Geochemical exploration: getting rid of some deeply rooted flawed processes

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ABSTRACT

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What is best practice in geochemical exploration? In my opinion, there are three important questions that must be considered when planning a geochemical survey in mineral exploration, and through addressing these, best practice may be achieved: (1) what is the type and nature of the samples? (2) what is the analysis method, is it appropriate and are you getting as many elements as possible? and (3) are data treated properly to avoid identification of spurious or fictive relationships? I explore these three questions below and outline some of the flawed processes that I have encountered at each step.

NATURE OF SAMPLES

Modern analytical methods – such as multi-acid digests followed by ICP-MS analysis – provide data with detection limits of ppb for many elements. However, this does not account for the variance that is introduced by inherent variability or sampling errors. While there is undoubtedly utility for ultra-low-detection limit techniques in quantifying low-level variations in path-finder elements, if duplicate samples from the same location (soil sample or stream sediment), outcrop (rock chips) or drill core do not have a commensurately high reproducibility, then the utility of the ultra-low-detection limit techniques may be limited.

The reproducibility of samples should be assessed as part of an orientation survey *at the start* of a geochemical survey. The orientation survey should aim to sample all the different intended sample media at a given sample point, and test potential laboratory methods that might be applicable to these samples. Often, orientation surveys are not completed, and procedures that are used are simply a 'copy and paste' from the previous job worked on by the geologist in charge or are company favourites. Every geochemical survey has different characteristics and local geology; accordingly, the optimal sampling strategy and laboratory method will change survey to survey.

For example, Figure 1a presents an *in-situ* regolith profile from a project in Zambia where 12 samples at 0.2-m intervals were sampled from the wall of an artisanal pit over the top of *in-situ* Au-Cu mineralisation (up to 26 ppm Au and 0.7% Cu). The style of mineralisation is unclear at this time as it has only been encountered in oxidised surface sample; but the high-grade mineralisation typically contains >50% Fe, but less where it is quartz veined. In addition to significant Cu and Au content, it is anomalous in Bi, Te, In, Sb, and Hg. The pit-wall samples were analysed by method ME-MS61 at ALS Geochemistry, Johannesburg: a four-acid digest followed by ICP-MS/OES analysis. The plot of K/Al indicates that the different sized samples are correctly correlated, i.e. that there is not a sampling error, that has resulted in the divergent performance in Cu and Fe in the two size fractions (Figure 1b). Traditionally, the <180 μm size fraction would have been selected for soil sampling in this project; however, the Fe and Cu contents are highest in the 180–2000 μm size fraction (Figure 1c,d), by almost a factor of five. When geochemical anomalies are a modest expression of subsurface mineralisation, sampling the correct sample media is critical to effectively detect the presence, let alone to map the extent, of mineralisation.
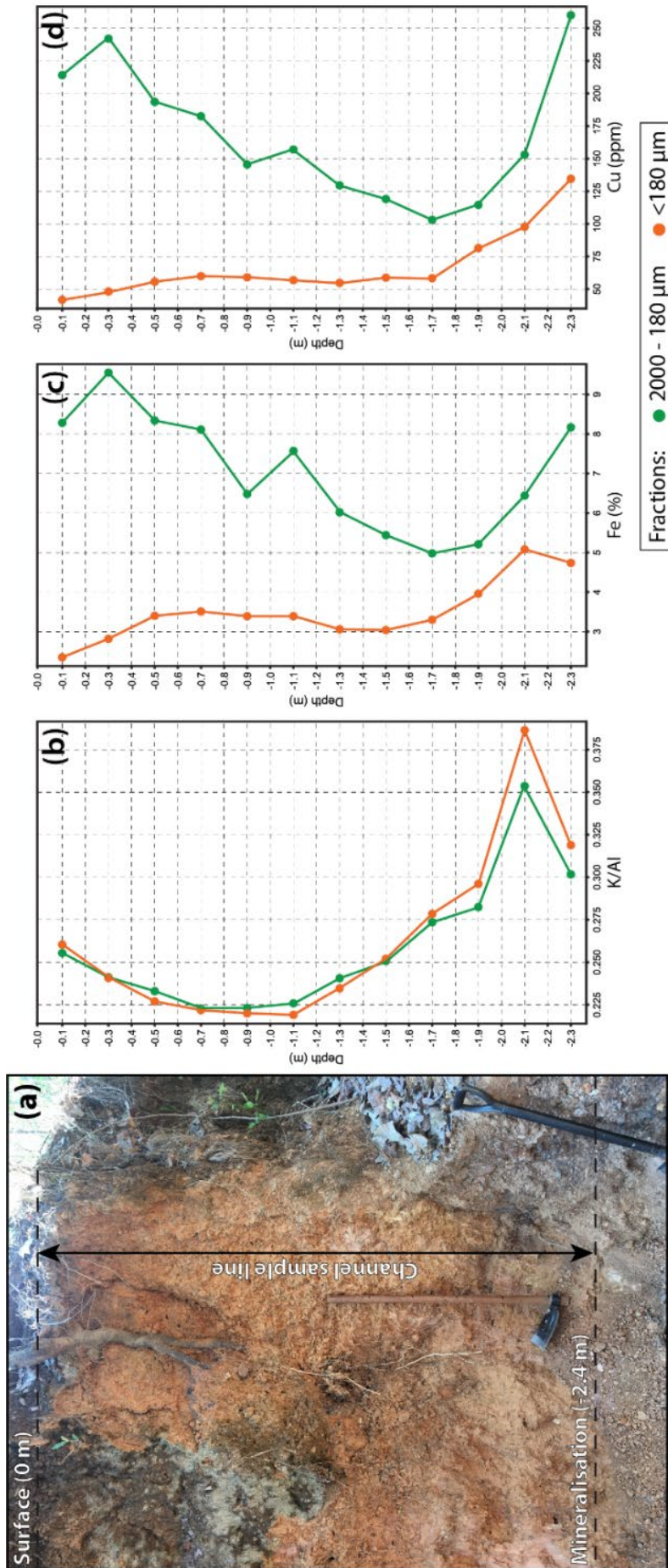
Figure 1 (a) Photograph of a 2.4-m thick regolith profile from a project in Zambia over the top of mineralisation; (b) K/Al for two size fractions (green = 2000–180 µm; orange <180 µm); (c) as for b, but for Fe (%); (d) as for b, but for Cu (ppm).

ANALYTICAL METHOD

Sadly, many geologists pick the cheapest analytical method that gives them the element suite that they are interested in. There seems to be little appreciation that different laboratory methods will result in significantly different results when the same sample is analysed. The same can be said about certified values of certified reference materials (CRMs); for some CRMs there may be multiple certified values for a given element, certified for different analytical methods through round robin analysis at multiple laboratories. For example, Zn in CRM OREAS25a has certified multielement data for three methods: fusion ICP-MS/OES (46.8 ppm), four-acid digest ICP-MS/OES (44.4 ppm), and aqua-regia digest ICP-MS/OES (30.1 ppm). All these values for Zn are certified, yet they are all different; so, care must be taken to match the analytical methods as aqua regia digest, which is typically the cheapest method, is not a total digest. That is to say, it does not extract all of the element's concentration from the sample, which is why Zn by this method is so much lower than Zn by fusion (a total method) and four-acid digest (a near-total method).

Portable XRF (pXRF) technology allows the generation of large geochemical datasets at little cost. With an appropriate workflow, pXRF data can be both reliable and robust for more than 24 elements. Indeed, pXRF data have a distinct advantage over multi-acid digest data in that they provide Si (which cannot be determined by an acid digest involving hydrofluoric acid due to silica loss) and Zr (which is seldom completely dissolved by acid digest). Four-acid digest followed by ICP-MS/AES analysis coupled with pXRF for Si and Zr, and Au, either by fire assay or aqua regia digest, provides a robust dataset of 50 elements in a cost-effective manner. However, building on the previous point, when picking element concentration values to calibrate a pXRF instrument, care must be taken to ensure that a (near-)total method is used; i.e. if fusion data are available, use that, if not, four-acid digest. Uncertified LA-ICP-MS or XRF data may be useful in the absence of (near-)total methods.

Finally, the laboratory is not always right – there will be errors (probably few and far between) and batch effects. Different laboratories have different methodologies (e.g. duration, temperature, or acid concentration(s)), even if the high-level method description is the same (e.g. four-acid digest). Thus, care needs to be taken comparing data from different laboratories within a project. The use of CRMs may also allow datasets from different laboratories or analysed at different times to be levelled against each other.

DATA TREATMENT

There is a growing body of literature around best-practice to mitigate the effect of compositional closure in geochemical data; however, this does not appear to be common-practice. Because geochemical data are compositional and thus typically total 100% or 1,000,000 ppm, they are not independent and consequently do not naturally inhabit a real-number space or a Euclidean number space (e.g. Aitchison, 1982, 1986; Aitchison *et al.*, 2000). Geochemical data cannot be subjected to standard statistical methods (e.g. parametric techniques) or even plotted meaningfully on element-element plots without producing spurious correlations in the data. There are numerous approaches to treating geochemical data to prevent this. Indeed, single-element maps or plots are the go-to for many exploration and mine geologists; but, a number of workers have argued correctly that single-element maps are not good practice (e.g. McKinley *et al.*, 2016). Best-practice requires samples to be collected and handled representatively, good performance of duplicate samples, use of appropriate analytical techniques with analysis of as many elements as possible, and proper treatment of the geochemical data at the interpretation step (e.g. Singer & Kouda, 2001; Buccianti & Grunsky, 2014; Gazley *et al.*, 2015, 2020; McKinley *et al.*, 2016).

Here, I present an example where a centred log ratio (CLR) transform has been used, which opens the dataset by transforming it such that the components are no longer dependent. In a geometrical sense CLR transforms the dataset from a simplex space to a real number space or a Euclidean space (e.g. Aitchison, 1982, 1986; Aitchison *et al.*, 2000). Assessing the dataset using the CLR transformed data allows for new insights than provided by the raw elemental data alone, as the CLR values account for variation in the other elements in the sample, rather than just considering a single component in a compositionally-closed space.

A synthetic dataset was generated in a uniform (unitless) grid of 6 x 7 samples (Figure 2). Two uniform anomalies each of 500 ppm As were created. In the western half of the map, the amount of Si was doubled (on a molar basis)

in the three samples that were coincident with the As high in an E-W direction. To the north and south of this line, the increase in Si (on a molar basis) was 75%, 50% and 25%. The bulk composition was then recalculated for each point in the grid that was affected; this increased the Si content from 31.19% to 38.30% in the sample that was previously 500 ppm As (Figure 2a), which decreased to 307 ppm (Figure 2b). The change in As concentration occurs despite the change in the composition being to Si, not As. This demonstrates the effect of compositional closure and how changes in processes that nominally only affect one element have flow on affects to all elements in the composition. Once a CLR is applied to the dataset, both As anomalies are equal at ~-3 as per the original starting composition where they were both 500 ppm (the small difference between values is due to the number of samples in the CLR, the bulk compositions of which influences the geometric mean of each element). In concentration (ppm) space, which is compositionally closed, an incorrect assessment of which anomaly was more significant would have been made. This example underscores the importance of *not* plotting only single element maps or plots in a compositionally closed space (e.g. ppm or %). Furthermore, multivariate data analysis or machine learning should not be conducted on data that inhabit a compositionally closed space.

CONCLUSION

This paper highlights some of the challenges that are related to geochemical sampling, and some of the deeply rooted and flawed processes that are continued to this day. With careful choice of sample media and laboratory methods, large geochemical sample sets can be generated in a cost-effective manner that maximise the chance of detecting the signature of hydrothermal or mineralising processes. However, these datasets must be treated properly to avoid identification of spurious or fictive relationships. To do this requires an understanding that geochemical data are compositional and that, in their raw form (ppm or %), they cannot be subjected to standard statistical methods (e.g. parametric techniques), plotted meaningfully on element-element plots, or plotted as single element maps without producing spurious correlations in the data. Numerous approaches are available to ensure that geochemical data are appropriately examined – as discussed here a CLR is just one of them.

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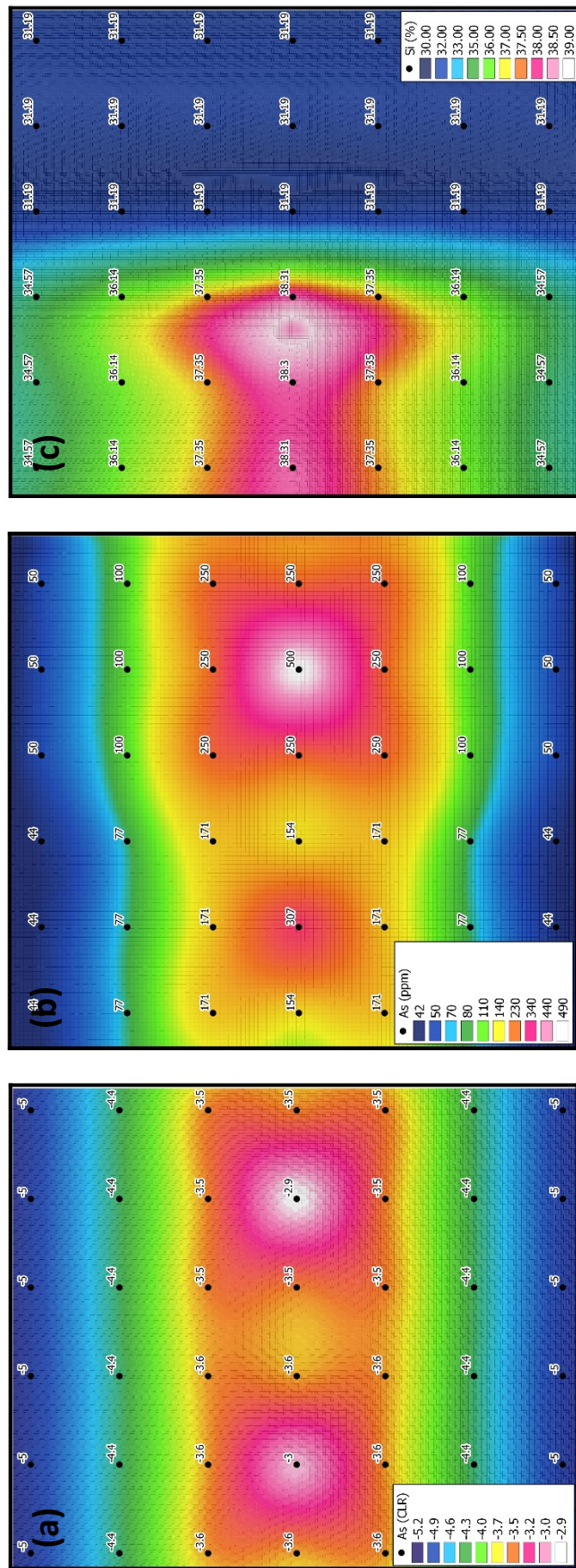
Figure 2 (a) contoured Si (%) of the synthetic dataset after modification; (b) contoured As (ppm) of the synthetic dataset after modification; and (c) contoured CLR As of the synthetic dataset after Si addition; and (c) contoured CLR As of the synthetic dataset after modification.