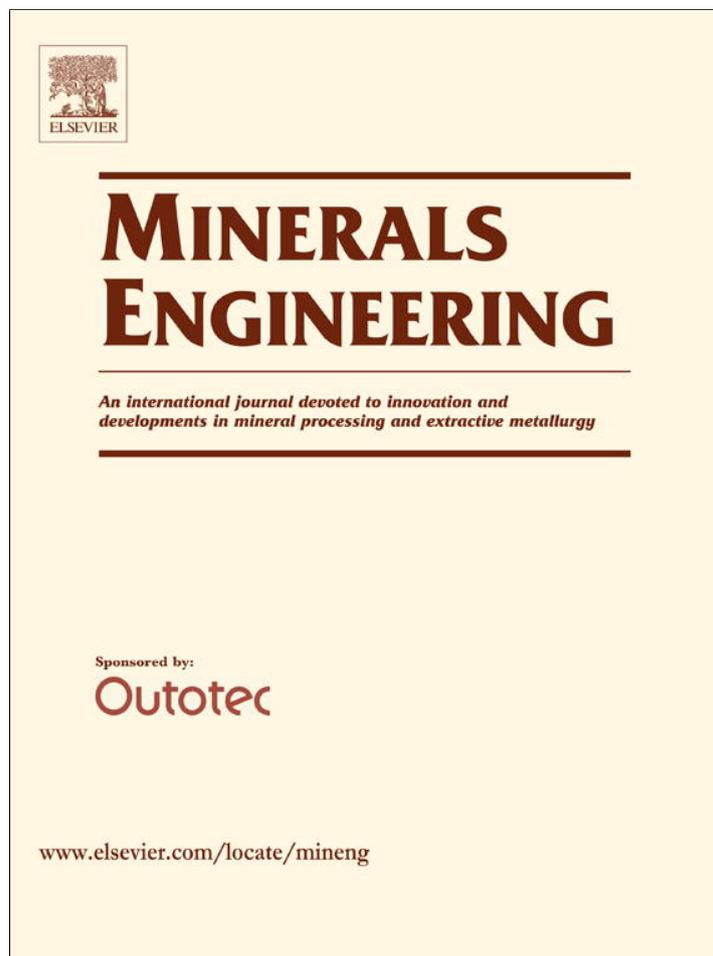


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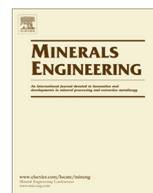
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Technical note

Study the relationship between the compositional zoning of high iron content pyrochlore and adsorption of cationic collector

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ABSTRACT

The matrix composition and surface chemistry of high iron pyrochlore (Fe pyrochlore) grains from Niobec (St-Horone carbonatite deposit) were analyzed, in order to identify a potential relationship between Fe pyrochlore matrix composition and the related effect on cationic collector adsorption (tallow diamine). SEM-EDX analyses indicate compositional zoning in the structure Fe pyrochlores. TOF-SIMS was used to analyse the surface of different compositional zones of Fe pyrochlore, in order to identify their related effects on tallow diamine adsorption. Surface analyses of high and low iron zones of treated Fe pyrochlore show that species indicative of the collector favour the regions of low iron content. The low iron areas also show a lower relative proportion of species indicative of oxidation. This study identifies the link between Fe pyrochlore compositional zoning, surface oxidation and, area selective collector loading.

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1. Introduction

In North America, Niobec is the only operating Nb extraction facility which has recovered pyrochlore ((Na,Ca)₂Nb₂O₆(OH,F)), the most abundant niobium containing mineral, from the St-Honoré carbonatite deposit by froth flotation. In Niobec plant, the pyrochlore surfaces in the desired pH (6–7) flotation range were negatively charged and therefore flotation of the pyrochlore was accomplished by the cationic collector, tallow diamine acetate (Dufresne and Goyette, 2004; Belzile, 2009).

Poor flotation of high iron pyrochlore is noted in the plant (Rao et al., 1988; Chehreh Chelgani et al., 2012a). Investigations indicated that the Fe increase in the pyrochlore is not as a result of Fe rich inclusions, rather it has been identified as an increase in matrix Fe content, and also suggested that poor floatability is linked to higher matrix Fe content (Chehreh Chelgani et al., 2012a). Surface chemical analyses of high and low iron pyrochlores by TOF-SIMS verified a relationship between pyrochlore surface reactivity and Fe content in the mineral matrix, and demonstrated the intensity of collector species was significantly higher on the surface of the Fe poor pyrochlore. Surface analyses released that the flotation selectivity of low Fe pyrochlore grains relative to high Fe pyrochlore grains, was in response to surface oxidation of the

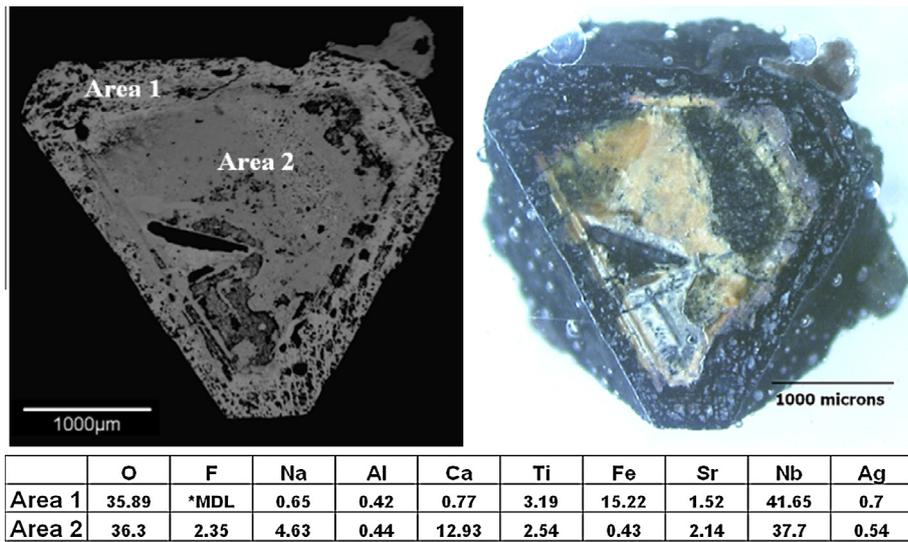
high Fe pyrochlore resulting in diminished collector attachment and poor recovery (Chehreh Chelgani et al., 2012b).

Zonation in pyrochlore (A₂B₂O₇) mineral groups is well recognized but less well understood. This is due, in part, from failure to recognize secondary alteration (replacement) phenomena and to distinguish them from primary (growth) features (Sharygin et al., 2009). Lumpkin and Ewing (1995, 1996) described alteration trends in pyrochlore from a range of parageneses and weathering environments. They identified three trends relating to alteration “primary”, “transitional”, and “secondary”. The distinction is compositionally related, using triangular diagrams with apices corresponding to divalent A-site cations (Zurevinski and Mitchell, 2004).

In this study, the relationship between compositional zoning and surface chemistry of high iron pyrochlore grains from the Niobec deposit were investigated. To the authors' knowledge, it is the first record of compositional zoning in Fe pyrochlore for St Horone deposit. This work describes zoning and chemistry of the Fe pyrochlore mineral, which is the main source of Nb. The study utilised energy dispersive X-ray spectroscopy (EDX) to measure concentrations of the main matrix elements in zoned areas of Fe pyrochlore grains which ultimately will affect the surface chemistry and factors controlling collector attachment. Time of flight secondary ion mass spectroscopy (TOF-SIMS) analyses were performed to examine the surface chemistry of Fe pyrochlore grains from the various areas in order to identify variability in reagent adsorption along with possible factors affecting the adsorption. The main aim of this study is to link pyrochlore matrix composition to surface chemistry in an attempt to relate the noted

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*MDL: Method detection limits, elements may be present but are below for detection.

Fig. 1. Optical microscopic (right) and BSE images (left), and EDX analysis of a Fe pyrochlore grain at wt.%.

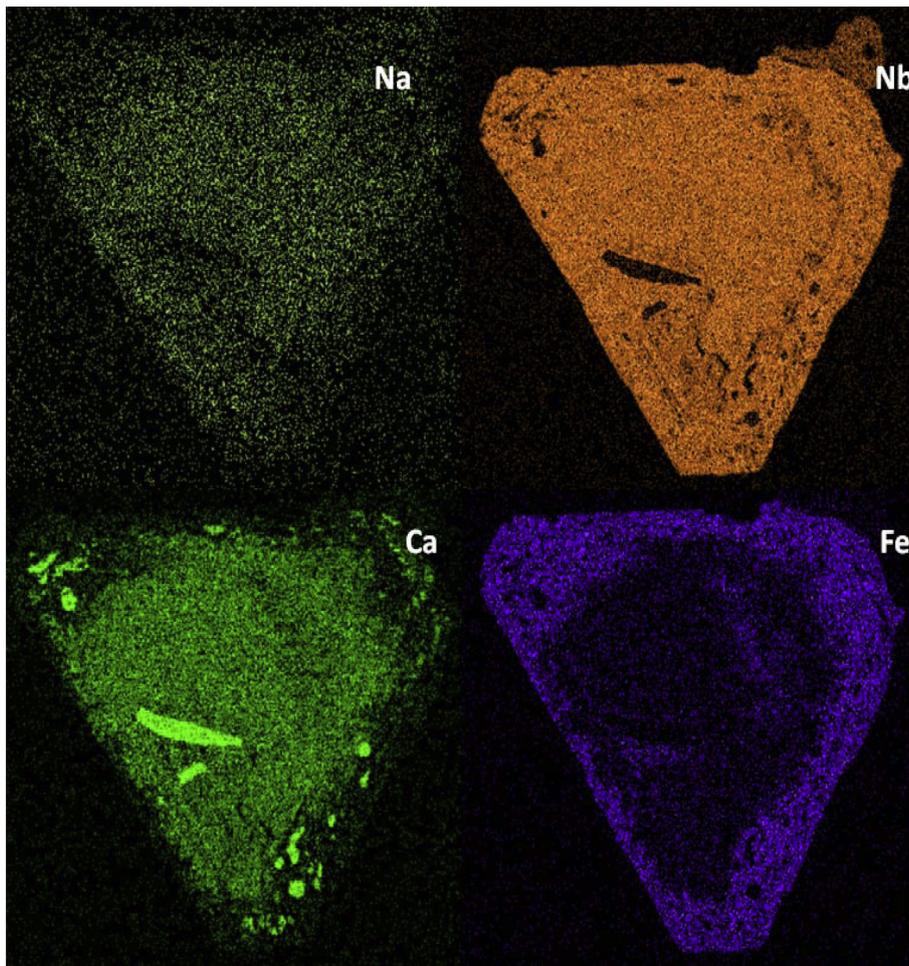


Fig. 2. Elemental maps for zoned crystal of the Fe-pyrochlore for St-Horone deposit.

variability in flotation recovery to compositional zoning. The results will be used to better understand the effect of compositional zoning on collector loading, the collector adsorption mechanism, and selective flotation.

2. Experimental

The concentration of matrix elements were measured in the Fe pyrochlore grains with a LEO 440 SEM equipped with a Gresham

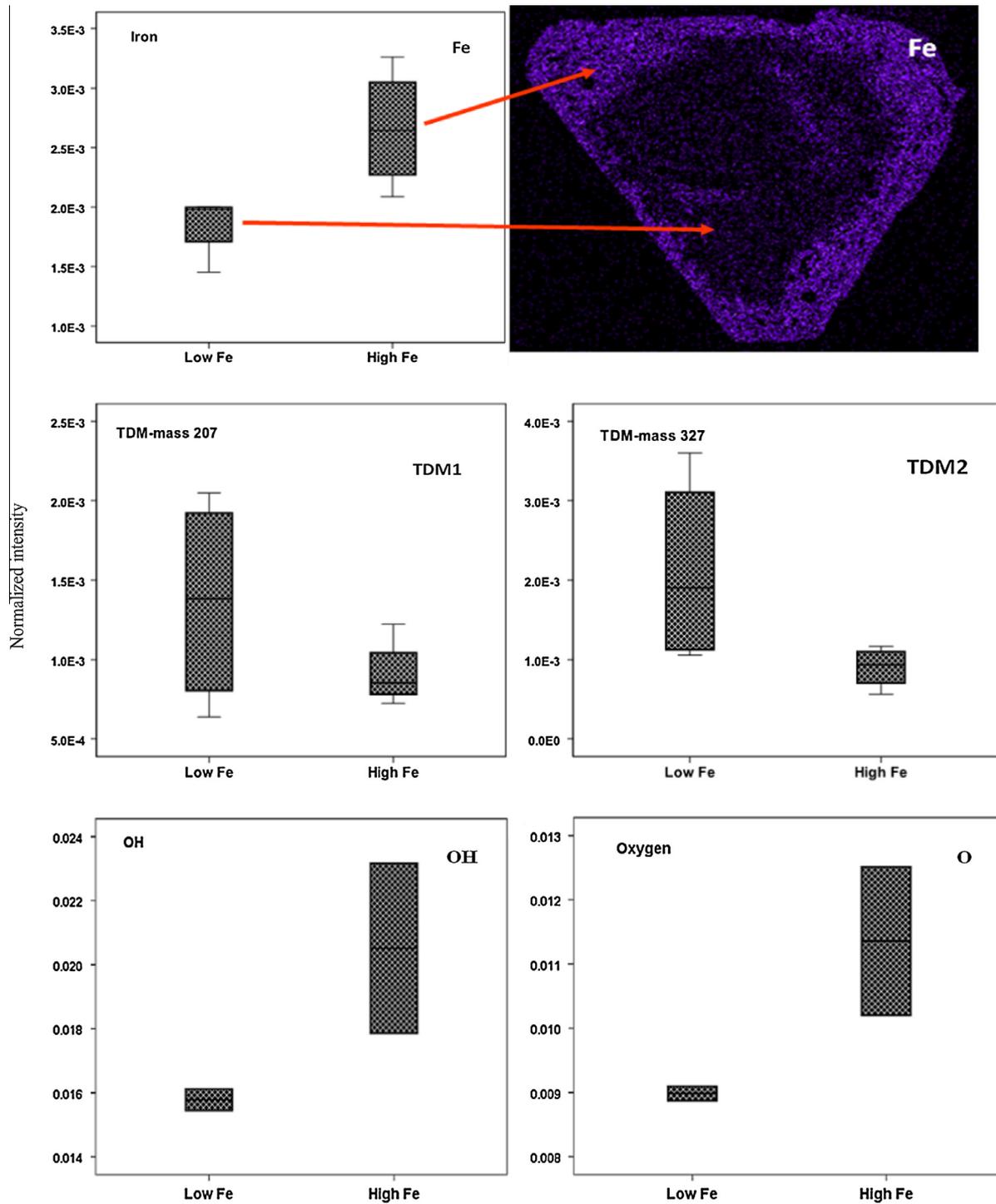


Fig. 3. Box and whisker plots illustrating the relative intensity of oxygen, hydroxide and cationic collector mass species on the surface of the conditioned high and low iron compositional zones of Fe pyrochlores. The horizontal bar in the boxes represents the median (mean of the data).

light element detector and a Quartz XOne EDX system. The instrument was operated at 20 kV, 400 pA. Samples were sputter-coated with carbon in order to prevent charging during analyses.

In order to evaluate collector adsorption variability and potential causes for identified differences, samples of Fe pyrochlore (6 large pyrochlore grains (3–6 mm)) were freshly fractured, polished and conditioned with tallow diamine at plant operating conditions. Test conditions were as follows; agitation of the minerals for 10 min in 227 ml deionised water (DIW) (pH 6.2) mixed with

0.05 ml tallow diamine. After 10 min the samples were removed, repeatedly rinsed with DIW (pH 6.2) then immediately transferred to the instrument for analysis.

To analyze the outer most layer of samples an ION-TOF, TOF SIMS IV secondary ion mass spectrometer used in this study. An isotopically enriched $^{209}\text{Bi}^+$ (Bismuth) primary ion beam is rastered across an area of interest on the sample surface. The raster size used was $\sim 300 \mu\text{m}$ with an acquisition pattern comprised of 100 scan lines. In order to examine the surface chemistry of com-

positional zones and also to identify variability in reagent adsorption in different zones, the surface of fresh and conditioned samples were analysed and then compared. Spectral mass positions representative of tallow diamine occur at mass 207 amu (TDM-1), and 327 amu (TDM-2) (S. Chehreh chelgani et al., 2012b, 2013).

3. Result and discussion

3.1. EDX

In general, alteration of pyrochlore ($A_2B_2O_7$) involves loss of F, Na, and Ca driving the altered Fe pyrochlore composition toward the A^{2+} cation-vacancy (Lumpkin and Ewing, 1996). At St Horone, pyrochlore formed throughout the magmatic crystallization (Fournier, 1993). Pyrochlore minerals at St Horone have A sites commonly occupied by Ca, Na, Sr and Fe. Their B sites are commonly occupied by Nb, and Ti. In Fe pyrochlores, the grains exhibit compositional zonation, reflecting changes in the fluid composition during crystal growth (Hogarth et al., 2000). An optical microscope, and back-scattered electron images along with semi-quantitative elemental analyses of selected areas on a Fe pyrochlore grain is given in Fig. 1. X-ray concentration maps for the same pyrochlore grain are given in Fig. 2. All images reveal structure and compositional zoning in the Fe pyrochlore samples. Denomme et al. (1982) considered that ferro pyrochlores having zonation formed from pyrochlore by addition of iron.

3.2. TOF-SIMS

The dominant peak positions for the cationic collector (tallow diamine acetate) examined and the parent and mass fragment positions (207 and 327 amu) were used to identify the presence of the reagent and assess variations in loading between different compositional zones of the samples investigated.

The relationship between collectors and Fe intensity is clearly illustrated graphically where intensities of various species on the surface of different compositional zones of the Fe pyrochlore grains are compared. A comparison of the normalised intensities of 207 amu, and 327 amu mass positions for treated samples reveals a preference for these species for the surface of the low Fe areas relative to the high Fe areas (Fig. 3). Discrimination for surface species Fe, O, and OH in favour of Fe rich areas was also observed (Fig. 3).

The data indicate that high iron zones have, on average, less tallow diamine on their surfaces when compared to the low iron content zones. Moreover, high Fe parts have more Fe along with OH and O on their surface, potentially indicative of preferential oxidation or at the very least, a greater proportion of surface oxidation species. The link between diminished collector loading and a greater presence of oxidized species suggests that attachment is not fa-

voured where oxidation occurs. Moreover, these areas are consistently higher Fe in content suggesting that areas of preferential oxidation and poor collector loading are linked to mineral matrix composition. These here are in agreement with the previous studies by Rao et al. (1988) and Chehreh Chelgani et al. (2012a), who noted that poor flotation of iron pyrochlore in the plant. The results here reveal that pyrochlore grains with outer Fe rims may not be easily recovered in the current flotation process.

4. Conclusion

SEM-EDX analysis of Fe pyrochlore has identified that the high iron content pyrochlores are compositionally zoned. The TOF-SIMS results verify a relationship between pyrochlore compositional zoning and collector loading. The surface analysis demonstrated that the intensity of the oxidized species O and OH was greater in zones corresponding to high matrix Fe content. The surface analysis also revealed that collector loading favours zones with low matrix Fe content, indicating that oxidation particular to the Fe ones inhibits collector attachment. This study identifies the link between collector attachment and compositional zoning in Fe pyrochlores.

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