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Chemical differentiation between immersed and dry wood samples in Nunavik (northern Quebec, Canada): preliminary results

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A B S T R A C T

The primary aim of this study was to differentiate immersed wood samples from dry wood samples based on chemical analysis. The method has been developed to be applied to wood found in archaeological sites to distinguish between driftwood and wood that was cut in the forest tundra and then transported to the sites. The results of our research show that Na concentrations in the immersed samples were much higher than in the dry samples for coniferous and deciduous wood samples. Principal components analysis (PCA) based on the element concentrations normalized to the total cation concentrations show that the data from the immersed wood samples and the dry wood samples clustered into two separate groups.

Introduction

Several wood resources were found at Arctic archaeological sites and provide evidence of the importance of wood in the daily lives of the Paleoeskimo and Neoeskimo peoples (e.g., Laeyendecker, 1993a, 1993b; Arnold, 1994; Gronnøw, 1996; Alix, 2004; Desrosiers et al., 2010). Wood was used to build boats, kayaks, sleds, houses, hunting tools, and to make fire. However, since this raw material was rare in this treeless region of the tundra, it is necessary to ask whether the wood found at archaeological sites came from driftwood collected near the sites or from trees cut at the edge of the boreal forest farther south. In particular, what is the origin of archaeological wood found at the IbGk-3 site (Qijurittuq) on Drayton Island, which is located in the treeless tundra about 20 km south of Inukjuak (northern Quebec, Canada) (Fig. 1) (Avataq Cultural Institute, 2008, 2009; Desrosiers et al., 2010; Lemieux et al., 2011; Steelandt et al., 2013). Spruce (*Picea* sp.), larch (*Larix* sp.), willow (*Salix* sp.), poplar (*Populus* sp.), and alder (*Alnus* sp.) were the main species of driftwood and archaeological wood specimens found in this area (Steelandt, 2015).

With regard to driftwood, very few studies have used different methods in order to distinguish driftwood that underwent river and sea transport from living wood that was deliberately cut. Some, for example, have focused on the presence of marine fungi as an indicator of floating in marine waters (Strongman and Rand, 1991; Abdel-Wahab and Jones, 2000). Entomological studies can also detect the presence of marine encrusters and borers in floating driftwood, including isopods such as *Limnoria lignorum* (Hill and Kofoid, 1927; Noda, 1981), or marine mollusks that specialize in wood boring such as *Teredo navalis* (Paalvast and van der Velde,

FIGURE 1. Location of wood sampling sites and fieldwork sites in Umiujaq and Kuujjuarapik (black dots) (Nunavik) and the IbGk-3 archaeological site on Drayton Island in Inukjuak (black square and map on the left).

2011; Eriksen et al., 2014) or *Teredo bartschi* (Cragg et al., 2009). However, the absence of these organisms on the large wood samples is not a conclusive proof that they had not been immersed in water.

Other studies have attempted to detect changes in the physical and mechanical properties of immersed wood. Notably, some anatomical and physical changes were found in the outer part of sapwood that resulted from bacterial action after a long immersion in water (Clausen, 2010). In contrast, no differences in compressive strength, flexural strength, and modulus of rupture were noted in fir (*Abies* sp.) and spruce (*Picea* sp.) (Bues, 1986) or in pine (*Pinus taeda*) (Syme and Saucier, 1995). Alix (2001) found no significant difference in density between driftwood from spruce in Victoria Island and from nonfloated spruce around Yellowknife. She also noted that seawater does not have a high enough concentration of salt to act on the physical properties of the wood.

In addition to examining the physical characteristics of driftwood, some chemical studies and experiments were conducted to distinguish driftwood from cut green wood and archaeological wood, as well as to identify specific degradations in driftwood or waterlogged wood. Typically, the study of chemical changes in wood that has come into contact with water is done in order to prevent or assess the deterioration of waterlogged archaeological wood or to improve conservation techniques. Gravimetric techniques are used to isolate and quantify the elements, but instrumental techniques such as Raman, nuclear magnetic resonance (NMR), Fourier transform infrared (FT-IR) spectroscopy, and pyrolysis are also used (e.g., Christensen et al., 2006; Tamburini et al., 2014). Molecular analysis of polysaccharide content also highlights potential alterations in archaeological objects after prolonged periods in aqueous environments or following attack by wood-degrading bacteria and fungi (Łucejko et al., 2012). Fengel and Wegener (1988) showed that the amount of lignin and secondary compounds slightly decrease in the trunks of fir (*Abies* sp.) and spruce (*Picea* sp.) that were immersed in fresh water for over 17 years, while the amount of cellulose and hemicellulose remained the same.

In the scholarly literature, only a few studies have focused on variations in chemical composition. In a leading study, Alix and Stimmell (1996) compared the relative changes in the concentration of elements between driftwood, deadwood, green wood, and archaeological wood using neutron activation analysis. They hypothesized that driftwood and archaeological wood may have undergone various chemical exchanges (i.e., absorption or leaching) while they were immersed in the water or buried in the soil. Four driftwood specimens from Victoria Island in the Arctic Ocean and seven deadwood

specimens and three green wood specimens from Yellowknife in the Northwest Territories (Canada) were subjected to chemical analysis. All of them were coniferous trees, either spruce (*Picea* sp.) or larch (*Larix* sp.). Their results revealed a strong enrichment in sodium (Na) and chloride (Cl), which are the main chemical elements in seawater, as well as enrichment in iodine (I), bromine (Br), and uranium (U) for driftwood samples compared to deadwood and green wood samples. However, all of these elements presented a wide range of concentrations for which there was no systematic explanation, which reflects the complexity of chemical exchanges between wood and environmental media.

In another important study of chemical changes in wood, Caruso Fermé et al. (2014) compared wood samples of *Nothofagus pumilio* and *Berberis* sp. from different forest, coastal marine, and lake areas in Patagonia with woody remains of the same species from the Orejas de Burro 1 archaeological site (Argentina) using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM–EDX). They found that burned driftwood preserved the chemical signal of seawater and could serve as a means of detecting marine driftwood. This recent study shows that the modern reference charcoal samples are mainly composed of C, O, and probably Ca and K, which are components of organic plant tissues; by contrast, the modern and archaeological charcoal and wood samples present additional chemical elements (Al, Si, Fe, Na, Mg, K, Cl, and Ca) and/or minerals.

This paper presents the findings of a novel study that sought to analyze how seawater may influence multiple concentrations of chemical elements on deciduous and coniferous wood specimens that were immersed under controlled conditions in Nunavik (Canadian Low Arctic) based on the total acid digestion of wood samples.

Materials and Methods

Fieldwork and Sampling

During the fieldwork campaigns of 2008, 2010, and 2011, eight taxa of driftwood were found on the beaches on the west coast of Nunavik. Deciduous species included willow (*Salix* sp.), alder (*Alnus* sp.), poplar (*Populus* sp.), and birch (*Betula* sp.); coniferous wood species included spruce (*Picea* sp.), larch (*Larix* sp.), white cedar (*Thuja* sp.), and fir (*Abies* sp.). On average, deciduous driftwood pieces were 22.93 ± 2.43 yr old (n = 504) with an average diameter of 3.79 ± 1.66 cm (n = 527), while coniferous driftwood pieces were 62.85 ± 7.19 yr old (n = 424) with an average diameter of 7.11 ± 0.7 cm (n = 484) (Steelandt et al., 2015).

For this preliminary study, only the main species found in driftwood clusters in Nunavik were considered. Two wood samples between 20 and 30 cm in length were collected from green willow (*Salix* sp.) and alder (*Alnus* sp.) shrubs around Umiujaq and from green larch (*Larix* sp.) and spruce (*Picea* sp.) trees around Kuujjuarapik-Whapmagoostui (Fig. 1). The two willow samples were 10 and 6 yr of age with a diameter of 8.4 and 7 mm, respectively; the two alder samples were 11 and 7 yr of age with a diameter of 8.6 and 5 mm, respectively; the two spruce samples were 20 and 30 yr of age with a diameter of 5 and 4 mm, respectively; the two larch samples were 15 and 11 yr of age with a diameter of 4 and 4.5 mm, respectively. Each wood sample was cut into two parts. One part was kept dry in an airtight bag in order to avoid seawater contamination, while the other was immersed in Hudson Bay for a week (field period) (Fig. 1). Each of the parts was kept under the same climatic conditions during the experiment.

Analytical Procedures

The wood samples were stripped of their bark, cleaned for 5 min in deionized water in order to remove any seawater, and then dried at 50 °C in a stove. Approximately 0.5 g from the last three rings of the deciduous samples and the last seven rings of the coniferous samples were collected by scraping with a ceramic knife. The samples were then ground in an agate mortar with a few drops of liquid nitrogen and homogenized for acid digestion.

All of the wood samples were chemically digested in a cleanroom. Approximately 0.15 g of wood powder was mixed with 6 mL of concentrated HNO_3 in a clean Savillex® digestion vessel. The vessel was then closed and heated on a hot plate (80 °C) for 48 h. Afterwards, the solution was evaporated. This step was repeated a second time with 4 mL of concentrated HNO_3. Then, 20 drops of ultrapure hydrogen peroxide (H_2O_2) were added to the samples in order to ensure the total oxidation of organic matter. The closed beakers were heated on a hot

plate at 80 °C for 24 h and the solution was evaporated. The samples were then dissolved in 0.37N HNO_3 and analyzed for major and trace elements using an Agilent Technologies TM HP4500 inductively coupled plasma mass spectrometry (ICP-MS) instrument at Rennes University. Indium (In) was used as an internal standard. The ICP-MS technique only detects the concentrations of cations, so the anion concentrations were not determined in this study. The international geostandards SLRS-4 (riverine water reference) and SRM1573a (tomato leaves reference) were used to check the validity and reproducibility of the analyses. The concentrations of 14 elements were determined: Na, Ca, Mg, K, Al, Si, Mn, Fe, Cu, Zn, Sr, Ba, Pb, and B. Typical rates of uncertainty (including all error sources) are <5% for all trace elements, whereas for major anions the uncertainty lies between 2% and 5%, depending on the concentration levels.

Statistical Analysis

In order to test the hypothesis that immersion in seawater may change the chemical composition of driftwood, principal components analysis (PCA) was performed on the original data from the wood samples. This method is useful for revealing correlation patterns in complex databases (e.g., Derrien et al., 2012). The 14 ICP-MS element concentrations (variables) in 16 wood samples (individuals) were analyzed using multivariate analysis (PCA). The PCA was based on a correlation matrix, whereby the data set was standardized and normalized. The PCA and relative statistical tests were performed with XLSTAT (Addinsoft, v. 7.5), using nonparametric tests for small samples of unknown distribution (Mann-Whitney).

Results and Discussion

Very few studies have concentrated on changes in the chemistry of wood. Some studies have focused on the organic components (Filley, 2003) and their decomposition over time (Waksman and Stevens, 1929); other studies have focused on the inorganic chemical composition of wood in order to distinguish green cut wood from driftwood (Alix and Stimmell, 1996) or on the chemical composition of particles contained in the structure of the wood in order to determine whether the wood was in contact with river water or seawater (Caruso Fermé et al., 2014).

Major and Trace Element Concentrations in the Dry and Immersed Wood Samples

Driftwood logs that have been transported by river and/or seawater may absorb some elements directly from the water. Some elements may also be leached from the wood into the water or vice versa. Accordingly, the chemistry of the wood may be different for driftwood as compared to dry wood, making possible the identification of a chemical fingerprint that may be used to distinguish dry wood from immersed wood. In this study, the concentrations of cation elements were determined for both dry and immersed pieces of the same original wood samples in order to highlight the potential influence of a short period of immersion in seawater on the wood chemistry.

The results of our experiments on the chemical composition of dry wood samples and wood samples that were immersed in seawater for one week are presented in Figure 2 and Table 1. In Figure 2, the chemical compositions of the immersed and dry wood samples are compared by plotting the ratio of element concentration of immersed to dry samples. This ratio highlights the enrichment (positive number) or depletion (negative number) of an element due to immersion. The range of element concentrations is wide and depends on the particular element and the wood species. All of the results were compared to those published in Alix and Stimmell (1996) and Caruso Fermé et al. (2014). However, a comprehensive comparison could not be performed because the three studies focus on different elements.

In general, the dry wood samples have low Na concentrations, less than 65 ppm, with an average of 46.34 ± 15.58 ppm for the coniferous samples and less than 249 ppm with an average of 124.9 ± 85.3 ppm for the deciduous samples. The corresponding immersed wood samples have Na concentrations 23 to 103 times higher than the dry wood samples, with an average of 1622 ± 782 ppm for the coniferous samples and 4165 ± 1662 ppm for the deciduous samples. A slight Mg enrichment is also observed in the immersed wood samples as compared to the dry wood samples with mean val-

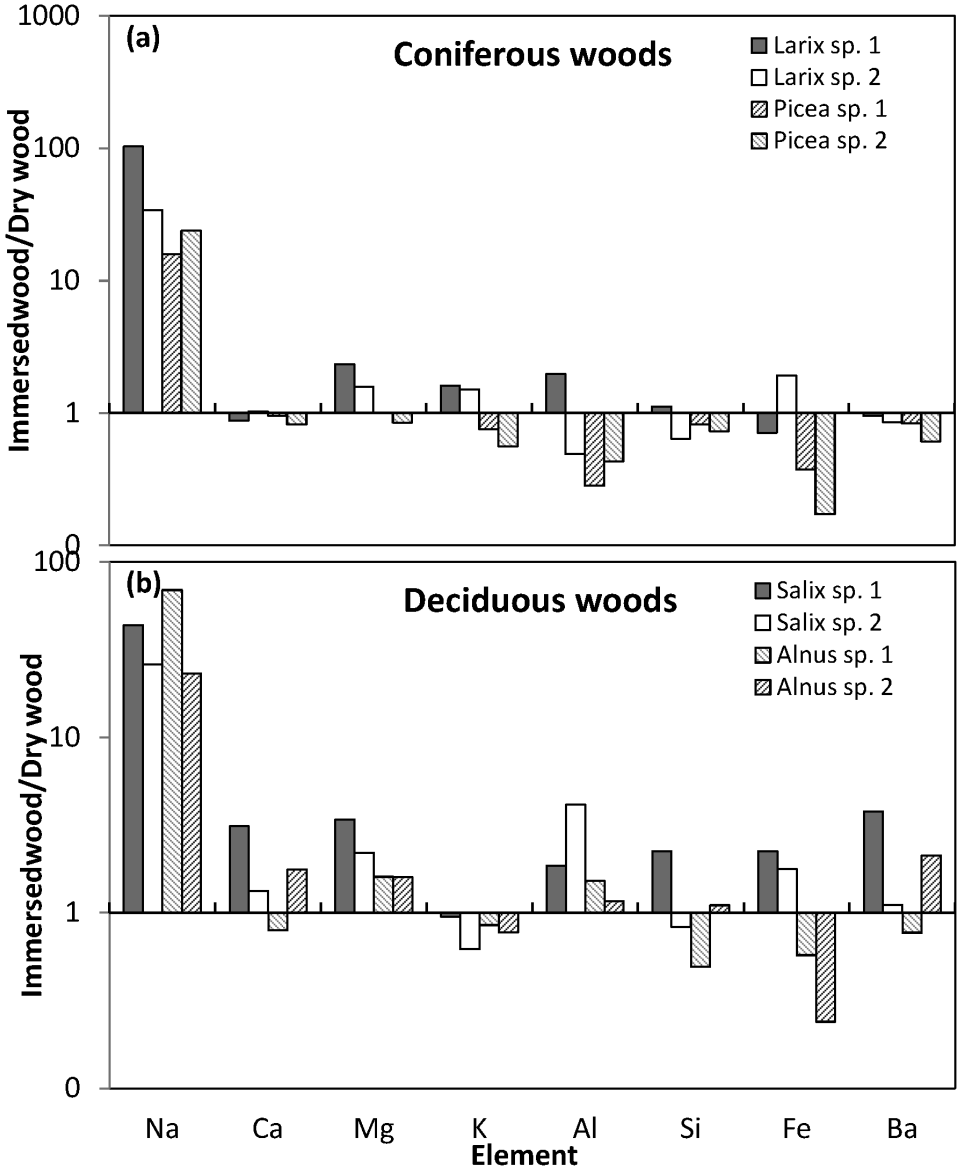

FIGURE 2. Concentrations of Na, Ca, Mg, K, Al, Si, Mn, Fe, and Ba in ppm in the immersed wood samples relative to dry wood samples for: (a) coniferous wood samples, and (b) deciduous wood samples. Values higher than 1 indicate the addition of elements through immersion in seawater; values less than 1 indicate a leaching of elements into seawater.

ues of 264.69 ± 71.47 ppm and 361.91 ± 138.05 ppm in the dry and immersed coniferous wood samples, respectively, and of 604.71 ± 263.71 ppm and 1296.09 ± 636.04 ppm in the dry and immersed deciduous wood samples, respectively. Na and Mg are the most common elements in seawater and Hudson Bay water (Obbard et al., 2009), so it is reasonable to expect that these elements would be incorporated into driftwood, either as particles or salt precipitates (e.g., Caruso Fermé et al., 2014). These Na and Mg enrichments observed in the immersed wood samples as compared to the dry wood samples in this study were also observed in Alix and Stimmell (1996) and Caruso Fermé et al. (2014). However, the Na concentration levels in the immersed coniferous wood samples are 2 to 7 times lower than in the driftwood samples of the same species analyzed by Alix and Stimmell (1996). The lower Na concentrations in our samples may be due to either the lower salinity of Hudson Bay water (Obbard et al., 2009) or the short immersion period for our samples. Indeed, in most Canadian coastal areas, salinities are lower than the oceanic average because freshwater inputs are plentiful and evaporation rates are relatively low due to the cooler climate (Harrison et al., 1983). Thus, in contrast to the Arctic Ocean surrounding Victoria Island and other ocean surface water (ranged from 32‰–38‰) (Kalle, 1971), Hudson Bay has a lower average salinity (ranged from 17‰–32‰) (NOAA, 2001) because of its low rate of evaporation, the large volume of freshwater entering the bay, and the

TABLE 1

Element concentrations (ppm or μg g^{-1} of wood) in dry, immersed wood samples.

Sample	Na	Ca	Mg	K	Al	B	Si	V	Mn	Fe	Cu	Zn	Sr	Ba	Pb
CONIFEROUS WOOD SAMPLES															
Wet *Picea* sp. 1	1020	1367	362	612	6.1	3.8	54.0	0.013	106.3	7.3	1.9	41.0	8.2	26.1	0.154
Dry *Picea* sp. 1	65	1427	358	811	21.6	3.3	51.3	0.035	129.3	19.6	1.5	38.4	9.1	31.3	0.150
Wet *Picea* sp. 2	1138	827	233	551	18.8	3.2	46.5	0.020	48.3	9.6	2.1	22.3	5.9	12.1	0.069
Dry *Picea* sp. 2	48	1006	275	979	43.5	2.3	102.2	0.107	66.1	55.7	2.1	24.3	6.4	19.7	0.157
Wet *Larix* sp. 1	2735	625	553	625	20.0	4.2	59.9	0.009	86.4	6.0	1.0	19.1	10.3	20.6	0.082
Dry *Larix* sp. 1	26	713	237	390	10.1	2.2	52.7	0.012	77.0	8.4	1.3	11.5	8.0	21.7	0.090
Wet *Larix* sp. 2	1597	540	299	695	5.8	3.1	46.7	0.007	67.6	10.4	1.0	18.1	7.7	13.2	0.442
Dry *Larix* sp. 2	47	524	189	459	11.9	2.2	50.7	0.010	105.8	5.4	1.1	8.3	7.5	15.4	0.072
DECIDUOUS WOOD SAMPLES															
Wet *Salix* sp. 1	3686	2851	1362	1018	8.6	18.6	83.9	0.037	66.0	16.6	9.3	147.1	28.6	39.1	0.402
Dry *Salix* sp. 1	84	917	401	1071	4.6	5.1	94.7	0.011	29.4	7.4	7.5	44.9	7.4	10.3	0.098
Wet *Salix* sp. 2	6471	3313	2164	1130	52.6	20.3	123.0	0.140	81.5	66.8	11.9	110.8	34.5	39.0	0.359
Dry *Salix* sp. 2	249	2486	984	1821	12.7	8.5	64.3	0.016	98.3	37.5	7.5	86.0	19.7	35.2	0.103
Wet *Alnus* sp. 1	3990	1709	929	656	13.2	12.5	50.5	0.071	41.4	26.9	3.5	102.1	18.0	25.5	0.550
Dry *Alnus* sp. 1	58	2146	579	769	8.6	6.8	41.3	0.029	83.8	46.9	3.7	109.9	14.8	33.1	0.361
Wet *Alnus* sp. 2	2517	1204	729	1038	5.8	10	46.9	0.020	96.4	9.1	3.5	145.2	11.4	22.5	0.318
Dry *Alnus* sp. 2	109	681	455	1339	5.0	4.9	59.4	0.012	87.1	37.9	3.1	71.0	4.7	10.6	0.382

limited circulation of this brackish water with the Atlantic Ocean (Howarth and Mohan, 2013).

Moreover, compared to the one-week immersion of our samples, the driftwood spruces of Victoria Island that likely originated from boreal forests in North America may have travelled several weeks, months, or years (Dyke et al., 1997; Dyke and Savelle, 2000). Such a long period of immersion may have caused the incorporation of Na (and Cl) and precipitated the entry of more salt minerals into the wood structure. Finally, it has been shown that a longer immersion time promotes the physico-chemical or biological weathering of dead wood (Vannote et al., 1980; Bilby and Ward, 1989, 1991). The increased degradation of the driftwood may facilitate its enrichment by elements such as Na and Cl. On the other hand, the nature of the soil and bedrock on which the tree grew (in Kuujjuarapik-Whapmagoostui) also has to be taken into account. Indeed, this soil may be depleted in Na compared to the soils on which the driftwood samples from Victoria Island grew. However, because of the unknown origin of the wood samples, this hypothesis cannot be confirmed.

The Na and Mg enrichment in the immersed wood samples is also accompanied by a slight enrichment in B in both the coniferous and deciduous wood samples. The mean B concentrations were 3.58 ± 0.52 ppm and 2.49 ± 0.52 ppm in the immersed and dry coniferous wood samples, respectively, while those in the immersed and dry deciduous wood samples were 15.36 ± 4.92 ppm and 6.33 ± 1.70 ppm, respectively.

Conversely, K was slightly depleted in all of the deciduous wood samples after immersion in seawater, with mean values ranging from 1250.14 ± 446.27 ppm to 960.49 ± 209.72 ppm in the dry and immersed deciduous wood samples, respectively.

Terrigenous elements such as Al and Si that are derived from alumino-silicate minerals are found to be relatively concentrated in both deciduous and coniferous wood samples. The respective mean Si concentrations in the dry and immersed coniferous

wood samples are 64.22 ± 25.33 ppm and 51.78 ± 6.45 ppm, respectively, while they are to 64.94 ± 22.18 ppm and 76.08 ± 35.45 ppm in the dry and immersed deciduous wood samples, respectively. Al has a three to four times lower concentration than Si in both deciduous and coniferous wood samples. The concentrations of this element (Al) only increase in the immersed deciduous wood samples, with mean values from 7.74 ± 3.77 ppm to 20.04 ± 21.89 ppm for dry and immersed deciduous wood samples, respectively. Alix and Stimmell (1996) noted a higher concentration of Al in the driftwood spruce samples as compared to the dead spruce samples, whereas we observed in our study a depletion of this element in the immersed spruce samples as compared to the dry spruce samples. This difference may be explained by the fact that our samples were not dead wood samples taken on the floor as was the case in Alix and Stimmell (1996). The contact between wood pieces and the soil or soil litter may have caused the exchange of Al from the soil to the wood.

The concentrations of some trace metals such as Mn, Zn, and Fe are relatively high in both deciduous and coniferous wood samples, ranging from 29 to 129 ppm for Mn, from 5 to 67 ppm for Fe, and from 8 to 147 ppm for Zn. Moreover, the deciduous wood samples also have greater concentrations of Zn, Fe, and Cu than the coniferous wood samples. However, no systematic increase or decrease of concentrations for these elements were observed that could be used to differentiate immersed wood samples from dry wood samples. Strontium (Sr) and barium (Ba) are also relatively concentrated in all of the wood samples, but they are more concentrated in the deciduous samples as compared to the coniferous samples by an average factor of 2. Sr also increases in all of the immersed deciduous wood samples, with an average value of 11.67 ± 6.85 ppm and 23.12 ± 10.39 ppm for the dry and immersed deciduous wood samples, respectively. Lead (Pb) is the only heavy metal that was identified, with a concentration averaging 0.2–0.4 ppm. Additional elements such as U, Th, Ga, Rb, Ni, and rare earth elements (REE) were also detected, but they are present in very low concentrations and will not be discussed in this paper.

Our results indicate that chemical exchanges after immersion in seawater were more common in the deciduous wood samples (*Salix* sp. and *Alnus* sp.) than in the coniferous wood samples (*Picea* sp. and *Larix* sp.). In addition to enrichment in Na, B, and Mg in the immersed coniferous and deciduous wood samples, all of the deciduous wood samples in this study were enriched in Al, Sr, and V, but relatively depleted of K after being submerged in seawater (Table 1 and Fig. 2). The systematic variations in cation concentrations (i.e., enrichment and loss) were more prevalent in the deciduous samples than in the coniferous samples, which may be explained by the fact that the porous structure of deciduous wood allows a greater absorption of elements as compared to coniferous wood, whose anatomy is devoid of vessels (Schweingruber, 1990).

Many variations in concentration were detected in samples from the same species even though they came from the same location and were subjected to the same experimental conditions. These differences may be explained by the different ages of the wood samples and by the difficulty of scraping the matching tree rings with the ceramic knife. In comparison to the others studies, the green twigs used in this study (especially for the spruce and larch samples) were younger and smaller than the driftwood typically found on the beaches. Moreover, the concentration of the elements varies longitudinally in the tree itself, with greater concentrations in areas where photosynthesis occurs. Consequently, the different concentrations observed in the same species may be related to the differences in their nature (parts of the trees), ages, and dimensions.

In this study, the bark on each wood sample was intentionally kept on before the immersion in order to reproduce the conditions of living trees falling into the water during floods. However, the bark also plays a role as a barrier to absorption. Indeed, the removal of bark can accelerate water infiltration and increase the salinity of the wood (Häggblom, 1982). In nature, trees lose their bark relatively quickly once they fall into the water, which facilitates the exchange of elements with their environments. We can also suppose that the chemical exchange between the wood and the water will increase after a longer time of immersion. Nevertheless, our study shows that even a short (7 day) period of immersion in seawater for living wood that retained its bark altered its chemical composition.

Multivariate Data Analysis

Given the relative variations in the absolute element concentrations between and among the different wood species, it was difficult to differentiate immersed wood from dry wood. To refine the process, the concentrations of each element were normalized to the total cation concentrations in order to consider the dilution factor of the absolute concentrations and the relative proportion between the elements. Principal component analysis (PCA) was also used to identify potential processes controlling the geochemical fingerprint of each wood sample. Indeed, PCA is one of the best multivariate statistical techniques for extracting linear relationships among a set of variables (Simeonov et al., 2003; Singh et al., 2004). PCA is typically used in environmental organic geochemistry to highlight different sources of water contamination (Huang et al., 2010; Juahir et al., 2011; Derrien et al., 2012), but this method has also been applied to archaeological samples in order to identify the potential influence of geochemical processes in the geochemical signature of driftwood (Caruso Fermé et al., 2014).

In the present study, PCA was used to assess the initial data set of wood samples and to represent the relationship among groups and individual samples on a graph using a linear combination of variables. After running the PCA on the 16 wet and dry samples, significant moderate low-dimensional structures were revealed (Fig. 3, parts a and b). This model is considered to be well-suited for studying the correlations between the key variables of interest. The first principal component (PC1) explained 36% of the total variance, while the second principal component (PC2) explained 23% and the third principal component (PC3) explained 14% of the total variance. Taken together, the first three PCA tests explained 73% of the total variance in the data set. For PC1, the elements with the major positive loadings were Ca, Si, and Ba, and the elements with the negative loading were Na. For PC2, B and Zn had the major positive loadings, while Al had the major negative loading. For PC3, Fe and Sr were the major positive and negative loadings, respectively. The Na concentrations significantly influenced the position of the immersed and dry samples in the PCA (Fig. 3, parts a and b). Therefore, PC1 reveals the influence of seawater leaching in the wood samples. Indeed, as Na is the main cation in seawater, it may be significantly absorbed into the wood structure, which causes it to dominate the cation load.

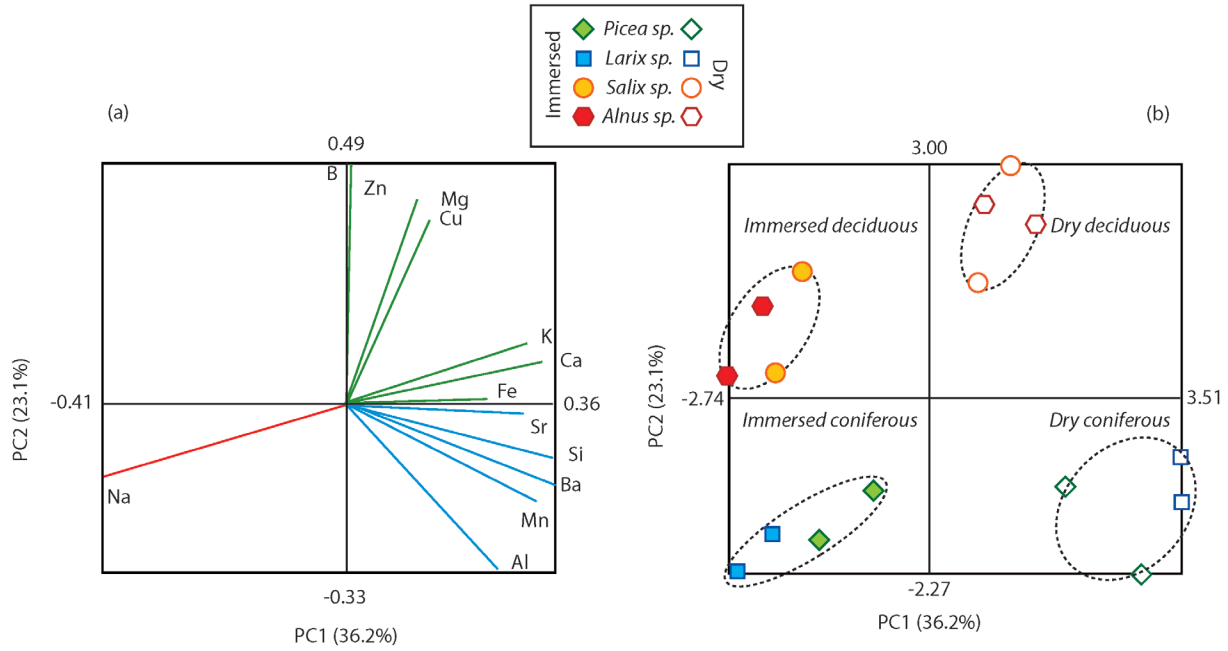

FIGURE 3. Principal components analysis (PCA) scores from concentrations of 14 elements normalized to the total cation concentrations for dry, immersed, and archaeological wood samples. PC1 and PC2: principal components 1 and 2. PC3 not shown here.

On the other hand, Ca, Si, and Ba (which are the main cations with positive loadings on PC1) indicate the influence of soil chemistry. Ca and Si are the main cations in alumino-silicate minerals, and Ba may be linked to atmospheric wet deposition in Arctic forests. The PC2 distinguished wood families (deciduous vs. coniferous) based on Al concentrations, and to a lesser extent based on Si and Mn concentrations, which are higher in coniferous wood samples than in deciduous wood samples. The results of the PCA also showed a redundancy between two variables (Ca and Sr) and a low contribution to the F1 axis (<5%) for three variables (Mg, Cu, and B). A second PCA was performed on only eight element concentrations normalized to the total cation concentration without Na/cations, which had a high correlation factor. This new PCA did not show any significant changes relative to the previous PCA model. In this model, PC1 explained 44% and PC2 explained 24% of the total variance in the data set. In summary, the individual distributions on PC1 and PC2 showed a clear separation between immersed wood samples (on the left side) and the dry wood samples (on the right side). In addition, for both the dry and immersed wood samples, the deciduous and coniferous wood samples clustered on the lower side and upper side of the graph, respectively (Fig. 3, part b).

The PCA model based on the concentrations of 14 elements showed that Na concentrations significantly influenced the position of the immersed and dry samples on the graph, which were separated into two groups. Score plots also indicated a separation between deciduous and coniferous wood samples. These findings are very encouraging and suggest that it will be possible to isolate chemical characteristics that will allow us to differentiate dry and immersed wood species. Future research should apply PCA to additional samples in order to verify that there is no overlap between the different clusters. In particular, some of the variables in the PCA models seem to be orthogonal to each other and may indicate a correlation, such as the Ba/cations versus Zn/cations or the Mg/cations versus Mn/cations (Fig. 3, part a). The further comparison of these results with data obtained from archaeological wood samples would highlight the robustness of this PCA based on coniferous and deciduous samples. Moreover, archaeological wood samples would also provide information about the influence of burial in the soil. Indeed, possible chemical exchange between soil and wood may cause enrichment and depletion of some elements depending on meteorological and weathering conditions.

Conclusion and Perspectives

In this preliminary study, an experiment was conducted in the field in order to detect potential changes in the chemical composition of coniferous and deciduous samples during a short period of contact with seawater. The chemical composition was determined on the wood samples by means of ICP-MS. A significant change in the chemical composition was observed when wood had been in contact with seawater as compared to dry wood. Indeed, Na concentrations (and to a lesser extent Mg and B concentrations) were more enriched in the immersed wood samples than in the dry wood samples. Moreover, systematic variations in the concentration of the elements (i.e., enrichments and impoverishments) seemed to be more numerous in the immersed deciduous wood samples than in the coniferous wood samples, likely because of their more porous anatomical structure. However, we did not notice a definitive set of markers that would allow us to conclusively determine seawater contamination.

A more complete analysis of anions such as Cl (which constitutes 55% of the mass of the salt content in seawater) using ion chromatography would be needed in order to confirm these findings. Moreover, additional geochemical analyses should be carried out on archaeological woods and soils; on more samples from cut, green, dead, drift, and immersed wood samples; and on modern wood samples placed in the soil for several periods of time, taking into account differences between coniferous and deciduous species.

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