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. Some X-Ray signals were recorded in order to investigate the behaviour of the Na $K\alpha$ and F $K\alpha$ X-ray counts with the elapsed time. The incident beam current was also recorded at the same time. In a clear contrast to what happens in the EPMA analysis of aluminosilicates and silicate glasses, we found that Na X-ray counts increase with time. This grow-in 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.

1. Introduction

Cryolite (Na_3AlF_6) 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 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, 5, 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

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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. Some X-Ray count rates were recorded in order to investigate the behaviour of the Na $K\alpha$ and F $K\alpha$ X-ray counts with the 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 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 $K\alpha$), albite (Na $K\alpha$) and orthoclase (Al $K\alpha$). Only one WDS spectrometer was used, equipped with a TAP crystal to analyze Na and Al and a LDE1 crystal was used to analyze F. All elements were analysed with 20 s counting times.

The XRD spectra were obtained using a Philips X'Pert, at 40 kV and 35 mA, with Co radiation ($\lambda\alpha1$=0.178896 nm and $\lambda\alpha2$=0.179285 nm), equipped with collimator and Bragg–Brentano geometry, at University of Coimbra. A cryolite was heated from room temperature to 300ºC, at 5ºC·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 20–80º range. The heating was performed at 5ºC·min-1 and after a 5 minute wait at each of the pre-defined temperature the spectra collection begun. The temperatures were: room temperature (RT), 60ºC, 100ºC, 205ºC, 300ºC and room temperature after cooling. The diffraction spectra were compared with ICDD (International Center for Diffraction Data) pattern nº82-0216, which corresponds to monoclinical cryolite.

3. Results

Time-dependent X-rays intensity variation of Na $K\alpha$ and F $K\alpha$ 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's a decrease of F cps and an increase of Na cps with time (figure 1a, 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 its drop off (figure 1a). The same phenomenon of F decrease and Na grow-in was observed at higher current beam (10 nA), but, for larger beam diameters, there was an increase in the F cps (figure 1c).

When using a lower accelerating voltage (6kV), again the F count rate decreases with time as opposed to the increase of Na count rate, although the slopes of these variations are smaller (figure 2). At this accelerating voltage, when Na is the second element to be analysed and the beam diameter is 5 μm, the Na $K\alpha$ intensity is too high and leads to a excessive Na weight % concentration (table 1).

The *grow-in* 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, 2). This phenomenon is a clear contrast to what happens during EPMA analysis of aluminosilicates, feldspars and silicate glasses, where there is a decrease in Na $K\alpha$ intensities, as Na⁺ ions move away from the bombarded area [7, 8]. 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 Na $K\alpha$ counts on cryolite. For the same time interval (160 s), F $K\alpha$ dropped about 16 % in cryolite and only 6 % in fluorite. The Na $K\alpha$ count rates increased about 9 % in cryolite and decreased 6 % in albite (figure 3).
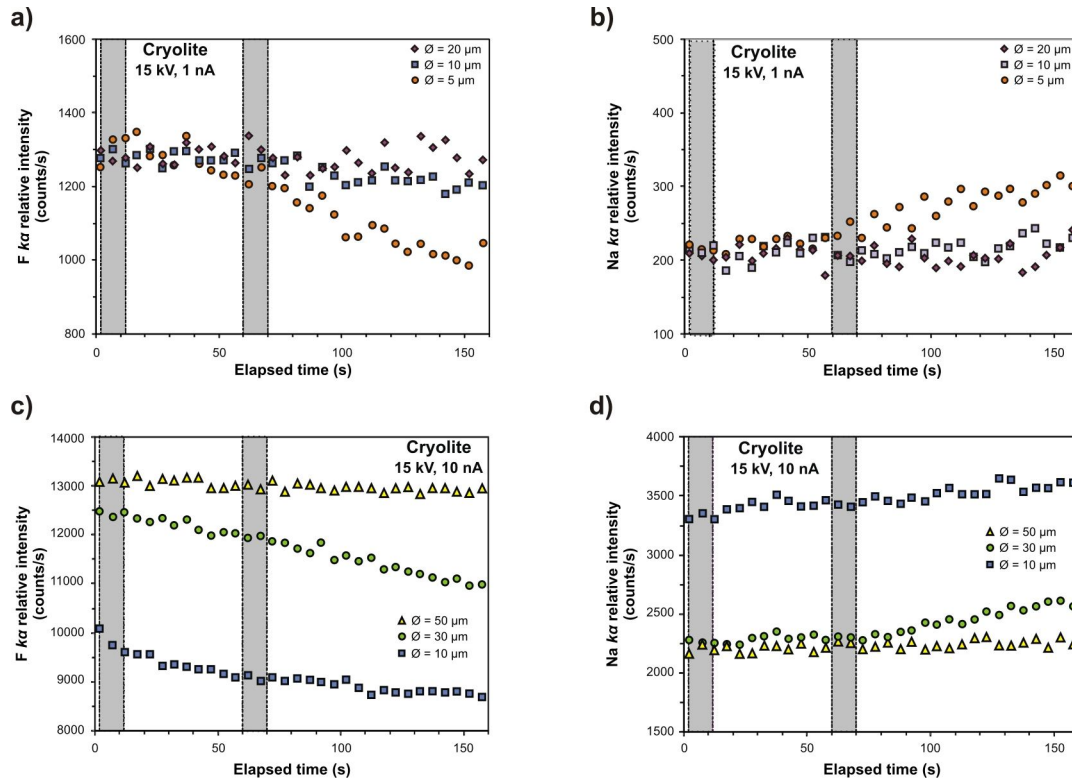
Figure 1. Plots showing the F (a, c) and Na (b, d) count rates in cryolite *versus* beam exposure time, with 15 kV accelerating voltage and a beam current of 1 nA (a, b) and 10 nA (c, d). Each point represents the average of the number of X-rays obtained in 10 readings in a 5 s interval, starting from t=2.08 s. The shaded areas represent the time intervals of F and Na X-rays peak measurements during cryolite analysis. All elements were analysed with 20 s counting times.
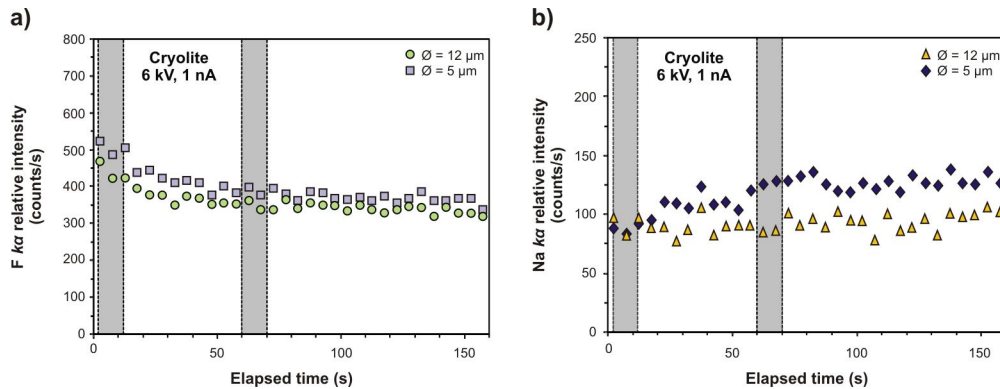

Figure 2. Plots showing the F (a) and Na (b) count rates in cryolite *versus* beam exposure time, with 6 kV accelerating voltage and a beam current of 1 nA. Each point represents the average of the number of X-rays obtained in 10 readings in a 5 s interval, starting from t=2.5 s. The shaded areas represent the time intervals of F and Na X-rays peak measurements. All elements were analysed with 20 s counting times.
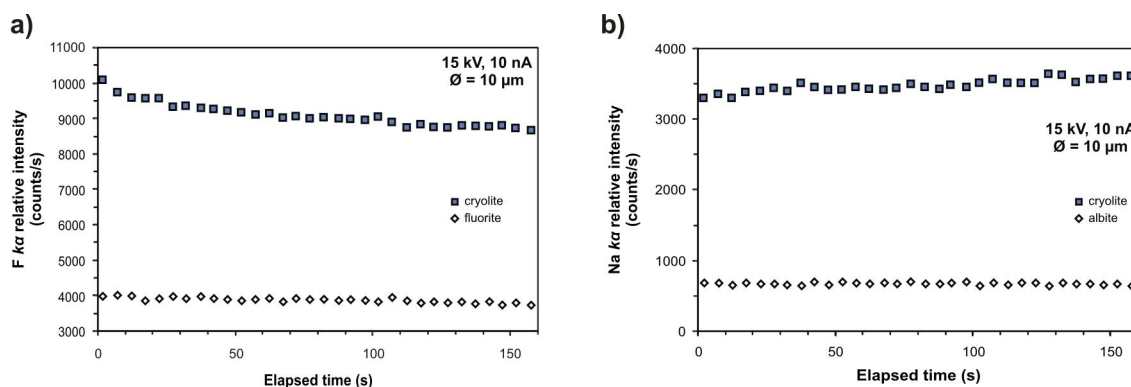
Figure 3. F (a) and Na (b) count rates variation with time in cryolite, fluorite (F) and albite (Na), at 15 kV, 10 nA and 10 μm beam diameter. Each point represents the average of the number of X-rays obtained in 10 readings in a 5 s interval, starting from t=2.08 s. Note that the decrease in F $K\alpha$ intensities is accompanied by an increase in Na $K\alpha$ 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 15kV and 3 different probe currents: 0.5nA, 1nA and 10nA. It is evident the surface damage induced by the electron beam on cryolite, and, as it would be expected, higher incident beam currents induce higher radiation damage in the mineral surface (figure 4).
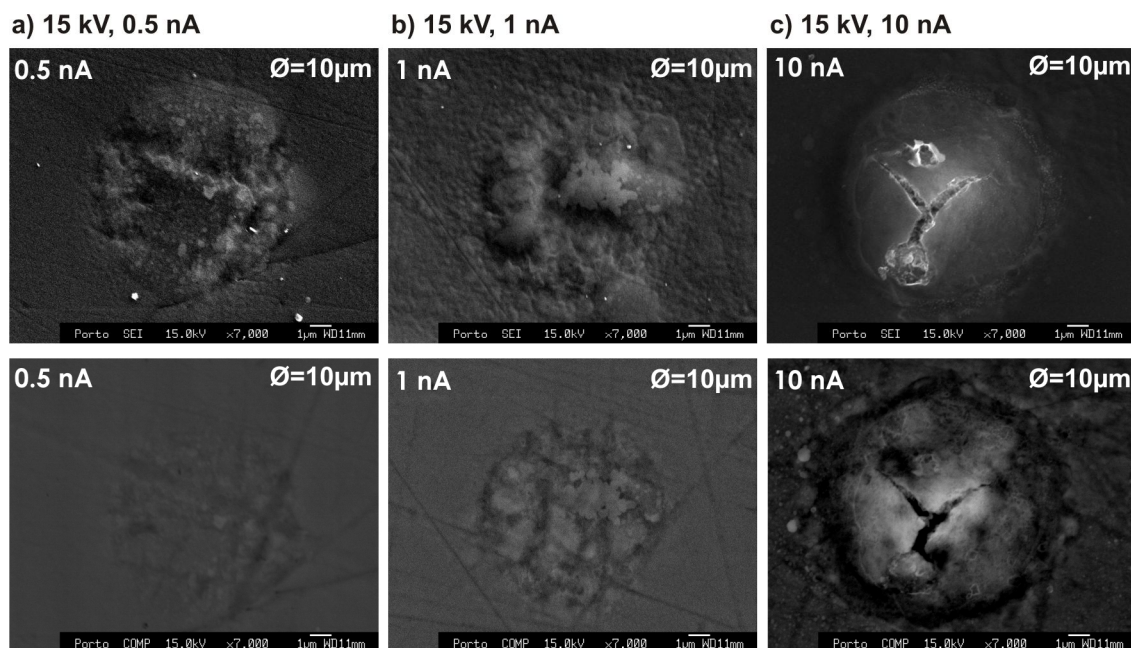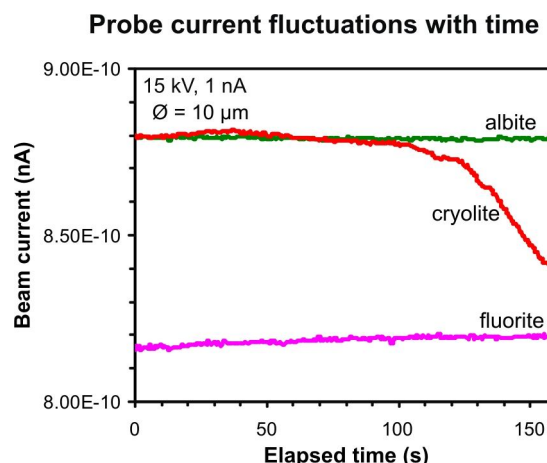

Figure 4. Secondary electron images (SEI) and backscattered electron images (COMP) of cryolite after EPMA analyses with 20 s counting times for each element. Only one WDS spectrometer was used to analyse the 3 elements (F, Na and Al).

In addition to the damage of the mineral surface, one could also register fluctuations on probe current with the elapsed time (figure 5). For 15kV, 1 nA and Ø=10µm, probe current decreases drastically after about 105s for cryolite and remains relatively unchanged for albite and fluorite.

Probe current fluctuations with time

Figure 5. Fluctuations of probe current (set at 1 nA) *versus* time, in albite, fluorite and cryolite, with 15 kV and a 10 µm beam diameter. Current probe decreases drastically after about 105 s exposure time in cryolite.

Being cryolite a low thermal conductivity material, it is expected that a considerable local rise in temperature may occur, induced by the electron beam [8].

In order to investigate the influence of 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 until 300ºC does not change the structure of the mineral (figure 6). Therefore, the observed cryolite surface damage may not be attributed to a temperature increase, but to the electron beam interaction with the structural lattice.

Figure 6. Some XRD spectra obtained during heating of a cryolite sample, showing that from room temperature (RT) to 300º C there is no structural dissociation of cryolite.
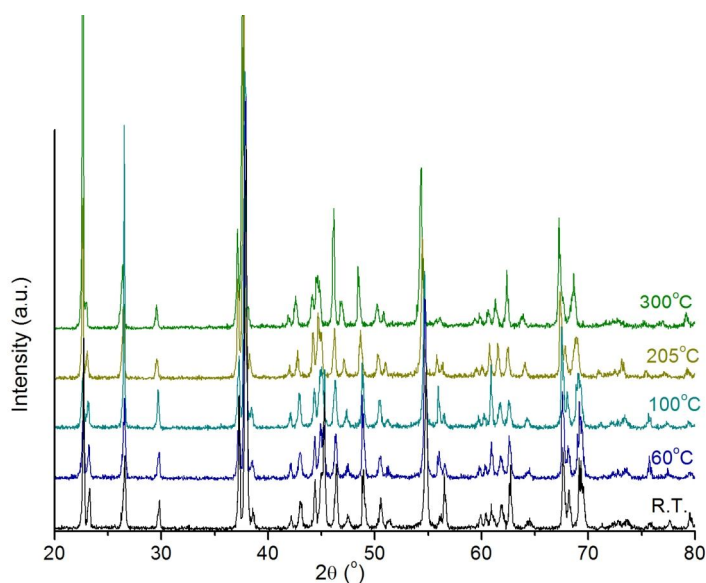
Table 1 presents some results of WDS analysis on cryolite performed with only 1 spectrometer for 2 values of accelerating voltage: 15 kV and 6 kV, 2 sequences of analysis (F-Na-Al and Na-F-Al) and several incident beam currents and beam diameters. Some WDS analysis were also performed scanning the beam in a raster (15kV, 1 nA) for the sequence of analyse Na-F-Al, but the results were

unacceptable for fluorine (F= 57,69% average of 4 analysis), although not so bad for the determination of sodium (Na =31.38%).

Table 1. Electron microprobe analysis of cryolite (wt. %), under different operating conditions.

Accelerating voltage	15 kV							
Sequence of analysis	F – Na – Al				Na – F – Al			
Probe current (nA)	0.5 nA	1 nA	5 nA	10 nA	**0.5 nA**	**1 nA**	**5 nA**	10 nA
Beam size (µm)	2 µm	5 µm	12 µm	20 µm	**2 µm**	**5 µm**	**12 µm**	20 µm
F	57.70	58.38	58.05	57.68	**54.18**	**55.02**	**53.85**	56.78
Na	37.25	34.47	34.54	32.86	**31.22**	**32.04**	**31.68**	32.09
Al	13.35	13.66	14.14	12.78	**14.03**	**13.31**	**13.94**	13.01
Total	108.30	106.51	106.73	103.32	**99.43**	**100.37**	**99.47**	101.88
n	6	2	4	6	4	6	9	12

Accelerating voltage	6 kV						
Sequence of analysis	F – Na – Al		Na – F – Al				
Probe current (nA)	1 nA	1 nA	1 nA	**1 nA**	Pure cryolite [a]		
Beam size (µm)	5 µm	12 µm	5 µm	**12 µm**			
F	55.06	57.76	40.68	**54.67**	F	54.29	
Na	43.66	32.36	40.42	**31.47**	Na	32.86	
Al	15.20	13.72	15.23	**13.70**	Al	12.85	
Total	113.92	103.84	96.33	**99.84**	Total	100.00	
n	5	5	4	5			

[a] Palache *et al.* [6]; n – number of analysis.
Values shown in bold are in good agreement with the ideal cryolite composition.

4. Conclusions

Cryolite is highly sensitive to electron beam radiation even with a defocused beam. The problem rises 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 probe current (figure 5) is an indication of a clear damage in the structure. As has been demonstrated by [10] an electron beam induced dissociation occurs on cryolite. They proved to exist fluorine loss from the electron bombarded cryolite, due to the emission of fluorine atoms and, simultaneously, diffusion of fluorine ions into the area depleted by electron bombardment. However, no desorbed F was observed when heating the sample at ≈200 ºC. This electron induced dissociation of cryolite also occured under the operating conditions used in this study. The balance between desorbed F atoms and adsorbed F⁻ ions may explain the difficulties in the analysis of F.

Heating tests followed by XRD spectra acquisition showed that heating a cryolite sample until 300ºC does not change the structure of the mineral (figure 6). Therefore, the observed cryolite surface damage may not be attributed to a temperature increase, but to the electron beam interaction with the structural 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 sequence of analyse;
- F is the second element in the sequence of analyse;
- a low probe current is used;
- the beam must be defocused within a limited range.

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