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Methods to analyze metastable and microparticulate hydrated and hydrous iron sulfate minerals

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Abstract

We evaluate analytical methods for characterizing hydrated and hydrous iron sulfate minerals (HHIS) that are typically metastable in air or vacuum, commonly form micrometer-sized particles, and contain multi-valent and light elements (Fe^{2+}, Fe^{3+}, OH^-, and H_2O) that may be challenging to quantify. We synthesized or obtained HHIS—szomolnokite, melanterite, rhomboclase, schwertmannite, ferricopiapite, paracoquimbite, and jarosite—as well as Fe-oxides. These nominally pure samples were characterized with X-ray diffraction (XRD), and then used to evaluate bulk analyses obtained from combined inductively coupled plasma, optical emission spectroscopy (ICP-OES), ion chromatography (IC), Mössbauer spectroscopy, and mass spectrometry. Integrated bulk analyses showed excellent agreement with the nominal formulas for the minerals.

Because HHIS commonly form micro-sized particles—for example, HHIS found in acid mine drainage (AMD) environments and in martian meteorites—it is necessary to develop micro-analytical techniques. Microscopic mid-infrared spectroscopy allows the analyst to successfully discriminate among HHIS with minimal sample preparation on the small scale (~40×40 μm). For chemical analysis, electron probe microanalysis (EPMA) is preferred for samples that can be mounted, polished, coated, and that are stable under high vacuum; however, few HHIS meet those criteria. To characterize HHIS compositions, we show that multiple low-vacuum scanning electron microscopy (SEM) analyses of the same uncoated, unpolished mineral are required. Analysis of each mineral shows linear trends on ternary diagrams of $5\times$Fe-SO_4-O (where oxygen is in O, OH, and H_2O) that may be used to narrow down the HHIS mineralogy. Low-vacuum SEM also provides invaluable information about the geochemical and textural context of the samples. Our study provides protocols for microanalysis of these challenging, fine-grained, and metastable HHIS that may also be applied to other mineral groups.

Keywords: Bulk analysis, microanalysis, light element analysis, low-vacuum SEM, micro-infrared spectroscopy, Mössbauer