Natural solid-state ion conduction induces metal isotope fractionation

Calvin J. Anderson¹, Ryan Mathur², John Rakovan³, and Anton S. Tremsin³
¹Department of Geology and Environmental Earth Science, Miami University, 118 Shideler Hall, 250 S. Patterson Avenue, Oxford, Ohio 45056, USA
²Geology Department, Juniata College, 1700 Moore Street, Huntingdon, Pennsylvania 16652, USA
³Space Sciences Laboratory, University of California at Berkeley, 7 Gauss Way, Berkeley, California 94720, USA

ABSTRACT
Solid-state ion conduction (SSIC) occurs in the formation of natural and synthetic wire silver and causes consistent isotope fractionation of the mobile ion, favoring the heavy isotope. Textural analysis of natural and synthetic samples revealed that wire silver is a mosaic-like polycrystalline aggregate with superimposed striations, consistent with very rapid basal addition of Ag atoms constrained within a lateral growth footprint at the Ag-Ag₂S interface. Growth experiments demonstrate that this process is fundamentally dependent not on the chemical environment, but only on the SSIC ability of the substrate, readily provided in this case by argentite (Ag₂S), a superionic-conducting material. Stable Ag isotope analysis of wire silvers provides a means to observe the geochemical effects of SSIC in Ag₂S. Natural samples were found to be enriched in the heavy isotope with a median (interquartile range) of +0.283‰ (+0.145‰ to +0.453‰). Furthermore, ¹⁰⁷Ag enrichment was amplified by an order of magnitude in synthetic samples grown at high temperature (>450 °C), which had a median δ¹⁰⁷Ag of +2.788‰ (+1.829‰ to +3.689‰). Known isotope fractionation mechanisms would indicate that SSIC products should have negative δ isotope values because normal reaction kinetics are more likely to mobilize the lighter isotope. This indicates a previously unrecognized isotope fractionation mechanism associated with SSIC in nature, and has important implications for the geochemistry of ore deposits where SSIC phases are present.

INTRODUCTION
Our understanding of the geochemistry and transport of metals in nature is mostly built on liquid-phase interactions. The possible roles of solid-state processes, however, have remained relatively unexplored. This is surprising given that a number of important sulfide, halide, and sulfosalt minerals are documented solid-state ion conductors (Hull, 2004; Bindi et al., 2006; Bindi and Menchetti, 2011). Solid-state ion conduction (SSIC) describes the process by which metal ions can be rapidly transported through a crystal lattice in response to a thermoelectric potential, in contrast to diffusion, which is comparatively much slower and whose driving force is a concentration, stress, or thermal gradient. However, evidence of SSIC by natural geologic processes has not been previously identified.

To investigate the possibility of SSIC in natural systems, we chose to study the mineral acanthite (Ag₂S) for several reasons: (1) its high-temperature polymorph argentite possesses the highest ionic conductivity of any known material (Hull, 2004; Kato et al., 2016), (2) it is an important and relatively common ore mineral (commonly found as paramorphs after argentite) (Ercker, 1951; Fontboté et al., 2017), and (3) it is sometimes intimately associated with native silver, commonly called “wire silver” (see Figs. DR1 in the GSA Data Repository; Anderson and Rakovan, 2017; Böllinghaus et al., 2018).

Observations from previous experimental studies strongly suggest that solid-state processes are involved in wire silver formation. Wire silver can be grown by simply heating acanthite (Ercker, 1951), and if carried out in contact with solid Ag, the native Ag dissolves into the sulfide resulting in excessive wire growth (Beutell, 1919). Provided that the thermal gradient is maintained (Beutell, 1919), this reaction can proceed in air (Edwards, 2001), water (Jensen, 1939), and even a vacuum with no other reagents (Kohlschütter and Eydmann, 1912), which implies that Ag₂S and its physical properties alone are sufficient for wire silver growth to occur.

We report the first direct evidence that not only does SSIC occur in natural systems, but can also result in geochemically significant metal mobilization and isotope fractionation. Two lines of inquiry were followed to identify SSIC in native wire silver formation through comparison of natural and synthetic samples. First, textural-mineralogical analysis served to evaluate the role of SSIC in wire silver growth. Then, stable Ag isotope analysis of wire silver provided a means to determine the geochemical effects of SSIC on the mobile ions.

METHODS
Wire Silver Synthesis
Synthetic wire silvers were grown at high temperature with open-flame methods inspired by the literature (Bischof, 1843; Kohlschütter and Eydmann, 1912; Beutell, 1919; Edwards, 2001; Ercker, 1951). Wires 3–8 mm long could be grown in as little as a half-hour (Figs. DR2 and DR3). In some experiments, plates of solid silver were placed in contact with the acanthite, which dramatically increased the volume of wire growth. Due to the nature of an open flame, it was not possible to exactly monitor the local temperature of the sample within the cone; only the minimum and maximum threshold temperatures of ~450 °C and 700 °C (melting point of Ag₂S; Frueh, 1961) respectively. In order to better imitate the conditions of wire silver–bearing...
ore deposits, several wires were also grown from hydrothermal solutions by following procedures from Jensen (1939).

Texture Analysis

Because Ag has a fairly short X-ray attenuation length (~4.6 µm), the bulk crystallinity of natural and synthetic wire silver was probed with energy resolved neutron imaging (ERNI) with a spatial resolution of ~200 µm (Tremsin et al., 2017). ERNI was conducted at the Japan Spallation Neutron Source (JSNS; Tokai, Japan).

Surface textures were analyzed with scanning electron microscopy (SEM) (Anderson and Rakovan, 2017). Neutron transmission data (Figs. DR8–DR10), SEM images of various specimens (Figs. DR3–DR7), and real-time observation of silver “blooming” from Ag,S substrates (Figs. DR1land DR12) can be found in the Data Repository. SEM analysis was conducted on the Zeiss Supra 35 VP FEG SEM equipped with electron backscatter diffraction (EBSD) at Miami University’s Center for Advanced Microscopy and Imaging (Oxford, Ohio, USA).

Stable Ag Isotope Analysis

Stable Ag isotope chemistry (109Ag/107Ag) of wire silvers and acanthites was measured with multicollector inductively coupled plasma mass spectrometry (MC–ICP-MS) on the Thermo Scientific Neptune Plus at Penn State University (University Park, Pennsylvania, USA). In refining our sampling procedure, we determined that a sample size of at least 1 mg was required for consistent results. For this reason, only three hydrothermal synthetic wires were suitable for analysis. Wires were dissolved in 4 ml of 8N HNO3, and then purified using ion exchange chromatography (Mathur et al., 2018). The U.S. National Institute of Standards and Technology (NIST) standard used had a 109Ag/107Ag ratio of 1.07638. Sample preparation was carried out according to published methods, and mass bias was corrected using Pd (Mathur et al., 2018).

Recently, concerns were raised about the reliability of 109Ag/107Ag ratios when the dissolved system contains Cl resulting in incomplete recovery of Ag (Fujii and Albarede, 2018). Therefore, great caution was taken during preparation to eliminate possible contamination, and our samples were essentially Cl free. Data plots and sample statistics were generated with R software (https://www.r-project.org; R Core Team, 2018).

Tabular data (Table DR1) and sample statistics (Table DR2) are included in the Data Repository.

RESULTS

Textural Evidence for Solid-State Ion Conduction in Nature

Wire silver, both natural and synthetic, was found to be a mosaic-like polycrystalline aggregate composed of elongate crystallites, commonly with a low aspect ratio (Fig. 1A). This texture is in stark contrast to that of metal whiskers (e.g., Sn, Cd, Li), which are generally low-defect single crystals that form by pressure gradients or screw dislocations (Compton et al., 1951; Morris and Bonfield, 1974; Galyon, 2004; Li et al., 2011). The longitudinally parallel striations, which give wire silver its characteristic bundle-like morphology, are commonly crosscut by crystallites, indicating that the striations are not controlled by planes of coherent grain boundaries, but rather by an external constraint during growth. These morphological-textural relationships are consistent across a wide range of growth conditions and scales (Figs. DR5–DR8) and with published EBSD pole figure maps of wire silver crystal sections (Böllinghaus et al., 2018). It bears repeating that the morphological and textural characteristics of natural and synthetic wire silvers are virtually indistinguishable.

Only two processes, namely, mechanical extrusion or laterally constrained base growth, could produce this combination of unique morphology and internal texture. However, mechanical extrusion can be ruled out because (1) the crystal growth steps would have been erased, but instead were commonly observed on wire surfaces, (2) Ag,S is too malleable to provide a rigid mechanical counterpressure (Liversidge, 1877), and (3) we observed no conduits or apertures in the host acanthite through which extrusion would have occurred. In contrast, laterally constrained base growth at the Ag-Ag,S interface can simultaneously explain the unique striated morphology and the polycrystalline texture of wire silver.

Scanning electron microscopy (SEM) not only yielded information about the surface texture of wire silver, but also provided direct observation of the initial stages of growth in real time. Upon prolonged exposure of Ag,S to the electron beam, horn-like growths of Ag spontaneously “bloomed” from the surface (see Fig. 1B). As growth progressed, patches of these blooms coalesced and became raised up on Ag,S pedestals (Fig. DR9) similar to pedestals observed on many natural and synthetic wire silver specimens (Fig. 1C; Fig. DR11). This phenomenon has been reported before by Sadovnikov et al. (2015), who showed it to be accompanied by a transformation of the acanthite substrate (space group P21/n; Hahn, 2005) into argentite (space group I3m; Hahn, 2005) caused by “radiation heating.” Although that study misidentified the blooms themselves as Ag,S, we confirmed with EBSD that the blooms are indeed native Ag (Fig. DR12).

Previous studies have shown that during wire silver growth, Ag+ ions migrate through the bulk solid to the growth interface, even in a vacuum (Kohlschütter and Eydmann, 1912; Beutell, 1919). There are only two mechanisms by which this entirely solid-state migration could occur: diffusion or SSIC. However, the extremely rapid growth rate of wire silver in our experiments (millimeters and centimeters in seconds and minutes) indicates extremely rapid migration of Ag, much too great to be explained by simple diffusion.
Therefore, we propose a new growth mechanism for wire silver that involves base growth by SSIC of Ag\textsuperscript{+} ions via a local displacive phase transformation of Ag\textsubscript{2}S from acanthite to argentite, where variable but high ion flux leads to a high number of defects, and in turn, generates many crystallites, which are constrained laterally by the argentite footprint (Fig. 2). Given that the morphological and textural characteristics of natural and synthetic wire silver are virtually indistinguishable, this appears to represent the first mineralogical evidence for SSIC in naturally occurring samples.

**Stable Ag Isotope Analysis**

Stable Ag isotope analysis (Fig. 3) revealed that natural wire silvers are generally enriched in the heavy isotope \(^{109}\text{Ag}\), with a \(\delta^{109}\text{Ag}\) of median (interquartile range) +0.283\%e (+0.145\%e to +0.453\%e). Low-temperature (LT) synthetic wires were generally consistent with the range for natural wire silver. High-temperature (HT) synthetic wires were significantly more enriched in \(^{109}\text{Ag}\), with a median \(\delta^{109}\text{Ag}\) of +2.788\%e (+1.829\%e to +3.689\%e), and values as large as +6.218\%e were observed. This is an order of magnitude more fractionation than that of any natural silver system. The disparity between LT and HT wire silvers mirrors the fact that the rate of SSIC in argentite is greater at high temperatures (Hull, 2004). Thus, the large spread in the HT data is likely due to variations in the \(\text{Ag}^+\) ion conduction rate, possibly caused by variable hindrance of SSIC by minor and/or trace element impurities, or by temperature fluctuations inherent in the growth method (see Methods). There was no apparent correlation between the \(\delta^{109}\text{Ag}\) values of synthetic wires and the initial \(\delta^{109}\text{Ag}\) of their respective acanthites.

**DISCUSSION**

The most interesting result is that the heavy-isotope enrichment we observed, especially from the HT wire syntheses, is opposite of that predicted by known fractionation mechanisms. These include mass-dependent, kinetic, equilibrium, and redox isotope effects. Mass-dependent isotope effects driven by passive diffusion would produce enrichment in \(^{109}\text{Ag}\) because it is lighter and would have a higher diffusion rate, and although this should increase with temperature, it would still be several orders of magnitude too small to explain the huge increase in Ag fractionation in our HT wires (Criss, 1999). A kinetic isotope effect would lead to an expectation that \(^{109}\text{Ag}-\text{S}\) bonds would have a lower zero-point energy than \(^{107}\text{Ag}-\text{S}\) bonds and be harder to break, and thus \(^{109}\text{Ag}\) would be less mobile in the lattice, leading to wire enrichment in the more mobile \(^{109}\text{Ag}\) (Criss, 1999). In equilibrium fractionation, \(^{109}\text{Ag}-\text{Ag}\) bonds would have a higher vibrational energy because \(^{109}\text{Ag}\) is lighter, and so the isotope exchange reaction would favor the formation of \(^{109}\text{Ag}-\text{S}\) bonds, freeing more \(^{107}\text{Ag}\) to enrich the wire silver; moreover, the magnitude of this effect would decrease with increasing temperature (Criss, 1999). Recently, a redox isotope effect was observed by Mathur et al. (2018) where precipitation (involving reduction) of native Ag resulted in a shift toward more negative \(\delta^{109}\text{Ag}\) values in the newly deposited silver. Because wire silver growth also involves a reduction of \(\text{Ag}^+\), enrichment in \(^{109}\text{Ag}\) would be expected.

Other, less-common mechanisms also fall short of explaining the inverse isotope values. The superconductor isotope effect has been known for a long time (Maxwell, 1952), but is a fundamentally different phenomenon from that observed in wire silver growth and does not apply to the case of SSIC (see note in the Data Repository). Magnetic isotope effects typically have strong temperature dependence (Buchachenko, 2013), and it has been predicted that superionic conduction could lead to significant fractionation of isotopes with different nuclear spins (I) (Kimball and Eswaran, 1976). However, this cannot explain fractionation of Ag because both isotopes have identical spin (\(I = 1/2\)). The probability of spin-selective interactions also depends on the nuclear magnetic moment (\(\mu\)) (Buchachenko, 2001), which is ~15% larger for \(^{109}\text{Ag}\) than for \(^{107}\text{Ag}\) (Haynes et al., 2017); it is currently unclear whether SSIC is truly spin-selective.

There remains one possible fractionation mechanism, but which has not yet been found in nature. Electron excitation of molecules can cause isotope fractionation based on preferential predissociation of one isotope’s bonds (Kato and Baba, 1995; Jensen et al., 1995). During SSIC in argentite, the \(\text{Ag}^+\) current is accompanied by a much greater free-electron current, some of which no doubt collides with \(\text{Ag}^+\) ions, possibly pumping them into an excited electronic state. Which Ag isotope, if either, could undergo predissociation would intimately depend on the isotope-specific vibronic structure of the Ag-S bonds (Fig. DR13). If, hypothetically, predissociation was an additional pathway by which \(^{109}\text{Ag}\) could preferentially break its bonds, then it would be the more mobile isotope, leading to the observed positive \(\delta^{109}\text{Ag}\).
values in wire silver. Because thermal vibrations (phonons) are the largest contribution to vibrational energy at high temperatures, we would also anticipate a significant increase with temperature. Unfortunately, available data are currently insufficient to determine whether this mechanism can account for our observed isotope values. If it is later confirmed, it would open up new lines of inquiry regarding the possible roles of excited states in native and sulfide mineral-forming and mineral-transforming reactions.

Finally, we note that acanthite, although not statistically different from non-wire silver, tends to be negatively skewed toward isotopically heavy compositions. This can be explained if some of the analyzed acanthites acted as conduits of SSIC at some point in their geologic history. This may help explain other cases where SSIC minerals have been associated with anomalously heavy metal isotope values (Wilson et al., 2016).

CONCLUSIONS

Textural analysis of wire silver, combined with data from historical experiments and real-time observations, strongly indicates that naturally heavy compositions. This can be explained if any of the acanthites acted as conduits of SSIC at some point in their geologic history. This may help explain other cases where SSIC minerals have been associated with anomalously heavy metal isotope values (Wilson et al., 2016).

REFERENCES CITED


Printed in USA