

Author:

Wesley Ingram, Ph.D., Consultant Geology and Geochemistry

Title:

Elemental analysis of commercial climbing chalks

Abstract:

A total of five powdered samples were selected for elemental analysis to compare chemical variation between several commercially available climbing chalks. The chalk samples were measured for their respective elemental components using a Bruker Tracer III portable X-ray Fluorescence instrument. Elemental results provided here rank the five climbing chalk samples by their respective purity, those containing the highest inferred magnesium carbonate (MgCO_3) content along with the lowest amounts of other impurities such as Si, S, Ca, Ti and Fe.

Introduction:

The goal of this study is compare the elemental composition of powdered climbing chalks from five different commercial vendors to determine their relative purity. X-ray Fluorescence (XRF) methods were used to determine the elemental chemistry and define bulk-rock forming minerals. Climbing chalk is routinely marketed as magnesium carbonate (MgCO_3). XRF technology provides the opportunity to quickly measure the relative proportion of elements in such geologic samples; hence it is suitable for this comparative analysis focusing on Mg along with other elements (Richter et al., 2006). As part of a typical scan for major elements (Materials and Methods Section), additional elements are detected, they include Si, S, K, Ca, Ti, Mn, Fe and Ni (Figure 1). For this study, the climbing chalks are assigned arbitrary designations A, B, C, D and E to insure unbiased interpretation; henceforth referred to in this manner. The chalk samples are then ranked based on interpretation of the elemental XRF data.

Material and Methods:

The materials used for this report include five powdered climbing chalk samples. The grain size is not known, however all samples have the appearance of fine powder (likely less than 200 μm); thus are suitable for XRF measurement and reduced matrix effects. The powdered chalk samples were placed into cylindrical containers, covered with ultra-thin film (4 μm or less), then lightly tamped to ensure a cohesive surface under the thin film. The powdered chalk was then placed over the XRF detector window, thin film facing down, and measured for 60 seconds. The sample preparation procedure outlined above was replicated providing comparative results for all samples.

Samples were measured using the Bruker Tracer III XRF analyzer, an instrument that allows specific control of XRF scanning parameters generating optimal XRF spectra for elements of similar atomic weight. The scanning parameters used are similar to major element settings and are specifically suitable for elements ranging from Mg to Fe. All samples were measured using the following XRF settings: (1) voltage of 15 keV, (2) current of 25 μA , (3) timed assay of 60 s, (4) no filter, and (5) vacuum atmosphere. The selected energy is appropriate for light elements, and the vacuum system used here is critical for effective detection of Na and Mg, which eliminates atmospheric effects (Jenkins, 2000). The current controls the rate of X-ray emission and no filter is required when measuring for major elements of low atomic weight. This XRF unit uses a Rhodium (Rh) X-ray tube, which generates reflection visible as a large peak (Figure 1); hence it is not associated with Rh in the sample.

Results and Discussion:

The XRF results presented in this report rank each chalk sample (A, B, C, D and E) based, in part on the highest interpreted concentration for Mg followed by the lowest concentration of other elements (considered impurities), which include Si, S, Ca, Ti and Fe (Figure 1; Table 1). While samples contain impurities, bulk composition of the samples are considered to be clean Ca-Mg carbonates as all samples are white powdered chalks; thus little to no clay content. Given the apparent lack of clay, it is reasonable to assume Mg is contained in the carbonate phase (MgCO_3). The measured data is in XRF counts; thus concentration and/or mineral content are interpretations.

XRF results indicate chalk Samples B and C have the highest counts for Mg, Sample C slightly higher with 6699 counts followed closely by Sample B with 6387 counts (Table 1). Based on this data,

Sample C has the highest Mg content. However, higher XRF Mg counts are potentially due to higher density or tightly-packed grains, and this would be reflected by higher counts for other elements as well. However, this is not the case as Sample C also yields the lowest counts for other elements Si, S, Ca, Ti and Fe (Table 1). Taken together (XRF counts of all elements, Table 1), these data indicate that Sample C is the purest of the chalk samples, hence it is ranked 1st in chemical purity.

The ranking for the 2nd most pure sample is not as obvious, for instance the Mg concentration for Sample B is higher than Sample E, while the latter contains lower amounts of S, Ca and Fe (Table 1). Sample E also exhibits higher Ti and Si counts, elements associated with siliciclastics (sands and silts) in geologic samples. Sample E is interpreted as slightly more pure based on estimates of Mg contained in the carbonate phase. From mineral stoichiometry and atomic weights, carbonates (CaCO_3) are heavier than siliciclastics, which are presumably oxides (TiO_2 and SiO_2). Hence, the ratio of Ca/Mg can be used to differentiate the sample that contains more Mg in the carbonate phase, thereby comprising the greater proportion of Mg minerals by weight. Using this method, Sample B yields Mg/Ca ratio of 0.320 and Sample E 0.388, thus the latter has greater Mg carbonate. Thus, it is interpreted as more pure, while acknowledging it also contains more Ti and Si - siliciclastics from silt or clay particles in the chalk. This Mg/Ca ratio does not account for Fe in the carbonate phase; however it does not change the interpretation as Fe is lower in Sample E (Table 1), consistent with higher purity. Based on these reasons, Sample E is interpreted as the 2nd most pure and Sample B is 3rd.

Applying the same method as above, it is apparent that Sample A has greater Mg relative to Ca than Sample D, while the latter has higher Mg XRF counts (Table 1). Thus, ranking the remaining chalk samples is also not obvious. Sample A contains more Mg in the carbonate phase based on the ratio Mg/Ca ratio (Sample A: 0.093 versus D: 0.078); yet this is still not straightforward as it also contains more Fe (Table 1). While Fe is associated with carbonates, clay content and/or siliciclastics, it is reasonable to assume Fe in a clean chalk is predominately in the carbonate phase; hence the Mg/Ca can be misleading without also considering Fe content. In fact, by taking the ratio of Fe/Ca for each sample, it is apparent that Sample A (Fe/Ca: 0.767) contains much more Fe in the carbonate phase, than does Sample D (Fe/Ca: 0.208). Based on the above, Sample D is considered more pure than Sample A due to the much lower Fe content, also likely in the carbonate phase. The Fe content is the differentiating factor here, as Si, S and Ti are similar for both samples (Table 1). Hence, Sample D is the 4th most pure and Sample A is the 5th ranked sample in chemical purity.

Conclusion:

XRF analysis indicates that the analyzed climbing chalks are chemically different; this variation can be used to rank the relative elemental purity, e.g. chalks most similar to MgCO_3 . This ranking is defined as those chalks that contain higher Mg content, along with lower amounts of other elements. Based on XRF data, none of the chalks are pure MgCO_3 and are more accurately described as Mg-Ca carbonates. Chalks are assigned the following rankings, Sample C, E, B, D and A, in order from most to least pure as it is defined in this study. While some rankings are interpretative, Chalk C yields the highest Mg detection. Chalk C also yields much lower XRF counts for the other elements; hence this particular sample is the most chemically pure based on the elements considered.

References:

Jenkins, R., 2006. X-ray Techniques: Overview, *in* Meyers, R.A. (eds.) *Encyclopedia of Analytical Chemistry* pp. 13269-13288.

Richter et al., 2006. The Avaatech Core Scanner: Technical description and applications to NE Atlantic sediments. *In*: Rothwell, R.G. (eds.), *New ways of looking at sediment core and core data. Geological Society Special Publication*, London, pp. 39-50.

Table 1. XRF Net Photons

Chalk-ID	Mg	Si	S	Ca	Ti	Fe
A	2640	649	1689	28313	1300	21715
B	6387	875	3341	21339	2219	10301
C	6699	608	1882	8844	1573	8160
D	3411	612	2022	43654	2081	9060
E	5664	3622	2519	14610	2247	8884

Table Caption 1. Tabulated data of net photons detected using the Bruker Tracer III. This instrument uses Rhodium X-ray tube to induce fluorescence for the elements listed (Mg, Si, S, Ca, Ti and Fe) as part of a scan for major elements (See Materials and Methods for scanning parameters). Fluorescence is measured using a Silicon Drift Detector. Photons hitting the detector are counted and binned by their respective energy; this fluorescent light is specific to the element in the sample. These XRF data are not corrected to standards, yet counts are directly proportional to concentration of the elements analyzed; therefore are appropriate for comparative analysis used here.

Figure 1. XRF Spectra

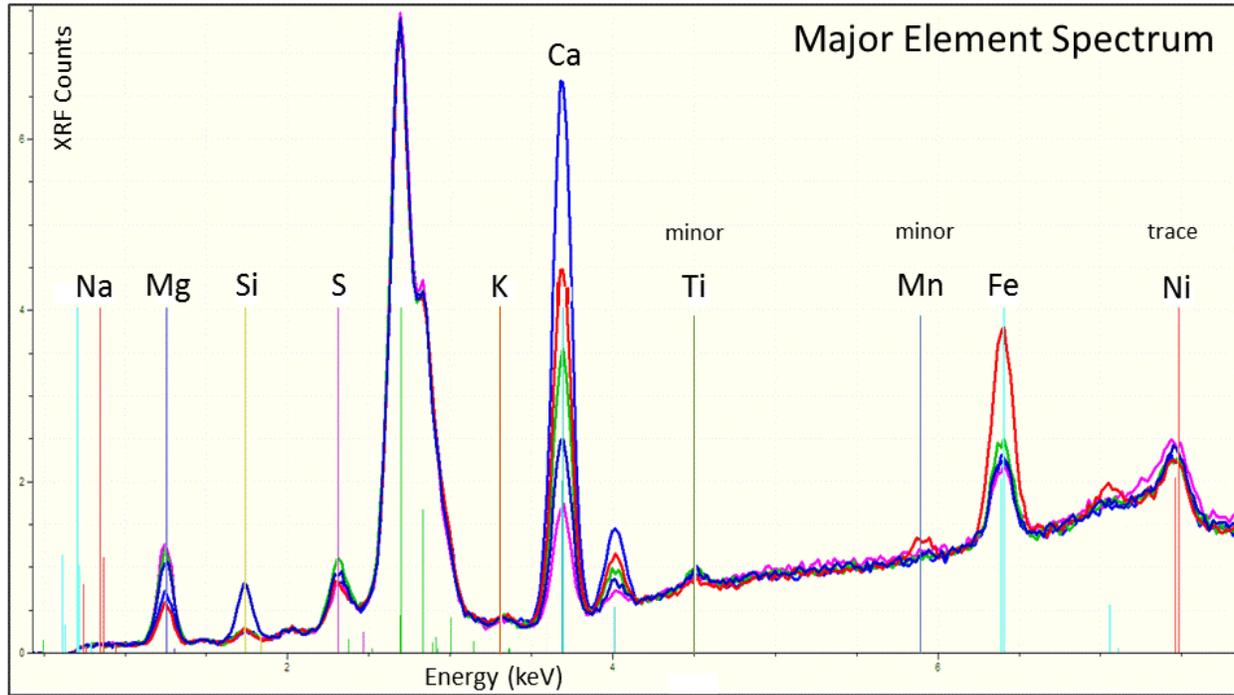


Figure Caption 1. XRF spectra for typical major element scan, the parameters used are specifically suitable for elements ranging from Mg to Fe (See Materials and Methods). Energy in kilo-electron volts (keV) on the horizontal axis and the number of photons on the vertical axis are measured by the Silicon Drift Detector. The height of the elemental peak (XRF counts) is directly proportional to concentration of the element in the sample and the energy is specific to the element. This major element scan includes Na, Mg, Si, S, K, Ca and Fe (not labeled), as well as minor elements Ti and Mn and finally the trace element Ni as labeled on the figure. The largest and broadest peak left of center is the Rhodium reflection from the Rh-target X-ray tube used to induce elemental fluorescence; hence has no relation to concentration of the element in the sample.