

# Pyrochlore surface oxidation in relation to matrix Fe composition: A study by X-ray photoelectron spectroscopy



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## ARTICLE INFO

### Article history:

Received 12 July 2013

Accepted 10 October 2013

Available online 2 November 2013

### Keywords:

Pyrochlore

Flotation

Oxidation state

Compositional zoning

XPS

Surface analysis

## ABSTRACT

The flotation recovery of pyrochlore from the Saint-Honore Carbonatite ore has been related to the variability in the mineral matrix Fe content; high Fe pyrochlore grains consistently report to the tails. Previous research has tentatively suggested that surface oxidation of high Fe pyrochlore grains may be driving partitioning of the pyrochlore grains to the tails. X-ray photoelectron spectroscopy (XPS) was used to examine the relationship between matrix Fe content and surface oxidation in high Fe pyrochlore grains and high Fe zoned regions in pyrochlore grains from the Carbonatite ore. XPS analyses of pyrochlore grains showed that a greater proportion of surface oxidation species corresponded to the zones with high matrix Fe content. The XPS data along with previously presented Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) data demonstrates a relationship between matrix Fe content and collector attachment. The Fe rich pyrochlore grains or zones show a higher degree of oxidation relative to the Fe poor grains or zones. The data reveal that collector attachment favors low Fe grains or zones, likely in response to a lower degree of surface oxidation.

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## 1. Introduction

The separation of pyrochlore, main source of niobium (Nb), from the remainder of the gangue phases in the Saint-Honore Carbonatite Nb deposit (Niobec) is accomplished by froth flotation. The overall Nb recovery at Niobec is less than 60%. Investigations directed towards understanding factors leading to poor recovery include: Gomez et al. (1987a); Gomez (1987b) who studied the influence of surfactants and type of water to optimize pyrochlore recovery and grade during flotation and showed plant recycle water decreased selectivity and increased reagent consumption; Rao et al. (1988) who noted that poor flotation of Fe pyrochlore in the plant; Dufresne and Goyette (2004); Belzile (2009); Ni et al. (2012) reported that 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.

Recent work by Chehreh Chelgani et al. (2012a) using the SEM–EDX analyses revealed that the Niobec deposit contains pyrochlore grains of both high (Fe-pyrochlore) and low Fe (pyrochlore) contents. The study also revealed that high Fe pyrochlore grains appear to be less recoverable than those with a lower Fe content, suggesting that pyrochlore flotation is at least partially linked to a mineral composition.

Further work by the same group using TOF-SIMS analyses identified a potential relationship between pyrochlore matrix composition and collector adsorption (Chehreh Chelgani et al., 2012b). The study showed that species indicative of the cationic collector (identify the collector) favor the surface of Fe poor pyrochlore relative to the Fe rich variety. The TOF-SIMS analyses also revealed a negative relationship between collector loading and the presence of Fe and related oxidation species. These results suggested a potential scenario where higher surface Fe content could promote preferential oxidation or at the very least, is linked to a greater proportion of surface oxidation species thereby interfering with collector adsorption.

Zonation in pyrochlore ( $A_2B_2O_7$ ) mineral groups is well recognized but less well understood. This is due, in part, to difficulties in recognizing and distinguishing secondary alteration (replacement) phenomena from primary (growth) features (Sharygin et al., 2009). Recent work by Chehreh chelgani et al. (2013) identified compositional zoning in the structure of Fe-pyrochlore grains from Niobec; two distinct zones were observed, high Fe and low Fe zones. TOF-SIMS analyses of pyrochlore grains conditioned with the reagent (tallow diamine acetate) identified that the mass species indicative of the collector favor the regions of low Fe content. Furthermore the low Fe areas also show a lower relative proportion of species indicative of oxidation. The results identified the link between Fe pyrochlore compositional zoning, and area selective collector loading (Chehreh Chelgani et al., 2013).

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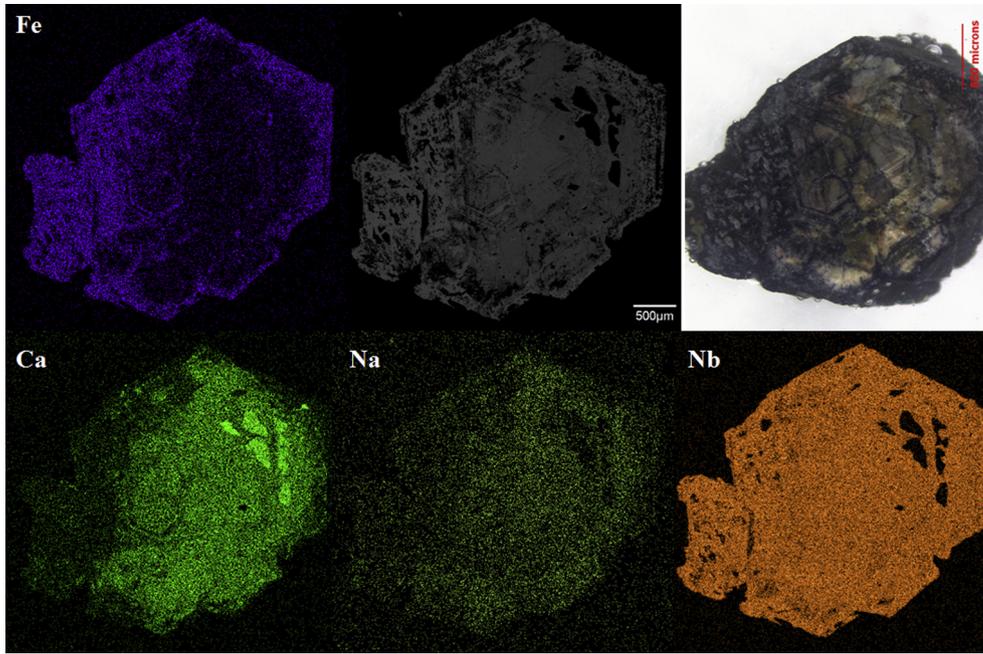


Fig. 1. Optical microscopic image, BSE image, and elemental maps for zoned Fe-pyrochlore from the St-Honore deposit.

Table 1

EDX analysis of different zones in Fe-pyrochlore grains from Niobec. The concentration data is expressed by weight%.

Fe zone	Minimum	Maximum	Mean	Std. deviation	Low Fe zone	Minimum	Maximum	Mean	Std. deviation
Oxygen	35.89	36.89	36.48	.52	Oxygen	33.65	37.78	35.91	2.09
Fluorine	<sup>a</sup> MDL	<sup>a</sup> MDL	<sup>a</sup> MDL	<sup>a</sup> MDL	Fluorine	2.35	3.45	2.83	.56
Sodium	.57	.90	.71	.17	Sodium	4.63	6.08	5.15	.81
Aluminum	.32	.49	.41	.085	Aluminum	.31	.45	.40	.08
Calcium	.70	1.09	.85	.21	Calcium	11.23	12.93	11.80	.98
Titanium	2.50	3.19	2.74	.39	Titanium	1.80	2.74	2.36	.49
Iron	11.81	15.22	13.73	1.74	Iron	<sup>a</sup> MDL	.94	.46	.47
Strontium	1.52	1.69	1.58	.093	Strontium	1.16	2.14	1.71	.50
Niobium	41.48	43.69	42.27	1.23	Niobium	36.30	37.85	37.28	.85

<sup>a</sup> MDL = method detection limits, elements may be present but are below for detection.

Surface sensitive techniques, scanning Auger microscopy (SAM), scanning tunneling microscopy (STM), atomic force microscopy (AFM), SEM and X-ray photoelectron spectroscopy (XPS) along with the more indirect methodologies like zeta potential, cyclic voltammetry (Smart, 1991; O' Connor et al., 1992; Laajalehto et al., 1993; Hochella, 1995; Kim et al., 1995; Peng et al., 2012) have been used for more than 20 years in a variety of studies related to the mechanisms of oxidation in mineral flotation. Among these techniques, XPS is the most suitable for identifying surface oxidation products and has probably contributed more understanding on the mechanisms of surface chemical actions in flotation than any other surface analytical technique (Buckley and Woods, 1985a,b, 1987, 1991; Smart, 1991; Smart et al., 1999, 2000, 2003a, 2003b, 2007; Jones et al., 1992; Fornasiero et al., 1994; Prestidge and Ralston, 1995; Descostes et al., 2000; Hart et al., 2006; Fredriksson and Holmgren, 2007; Gerson and Jasieniuk, 2008; Olsen et al., 2012). It is well established that metal sulfide minerals exhibit oxide and hydroxide species on their surface after exposure to air or aqueous solution during mineral processing. However, information regarding the surface chemistry and changes for oxides or silicates in response to variability in pulp conditions both experimental and from plant environments, is limited (Kim et al., 1995; Smart et al., 1998).

In this study XPS analyses were performed to examine the variability in surface oxidation of compositional zoning in pyrochlore

grains with different Fe content. The aim of the study is to link pyrochlore matrix composition to variability in surface oxidation in order to evaluate this relationship to the observed mineral recovery. The results will provide understanding regarding the loss of selected pyrochlore grains. The results will also be used towards the selection of potential alternative commercial reagents, for optimizing selectivity and recovery, or to help design reagents particularly suited for pyrochlore in this flotation context.

## 2. Experimental

Pyrochlore grains were collected from the St-Honoré carbonatite deposit, Niobec, Quebec, Canada. The concentration of matrix elements was measured in pyrochlore grains with a LEO 440 SEM equipped with a Gresham 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.

The XPS analyses were carried out with a Kratos Axis Ultra spectrometer using a monochromatic Al K $\alpha$  source (15 mA, 14 kV). The instrument work function was calibrated to give a binding energy (BE) of 83.96 eV for the Au 4f<sub>7/2</sub> line for metallic gold and the spectrometer dispersion was adjusted to give a BE of 932.62 eV for the Cu 2p<sub>3/2</sub> line of metallic copper. Binding energy accuracy

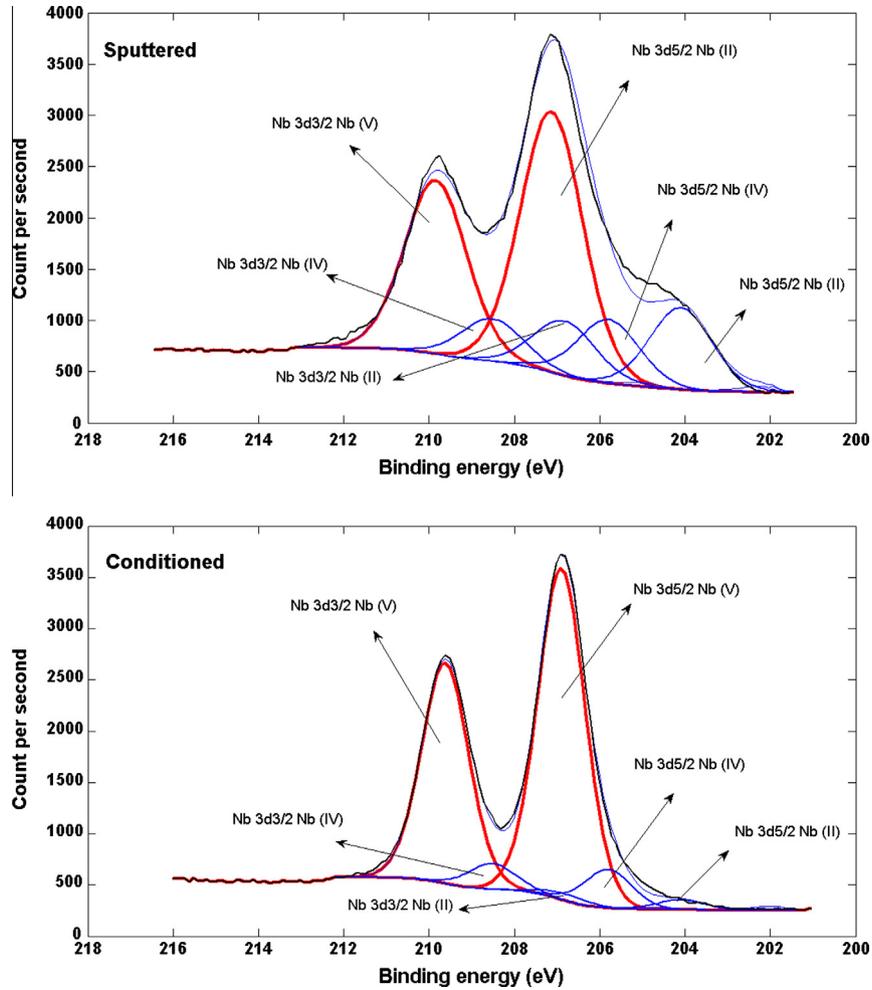


Fig. 2. Niobium states on the surface of a sputtered and conditioned pyrochlore grain.

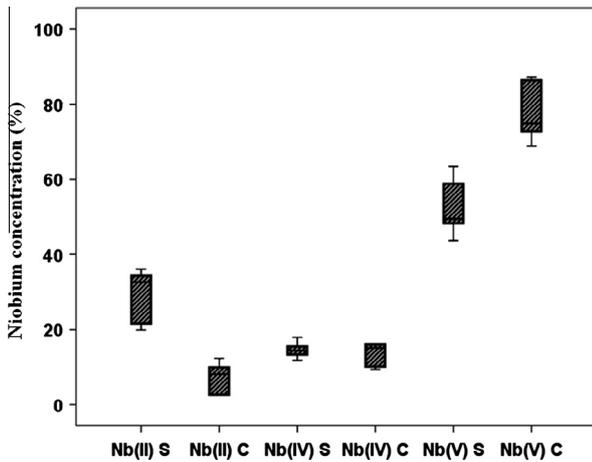


Fig. 3. Relative proportion of Niobium species measured on the surface of the sputtered (S), and conditioned (C) pyrochlore grains.

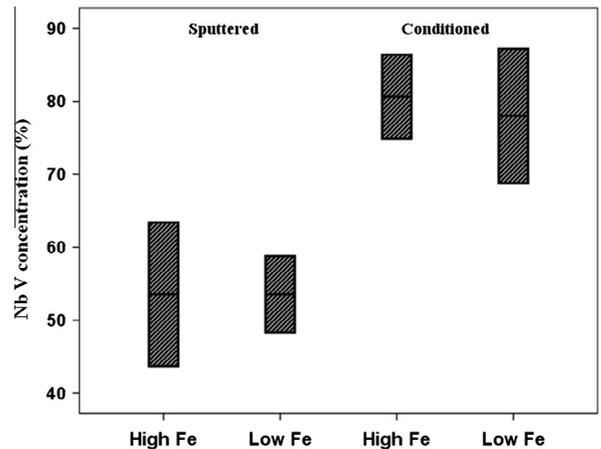


Fig. 4. Concentration of Nb(V) on the surface of high and low iron pyrochlore zones.

is  $\pm 0.025$  eV. The Kratos charge neutralizer system was used on all specimens. Survey spectra were collected with a pass energy of 160 eV from an analysis area of  $\sim 300 \times 700 \mu\text{m}$ . High-resolution spectra were obtained using either a 20 eV or 40 eV pass energy and an analysis area of  $\sim 300 \times 700 \mu\text{m}$ . Spectra were analyzed using CasaXPS software (version 2.2.107) (Fairley, 1999–2005).

In order to develop a baseline for comparative analyses between high and low Fe zones, selected grains were mounted in epoxy and polished to a  $0.3 \mu\text{m}$  finish. The grains were then sputtered in vacuum (4 days for all grains) in order to generate fresh surfaces for analyses then subsequently analyzed. To examine differences in surface species in relation to oxidation, the fresh samples (subsequent to sputtering) were removed from the instrument and

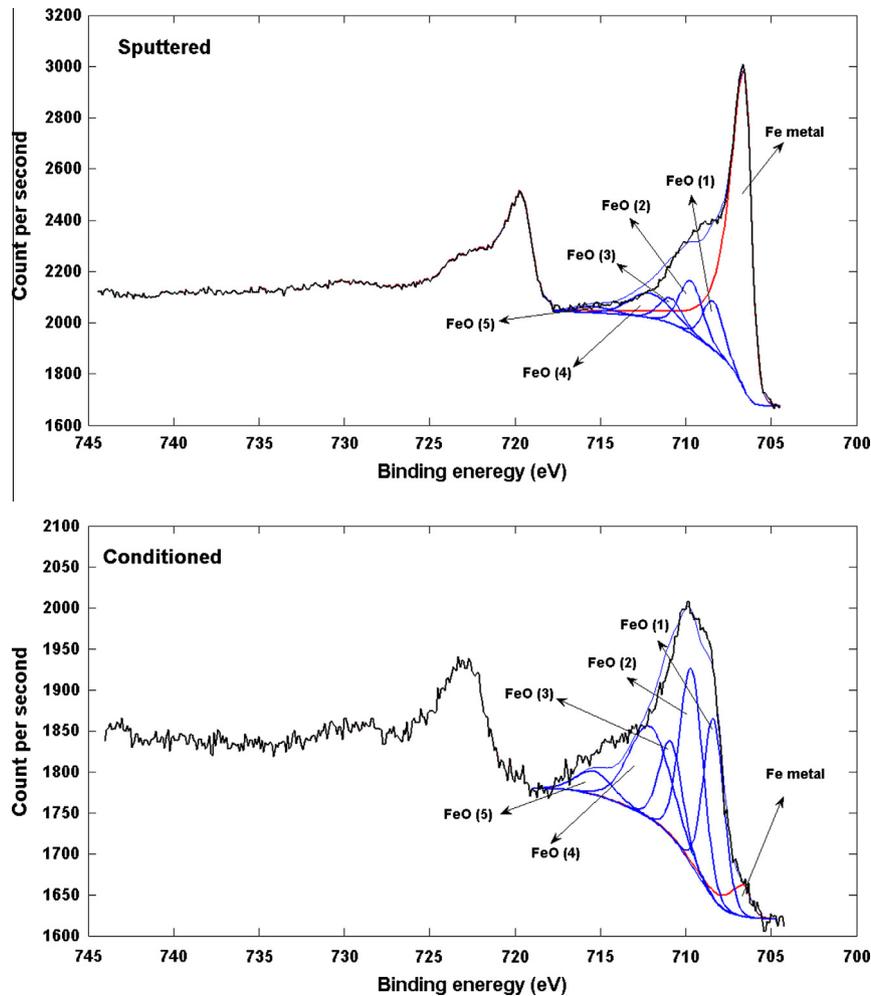


Fig. 5. Iron states on the surface of a sputtered pyrochlore and immediately conditioning.

placed in oxygen saturated deionised water (pH 6.2) for 30 min. After reaction the samples were removed, placed immediately into the instrument and analyzed.

### 3. Results

SEM–EDX analysis has identified that the Fe-pyrochlores grains are compositionally zoned. X-ray concentration maps for Fe-pyrochlore grain is given in Fig. 1. The EDX analysis of different zones is presented in Table 1.

#### 3.1. XPS survey spectra and high resolution Nb 3d<sub>5/2</sub>

The various Nb species were assigned based on the binding energy data provided by the NIST data base, these are: Nb<sub>2</sub>O<sub>5</sub>: 207.4 eV, NbO<sub>2</sub>: 206.2 eV, and NbO: 203.7 eV (Naumkin et al., 2000; Cooley and Sibener, 2007).

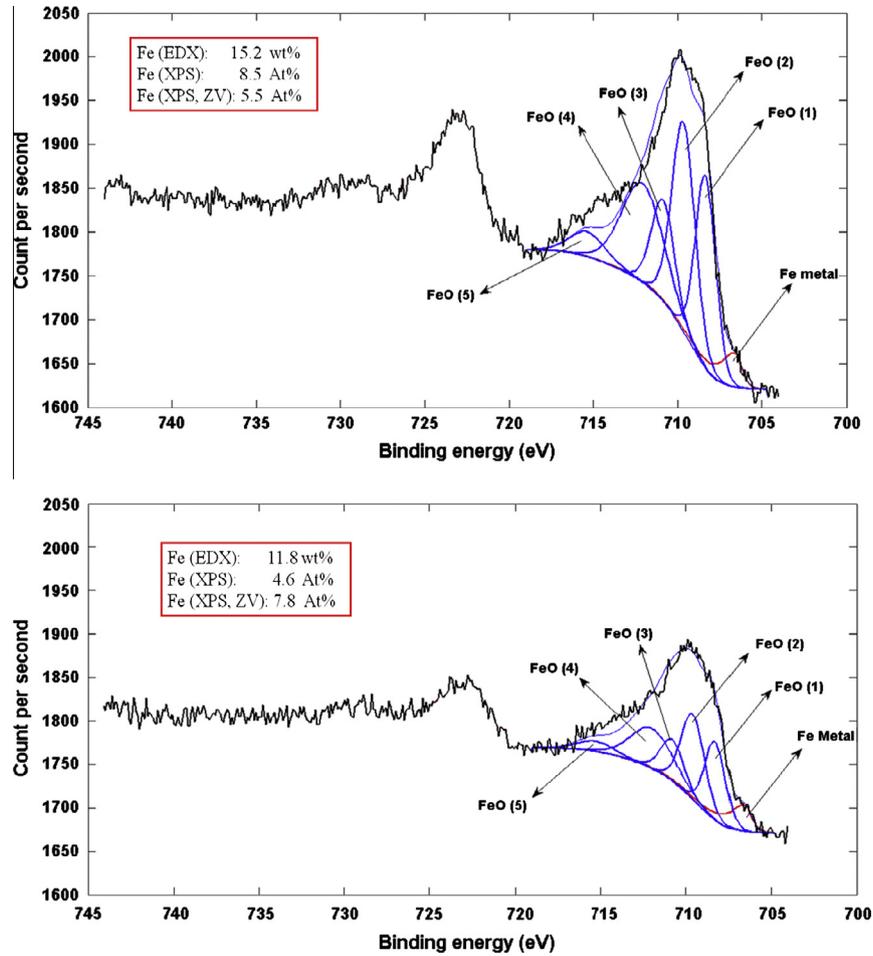
Fig. 2 shows the binding energies of the Nb 3d<sub>5/2</sub> electrons from the analyses of a high Fe pyrochlore before and after treatment. Comparison of the sputtered pyrochlore surfaces with those after conditioning show a significant change in the relative proportion of Nb species. The doublet at binding energy 207 eV representing Nb(V) shows a significant increase in the conditioned sample relative to those at 204 and 206 eV representing Nb(II) and Nb(IV) respectively (Fig. 3). The data indicates an increase in the proportion of oxidized Nb species present on the surface of grains after conditioning. A comparison between the high and low Fe zones re-

vealed that the actual amount of Nb(V) was the same on both grains before conditioning. After conditioning the surface proportion of Nb(V) increased on both high and low Fe zones, however the average surface proportion of Nb(V) on low Fe zones is slightly less than the high Fe zones (Fig. 4).

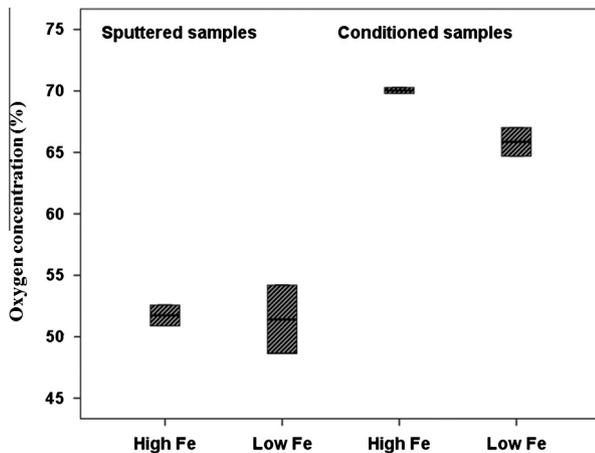
#### 3.2. XPS survey spectra and high resolution Fe 2p<sub>3/2</sub>

Compared to the other transition metal species, the complex multiple species fitting of Fe is the most problematic. Pratt et al. (1994) used a series of multiplet peaks to curve fit oxidized Fe sulfide (pyrrhotite) surfaces. Biesinger et al. (2011) presented a summary of full fitting parameters for Fe including the multiplet and satellite structure. The paper clearly illustrates that, materials with numerous possible species showing overlapping binding energies can result in erroneous interpretations. They went onto indicate that two distinct species can likely be fitted accurately, fitting three is difficult fitting four very problematic and must only be looked at as indicative. Given that, from a comparative analytical perspective, XPS Fe data in this study is of value in that it can provide information related to the process based on the relative changes in the proportion of species identified on the surface of the mineral phases. The Fe 2p<sub>3/2</sub> peak fitting parameters identified in Biesinger et al. (2011) have used for specie identification.

The pyrochlore family is complex. The general mineral formula can be given by: A<sub>2–m</sub>B<sub>2</sub>O<sub>6</sub>(O, OH, F)<sub>1–n</sub>, pH<sub>20</sub> where A = Na, Ca, K, Sr, Ba, Mn, Fe<sup>2+</sup>, Mg, Sn, Pb, Bi, Cs, Sb<sup>3+</sup>, Th, U, Y, Ce, Nd, La and



**Fig. 6.** Comparison of the high resolution XPS spectra between grains with different Fe content after conditioning. Included for each grain examined is the weight% Fe, as determined by EDX, along with the relative proportion surface Fe (At%) from the XPS broad scan data and the proportion of Fe metal (At%) as determined in the high resolution XPS scans. Fe(XPS ZV) refers to the Fe metal in the spectra.



**Fig. 7.** Box and whisker plots illustrating the relative intensity of oxygen on the surface of the sputtered and conditioned high and low iron compositional zones of Fe pyrochlores.

B = Nb, Ta, Ti, Zr,  $\text{Fe}^{3+}$ , Al (Vlasov, 1966; Hogarth, 1977; Fleischer, 1987). Since the assignment of Fe can either occur in the A or B positions correct position of Fe and therefore its valence state in the structure of pyrochlore from Niobec is generally unknown. Investigations by Zurevinski and Mitchell (2004) mentioned that it would not be surprising if  $\text{Fe}^{2+}$  is present at the A sites, where

the cation exchange reactions occur more easily. Recent studies (Chehreh Chelgani et al., 2012a) using statistical analyses of EDX data from Niobec pyrochlore grains indicated that the Fe in the matrix is primarily located at the A position.

Unfortunately, the concentration of Fe in the low Fe pyrochlore grains did not allow for the collection of spectra amenable to reasonable interpretation. Hence a direct comparison between the development of Fe species on grains with very low Fe contents was not possible. What follows is a comparison between grains considered as high Fe pyrochlore grains with differing Fe contents. The objective is to determine if there are reasonable, measurable chemical state differences similar to those observed in the TOF-SIMS analyses which can be potentially linked to the observed flotation response. Representative XPS spectra of Fe on the surface of sputtered and conditioned high Fe pyrochlore zones are shown in Fig. 5. The sputtering process results in the removal of Fe-oxides and the reduction of Fe giving rise to the zero valent Fe peak (Fe metal) at a BE of 706 on the sample. The conditioning process resulted in the development of significant Fe oxide on the surface of the pyrochlore. Evaluation of the spectra reveals that the process resulted in the generation of  $\text{Fe}^{2+}$ , identified as FeO, along with minor and varying proportions of  $\text{Fe}^{3+}$  as  $\text{Fe}_2\text{O}_3$ . A positive identification of FeOOH was not accomplished due to the complicated nature of the spectrum, however its presence is indeed possible. Comparison of the spectra from pyrochlore grains with relative high and lower Fe contents after conditioning reveals several significant differences: (i) surface Fe content is significantly higher

**Table 2**

High resolution XPS data for Nb as measured on the surface of conditioned high and low Fe pyrochlore zones. All data in relative %.

	Nb(O)	Nb(II)	Nb(IV)	Nb(V)
High Fe	0.9	2.6	10.1	86.4
Low Fe	0.8	2.6	9.4	87.2
High Fe	0.0	2.7	9.7	87.7
Low Fe	1.9	8.1	15.1	74.9
High Fe	1.2	9.9	16.0	72.8
Low Fe	2.7	12.3	16.2	68.8

in the high matrix Fe content sample, (ii) the proportion of zero valent Fe (Fe-metal) is higher on the surface of the low Fe pyrochlore sample and (iii) there is a greater proportion of Fe–O species on the surface of the high Fe pyrochlore grains (Fig. 6).

### 3.3. Oxygen

The XPS was used to examine the development of surface oxidation species in relationship to pyrochlore matrix compositional zones. XPS spectra were collected from low Fe and high Fe compositional zones after sputtering, and after conditioning (Fig. 7). The data from the sputtered samples reveals no difference in the surface oxygen content between the high and low Fe content zones. After conditioning however the high Fe content zones showed overall higher oxygen content (~5%) as compared to the low Fe zones.

## 4. Discussion

Observations by Abeidu (1974) showed pyrochlores with high Fe content appear to be less recoverable than those of low Fe content. He speculated that the flotation selectivity can possibly be related to preferential surface oxidation of the Fe rich mineral rendering the surface unsuitable for collector attachment. Investigations on the effects of surface oxidation and/or the precipitation of oxidative species indicated that, as the mineral surface becomes increasingly covered with metal oxide/hydroxide species the surface becomes increasingly less negative and can even become positively charged (Fornasiero et al., 1992; Fornasiero et al., 1994; Witika and Dobias, 1993; Fairthorne et al., 1997; Fullston et al., 1999; Barnes et al., 2009). The data gathered from the surface evaluation of pyrochlore grains from the Niobec operation by (Chehreh Chelgani et al., 2012a,b) indicate that differential cationic collector attachment efficiency is linked to Fe content in the pyrochlore grains. Given this observation, a potential scenario for flotation selectivity in relation to matrix Fe content is put forward: inhibition of collector attachment due to preferential oxidation of the high Fe pyrochlore grains or regions in zoned pyrochlore grains during the recovery process.

Previous investigations at Niobec have shown that a higher concentration of matrix Fe in pyrochlore grains can potentially be linked to poor selectivity (Rao et al., 1988; Chehreh Chelgani et al., 2012a). Surface analyses by TOF-SIMS demonstrated that the intensity of oxidative species O, OH and FeOH was greater on the surface of high Fe pyrochlore grains in comparison with low Fe pyrochlore grains (Chehreh Chelgani et al., 2012b).

While the XPS analyses was not able to fully differentiate the types of Fe oxidation species on the surface of the pyrochlore grains, variations in the relative proportions of oxidation products demonstrate a number of factors in support of the contention that collector attachment is linked to preferential surface oxidation of Fe rich grains or regions. A significant line of support comes from the oxygen data which shows an overall higher O content on the surface conditioned Fe rich pyrochlore grains or zones relative to

the low Fe pyrochlore particles or zones (Fig. 6). This is in agreement with the TOF-SIMS data which linked higher O contents to Fe rich pyrochlore grains and zones with diminished collector presence (Chehreh Chelgani et al., 2012b). There is also a curious overall greater proportion of oxidized Nb on the surface of the high Fe grains accompanied with a greater proportion of more reduced Nb species on the low Fe grains or regions (Table 2). While it is not clear if the degree of Nb oxidation and the resulting proportional difference of oxidized Nb species is facilitated by matrix Fe content, it is clear that in zones or grains with higher Fe content, there is a greater proportion of both Nb and Fe oxidation products. Although the argument can be made that the greater proportion of these species on the surface of the Fe rich pyrochlores could be related to a precipitation phenomenon, the data for pyrochlores with variable Fe contents provides evidence that the process is related to preferential surface oxidation. The XPS data clearly shows that the proportion of surface oxidation products increases proportionally to the matrix Fe content of the grain; a similar link is highly unlikely to be shown by a precipitation mechanism. Thus, the established link between poor pyrochlore recovery and matrix Fe content from the previous SEM-EDX and TOF-SIMS studies (Chehreh Chelgani et al., 2012a,b, 2013) is related to a greater degree of both Fe and to some degree Nb oxidation which results in zones or grains that preferentially inhibit collector attachment and therefore show poor recovery.

## 5. Conclusions

Previous studies of pyrochlore grains have linked poor flotation performance to an increase of Fe content in the matrix of grains. One possible explanation linking high Fe content to poor recovery suggested that high Fe content resulted in a variable degree and rate of surface oxidation. Surface analysis techniques such as XPS allow for a direct ex situ determination of the degree of oxidation on the surface of minerals. The present study utilizes the XPS technique to investigate the oxidation states on the surface pyrochlore of different Fe content and grains that are compositional zoned pyrochlores (areas of high and low Fe content). Bench testing and XPS analyses of variable Fe content pyrochlore grains verify a relationship between pyrochlore surface oxidation and Fe content in the mineral matrix. It was demonstrated that on the surface of conditioned samples, a greater proportion of oxygen was identified in high Fe zones in comparison to those with low Fe contents. Furthermore, the analyses revealed that there was a greater proportion of higher valence state Fe and Nb species developed on the surface of the high Fe pyrochlore zones during the conditioning tests. These data provide evidence that the previously identified link between matrix Fe content and collector attachment is likely in response to selective oxidation on the surface of Fe rich pyrochlore grains or zones within the pyrochlore grains. The data may be of significant value as they can be applied to testing scenarios designed in order to evaluate to flotation improvement strategies.

## Acknowledgements

This work was partially completed with funding provided by the Natural Sciences and Engineering Research Council of Canada (NSERC Grant # CRDPJ 364576-07).

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