ELECTRON MICROPROBE ANALYSIS OF CRYOLITE

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Cryolite (Na_3AlF_6) is an uncommon aluminofluoride, with a chemical composition 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. After the exhaustion of Ivigtut deposit, another outstanding deposit of cryolite was found in the Pitinga mining district, Brazil. Minor occurrences of cryolite and other aluminofluorides occur around the world, 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.

References to electron microprobe analysis of aluminofluorides in the literature are vague and the authors did not find any published quantitative analysis of cryolite by WDS. A sample of cryolite from the Academia das Ciências de Lisboa Museum was studied with a JEOL JXA 8500-F electron microprobe under several operating conditions. A TAP crystal was used to analyze Na and Al and a LDE1 crystal to analyse fluorine.

As F and Na are both highly volatile elements, 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 beam current, spot size or counting times.

Some X-ray signals were recorded in order to investigate the behaviour of the Na Kα and F Kα 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 15 kV accelerating potential and several incident beam currents.