

## Electron microprobe analysis of cryolite

F Guimarães<sup>1</sup>, P Bravo Silva<sup>1</sup>, J Ferreira<sup>1</sup>, A P Piedade<sup>2</sup> and M T F Vieira<sup>2</sup>

<sup>1</sup> LNEG - National Laboratory of Energy and Geology, Rua da Amieira, Ap. 1089, PT-4466-901 S. Mamede de Infesta, Portugal

<sup>2</sup> University of Coimbra, Faculty of Sciences and Technology, Department of Mechanical Engineering, Rua Silvio Lima, PT-3030-790 Coimbra, Portugal

E-mail: fernanda.guimaraes@lneg.pt

**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 K $\alpha$  and F K $\alpha$  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 (Na<sub>3</sub>AlF<sub>6</sub>) 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,

