2010 Synchrotron Ice Project Summary Report

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Executive Summary

The Bosworth Creek Monitoring Project (BCMP) is a multi-disciplinary, long-term study of a local watershed by high school students from Mackenzie Mountain School, Norman Wells, NT, local residents, and researchers from universities and government agencies. The four seasonal phases of the creek (open water, freeze-up, frozen and break-up) are sampled for biological and chemical baseline inventories that help monitor potential impacts resulting from industrial activities and climate change. A close working relationship with scientists from southern universities, government agencies and industry provides northern high school students with exceptional scientific career opportunities.

Introduction and Program Overview

The Bosworth Creek Monitoring Project (BCMP) was initiated in 2006 following concerns raised by local residents about fish stocks following the removal of a weir. The weir was constructed in 1960 to create a pond needed to run a power generation station for an oil refinery. Closure of the refinery resulted in dismantling the weir in 2005 by Imperial Oil Resources NWT Limited under a Reclamation and Restoration Plan. The Sahtu Renewable Resources Board (SRRB) contacted the Department of Fisheries and Oceans (DFO) about the logistics involved in restocking the creek. It was decided that fish would likely re-inhabit the creek on their own and the project was created to allow local youth an opportunity to track these changes over time. The BCMP is looking at most aspects of the 125 square kilometre watershed including flora, fauna, geology, geography, climatology, and chemistry. The BCMP is aimed at local youth comprised of approximately 55% Dene and Métis and 45 % of other ethnic origins. The project includes approximately equal participation by both genders and encourages and supports young women to pursue careers in the sciences.

The BCMP has acquired the most extensive chemistry data set for any creek in the NWT. These samples were collected over three and a half years and include approximately 55 sediment, 61 water and 17 ice samples. During the course of these collections, it became apparent that there were three kinds of ice at Bosworth Creek. The first two are chemically related and include frozen creek water and blue-green overflow. Blue-green overflow (Figure 1) is well known by northerners and results from groundwater forcing its way through a frozen surface layer and causing local flooding events that lead to successional layers of ice on top of the original surface. This type of overflow is the same ground water that normally flows in creeks during the summer, and for many creeks like Bosworth, throughout the winter under the ice.

Blue-green overflow may exit through fissures in creek or lake ice where pressure ridges separate. However, the most common source flows through terrestrial sediments that either border waterways, or occur in areas were ground water doesn't normally flow; such as seismic lines, roads and low-lying topography. Slight differences in chemistry compared to creek water may reflect this interaction and appears to be marginally influenced by local differences in soil chemistry. Regardless, this ground water does not undergo significant changes and does not pose any potential health concerns to local wildlife or people.

The third type of ice is yellow-brown in colour (Figure 2) and exhibits elevated levels of most heavy metals (Table 1) and some other properties. These differences in chemistry prompted further investigation that identified this type of ice occurring throughout much of the Sahtu Settlement Area. Moreover, local elders and others do not recall seeing this type of ice in the past; while recently, reports have accumulated about first time appearances at places where it never occurred before.

Since this ice seems to be increasing in both prevalence and abundance, local Aboriginal leaders and community members are becoming concerned about the possible impacts to the health of their people, and the wildlife that are essential for Dene and Métis subsistence and identity.

It was decided that a more thorough investigation was required following the preliminary analysis of the elemental ice chemistry. An application was submitted to the Canadian Light Source Inc. (CLSI) at the University of Saskatchewan to undertake synchrotron x-ray analysis of the soil and both types of overflow. This world class research facility provides limited time annually for high school youth to undertake original science projects through the Students on the Beamline Program. Our application was approved following extensive peer review and samples were obtained from soil and both, yellow-brown and blue-green overflows. These samples were analyzed by three students from two Sahtu communities and included Chantal Bavarad (Chief Albert Wright School [CAWS], Tulita) and Siobhan Quigg and Nigel Gregory (Mackenzie Mountain School [MMS], Norman Wells).

Methods

The "Ice Team" collected samples of both kinds of ice and processed them into dry powder (Figure 3). This was a laborious task that produced approximately 10g of precipitate for every 5L of yellow-brown ice water and 1g for every 5L of blue-green ice water. Samples were obtained by the students from Bosworth Creek, Norman Wells and Four Mile Creek, Tulita. Following processing, the samples and team members travelled to Saskatoon to run experiments at the CLSI Synchrotron March 2-4, 2010. This is a student driven project and they actively participated in all aspects of experimental design and procedures including sample collection, local preparation of samples, sample preparation at CLSI, data collection, data analysis, and will be contributing to a Poster Presentation, and co-authoring a publication with the beamline scientist on their findings.

A synchrotron is a machine that produces brilliant light by forcing electrons to change direction with powerful magnets. Basically, the procedure employs an electron gun that supplies a linear accelerator with electrons that are accelerated by microwave radio frequency to 250 million electron volts (MeV). The electrons are then sent to the inner booster ring where further microwave fields increase the energy to 2,900 MeV. This energy produces an electron flow that travels approximately 99.999998% light speed, or 4.7 m/s slower than the speed of light. When the electrons reach 2,900 MeV, they are transferred by an injection system into the outer storage ring where they circulate for 4 to 12 hours. The circular looking storage ring is composed of 12 straight sections that bend the electrons into a circular path with powerful magnets. Photons are produced every time the 6,800 kg dipole magnets change the direction of the electron flow and other types of magnetic or insertion devices called wigglers and undulators produce a very high flux of photons along the beamline. The wigglers produce a wide range of high energy x-rays, while undulators produce higher intensities of x-rays with a narrower range of energies (Walker 2009).

The photons are then passed through a monochronometer at the beginning of each beamline that allows researchers to choose which wavelength they require. Different beamlines employ specific kinds of monochronometers and this project was granted an 8 hour shift on the Spherical Grating Monochronometer (SGM) Beamline on March 3. This beamline employs soft x-rays ranging between 250 - 2,000 eV and is typically used for studying materials containing elements with low atomic numbers (Walker 2009).

The students spent March 2 learning about and touring the facility (Figure 4) and included radiological safety orientations, other housekeeping duties and specimen preparations (Figure 5) so that they were fully prepared at the beginning of their shift the following morning. The shift began at 8AM and the first samples were loaded into the endstation (Figure 6) and a vacuum of 10^{-11} torr was achieved by 8:40AM (1 atmosphere Pressure = 760 torr). This level of vacuum is required to minimize electron and photon interactions with other atoms and molecules and there are fewer molecules in the system than there are in space surrounding the international space station (Walker 2009). However, this process is time consuming and care must be taken in choosing samples and procedures to best maximize the limited time available.

The students were responsible for undertaking the experiments. Assistance was provided by Dr. Robert Blyth, Assistant Director of Research, Tracy Walker, Education Outreach Coordinator, Ronda Martens (CLS) and Jamie Mackenzie (CLS). However, all decisions regarding sample priorities, the level of scrutiny, and direction of research were made by the students.

This was significant for two reasons. First, each experiment that was preformed on a particular sample was time consuming in itself, particularly if the range of investigation leads to unexpected results. This occurred on several occasions throughout the shift and the students had to decide 'on the fly' as to their next course of action. Second, their decisions led to the discovery of two previously unknown phenomena; (1) the ability to image strontium with this beamline and (2) the possible discovery of a new species of oxygen.

Each student took turns operating the computer, while the other two were occupied with data recording duties. Except for brief washroom breaks, the students only took 10 minutes off each, for lunch. The shift ended at 4PM precisely.

March 4 was a very hectic day in which the students compared their data with published values, recorded their observations and drew their conclusions. These were used to create a PowerPoint presentation that the students gave to CLSI staff that included more than a dozen beamline scientists and technicians at 3:30PM that afternoon (Figure 7).

Results and Observations

Elemental chemistry of blue-green and yellow-brown overflow has shown that the latter contains higher concentrations of measured parameters (refer to Table 1), but that both share similar relative abundances of these elements (Figures 8 and 9). In fact, there appears to be as much variation in the relative abundances within each type of ice, as there are between them.

Soils demonstrate variations between samples to a lesser degree and may reflect examples of local industrial contamination, other human activities and local geological characteristics.

However, the relative abundance of comparable elements indicates very little, if any relationship between the soils and ice (Figure 10). This suggests that the impact on both kinds of ice from soil chemistry is either uniform or insignificant.

Synchrotron light analyses provide an avenue of investigation that cannot be undertaken through regular elemental analyses. The Spherical Grating Monochronometer (SGM) provides information about the structure of a substance or compound. As the x-rays interact with the sample, the amount of photon absorption can be measured as the Total Electron Yield (TEY). This value occurs at known energy levels for each element (Figure 11). If a particular element is present, then it will not only occur at the known energy level, but it will also profile a unique signature that is associated with a particular compound. For example, elemental calcium produces a TEY between approximately 348 eV and 356 eV and resembles a single peak sine wave. The Ca in the soil and both ice samples closely matches the spectrum for calcium carbonate ($CaCo_3$) as seen in Figure 12. This is expected since limestone dominants the landscape.

The drawback of this method lies in the apparent lack of a general key for identifying elemental compounds, necessitating exhaustive literature reviews. An example of this can be seen in the sodium profiles (Figure 13). Each ice has a distinct and different sodium compound. It was initially believed that the yellow-brown ice contained sodium chloride (NaCl) but this was dismissed because first peak is too short. It is unclear as to which compounds either of these sodium spectra relates. Oxygen provides another example of unknown compounds (Figure 14). The two forms of ice share similar spectra, although a difference resides between the two at approximately 543 eV. Both share minor resemblances to compounds such as calcium oxide (CaO) and strontium oxide (SrO) (after Nakai et al. 1987) but significant differences preclude their identification. It is possible that these compounds are either unknown, or have never been previously investigated using synchrotron radiation. Moreover, these profiles differ completely with that of soil which illustrates a typical signature (Figure 14a).

This project produced the first SGM spectra for strontium in the facility's history (Figure 15). This occurred because strontium lies at the extreme imaging end of SGM resolution and was previously not attempted. It is currently not known if this has been replicated by other facilities and these spectra may be the first SGM baseline data for this element.

Discussion

Blue-green overflow exhibits very similar chemistry to ordinary creek water and likely originates from the same source as most flowing creeks throughout the summer. This ice is well-known by local people and has been around as long as anyone can remember. It often poses serious threats to travelers while in its slushy state but does not pose any chemical health concerns. Blue-green overflow generally occurs at predictable locations where ground water is halted by the formation of frost walls in creek substrate or in areas dominated by springs.

The yellow overflow is different. While its elemental chemistry is similar to blue-green overflow and creek water in relative abundances, the levels of many elements including Calcium (Ca), Potassium (K), Magnesium (Mg), Sodium (Na), Iron (Fe), Manganese (Mn), Aluminum (Al), Arsenic (As), Boron (B), Barium (Ba), Copper (Cu), Lithium (Li), Molybdenum (Mo), Nickel (Ni), Lead (Pb), and Uranium (U) occur at levels ten times or higher.

Another characteristic of this ice is its presence at so many different kinds of locations. Yellow overflow occurs in some areas of disturbance and some areas that have never been disturbed by industry. It sometimes occurs in association with blue-green overflow and known locations of springs. However, it also occurs independently of blue-green overflow and in locations that are not associated with springs. It appears to be forming at new locations as evidenced by several examples this winter. Areas that are known to exhibit this ice also appear to be increasing in volume annually. Given the broad range of variables and its concentrated nature, yellow-brown overflow must be coming from a different source than regular ground water. The most plausible reservoir is permafrost.

This poses a serious concern. While, its presence may not be that significant in itself, the potential cumulative effect is enormous and has prompted a call for testing country foods for uranium and other related elements. Since this overflow inundates areas rich in lichens, mosses and shrubs that are consumed by caribou, moose and other important subsistence species, there is potential for long-term accumulation of these contaminants by people

Finally, the issue of colour remains unresolved. The yellow-brown overflow may be caused by sulphur as this yellow metal is known to occur in both the sediments and waters in and around Bosworth Creek. Sulphurous vapours are ever-present in some areas along the creek and arise from springs that flow at well-known locations. This water produces a strong sulphur smell but is transparent, whereas, the yellow-brown ice has no smell and does not produce one when melted, while still retaining colour. Therefore, sulphur does not account for the yellow-brown colour of the ice.

Conclusions

Yellow-brown overflow ice contains elevated levels of several elements that can become toxic to people and wildlife through bioaccumulation. This ice seems to be increasing in prevalence and occurs at both predictable and unpredictable locations. Local community residents are concerned about the potential negative impacts that this ice could have on their health and their traditional subsistence practices. The SRRB will initiate a testing program in response to these concerns that will investigate potential contamination of country foods in the Sahtu Settlement Area. These studies will address major subsistence species including moose, caribou and several predatory fish that are prone to bioaccumulation.

The source of this ice remains unknown but it seems to be arising from a different source than the blue-green overflow or general creek water; making permafrost a likely candidate. If this is the case, then the problem will escalate and may do so very rapidly given the current rate of permafrost degradation throughout the north. The preliminary results from elemental chemistry and synchrotron X-ray bombardment suggest that this is a very complicated issue and that further sampling and analyses are required to establish baseline information. These studies will provide tools necessary for mitigating potential negative health impacts to the people of the north.

Figure 1: Typical blue-green overflow ice.

Figure 2: Typical yellow overflow ice.

Table 1. Elemental chemistry of some creek water and blue-green and yellow-brown overflow ice

mg/L	Creek Water	Blue-Green	Yellow-Brown	Yellow-Brown
Calcium (Ca)	120	164	1540	1710
Potassium (K)	1.83	2.47	74.4	70.3
Magnesium (Mg)	47.3	66.6	773	983
Sodium (Na)	31	55.2	1020	670
Iron (Fe)	0.034	0.0406	0.986	0.243
Manganese (Mn)	0.0056	0.0116	0.734	0.0926
Aluminum (Al)	0.01	0.023	0.326	0.072
Boron (B)	<0.050	0.057	0.609	0.852
Barium (Ba)	0.0861	0.112	1.32	0.998
Cobalt (Co)	<0.0020	<0.0020	0.0036	0.0021
Copper (Cu)	<0.0010	0.0037	0.0226	0.0222
Lithium (Li)	0.013	0.016	0.237	0.282
Molybdenum (Mo)	<0.0050	<0.0050	0.018	0.0478
Nickel (Ni)	0.0034	0.0041	0.0398	0.0381
Lead (Pb)	<0.00010	0.00086	0.00869	0.00418
Antimony (Sb)	<0.00040	<0.00040	0.00116	0.0016
Titanium (Ti)	0.0012	<0.0010	0.0133	0.0084
Uranium (U)	0.00178	0.00362	0.0203	0.0387
Vanadium (V)	<0.0010	<0.0010	0.0035	0.0020
Zinc (Zn)	<0.0040	0.0108	0.187	0.039

Figure 3. Collection and preparation of the samples. 3a: science teacher Kit Dennis-Walker and Chantal Bavard from Chief Albert Wright School, Tulita; 3b: Siobhan Quigg and Nigel Gregory from Mackenzie Mountain School, Norman Wells; 3c: melting yellow-brown overflow ice in a beaker; 3d: precipitate that rises to the top of the ice during melting at room temperature; 5e: the dried precipitate that was ground in a mortar and pestle to create very fine powder.

Figure 4. March 2, 2010. 4a: writing the radiation safety exam; 4b touring the facility (the large animal receiving bay where they are able to image live animals as large as bison); 4c: the synchrotron control room; 4d: the Spherical Grating Monochronometer beamline; 4e: the endstation where the samples are placed for analyses.

Figure 5. Preparation of the samples for the beamline. Each sample is prepared by covering a piece of carbon tape with the powdered precipitate. 5a: Tracy Walker (CLS) and Chantal Bavard discussing technique with Siobhan Quigg and Jamie Mackenzie (CLS) working on another sample; 5b: Chantal and Siobhan working intently with Jamie looking on; 5c: Tracy, Nigel Gregory, Siobhan and Jamie; 3d: the final stages of preparation; 5e: the finished sample ready for the endstation.

Figure 6. March 3, 2010. 6a: the first samples are loaded into the endstation; 6b: Siobhan at the controls; 6c:checking another sample before loading it into the endstation; 6d: finding something unusual; 6e: conducting original science.

Figure 7. March 4, 2010. Presentation to CLS staff. 7a: Jamie and Siobhan looking over notes for the presentation; 7b: Chantal Bavard; 7c: Nigel Gregory; 7d: Siobhan Quigg; 7e cookies and coffee following a successful presentation.

Figure 8. Relative abundance of comparable yellow-brown ice values.

Figure 9. Relative abundance of comparable blue-green ice values.

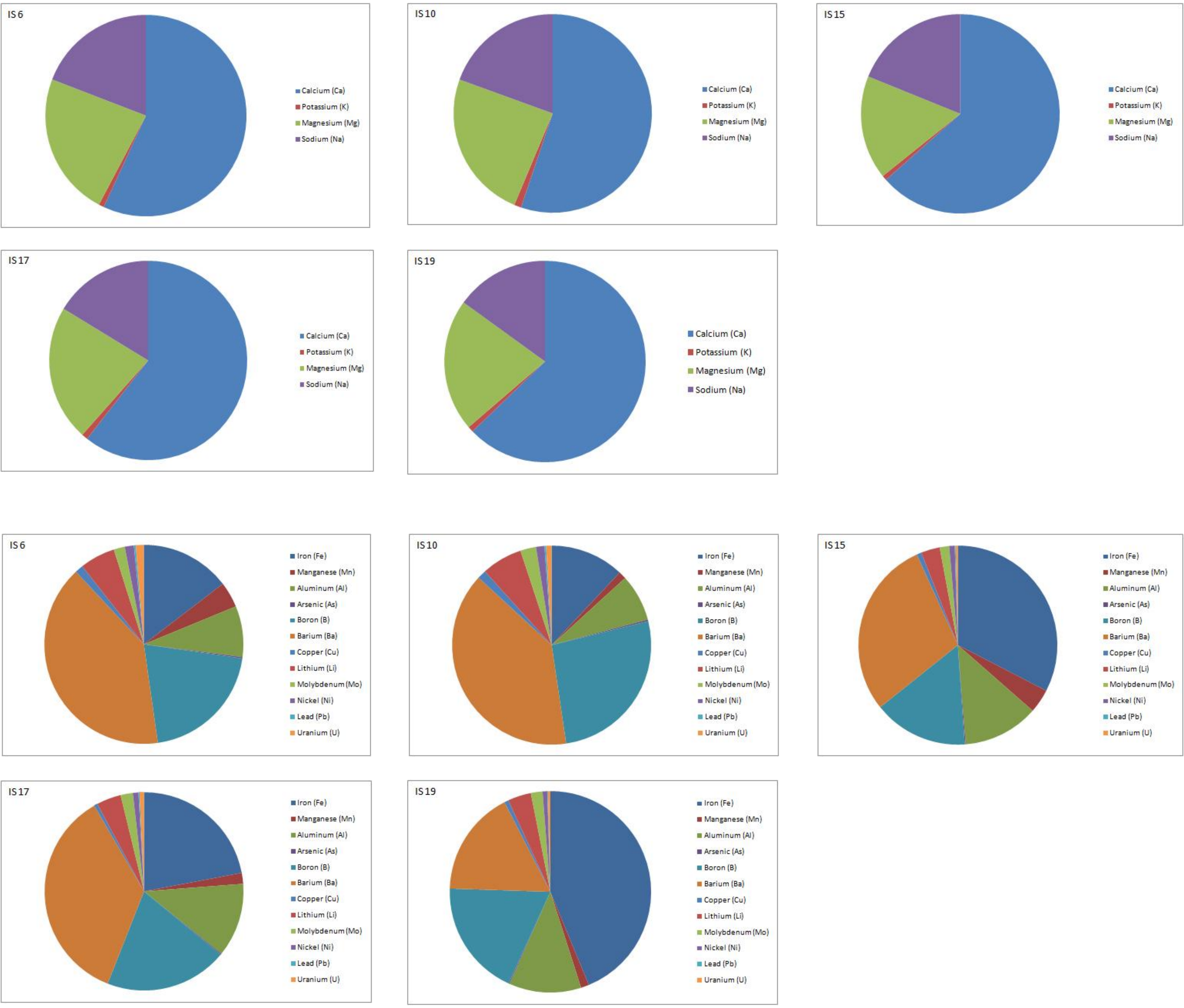
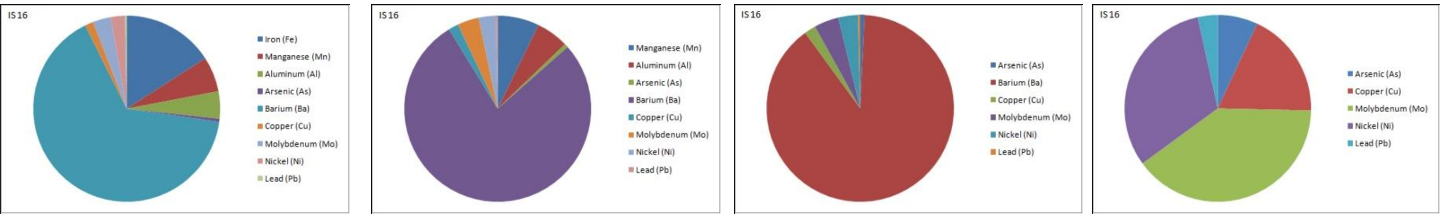
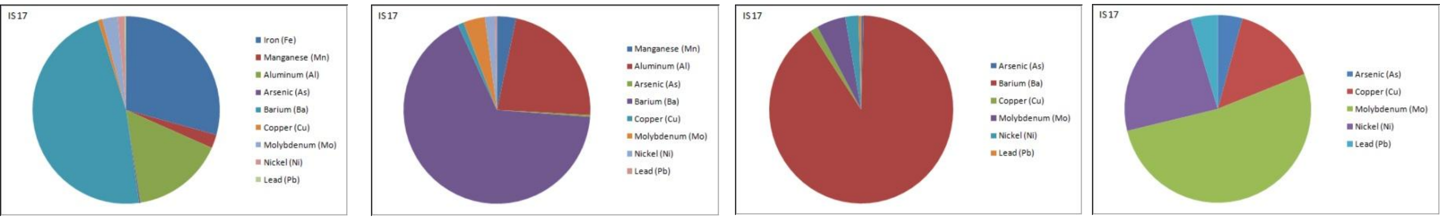


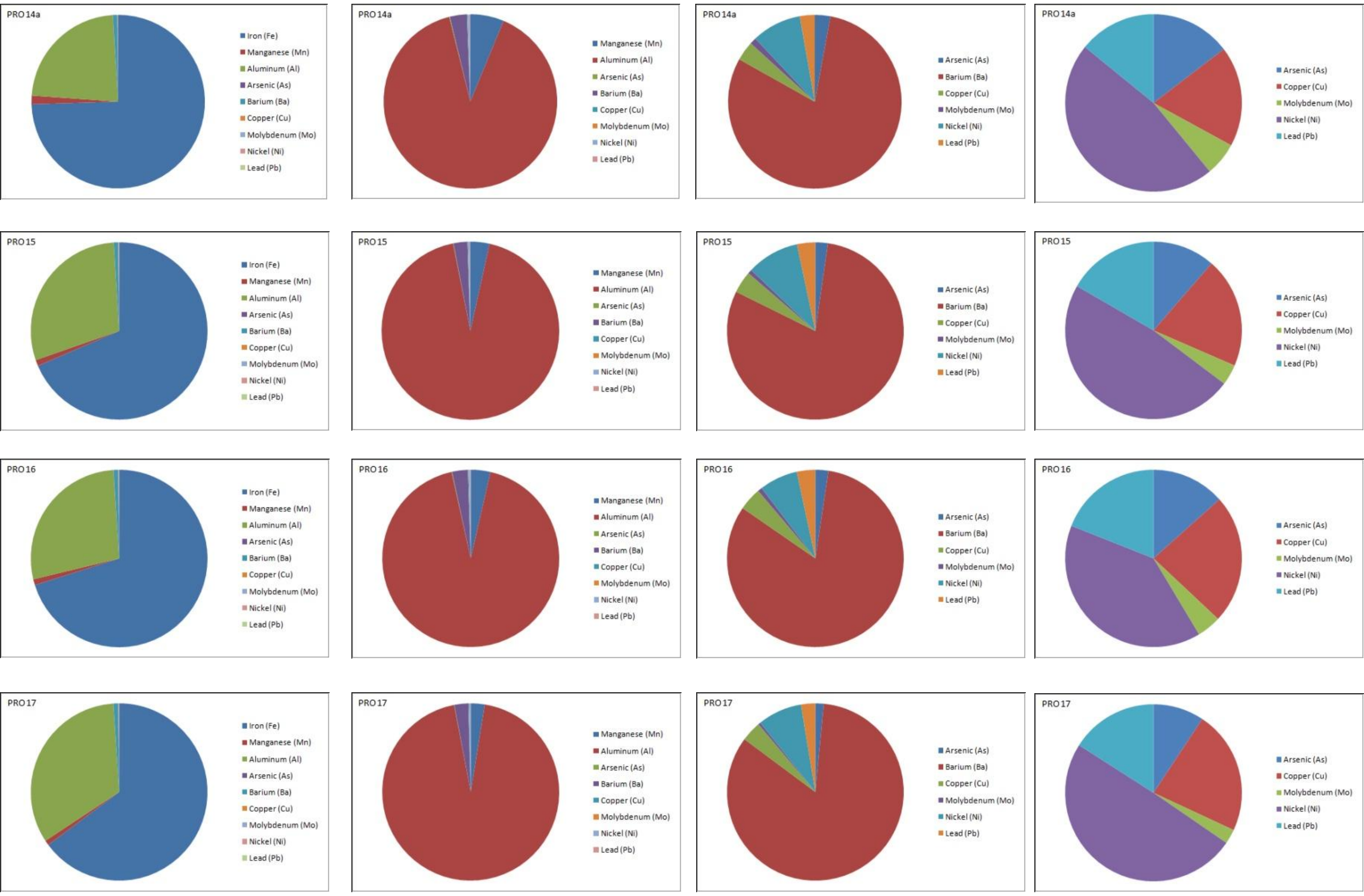
Figure 10. Relative abundance of comparable ice and soil values



Ice : IS 16 (Y-B)



Ice : IS 17 (B-G)



Soils: PRO 14a, PRO 15, PRO 16, PRO 17

Figure 11. Total Electron Yields (TEY) for carbon (C), oxygen (O), sodium (Na), magnesium (Mg), aluminium (Al), and silicon (Si). Each spectrum occurs at specific energy levels and pure elements produce these sign wave patterns (from Walker 2009).

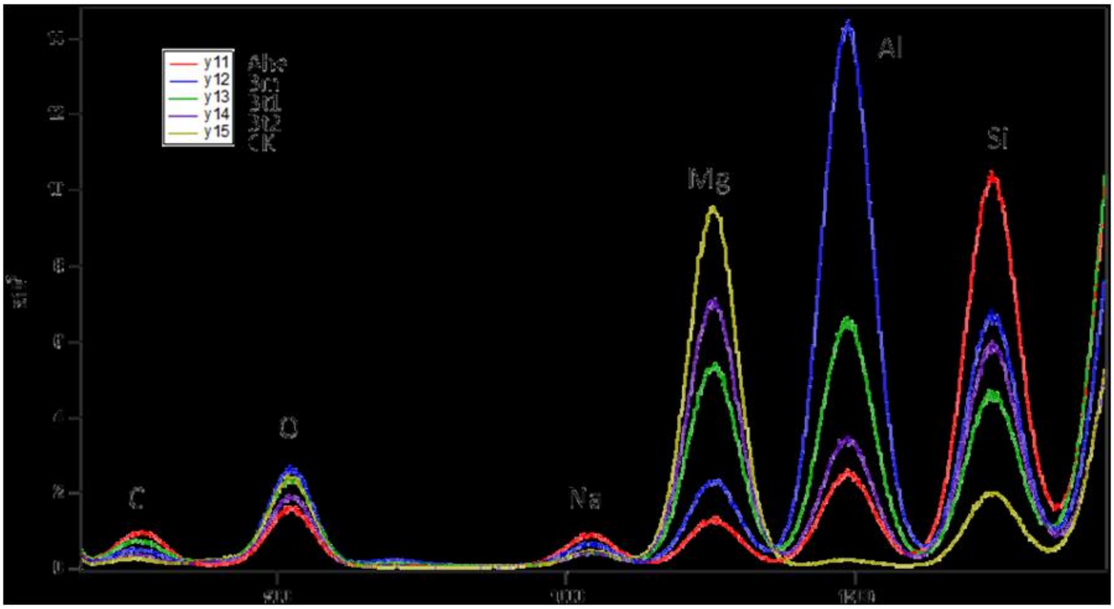
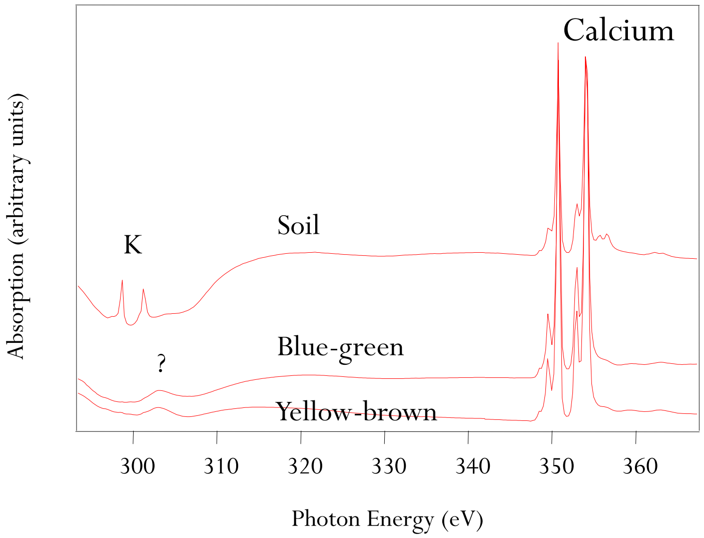


Figure 12. TEY Ca spectrums of soil and both types of ice from Bosworth Creek. These signatures closely resemble a CaCo3 spectrum (From Ko et al. 2007) and occur within the expected energy range of Ca. K appears in the soil sample but is absent from both ice samples, although each exhibits unknown signatures that occur beyond the eV range for K.



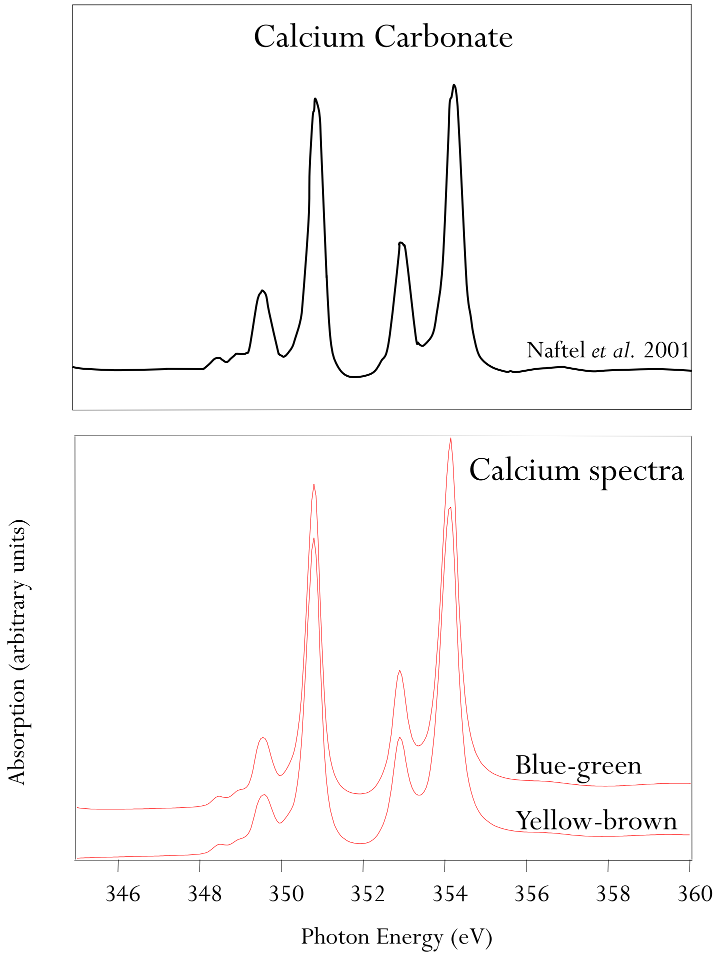


Figure 13. Calcium eV range TEY spectrums of both types of ice from Bosworth Creek. These signatures closely resemble a $CaCo_3$ spectrum (From Ko et al. 2007) and are assumed to be calcium carbonate.

Figure 14. TEY Na spectrums of both types of ice from Bosworth Creek. These spectra were initially thought to be the result of Cl addition, resulting in NaCl. However, the lack of peak signatures precludes NaCl as the likely compound and both ice samples exhibit different compound structural edges. Further investigation is required.

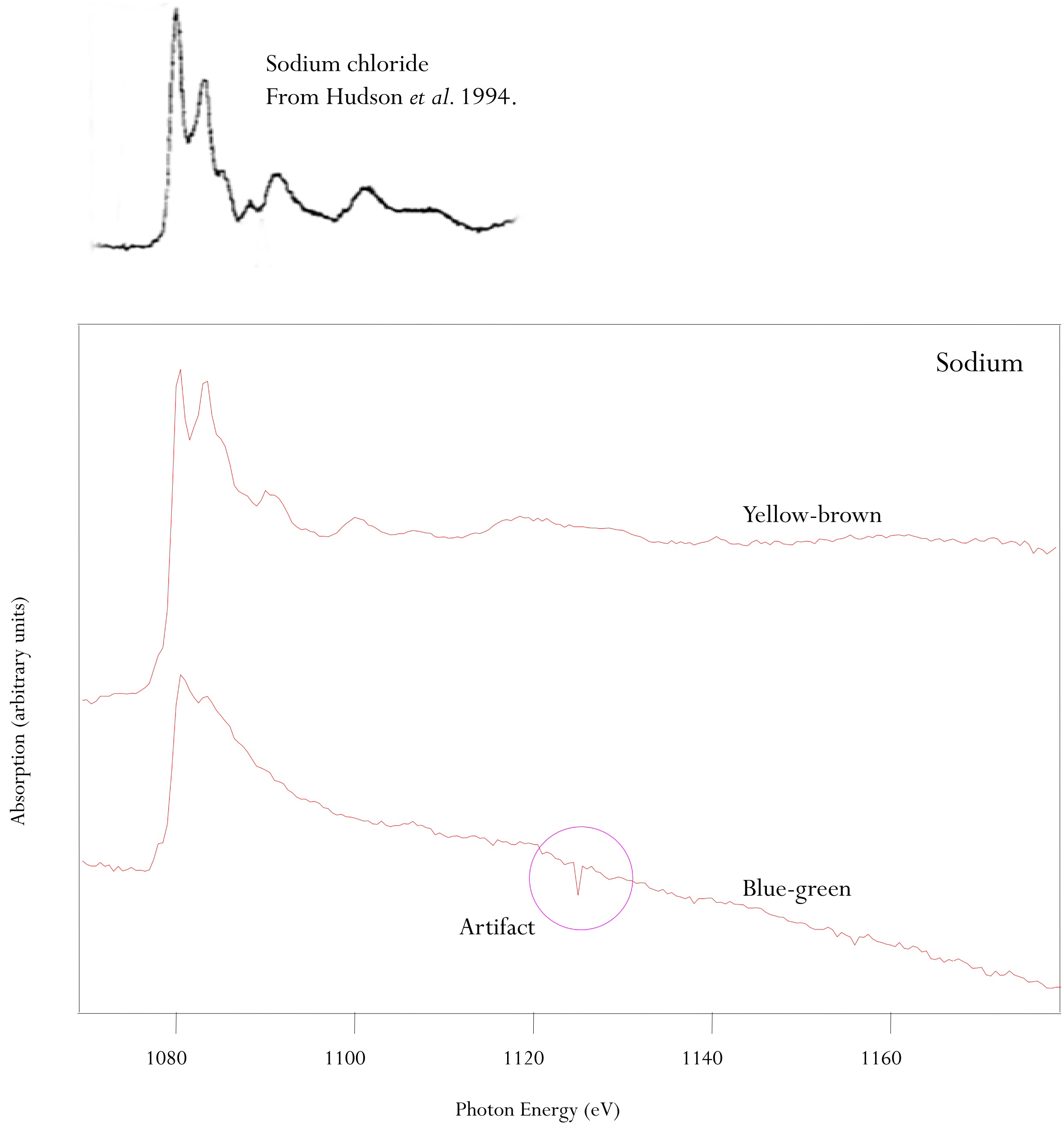
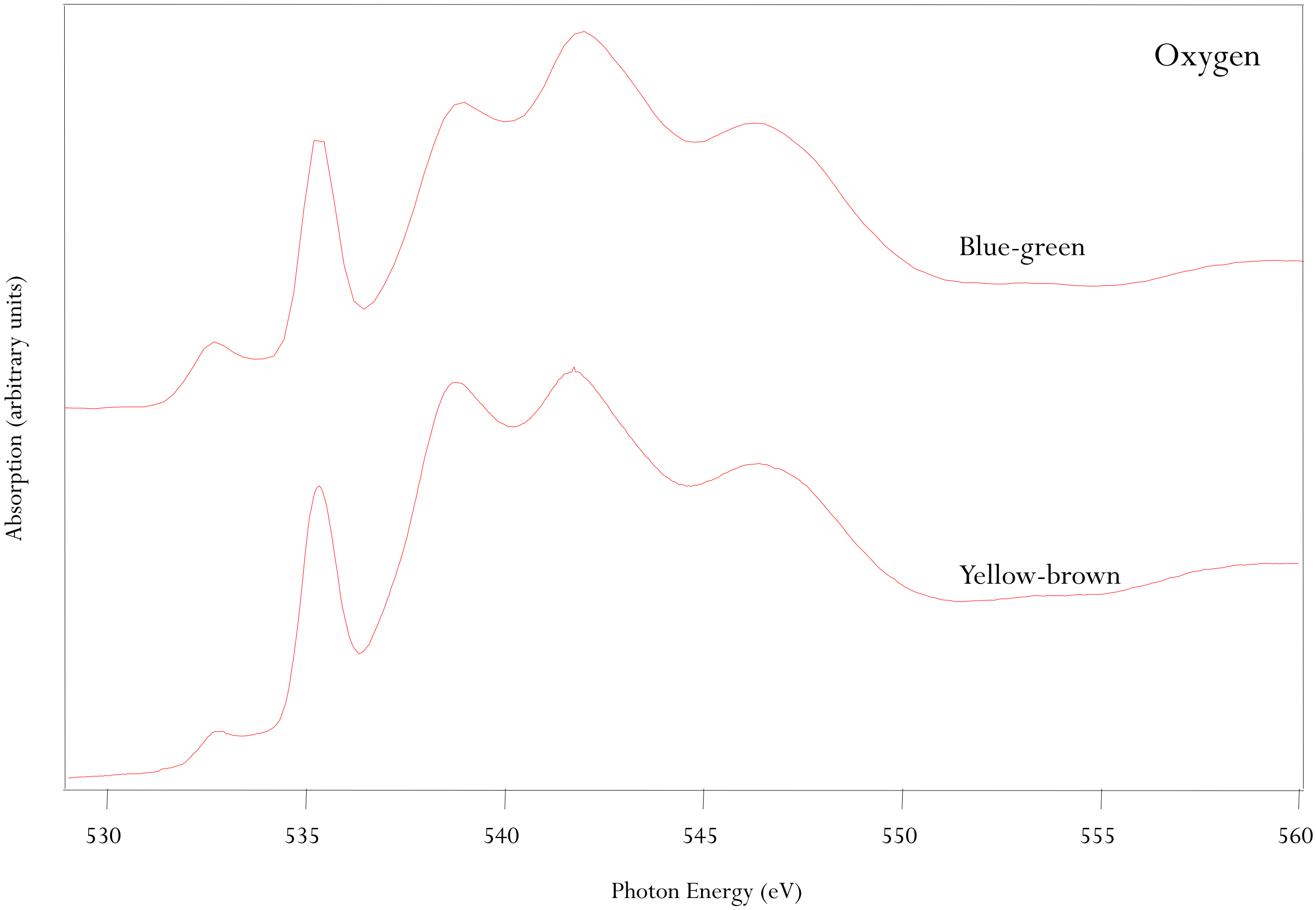


Figure 15. TEY O spectrums of both types of ice from Bosworth Creek are currently unknown and may represent an unknown species or compound. The TEY O spectrum for soil (not shown) is a typical signature also occurring within the expected eV range for O.



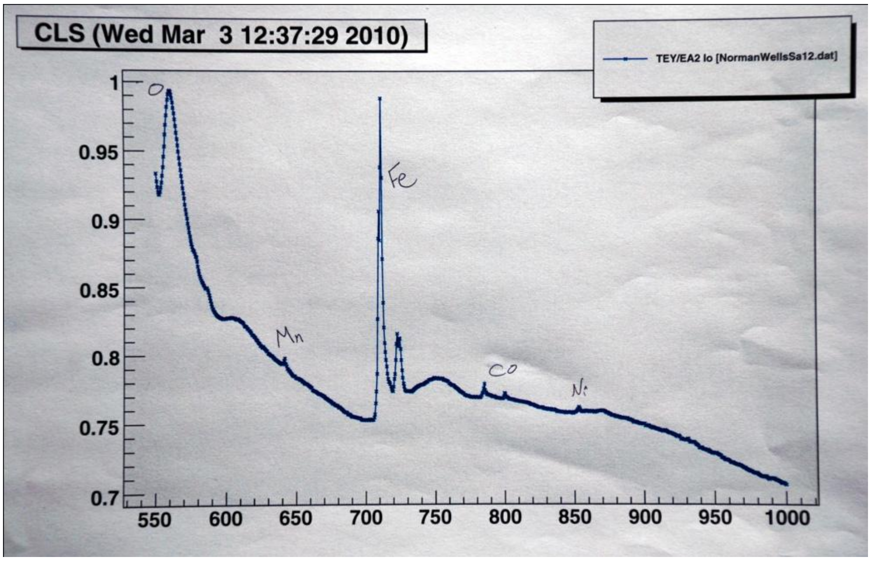
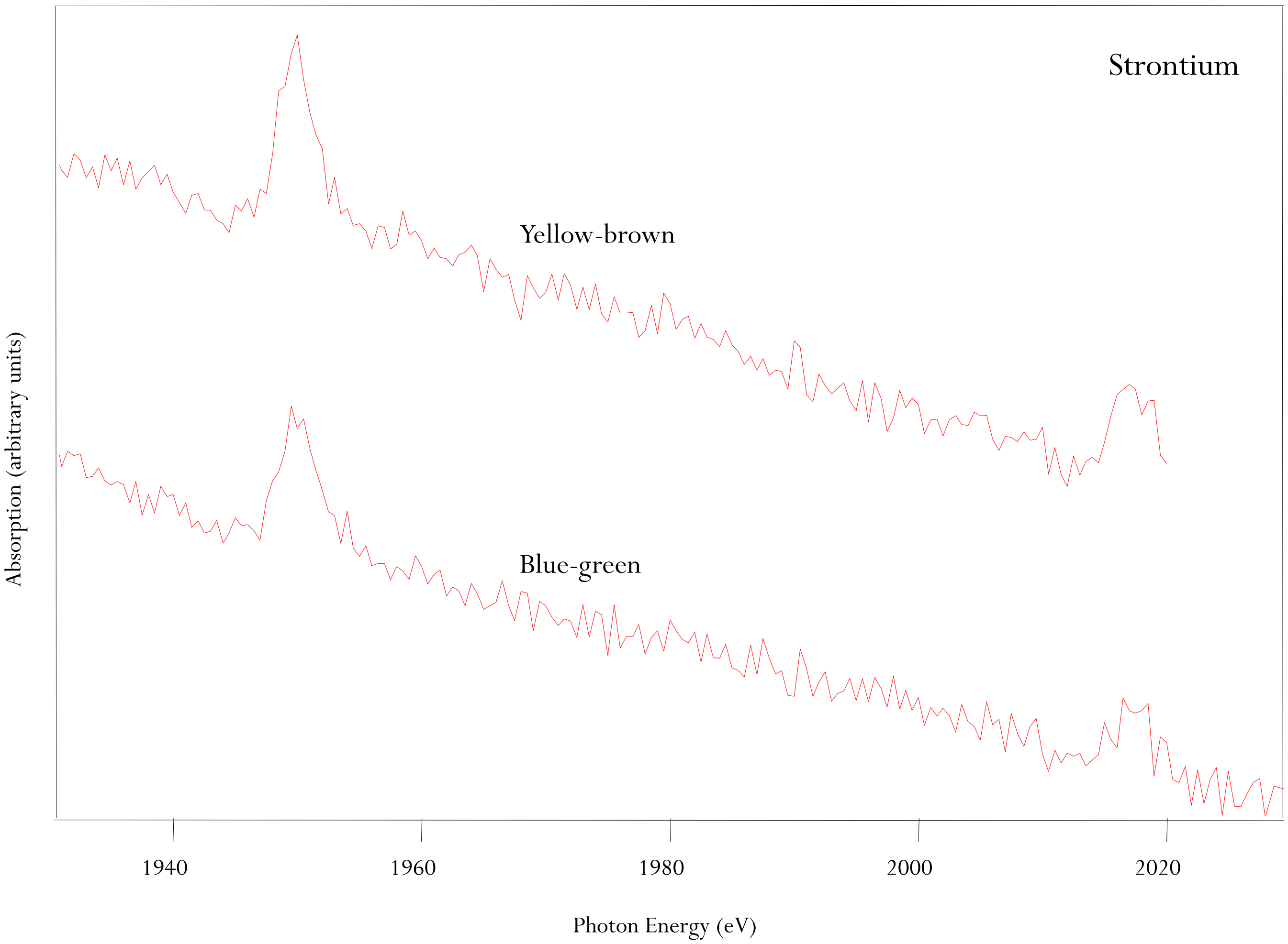


Figure 15a. The TEY spectrum for oxygen in soil is a typical signature occurring near the 550 eV range. Other elements occurring in this sequence include manganese, iron, cobalt and nickel.

Figure 16. TEY Sr spectrums of both types of ice from Bosworth Creek. These are the first Sr spectra imaged by SGM in the CLSI facility. These may be the first SGM baseline spectra for Sr, as this element occurs at the far range of SGM beamline energy. The peak that occurs near 1940 eV represents the $L_3 2p_{3/2}$ orbital and the peak on the right represents the $L_2 2p_{1/2}$ orbital.



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