

## Study of pyrochlore surface chemistry effects on collector adsorption by TOF-SIMS

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### ARTICLE INFO

#### Article history:

Received 8 June 2012

Accepted 28 July 2012

#### Keywords:

Pyrochlore  
Collector adsorption  
Surface chemistry  
TOF-SIMS

### ABSTRACT

Time of flight secondary ion mass spectrometry (TOF-SIMS) was used to analyse the surface of two different types of pyrochlore, high Fe pyrochlore and low Fe pyrochlore, from Niobec Saint-Honore mine deposit. Pyrochlore grains were analysed in order to identify a potential relationship between pyrochlore matrix composition, the corresponding surface expression and the related effect on cationic collector adsorption. TOF-SIMS analyses of pyrochlore surfaces from a conditioning test show that the species indicative of the cationic collector, favour the surface of Fe poor pyrochlore relative to the Fe rich variety. Lower collector signals on the surface of the Fe-pyrochlore are matched by higher relative intensities of Fe, OH, O and FeOH. The TOF-SIMS results illustrate a negative relationship between a cationic collector adsorption and the presence of Fe and Fe oxidation species on the surface of pyrochlore grains, and supports previous work which identified a negative correlation between matrix Fe content and pyrochlore floatability. The surface analysis illustrates the link between pyrochlore matrix chemistry, the expression of surface species and their effect on collector adsorption.

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### 1. Introduction

Pyrochlore, the most abundant niobium containing mineral (Perrault and Manker, 1981) is economically recovered in Brazil, China, and Canada (Kouptsidis et al., 2008).

Flotation is the preferred and most cost-effective method for pyrochlore recovery (Burks, 1958; Shapolov and Polkin, 1958; Zakharov et al., 1967; Razvozzhaev and Nikiforov, 1972; Bogdanov et al., 1973; Abeidu, 1974; Raby and Desrochers, 1975; Wilson, 1979; Biss and Nadeau, 1982; Biss, 1985). The Saint-Honore mine (west of Saint-Honore near Chicoutimi, Quebec) is the largest deposit of pyrochlore in North America. Economic recovery of pyrochlore by Niobec Inc. has continued since 1974 (Kouptsidis et al., 2008).

Numerous experiments were performed on the influence of surfactants and type of water to optimise pyrochlore recovery and grade during flotation (Gomez et al., 1987; Rao et al., 1988; Dufresne and Goyette, 2004; Belzile, 2009). These investigations showed 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 mild cationic collector, tallow diamine acetate (Dufresne and Goyette, 2004; Belzile, 2009).

Recent mineralogical investigations on samples from the rougher banks at the Niobec plant have shown that pyrochlore grains with high Fe content appear to be less recoverable than those with a lower

Fe content. The analysis identified that the flotation response is related to matrix (structural) Fe rather than Fe occurring as inclusions within the pyrochlore and suggest that poor floatability is linked to matrix composition (Chehreh Chelgani et al., 2012).

Surface chemistry is the principal determinant for selective separation of the various mineral phases. With a rise in the complexity of the ores processed by flotation, understanding the reactivity of mineral surfaces in this context is becoming increasingly more important. Advanced surface analytical tools are unique in that they have the capacity to link mineral surface characteristics, to process parameters in order to better understand a flotation response (Hart et al., 2006; Biesinger et al., 2007). Several studies have shown that Time of Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) has the capacity for measuring the relative loading characteristics of surface species, mapping their distribution between phases and streams, and therefore can be utilised as a diagnostic tool for process optimisation (Chryssoulis et al., 1995; Nagaraj and Brinen, 1996, 1997, 2001; Smart et al., 2000, 2006; Piantadosi et al., 2000; Piantadosi and Smart, 2002; Hart et al., 2006).

The purpose of this study is to investigate the surface chemical factors affecting the adsorption of the cationic collector tallow diamine on both high iron (Fe-pyrochlore) and low iron pyrochlore (pyrochlore). The investigation is a follow-up to previous work where flotation recovery was linked to matrix Fe content. TOF-SIMS was used to explore the possible factors affecting reagent adsorption on the pyrochlores. These investigations will potentially aid in modelling molecular interactions of the collector and the pyrochlore surface under specific conditions. The results

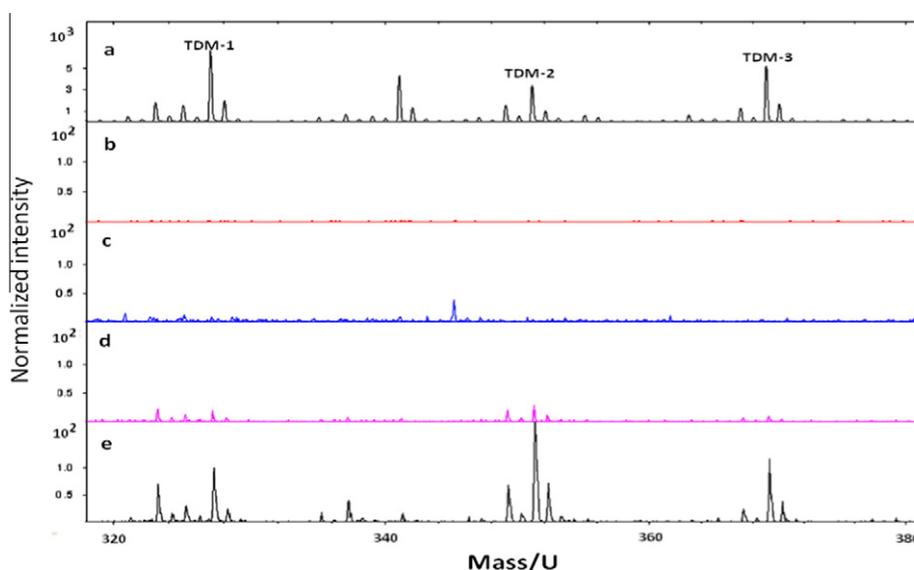
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**Table 1**  
EDX analysis of high iron content (Fe-pyrochlore) and low iron content (pyrochlore) pyrochlore grains. The concentration data is expressed 1 wt.%.

Fe-pyrochlore	Minimum	Maximum	Mean	Std. deviation	Pyrochlore	Minimum	Maximum	Mean	Std. deviation
O	31.65	41.12	36.06	3.89	O	36.12	47.06	41.00	5.37
Na	0.76	1.21	0.93	0.2	Na	2.88	5.91	3.93	1.35
Mg	0.44	0.59	0.51	0.06	Mg	*MDL	0.73	0.37	0.30
Ca	0.47	1.03	0.72	0.23	Ca	6.62	12.82	9.49	2.73
Ti	2	3	2.63	0.28	Ti	2	3	2.27	0.43
Fe	14.28	20.30	16.63	2.58	Fe	*MDL	1.72	0.81	0.7
Sr	1.26	1.94	1.53	0.29	Sr	1.15	5.62	3.82	1.96
Nb	35.28	39.22	37.97	1.83	Nb	28.79	37.25	33.33	3.54
F	*MDL	*MDL	*MDL	*MDL	F	2.92	5.59	4.57	1.17

\*MDL = method detection limits, elements may be present but are below for detection.



**Fig. 1.** Positive ion ToF-SIMS spectrum for tallow diamine (collector), high and low iron content pyrochlore (pyrochlore and Fe-pyrochlore) with and without treatment ((a) collector, (b) Fe-pyrochlore without conditioning, (c) pyrochlore without conditioning, (d) Fe-pyrochlore after conditioning, and (e) pyrochlore after conditioning).

may be used to select the most suitable commercial reagents to optimise selectivity and recovery, or help to design reagents particularly suited to the mineral in this flotation context.

## 2. Experimental methodology

Samples (Fe-pyrochlore and pyrochlore) were obtained from the Niobec mine. In order to evaluate collector adsorption variability and potential causes for identified differences, samples of both high and low Fe pyrochlore were freshly fractured 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.

The instrument used in this work is an ION-TOF, TOF SIMS IV secondary ion mass spectrometer. This technique allows for the analysis of the outermost atomic layers of a surface by mass spectrometry. 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 time of 100 scans. The bombardment of the surface with the bismuth primary ion beam induces the emission of positively and negatively charged secondary ions from the sample surface. These secondary ions are extracted from the sample surface and mass analysed using a time-of-flight mass spectrometer. A plot of secondary ion

**Table 2**

Pearson correlation ( $r$ ) between the average normalised mass intensities for selected species measured on the surface of both high and low iron content pyrochlore gains.

Ions	Nb	Na	Ca	Fe	Sr
Nb	1.000	–	–	–	–
Na	0.954	1.000	–	–	–
Ca	0.929	0.932	1.000	–	–
Fe	–0.111	–0.244	–0.250	1.000	–
Sr	0.718	0.792	0.869	–0.186	1.000
*TDM-1	0.709	0.674	0.486	0.032	0.259
*TDM-2	0.532	0.585	0.379	0.027	0.276
*TDM-3	0.495	0.631	0.437	0.118	0.373

\*TDM-1, \*TDM-2, \*TDM-3 peaks for tallow diamine molecular ion at mass 327, 351, and 369 amu respectively.

intensity versus mass results in a traditional first order mass spectrum, with a resolution of 10,000 above 200 atomic mass units (amu). TOF-SIMS can detect species with concentrations in the ppm range. The data were recorded with full mass spectra in  $256 \times 256$  pixels using a hybrid focussed bunched mode  $^{209}\text{Bi}_3^+$  cluster ion beam with the following beam conditions for spatial resolution:

Ion source: 25 kV  $\text{Bi}^+$ .  
Current:  $\sim 0.3 \mu\text{A}$ .  
Pulse: 1 ns.  
Beam spot size:  $\sim 1 \mu\text{m}$ .

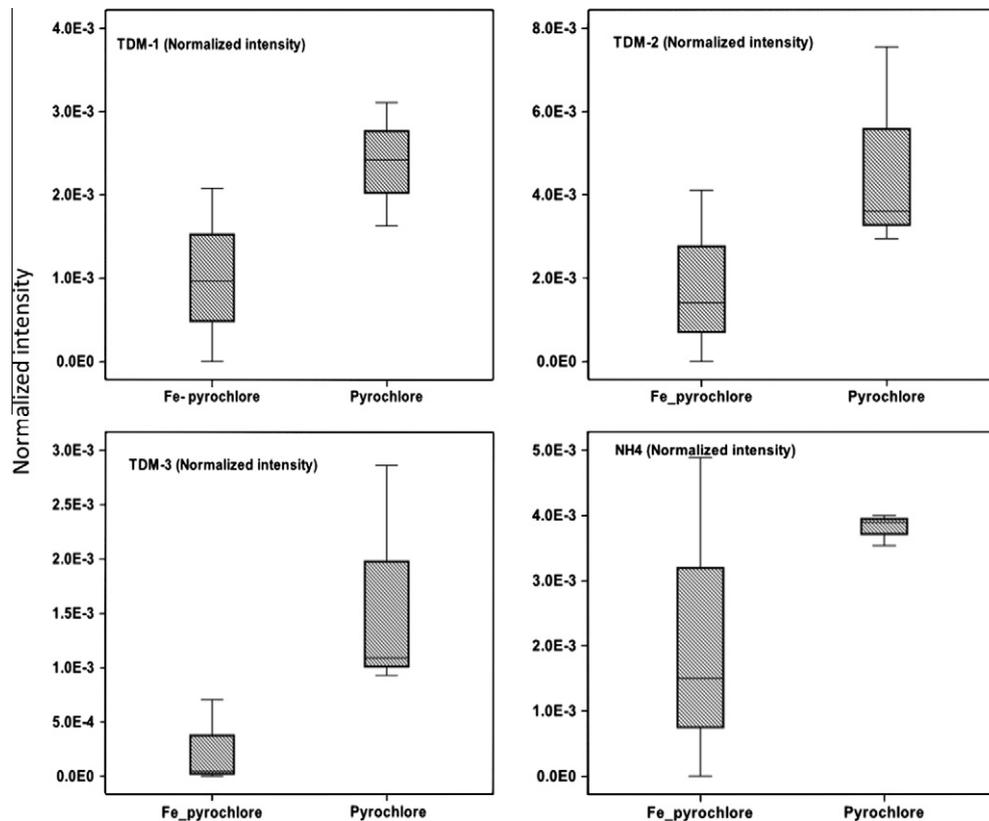


Fig. 2. Box and whisker plots illustrating the relative intensity of cationic collector mass species on the surface of the conditioned Fe-pyrochlore (high iron) and pyrochlore (low iron) grains.

Raster area: generally  $300 \times 300 \mu\text{m}$  (variable).

Mass range: 1–850 amu.

Mass resolution: 10,000 amu.

Sample charging was neutralised with an electron flood gun.

### 2.1. Data treatment

Prior to analysis of the test samples, TOF-SIMS mass spectra of unconditioned freshly fractured high and low Fe pyrochlore grains, and tallow diamine were obtained. All raw spectra were processed using the IONTOF software. Peaks in the calibrated spectra were assigned to specific isotopes in accordance with their atomic mass unit (amu) and similarly peaks reflecting molecular species of the collector were assigned mass positions. The corrected ion intensity for each mass position, measured as the integrated area under each peak corrected for dead times can be related to abundance of the particular specie. In order to compare intensities between areas of different dimensions, corrected intensities were normalised to the total number of counts for the areas examined.

The analytical approach was to conduct comparative surface analyses of the different pyrochlore grains in order to determine statistically significant differences in the surface composition of species particularly related to collector adsorption and potential factors affecting adsorption. The analysis provides a comprehensive survey of the surface species on the mineral grains.

## 3. Results

Samples (Fe-pyrochlore and pyrochlore) were obtained from the Niobec mine. The elemental composition of these samples, determined with energy dispersive X-ray spectroscopy (EDX) is shown in Table 1.

TOF-SIMS spectra in the specified mass position representative of the collector, pyrochlore and Fe-pyrochlore, without conditioning, and after conditioning with tallow diamine are given in Fig. 1. Spectral mass positions representative of tallow diamine occur at mass 327 amu (TDM-1), 351 amu (TDM-2), and 369 amu (TDM-3). None of the diamine representative peaks were identified in the spectra of the untreated pyrochlore samples. The overlain spectra illustrate that the intensity of the collector appears to be stronger on the surface of the pyrochlore grains relative to the Fe-pyrochlore grains (Fig. 1).

The correlation between two variables reflects the degree to which the variables are related. The most common measure of correlation is the Pearson Product Moment Correlation (called Pearson's correlation). The value for a Pearson's correlation can fall between 0 (no correlation) and 1 (perfect correlation). In order to evaluate the relationship between species identified on the surface of pyrochlore grains Pearson correlations were performed on the species intensity data. Inter-correlations between selected ions on the surface of treated pyrochlore and Fe-pyrochlore grains are given in Table 2. These results indicate that there is no significant linear correlation between Fe and the collector species TDM-1, TDM-2, and TDM-3.

While the linear correlation data suggests that there is no relationship between collectors and Fe intensity, the relationship is clearly illustrated graphically where intensities of various species on the surface of the pyrochlore grain are compared. A comparison of the normalised intensities of  $\text{NH}_4$ , TDM-1, TDM-2, and TDM-3 mass positions (representative of the tallow diamine) for treated samples reveals a preference for these species on the surface of the pyrochlore relative to the Fe-pyrochlore (Fig. 2). Discrimination in surface species in favour of Fe rich pyrochlore grains was also noted for Fe, O, OH and FeOH (Fig. 3). Discrimination in favour of

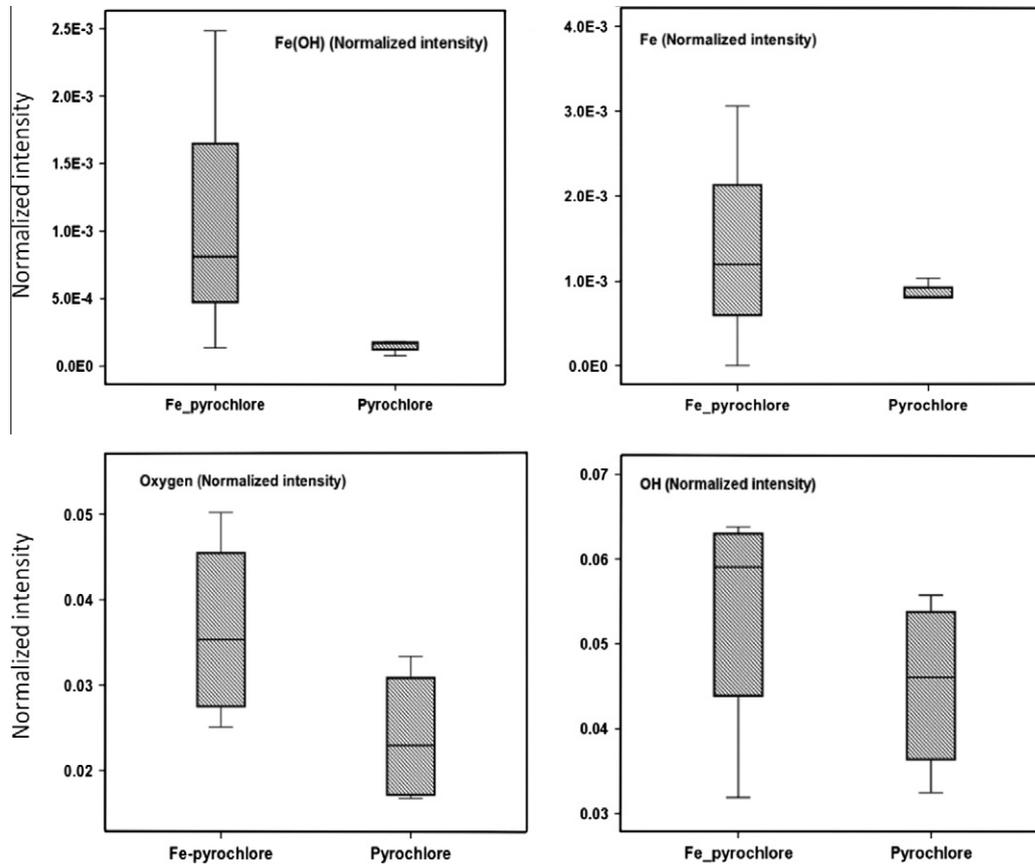


Fig. 3. Box and whisker plots illustrating the relative intensity of oxygen and hydroxide on the surface of conditioned pyrochlore particles.

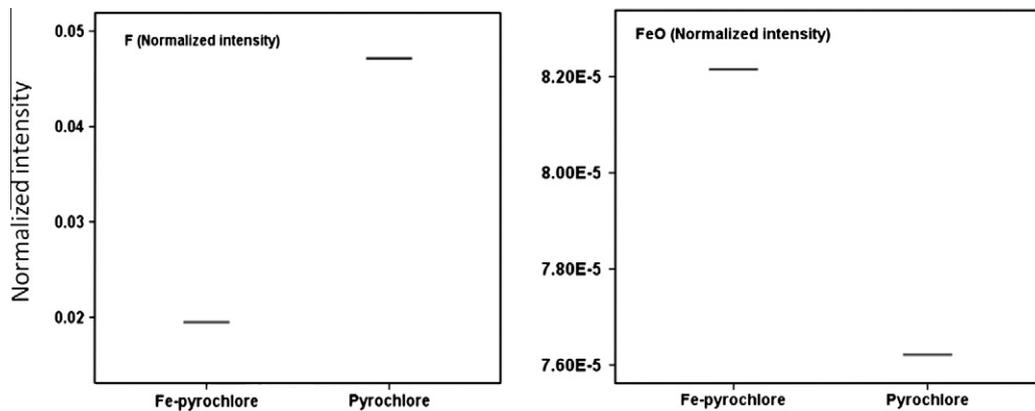


Fig. 4. Box and whisker plots illustrating the relative intensity of F and FeO on the surface of untreated pyrochlore grains.

Fe poor pyrochlore grain surfaces was noted for fluorine (without conditioning samples) (Fig. 4).

#### 4. Discussion

The data suggest that Fe-pyrochlore had, on average, less tallow diamine on their surfaces when compared to the low iron content pyrochlore. Moreover, Fe-pyrochlore grains have more Fe along with FeOH, OH and O on their surface, potentially indicative of preferential oxidation or at the very least, a greater proportion of surface oxidation species. These results are in agreement with the previous studies, suggesting that iron oxide/hydroxide can

cover the surface of pyrochlore, thereby interfering with collector adsorption (Rao et al., 1988). Observations by Abeidu, 1974 and Chehreh Chelgani et al., 2012, that indicate pyrochlore grains with high Fe content appear to be less recoverable, can possibly be related to preferential surface oxidation of the Fe rich pyrochlore rendering the surface unsuitable for collector attachment. Previous investigations have also suggested that a higher proportion of Fe possibly decreases the negative surface charge on grains, potentially preventing the adsorption of the cationic amine collectors (Barros et al., 2008; Chehreh Chelgani et al., 2012).

From this study, it is evident that the surface of Fe-pyrochlore grains contains a greater intensity of species indicative of oxidation

relative to the low Fe pyrochlore. In oxide minerals, the magnitude of the negative surface charge is determined by the density of the structural (matrix compound) or adsorbed potential-determining negative ions (i.e.  $\text{N}^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ , etc.) (Somasundaran and Agar, 1967; Somasundaran, 1968; Elimelech et al., 1994). According to the previous studies on Niobec samples, the surface of pyrochlore was negatively charged in the 6–7 pH range (Dufresne and Goyette, 2004; Gomez, 1987; Rao et al., 1988; Belzile, 2009). Although there was little discussion on surface charge in relation to matrix chemistry, the exhibited negative surface charge may be related to the presence of negative ions in the matrix or attached to the surface. According to the results in this study (Fig. 4), the average normalised intensity of fluorine on the surface of pyrochlore is greater than that on the surface of Fe-pyrochlore particles. Higher fluorine contents in the low iron pyrochlore grains were also detected in the EDX analysis (Table 1), suggesting that the F surface expression may be related to the matrix composition.

From these analyses better flotation performance by the low Fe pyrochlore grains is likely in response to the greater proportion of cationic collectors attached to their surface. Their preference for attachment may be related to a higher proportion of near surface negatively charged matrix ions effectively increasing the negative surface charge. Poor collector attachment to the Fe-pyrochlore grain surface may be related to the presence of oxidative species (Fig. 3). As the mineral surface becomes increasingly covered with metal oxide/hydroxide species the surface become increasingly less negative and can even become positively charged (Fornasiero et al., 1992, 1994; Witika and Dobias, 1993; Fairthorne et al., 1997; Fullston et al., 1999; Barnes et al., 2009). From this data, it appears that surface oxidation negatively effects collector attachment and, that an increase in surface oxidation is linked to higher proportions of matrix Fe in the pyrochlore structure.

## 5. Conclusion

Surface composition controls the surface reactivity and consequently plays an important role in determining flotation behaviour of minerals. Surface analysis techniques such as TOF-SIMS allow for a direct ex situ determination of the degree of collector adsorption on the surface of minerals. The present study utilises the TOF-SIMS technique to investigate the adsorption of the cationic collector, tallow diamine, on the surface of different types of pyrochlore (high iron and low iron content). The TOF-SIMS results verify a relationship between pyrochlore surface reactivity and Fe content in the mineral matrix. It was demonstrated that the intensity of the oxidative species O, OH and FeOH was greater on the surface of high Fe pyrochlore particles in comparison with low Fe pyrochlore particles. Furthermore the intensity of collector species was significantly higher on the surface of the Fe poor pyrochlore. The link between surface and matrix chemistry is identified. The results from these tests at least partially explain the flotation selectivity of low Fe pyrochlore grains relative to high Fe pyrochlore grains, where preferential surface oxidation favours the high Fe pyrochlores resulting in diminished collector attachment and poor recovery.

## Acknowledgment

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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