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Halogens in hydrothermal sphalerite record origin of ore-forming fluids

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ABSTRACT

The halogens Cl and Br are sensitive indicators for the origin of ore-forming fluids. Here, we use a combination of microchemical and microscopic methods to show that measurable concentrations of these elements commonly occur as atomic-scale substitutions within hydrothermal sphalerite. Furthermore, the Cl/Br ratios of the halogen-rich sphalerites investigated in this study are indistinguishable from those of the corresponding ore fluids. Thus, they record fluid compositions, which are in turn closely related to fluid origin. Given the abundance of sphalerite in hydrothermal base-metal deposits, as well as the relative ease of conducting in-situ microchemical analyses, the halogen signature of sphalerite has the potential to become a sensitive proxy to distinguish between different ore-forming environments.

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INTRODUCTION

Due to their ability to form stable complexes with many metals in aqueous solutions, halogens play a key role in mass-transfer processes on Earth and other planetary bodies (Harlov and Aranovich, 2018). Not only are they heavily involved in the formation of most hydrothermal ore deposits (Pirajno, 2018), but they also critically affect the nature and rate of various magmatic and metamorphic processes (Dolejš and Zajacz, 2018; Hammerli and Rubenach, 2018).

Because they generally behave conservatively during fluid-rock interaction and show distinctive signatures for different crustal reservoirs, Cl and Br have seen extensive use as tracers for the origin of ore-forming hydrothermal fluids (Lecumberri-Sanchez and Bodnar, 2018). While previous studies primarily relied on either the analysis of fluid inclusions or rare silicate minerals such as scapolite to constrain fluid compositions (e.g. Kesler et al., 1995; Hammerli et al., 2013), this article is the first to demonstrate the in-situ measurement of Cl and Br in hydrothermal sphalerite.

Background

Sphalerite, the cubic polymorph of ZnS, is a common mineral in many types of hydrothermal base-metal deposits. It is well known for its diverse trace element chemistry (Cook et al., 2009; Belissont et al., 2014), recording critical information about the physico-chemical conditions of ore formation (Frenzel et al., 2016). Although high concentrations of Cl in sphalerite have previously been reported (Taylor and Radtke, 1969; Barrie et al., 2009), there is a lack of systematic data on the general prevalence of Cl and other halogens in natural samples, as well as the likely significance and implications of this phenomenon.

Because they are not part of the classic suite of chalcophile elements, the halogens are not commonly included in the set of minor and trace elements analyzed in sulfide minerals. This is despite the fact that 1) the Cl^- ion is virtually the same size as S^{2-} (Shannon, 1976) and would therefore be expected to readily substitute into sulfide minerals (Blundy and Wood, 2003); and 2) Cl/S ratios in hydrothermal fluids are generally high (Yardley, 2005). Of the other halogens, Br^- in particular would also be expected to substitute for S^{2-} for similar reasons. These considerations provided the major motivation for this work. As our data shows, halogen substitution into hydrothermal sphalerite may be a common phenomenon, particularly in low-temperature deposits.

MATERIALS AND METHODS

To study the occurrence of Cl and Br in natural sphalerite, we selected 12 samples from a diverse range of ore deposits, covering five geological types (Table DR1)[1]. Chlorine concentrations were first measured in all samples using electron-probe micro-analysis (EPMA), since this technique offers the best detection limits for Cl. EPMA measurements were supplemented by laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) to independently verify the occurrence of Cl and determine the abundances of Br and other relevant trace elements (Ga, Ge, In, Co, Tl, Na etc.). Samples with high Cl concentrations were then selected for detailed mapping of Cl distribution by EPMA (µm-scale) and scanning transmission electron microscopy (STEM) coupled with energy-dispersive x-ray spectroscopy (EDX) (nm-scale) to study the spatial distribution of Cl within samples at different scales, and determine its mode of occurrence (substitution or inclusions). Full details of all analytical methods are given in the GSA Data Repository[1] 201Xxxx (Appendix DR1).

RESULTS

EPMA measurements showed that appreciable Cl concentrations occur in three out of the 12 investigated samples, ranging from 46 – 4,900 µg/g on average (Table 1). In most samples, however, Cl concentrations were below the detection limit of the EPMA (~30 µg/g). Where Cl concentrations exceeded ~100 µg/g, they were also measurable by LA-ICP-MS and were accompanied by measurable Br and Na concentrations. Laser ablation traces of Cl, Br and Na were generally smooth (Fig. DR1), indicating homogeneous distribution of these elements within the sphalerite matrix at the scale of ablation.

Exploratory analysis of the micro-chemical dataset showed that the halogen-rich sphalerites are characterised by significantly higher concentrations of Tl and Ge, and lower Mn concentrations compared to the halogen-poor ones (Appendix DR1). Other trace elements (Cd, Co, Fe, Ga, In etc.) do not show significant correlations with halogen content.

Due to their very high halogen contents, the samples from Lisheen (Li-HS-86) and Baisoara (BS7b) were selected for further investigation by EPMA mapping and STEM-EDX imaging. Sample Li-HS-86 is dominated by fine-grained, colour-banded colloform sphalerite, while sample BS7b features more coarsely crystalline black to yellowish-translucent sphalerite.

Figure 1 illustrates the results of EPMA mapping for sample Li-HS-86. The corresponding figure for sample BS7b is included in Appendix DR1 (Fig. DR6). In general, the EPMA maps show that:

1) Cl distribution from the mm- to µm-scale is characterized by complex, sometimes oscillatory, growth zoning qualitatively similar to that shown by the other investigated elements (Cd, Cu, Pb, Fe, where measurable).
2) In the highest-resolution element maps (step size: 1 µm), Cl is homogeneously distributed within zones of similar composition. There is no evidence for Cl-rich inclusions at this scale.

Further examination of Cl-rich areas by high-angle annular dark field (HAADF)-STEM imaging showed that both samples have complex nanostructures featuring nano-scale porosity, inclusions, and sub-grain boundaries (Fig. 2 for Li-HS-86; Fig. DR7 for BS7b). In addition, STEM-EDX-mapping and semi-quantitative analysis allowed for the examination of Cl-distribution at the nano-scale. Here, there are marked differences between the two samples:

- **Li-HS-86** contains a substantial amount of Pb-Cu-Cl-rich inclusions of unknown speciation that are often associated with porosity. Nevertheless, an appreciable amount of Cl is still homogeneously distributed throughout the material at the investigated scale (~ 1 nm), suggesting it is present as atomic-scale substitutions in the sphalerite (Fig. 2). In fact, a mass balance calculation using LA-ICP-MS data for Cu, Pb and Cl indicates that at least 75% of the total Cl content in Li-HS-86 is hosted as substitutions in the sphalerite rather than as Pb-Cu-Cl-rich inclusions (cf. Appendix DR1).
- **BS7b** shows no evidence of Cl-rich inclusions, and Cl appears to be homogeneously distributed throughout the material at the investigated scale (~ 1 nm). This suggests it is present exclusively as atomic-scale substitutions in the sphalerite (Fig. DR6).

Thus, both samples appear to contain considerable amounts of Cl as homogeneously distributed atomic-scale substitutions in the sphalerite lattice. Unfortunately, the µm- and nm-scale distribution of Br and Na could not be investigated in detail due to their considerably lower concentration levels (rarely exceeding tens of µg/g, cf. Table 1), as well as interference from other elements (e.g. Zn on Na). However, no Br- or Na-containing nano-inclusions were found during STEM-EDX work in either of the two samples, suggesting these elements are also present as atomic-scale substitutions.

DISCUSSION

Our analytical data strongly suggests that Cl, Br and Na are mostly present in sphalerite as atomic-scale substitutions, rather than solid or fluid inclusions. This observation has several important implications, which we briefly discuss below. Specifically, we consider the likely substitution mechanisms of the three elements, as well as potential applications to the study of mineral deposits.

Substitution mechanisms

Since chloride and bromide ions probably substitute for sulfide ions, their incorporation is expected to introduce a net positive charge on the sphalerite crystal lattice. Therefore, a compensation mechanism is required to maintain charge balance. There are two potential candidates for this mechanism:

1) **Coupled substitution**, where the introduction of Cl^- (or Br^-) is accompanied by the exchange of Zn^{2+} for a monovalent cation A^+ (e.g. Cu^+, Ag^+, Tl^+ or Na^+) on the zinc sublattice, such that:

$$ZnS_{sph} + Cl_{aq}^{-} + A_{aq}^{+} \leftrightarrow ACl_{sph} + Zn_{aq}^{2+} + S_{aq}^{2-} \quad (1)$$

where the subscripts aq and sph denote the hydrothermal fluid and the sphalerite solid solution, respectively.

2) **Vacancy generation**, where a vacancy is created in the zinc sublattice to compensate for two substituted Cl^- ions:

$$2\ ZnS_{sph} + 2\ Cl_{aq}^{-} \leftrightarrow 2\ ZnCl_{sph}^{+} + \square S_{sph}^{2-} + S_{aq}^{2-} \quad (2)$$

Here, $\square S_{sph}^{2-}$ denotes a Zn vacancy.

Several studies have demonstrated that equivalent compensation mechanisms can explain the substitution of tri- and tetravalent cations for Zn^{2+}, which would otherwise also introduce a net positive charge (e.g. Cook et al., 2012; Cook et al., 2015; Belissont et al., 2016). Comparable mechanisms likely also apply to the incorporation of Na^+, which would be expected to substitute for Zn^{2+}.

To test which mechanism is most likely to be relevant in the investigated samples, we plotted the net negative lattice charge introduced into the sphalerite by mono-, tri- and tetravalent cations against Cl + Br concentrations (Fig. DR5). This showed that approximate charge balance is only maintained in sample BS7b, indicating coupled substitution as the main incorporation mechanism in this sample. In samples Li-HS-86 and TM06.2 on the other hand, there are large imbalances between the net lattice charges introduced by substituting cations and anions, indicating incorporation of Cl^- and Br^- by Zn-vacancy generation. We note that available XANES data for Ge in TM06.2 (Cook et al., 2015) is also consistent with Zn-vacancy generation as the major charge compensation mechanism in this sample. Thus, incorporation mechanisms vary by sample, with either (1) or (2) more relevant in different cases.

While similar charge balance plots as in Fig. DR5 have been used in previous studies to check for the coupled substitution of different cations (e.g. Johan, 1988; Belissont et al., 2014), we note that these studies generally omitted Cl, Br and Na. Given the presence of high Cl concentrations in some sphalerites, the previous conclusions derived from such plots regarding the incorporation mechanisms of Ga, Ge and other tri- and tetravalent ions into the sphalerite lattice may therefore be erroneous and require re-examination in light of our new results.

Potential applications

Two major geological applications can be envisaged for measurements of Cl, Br and Na concentrations in sphalerite. First, they may be useful as tracers of fluid origin. Second, it may be possible to use them as indicators for fluid salinity. Together with existing sphalerite geothermometers (Keith et al., 2014; Frenzel et al., 2016), this would enable the characterization of formation temperature, fluid salinity and fluid origin for a sphalerite sample based on only a small set of in-situ microchemical analyses. Given the current need to combine time-consuming microthermometric measurements with at least one other technique (LA-ICP-MS or crush-leach analyses) to yield the same information (Kesler et al., 1995; Seo et al., 2011; Hammerli et al., 2013), this would constitute a substantial step forward.

Figure 3 shows that Cl/Br ratios in the investigated sphalerite samples are similar to the ratios of the corresponding ore-fluids. This indicates that no major fractionation occurs between Cl and Br when partitioning from the fluid into the sphalerite, making them suitable as tracers of fluid composition and origin. Agreement between sphalerite and fluid composition is particularly good for samples Li-HS-86 and TM06.2, which show clearly distinct Cl/Br ratios, yet lie within the range expected for their corresponding ore-fluids (Irish-type and MVT fluids). Only in sample BS7b is the Cl/Br ratio somewhat lower than expected for a skarn fluid. However, it still lies within the range covered by the fluid data (incl. outliers). We also note that the skarn dataset available for comparison is extremely limited, deriving from only two ore deposits.

Another potential application for Cl, Br and Na in sphalerite is their use as a proxy for fluid salinity. To first order, absolute concentrations of Cl, Br and Na in sphalerite should be controlled by their respective concentrations in the ore-forming fluid (McIntire, 1963). Since NaCl is the major source of salinity in crustal fluids (Yardley, 2005; LeCumberri-Sanchez and Bodnar, 2018), such relationships should be usable in a sphalerite salinometer. However, the fact that high Cl, Br and Na concentrations are only present in low-temperature sphalerites (cf. Appendix DR1) suggests that some temperature control may also exist. A correction for such a dependence would need to be incorporated into any potential salinometer.

Overall, the use of element ratios such as Cl/Br shows the greatest potential for direct application in economic geology. Sphalerite salinometry may become feasible in the near future as more analytical data becomes available, allowing for the calibration of Cl and Na concentrations in sphalerite against fluid salinity and potential temperature effects.

CONCLUSIONS

To conclude, we have shown that the atomic-scale substitution of Cl and Br for S, and Na for Zn in hydrothermal sphalerite commonly leads to measurable concentrations of all three elements in sphalerite, particularly in base-metal deposits formed at low temperatures (< 200°C). Furthermore, Cl and Br are incorporated without fractionation, such that the Cl/Br ratio in sphalerite records the signature of the ore-forming fluids, in turn allowing for the identification of the fluids' origin.

In the future, it may also be possible to infer fluid salinity from absolute Cl and Na concentrations in sphalerite. In combination with existing geothermometers (Keith et al., 2014; Frenzel et al., 2016), this would make the trace-element signature of sphalerite an invaluable indicator in the study of hydrothermal ore deposits. Its major advantages compared to current methods used to determine the temperature, salinity and halogen signature of ore-fluids are the relative ease of sample preparation and analysis compared to fluid inclusion studies, the generally much greater abundance of sphalerite than scapolite in many base-metal deposits, as well as the better control over the geological significance of the sample material compared to crush-leach analyses.

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FIGURE CAPTIONS

Figure 1. EPMA maps at different scales for sample Li-HS-86 (sph II) showing Cl, Pb and Cu distribution, superimposed on high-contrast BSE images of the polished sample surface: A) mm-scale distribution, B) intermediate scale, C) micron-scale.

Figure 2. Summary of STEM and STEM-EDX imaging in sample Li-HS-86 (sph II): A) overview of sample foil with corresponding SAED pattern in lower left-hand corner; B) and C) detailed HAADF-STEM images of A) as indicated; D) detail of B) showing close-up of nano-porosity; E) detail of C) showing inclusions; F) detail of E) showing close-up of inclusion hosted in nano-pore; G) detail of C) and EDX maps of same area; H), I) and J) summed EDX spectrum for different parts of the map area shown in G) as indicated (grey line – data, red line – fitted spectrum, green line – fitted background). Note complex nanostructure of the material (different domains, pores, bright inclusions) and high Cl contents hosted in bright inclusions as well as sphalerite matrix.

Figure 3. Comparison of Cl/Br ratios in halogen-rich sphalerite samples from this study with literature data on relevant ore-forming and crustal fluids (see Appendix DR4 for complete fluid dataset including a reference list).

[1]GSA Data Repository item 201Xxxx, including Appendixes DR1 (detailed methods and summary of analytical results), DR2 (full EPMA dataset), DR3 (full LA-ICP-MS dataset) and DR4 (fluid database used for Fig. 3), is available online at www.geosociety.org/pubs/ft20XX.htm, or on request from editing@geosociety.org.