Electron microprobe analysis of cryolite

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Abstract. A sample of cryolite was studied with a JEOL JXA 8500-F electron microprobe under several operating conditions. A TAP crystal was used to analyse Na and Al and a LDE1 crystal to analyse F. As F and Na are both highly “volatile” elements, special care must be taken during analysis. The measurement order of Na, F and Al is not irrelevant and optimum conditions may also result in different combinations of accelerating voltage, beam current, beam size or counting times. Relevant X-ray signals were recorded in order to investigate the behaviour of the Na Kα and F Kα counts with elapsed time. The incident beam current was also recorded at the same time. In a clear contrast to what has normally been reported in the EPMA analysis of aluminosilicates and silicate glasses, we found that the Na X-ray counts increase with time. This increment of X-rays intensities for sodium in cryolite depends on the operating conditions and is accompanied by a strong migration of fluorine from the beam excitation volume, leading to a decrease in F X-ray counting rates. It was also observed that higher incident beam currents induce higher radiation damage in the mineral. The current instability is consistent with possible electron induced dissociation in the cryolite structure. An analytical protocol was achieved for 6 kV and 15kV accelerating voltage for the correct EPMA analysis of cryolite.

1. Introduction

Cryolite (Na₃AlF₆) is an uncommon mineral, although it is the most frequent aluminofluoride in nature [1]. Its chemical composition is extremely rich in fluorine and sodium (F: 53 – 54 %; Na: 32 – 34 %). Historically, natural cryolite has been used as an aluminium ore and, more recently, as a solvent for bauxite in the electrolytic refining of aluminium, and also as a pesticide. Natural cryolite was only extracted in large quantities from a world-class deposit within a granite stock in Ivigtut, Greenland [1]. After the exhaustion of the Ivigtut deposit, another outstanding deposit of cryolite was found in the Pitinga mining district, Brazil [2, 3]. Minor occurrences of cryolite and other aluminofluorides occur around the world, mostly in peralkaline granites and pegmatites, but its rarity precludes their economic application. The unavailability of natural cryolite in economic quantities led to the production of synthetic cryolite, which is widely used in the electrolytic processing of alumina. In the last few years, there has been a growing interest on cryolite as a preferred component for thermodynamic models of peralkaline granitic and rhyolitic systems [4-6].

References to electron microprobe WDS analysis of aluminofluorides are rare in the literature, as accurate fluorine determination is still a difficult task, especially in F-rich minerals. In the case of cryolite, this analytical problem gets worse due to the coexistence of two highly “volatile” elements,
(F and Na). In this study, several WDS analyses on a cryolite sample from the Academia das Ciências de Lisboa Museum were performed under different operating conditions. Relevant X-ray count rates were recorded in order to investigate the behaviour of the Na Kα and F Kα X-ray with elapsed time. The incident beam current was also recorded at the same time in cryolite, and also in the calibrating standards used for Na (albite) and F (fluorite). The measurement order of the elements Na, F and Al was also taken into account. Both sequences F-Na-Al and Na-F-Al were used for analyses. In order to determine the effect of temperature on the cryolite structure, some heating tests followed by XRD spectra acquisition were performed at the Faculty of Sciences and Technology of Coimbra on another cryolite sample.

2. Analytical methods
The EPMA analyses were performed with a JEOL JXA 8500-F electron microprobe, at LNEG, under several operating conditions. The following standards were used for all the quantitative determinations: fluorite (F Kα), albite (Na Kα) and orthoclase (Al Kα). One WDS spectrometer, equipped with a TAP crystal, was used to analyse Na and Al and a LDE1 crystal was used to analyse F. All elements were analysed with 20 s counting times. The sample and standards were carbon coated (approx. 30 nm thickness).

The XRD spectra were obtained using a Philips X’Pert powder diffractometer, at 40 kV and 35 mA, with Co radiation (λα1 = 0.178896 nm and λα2 = 0.179285 nm), equipped with collimator and Bragg-Brentano geometry, at University of Coimbra. A cryolite was heated from room temperature to 300 °C, at 5 °C·min⁻¹ and 150 mbar against a blank of pure alumina with equivalent weight. All the tests were performed with a step size of 0.025º and a time per step of 0.5 s, in 20° - 80° range. The heating was performed at 5 °C·min⁻¹ and, after a 5 minute wait at each of the pre-defined temperatures, the spectra collection begun. The temperatures were: room temperature (RT), 60 °C, 100 °C, 205 °C, 300 °C and room temperature after cooling. The diffraction spectra were compared with ICDD (International Center for Diffraction Data) pattern no. 82-0216, which corresponds to monoclinic cryolite.

3. Results
Time-dependent X-rays intensity variation of Na Kα and F Kα in cryolite is presented in figure 1. The shaded areas show the 10s intervals of F and Na peak measurements during cryolite analysis.

At 15 kV and 1 nA, F and Na counts/s (cps) have opposite behaviours. In general, there is a decrease of F cps and an increase of Na cps with time (figures 1a and b). Furthermore, the slopes of F count rates decrease and Na count rates increase are higher for a beam diameter of 5 µm. However, in the first 10 s an increase on F count rates was recorded before it starts to drop off (figure 1a). The same phenomenon of F decrease and Na increase was observed at higher current beam (10 nA), but, for larger beam diameters, there was an increase in the F cps with time (figure 1c).

When using a lower accelerating voltage (6 kV), again the F count rate decreases with time as opposed to the increase of Na count rate, although the slopes of these variations are less steep (figure 2). At this accelerating voltage, when Na is the second element to be analysed and the beam diameter is 5 µm, the Na Kα intensity is comparatively too high and leads to an excessive Na wt% concentration (Table 1).

The increment of X-ray intensities for sodium (Na) in cryolite depends on the operating conditions and is accompanied by a strong migration of fluorine (F) from the beam excitation volume, leading to a decrease in F X-ray counting rates (figures 1 and 2). This phenomenon is in clear contrast with what has been reported to occur normally during EPMA analysis of aluminosilicates, feldspars and silicate glasses, where one usually observes a decrease in Na Kα intensities, as Na⁺ ions move away from the bombarded area [7-10]. A comparison between F and Na X-rays intensities variation has been made for cryolite, and for the calibrating standards fluorite and albite (figure 3). As can be observed, there is always a decrease in the number of X-rays counts, when compared to their initial values, except for
Figure 1. Plots showing the F (a, c) and Na (b, d) count rates in cryolite versus beam exposure time, with 15 kV accelerating voltage and a beam current of 1 nA (a, b) and 10 nA (c, d). Each point represents the average of the number of X-rays obtained in 3 seconds every 5.2 seconds, starting from $t = 2.08$ s. The shaded areas are the moments (10 s) of peak measurement, either for F or Na, during analyses (which last about 150 s each).

Figure 2. Plots showing the F (a) and Na (b) count rates in cryolite versus beam exposure time, with 6 kV accelerating voltage and a beam current of 1 nA. Each point represents the average of the number of X-rays obtained in 3 seconds every 5.2 seconds, starting from $t = 2.08$ s. The shaded areas are the moments (10 s) of peak measurement, either for F or Na, during analyses (which last about 150 s each).
**Table 1.** Electron microprobe analysis of cryolite (wt%), under different operating conditions.

| Accelerating voltage | 15 kV | 6 kV |
|----------------------|-------|------|
| Sequence of analysis | F – Na – Al | Na – F – Al | Pure cryolite a |
| Probe current (nA)   | 0.5 nA | 1 nA | 1 nA | 1 nA |
| Beam size (µm)       | 2 µm | 5 µm | 12 µm | 20 µm |
| F                    | 57.70 | 58.38 | 58.05 | 57.68 | 54.18 |
| Na                   | 37.25 | 34.47 | 34.54 | 32.86 | 31.22 |
| Al                   | 13.35 | 13.66 | 14.14 | 12.78 | 14.03 |
| Total                | 108.30 | 106.51 | 106.73 | 103.32 | 99.43 |
| n                    | 6     | 2    | 4     | 6     | 4     |

a Palache et al. 1951 [14]; n = number of analysis.

Values shown in bold are in good agreement with the ideal cryolite composition.

Na Kα counts on cryolite. For the same time interval (160 s), F Kα dropped about 16 % in cryolite and only 6 % in fluorite. The Na Kα count rates increased about 9 % in cryolite and decreased 6 % in albite (figure 3).

![Figure 3](image)

**Figure 3.** F (a) and Na (b) count rates variation with time in cryolite, fluorite (F) and albite (Na), at 15 kV, 10 nA and 10 µm beam diameter. Each point represents the average of the number of X-rays obtained in 3 seconds, every 5.2 seconds, starting from t = 2.08 s. Note that the decrease in F Kα intensities in cryolite is accompanied by an increase in Na Kα count rates during time, and neither of these situations occur in fluorite or albite at the same operating conditions.
Some secondary electron images (SEI) and electron backscattered images (COMP) were taken at the end of three WDS quantitative analysis on cryolite, all at 15 kV and 3 different probe currents: 0.5 nA, 1 nA and 10 nA. The electron beam damage induced on cryolite is evident, and, as it would be expected, higher incident beam currents induce higher radiation damage in the mineral (figure 4).

![Figure 4](image)

**Figure 4.** Secondary electron images (SEI) and backscattered electron images (COMP) of cryolite after EPMA analyses with 20 s counting times for each element. Only one WDS spectrometer was used to analyse the 3 elements (F, Na and Al).

In addition to the beam damage induced within the interaction volume in the mineral, one could also observe considerable fluctuations on sample current (probe current measured from the sample) with the elapsed time (figure 5). For 15 kV, 1 nA (nominal beam current) and Ø = 10 µm, the sample current measured decreases drastically after about 105 s for cryolite and remains relatively unchanged for albite and fluorite.

Some calculated and experimental data on thermal conductivity for NaF-AlF₃ molten mixtures have been published [11, 12]. However, the authors are unaware of the exact value of solid cryolite thermal conductivity, which precludes the application of the equation proposed by Castaing to calculate the temperature rise under electron bombardment [13]. Nevertheless, assuming that cryolite might have a low thermal conductivity value, one may expect a considerable local rise in temperature induced by the electron beam.

In order to investigate the influence of the temperature rise in the cryolite structure, several heating tests followed by XRD spectra acquisition were performed. The results obtained showed that heating a cryolite sample up to 300 °C does not change the structure of the mineral (figure 6). Therefore, the observed damage induced on cryolite may not be attributed to a temperature increase, but to the electron beam interaction with the structural lattice.
Figure 5. Fluctuations of sample current (nominally set at 1 nA) versus time, in albite, fluorite and cryolite, with 15 kV and a 10 µm beam diameter. Sample current decreases drastically after about 105 s exposure time in cryolite.

Figure 6. Some XRD spectra obtained during heating of a cryolite sample, showing that from room temperature (RT) to 300 ºC there is no structural dissociation of cryolite.

Table 1 presents some results of WDS analysis on cryolite performed with only 1 spectrometer for 2 values of accelerating voltage: 15 kV and 6 kV, 2 sequences of analysis (F-Na-Al and Na-F-Al) and several incident beam currents and beam diameters. Some WDS analysis were also performed scanning the beam in a raster (15 kV, 1 nA) for the analysis sequence Na-F-Al, but the results were unacceptable for fluorine (F = 57.69 % average of 4 analysis), although acceptable for the determination of sodium (Na = 31.38 %).

4. Discussion
Variations in time of the apparent concentrations of sodium and/or fluorine upon electron bombardment of minerals and glasses have been described over the years [7-9, 15-18]. Sample damage under electron beam bombardment and an unexpected behaviour of the so-called sodium migration in alkali silicate glasses have also been discussed earlier [15, 16]. These authors had observed that, after an initial loss of Na within the first seconds, there is a reversal effect with increasing Na cps values, in particular when using small beam diameters and relatively high probe currents. A similar behaviour of Na migration during electron probe microanalysis was described for hydrated silicate minerals, such as zeolites [19, 20]. Even minerals like petzite, a silver-gold telluride
made up of conductive heavy elements, can reveal significant compositional changes during electron microprobe analysis, which can be ascribed to the semi-conducting properties of the mineral [21].

The charging effects due to electron bombardment on metallic coated insulators have been studied previously [22]. The model calculates the non-uniform electric field distribution which influences the secondary electron yield value ($\delta$) and the surface potential ($V$), causing the ion migration. The oxygen desorption from glasses, measured by mass spectrometry [7], can be explained by this model, as well as the local compositional changes in alkali silicate glasses [15].

In the specific case of cryolite, a superionic compound [23], the diffusion of fluorine and sodium under electron bombardment is clearly enhanced.

During an investigation on the effect of electron bombardment on the secondary electron emission from cryolite, at a low value of primary energy beam (~ 400eV), it was observed that, while the secondary electron emission coefficient ($\delta$) was falling, fluorine atoms escaped from the surface, eventually producing a surface metallic layer of Al and Na [24]. As demonstrated by [25], electron beam induced dissociation occurs in cryolite. Fluorine loss from the electron bombarded cryolite was observed and attributed to the emission of fluorine atoms and, to a lesser extent, simultaneous diffusion of fluorine from the surrounding mineral structure into the area depleted by the electron bombardment. However, no desorbed F was observed when heating the sample at $\approx 200$ °C [25]. This electron induced dissociation of cryolite can be inferred to have also occurred under the operating conditions used in this study. The imbalance between desorbed F atoms and adsorbed F- ions that occur at different operating conditions, may explain the difficulties in obtaining reliable analyses of F in this mineral.

5. Conclusions
Cryolite is highly sensitive to electron beam radiation even with a defocussed beam. The problem gets worse with the increase of beam current. Cryolite damage observed under the electron bombardment may occur sooner (higher currents), or later (lower currents). The high drop of sample current, as shown in figure 5 after about 105 s elapsed time, is an indication of a severe damage to the structure.

Heating tests followed by XRD spectra acquisition showed that heating a cryolite sample up to 300 °C does not change the structure of the mineral (figure 6). Therefore, the observed cryolite damage may not be solely attributed to the temperature increase, but mainly to the electron beam interaction with the structure lattice.

Despite these problems, it is possible to perform quantitative EPMA analysis of cryolite, using only one WDS spectrometer, providing that:
- short counting times are used;
- Na must be the first element in the analysis sequence;
- F is the second element in the analysis sequence;
- a low probe current is used;
- the beam must be defocused within a limited range.

Acknowledgments
This research is partially sponsored by FEDER funds through the programme COMPETE (Programa Operacional Factores de Competitividade) and by national funds through FCT (Fundação para a Ciência e a Tecnologia), under the project PEst-C/EME/UI0285/2013. This paper was substantially improved by the helpful comments of Prof. Romano Rinaldi and an anonymous reviewer.

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