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Improving lithological discrimination in exploration drill-cores using portable X-ray fluorescence measurements: (2) applications to the Zn-Cu Matagami mining camp, Canada

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ABSTRACT

A new geoscientific application of portable XRF (pXRF) analysers is the acquisition of high-spatial resolution down-hole geochemical profiles obtained *in-situ* on exploration drill-cores. One advantage of such profiles over traditional laboratory geochemistry, apart from the non-destructive aspect of pXRF, is that they are obtained quickly, in the field. So they can help exploration companies take important decisions such as "has a target stratigraphic horizon been reached, or should we drill deeper?" For example, in the Matagami mining camp, pXRF data permits the rapid distinction of two visually similar and variably altered rhyolites in the Persévérance mine area, based on a plot of Ti/Zr vs. Al/Zr. The corrected pXRF data plots within the same fields as the traditional geochemical analyses for these rhyolites. Another advantage of pXRF profiles for exploration companies, geological surveys or academic researchers is the ability to locate lithological contacts better, and in general improve down-hole lithological discrimination, especially for fine-grained and/or hydrothermally altered lithologies. For example, in the Caber volcanogenic massive sulfide deposit area, there are abundant intrusions which makes it difficult to follow the volcanic stratigraphy between drill holes and sections. In the drill hole studied the pXRF data, plotted as down-hole profiles of elements/oxides and ratios, allows several previously unidentified altered dykes to be distinguished from altered rhyolites.

KEYWORDS: *portable XRF, drill-core, Matagami, volcanogenic massive sulfides, submarine volcanic rocks*

INTRODUCTION

During major mineral exploration programs, thousands of meters of drill-core are generated. The primary goal of diamond drilling is to discover or delineate ore deposits, so any core interval thought or known to potentially contain the sought-after elements (e.g. Ag, Au, Cu, Mo, Ni, Pb, Pd, Pt, Sn, W, Zn) will be assayed by the exploration companies. Many companies also send unmineralized samples to geochemical laboratories for whole rock analyses. These analyses can be used to assess hydrothermal alteration or to identify what lithological units the drill-hole has crossed. Obtaining geochemical data is especially important when working on fine-grained, altered, or deformed rocks, which are difficult to sort otherwise. Traditional laboratory geochemistry is normally accurate, precise, and potentially complete in terms of the range of elements obtained, but typically this approach has a low spatial resolution (10s of meters between samples) and suffers from a long time between the decision to sample and the arrival of the analyses back from the laboratory.

An emerging complementary method is the use of portable X-ray florescence (pXRF) devices. These analysers give immediate *in-situ* (non-destructive) measurements and spatial resolution (analysis spacing) can be down to centimeters if needed. More realistically, users of pXRF analysers on long exploration cores can make measurements every meter or less to obtain relatively high-spatial resolution geochemical profiles for certain elements, which will allow them to produce improved geological logs, sections and maps. Under certain circumstances, acquiring pXRF data on drill-cores may even allow rapid well-informed decisions on whether to continue deepening a drill-hole targeting a certain stratigraphic contact or horizon, for example.

In this paper, we use an extensive pXRF database from the Matagami mining camp in Canada to illustrate the usefulness of high-spatial resolution pXRF profiles on drill-cores to improve lithological discrimination. The companion paper (Ross *et al.* this volume) discusses the use of pXRF analysers *in-situ* on rock cores and presents the tests we have carried out with three analysers to quantify precision and accuracy.

GEOLOGICAL SETTING

The Matagami mining camp is located in the northern Abitibi Subprovince (Superior Province), Québec, Canada (Figs. 1a, 1b). Some 19 Zn-rich volcanogenic massive sulfide (VMS) deposits are currently known in the camp (Fig. 1c), of which 10 have been mined out, one is currently mined (Persévérance), and another will begin production in 2013 (Bracemac-McLeod). The cumulative production at year-end 2010 was 46.5 Mt of ore at average grades of 9.1% Zn, 0.9% Cu, 28 g/t Ag and 0.5 g/t Au (Ross *et al.* in press).

The *c.* 2.7 Ga geology of the area is dominated by a sequence of submarine subalkaline volcanic rocks, with mafic to intermediate rocks being more abundant than their felsic counterparts (e.g. Piché *et al.* 1993; Ross *et al.* in press). The volcanic sequence is intruded by a layered mafic intrusion, the Bell River Complex, thought to be the heat source for VMS hydrothermal cells (Carr *et al.* 2008). Volcanic rocks are also invaded by synvolcanic to post-volcanic intermediate to felsic plutons such as the McIvor Pluton. Mafic to intermediate sills and dikes cross-cut and inflate the volcanic sequence.

The felsic volcanic rocks and the spatially associated VMS deposits occur in three trends, orientated NW-SE to WNW-ESE, that subcrop below significant Quaternary cover: the South Flank, the North Flank, and the West Camp (Fig. 1c). Volcanic rocks generally dip at medium to high angles toward the SW in the South Flank, and are sub-vertical in the other two trends. An exception is the Persévérance Mine area where the strata are sub-horizontal. The stratigraphic facing direction is to the NE in the West Camp, to the north in the North Flank and toward the SW in the South Flank. The pXRF data we will discuss in this paper come from drill-holes chosen in the South Flank and the West Camp.

In the South Flank, the submarine volcanic package can be divided into two main stratigraphic units, the Watson Group at the base and the Wabassee Group at the top (Piché *et al.* 1993). The Key Tuffite, a volcano-exhalative horizon, lies between the two groups and marks the position of most of the VMS deposits. The Watson Group contains a dacite overlain by a rhyolite. The Wabassee Group is dominated by pillowed to massive mafic lavas, but contains minor felsic volcanic units, called the Bracemac Rhyolite and the Dumagami Rhyolite. The former is restricted to the Bracemac-McLeod area, whereas the former is found in the central and NW portions of the South Flank.

The geology of the West Camp is less well understood, but in general is thought to be at least partly correlative with that of the South Flank (Ross *et al.* in press). At the Caber VMS deposit, where some of our pXRF data was acquired, the volcanic sequence starts with a correlative of the Watson Rhyolite (Masson 2000). This is overlain by a tuffite equivalent to the Key Tuffite or by VMS mineralization. Above that are some mafic to intermediate lavas, and the whole package including the Caber VMS deposit is cross-cut by the McIvor Pluton.

In general, at Matagami, the paucity of outcrop means that the details of geology and volcanic stratigraphy are mostly known from diamond drill-holes and cross-sections drawn almost exclusively from drilling information. In this context, a detailed volcanic chemo-stratigraphy established from down-hole geochemical profiles in key areas is valuable, since VMS deposits tend to occur at specific stratigraphic positions. Another common issue at Matagami is separating intrusions from lavas in drill-cores when the rocks are massive and fine-grained, and/or hydrothermally altered.

MATAGAMI PXRF DATA-SET

INRS owns two Delta Premium pXRF analysers from Olympus Innov-X, and previously had access to an Alpha model from the same manufacturer. Using the Alpha analyser in soil mode, we have collected a total of 2028 pXRF measurements in three South Flank diamond drill-holes representing 2817 m of core during summer-fall 2010 and winter 2011 (Ross *et al.* 2011). The integration time was 60 s for each measurement.

Then, using the two Deltas in ‘mining plus’ mode, we have collected a total of 12 181 pXRF measurements in 10 diamond drill-holes representing 6942 m of core during summer 2011 (Ross *et al.* 2012). The targeted measurement spacing was *c.* 0.5 m and the integration time was 60 s, i.e. 30 s per beam. These drill-holes came from the South Flank (n = 6), the North Flank (n = 3) and the West Camp (n = 1). The 10 holes logged with the Deltas include re-measuring the three holes originally studied with the Alpha, to create a consistent database.

The data from the two Delta analysers, referred to as Delta-A and Delta-B, were leveled to compensate from inter-analyser differences[1]. For the elements for which this was possible, the Alpha and Delta data were also corrected to compensate for systematic errors (see the companion paper for methodology).

In the following sections we use a subset of this extensive database to compare the Alpha and Delta analysers on entire drill-holes, show that visually similar lithological units can be quickly distinguished with pXRF data to aid mineral exploration decisions, and illustrate how the data can help to improve down-hole lithological discrimination in general.

Comparison of the Alpha and Deltas on the same drill-hole

Logging the core from three entire drill-holes with both the Alpha and Deltas analysers allows us to compare geochemical profiles obtained with different generations of instruments from the same manufacturer. We present the data for one of these holes, from the Bracemac-McLeod area in the SE portion of the South Flank. MC-05-18 is a 1146 m-deep exploration drill-hole that crosses, from top to bottom, mafic to intermediate lavas, the Bracemac Rhyolite, massive sulfides and the Key Tuffite, and the Watson Rhyolite (Fig. 2). Although over 1000 measurements were made with the Alpha analyser, and over 2000 with the Deltas, only 526 depths were measured with both models due a change in sampling strategy.

These common points are plotted in Figure 2 as corrected down-hole profiles of Zr. Taking into account that the measurements, although intended to be made at the same depth, can't have been made *exactly* on the same spot[2], the unsmoothed corrected profiles are reasonably similar (not shown). Applying a three-point moving average smoothes away most of the mineralogical variation due to slightly different measuring positions, and yields the very similar profiles shown in Figure 2. There is also a good correspondence between the corrected pXRF profiles and traditional laboratory geochemistry. Note that the samples for laboratory geochemistry were collected before the pXRF data were acquired, and therefore not measured by pXRF.

Figure 3 shows binary plots of Zr or TiO_2 for the Alpha vs. the Deltas. The plot for uncorrected TiO_2 shows significant scatter, with a trend quite different from the 1:1 line (slope = 0.44 for a linear regression passing through the origin). Correcting both data-sets to remove the systematic error (as explained in the companion paper), and taking a three-point moving average down-hole to reduce the scatter, improves the correlation from 82% to 91% and brings the data toward the 1:1 line. The correspondence between the uncorrected Zr data-sets was better than for Ti (with a 87% correlation and the data plotting near the 1:1 line). Correcting both data-sets to remove the systematic error, and taking a three-point moving average down-hole, improves the correlation to 94%.

The remainder of this paper utilizes the Delta data only.

Distinguishing visually similar units on-site

The Dumagami Rhyolite and the Watson Rhyolite are two submarine felsic units dominated by massive and lobate facies. Both are quartz-phyric and can locally be amygdaloidal and spherulitic. Hydrothermal alteration ranges up to intense and pervasive chlorite replacement near VMS deposits. In other words, the two rhyolites are not easily distinguishable in drill-core without the help of geochemistry. In the Persévérance mine area of the South Flank, the two rhyolites lie on top of each other (Dumagami above, Watson below) without intervening mafic or intermediate volcanic units (Fig. 4). Mineralization typically occurs on top of, or within the uppermost portion of, the Watson Rhyolite. So if a company drills a new hole in this area, how can it be sure that the proper stratigraphic target (i.e. the top of the Watson Rhyolite) has been reached? Using pXRF could help.

Diamond drill-hole EQ-00-41: distinguishing two rhyolites To illustrate this idea we examine the diamond drill-hole EQ-00-41, which crosses both rhyolites and a fault zone probably occupied by altered dikes (Fig. 4a). Between the two rhyolites there is the Key Tuffite, which is a very useful marker horizon, but it can sometimes be missing from the sequence or could be confused with other tuffites. So a geochemical confirmation that the Watson Rhyolite has been reached is important. Figure 5 shows the unsmoothed

[1] For seven drill-holes, both Delta analysers were used; for the other three drill-holes, only the Delta-A device was used. When both analysers were used on the same hole to save time, the first two core boxes were analysed with the Delta-A, then the following two boxes were analysed with the Delta-B, and so on. This means that approximately the same number of measurement points were taken in each lithology with each analyser. The leveling process first involved compiling pXRF data for the drill-holes where both analysers had been used into two data files (one per analyser). For each element and each analyser, average concentrations were calculated. For each element, a leveling factor based on the ratio of these averages was applied to the Delta-B data, to level it with the Delta-A data.

[2] The procedure for locating a measurement spot involves rotating the core 180° relative to its attitude in the core box to expose the cleaner underside, and measuring depth with a tape measure relative to the top of the section. After this was done for the Alpha measurements, the core was returned to its boxes in its original position, and the boxes were moved back to their storing racks. One year passed, then the procedure was repeated for the Delta analysers. Depth-wise, the correspondence between the measurement spots for the Alpha vs. Deltas is probably within 1 cm on average, but there is the additional possibility of core rotations by maybe up to 20°. Note that the cores were always cleaned just before measurements.

down-hole variations in SiO_2, TiO_2, Al_2O_3, Fe_2O_3, MnO, Zr, Ti/Zr and Al/Zr, with an average measurement spacing of 55 cm (359 pXRF measurements). Compared to the Dumagami Rhyolite, the Watson Rhyolite has lower values of TiO_2, higher Zr, lower Ti/Zr, and somewhat lower Al/Zr.

It is best to use ratios of immobile elements when dealing with hydrothermally altered volcanic rocks (e.g. Gifkins *et al.* 2005), so Figure 6a shows corrected pXRF-derived Al/Zr vs. Ti/Zr, compared with laboratory geochemistry in the same drill-hole. There is no overlap between the two rhyolites in the corrected pXRF data, and the measurements are well clustered near the middle of each field. Thus, to answer the question 'have we reached the targeted rhyolite?', a technician or geologist could collect a pXRF measurement at regular intervals after opening the newly drilled core boxes, and plot the corrected data in the manner of Figure 6a.

Diamond drill-hole PER-00-45: distinguishing two rhyolites To validate the conclusion made for EQ-00-41, we perform the same exercise for another drill-hole in the Persévérance mine area, PER-00-45 (Fig. 4b). Some 557 pXRF measurements are available, of which 390 were made in the two rhyolites of interest. Figure 6b shows corrected Ti/Zr vs. Al/Zr for this drill-hole. Again there is no overlap between the field of the Dumagami Rhyolite and that of the Watson Rhyolite, although with more data points for this drill-hole, the gap between the fields is much narrower. Still, the corrected pXRF data points are well clustered in the middle of the two fields, near the position of most laboratory analyses. Note that both fields in this plot include measurements made in intervals described as moderately to intensely chloritized. So hydrothermal alteration does not blur the distinction between the two rhyolites.

Using down-hole profiles to improve lithological discrimination

It is common to assign entire core intervals to a certain lithology based on one whole-rock sample analysed by traditional laboratory methods. This procedure assumes that the sampled material is representative of the entire interval. Often this is correct, but when alteration and/or tectonic fabrics hide primary textures, the core is broken, etc., multiple lithologies may be hiding within one interval, or the lithological contacts may be misplaced.

To illustrate how down-hole pXRF profiles can improve lithological discrimination, we use as an example a drill-hole from the Caber deposit in the West Camp. This unmined VMS deposit contains historical resources of 0.48 Mt @ 11.7% Zn, 1.0% Cu, 14 g/t Ag and 0.2 g/t Au (Masson 2000). Stratigraphically under the mineralization, a quartz-phyric rhyolite is found (Fig. 7). Mafic to intermediate lavas occupy the hanging wall position, on the NE side. This area is characterized by numerous intrusions, mostly sub-concordant, which in the presence of hydrothermal alteration (e.g. intense pervasive chlorite) can be difficult to separate from the lavas. Several faults also occur in the area. Better tools are needed to separate volcanic rocks (which can be correlated from section to section) and intrusions (which often cannot).

Diamond drill-hole NCB-98-38 was drilled directly through the Caber VMS deposit and crosses the footwall rhyolite and hanging wall mafic to intermediate lavas (Fig. 7). There is 378 m of core for this hole and 646 pXRF measurements were made, for an average spacing of 59 cm. In Figure 8 we plot two immobile element ratios and a number of elements/oxides as down-hole profiles. The mineralized zone shows elevated Cu, Fe and Zn, with Cu more abundant at the stratigraphic base as is typical of such deposits. The main interest here is the abundance of newly proposed dikes in the rhyolite. The Ti/Zr and Al/Zr profiles show that theses dikes were underestimated in the original geological description of the core: only about half were identified. The interval 308.05-314.20 m, stratigraphically just below the mineralization and originally described as a 'carbonate-altered rhyolite with locally intense chlorite', probably consists entirely of one or several mafic to intermediate dikes.

DISCUSSION AND CONCLUSIONS

We have acquired a substantial amount of *in-situ* pXRF data on cores from the Matagami mining camp, in the form of down-hole profiles. These high-resolution multi-element geochemical profiles have sufficient precision and accuracy to be quite useful; such profiles would not be easily obtainable otherwise. They will lead, together with other types of studies, to a better understanding of the volcanic stratigraphy, volcanic architecture and hydrothermal alteration in the Matagami area. This will contribute to ongoing academic, industrial and governmental geoscience investigations. Specifically, in this paper, we have illustrated two successful applications based on immobile element ratios: distinguishing two visually similar rhyolites in the Persévérance mine area, and improving down-hole lithological discrimination in the Caber VMS deposit area.

The use of pXRF analysers *in-situ* on rock cores will not replace destructive laboratory geochemistry because the latter type of analysis is more precise and accurate, and also allows a lot more material to be measured in one analysis, eliminating the effect of small-scale mineralogical heterogeneity. Further, many elements are currently not well measured, or even detected, by pXRF: this includes many HFSE and REE useful for spidergrams or tectonic discrimination diagrams, precious metals at low concentrations, and even major elements Na and Mg, essential for the calculation of many hydrothermal alteration indices. But obtaining both laboratory geochemistry and pXRF data on the same drill-hole is very advantageous, especially in association with measurements of physical properties and mineralogy (Ross et al. submitted).

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Figure captions

Figure 1. (a) Location of the Abitibi greenstone belt in eastern Canada. (b) Simplified geological map of the Abitibi greenstone belt showing the location of the Matagami mining camp. (c) Simplified geological map of the Matagami area, modified from Roy & Allard (2006). Grid is UTM Nad 83, zone 18.

Figure 2. Down-hole profiles of Zr in drill-hole MC-05-18 from the McLeod VMS deposit area, using corrected pXRF data from the Alpha and Delta analysers (3-point moving average). Traditional geochemistry from INRS (n = 49) and Xstrata Zinc Canada (n = 38, i.e. one sample every 30 m on average) is shown for comparison. Stratigraphic top is towards the top of the hole. Massive sulfides ("M. sulfides") could not be analyzed by pXRF in this hole. I1: felsic intrusive, I2: intermediate intrusive; I3: mafic intrusive; I3A: gabbro; Rhy: rhyolite.

Figure 3. Direct comparison of the Alpha and Delta pXRF data in drill-hole MC-05-18 at nearly the same depths (see text for discussion of depths), for TiO_2 (%) and Zr (ppm). Dashed lines have a slope of 1, pass through the origin, and are shown for reference.

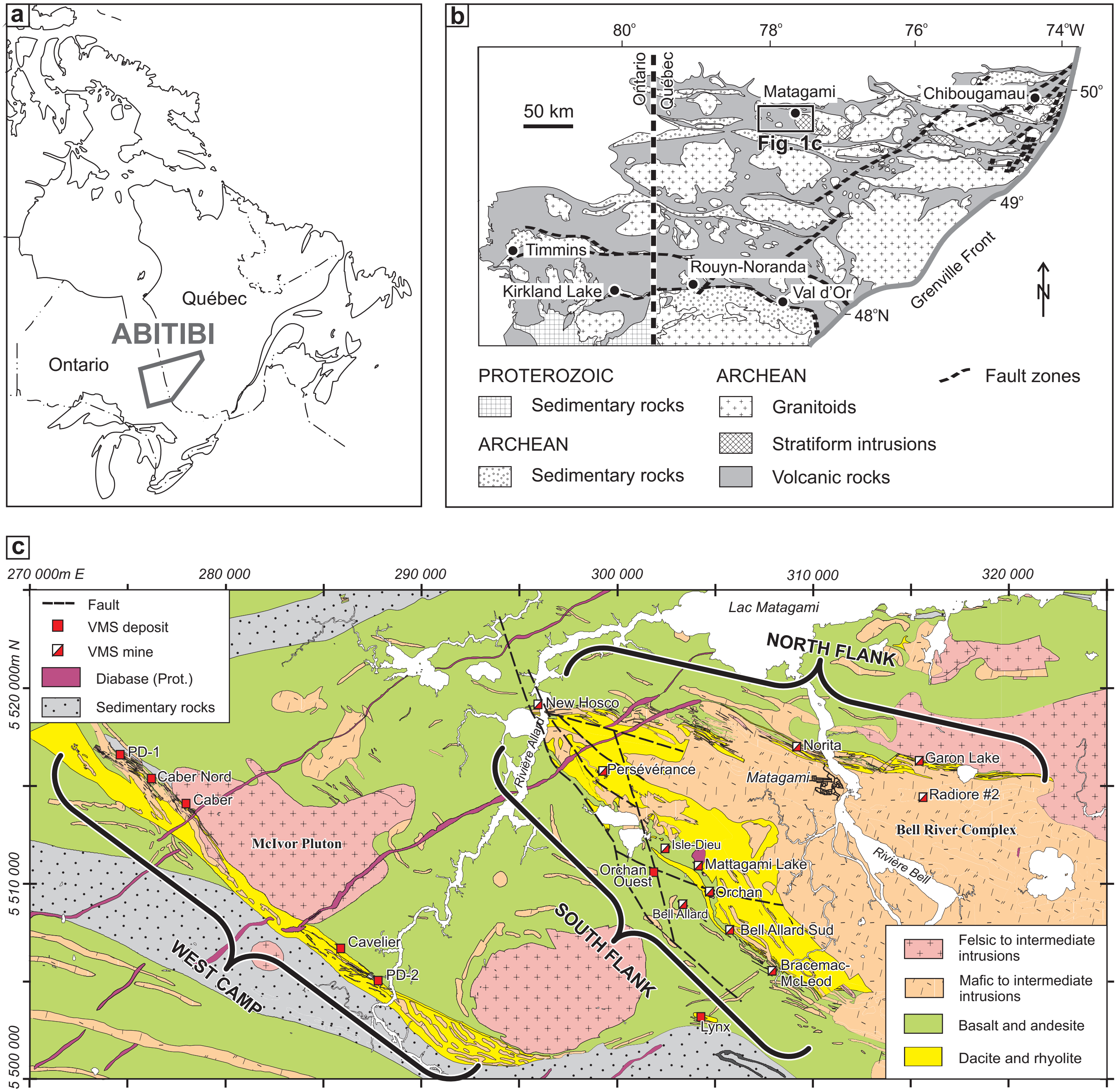
Figure 4. Geological cross-sections through the Équinoxe and Persévérance ore lenses, Persévérance mine, showing the location of the drill-holes analysed in this study (EQ-00-41 and PER-00-45), modified from Arnold (2006).

Figure 5. Down-hole geochemical profiles based on pXRF data for drill-hole EQ-00-41 from the Persévérance mine area. Stratigraphic top is towards the top of the hole. See text for discussion of geology. The two Deltas analysers were used; Ti/Zr and Al/Zr are corrected data, other elements/oxides are leveled data. Anomalies marked 'D' on the Ti/Zr profile are interpreted dikes, not noted in the original log except for the one where the "D" is underlined.

Figure 6. Plots of Ti/Zr vs. Al/Zr for two Matagami drill-holes from the Persévérance mine area: (a) EQ-00-41 and (b) PER-00-45. The corrected pXRF data can discriminate between the Dumagami Rhyolite and the Watson Rhyolite. Laboratory geochemistry for the same holes is shown for comparison (unpublished data from Xstrata Zinc Canada and INRS using a combination of wdXRF, fusion ICP-AES and fusion ICP-MS). For EQ-00-41, the two Delta analysers were utilized, whereas for PER-00-45, only the Delta-A was used. 'Other' lithologies are mostly intrusive rocks, including inferred dikes not reported in the original descriptions.

Figure 7. Geological cross-section through the Caber VMS deposit, showing the location of the drill-hole analysed for this study (NCB-98-38), modified from Masson (2000).

Figure 8. Down-hole geochemical profiles for drill-hole NCB-98-38 through the Caber VMS deposit. Stratigraphic top is towards the bottom of the hole. See text for discussion of geology. The two Deltas analysers were used; Ti/Zr and Al/Zr are corrected data, other elements/oxides are leveled data. Anomalies marked 'D' on the Ti/Zr profile are interpreted dikes, not noted in the original log except for those where the 'D' is underlined. Other abbreviations: I2: intermediate intrusive, I3: mafic intrusive, MS = massive sulfides, SMS = semi-massive sulfides.



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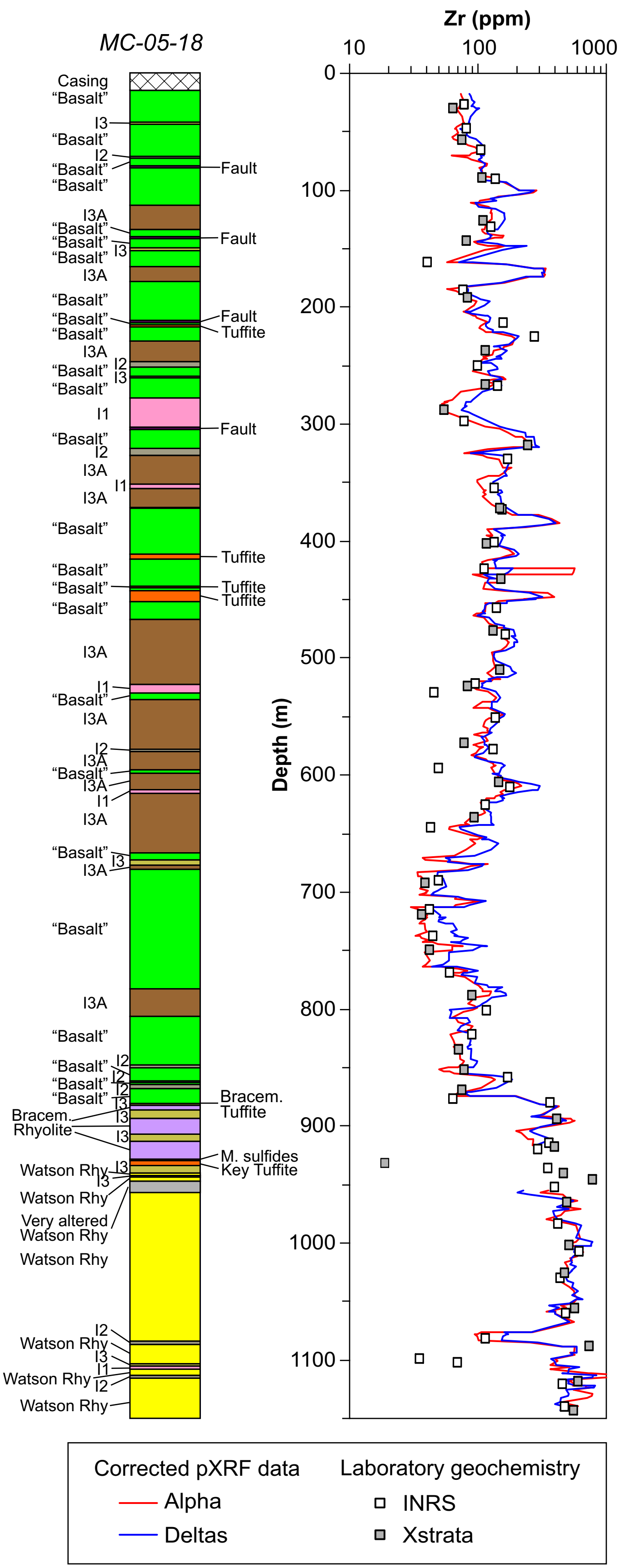

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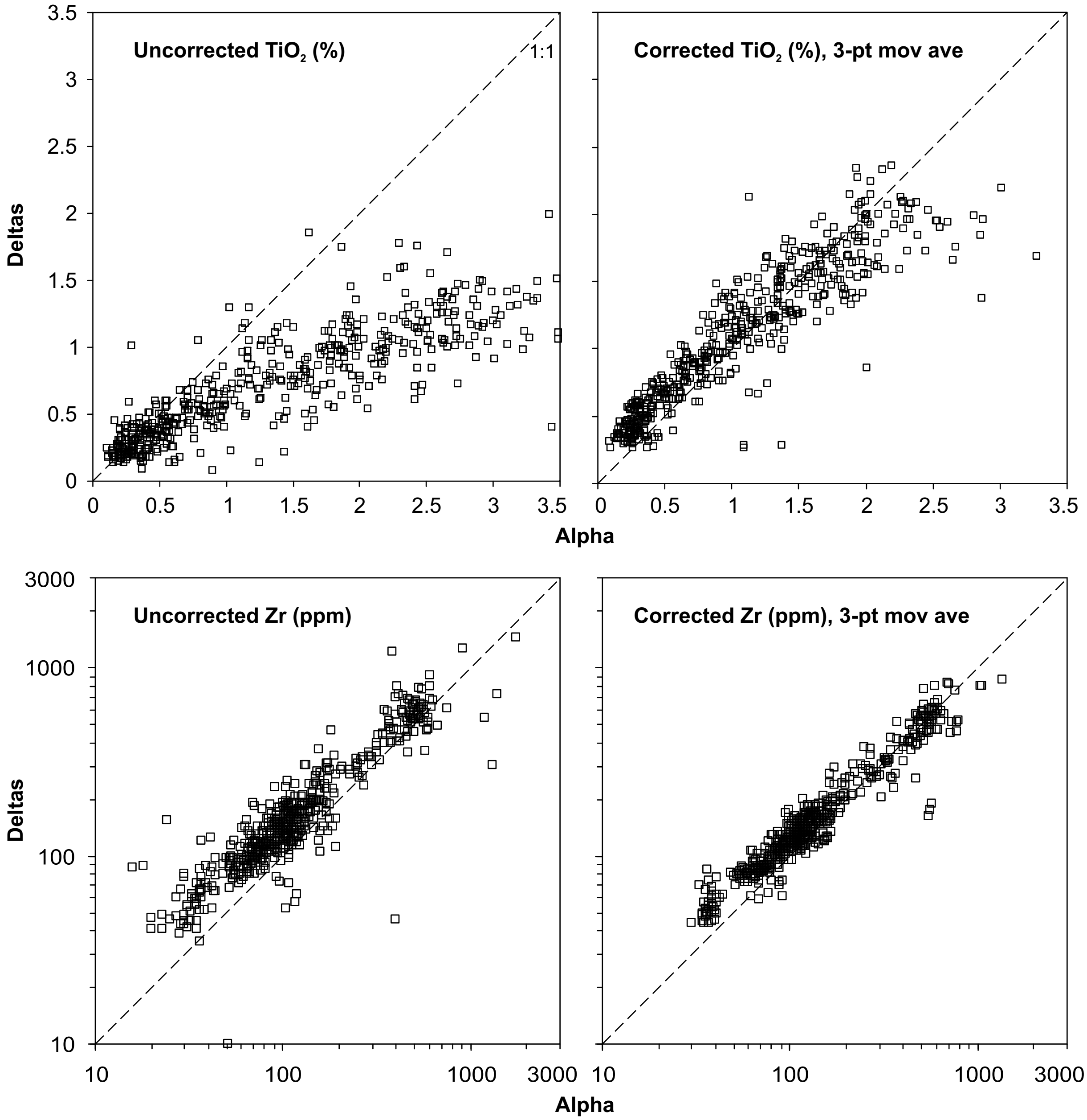

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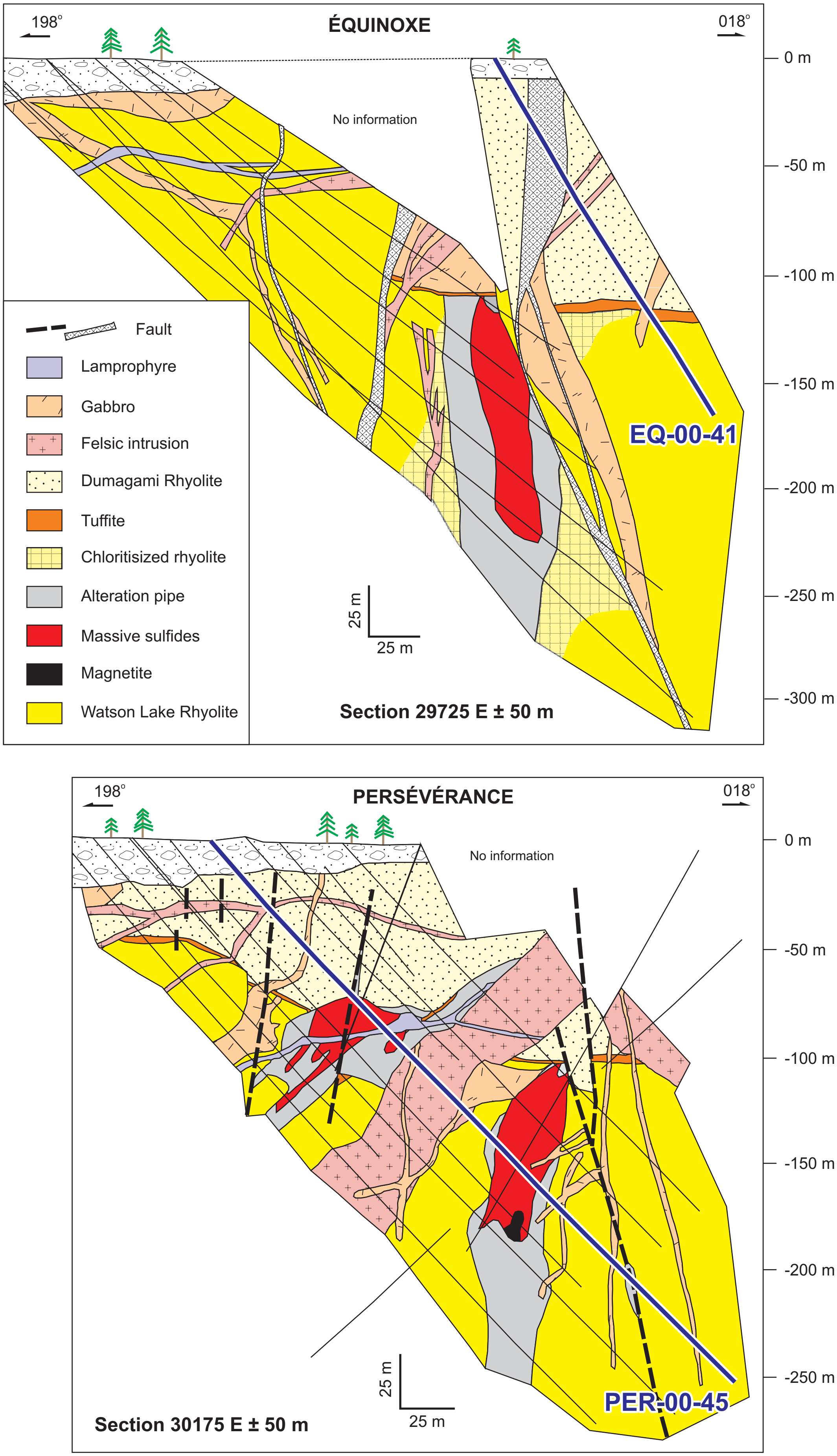

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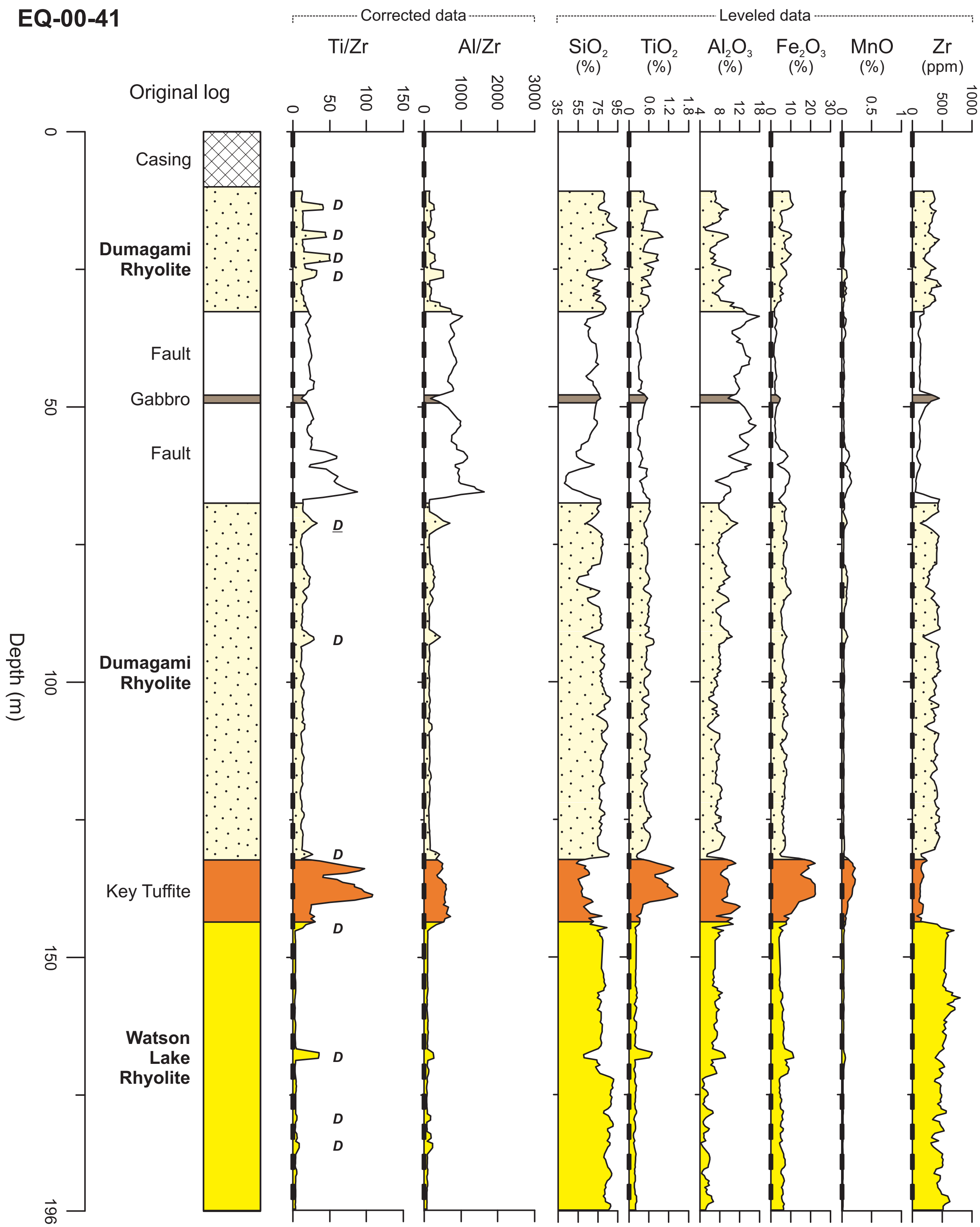

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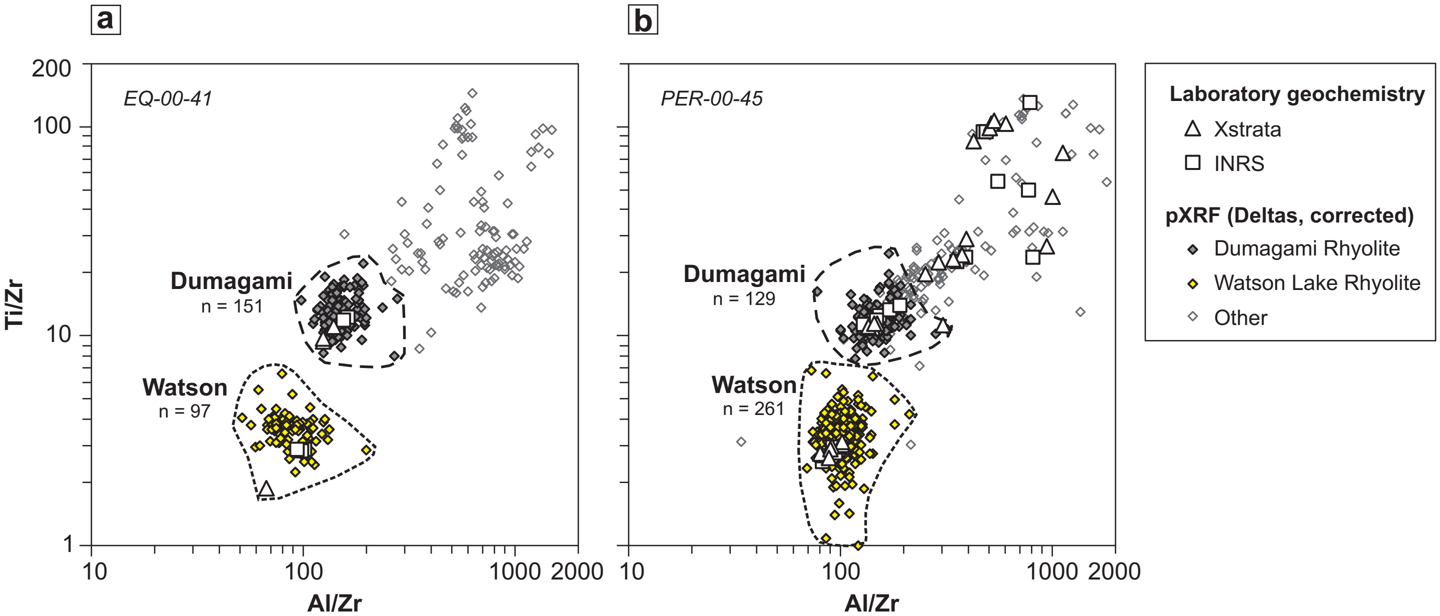

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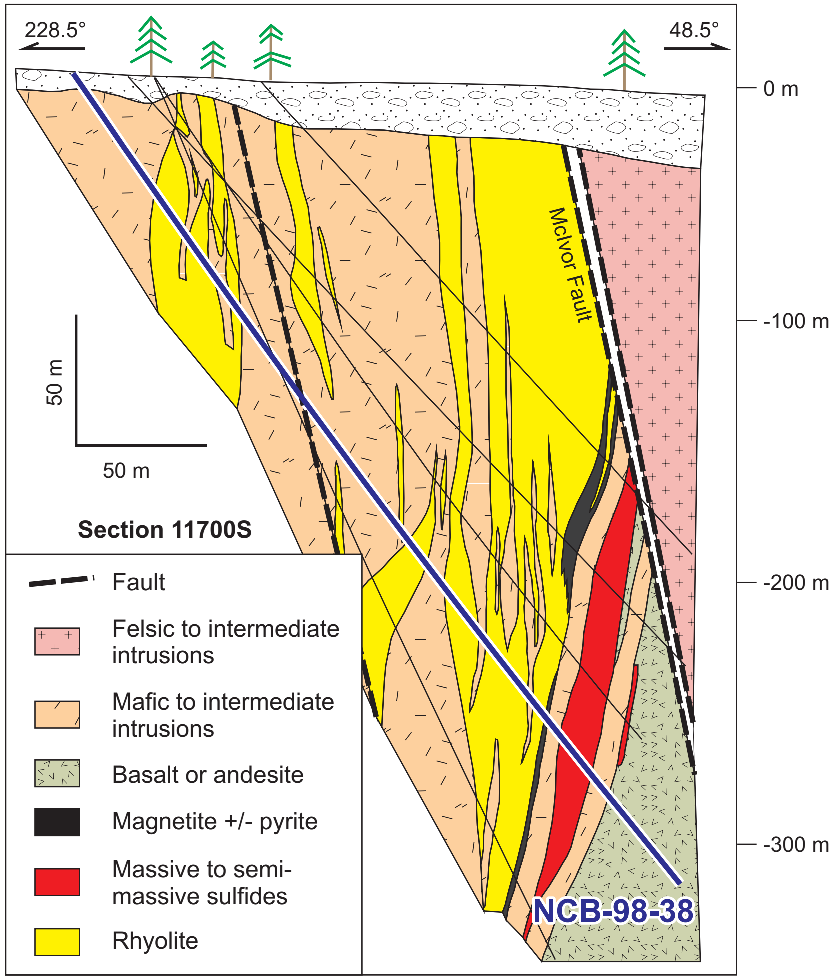

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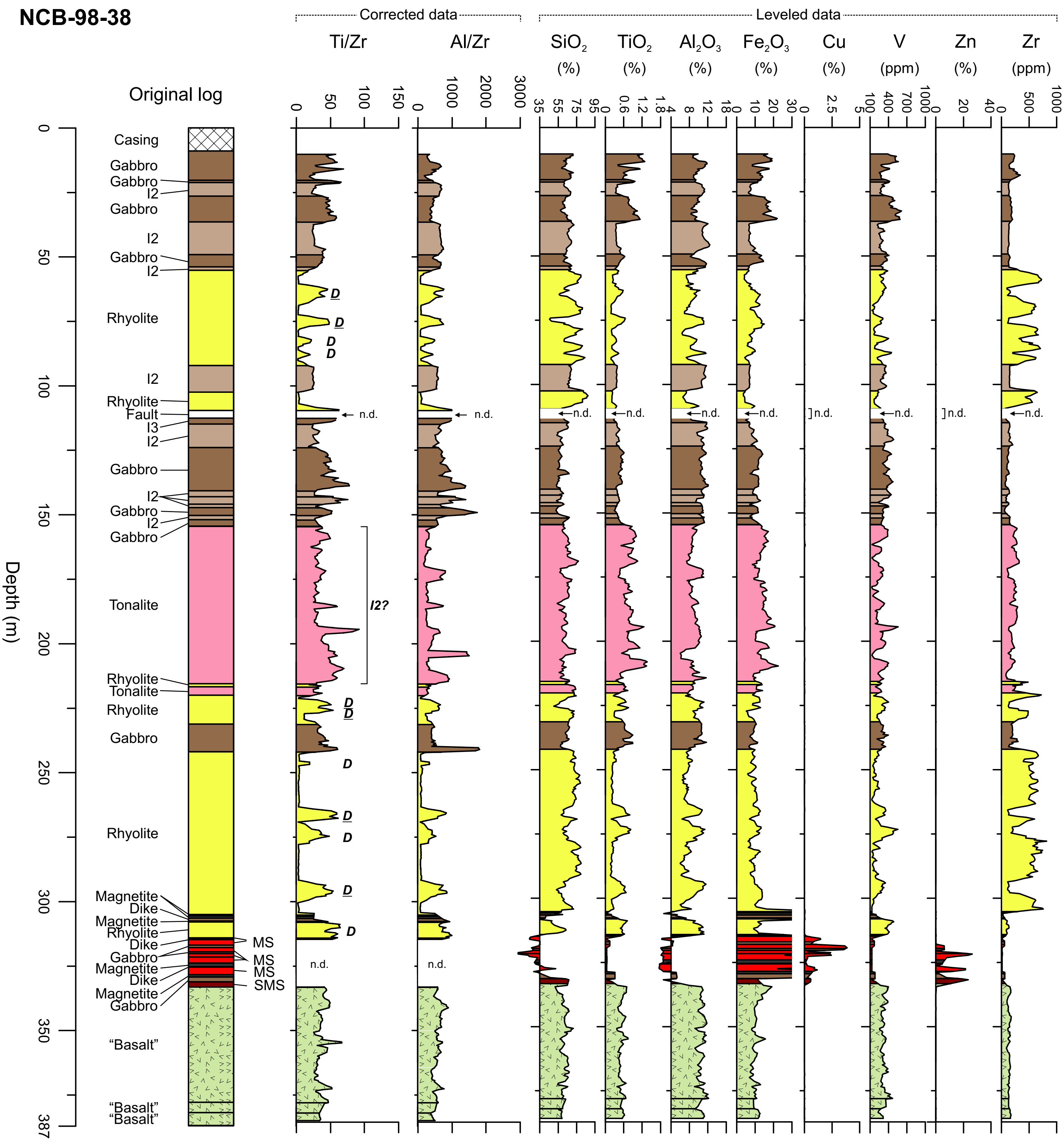

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