FLUORIDE IN NEWFOUNDLAND TILLS

S.D. Amor

Open File NFLD/3344

St. John’s, Newfoundland
December, 2018
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ABSTRACT

Fluoride data for 18 141 till samples, collected in Newfoundland between 1985 and 2017, and analyzed by ion-selective electrode determination after alkaline fusion, are released. The data have been subjected to standard quality-assurance procedures, and are considered satisfactory.
INTRODUCTION

Fluoride analyses are complete for all till samples collected in Newfoundland, up to and including the 2017 field season. Analytical data for other elements associated with these samples, with the exception of those collected in 2017, are available in a series of open-file reports (Batterson et al., 1998, 2001, 2003, 2004, 2006, 2009a, b, c; Brushett, 2011, 2012, 2014; Brushett and Amor, 2016; Campbell, 2018; Davenport et al., 1996; Liverman et al., 1993, 2000, 2001; McCuaig, 2002; McCuaig et al., 2006; Organ, 2014; Organ and Amor, 2017a, b; Smith et al., 2009) and are available for download from the Geoscience Atlas (geoatlas.gov.nl.ca) or from the Geofiles database (gis.geosurv.gov.nl.ca/minesen/geofiles). Fluoride analyses are now a component of the analytical suite for all till-geochemical samples in the province, and will be reported with the other elements in future open-file reports.

COVERAGE

The till-sampling program of the island of Newfoundland is ongoing and the coverage to date is documented in the till geochemical index of the Geoscience Atlas (geoatlas.gov.nl.ca). Sampling coverage is neither complete, nor is it evenly distributed, and it is anticipated that analytical results from ongoing work will be released in future open-file reports. However, given the current interest in fluorite (Adams and Kerr, 2013; Magyarosi, 2018), and the critical metals associated with fluoride enrichment (e.g., W, Mo, rare-earth elements), all available fluoride analyses, from both re-analyzed and newly submitted samples, are being released as a stand-alone report, without delay. The fluoride analyses have been divided up into nine regions, as described in Table 1, which also lists the open-file reports in which the original sampling work, and analytical data, were described. Figure 1 shows the areal distribution of the samples; there are too many for sample numbers to be posted on this map, but coordinates are listed in Appendix A.

DATABASE

The database consists of fluoride analyses of 18,141 till samples, collected between 1985 and 2017. The samples were analyzed for fluoride ion (F-) by alkaline fusion with ion-selective electrode determination (Finch et al., 2018). A few samples had previously been used up and were, therefore, not available for fluoride analysis. The data, accompanied by relevant field observations, comprise Appendix A.

QUALITY ASSURANCE

STANDARDS

The till reference standards routinely inserted into the sample flow are supplied by Natural Resources Canada, and the parameters for which recommended values and ranges are provided (Lynch, 1996), do not include fluoride. It is necessary, therefore, to create control charts based on the means and standard deviations of the GSNL lab’s own analyses. These are summarized in Table 2. Clearly, there is an element of bias in this method because the charts will not indicate if there has been consistent underestimation, with respect to a “true” or “accepted” value through-
<table>
<thead>
<tr>
<th>Region</th>
<th>NTS Map Areas</th>
<th>Number of Samples</th>
<th>Open Files</th>
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<tr>
<td>Southwest</td>
<td>11O/09, 16; 11P/13; 12A/04, 05, 06, 07</td>
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<td>NFLD/2871, 12A/1449, 12A/1562</td>
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<td>West</td>
<td>12A/10, 11, 12, 13, 14, 15; 12H/02, 03, 04, 06, 07</td>
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<td>North</td>
<td>02E/12; 12H/09, 10, 11, 12, 15</td>
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<td>NFLD/2611, NFLD/2823, S. Hashmi (pers. comm.)</td>
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<tr>
<td>Northeast</td>
<td>02C/13; 02D/15, 16; 02E/01, 02, 07, 08, 09, 10; 02F/04, 05</td>
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<tr>
<td>North central</td>
<td>02D/13, 14; 02E/03, 04, 05, 06, 11; 12A/16; 12H/01, 08</td>
<td>2983</td>
<td>NFLD/2611, 12A/1562, NFLD/2664, 12H/2212, NFLD/2704</td>
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<tr>
<td>South central</td>
<td>01M/13; 02D/03, 04, 05, 06, 10, 11, 12; 11P/09, 16; 12A/01, 08; 12A/09</td>
<td>2450</td>
<td>NFLD/3273, 12A/1562, NFLD/3341</td>
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<td>Burin</td>
<td>01L/13, 14; 01M/02, 03, 04, 05, 06, 07, 08, 09, 10, 11, 12</td>
<td>1496</td>
<td>NFLD/3043, NFLD/3273</td>
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<tr>
<td>Bonavista</td>
<td>01M/15, 16; 01N/13; 02C/04, 05, 06, 11, 12; 02D/01, 08, 09</td>
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<tr>
<td>Avalon</td>
<td>01K/11, 12, 13, 14, 15; 01L/16; 01M/01; 01N/02, 03, 04, 05, 06, 07, 10, 11, 12, 14, 15; 02C/02, 03</td>
<td>2967</td>
<td>NFLD/2824, NFLD/2869, NFLD/3026</td>
</tr>
</tbody>
</table>

**Note:** One additional sample was collected in map area 12I/04.
Figure 1. Sample location map.
out the analytical program. For exploration geochemical purposes, this is not a serious problem because local maxima will still appear as such; and it is also possible to use the charts to identify seriously deviant analyses or sequences of analyses, and upward or downward trends.

The control charts are shown in Figures 2 and 3.

**DUPLICATES**

The Thompson-Howarth (1978) plot (Figures 4 and 5) offers a visual estimate of the precision represented by each of the analytical and field duplicate pairs and, in particular, of duplicate pairs whose spread is unusually great for the mean concentration level. There are no such duplicate pairs in the fluoride analyses.

Precision, as measured from duplicate analyses, can be expressed in a number of ways. The overall precision, at the 5% (also referred to as 95%) confidence level can be expressed from the analytical duplicate pairs as a single statistic; this figure computes to ±26.3% for the analytical duplicates and ±54.0% for the field duplicates. However, this method of calculation does not take into account the variation of precision with concentration level, in particular that the absolute value of the precision tends to be highest at lowest concentration levels. Furthermore, because of the positive skew of most geochemical frequency distributions, the overall precision will tend to be weighted in favour of the lower concentration levels where the absolute value of the precision is higher.

As shown in Figure 6, there is a linear relationship (although not straight-line) between concentration level and precision at the 95% confidence level, which enables duplicate pairs with an unacceptably large spread to be quickly identified. There are no duplicates whose spread gives cause for concern.

**ACKNOWLEDGMENTS**

Heather Campbell is thanked for reviewing an early version of this report.

<table>
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<tr>
<th>CRM Standards</th>
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<th>Mean (Expected Value)</th>
<th>Upper Limit (Mean +2σ)</th>
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<td>313</td>
<td>381</td>
<td>449</td>
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<tr>
<td>TILL-2</td>
<td>264</td>
<td>370</td>
<td>477</td>
<td>584</td>
</tr>
<tr>
<td>TILL-3</td>
<td>272</td>
<td>217</td>
<td>261</td>
<td>306</td>
</tr>
<tr>
<td>TILL-4</td>
<td>262</td>
<td>309</td>
<td>382</td>
<td>455</td>
</tr>
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</table>
Figure 2. Control charts for certified reference standards TILL-1 and TILL-2. Symbols indicate the geologist who originally collected the samples, and the year in which the fluoride analyses were performed. Values in ppm.
Figure 3. Control charts for certified reference standards TILL-3 and TILL-4. Symbols indicate the geologist who originally collected the samples, and the year in which the fluoride analyses were performed. Values in ppm.
Figure 4. Thompson-Howarth plot: analytical duplicates. Values in ppm.

Figure 5. Thompson-Howarth plot: field duplicates. Values in ppm.
Figure 6. Relationship between analytical precision and concentration level (in ppm).

\[ y = 2.0957x^{-0.427} \]
\[ R^2 = 0.5059 \]

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Thompson, M. and Howarth, R.J.
APPENDIX

APPENDIX A: Fluoride in Tills 1985-2017
The data are available as a digital comma-separated file (.csv) through this link:
http://www.nr.gov.nl.ca/nr/mines/geoscience/publications/openfiles/OF_NFLD_3344/OF_NFLD_3344_AppendixA.csv