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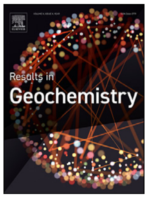

Short Communication

The occurrence of Hg, Se, S, Ni, Cr, and Th in Talc Ore: A scanning electron microscopy (SEM) study of historical samples from the Willow Creek Mine, Montana

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ABSTRACT

Due to short timeframes over which small-scale talc mines operate (approximately 1 to 10 years), detailed characterization of their mineralogy and geochemistry in the peer-reviewed literature is limited. Investigation of sample 1497 of the Willow Creek Mine, Montana by scanning electron microscopy using back scatter detection (SEM-BSD) indicates a complex minor mineral assemblage. Hg-Se-S minerals are associated with graphite whereas Zn-Cr-Ni minerals and Th minerals are dispersed in the talc matrix. Notably, Hg, Se, Zn, Cr, and Ni are of human health concern. Minerals with these elements are ~ 20 to 0.4 µm in diameter, and all have examples in the PM_{10} or $PM_{2.5}$ size fraction. These minerals would likely not be separated out during processing of talc ore and would be inhalable. Results indicate a need for detailed SEM-BSD investigations of historic talc products from the Willow Creek Mine and for investigating ore from similar settings in Montana.

1. Introduction

Talc products and talc sources have become of interest owing to extensive litigation of consumer products based on asbestos content (Petter, 2020, NBC 2019, Girion, 2018). One component that has not been well established in talc ore and talc products in the peer-reviewed literature is the occurrence of other minerals such as oxides and sulfides that may be present as inclusions in talc ore and talc products which have the potential to contain elements of environmental health concern.

Talc ore deposits are metamorphic rocks that are long recognized to commonly occur in two broad classes: (1) mafic and ultramafic protolith settings and (2) carbonate (marble) settings (Chidester, Engel & Wright, 1964). Although talc has been extensively mined and used globally for decades in a wide variety of products such as seed coatings, paints, plastics and cosmetics, there are several characteristics of talc deposits which have not been thoroughly studied. Talc deposits are often omitted in ore geology text books (Ridley, 2013). Presumably this is because these deposits have not been as extensively researched as others (e.g., SEDEX, epithermal gold, diamondiferous kimberlites) and are not as well understood. There are comparatively few detailed investigations of the mineralogy and geochemistry of talc ore deposits using scanning electron microscopy (SEM) in the peer-review literature. Prior geologic SEM research of talc has focused primarily on its occurrence as an alteration product of minerals (Polovina, Hudson & Jones, 2004). Prior SEM investigations on talc specifically related to mineral products from ores is far more common, but they do not usually use back scatter detection (BSD) to look for impurities (Delgado et al., 2020, Yekeler, Ulusoy & Hiçyılmaz, 2004, Premalal, Ismail & Baharin, 2002). SEM studies relating to talc ores are done mainly in the context of mineral processing (Baba et al., 2015). Detailed geochemical studies of talc-bearing units are uncommon (Powell, Johnston, Collom & Johnston, 2006, Shin & Lee, 2002).

In the global history of talc production, many historic mines were operated and often over a limited or over variable window of time. Many of these mines do not have their mineralogy investigated in detail systematically in the peer-reviewed literature. Thus, comprehensive mineralogical data on such mines is lacking and this is critical for understanding the geologic and geochemical evolution of these deposits. This is also important for providing context for environmental properties of derived products.

2. Setting, materials and methods

According to the USGS currently Montana is the leading talc producer in the U.S. (U.S.G.S. 2020). The talc corridor of Montana is hosted in Achaean marbles and is an east to west zone over approximately 1600 km^2 (Van Gosen, Berg & Hammarstrom, 1998). Located in this corridor is the Willow Creek Mine. Berg (1979) provides a description of the Wil-

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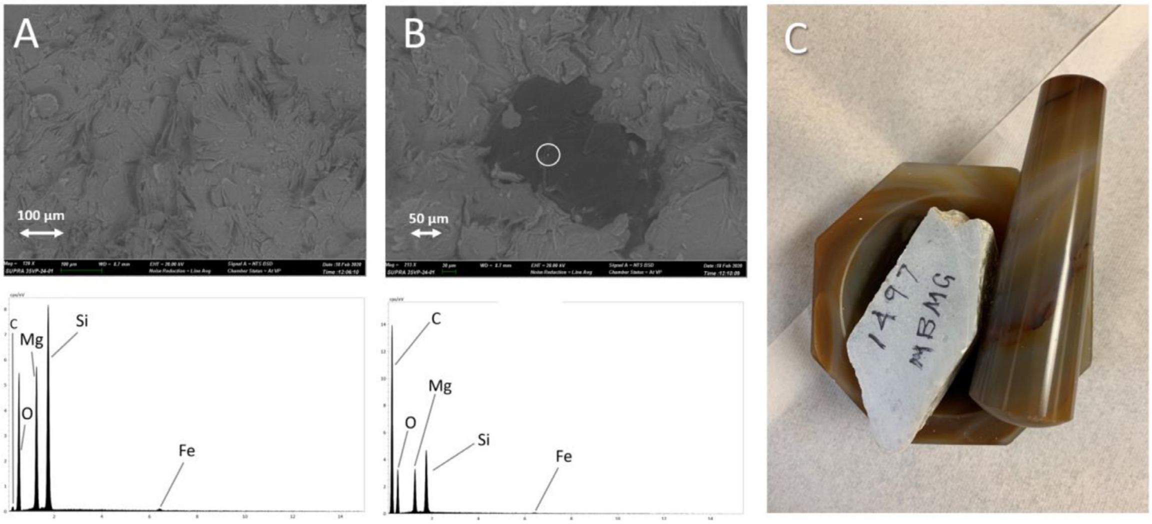

Fig. 1. (A) BSD image of the general texture of talc showing foliated subhedral talc crystals. EDS spectrum for the entire image is shown below. (B) BSD image of a representative crystal of graphite (dark mineral) in talc matrix with a circle on a Se-rich mineral inclusion. EDS spectrum for a ~150 × 150 µm area to the right of the white circle is shown below. (C) Image of the sample chip used in this study showing sample number and clean agate mortar and pestle. The sample is approximately 6 cm in length and 1 cm thick.

low Creek Mine (also sometimes referred to as the Ruby Ridge Mine) which states the mine is located 16 miles southeast of Alder, Montana with small levels of production from underground operations several decades prior to the 1970s with more significant production occurring between 1970 and 1979. Further information indicates that the mine produced talc in the 1970s but production ceased owing to a large high wall landslide that infilled the deposit under barren footwall rocks during 1980 (Van Gosen, Berg & Hammarstrom, 1998, Berg, 1979). As a result, the ore body of the mine has not been accessible since. Descriptions indicate that the mine occurs in a small body of marble which is in turn is enclosed by gneiss (Berg, 1979). The hanging wall and footwall of the marble consist of chloritically altered quartzofeldspathic gneiss and garnetiferous biotite gneiss with minor hornblende gneiss and amphibolite (Berg, 1979). These are Precambrian in age and have been deformed such that they sit on Paleozoic rocks (Berg, 1979). The talc body and enclosing metamorphic rocks strike northeast and dip at varying angles from 40 to 70° to the northwest and talc mineralization extends approximately 300 m along strike (Berg, 1979).

Six samples of ore of the Willow Creek Mine were acquired from the geological repository of the Montana Bureau of Mines and Geology in October 2019 for study with the aid of Dr. Dick Berg who collected the samples in the 1970s. For the purpose of this study, one of the samples (1497 MBMG) has been characterized in detail via SEM. A Zeiss SUPRA 35VP Field Emission Scanning Electron Microscope (FE-SEM) was used at Miami University's Center for Advanced Microscopy and Imaging (CAMI) to acquire backscattered electron (BSD/BSE) micrographs. The instrument has a Bruker Xflash 5010 Energy Dispersive X-Ray Spectroscopy (EDS) detector to collect elemental data with a detection limit of approximately 0.08 wt.% (Kuisma-Kursula, 2000). EDS data was processed using eSpirit 2.

3. Results

Visual inspection of the sample indicates that talc (~95%) and graphite (~3–5%) appear to be the primary minerals present (Fig. 1). Graphite is somewhat obscured visually in the sample chip owing to the soft nature of talc which envelopes graphite crystals. SEM data indicate that much of the sample is comprised of subhedral to near euhedral foliated talc crystals with diameters of ~50 to 800 µm, however much smaller (< 1 to 10 µm ~5%) and larger (>1 mm, 2–3%) crystals do occur (Fig. 1). Graphite occurs as euhedral crystals with irregular to near hexagonal forms approximately 350 to 500 µm in diameter (Fig. 1). Within graphite crystals, bright contrast minerals occur which contain Hg, Se, and S. These phases tend to be located near the center of the graphite crystals, are anhedral to subhedral in nature, and all are approximately 2 to 3 µm in maximum dimension (Fig. 2). All EDS spectra have lines for Se and more variably, lines for S and/or Hg which are very near each other. A dominant peak for C is observed as are peaks from the underlying talc such as O, Mg, Si, and Fe.

Within the matrix a common subhedral to anhedral mineral phase approximately 10 to 0.6 µm in diameter with detectable Zn, Cr, and Ni occurs (Fig. 3). The Fe peak in these mineral spectra are more intense and thus Fe is the likely a component of this mineral. Thorium also occurs in the sample in a crystal that is approximately 8 µm in diameter and in smaller nanoscale particles surrounding it.

4. Interpretations and implications

The majority of the sample is dominated by talc however there are other minerals present. Graphite hosts an unusual mineral (or minerals) with EDS spectra characterized by Hg-Se-S peaks but notably, no Hg-Se-S peak ratios observed in these phase(s) were similar. The association of graphite and Hg-Se-S mineral compositions appears to be a new mineralogical association, with no prior associations found in the literature or the mindat database. The exact identification of the Hg-Se-S minerals is unclear owing to the nature of their occurrence in the graphite and talc substrate, and the fact that the particles are too small to be picked and selected for single crystal and/or powder X-ray diffraction. Potential mineral candidates are tiemannite (HgSe) or hypothetical variants thereof. The mineral may likely be mixed with cinnabar which is a known mineral associated with tiemannite. A range of Hg-Se compositions are experimentally possible and can form over a wide temperature range from ~250 to ~800 °C (Boctor & Kullerud, 1986). Similarly a range of Se-S compositions are also experimentally possible and form over a temperature range of 102 to 216 °C (Boctor & Kullerud, 1987). The Hg-Se-S minerals present in the sample are therefore inferred to be mixtures, or have an intermediate composition broadly similar to that in the experimental work (Boctor & Kullerud, 1986, Boctor & Kullerud, 1987).

The Zn, Cr, and Ni (±) Fe-bearing mineral may be a substituted variation of zincochromite (Levy et al., 2005). Alternatively, the mineral may be an admixture of zincochromite and Ni-bearing magnetite. Although

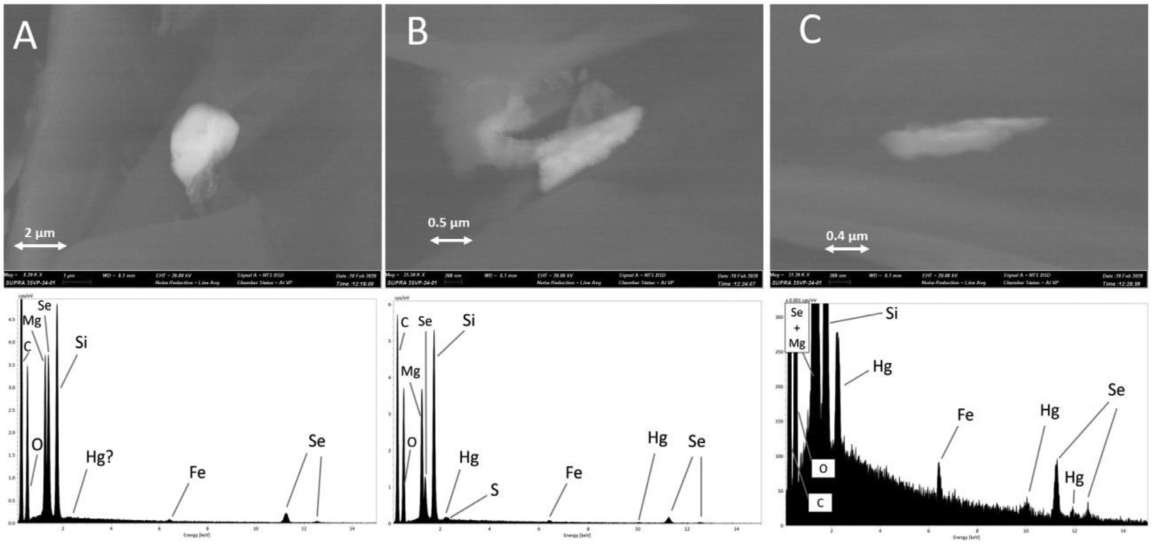

Fig. 2. BSD and EDS data of Hg-Se-S mineral inclusions in graphite. All are approximately 2 −3 µm in diameter. (A) BSD image of subhedral Se-rich particle shown in Fig. 1b. EDS spectrum for this grain is below and shows three peaks for Se and one peak near detection limit for Hg. Other peaks are interpreted to be from talc substrate. (B) BSD image of subhedral Hg-Se-rich particle, with minor S. EDS spectrum for this grain is below and shows three peaks for Se and two peaks near detection limit for Hg. The major S peak is present and is next to the Hg peak which has a net effect of having a double peak with a broad topology. Other peaks are interpreted to be from talc substrate. (C.) BSD image of subhedral Hg-Se-rich particle, with enlarged EDS spectra showing no S peak near the major line of Hg.

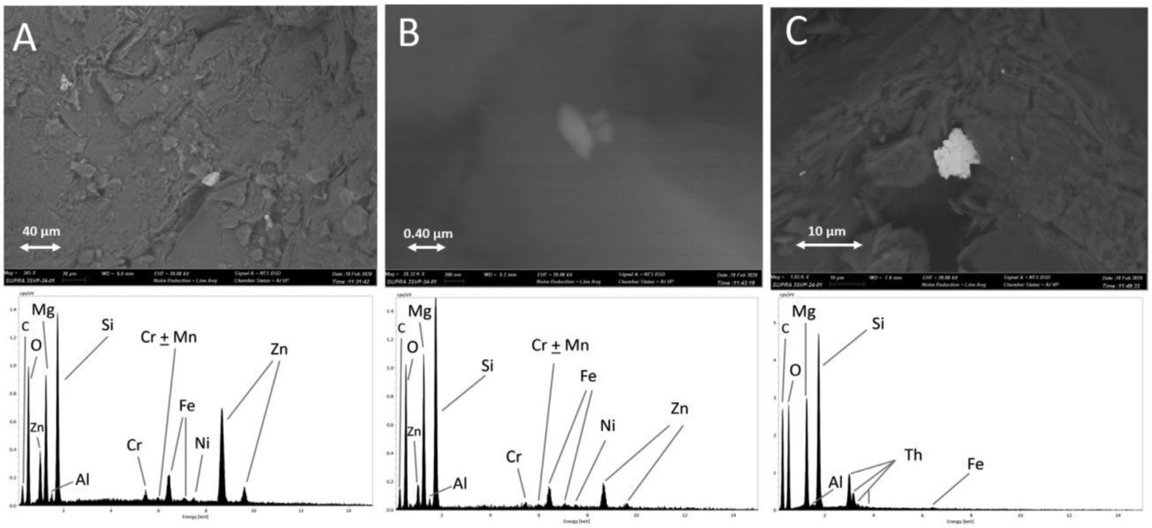

Fig. 3. (A) BSD image showing center bright particle of Zn-Cr-Ni (±) Fe mineral with EDS spectra below. (B) BSD image showing a pair of submicrometer scale particles of Zn-Cr-Ni (±) Fe mineral with EDS spectra below. (C) BSD image of platy Th-rich particle with EDS spectra below showing elements from talc and Th. Si may or may not be associated with the Th-rich particle thus it may be thorianite (ThO_2) or thorite ($ThSiO_4$).

a specific species cannot be identified among the spinels, this mineral group is well recognized for having extensive solid solution amongst transition metals. This Zn, Cr, and Ni (±) Fe-bearing mineral has not been previously reported in talc deposits. For the Th-bearing mineral, EDS spectra show no presence of phosphate and the mineral is interpreted as either thorite ($ThSiO_4$) or as thorianite (ThO_2), both being consistent with the EDS spectra on the talc substrate.

SEM-EDS analysis enables the identification of elements present in spatial context however there are limitations of exact identification when considering the range of potential chemical compositions of targeted minerals as determined with unavoidable substrate signal which may or may not coincidentally have elements also inherent to the targeted minerals such as Si, or Fe. Nonetheless the unique chemical compositions and textures observed using BSD here provide new constraints on this deposit. The mineral assemblage of the Willow Creek Mine is more mineralogically diverse and complex than previously recognized and results indicate detailed bulk chemical study and transmission electron microscopy is warranted.

There have been recent investigations of the Willow Creek Mine material with mineralogical and isotopic work (Buzon & Gunter, 2016, Hill, 2018). Previous mineralogical investigations of samples of Willow Creek, did not prepare powder X-ray diffraction samples properly, as they ground them and did no additional treatments normally used for phyllosilicate determinations (Buzon & Gunter, 2016, Moore & Reynolds, 1997). They did not use heavy liquids to concentrate minor minerals for study. This study investigated a few samples of Willow Creek by bulk X-ray fluorescence and present concentrations of 18–22 ppm for Cr, 16–25 ppm for Ni, and 13–21 ppm for Zn and they present 0 ppm for Th, and no analytical data for Se or Hg (Buzon & Gunter, 2016). This study does present SEM data for Willow Creek samples using BSE, yet the scale appears to be far too low a resolution (field of view ~1.8 mm) to detect the Hg-Se-S minerals, the Zn-Cr-Ni minerals, and the thorianite (or thorite) (Buzon & Gunter, 2016). Data from this previous study is broadly consistent with findings here.

The observation of Hg-Se-S minerals, the Zn-Cr-Ni minerals, and the thorianite (or thorite) in the talc ore is of health concern as these minerals may have been included in final talc product produced from Willow Creek. Examples of these minerals occur in PM_{10} and $PM_{2.5}$ size fraction and thus could be inhaled during processing or product use. Berg's work provides some insight into mine operations and indicates that in the 1970s talc ore was hauled to a sorting yard where after it was sorted the talc of quality was then trucked to Alder for rail shipment (Berg, 1979). The implication here is that talc was sorted by hand. As the minerals of concern observed occur or can occur in PM_{10} or $PM_{2.5}$, and are intimately mixed with the talc ore matrix, it is highly unlikely that they could have been effectively removed by handpicking or other techniques.

Components of the Hg-Se-S minerals (Hg, Se), the Zn-Cr-Ni mineral (Zn, Cr, Ni), and the thorianite or thorite (Th) are well recognized as toxic (Agency for Toxic Substances & Disease Registry (ATSDR) 2020). The nature and extent of Hg, Se, Zn, Cr, Ni, and Th in historical product derived from the Willow Creek Mine should be investigated further to assess potential historic human exposure. Moreover, talc from in the talc corridor of Montana and elsewhere should be investigated using SEM-BSD-EDS techniques at magnifications to observe sub-micrometer particles. Systematic bulk chemical techniques are warranted including ICP-MS for appropriate transition metals (e.g., Zn, Cr, Ni) and USEPA Method 7473 for Hg and USEPA Method 7742 for Se (U.S. Environmental Protection Agency (EPA) 1998, U.S. Environmental Protection Agency (EPA) 1994). Hg analysis by ICP-MS can be problematic and ICP-MS for Se can be challenging owing to interferences (Li et al., 2006, Kovacs, Szeles & Prokisch, 2008). Future bulk chemical work should be done cognizant of analytical issues and limitations for determining Hg and Se concentrations in talc ore as potential exists for significant error.

5. Summary

This is the first detailed SEM-BSD-EDS study of minor minerals in the Willow Creek Mine. Hg-Se-S minerals, Zn-Cr-Ni minerals and Th minerals occur in PM_{10} to $PM_{2.5}$ size fraction, being inhalable. These minerals provide justification for further bulk geochemical work using ICP-MS and USEPA methods and also indicate some level of concern for the environmental health properties of derived historical talc products and wastes in the Willow Creek Mine and similar deposits. The extent and nature of minor minerals with elements of environmental concern should be investigated more broadly using TEM and electron energy loss spectroscopy (EELS) to identify the concentrations, valence state (e.g., Cr^{3+}/Cr^{6+}), and mineral form of elements of concern.

Declaration

Dr. Krekeler serves as an expert witness in talc and asbestos litigation for the Simmons Hanly Conroy, Kazan Law, and Motely Rice firms. These firms did not provide financial support for this study.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

I (Mark Krekeler) work as an expert witness in asbestos litigation cases in the United States. I specifically work for the Simmons Hanly Conroy, Kazan Law, and Motely Rice firms. These firms did not provide financial support for this study. To be clear, I travelled to Montana in October of 2019 to obtain research samples from Dr. Dick Berg and travel was supported by myself.

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