of the portlandite. Further into the sample aragonite and
220 vaterite, the two metastable calcium carbonate phases, occur. The formation and stability of these
221 two phases are favored over calcite at temperatures above 40°C [23,24]. The overall thickness of
222 the carbonated zone, defined by the presence of calcium carbonate phases, is about 3500 µm, for
223 both irradiated and non-irradiated samples (Fig. 4).

224 Samples treated in the climatic chamber exhibited cracking after three days of treatment (Fig. 5),
225 probably due to the enhanced drying process.

226 3.3 Leaching results

227 Leaching experiments were performed for samples exposed to various aging treatments as well as
228 for untreated reference samples. Figures 6 and 7 present the average cumulative fraction of Sr and
229 Ca ions leached for the different samples vs. square root of time.

230 The overall cumulative fraction values obtained for Sr were higher than for Ca, although the trends
231 were similar. For the reference sample, for example, the cumulative fraction of Sr was five times
232 higher than for Ca (0.09 and 0.018 respectively).

233 For samples aged under atmospheric conditions, and hence exposed to carbonation, the cumulative
234 fraction of both Sr and Ca ions leached was lower than for untreated reference samples, with no
235 apparent difference between the irradiated and climatic chamber samples.

The sample that has been exposed to irradiation under inert atmosphere showed a slight increase in the cumulative Sr and Ca leached fraction compared with the reference sample. Significant increase in the leached fraction of Sr and Ca was obtained for the samples that were treated in the climatic chamber under inert atmosphere. For these samples the Sr and Ca cumulative fractions increased from values of 0.09 and 0.018 in the reference sample, to values of 0.35 and 0.044; respectively.

The difference between the results obtained for irradiated and climatic chamber samples treated under inert atmosphere could be a result of differences in the sample pre-treatment. As presented in section 3.2.1, the irradiated sample showed a thin carbonation zone. Such carbonation zone was not found for the samples treated in the climatic chamber, which were polished before treatment.

The effect of initial Sr concentration on the Sr retention can be studied from the leaching curves of the two samples irradiated under inert conditions (Fig. 8), one doped with Sr and the other containing the native Sr content from CEM I cement (3660 ppm vs. 250 ppm respectively). Despite the large difference in the initial Sr concentration the cumulative leached fractions obtained were almost similar. Similar leachabilities were observed for both samples during the early stages of leaching, while a slightly higher leached fraction for the sample doped with Sr was measured at the later stages of the experiment.

3.4 Post leaching characterization

The distribution of the alkaline earth elements Sr, Ba and Ca within the leached samples, as obtained from LA-ICP-MS, will be presented together with the phase distribution as obtained from XRD depth profile measurements and complemented with EPMA images. Sr was considered as waste simulant, while Ca is a major cement component and Ba is a trace element present in cement.

Both Sr and Ba may substitute Ca in various mineral phases (especially carbonates) with high compatibility [25].

3.4.1 Post-leaching characterization of untreated reference sample

The untreated sample that served as a reference for the leaching test was analyzed after leaching. Figure 9 presents the EPMA BSE image of the sample. A very distinct disturbed zone can be detected at the surface. This zone, which is composed of several sub-zones, has an overall thickness of 700 μm .

The Sr, Ca and Ba relative concentration profiles along this reference sample are presented in Figure 10. All three elements show a decrease in relative concentration moving from the inner undisturbed zone ($C/C_0 = 1$) towards the surface of the sample.

For all three elements, the concentration is relatively constant along the outer 700 μm , except for the outermost ~ 150 μm , where a large dispersion of the concentrations was found. This region roughly corresponds to the disturbed zone in figure 9. Further into the sample a relatively constant increase in the Sr concentration, with no corresponding morphological changes in the BSE image, is obtained until ~ 1600 μm , where the concentration levels to $C/C_0 = 0.8$. A further increase in the C/C_0 is observed at ~ 3000 μm reaching the level of $C/C_0 = 1$ at ~ 4000 μm . For both Ca and Ba the concentration reaches the level of $C/C_0 = 1$ at ~ 1000 μm .

Figure 11 presents the XRD profile of the same sample. At the surface, a carbonated zone is detected, indicated by the presence of calcite together with a reduction in the portlandite intensity.

The normalized intensity for calcite is relatively high for the first 300 μm from the surface of the sample and then is gradually decreases up to a depth of approximately 800 μm into the sample, roughly corresponding to the disturbed depth as observed by EPMA (Fig. 9) and to the constant concentrations of all three elements studied (Fig. 10).

3.4.2 Post-leaching characterization of samples aged under inert conditions

Figure 12 presents an EPMA BSE image of the sample treated in the climatic chamber under inert conditions. The image presents a highly porous, irregular dark area at the sample surface and along two deep cracks which are perpendicular to the surface. These cracks seem to be inter-connected and penetrate approximately 1000 μm into the sample. The bulk of the sample contains a brighter, denser looking material.

Figure 13 presents the element concentrations along a cross-section of the samples aged under inert conditions. Both samples show relatively large scatter of all three elements within the 100 μm nearest to the surface, followed by a relatively constant concentration of all three elements up to a depth of 500-700 μm .

Further into the sample, the Sr concentration gradually increases until reaching values similar to those of the undisturbed region ($C/C_0 = 1$) at a depth of about 3000 μm for the irradiated sample and 3800 μm for the sample treated in the climatic chamber. The Ca and Ba concentration profiles show a step-like increase at a depth of 700 μm , reaching a constant value of $\sim C/C_0 = 1$.

XRD measurements of the above samples reveal the depletion of portlandite from the outermost region. Portlandite is detected at a depth of approximately 500-700 μm from the surface, in accordance with the Ca concentration profile. Both samples show the presence of calcite at the sample surface, gradually decreasing to a depth of approximately 500-700 μm (Fig. 14). Higher intensity values of calcite were measured for the irradiated sample, in accordance with the higher scatter at the surface probably due to an initial carbonation layer present in the sample, as previously discussed in sections 3.2.1 and 3.3.

3.4.3 Post-leaching characterization of samples treated under atmospheric conditions

Figure 15 presents an EPMA BSE image of the sample treated in the climatic chamber under atmospheric conditions. A thin (50-80 μm) porous rim is observed at the outer surface of the sample. Porous regions are also observed along cracks which are perpendicular to the surface and penetrate up to 300 μm . Beyond this porous rim, a zone of denser and brighter material, having a thickness of 200 μm , is observed. The inner part of the sample keeps a relatively uniform appearance.

Figure 16 presents the Ca, Sr and Ba relative concentration cross section along two samples exposed to atmospheric conditions, either irradiated or treated in the climatic chamber. Both samples show significant scatter near the surface. For the sample treated in the climatic chamber, all three elements are depleted in the outermost 100 μm . For the irradiated sample Sr and Ba are enriched in the outermost 100 μm . The concentration of all three elements was found to increase from a depth of ~ 100 to ~ 1000 μm . The Ca concentration reaches its undisturbed concentration ($C/C_0 \sim 1$) at ~ 1000 μm into the sample. For Sr and Ba, however, enrichment relative to the initial concentration ($C/C_0 > 1$) is observed at a depth range of 700-4000 μm , with a gradual decrease back to the undisturbed value.

Figure 17 presents the XRD measurements of the above samples. In both cases portlandite is depleted from the surface up to a depth of 250-300 μm . From this depth inward there is a gradual increase in portlandite to its maximal intensity.

Calcite was found at the surface of both samples. Its intensity decreases towards the inner part of the sample and levels off at around 300 μm depth. The vaterite and aragonite phases are present up to 3500 μm from the surface. The intensity curves slightly differ between the two samples. While for the sample treated in the climatic chamber maximal intensity for both phases was detected at around 50-100 μm from the surface, for the irradiated sample both carbonate phases

were not detected at the surface and appeared at a depth of 100 μm with a maximal intensity around 150 μm . For both samples the normalized intensity of vaterite was higher than that of aragonite.

4. Discussion

4.1 Leaching effect – samples treated under inert conditions

The post-leaching reactive concentration profiles obtained for samples aged under inert atmosphere, present an extended disturbed profile for all three examined elements, as compared to the reference sample. This corresponds well with the higher cumulative leached fraction obtained for these samples, possibly due to the formation of microcracks, which is known to occur during the enhanced drying process.

When comparing the two samples treated under inert conditions, it can be seen that the sample treated in the climatic chamber shows much higher leachability and deeper depletion profile relative to the sample exposed to irradiation.

As already discussed in section 3.2.1, the major difference between these two samples was the very thin carbonated layer present in the irradiated sample which was prior to treatment removed by polishing from the sample placed in the climatic chamber. This carbonated layer, a few tens of micrometers thick, may contribute to the reduced leachability of the sample irradiated under inert atmosphere.

An additional reason for the difference between the two samples could be the increased dehydration and consequent cracking due to the lower RH conditions (32%) fixed in the climatic chamber, compared to the irradiated sample sealed in an ampoule and thus exposed to much higher relative humidity (>80%).

The cumulative leaching fractions of samples with different initial Sr concentration (3660 ppm vs. 250 ppm Sr) were almost similar. A slightly higher leached fraction for the sample doped with Sr, may result from a higher fraction of Sr residing in the interstitial pores for the doped sample relative to the non-doped one, where a higher fraction of Sr is probably bound within the lattice sites.

4.2 Leaching effect – samples treated under atmospheric conditions

In the present study samples were exposed to carbonation at 40°C either in a climatic chamber or during the irradiation process. Both samples exhibit a ~3500 µm thick carbonated layer, composed mainly of metastable calcium carbonate phases (vaterite and aragonite). The dominance of vaterite and aragonite in the carbonated layer is in agreement with previous studies showing that hexagonal vaterite precipitation predominates at 40°C, a temperature at which orthorhombic aragonite starts to form as well [26]. It was further shown that a high Sr concentration enhances aragonite precipitation [24,27]. Additionally Roncal-Herrero *et al.* [28] have shown that in the presence of Sr, vaterite can become the dominant carbonate phase even at relatively low temperatures (25°C).

The ~3500 µm thick carbonated front leads to the reduced leachability of the Sr ions, compared to the untreated sample. One possible mechanism for the reduction in ion leachability is porosity clogging which is characteristic to carbonated samples [29,30] as indicated by the densification of the carbonated zone observed in this study (Fig 15). Furthermore, it was shown that vaterite, which was found here as the dominant carbonate phase for these samples, has the lowest density among these carbonate polymorphs, and therefore could lead to increased pore clogging [31].

369 An additional process that can lead to reduced leachability of Sr is the co-precipitation of Sr into
370 carbonate phases. Aragonite and vaterite have high coordination lattice sites for Sr and Ba and can
371 easily accommodate these larger ions [24,32]. The measured partition coefficient values for Sr in
372 aragonite is of the order of 1.1 at 40°C [33].

373 The effect of Sr co-precipitation in the metastable carbonate phases can be demonstrated by
374 comparing Ca/Sr weight ratios in the cement paste and in the leachate solutions. In the original
375 cement paste the Ca/Sr ratio is approximately 120. However, a much lower value of 30 was
376 obtained for this ratio in the leachate of the reference sample, due to the preferential incorporation
377 of Ca into crystalline phases and the C-S-H phase, whereas the Sr remains largely interstitial and
378 more available to leaching. In the leachate of the carbonated samples the Ca/Sr ratio is ~45,
379 indicating preferred Sr retention compared to the non-carbonated reference sample. This
380 emphasizes the effect of Sr co-precipitation in aragonite and vaterite, increasing the Sr retention
381 in the paste and thus reducing its relative leachability.

382 Therefore we may conclude that the clogging effect, which is expected to affect equally all ion
383 mobilities and not to change the Ca/Sr ratio, is secondary in this case.

384 Additional evidence to the increased Sr retention induced by co-precipitation in aragonite and
385 vaterite phases can be observed by the analysis of the solid matrix. The $[Sr]/[Sr]_0$ ratio within an
386 unleached sample is ~1 throughout the sample, with the exception of the outer surface zone where
387 a large scatter in the results was detected (see section 4.4). All the leached samples that were treated
388 under inert conditions as well as the reference sample show a decrease in the $[Sr]/[Sr]_0$ ratio from
389 a value of 1 in the undisturbed zone to a lower value towards the surface. However, in the samples
390 treated under atmospheric conditions a local enrichment in the $[Sr]/[Sr]_0$ ratio is measured within
391 the aragonite/vaterite precipitation zone, where this ratio reaches the range of 1.2 - 1.4 (Fig. 16).

The relative enrichment of Ba in the carbonated front may be related to a similar process occurring due to preferred Ba precipitation in aragonite [34].

It is suggested that this enrichment has occurred during the initial carbonation process. Vaterite/aragonite precipitation during the treatment has reduced the local Sr concentration in the pore solution, creating a local gradient in Sr concentration and thus yielding a driving force for Sr diffusion from the surrounding areas to the carbonate precipitation zone. Continuous precipitation of Sr and Ba caused the observed relative enrichments, and thus increased the Sr and Ba ions retention within the sample.

It is interesting to note that although the sample carbonated in the climatic chamber showed evidence of cracking at an early stage of the treatment (Fig. 5), this cracking did not lead to higher Sr leachability, supporting the suggestion that Sr immobilization is dominated by its enhanced co-precipitation in the carbonated layer.

4.3 The calcite surface layer effect

In the analyzed unleached sample, the relative concentration of Ca, Sr and Ba at the outer surface layer showed a large scatter with values ranging between 0.6 and 1.4 (Fig. 3). We suggest that this phenomenon is related to calcite precipitation during sample handling at atmospheric conditions, creating a very thin (10-100 μm) carbonated layer.

Additionally, in all leached samples, either treated or untreated, a calcite layer was detected at the outer surface of the sample with thickness varying between 100-500 μm .

Calcite precipitation during leaching is reflected in the leaching curves where a change in the slope develops over the square root of time (Figures 6 & 7). A steeper slope was measured over the first 7 days of leaching, whereas a more moderate slope persists over the remaining leaching process.

This effect was clearly demonstrated for the samples treated in the climatic chamber which have been polished before treatment and therefore they were lacking the initial calcite layer, making the effect more pronounced. This behavior is typical to the formation of a dense impervious carbonation layer and is consistent with previous results by Andac and Glasser [31]. Various other studies investigating the leaching of Portland cement pastes by hydrogeno-carbonate solutions [35,36] or natural waters containing CO₂ [37,38] have shown the formation of a calcite crust, at or near the paste–leachant interface, which strongly slows down the degradation process.

Within the near surface calcite layer significant scatter of the Ca, Sr and Ba concentrations occurs. When observing the chemical composition of this layer in leached samples under all treatments, Ca and Sr usually show a reduction in their relative concentration, whereas Ba shows a significant increase in its relative concentration (Figures 10,13&16)

The reason for this different behavior is related to the two simultaneous processes of leaching and calcite precipitation. Ca, as a major element, is effectively leached from the sample. Due to its high concentration in the matrix, the small amount of calcite precipitated does not affect the overall trend of the reduction in the Ca relative concentration.

On the other hand, Ba, being a trace element is significantly affected from minor precipitation processes. The relatively high Ba enrichment with respect to Sr is mainly the outcome of its lower concentration in the paste and hence higher sensitivity to precipitation processes. This phenomenon is widely used in geological studies, where trace elements are used to emphasize the precipitation of crystalline phases [39].

Moreover, the magnitude of this scatter for all three elements is much smaller for the samples treated in the climatic chamber (Fig. 13a) compared with the irradiated samples (Fig. 13b). This is

probably the consequence of the presence of the pre-leaching calcite layer in the later increasing the relative amount of calcite in the sample surface and therefore leading to higher scatter in the element concentrations.

5. Conclusions

The use of local chemical analysis (LA-ICP-MS) together with crystallographic analysis (XRD), supplemented by EPMA imaging, enabled us to link between the crystallography, texture and the composition of the treated samples and their ability to retain Sr ions in the system.

The cementation process is used for the conditioning of low and intermediate level radioactive waste; hence, the effects of irradiation and carbonation are intrinsic to the assessment of the process. However, in the present study no evidence of enhanced degradation mechanisms due to irradiation was found. Carbonation on the other hand, had shown a positive effect on the retention of Sr ions in the matrix with the formation of a distinct carbonated zone at the surface.

In the present study carbonation occurred in three different manners. 1) A very thin (up to 100 μm) carbonated zone was formed during sample preparation and handling. This thin calcite layer was removed for the samples treated in the climatic chamber, leading to an increased Sr leachability compared to samples which were not polished before treatment. 2) All samples exhibited some carbonation (100-500 μm) during the leaching test, performed according to the ANSI-16.1 procedure with no precaution taken to avoid exposure to the atmosphere. 3) For all samples exposed to enhanced carbonation at 40°C, a 3500 μm thick carbonated layer, composed of metastable calcium carbonates (aragonite and vaterite) was formed. These carbonate phases

possess high coordination lattice sites for Sr (and Ba) and therefore can easily accommodate these larger ions [32,24].

The crystallographic and chemical composition of the samples as well as the retention of Sr ions (representing the immobilized waste) was highly influenced by the latter carbonation process. The extent of carbonation, as well as the crystallography and the Sr retention were similar for both carbonated samples with no additional effect found for the irradiated sample. Thus, carbonation enhanced by temperature increase, is sufficient to explain the retention behavior of strontium under the present atmospheric conditions. The correlation found between relative Sr enrichment and the presence of Ca-carbonate phases, clearly leads to the conclusion that during the carbonation treatment Sr ions are preferentially fractionated into these metastable carbonate phases, leading to a higher retention in the cement paste.

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569 Table 1: Chemical composition of CEM I Val d’Azergues cement (wt%) (Producers data)

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	SO ₃	S ⁻²	Cl ⁻	P ₂ O ₅	LOI
20.6	3.6	5.0	64.3	0.7	0.7	0.2	2.7	0.01	0.06	0.4	1.1

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584 Table 2: List of samples (irradiation=IR, climatic chamber=CC, atmospheric=At, inert=In)

Sample experimental condition	Sr doping	Polished before treatment	Treatment	External conditions	leaching	comments
Reference	+	-	-	-	+	
Climatic chamber atmospheric	+	+	CC	At	+	
Climatic chamber inert	+	+	CC	In	+	
Irradiated atmospheric	+	-	IR	At	+	
Irradiated inert (blank)	-	-	IR	In	+	Natural Sr concentration
Irradiated inert (unleached)	+	-	IR	In	-	

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592 Table 3: Crystallographic data for the XRD RIR analysis (from ICSD using POWD-12++)

mineral	2 θ	RIR	peak fraction
Calcite	29.3	3.2	1
Aragonite	26.1	1.13	1
Vaterite	26.9	1.14	1
Portlandite	17.9	3.46	0.74

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Table 4: List of analyzed isotopes, their average limit of detection and average analytical error percent for the different spot sizes

Spot size	10 μm		50 μm		100 μm	
	LOD ($\mu\text{g/g}$)	% error	LOD ($\mu\text{g/g}$)	% error	LOD ($\mu\text{g/g}$)	% error
^{25}Mg	76	2.4	2.7	0.6	0.9	0.2
^{29}Si	3083	1.7	111	0.4	29	0.1
^{42}Ca	3696	1.0	94	0.1	26	0.1
^{43}Ca	1653	1.5	68	0.3	24	0.1
^{88}Sr	1.4	0.8	0.1	0.2	0.02	0.1
^{137}Ba	7.3	8.1	0.4	1.9	0.1	0.8

614 **Figure captions:**

615 Figure 1: The sampling spot size and relative concentration of Ca and Mg as a function of the
616 distance from the sample surface in a leached sample. C = the concentration at a specific distance,
617 C_0 = the concentration at the undisturbed inner sample volume.

618 Figure 2: EPMA BSE image of sample surface irradiated under inert atmosphere.

619 Figure 3: Relative concentration of Ca, Ba and Sr as obtained by LA-ICPMS along a cross section in a
620 sample irradiated under inert conditions

621 Figure 4: XRD profiles of samples treated under atmospheric conditions. (a) sample treated in
622 climatic chamber, (b) sample irradiated

623 Figure 5: Cracking on sample exposed to atmospheric conditions in the climatic chamber

624 Figure 6: Sr Cumulative fraction as a function of square root of leaching time. The error bars
625 represent the average deviation of duplicate samples.

626 Figure 7: Ca Cumulative fraction as a function of square root of leaching time. The error bars
627 represent the average deviation of duplicate samples

628 Figure 8: Sr Cumulative fraction for samples irradiated under inert conditions doped and un-doped
629 with Sr as a function of square root of leaching time.

630 Figure 9: EPMA BSE image of the untreated reference leached sample

631 Figure 10: the Sr, Ca and Ba concentration variation along a cross section in the
632 untreated reference leached sample

633 Figure 11: XRD profile of the untreated reference leached sample

Figure 12: EPMA BSC image of leached sample after treatment in the climatic chamber under inert atmosphere.

Figure 13: LA-ICP-MS Ca, Ba and Sr concentration variation along a cross section in the two leached samples after treatment under inert atmosphere.(a) climatic chamber (b) irradiated

Figure 14: Phase distribution along a cross section in the leached samples after treatment under inert atmosphere (a) in the climatic chamber (b) irradiated

Figure 15: EPMA BSE images of leached sample treated in the climatic chamber under atmospheric conditions. Zoom into the near edge area (surface on the top).

Figure 16: The Ca, Ba and Sr concentrations along a cross section in leached samples after treatment under atmospheric conditions; (a) in the climatic chamber (b) irradiated

Figure 17: Phase distribution along a cross section in the leached samples after treatment under atmospheric conditions (a) in the climatic chamber (b) irradiated

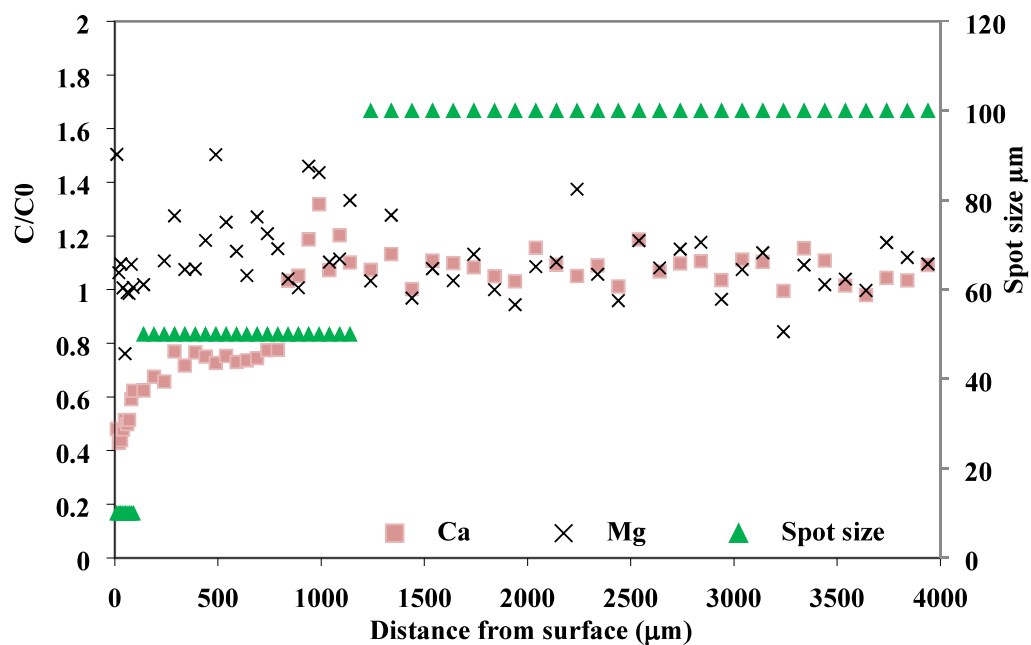


Figure 1: The sampling spot size and relative concentration of Ca and Mg as a function of the distance from the sample surface in a leached sample. C = the concentration at a specific distance, C_0 = the concentration at the undisturbed inner sample volume.

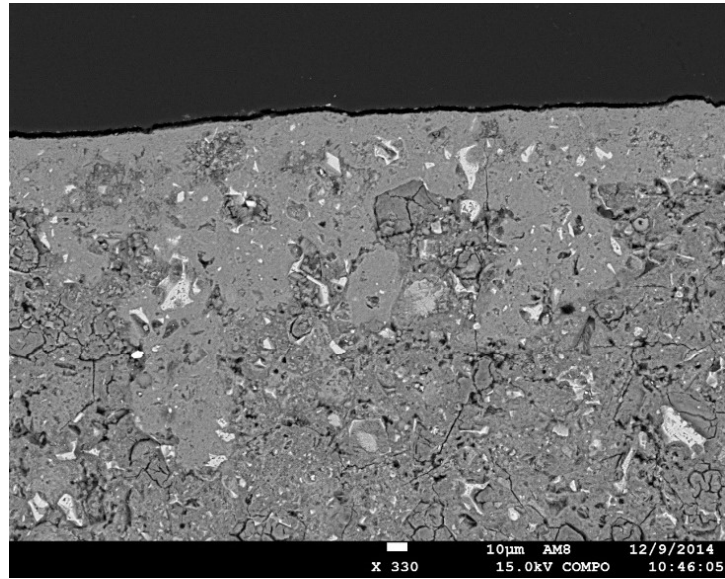


Figure 2: EPMA BSE image of sample surface irradiated under inert atmosphere.

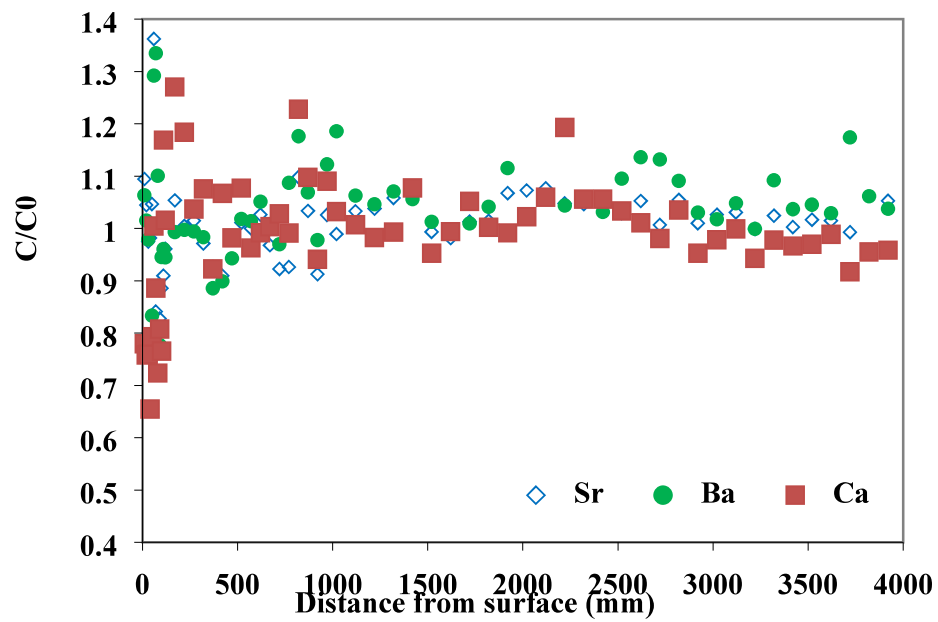


Figure 3: Relative concentration of Ca, Ba and Sr as obtained by LA-ICPMS along a cross section in a sample irradiated under inert conditions

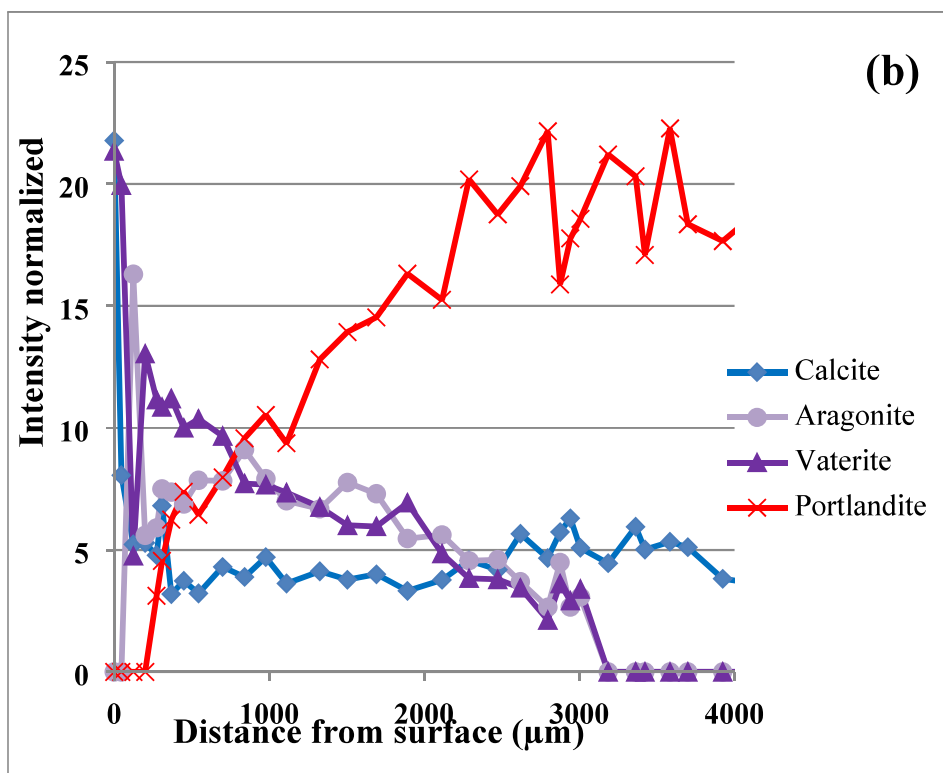
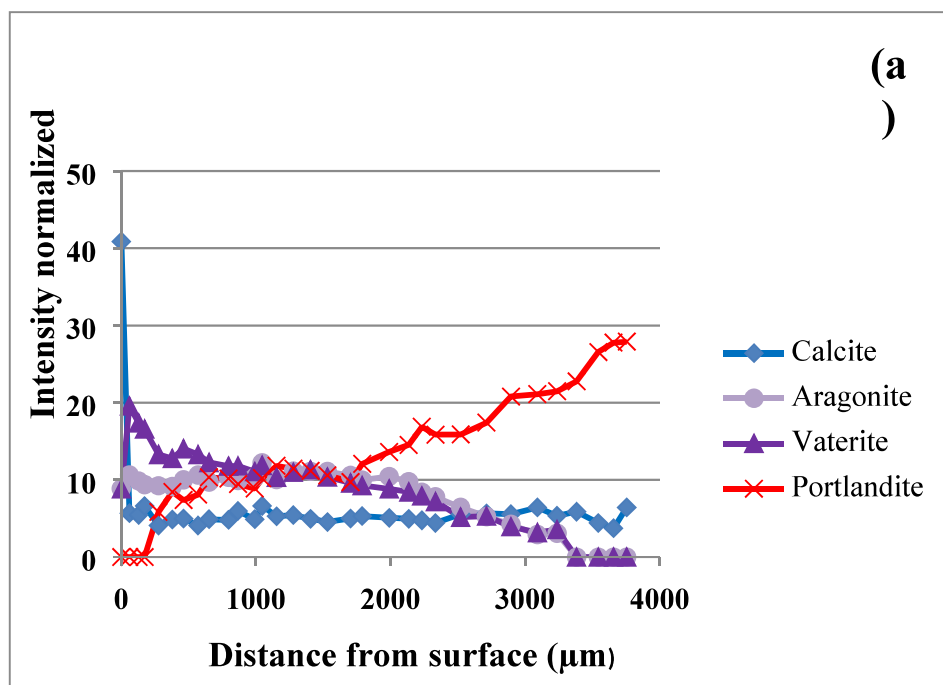


Figure 4: XRD profiles of samples treated under atmospheric conditions. (a) sample treated in climatic chamber, (b) sample irradiated

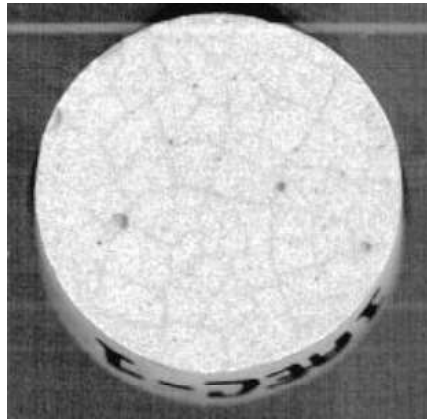


Figure 5: Cracking on sample exposed to atmospheric conditions in the climatic chamber

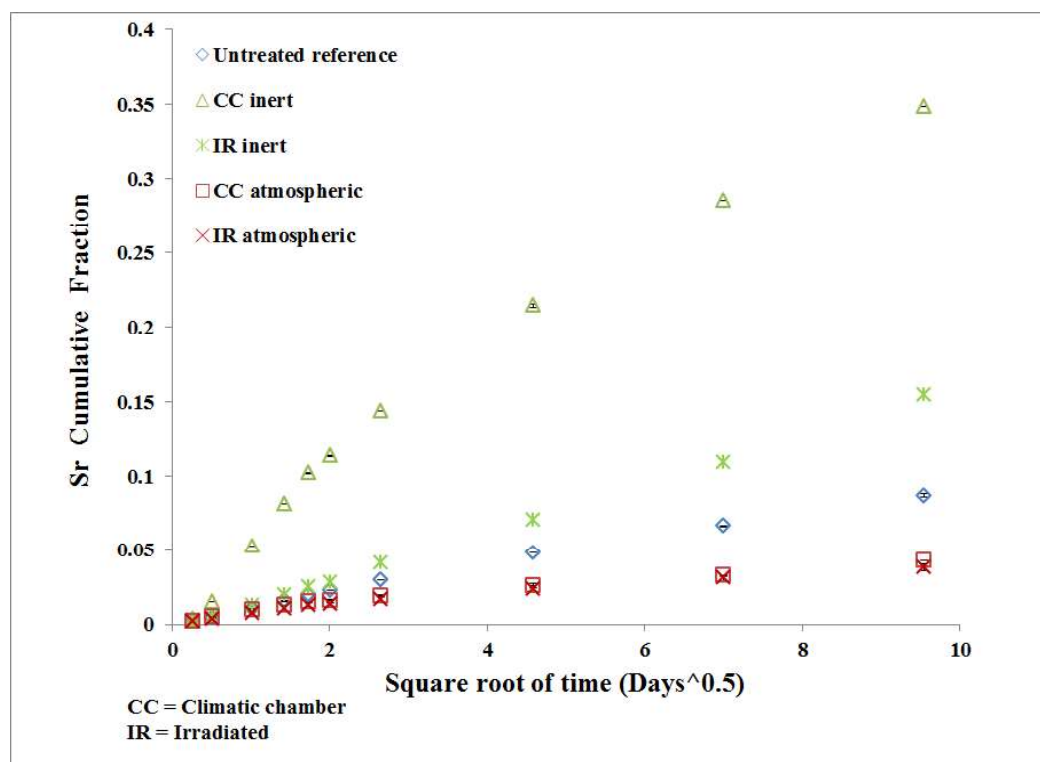


Figure 6: Sr Cumulative fraction as a function of square root of leaching time. The error bars represent the average deviation of duplicate samples.

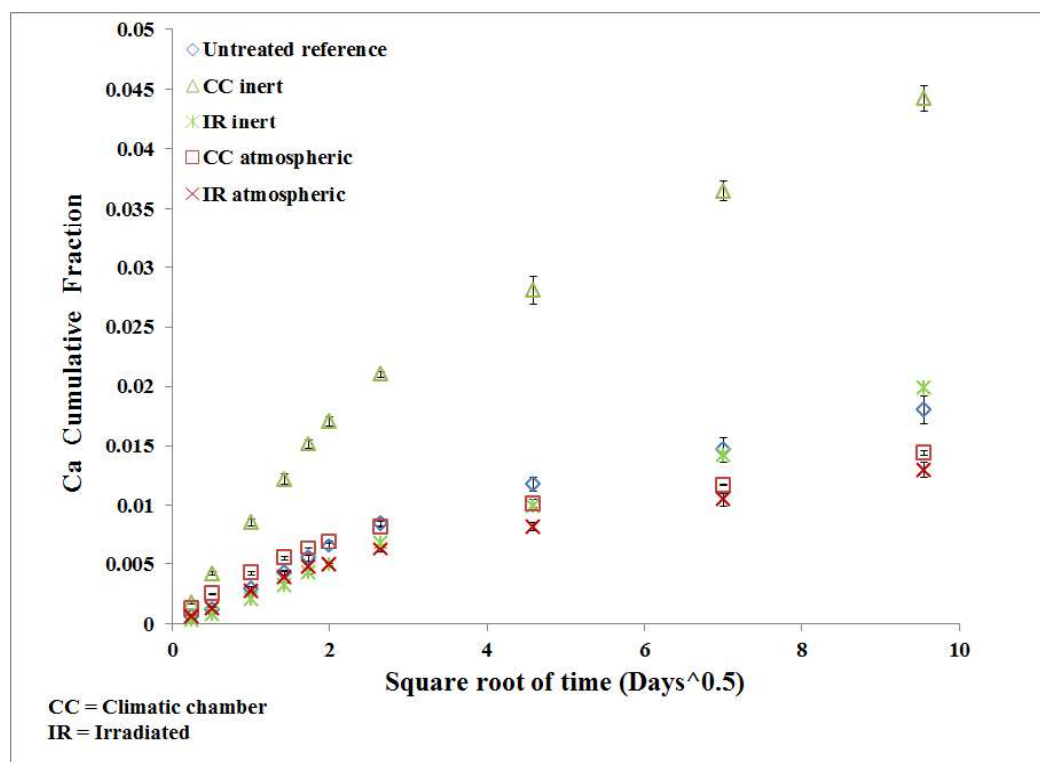


Figure 7: Ca Cumulative fraction as a function of square root of leaching time. The error bars represent the average deviation of duplicate samples

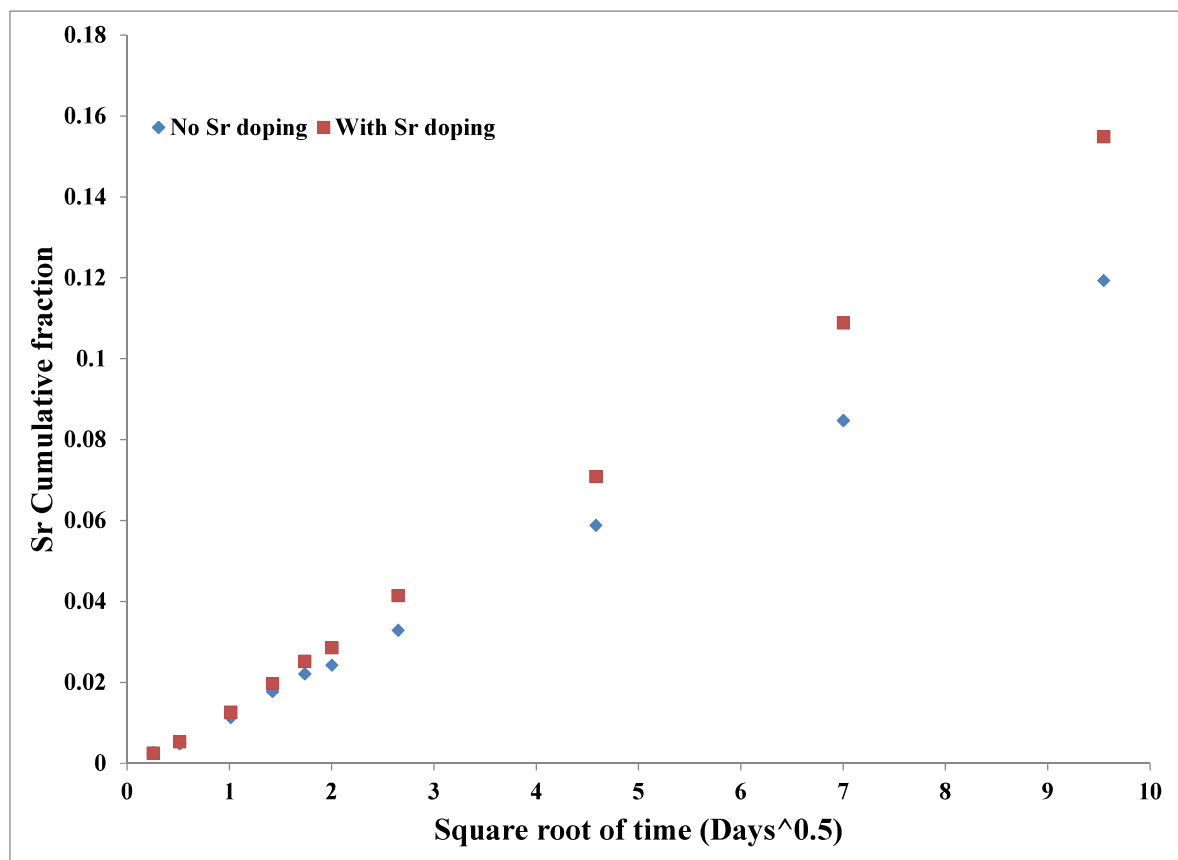


Figure 8: Sr Cumulative fraction for samples irradiated under inert conditions doped and un-doped with Sr as a function of square root of leaching time.

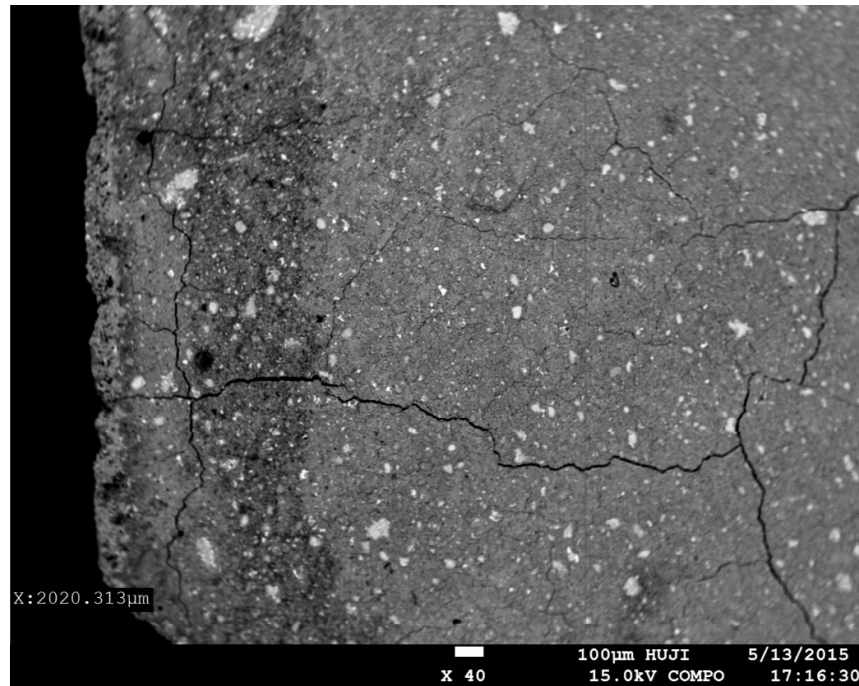


Figure 9: EPMA BSE image of the untreated reference leached sample

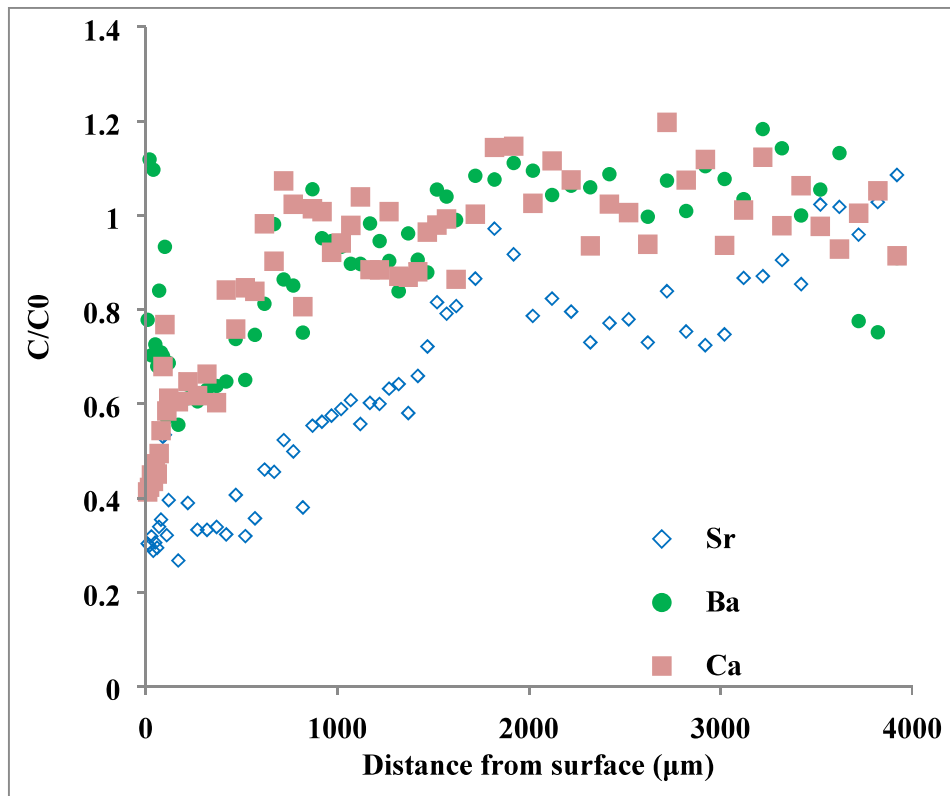


Figure 10: the Sr, Ca and Ba concentration variation along a cross section in the untreated reference leached sample

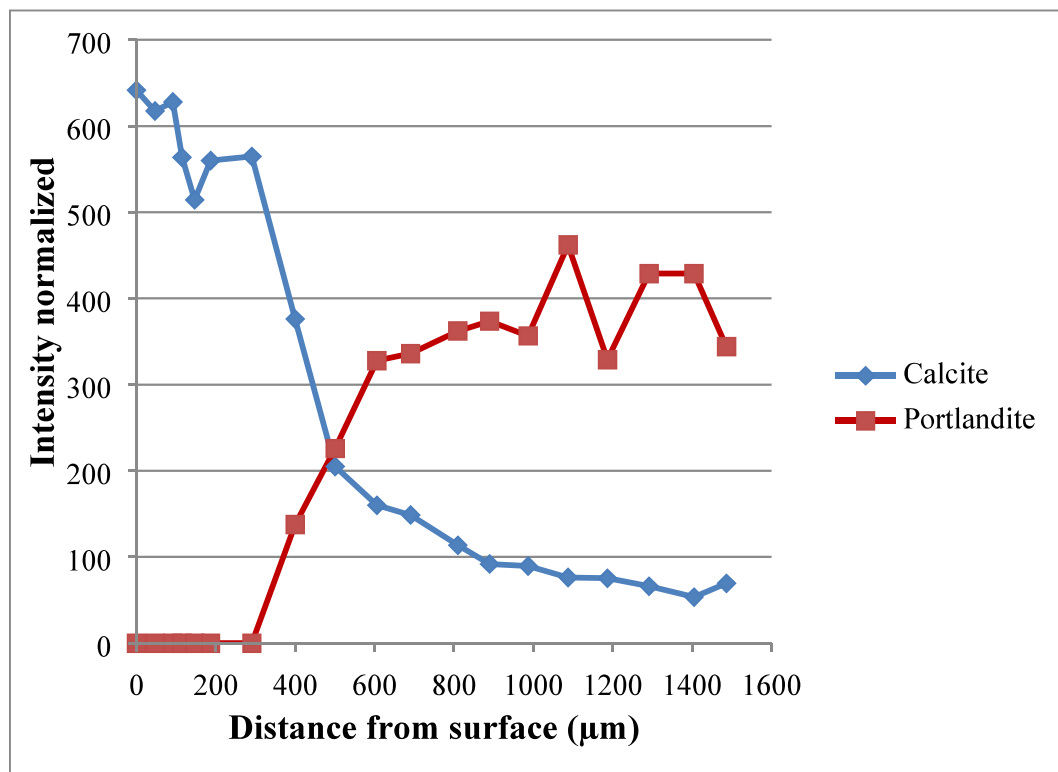


Figure 11: XRD profile of the untreated reference leached sample

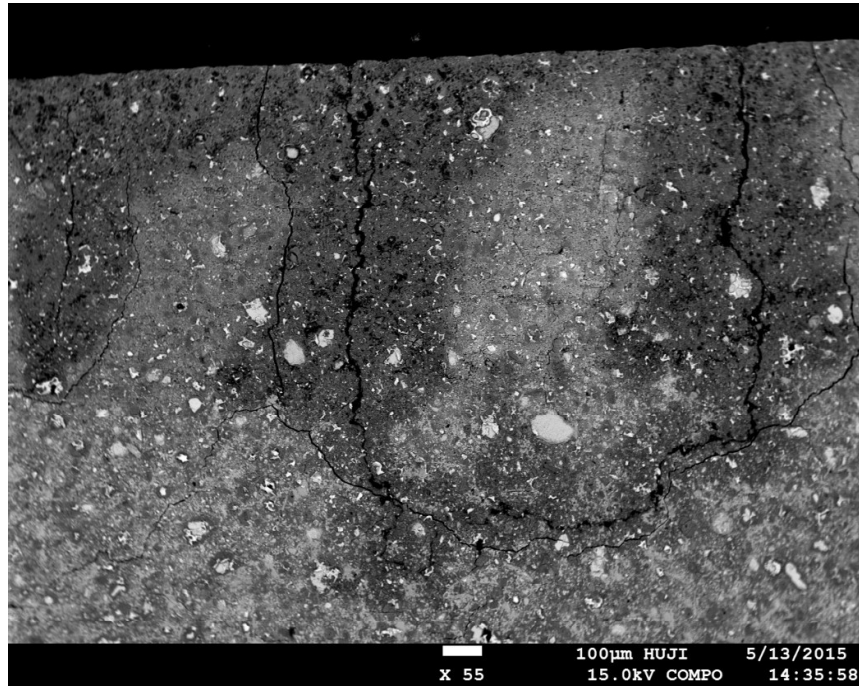


Figure 12: EPMA BSC image of leached sample after treatment in the climatic chamber under inert atmosphere.

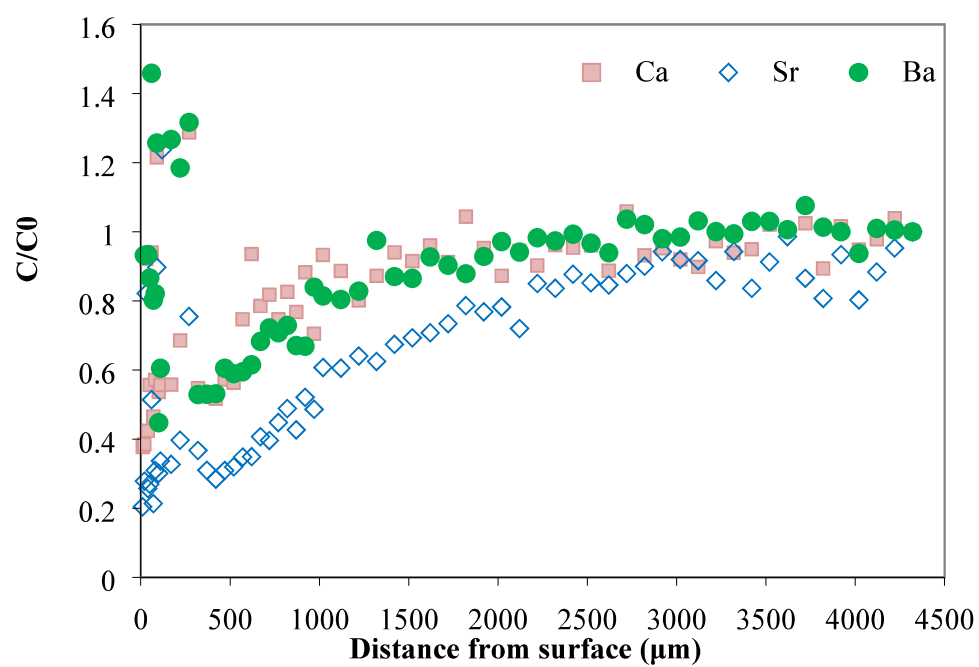
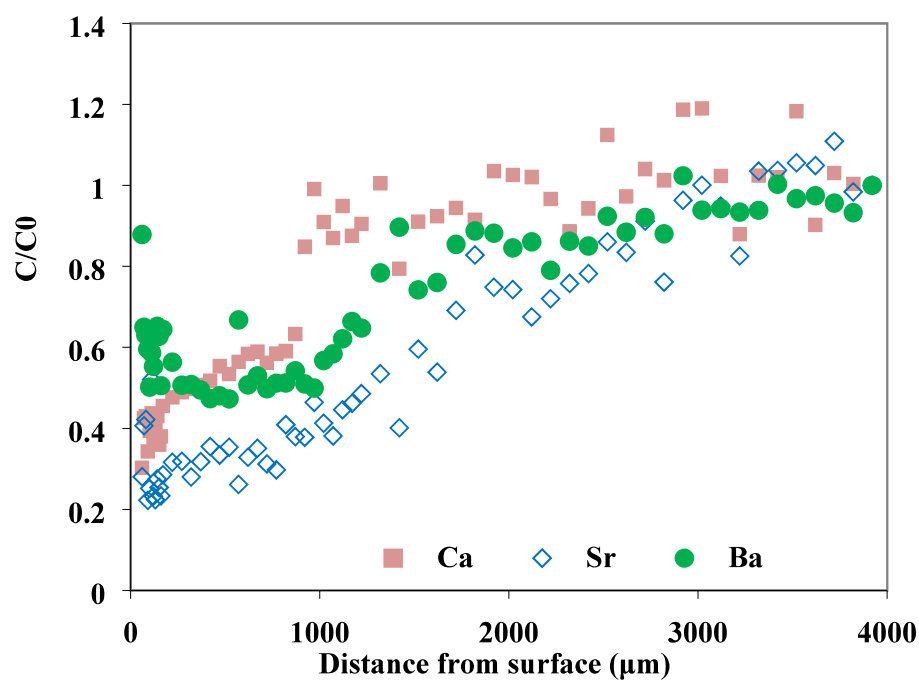


Figure 13: LA-ICP-MS Ca, Ba and Sr concentration variation along a cross section in the two leached samples after treatment under inert atmosphere:(a) climatic chamber (b) irradiated

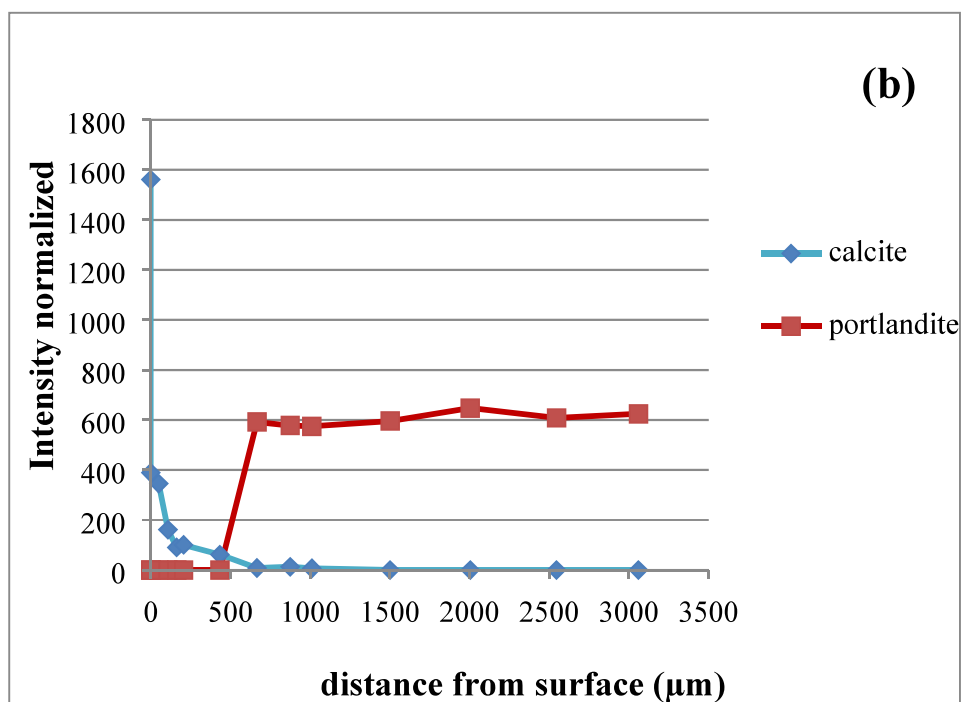
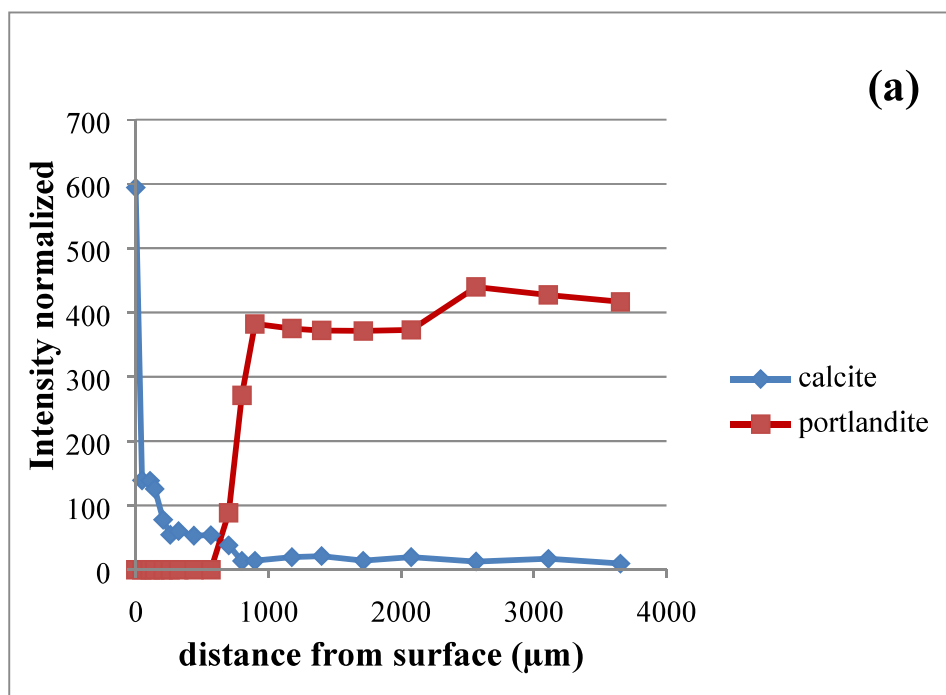


Figure 14: Phase distribution along a cross section in the leached samples after treatment under inert atmosphere (a) in the climatic chamber (b) irradiated

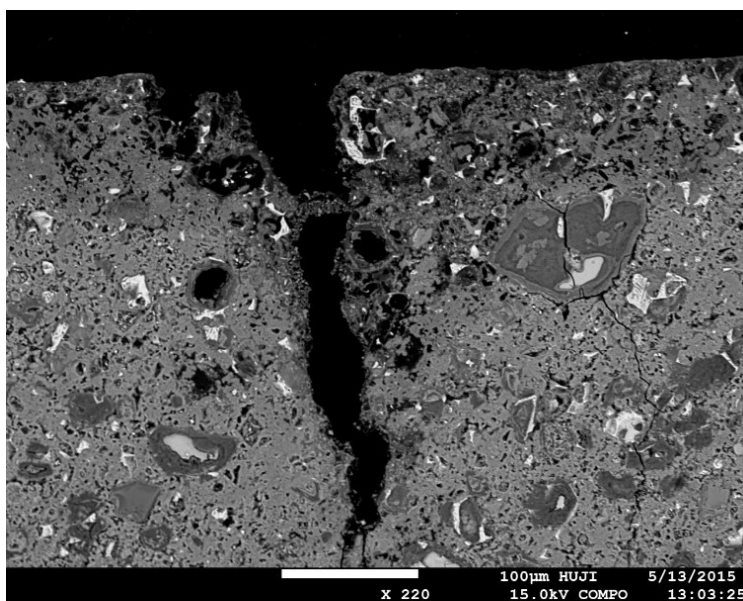


Figure 15: EPMA BSE images of leached sample treated in the climatic chamber under atmospheric conditions. Zoom into the near edge area (surface on the top).

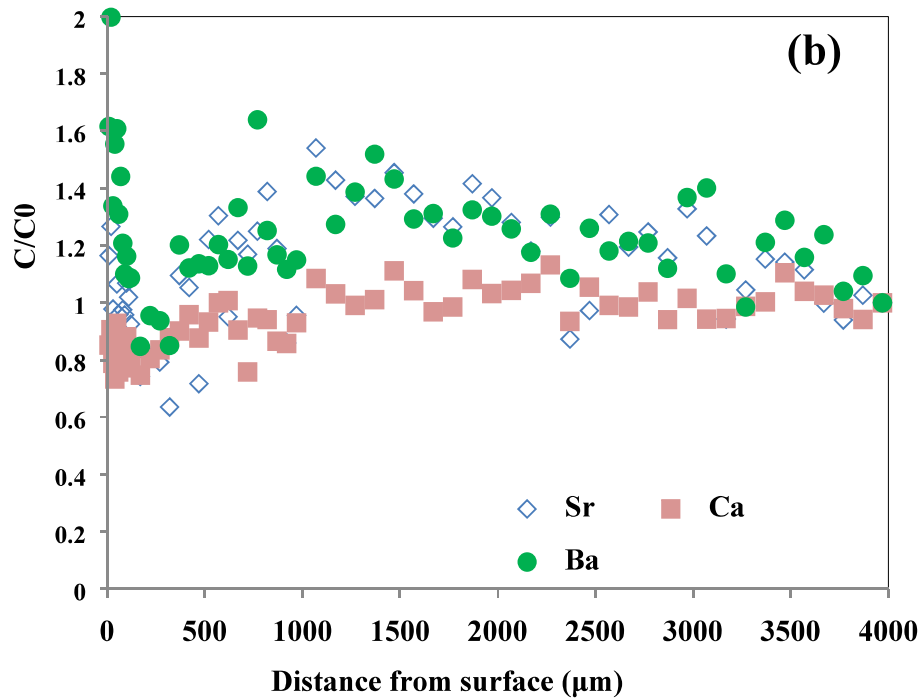
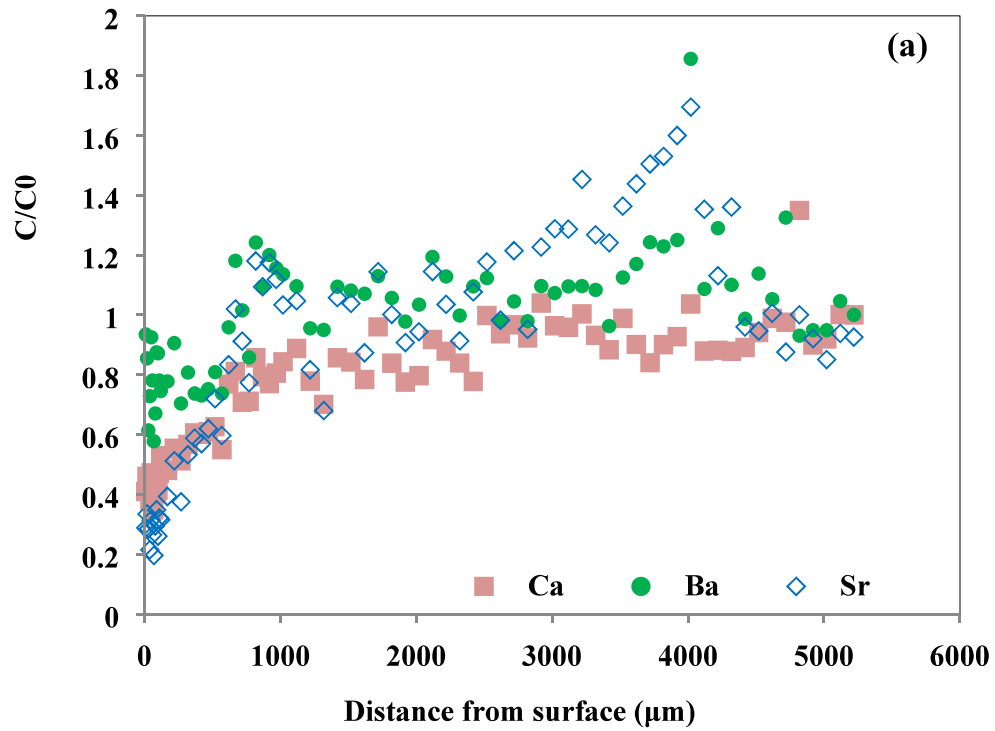


Figure 16: The Ca, Ba and Sr concentrations along a cross section in leached samples after treatment under atmospheric conditions; (a) in the climatic chamber (b) irradiated

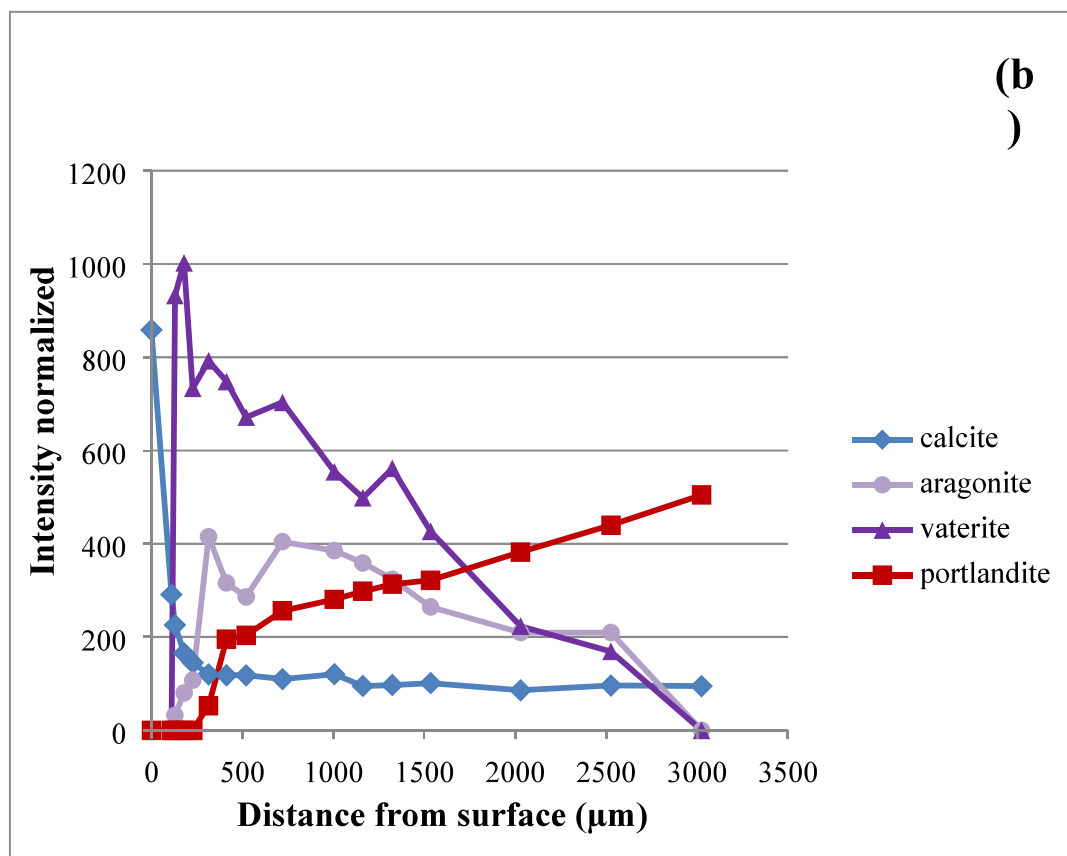
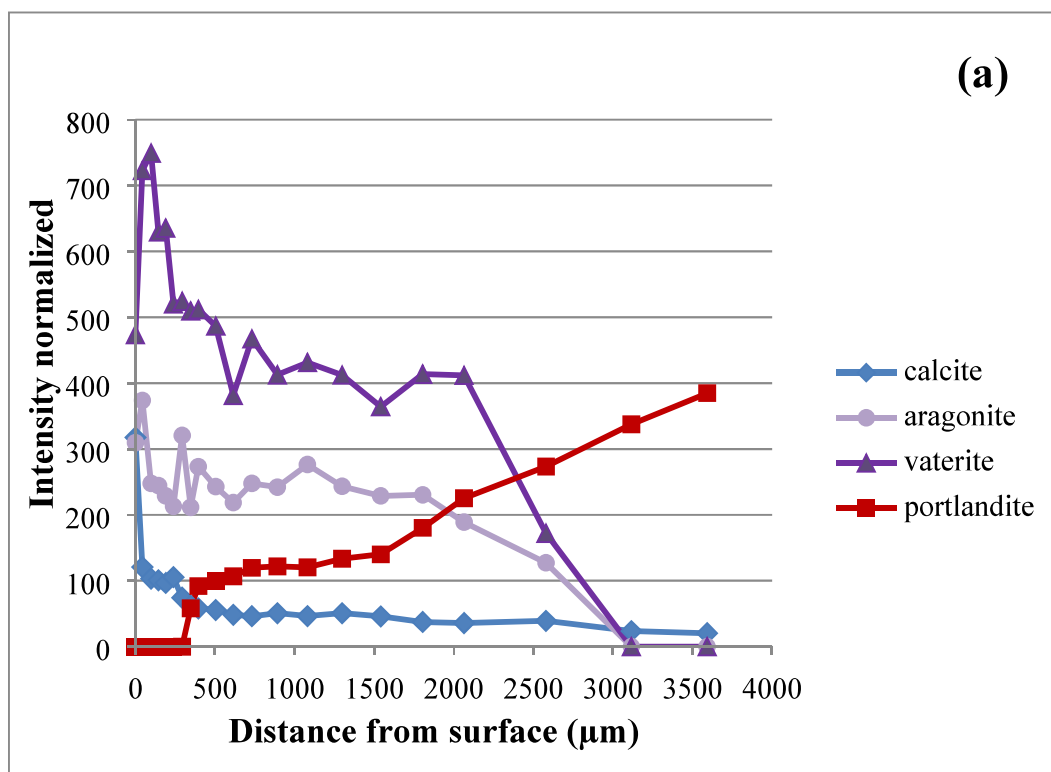


Figure 17: Phase distribution along a cross section in the leached samples after treatment under atmospheric conditions (a) in the climatic chamber (b) irradiated