Igneous lithogeochemistry data for the Dease Lake, Kitsault River, Galore Creek, Telegraph Creek, Foremore, and other areas in northwestern British Columbia

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Front cover: Interstratified volcanic flows, breccia and tuff of the Horn Mountain Formation (upper Hazelton Group), approximately 6 km northeast of Mount Sister Mary in the Dease Lake area. View to the south. **Photo by Bram van Straaten.**

Back cover: Pink granitic dikes of the Three Sisters pluton, potassic phase, cutting hornblende granodiorite of the Cake Hill pluton, Three Sisters Range, Dease Lake area. **Photo by Bram van Straaten.**

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Abstract

This release provides whole-rock lithogeochemical data for 555 Devonian to Quaternary rock samples from northwestern British Columbia. Samples were collected between 2003 and 2021 for petrogenetic studies, and are predominantly from Triassic to Jurassic igneous rocks within the Stikine terrane. The extensive dataset can be used to better understand the magmatic and geochemical evolution of the Stikine terrane, particularly as it relates to its large mineral endowment. We developed a new geoscientific metadata structure that allows for full capture and querying of bedrock geological unit information and better integration with data formats for these units in BC digital geology. We also evaluate 56 quality control samples.

Keywords: Whole-rock lithogeochemistry, igneous rocks, petrogenesis, metadata, data structure, quality control, Stikine terrane, Dease Lake, Galore Creek, Kitsault River, Telegraph Creek, Foremore, Red Mountain, Iskut River, Mount Blair, Stikine pluton, Spatsizi, Stikine assemblage, Tsaybahe group, Stuhini Group, Hazelton Group, Kinskuch unit, Betty Creek Formation, Spatsizi Formation, Horn Mountain Formation, Kitsault unit, Quock Formation, Bowser Lake Group, Gnat Lakes plutonic suite, Stikine Plutonic Suite, Galore plutonic suite, Tatogga plutonic suite, Texas Creek Plutonic Suite, Three Sisters Plutonic Suite, Hluey Lakes complex, Snowdrift Creek plutonic suite, Hyder Plutonic Suite

1. Introduction

Herein we present analytical results from whole rock lithogeochemical samples for petrogenetic studies collected in 2003-2005, 2011, and 2015-2021 during bedrock mapping in northwestern British Columbia (Figs. 1, 2). Three appendices are included (BCGS_GF2022-12.zip). Appendix 1 contains a Microsoft Excel file with all sample metadata and lithogeochemical data (Appendix 1a, 1b), a batch list with detection limits (Appendix 1c) and an explanation of the metadata structure (Appendix 1d). Appendix 2 contains a Microsoft Excel file with all quality control data. Appendix 3 contains all original analytical certificates.

2. Sample distribution and geology

This release contains 611 samples, including 555 routine (non-quality control) samples and 56 quality control samples (Fig. 1). The routine samples include 454 new samples, and 101 previously published samples (van Straaten et al., 2012; Logan and Iverson, 2013). The latter are re-released in digital format with revised unit assignments based on new mapping, petrographic, and geochemical studies by van Straaten et al. (2022). All sample metadata and analytical data are released digitally to allow for straightforward data import, manipulation, querying, and interpretation.

This data release includes samples that are from predominantly igneous rocks within the Stikine terrane; units sampled range from Devonian to Quaternary (Figs.1, 2). Samples analyzed were collected mainly from the Dease Lake, Kitsault River, Galore Creek, Telegraph Creek, and Foremore areas; a more limited number of samples are from the Red Mountain, Upper Iskut River, Mount Blair, Stikine pluton, and Spatsizi areas (Fig. 1). For further geologic information see: 1) Dease Lake, Logan et al. (2012), van Straaten et al. (2012), van Straaten and Nelson (2016), van Straaten and Gibson (2017), van Straaten

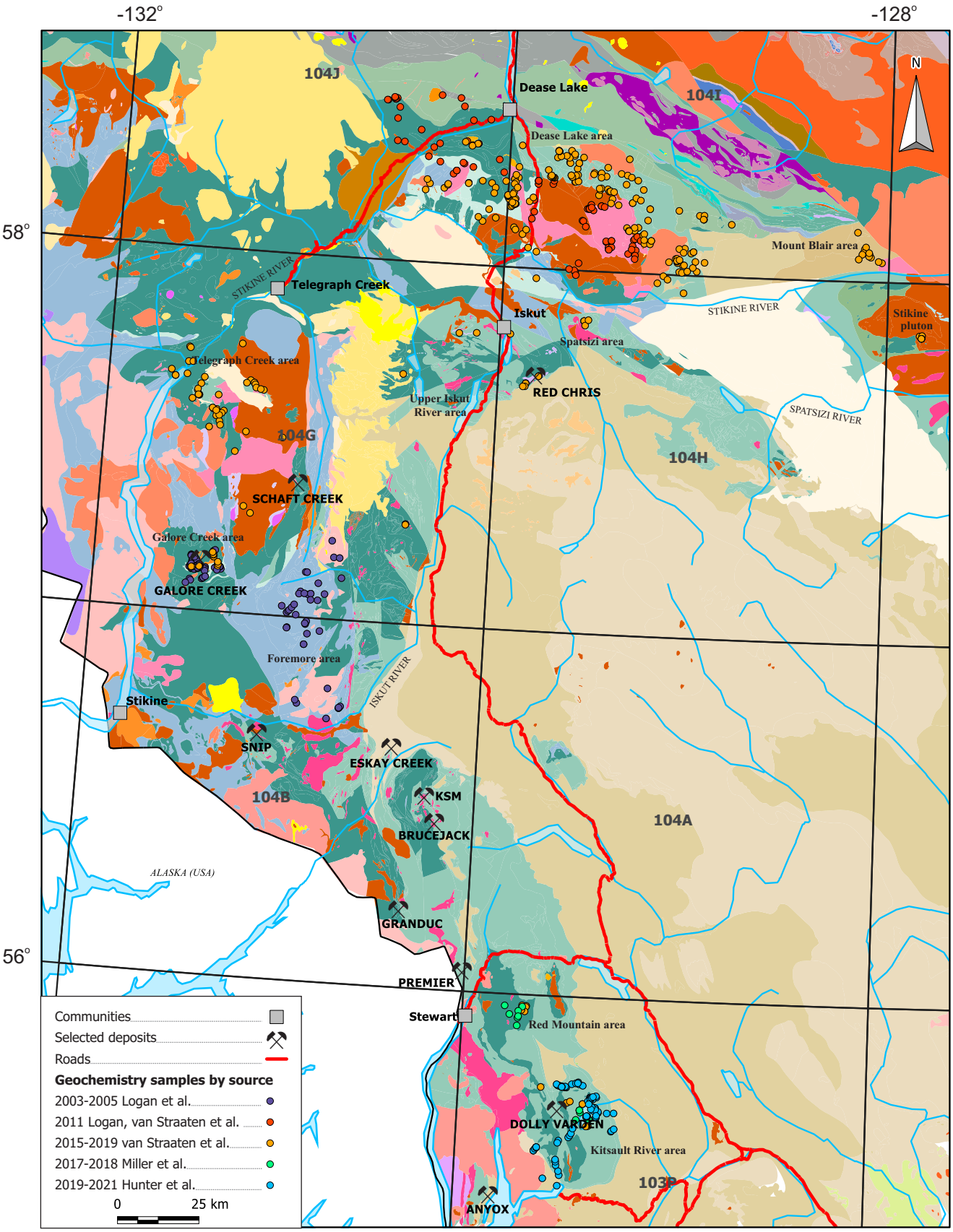

Fig. 1: Sample location map; geology from BC Digital Geology version 2021-10-06 (Cui et al., 2017).

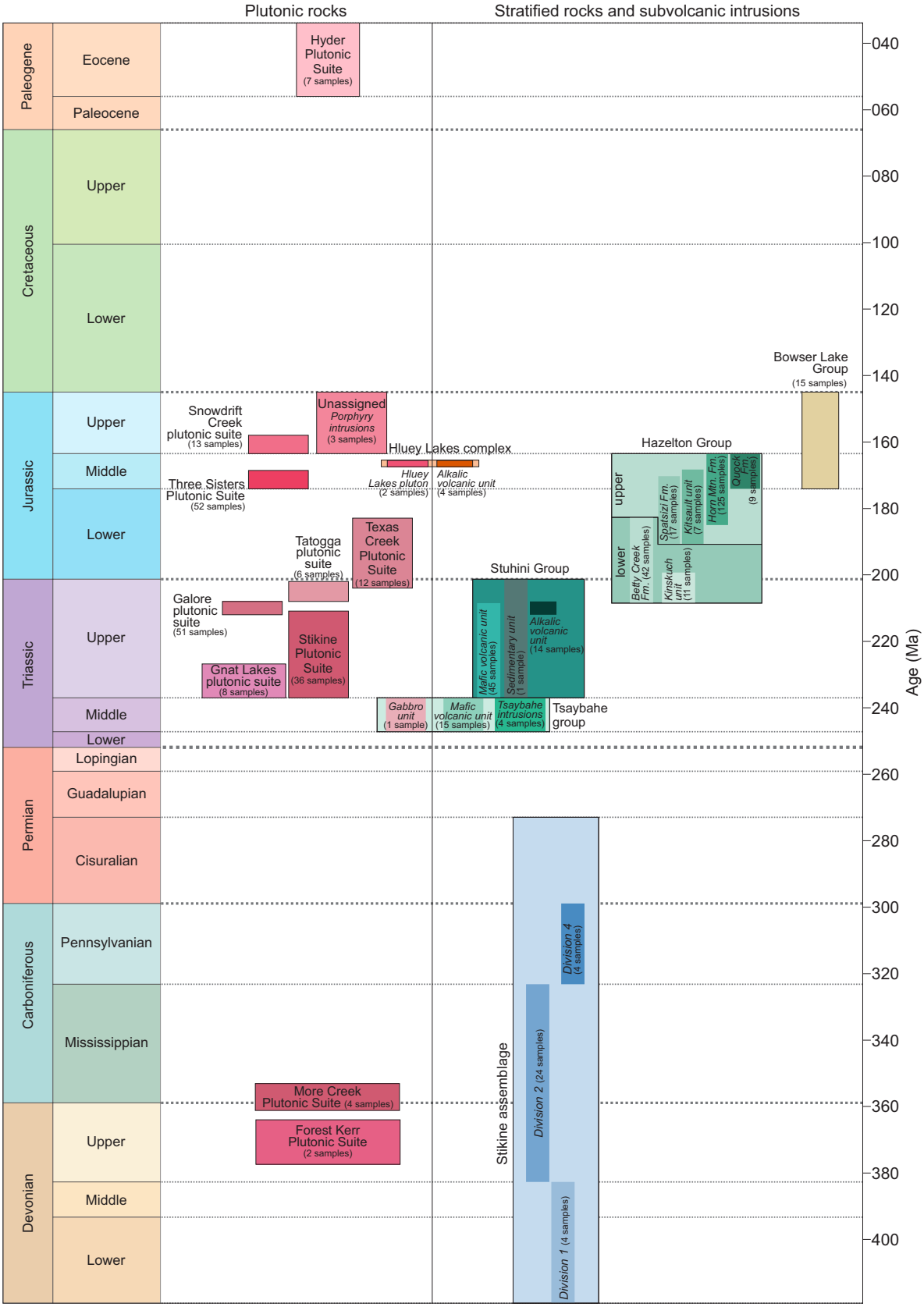

Fig. 2: Schematic Devonian to Eocene stratigraphic and magmatic framework displaying unit assignments for 538 out of 555 routine lithogeochemistry samples. Names at the rank of group or suite in large font, names at the rank of formation or lithodeme in smaller italic font. Geological timescale after Cohen et al. (2013).

and Bichlmaier (2018), van Straaten and Wearmouth (2019), van Straaten et al. (2022); 2) Kitsault River, Hunter and van Straaten (2020), Miller et al. (2020), Hunter et al. (2022); 3) Galore Creek, Logan and Koyanagi (1994), Enns et al. (1995), Logan (2005); 4) Telegraph Creek, Brown et al. (1996); and 5) Foremore, Logan et al. (2000), Logan (2004a, b).

The data presented herein include reanalysis of samples collected between 1989-1991 from the Foremore and Forrest Kerr-Mess Creek areas by Logan et al. (2000); both the original analytical results as compiled in Han et al. (2016) and new results are included in Appendix 1. Similarly, samples collected between 1988-1991 from the Telegraph Creek area by Brown et al. (1996) were reanalyzed and both the original results as compiled in Han et al. (2016) and new results are included in Appendix 1.

3. Sample collection, preparation, and analytical methods

During sample collection and preparation, we selected fresh material, avoiding and/or removing obvious surface weathering, altered areas, veins, and open-space fills. Least-altered and lichen-free rock samples were collected in the field as chips, then bagged and sealed. Where samples could not be cleaned in the field, altered and/or weathered material was removed using a rock saw at the British Columbia Geological Survey sample preparation facilities in Victoria.

3.1. 2003-2005 samples

Samples collected between 2003-2005 from the Foremore and Galore Creek areas were either pulverized in a Cr steel or W carbide mill at the British Columbia Geological Survey in Victoria or pulverized using a W carbide mill at Cominco Research (Global Discovery) Labs in Vancouver. Samples were analyzed for major oxides using a fused disc X-Ray Fluorescence (XRF) technique, FeO was determined by titration, and minor elements by a pressed pellet XRF technique at Cominco Research Labs. Minor and trace elements were determined using peroxide fusion inductively coupled plasma-mass spectrometry (ICP-MS) at the Memorial University of Newfoundland.

3.2. 2011 samples

Samples collected in 2011 from the Dease Lake area (batch 2011_03) were jaw crushed at the British Columbia Geological Survey in Victoria. The crushed samples were sent to Activation Laboratories in Ancaster (Ontario), where they were pulverized in a mild steel mill to prevent Cr and Ni contamination. Samples were analyzed for major oxides and minor and trace elements using a lithium metaborate plus lithium tetraborate fusion technique. The milled samples were mixed with a flux of lithium metaborate and lithium tetraborate and fused in an induction furnace at 1150°C. The melt was immediately poured into a solution of 5% nitric acid and mixed continuously until completely dissolved. This aggressive fusion technique ensures that the entire sample, including resistate phases, dissolves. The samples were analyzed for major oxides using an inductively coupled plasma-atomic emission spectrometry (ICP-AES) technique, and minor and trace elements, including rare earth elements, using an ICP-MS technique. Nickel was analyzed by an ICP-MS technique following a four-acid digestion, beginning with hydrofluoric acid, followed by a mixture of nitric and perchloric acid, and finally hydrochloric acid. With this near-total digestion technique, certain resistate phases (e.g., zircon, sphene, gahnite, chromite, cassiterite, rutile, and barite) may be only partly dissolved. Chromium was analyzed using instrumental neutron activation analysis (INAA), whereby samples were irradiated in a nuclear reactor, and, following a 7-day decay, gamma rays measured on germanium detectors.

Additional samples collected in 2011 from the Dease Lake area (batch 2012_05) were jaw crushed and pulverized in a W carbide mill at the Department of Geology, University of Wisconsin-Eau Claire. Prepared samples were analyzed for major oxides using a fused pellet XRF technique and for minor elements using a pressed pellet XRF technique at the University of Wisconsin-Eau Claire. Minor and trace elements were analyzed by lithium borate fusion at Activation Laboratories as described above.

3.3. 2015-2021 samples

Samples collected between 2015-2021 from the Dease Lake, Kitsault River, Galore Creek, and other areas in northwestern British Columbia were either jaw crushed and pulverized in a Cr steel mill at the British Columbia Geological Survey in Victoria and/or crushed followed by pulverization to 85% passing 200 mesh (75 µm) using a mild steel mill at Bureau Veritas Commodities Canada Ltd. in Vancouver. The samples were analyzed for major oxides and minor and trace elements at Bureau Veritas, where the prepared samples were mixed with a lithium metaborate/tetraborate flux, and crucibles fused in a furnace. The cooled bead was subsequently dissolved in American Chemical Society (ACS)-grade nitric acid and major oxides analyzed by inductively coupled plasma-emission spectrometry (ICP-ES), and minor and trace elements analyzed by ICP-MS. Loss on ignition (LOI) was determined by igniting a sample split at 1000°C then measuring the weight loss. Total carbon and sulphur were determined by Leco combustion. Gold and volatile elements were determined through digestion of a 0.5 g sample split in a modified aqua regia solution of equal parts concentrated HCl, HNO_3 and deionized H_2O for one hour in a heating block or hot water bath. The sample was then made up to volume with dilute HCl, and analyzed using ICP-MS.

4. Geoscientific data fields

4.1. New geoscientific metadata structure

We developed a new geoscientific metadata structure (Table 1) to fill several gaps in the current BCGS lithogeochemistry database (Han et al., 2016; Han and Rukhlov, 2020). Notably, the current BCGS database does not contain suitable fields to capture and query bedrock geological unit information such as geological age, numerical age or age range, group or suite name, formation or lithodeme name, and member or phase name. Also, the current BCGS database contains samples analyzed for a variety of purposes that cannot be easily separated (e.g., igneous lithogeochemistry data for petrogenetic studies vs. altered and/or mineralized samples analyzed to determine metal values).

The revised metadata structure used herein allows for full capture of bedrock geological unit information and includes a field for the sample purpose (Table 1, Appendix 1d). The data structure aims for better integration with data formats for geological units in BC digital geology (Cui et al., 2017),

Table 1. Geoscientific metadata fields used in the present release compared with other common lithogeochemical and other metadata structures: BCGS lithogeochemical database (Han et al., 2016; Han and Rukhlov, 2020); BC digital geology (Cui et al., 2017); EarthChem (bulk sample analyses template v.3.0, available from https://www.earthchem.org/ecl/templates/); System for Earth Sample Registration (SESAR; batch registration quick guide v.7, available from https://www.geosamples.org/); the Western North American Volcanic and Intrusive Rock Database (NAVDAT; see https://www.navdat.org/NavdatSearch/index.cfm); Yukon lithogeochemical database (Yukon Geological Survey, 2020); and Geological Survey of Canada Open File (Zagorevski, 2020). * see lookup table (Appendix 1d). Green fields are the same in both databases, yellow fields are similar.

This release			Others						
Gp.	**Data field**	**Explanation**	**BCGS litho-geochem**	**BC Digital Geology**	**Earth-Chem**	**SESAR**	**NAVDAT**	**YGS**	**GSC OF**
Sample ID	sample_name	Sample name	data_sample> sample_name		sample name	sample name	sample ID	sample_ num	sample
	lab_num	BCGS lab archive sample number	data_sample> lab_num			other name(s)			
	orig_lab_num	Original BCGS lab archive sample number							
Location	latitude	Latitude in decimal degrees	data_sample> wgs84_lat		latitude	latitude	latitude	latitude_ dd	latitude
	longitude	Longitude in decimal degrees	data_sample> wgs84_long		longitude	longitude	longitude	longitude_ dd	longitude
	easting	Easting in UTM				easting (m)			
	northing	Northing in UTM				northing (m)			
	srid_src	Spatial reference system identifier (EPSG) of coordinates used in source *							
	elevation	Elevation in metres above sea level	data_sample> wgs84_elev		elevation	elevation start			altitude
	coord_conf	Confidence of spatial accuracy *	data_sample> coord_conf				location precision	loc_ accur	
Sample info	qc_type	Routine or quality control sample *							
	sample_purpose	Purpose for sampling *				purpose			
	sample_disposition	Sample disposition *	data_sample> sample_type			sample type			
	collect_date	Date (yyyy-mm-dd) or year (yyyy) sample was collected	data_sample> collect_date		collection date	collection date		year	
	collector	Last, first name of person who collected the sample	code_geol> name		collector	collector/ chief scientist		geologist	
	location	Project area or general location for group of samples			location keywords	locality		project	
Unit	strat_age	Stratigraphic age or position range of unit at Epoch or Series level		strat_age	age	geological age	geological age	age_perio	revised_ epoch
	terrane	Geological terrane *		terrane					revised_ terrane
	gp_suite	Group, plutonic suite name or others at equivalent rank		gp_suite				p_suite	revised_ group
	sbgp_suite	Subgroup, subsuite name or others at equivalent rank		sbgp_suite					
	fm_lithodm	Formation, lithodeme name or others at equivalent rank		fm_lithodm				unit	revised_ formation
	mem_phase	Member, phase or others at equivalent rank		mem_phase					
	strat_name	Group/suite (subgroup/subsuite) - Formation/lithodeme - Member/phase	data_sample> rock_unit	strat_name		geological unit			
	orig_strat_unit_code	Original rock unit code							
	strat_unit_code	Rock unit code		strat_unit					
	strat_unit_reliability	Reliability of strat_age to strat_unit_code fields *							
	strat_unit_source	Source for strat_age to strat_unit_code fields							

Table1. continued

This release			Others						
Gp.	**Data field**	**Explanation**	**BCGS litho-geochem**	**BC Digital Geology**	**Earth-Chem**	**SESAR**	**NAVDAT**	**YGS**	**GSC OF**
Sample desc	rock_class	Rock class of sample *		rock_class		classification	material + rock type	rock_ class	type
	field_desc	Field description of sample							
	petrogr_desc	Petrographic description of sample, if available							
	sample_desc	Sample description. Derived from field_desc and/or petrogr_desc	data_sample> sample_desc			sample description		rock_type	
Unit age	age_max	Maximum numeric age of unit in million years		age_max_ mt		age (max)	max age		
	age_min	Minimum numeric age of unit in million years		age_min_ mt		age (min)	min age		
	age_ave	Average numeric age, (age_max + age_min)/2					age	chron_ age	age
	age_error	Error of numeric age, ((age_max + age_max_u) - (age_min - age_min_u))/2						age_error	age_plus + age_minus
	age_notes	Age constraint (e.g., U-Pb zircon) and reference(s) used for age_min and age_max fields		age_ method				source	age_ method
Analytical	sample_prep	Sample preparation: pulverizing mill type (lab)	code_prep> name + code_prep> prep_lab		sample preparation				
	batch_id	BCGS lab batch number (year_number)	data_sample> batch_id						
	analytical_desc	Description of analytical methods used (Appendix 1b only)						met_ major + met_trace	
	lab_certificate_no	Laboratory name: lab certificate number; Laboratory name 2: lab certificate number 2	code_lab> name					lab + cert	laboratory

and with proposed open data standards for geochemical data (EarthChem) and geoscientific sample material (System for Earth Sample Registration (SESAR), an International GeoSample Number (IGSN) allocating agent). We also compared our data structure with the Western North American Volcanic and Intrusive Rock Database (NAVDAT), Yukon lithogeochemistry dataset (Yukon Geological Survey, 2020) and a northern BC-southern Yukon lithogeochemical dataset (Zagorevski, 2020). A comparison of metadata fields is presented in Table 1. Most data fields are similar or identical between the different data structures (Table 1). One of the differences worth highlighting is the *age_max* and *age_min* fields, which together with the derived *age_ave* and *age_error* fields can be used to plot geochemical parameters against age. In this data release the quoted ages are for the unit (not for the sample, as in SESAR or NAVDAT); this has the advantage that the age ranges match those in BC digital geology and that samples from the same unit have the same age range. Sample ages can be extracted from the BC geochronology database (Han et al., 2020).

4.2. General notes

Original coordinates for most samples were given in UTM NAD83 zone 9 north, most 2004 sample coordinates were provided in latitude and longitude in WGS84, and 1989-1991 Telegraph Creek sample coordinates were given in UTM NAD27 zone 9 north. UTM coordinates were reprojected to latitude and longitude in WGS84 with 6 decimal places or better (<1 m resolution) using MapInfo Discover. Elevation data in italic font and light-yellow highlight for samples with high spatial accuracy are from the digital elevation model (DEM) of British Columbia (created from the 1:20,000 scale Terrain Resource Information Management DEM with a 25 m pixel size).

In cases where no group or suite name (*gp_suite* field, Table 1) was available, we used 'Unassigned' to avoid blank fields. We introduced several informal, temporary, and descriptive unit names in the formation/lithodeme (*fm_lithodm*) and member/phase (*mem_phase*) fields to increase the user's ability to filter by *strat_name* (e.g., Stuhini Group – Mafic volcanic unit). We subdivided the Stikine assemblage into informal Divisions 1, 2 and 4 as proposed by Logan et al. (2000). Galore intrusions were subdivided into twelve informal phases (I-1 to I-12) following Enns et al. (1995, Table 2). Samples from subvolcanic intrusions were typically assigned to the stratigraphic group and/or formation that the intrusions were feeding (following North American Commission on Stratigraphic Nomenclature, 2005), but with a distinct name at a lower rank (using either the *fm_lithodm* or *mem_phase* fields; e.g., Tsaybahe group – Tsaybahe intrusions). Where only a few subvolcanic intrusions were sampled, they are included with the volcanic unit they are interpreted to have fed.

Except for most of the Dease Lake area samples, sample descriptions are not based on petrographic studies, and unit assignments have not been evaluated using lithogeochemical data. As such, most unit assignments should be treated as preliminary. Mineral abbreviations used throughout Appendix 1 are after Siivola and Schmid (2007).

5. Geochemical data fields

The geochemical metadata structure (Appendix 1a) follows the BCGS lithogeochemistry database standards as summarized in Han et al. (2016) and Han and Rukhlov (2020), where each analyte header strings together the analyte, two- to three-letter analytical method code, and unit of measurement (e.g., SiO_2_XRF_pct, Cr_INA_ppm; see Appendix 1d for full details).

We also provide a more user-friendly data structure for easy data manipulation (Appendix 1b). This data sheet lists all major oxides, minor and trace elements analyzed by total determination methods (lithium borate fusion, sodium peroxide fusion, XRF, Cr by INAA, Ni by four acid digestion, LOI by gravimetric determination, FeO by titration, C and S by Leco combustion), followed by elements analyzed by partial determination methods (aqua regia). The Microsoft Excel sheet uses the total determination (TD) analytical method code for lithium borate fusion, sodium peroxide fusion, XRF, Cr by INAA and Ni by four acid digestion. In cases where an analyte was analyzed multiple times by different total determination methods, we selected the most suitable method. In such cases, measurements using lithium borate fusion were favoured over those by XRF (LIP > XRF); measurements using sodium peroxide fusion were typically favoured over those by XRF (SIP > XRF), except for Nb which appears more accurate and precise using XRF (see Appendix 2f); Cr by INAA was favoured over lithium borate fusion (INA > LIP, Appendix 2f); Ni by four acid digestion was favoured over lithium borate fusion (MIP > LIP, Appendix 2f); and, in general, modern analyses (2003-2021) were favoured over historic analyses (1988-1991). As an example, if both SiO_2_LIP_pct and SiO_2_XRF_pct were analyzed for the same sample, SiO_2 analyzed by lithium borate fusion (LIP) was used in Appendix 1b and listed as SiO_2_TD_pct. We also recalculated a variety of analytical values, so they are shown consistently throughout this spreadsheet tab. Lab certificates that listed Cr_2O_3_pct were recalculated to Cr_ppm, $C^{(T)}$ expressed as CO_2_pct to $C^{(T)}$_pct, and Ba_pct to Ba_ppm. Where $Fe_2O_3^{(T)}$_pct was not listed on a lab certificate it was calculated from Fe_2O_3_pct and FeO_pct; where Fe_2O_3_pct was not listed it was calculated from $Fe_2O_3^{(T)}$_pct and FeO_pct (see Appendix 1d). All totals were recalculated by summing of concentrations of SiO_2, TiO_2, Al_2O_3, $Fe_2O_3^{(T)}$, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, and LOI.

6. Quality control results

This data release contains 56 QC samples, including 28 standards, 25 duplicates, and 3 blanks. We did not review the data reliability of batches 2012_05 and 2015_04 due to a lack of quality control (QC) samples. The data reliability of batch 2015_03 was evaluated using the results of two repeat pulp analyses performed in 2017.

6.1. Accuracy

We reviewed the accuracy of the analytical data using certified reference materials (standards) and methods outlined in Abzalov (2008; 2011) and Piercey (2014). We used certified, recommended, and provisional reference material values only. Although we attempted to select appropriate standards, it was impossible to control all variations in sample matrix and

Table 2. Evaluation of accuracy of analytical results using standards. All standards that were analyzed at least two times per laboratory are shown. Abzalov (2008; 2011) statistical test, where analytical results are acceptable with regard to accuracy if ≤ 1. Percent relative difference (%RD), where analytical results are considered to have good accuracy if | RD% | ≤ 10% (Piercey, 2014). NA = Not analyzed; BDL = Below detection limit; NCV = No certified value; green fields pass, and red fields fail QC test.

Lab	Cominco		Memorial U		Bureau Veritas					
Standard	Std SY-4 (n=5)		Std SY-4 (n=5)		Std TDB-1 (n=7)		Std BCGS Till 2013 (n=8)		Std RGM-2 (n=2)	
Type	Abzalov	%RD	Abzalov	%RD	Abzalov	%RD	Abzalov	%RD	Abzalov	%RD
SiO_2_TD_%	0.14	0	NA	NA	NCV	-1	0.97	-1	0.09	0
TiO_2_TD_%	0.29	-2	NA	NA	NCV	2	0.17	0	0.43	8
Al_2O_3_TD_%	0.02	0	NA	NA	NCV	0	0.33	0	0.60	-3
$Fe_2O_3^{(T)}$_TD_%	0.16	-1	NA	NA	NCV	0	0.04	0	0.63	-3
Fe_2O_3_CALC_%	0.26	4	NA	NA	NA	NA	NA	NA	NA	NA
FeO_TIT_%	0.44	-6	NA	NA	NA	NA	NA	NA	NA	NA
MnO_TD_%	1.00	-7	NA	NA	NCV	-3	0.63	-2	NCV	NCV
MgO_TD_%	0.32	-5	NA	NA	NCV	0	0.44	1	0.12	-2
CaO_TD_%	0.10	0	NA	NA	NCV	1	1.18	2	0.16	-1
Na_2O_TD_%	0.16	-1	NA	NA	NCV	0	1.33	-2	0.74	-4
K_2O_TD_%	0.26	-3	NA	NA	NCV	0	0.60	-1	0.00	0
P_2O_5_TD_%	0.62	-15	NA	NA	NCV	-9	1.19	-5	0.36	-20
LOI_GRV_%	0.93	10	NA	NA	NCV	90	1.07	2	NCV	NCV
Total_TD_%	NCV	NCV	NA	NA	NCV	NCV	NCV	NCV	NCV	NCV
C_LE_%	NA	NA	NA	NA	NCV	NCV	0.77	5	BDL	BDL
S_LE_%	NA	NA	NA	NA	NCV	0	BDL	BDL	BDL	BDL
Ag_TD_ppm	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
As_TD_ppm	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Ba_TD_ppm	NA	NA	1.55	19	0.99	-11	0.50	-5	0.41	-4
Be_TD_ppm	NA	NA	NA	NA	NCV	NCV	0.62	120	NCV	NCV
Bi_TD_ppm	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Ce_TD_ppm	NA	NA	0.48	-6	0.43	-9	0.01	0	0.37	-5
Co_TD_ppm	NA	NA	NA	NA	3.76	-10	0.89	-9	0.30	-10
Cr_TD_ppm	NA	NA	NA	NA	0.27	-3	0.16	3	BDL	BDL
Cs_TD_ppm	NA	NA	NA	NA	NCV	NCV	0.49	-10	NCV	NCV
Cu_TD_ppm	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Dy_TD_ppm	NA	NA	0.02	0	0.95	-24	0.39	-3	NCV	NCV
Er_TD_ppm	NA	NA	0.17	-3	NCV	NCV	0.16	-2	NCV	NCV
Eu_TD_ppm	NA	NA	0.46	-5	1.22	-12	0.04	1	NCV	NCV
Ga_TD_ppm	NA	NA	NA	NA	0.57	-11	0.70	-4	0.70	-9
Gd_TD_ppm	NA	NA	0.13	-2	NCV	NCV	0.10	0	NCV	NCV
Ge_TD_ppm	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Hf_TD_ppm	NA	NA	0.29	5	0.70	-14	0.01	0	NCV	NCV
Ho_TD_ppm	NA	NA	0.23	-3	0.09	-6	0.19	-2	NCV	NCV
In_TD_ppm	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
La_TD_ppm	NA	NA	0.15	-2	0.08	-2	0.11	-1	0.10	-2
Lu_TD_ppm	NA	NA	0.22	-4	0.50	-12	0.09	1	NCV	NCV
Mo_TD_ppm	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Nb_TD_ppm	0.21	-9	NA	NA	NCV	NCV	0.09	-1	NCV	NCV

Table 2. continued

Nd_TD_ppm	NA	NA	0.10	-1	0.12	-1	0.09	-1	1.00	-11
Ni_TD_ppm	NA	NA	NA	NA	0.34	-5	0.14	-2	BDL	BDL
Pb_TD_ppm	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Pr_TD_ppm	NA	NA	NCV	-4	NCV	NCV	0.29	-4	NCV	NCV
Rb_TD_ppm	0.12	-3	NA	NA	1.02	-18	0.38	-6	0.59	-4
Sb_TD_ppm	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Sc_TD_ppm	NA	NA	NA	NA	0.12	-2	0.28	-3	1.67	-20
Sm_TD_ppm	NA	NA	0.18	-3	0.67	-5	2.26	-12	NCV	NCV
Sn_TD_ppm	NA	NA	NA	NA	0.14	-14	0.27	29	NCV	NCV
Sr_TD_ppm	0.10	1	NA	NA	0.33	-7	0.33	3	0.27	-3
Ta_TD_ppm	NA	NA	0.40	70	0.43	-21	0.34	-17	NCV	NCV
Tb_TD_ppm	NA	NA	0.03	0	0.90	-15	0.25	-4	NCV	NCV
Th_TD_ppm	NA	NA	0.13	-9	0.28	-6	0.16	4	NCV	NCV
Tl_TD_ppm	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Tm_TD_ppm	NA	NA	0.17	-4	0.59	-20	0.41	-5	NCV	NCV
U_TD_ppm	NA	NA	NA	NA	0.80	-17	0.33	9	0.11	-3
V_TD_ppm	NA	NA	NA	NA	0.25	-2	0.24	-2	NCV	NCV
W_TD_ppm	NA	NA	NA	NA	NCV	NCV	0.23	-14	NCV	NCV
Y_TD_ppm	NA	NA	0.59	-10	0.47	-10	0.25	-4	0.70	-12
Yb_TD_ppm	NA	NA	0.10	-2	NCV	NCV	0.51	-5	NCV	NCV
Zn_TD_ppm	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Zr_TD_ppm	NA	NA	1.18	27	0.04	-1	0.04	0	0.26	-4
Mo_AIP_ppm	NA	NA	NA	NA	0.54	-47	0.40	5	NCV	NCV
Cu_AIP_ppm	NA	NA	NA	NA	0.06	1	0.62	3	5.60	-92
Pb_AIP_ppm	NA	NA	NA	NA	0.29	-10	0.18	1	8.84	-93
Zn_AIP_ppm	NA	NA	NA	NA	2.48	-36	0.46	-2	7.75	-95
Ni_AIP_ppm	NA	NA	NA	NA	5.12	-67	0.24	1	NCV	NCV
As_AIP_ppm	NA	NA	NA	NA	0.65	-26	0.18	1	4.50	-82
Cd_AIP_ppm	NA	NA	NA	NA	NCV	NCV	0.32	3	BDL	BDL
Sb_AIP_ppm	NA	NA	NA	NA	0.71	-57	0.18	-2	NCV	NCV
Bi_AIP_ppm	NA	NA	NA	NA	NCV	NCV	1.01	-13	BDL	BDL
Ag_AIP_ppm	NA	NA	NA	NA	NCV	NCV	0.32	-2	BDL	BDL
Au_AIP_ppb	NA	NA	NA	NA	0.05	-2	0.26	11	NCV	NCV
Hg_AIP_ppm	NA	NA	NA	NA	BDL	BDL	0.34	-3	BDL	BDL
Tl_AIP_ppm	NA	NA	NA	NA	BDL	BDL	1.04	36	BDL	BDL
Se_AIP_ppm	NA	NA	NA	NA	NCV	NCV	0.69	32	BDL	BDL

analyte concentrations given the wide variety of rock types, up to 65 analytes, and only a handful of standards per laboratory.

Repeat analyses of a given standard at the same laboratory were used to evaluate if the analytical results were acceptable (Table 2, Appendix 2a) using equation 1 (Abzalov 2008, 2011) and equation 2 (Piercey, 2014).

$$\frac{|m-\mu|}{2\sqrt{\sigma_L{}^2+\frac{S_W{}^2}{n}}} \leq 1 \qquad \text{equation 1}$$

$$\%RD = 100\,\frac{m-\mu}{\mu} \quad \text{with } |\%RD| \leq 10\% \qquad \text{equation 2}$$

where

μ = certified mean for the reference material

σ_L = certified between-laboratory standard deviation for the reference material

m = arithmetic mean of the replicate analyses of the standard

S_w = estimated standard deviation of the replicate analyses of the standard

n: number of replicate analyses of the standard

%RD = percent relative difference

Eighty-seven percent of the analytical values satisfy the Abzalov test and 75% pass the percent relative difference test (Table 2; Appendix 2a). For most of the failed test results, the greater variability can be attributed to element concentrations in the standards close to their detection limit. Failed test results for elements analyzed by aqua regia digestion at Bureau Veritas (standards TDB-1 and RGM-2; Table 2) are because certified reference values for these standards are based on total, not partial, digestion methods, and are not a cause for concern.

Only a limited number of analytical values fail both the Abzalov and %RD test. For the 2003-2005 analytical data this is the case for Ba and Zr using standard SY-4 analyzed by sodium peroxide fusion ICP-MS at Memorial University (see Appendix 2f for more information); these values may need to be used with caution. For the 2015-2021 data this is the case for Eu and Rb using standard TDB-1, Sm using BCGS Till 2013, and Nd and Sc using RGM-2. For Eu, Sm, Nd, and Sc this does not appear to be a significant concern, because similar concentrations in other standards are acceptable and show excellent accuracy. Low Rb concentrations in TDB-1 fail both accuracy tests but accuracy is acceptable for other standards with higher Rb concentrations, suggesting potential caution may need to be applied when interpreting low Rb concentrations. Low Sc concentrations in RGM-2 are close to the detection limit, and failure to pass the accuracy tests at such low concentrations is not a cause for concern.

Appendix 2b and 2c list the performance of individual standards using the percent relative difference and equation 3 (Abzalov, 2011).

$$|X - \mu| \leq 2\,\sigma_C \qquad \text{equation 3}$$

where

μ = certified mean for the reference material

X = analytical value of the standard

σ_C = certified within-laboratory standard deviation for the reference material

6.2. Precision

We reviewed the precision of the analytical results using the average coefficient of variation calculated from duplicate pairs (equation 4; Stanley and Lawie, 2007; Abzalov, 2008; 2011; Piercey, 2014).

where

$$CV_{avg}\ (\%) = 100\sqrt{\frac{2}{N}\sum_{i=1}^{N}\left(\frac{(a_i-b_i)^2}{(a_i+b_i)^2}\right)} \qquad \text{equation 4}$$

a_i = original analysis for the i different pairs

b_i = duplicate analysis for the i different pairs

N = number of duplicate pairs

For most standard elements that are well above the detection limit the CV_{avg} (%) values should be less than 10% for field duplicates, and less than 5-7.5% for pulp or analytical duplicates (Piercey, 2014). Ninety-two percent of the $CV_{avg.}$ (%) values satisfy the above criterion, indicating good precision (Table 3, Appendix 2d). Of the 8% remaining analytes, the greater variability can typically be attributed to element concentrations in the duplicate samples close to their detection limit. Two repeat pulp analyses from batch 2015_03, performed in 2017, show good precision for values well above their detection limits (Appendix 2d). It suggests the data from this batch (which has no other QC samples) is reliable. Appendix 2e lists the coefficient of variation (CV) for individual duplicate pairs.

Table 3. Evaluation of precision of analytical results using duplicate sample pairs. Average coefficient of variation (CV_{avg} %) after Stanley and Lawlie (2007), Abzalov (2008; 2011) and Piercey (2014). For most standard elements that are well above the detection limit the values should be less than 10% for field duplicates, and less than 5-7.5% for pulp or analytical duplicates (Piercey, 2014). NA = Not analyzed; BDL = Some or all values below detection limit; green fields pass, and red fields fail QC test.

Lab	Cominco		Memorial U		ActLabs	Bureau Veritas	
Duplicate pairs	pulp (n=1)	chip (n=2)	pulp (n=1)	chip (n=1)	chip (n=4)	pulp (n=3)	chip (n=15)
Type	CV_{avg}	CV_{avg}	CV_{avg}	CV_{avg}	CV_{avg}	CV_{avg}	CV_{avg}
SiO_2_TD_%	0.37	0.10	NA	NA	1.14	0.56	0.41
TiO_2_TD_%	0.88	1.39	NA	NA	2.00	1.48	1.72
Al_2O_3_TD_%	0.52	0.36	NA	NA	1.35	0.35	0.79
$Fe_2O_3^{(T)}$_TD_%	0.17	0.20	NA	NA	3.60	3.30	1.11
Fe_2O_3_CALC_%	0.54	0.35	NA	NA	NA	NA	NA
FeO_TIT_%	0.86	0.00	NA	NA	NA	NA	NA
MnO_TD_%	10.88	0.00	NA	NA	3.40	1.54	4.44
MgO_TD_%	1.57	0.99	NA	NA	2.64	1.53	1.98
CaO_TD_%	0.43	0.74	NA	NA	3.91	1.20	7.07
Na_2O_TD_%	3.03	5.64	NA	NA	1.88	0.46	1.77
K_2O_TD_%	0.72	0.97	NA	NA	1.98	1.29	1.52
P_2O_5_TD_%	21.57	9.02	NA	NA	2.64	5.00	5.20
LOI_GRV_%	0.00	4.02	NA	NA	4.16	7.71	7.19
Total_TD_%	0.64	0.09	NA	NA	0.81	0.02	0.02
C_LE_%	NA	NA	NA	NA	NA	24.06	BDL
S_LE_%	NA	NA	NA	NA	NA	BDL	BDL
Ag_TD_ppm	NA	NA	NA	NA	BDL	NA	NA
As_TD_ppm	NA	NA	NA	NA	BDL	NA	NA
Ba_TD_ppm	NA	NA	1.27	0.47	0.79	3.36	3.23
Be_TD_ppm	NA	NA	NA	NA	BDL	BDL	BDL
Bi_TD_ppm	NA	NA	NA	NA	BDL	NA	NA
Ce_TD_ppm	NA	NA	1.18	0.98	1.41	1.48	3.96
Co_TD_ppm	NA	NA	NA	NA	4.95	5.34	2.99
Cr_TD_ppm	NA	NA	NA	NA	BDL	BDL	BDL
Cs_TD_ppm	NA	NA	NA	NA	6.28	5.80	17.96
Cu_TD_ppm	NA	NA	NA	NA	BDL	NA	NA
Dy_TD_ppm	NA	NA	1.25	0.44	2.57	2.27	3.83
Er_TD_ppm	NA	NA	0.69	2.95	1.39	4.24	4.05
Eu_TD_ppm	NA	NA	0.51	0.34	5.43	1.68	3.47
Ga_TD_ppm	NA	NA	NA	NA	2.02	2.97	2.71
Gd_TD_ppm	NA	NA	1.25	0.54	4.00	2.50	4.07
Ge_TD_ppm	NA	NA	NA	NA	20.35	NA	NA
Hf_TD_ppm	NA	NA	1.29	2.72	3.28	4.03	4.97
Ho_TD_ppm	NA	NA	1.56	3.86	3.09	2.67	5.50
In_TD_ppm	NA	NA	NA	NA	BDL	NA	NA
La_TD_ppm	NA	NA	2.25	1.30	1.95	2.42	3.22
Lu_TD_ppm	NA	NA	0.72	1.44	5.00	3.52	3.36
Mo_TD_ppm	NA	NA	NA	NA	BDL	NA	NA
Nb_TD_ppm	12.86	BDL	NA	NA	0.75	2.52	3.55

Table 3. continued.

Nd_TD_ppm	NA	NA	2.44	2.43	5.81	1.78	4.12
Ni_TD_ppm	NA	NA	NA	NA	4.71	BDL	BDL
Pb_TD_ppm	NA	NA	NA	NA	BDL	NA	NA
Pr_TD_ppm	NA	NA	2.17	2.57	1.92	1.63	3.21
Rb_TD_ppm	1.98	4.77	NA	NA	2.60	0.87	2.34
Sb_TD_ppm	NA	NA	NA	NA	BDL	NA	NA
Sc_TD_ppm	NA	NA	NA	NA	4.30	5.66	1.22
Sm_TD_ppm	NA	NA	0.20	0.70	3.48	4.37	3.03
Sn_TD_ppm	NA	NA	NA	NA	BDL	BDL	BDL
Sr_TD_ppm	0.08	0.77	NA	NA	1.68	0.83	3.60
Ta_TD_ppm	NA	NA	4.09	23.53	13.61	23.09	BDL
Tb_TD_ppm	NA	NA	2.34	0.29	3.19	2.21	3.02
Th_TD_ppm	NA	NA	0.51	1.00	7.86	3.53	5.43
Tl_TD_ppm	NA	NA	NA	NA	12.72	NA	NA
Tm_TD_ppm	NA	NA	2.22	1.79	2.33	3.40	2.97
U_TD_ppm	NA	NA	NA	NA	5.33	7.22	9.00
V_TD_ppm	NA	NA	NA	NA	3.88	6.26	3.91
W_TD_ppm	NA	NA	NA	NA	BDL	BDL	BDL
Y_TD_ppm	NA	NA	1.00	0.56	2.37	5.60	3.59
Yb_TD_ppm	NA	NA	0.54	0.71	3.82	4.78	4.55
Zn_TD_ppm	NA	NA	NA	NA	BDL	NA	NA
Zr_TD_ppm	NA	NA	0.32	1.65	4.29	0.84	2.82
Mo_AIP_ppm	NA	NA	NA	NA	NA	17.21	BDL
Cu_AIP_ppm	NA	NA	NA	NA	NA	8.15	22.88
Pb_AIP_ppm	NA	NA	NA	NA	NA	18.18	6.24
Zn_AIP_ppm	NA	NA	NA	NA	NA	6.08	5.45
Ni_AIP_ppm	NA	NA	NA	NA	NA	7.22	10.50
As_AIP_ppm	NA	NA	NA	NA	NA	BDL	BDL
Cd_AIP_ppm	NA	NA	NA	NA	NA	BDL	BDL
Sb_AIP_ppm	NA	NA	NA	NA	NA	BDL	BDL
Bi_AIP_ppm	NA	NA	NA	NA	NA	BDL	BDL
Ag_AIP_ppm	NA	NA	NA	NA	NA	BDL	BDL
Au_AIP_ppb	NA	NA	NA	NA	NA	BDL	BDL
Hg_AIP_ppm	NA	NA	NA	NA	NA	BDL	BDL
Tl_AIP_ppm	NA	NA	NA	NA	NA	BDL	BDL
Se_AIP_ppm	NA	NA	NA	NA	NA	BDL	BDL

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