Lithium in Portland cement clinker: absence of evidence is not evidence of absence

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R3 version

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Abstract

Lithium is a challenging element to analyse in mineral matrixes. The very low energy (54 eV) of its X-ray emission line makes it almost impossible to analyse by common methods such as energy dispersive spectroscopy. Hence, its localisation within cementitious phases is poorly known. Based on glow-discharge mass spectrometry (GD-MS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS), the present paper shows for the first time the repartition of Li at the scale of a microstructure of clinker with a 200 nm lateral resolution. Li is correlated to both Al and Fe in the interstitial phase, but also to Mg in periclase.

Keywords

Lithium, Portland cement clinker, ToF-SIMS, microstructure, microscopy

1 Introduction

"*Absence of evidence is not evidence of absence*" is a quote from the famous astronomer Carl Sagan (1934-1996), highlighting a deep reflection about, according to (Feres and Feres, 2023), the "*logical fallacy where a hypothesis is assumed to be true or false before being scientifically and satisfactorily investigated*". While all those implications are way beyond the topic of the present article, the above quote fits well to the quest of Li in cementitious materials.

Lithium (Z=3) is a light element widely used in the so-called Li-ion batteries, but it also covers a wide range of applications, from medicine to treat bipolar disorder (Jope, 1999) to lubricant in grease (Yonggang and Jie, 1998). Within the framework of its use in batteries, Li-bearing minerals and battery components are gaining interest in their microanalysis, since Li is complex to analyse using traditional materials science analytical devices such as energy dispersive spectroscopy (Hovington *et al.*, 2016; Grew, 2020; Thiéry and Bou Farhat, 2023)

2 Lithium in cementitious materials

Li has very specific uses in cementitious materials, as described below, but it is also present naturally in raw materials and fuels used in the burning of Portland cement clinker (PCC).

2.1 Li in the raw feed

Considering that the main part of the raw feed of cement clinker consists of a mixture of clay and limestone, which are natural materials, Li is likely to be present. Indeed, although the raw mix consists of sedimentary rocks where typical Li-bearing micas are unlikely to be present, the natural presence of Li in muscovite cannot be excluded (Korbel, Filippova and Filippov, 2023; Sulcek, Marler and Fechtelkord, 2023). Raw feed involving other types of rocks than

sedimentary ones, typically metamorphic rocks, are prone to a higher muscovite content (Korkmaz and Hacifazlioğlu, 2024).

2.2 Li in alternative fuels

Alternative fuels are widespread in cement plant in order to burn various wastes (Aranda Usón *et al.*, 2013; Rahman *et al.*, 2015). They can be both solid or liquid. Although environmental policies strongly promotes the recycling of domestic batteries, it cannot be excluded to find them in municipal solid waste (MSW) (Kayla Kilgo *et al.*, 2022).

3 Analytical challenges of Li in cementitious materials

Like in any inorganic material in Earth or materials sciences, Li is elusive and tricky to analyse in-situ (Thiéry and Bou Farhat, 2023). However, in the very specific case of cementitious materials, the analysis is made even more difficult considering their hydrous state, porosity, beam sensitivity and chemical variations at the micrometre scale (Diamond, 2004; Scrivener, 2004; Stutzman, 2004, 2012; Scrivener *et al.*, 2016; Thiéry, Trincal and Davy, 2017).

3.1 Is Li present in cementitious materials?

Prior to describing analytical possibilities to obtain qualitative or quantitative data for Li in those materials, it is worth recalling why this element is likely to be present. In the raw feed (Figure 1), clay and limestone are natural sources of Li. The Clarke (average content of an element in the continental crust) for Li is estimated at ca. 20 ppm (Teng *et al.*, 2004), which, of course, is likely to exhibit significant variations across the various geological layers. Moreover, Li seems to be almost absent from limestones, but rather concentrated in shales (Horstman, 1957). For example, Australian shales have yielded up to 109 ppm Li (Teng *et al.*, 2004), but limestone are down to 5 ppm (Horstman, 1957). However, the range of variation is really wide and highly dependent on the lithological type (Chan, Leeman and Plank, 2006).

Indeed, in sedimentary rocks, Li is associated with clay minerals (hence its presence in shales rather than in carbonates) (Zhao, Wang and Cheng, 2023).

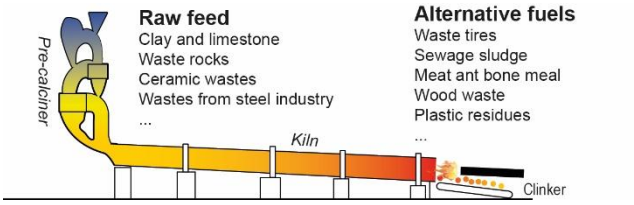

Figure 1. Schematic view of a Portland cement kiln and associated sources of Li

3.2 Analytical methods giving access to Li analysis

Laser ablation with inductively coupled plasma mass spectrometry (LA-ICP-MS) is widely used in Earth sciences but not so common in cement and concrete research (Decker *et al.*, 2021; Kleiner *et al.*, 2022). Although it yields compositional information for virtually the whole periodic table (including isotopes) down to the ppb level, the ablation crater, typically 100 micrometres in diameter, is way too large for analysis at the microscale.

Laser-induced breakdown spectroscopy (LIBS) can yield interesting results for Li analysis in solids (Gallot-Duval *et al.*, 2024). However, as for LA-ICP-MS described above, the analytical spots can in some cases exceed the size of crystals to be analysed in clinker (Sweetapple and Tassios, 2015), although recent developments in the technique allow to produce ablation craters around 5 micrometers in diameter (Berthou *et al.*, 2024).

Time of flight secondary ion mass spectrometry (ToF-SIMS) is a surface analysis technique where the sample is bombarded with short pulses of primary ions. Then secondary ions generated are collected from the first nanometers of the sample via a time of flight analyser. A spectra is then obtained with characteristic peaks of elementary and molecular ions. (Penen *et al.*, 2022). By focusing and scanning the primary ion gun, secondary ions can

be images with a lateral resolution up to 200 nm. This technique allows the analysis of all elements with a high sensitivity (ppm-ppb). However, it does not provide a quantitative estimation of the composition due to the variability of the probability of ionisation from one sample to another. It had been applied to the study of Li behaviour in concrete suffering from alkali-silica reaction (Leemann *et al.*, 2014, 2015; Bernard and Leemann, 2015).

3.3 Challenges in SEM-EDS and electron microprobe (WDS)

Although those challenges have recently been discussed (Hovington *et al.*, 2016; Thiéry and Bou Farhat, 2023), the main points will be briefly recalled here. Energy-dispersive spectroscopy (EDS, or EDX) is routinely used as an analytical tool under the SEM (Georget, Wilson and Scrivener, 2021), both as individual points or as chemical maps.

The Kα band of Li is located at 54 eV, belonging to the "ultra-soft" X-rays category. They are possible to analyse only using windowless detectors, which are not common under the SEM (Hovington *et al.*, 2016), or using very specific detectors in WDS (Polkonikov *et al.*, 2021).

3.4 Where is Li in Portland cement clinker?

In order to illustrate the above points of interest, the present study focuses on the simplest component of cement, namely Portland cement clinker. Indeed, it provides in itself enough complexity to illustrate future works related to the same topic.

Contrarily to glasses and ceramics in which the Li_2O-CaO-SiO_2 system is well known (West, 1978; Konar and Jung, 2020), scarce literature is available on the topic of Li incorporation in PCC phases. An experimental study carried out by (Woermann, Hahn and Eysel, 1979) revealed that Li is preserved during the formation of tricalcium silicate and can be incorporated up to 1,2 wt% LiO_2 in this phase. During clinkerization, it is known that a minor amount of Li_2O lowers the melting temperature, hence promoting the formation of the interstitial phase (Bhatty, 1995; Kolovos, Tsivilis and Kakali, 2002). At the microstructural

115 level, the incorporation of Li_2O in the raw feed of laboratory synthesized clinkers resulted in
116 the transformation of the borders of C_3S in a mixture of C_2S and lime (Boháč *et al.*, 2022). In
117 all examples, Li_2O was not quantified nor observed at the microstructural level.

118 Surrounding the calcium silicates in PCC, the so-called "interstitial phase" is a mixture of
119 tetra-calcium aluminate ferrite (C_4AF) with a brownmillerite structure (Colville and Geller,
120 1971), and tricalcium aluminate (C_3A). Only brownmillerite can accommodate Li in its
121 structure (Mohamed *et al.*, 2022). Hence, according to the above review, it seems that Li can
122 be present both in alite (C_3S) and ferrite (C_4AF), but this repartition has never been observed
123 experimentally.

124 **4 Materials and methods**

125 A sample of commercial Portland cement clinker was prepared for microscopy using common
126 resin embedding and polishing procedure, using water-free lubricants (Thiéry, Dubois and
127 Bellayer, 2022). To obtain the Li content of the sample, a raw chip of clinker was analysed
128 using a Nu-Astrum glow discharge mass spectrometer (GD-MS). The sample was placed on a
129 tantalum holder, within a Pin Cell cell type, under a constant flux or Ar, a glow discharge
130 potential of 1 kV with a 3 mA sample current.

131 ToF-SIMS analysis were performed on a TOF.SIMS^5 machine from IONTOF equipped with a
132 Bi primary ion source and with Cs and O_2 for sputtering. Prior to the analysis, sample was
133 eteched with O_2 sputter gun (2kV, 700nA) over an area of 700x700µm2 during 5 minutes.
134 This operation was performed in order to remove contamination induce during sample
135 preparation. Then an analysis were performed in the center of the O2 crater over an area of
136 200 x 200 µm2. Bi primary ion gun was used in burst mode (6 pulses) in order to combine
137 both a good lateral resolution and a correct mass resolution. Mass resolution obtain on this
138 condition was 2000 at m/z= 40 for Ca+. Cycle time was 70 µs and allowed us to obtain

masses up to 450 m/z. We chose 256 x 256 pixels for data acquisition and we cumulated 1000 scans to have significant intensity for Li^+ secondary ions.

5 Results and discussion

GD-MS gives a Li content of 130 ppm. This is in good agreement with the very low content of the initial raw materials used in the making of clinker's raw feed (§ 3.1 above), but also showing an enrichment relatively to its natural content in the continental crust (Teng *et al.*, 2004, 2008). The loss of volatiles during the clinkerization reactions (Kerton, 1993) might account for the concentration of Li during the firing of the raw feed.

The repartition of elements at the scale of the microstructure using ToF-SIMS is illustrated in **Erreur ! Source du renvoi introuvable.**. The results are similar to what could have been obtained with a common EDS detector: chemical maps account for a representation of the traditional phases. For instance, the correlation between Ca and Si allows to locate the calcium silicates. Ca, Al and Fe, on the other hand, are located in the so-called interstitial phase, surrounding the calcium silicates. However, the interest of ToF-SIMS in this case is to show the presence of Li, for which several correlations can be made. While there seems to be a low concentration through the entire microstructure, higher amounts, directly correlated to Al and Fe in the interstitial phase, can be seen. This is in good agreement with the description of Li substitution in ferrites and brownmillerites structures (Panda, Hota and Choudhary, 2023; Askarzadeh and Shokrollahi, 2024; Spanu *et al.*, 2024), which are classically considered as reference structures for phases from the interstitial phase of clinker. However, this had never been observed by ToF-SIMS mapping (or any other chemical map). Finally, the highest relative Li concentration in clinker is directly correlated to Mg only, implying the Mg-Li substitution in periclase MgO, which is a common (but not desirable) phase in clinker

(Song *et al.*, 2021). This substitution had already been described (Doman, Alper and Mcnally, 1968), and, interestingly, in the present case, there is no correlation with Al, while high temperature substitution of $LiAlO_2$ in the MgO lattice (Doman and McNally, 1973).

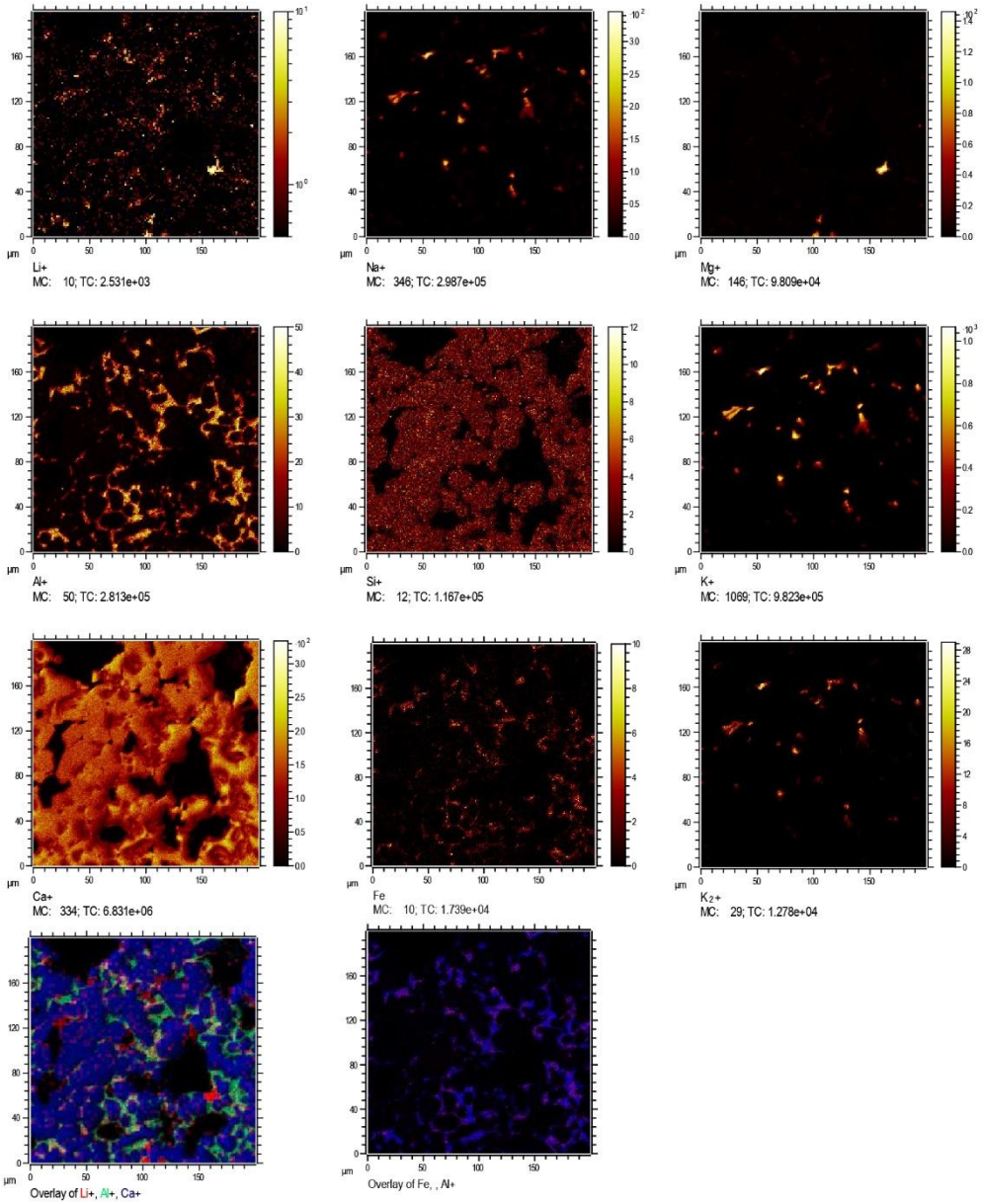

Figure 2. ToF-SIMS elemental maps on a polished section of Portland cement clinker.

ToF-SIMS hence proves itself as a really powerful tool to observe the repartition of elements such as Li within a cementitious matrix. This has already been shown for ASR mitigation (Bernard and Leemann, 2015), and in the present case it allows deciphering Li repartition in a complex matrix with a very low concentration (130 ppm). It gives perspectives for the characterization of Li-bearing products in cementitious matrix. Indeed, surface-finishing agent based on Li silicate are commonly used (Tung, Kitagaki and Yamakita, 2020; Song, Lu and Lai, 2021; Jansová *et al.*, 2023). While the effects on the water absorption and microstructure have been described, the mechanisms and the localization and nature of the Li hydrates within the cementitious matrix are unknown. In the same way, it is well known that Li has a positive effect for Portland cement setting (Witzleben, 2020), but once again, the nature and microstructure of Li-bearing hydrated cement paste is not known.

6 Conclusions

Techniques poorly used in cement science, such as GD-MS and ToF-SIMS, are currently almost the only ones yielding valuable results to quantify and localise Li in a cementitious material. Until now, the repartition of Li within the various clinker phases had never been observed. ToF-SIMS allowed us to locate its presence in the so-called interstitial phase as well as in periclase, at a very low concentration (130 ppm) in the sample.

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