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Fluid mixing forms basement-hosted Pb-Zn deposits: Insight from metal and halogen geochemistry of individual fluid inclusions

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ABSTRACT

Fluid mixing across unconformities between crystalline basement and overlying sedimentary basins is commonly invoked as an efficient chemical mechanism for ore deposition, but the origin of basement brines and the process of ore formation have rarely been linked by direct evidence. Using laser ablation–inductively coupled plasma–mass spectrometry microanalysis of individual fluid inclusions with an improved detection approach for anion components, we determined simultaneously the ore metal concentrations and the Cl/Br ratio in texturally well constrained inclusion assemblages from a basement-hosted quartz-fluorite-barite-Pb-Zn vein system. An inverse correlation between the Pb + Zn concentrations and the Cl/Br mass ratios in the fluid inclusions provides clear evidence for mixing of a basement-derived metal-rich brine and a metal-poor formation water that acquired its salinity from halite dissolution in Triassic evaporites of the sedimentary cover. This mixing of two distinct brines with comparable salinity is recorded during the growth of individual quartz crystals containing small galena inclusions, demonstrating the transient and episodic nature of fluid mixing during mineral deposition.

INTRODUCTION

Na-Ca–rich basement brines are widespread in the crystalline continental crust (Frape and Fritz, 1987). Although their mode of formation and the source of their salinity are still debated, they are increasingly recognized as a major agent in the formation of many world-class hydrothermal ore deposit types, including sediment-hosted and vein-type Pb-Zn deposits (Gleeson et al., 2001; Muchez et al., 2005; Leach et al., 2010; Wilkinson, 2010), shale-hosted Cu deposits (Koziy et al., 2009), and unconformity-related U deposits (Derome et al., 2007; Boiron et al., 2010; Richard et al., 2012). Prominent examples where basement brines have been invoked as the major transporter of ore metals are the Irish-type Pb-Zn deposits (Russell et al., 1981; Wilkinson, 2010), the Cu deposits of the Central African copper belt, and the Kupferschiefer in Europe (Muchez et al., 2005; Koziy et al., 2009). Evidence for the diverse origins of basement brines and their role in ore deposit formation comes from geological relations and radiogenic isotope studies that were able to conclusively trace metal sources to basement rocks (Dixon et al., 1990; Goldhaber et al., 1995), and from fluid inclusion analysis for conservative components like halogen ratios (Banks et al., 2000) and stable isotope studies (Stoffell et al., 2008; Wilkinson, 2010). Fluid inclusion data demonstrate the presence of unusually metal-rich saline brines that record a high-temperature origin, compatible with fluid-rock interaction in the crystalline basement underlying the sedimentary basins that host the ore deposits (Wilkinson et al., 2009; Richard et al., 2012).

The hot chloride-rich brines are able to transport high concentrations of Pb, Zn, and Cu, to thousands of μg/g (Wilkinson et al., 2009), from the crystalline basement to shallow crustal levels, due to the enhanced stability of metal chloride complexes at elevated temperatures (Yardley, 2005). The formation of major sediment-hosted ore deposits also requires substantial fluid focusing and a mechanism that efficiently supplies reduced sulfur, which is essential for precipitating sulfide ore minerals (Goldhaber et al., 1995; Wilkinson et al., 2005; Leach et al., 2010). Fluid mixing between metal-rich basement brines and reduced sulfur-bearing sedimentary formation waters has been suggested as the most efficient process for Pb-Zn ore mineral precipitation. Evidence for fluid mixing comes from fluid inclusion data and bulk halogen systematics (Derome et al., 2007; Stoffell et al., 2008; Boiron et al., 2010), stable isotope geochemistry (Goldhaber et al., 1995), and paleohydrological modeling (Plumlee et al., 1994; Garven et al., 1999). Despite considerable advances in understanding the chemistry of base metal ore fluids and the physical and chemical processes that control their formation (Stoffell et al., 2008; Wilkinson et al., 2009), some discrepancy remains with regard to the hydrological efficiency of fluid mixing compared to its expected effectiveness on geochemical grounds (Appold and Garven, 2000). Thus, while many studies infer the importance of mixing processes for the formation of ore deposits on basinal or district scales, direct evidence on the scale of individual ore veins that could potentially resolve this discrepancy is lacking.

Here we report the results of a fluid inclusion study of basement-hosted Pb-Zn veins from the Schwarzwald in southwestern Germany that reconstructs the fluid sources based on a combination of detailed textural analysis of fluid inclusion assemblages and laser ablation–inductively coupled plasma–mass spectrometry (LA-ICPMS) microanalysis of the fluid composition. Reflecting recent advances in analytical techniques (Seo et al., 2011), it was possible to measure ore metal (Pb, Zn, Ag, As, Sb) and halogen (Cl, Br) concentrations simultaneously in the same fluid inclusions. This revealed clear correlations between Cl/Br ratios and total metal content at the scale of single growth zones in quartz crystals, providing the first direct evidence for fluid mixing processes at the scale of individually trapped fluid pulses.

Pb-Zn VEIN MINERALIZATION IN THE VARISCAN BASEMENT

Post-Variscan Mesozoic vein-type Pb-Zn mineralization is widespread in large parts of western and central Europe, including Variscan basement complexes of Germany, France, England, and Spain (Muchez et al., 2005). Typical examples of Pb-Zn-fluorite-barite veins that form part of a long-lived crustal-scale hydrothermal system are exposed in the crystalline basement of the Schwarzwald, Germany (Fig. 1). The Schwarzwald forms part of the European Variscan orogen, comprising Paleozoic gneiss complexes crosscut by syntectonic to late tectonic Variscan granitoids (Hann and Zedler, 2008). The crystalline basement is unconformably overlain by Permian and Lower Triassic redbed sedimentary rocks and Middle Triassic to Jurassic carbonates with intercalated claystones and evaporites. Comparable sedimentary rocks underlain by Variscan basement are host to major Mississippi Valley–type Pb-Zn deposits in Upper Silesia, Poland (Muchez et al., 2005). Large-scale extensional tectonics that commenced in the Tertiary resulted in the formation of the Upper Rhine Graben rift zone. Rifting caused exhumation of the crystalline basement and erosion of the post-Variscan sedimentary cover rocks. The Schwarzwald hosts ~1000 known hydrothermal veins, which are mostly confined to basement rocks and rarely extend into the overlying sediments. The veins occurring throughout the district have been classified into several groups based on age and metal inventory, the most common type being Mesozoic

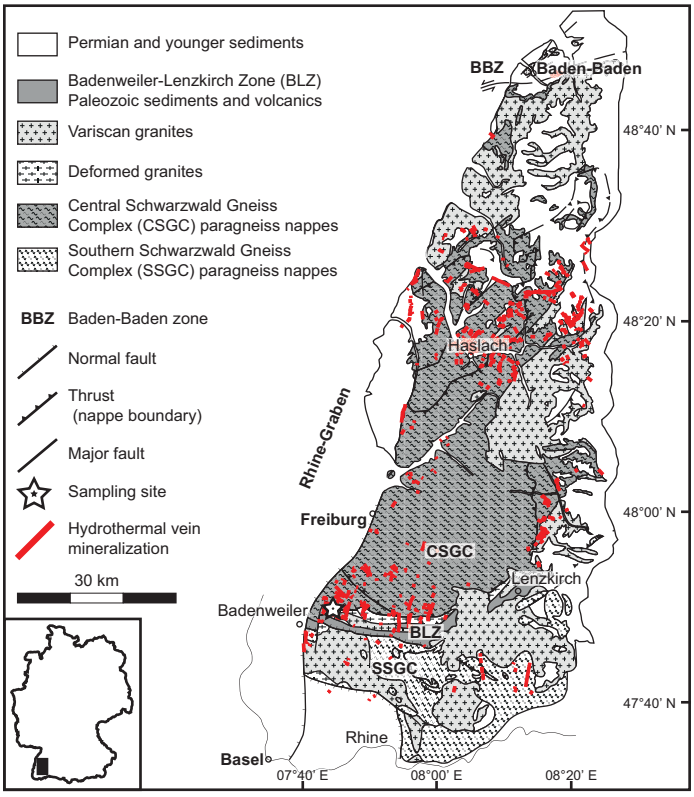

Figure 1. Geological map of Schwarzwald hydrothermal system (southwestern Germany) showing location of studied quartz-barite-fluorite-Pb-Zn vein mineralization (modified after Hann and Zedler, 2008).

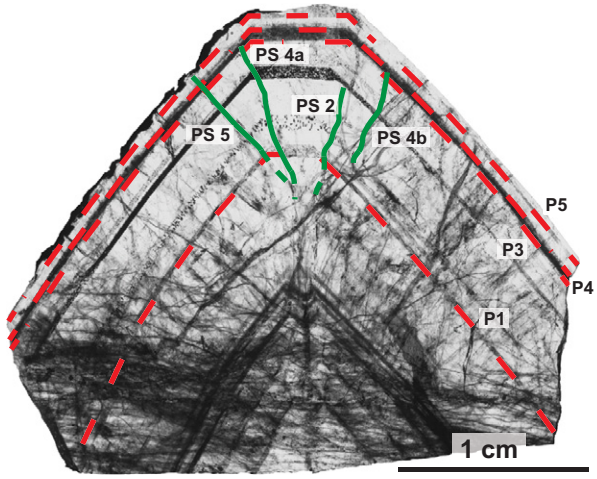

Figure 2. Fluid inclusion chronology in growth-zoned chevron quartz crystal. Growth zones hosting primary (P) fluid inclusions and pseudosecondary (PS) fluid inclusion trails are highlighted by dashed red lines and solid green lines, respectively.

quartz-fluorite-barite veins with Pb-Zn-Cu, Fe-Mn, or U-Bi-Ag-Co-Ni ore mineralization (Staude et al., 2009). The paleohydrological setting at the basement-cover interface makes the large-scale hydrothermal system of the Schwarzwald an ideal natural laboratory for investigating the interaction between basement-derived fluids and formation waters.

ANALYTICAL TECHNIQUES

Representative samples of quartz-barite-fluorite-Pb-Zn mineralization were selected for detailed texturally resolved fluid inclusion studies. The samples originate from a 10-m-thick cluster of hydrothermal veins north of the town Bad Sulzburg (southwestern Schwarzwald; Fig. 1). Massive barite veins are crosscut by hematite-bearing quartz veins, with euhedral chevron quartz crystals (to 5 cm in size) occurring inside open cavities. The crystals show pronounced growth zoning (Fig. 2) and several generations of well-preserved fluid inclusion assemblages. Galena inclusions occur along growth zones inside the quartz, whereas fluorite overgrows quartz and represents the latest hydrothermal mineral in this vein system.

Microthermometry was performed using a Linkam THMSG-600 cooling-heating stage, which was calibrated against synthetic fluid inclusion standards. LA-ICPMS microanalysis of individual fluid inclusions was performed with a Perkin Elmer Elan 6100 quadrupole ICPMS connected to a GeoLas 193 nm ArF excimer laser system. Analytical procedures were given by Heinrich et al. (2003) and Seo et al. (2011). LA-ICPMS analyses were done with two different element suites, the first containing 22 elements (Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, B, Fe, Mn, Zn, Pb, Ag, Tl, As, Sb, S, Cl, Br, and Si). The second one was optimized for high-precision analysis of Cl/Br ratios and contained only 9 elements (Na, Ca, Fe, Mn, Zn, Pb, Cl, Br, and Si). The external standardization was based on Na concentrations calculated from microthermometric data using the model system H_2O-NaCl-$CaCl_2$ (Steele-MacInnis et al., 2011). Data reduction was carried out using the SILLS (Signal Integration for Laboratory Laser Systems) software package (Guillong et al., 2008).

MAJOR ELEMENT CHEMISTRY OF FLUID INCLUSIONS

The vein quartz samples show well-developed growth zoning with fluid inclusions trapped on each major growth surface (Fig. 2) and on trails that crosscut some growth zones, allowing a complete reconstruction of the relative timing of sequentially trapped fluid inclusion assemblages. The fluid inclusion assemblages situated on one growth zone or one pseudosecondary trail were taken as coeval and then grouped as primary (P) and pseudosecondary (PS) assemblage groups (Fig. 2), with increasing numbers denoting younger age. All fluid inclusions are aqueous two phase (liquid-vapor) with a vapor bubble size of ~5 vol%, and contain both ice and hydrohalite after freezing. Sequential freezing and low heating rates of 0.2 °C/min were used to account for sluggish dissolution behavior of hydrohalite, which invariably melts a few degrees before ice upon heating. Figure 3 shows the bulk composition of 174 fluid inclusions in the H_2O-NaCl-$CaCl_2$ phase diagram. The data are remarkably consistent for fluid inclusion assemblages trapped on individual growth zones and pseudosecondary inclusion trails. Total salinities are fairly constant at 23 wt% (NaCl + $CaCl_2$), whereas Na/Ca ratios vary. This variation is based on differences in hydrohalite melting temperature of ~4 °C, well outside the analytical uncertainty (0.5 °C). Homogenization temperatures are fairly constant throughout all fluid inclusion assemblages and are in the range of 130–160 °C.

TRACE ELEMENT GEOCHEMISTRY OF FLUID INCLUSIONS

Microanalysis with LA-ICPMS was carried out on fluid inclusions of at least 25 µm to ensure low detection limits and acceptable counting statistics for trace ore metals and Br. We conducted 70 successful measurements on inclusions from all assemblage groups with the full element suite and 28 with the reduced element suite. The microthermometric and concentration data for all elements analyzed are available in Table DR1 in the GSA Data Repository[1]. Figure DR1 (in the Data Repository) contains two representative LA-ICPMS signals of fluid inclusions and the

[1]GSA Data Repository item 2013187, Table DR1 (microthermometric and concentration data) and Figure DR1 (representative LA-ICPMS signals of fluid inclusions and adjacent host quartz), is available online at www.geosociety.org/pubs/ft2013.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

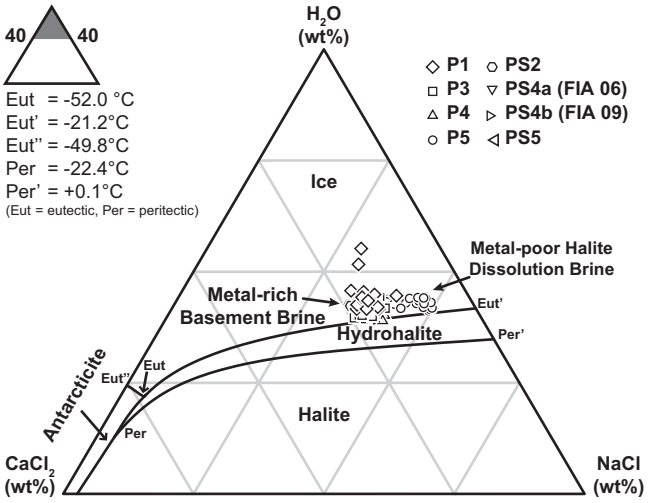

Figure 3. Fluid composition in ternary H_2O-NaCl-$CaCl_2$ system as determined by microthermometry, showing close overlap of two brine end members in terms of their major element composition. P—primary; PS—pseudosecondary; FIA—fluid inclusion assemblage.

adjacent host quartz. The LA-ICPMS data show that Zn, Pb, and Mn are the most important ore metals, with concentrations in the ranges of 10–770, 10–340, and 10–1650 µg/g, respectively. Sulfur concentrations were measured, but due to low signal to background ratios the analytical uncertainties are large, resulting in unsystematic variations in the range of 50–900 µg/g. Figure 4A shows Na/Ca ratios determined from microthermometry as a function of the concentration of Pb + Zn. Because accurate determination of Ca concentrations with LA-ICPMS is affected by mass interferences (Heinrich et al., 2003), we accepted the microthermometric data as the best estimate for the Na/Ca ratios. Combining the major and trace element data shows important correlations. The Na/Ca ratios are negatively correlated with the concentrations of Pb + Zn (Fig. 4A). Furthermore, the mass-based Cl/Br ratios show a distinct negative correlation with the concentration of Pb + Zn (Fig. 4B), whereas the Pb/Zn ratios are remarkably constant for all individual fluid inclusions and fluid inclusion assemblages regardless of their relative age (Fig. 4C).

The 1σ errors of measurements (relative standard deviation of element signals) with the full element suite are sometimes large for inclusions with high Cl/Br ratios, reflecting low absolute Br concentrations close to the detection limits. By contrast, the precision in Cl/Br ratios obtained with the reduced element suite is considerably better and the observed correlations are statistically significant.

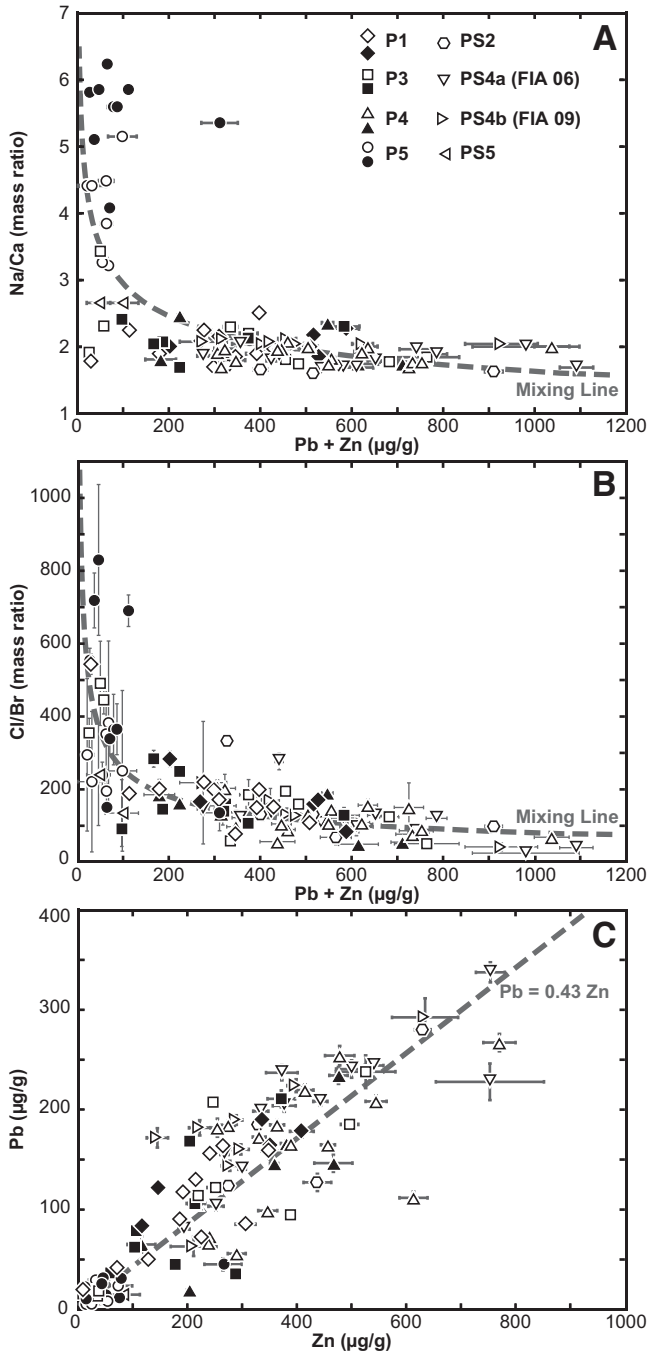

Figure 4. A: Microanalysis of single fluid inclusions shows close correlation between total base metal content (Pb + Zn) and Ca/Na ratio. P—primary; PS—pseudosecondary; FIA—fluid inclusion assemblage. B: Close correlation between Pb + Zn and Cl/Br ratio, resulting from mixing of two brines with similar total salinity (Fig. 3). C: Major variation of total metal content at constant Pb/Zn ratio reflects mixing of metal-bearing brine with metal-depleted fluid. Open and filled symbols denote analyses performed with full and reduced element suite, respectively.

DISCUSSION AND CONCLUSIONS

The fluid inclusion data show Cl/Br ratios between 80 and 780 that are negatively correlated with the ore metal concentrations. Low Cl/Br ratios (80–100) are typical of basement-derived brines that originated as residual brines after extensive evaporation of seawater, whereas high Cl/Br ratios above that of seawater (290) can be attained via halite dissolution when fluids percolate through evaporitic sequences (Frape and Fritz, 1987; Banks et al., 2000). The ore metal concentrations (Pb + Zn) are negatively correlated with the Cl/Br and Na/Ca ratios, both at the scale of different growth zones and within the same growth zone of individual quartz crystals. The data are best explained by fluid mixing processes that involve a metal-rich basement brine with low Cl/Br ratio and a metal-depleted halite dissolution brine with much higher Cl/Br ratio derived from evaporite-bearing Triassic sedimentary rocks. Elevated Ca concentrations in the latter are most likely related to Na-Ca exchange reactions along the flow path through the uppermost parts of the basement. The constant Pb/Zn ratios (Fig. 4C) support this interpretation, because crustal fluids typically show a linear correlation between both metals, which is controlled by sulfide saturation in the source aquifers and fluid salinity (Yardley, 2005). Dilution of a metal-bearing basement brine via mixing with a metal-depleted fluid would result in greater variation in the absolute concentrations of Pb and Zn without changing their ratio. The bulk salinity does not show large variations, suggesting that fluid mixing involved

two brines of very similar bulk properties but different Na/Ca ratios. This observation is in agreement with fluid inclusion data from post-Variscan basement-hosted vein mineralization (Staude et al., 2012) and the Soultz-sous-Forêts geothermal site in the Upper Rhine Graben, where brine inclusions with highly variable Cl/Br ratios were interpreted to record fluid mixing between a basement brine and formation water formed via halite dissolution (Boiron et al., 2010). The compositional variability we observe at the scale of individual growth zones and fluid inclusion trails suggests that the quartz crystals have trapped fluids that were not compositionally homogeneous and that fluid mixing processes are transient and can occur at a small scale. This supports earlier observations from unconformity-related ore deposits (U deposits in Canada, Australia, and Africa, and fluorite-barite-Pb-Zn mineralization in France), where variations in bulk salinity and homogenization temperatures of fluid inclusions trapped on individual microfractures were interpreted in terms of small-scale fluid mixing processes (Boiron et al., 2010).

In conclusion, our data clearly demonstrate that fluid mixing between a metal-bearing basement brine and a metal-depleted halite dissolution brine was responsible for formation of quartz-barite-fluorite-Pb-Zn vein mineralization. The data also show that geochemical signatures indicative of fluid mixing processes can be easily overlooked in conventional fluid inclusion data and bulk fluid analysis, and may require single-inclusion microanalytical data in order to be detected.

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REFERENCES CITED

Appold, M.S., and Garven, G., 2000, Reactive flow models of ore formation in the Southeast Missouri District: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 95, p. 1605–1626, doi:10.2113/gsecongeo.95.8.1605.

Banks, D.A., Green, R., Cliff, R.A., and Yardley, B.W.D., 2000, Chlorine isotopes in fluid inclusions: Determination of the origins of salinity in magmatic fluids: Geochimica et Cosmochimica Acta, v. 64, p. 1785–1789, doi:10.1016/S0016-7037(99)00407-X.

Boiron, M.C., Cathelineau, M., and Richard, A., 2010, Fluid flows and metal deposition near basement/cover unconformity: Lessons and analogies from Pb-Zn-F-Ba systems for the understanding of Proterozoic U deposits: Geofluids, v. 10, p. 270–292, doi:10.1111/j.1468-8123.2010.00289.x.

Derome, D., Cathelineau, M., Fabre, C., Boiron, M.C., Banks, D., Lhomme, T., and Cuney, M., 2007, Paleo-fluid composition determined from individual fluid inclusions by Raman and LIBS: Application to mid-Proterozoic evaporitic Na-Ca brines (Alligator Rivers Uranium Field, northern territories Australia): Chemical Geology, v. 237, p. 240–254, doi:10.1016/j.chemgeo.2006.10.015.

Dixon, P.R., LeHuray, A.P., and Rye, D.M., 1990, Basement geology and tectonic evolution of Ireland as deduced from Pb isotopes: Geological Society of London Journal, v. 147, p. 121–132, doi:10.1144/gsjgs.147.1.0121.

Frape, S.K., and Fritz, P., 1987, Geochemical trends for groundwaters from the Canadian Shield, *in* Fritz, P., and Frape, S.K., eds., Saline water and gases in crystalline rocks: Geological Association of Canada Special Paper 33, p. 19–38.

Garven, G., Appold, M.S., Toptygina, V.I., and Hazlett, T.J., 1999, Hydrogeologic modeling of the genesis of carbonate-hosted lead-zinc ores: Hydrogeology Journal, v. 7, p. 108–126, doi:10.1007/s100400050183.

Gleeson, S.A., Wilkinson, J.A., Stewart, F.M., and Banks, D.A., 2001, The origin and evolution of base metal mineralising brines and hydrothermal fluids, south Cornwall, UK: Geochimica et Cosmochimica Acta, v. 65, p. 2067–2079, doi:10.1016/S0016-7037(01)00579-8.

Goldhaber, M.B., Church, S.E., Doe, B.R., Aleinikoff, J.N., Brannon, J.C., Podosek, F.A., Mosier, E.L., Taylor, C.D., and Gent, C.A., 1995, Lead and sulfur isotope investigation of Paleozoic sedimentary rocks from the southern midcontinent of the United States; implications for paleohydrology and ore genesis of the Southeast Missouri lead belts: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 90, p. 1875–1910, doi:10.2113/gsecongeo.90.7.1875.

Guillong, M., Meier, D., Allan, M., Heinrich, C.A., and Yardley, B., 2008, SILLS: A MATLAB-based program for the reduction of laser ablation ICP-MS data of homogeneous materials and inclusions, *in* Sylvester, P., ed., Laser ablation ICP-MS in the Earth sciences: Current practices and outstanding issues: Mineralogical Association of Canada Short Course 40, p. 328–333.

Hann, H.P., and Zedler, H., 2008, Variscan Internides: Black Forest (Schwarzwald), *in* McCann, T., ed., The geology of Central Europe, Variscan tectonics, Volume 1: Precambrian and Palaeozoic: London, Geological Society of London, p. 599–665.

Heinrich, C.A., Pettke, T., Halter, W.E., Aigner-Torres, M., Audétat, A., Gunther, D., Hattendorf, B., Bleiner, D., Guillong, M., and Horn, I., 2003, Quantitative multi-element analysis of minerals, fluid and melt inclusions by laser-ablation inductively-coupled-plasma mass-spectrometry: Geochimica et Cosmochimica Acta, v. 67, p. 3473–3497, doi:10.1016/S0016-7037(03)00084-X.

Koziy, L., Bull, S., Large, R., and Selley, D., 2009, Salt as a fluid driver, and basement as a metal source, for stratiform sediment-hosted copper deposits: Geology, v. 37, p. 1107–1110, doi:10.1130/G30380A.1.

Leach, D.L., Bradley, D.C., Huston, D., Pisarevsky, S.A., Taylor, R.D., and Gardoll, S.J., 2010, Sediment-hosted lead-zinc deposits in Earth history: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 105, p. 593–625, doi:10.2113/gsecongeo.105.3.593.

Muchez, P., Heijlen, W., Banks, D., Blundell, D., Boni, M., and Grandia, F., 2005, Extensional tectonics and the timing and formation of basin-hosted deposits in Europe: Ore Geology Reviews, v. 27, p. 241–267, doi:10.1016/j.oregeorev.2005.07.013.

Plumlee, G.S., Leach, D.L., Hofstra, A.H., Landis, G.P., Rowan, E.L., and Viets, J.G., 1994, Chemical reaction path modeling of ore deposition in Mississippi Valley-type Pb-Zn deposits of the Ozark region, U.S. Midcontinent: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 89, p. 1361–1383, doi:10.2113/gsecongeo.89.6.1361.

Richard, A., Rozsypal, C., Mercadier, J., Banks, D.A., Cuney, M., Boiron, M.C., and Cathelineau, M., 2012, Giant uranium deposits formed from exceptionally uranium-rich acidic brines: Nature Geoscience, v. 5, p. 142–146, doi:10.1038/ngeo1338.

Russell, M.J., Solomon, M., and Walshe, J.L., 1981, The genesis of sediment-hosted exhalative zinc + lead deposits: Mineralium Deposita, v. 16, p. 113–127, doi:10.1007/BF00206458.

Seo, J.H., Guillong, M., Aerts, M., Zajacz, Z., and Heinrich, C.A., 2011, Microanalysis of S, Cl, and Br in fluid inclusions by LA-ICP-MS: Chemical Geology, v. 284, p. 35–44, doi:10.1016/j.chemgeo.2011.02.003.

Staude, S., Bons, P.D., and Markl, G., 2009, Hydrothermal vein formation by extension-driven dewatering of the middle crust: An example from SW Germany: Earth and Planetary Science Letters, v. 286, p. 387–395, doi:10.1016/j.epsl.2009.07.012.

Staude, S., Werner, W., Mordhorst, T., Wemmer, K., Jacob, D., and Markl, G., 2012, Multi-stage Ag-Bi-Co-Ni-U and Cu-Bi vein mineralization at Wittichen, Schwarzwald, SW Germany: Geological setting, ore mineralogy, and fluid evolution: Mineralium Deposita, v. 47, p. 251–276, doi:10.1007/s00126-011-0365-4.

Steele-MacInnis, M., Bodnar, R.J., and Naden, J., 2011, Numerical model to determine the composition of H_2O-NaCl-$CaCl_2$ fluid inclusions based on microthermometric and microanalytical data: Geochimica et Cosmochimica Acta, v. 75, p. 21–40, doi:10.1016/j.gca.2010.10.002.

Stoffell, B., Appold, M.S., Wilkinson, J.J., McClean, N.A., and Jeffries, T.E., 2008, Geochemistry and evolution of Mississippi Valley-type mineralizing brines from the Tri-State and northern Arkansas districts determined by LA-ICP-MS microanalysis of fluid inclusions: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 103, p. 1411–1435, doi:10.2113/gsecongeo.103.7.1411.

Wilkinson, J.J., 2010, A review of fluid inclusion constraints on mineralization in the Irish ore field and implications for the genesis of sediment-hosted Zn-Pb deposits: Economic Geology, v. 105, p. 417–442, doi:10.2113/gsecongeo.105.2.417.

Wilkinson, J.J., Everett, C.E., Boyce, A.J., Gleeson, S.A., and Rye, D.M., 2005, Intracratonic crustal seawater circulation and the genesis of subseafloor zinc-lead mineralization in the Irish orefield: Geology, v. 33, p. 805–808, doi:10.1130/G21740.1.

Wilkinson, J.J., Stoffell, B., Wilkinson, C.C., Jeffries, T.E., and Appold, M.S., 2009, Anomalously metal-rich fluids form hydrothermal ore deposits: Science, v. 323, p. 764–767, doi:10.1126/science.1164436.

Yardley, B.W.D., 2005, Metal concentrations in crustal fluids and their relationship to ore formation: Economic Geology and the Bulletin of the Society of Economic Geologists, v. 100, p. 613–632.

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