# A fluid inclusion study of the drusy quartz of the Potosi Dolostone, Southeast Missouri.

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Abstract-A fluid inclusion study of drusy quartz in the Potosi formation in the Southeast Missouri barite district (Washington County), north of the Viburnum Trend lead-zinc district, shows that the fluids which deposited the quartz were both less saline and hotter than the fluids which deposited the sulfides in either the Viburnum Trend or the barite district. The drusy quartz is thus apparently unrelated to either mineralization event.

#### 1. INTRODUCTION

Delineating the pathways followed by the fluids responsible for the extensive hydrothermal mineralization in southeastern Missouri has long proved to be a difficult problem. One aspect of this problem not often commented on is that, although there is much discussion of the sources of the fluids and their pathways *towards* the ore deposits, there is little discussion of their pathways *after* ore deposition, i.e., their *exit* paths.

A number of imaginative methods have been used to infer fluid directions towards the ores (Figure 1), and the idea that there may be more than one source and one direction has definitely not been ruled out, so the directions indicated are not necessarily mutually exclusive. There is widespread agreement that at least one source, perhaps the major source, first proposed by Leach and Rowan (1986), lies to the south, where the Ouachita/Allegheny Orogeny at the end of the Paleozoic provided a hydraulic gradient which could account for the regional flow. This is supported by several lines of evidence (Leach et al., 1991; Kaiser et al., 1987, after Leach et al., 1984; Farr, 1986; Leach and Rowan, 1986; Horrall et al., 1997), most recently a modeling study by Appold and Garven (1999). Arrow 1 in Figure 1 represents straight southto-north flow as implied by two-dimensional flow models along the Viburnum Trend, such as that of Appold and Garven (1999). However, there is evidence that flow was channeled through the Reelfoot rift, Bloomfield Lineament Zone, and/or northwesterly-trending faults (Horrall et al., 1997; see also He et al., 1997), represented in Figure 1 by arrow 4. Another suggestion made here is that, because model uplift contours in the Ouachitas (Beaumont et al., 1987, Figure 5) have a NW - SE direction, there would be a northeasterly component to the northward flow, which would be turned eastward in the vicinity of the Viburnum Trend because of the high permeability contrast across the Trend, the back-reef dolomites being highly permeable. This idea is represented by arrow 5 in Figure 1. An attractive feature of this idea is that it more easily accounts for the predominantly north-south mineral zoning in the Trend. Another suggestion (Gregg and Shelton, 1989a,b; Wagner, 1995) is that at least some flow is from north to south, represented by arrow 3, possibly from the Illinois basin to the northeast.

No matter where the fluids come from, they must exit the mineralized zones and go somewhere. In the case of the Viburnum Trend, there seem to be only two main possibilities, again not mutually exclusive. One is that they exited along the major fault zones to the north of the Trend, perhaps even being responsible for the barite-lead district in Washington County (arrow 2 in Figure 1). Kaiser and Ohmoto (1988) indicate that some of the structures in the region were active during mineralization. The other is that, as mentioned above, they exited through the backreef facies east of the Viburnum Trend. There are some chemical problems to be resolved in proposing that the barite-lead district mineralization was produced by exiting Viburnum fluids, but it is not impossible.

A very common feature of the dolostone host rocks in the barite-lead district is drusy quartz, the fluid inclusions in which are the focus of this study. According to Wagner (1973) the quartz is pre-barite, and unrelated to the barite-sphalerite-galena ores, but in the context of the exiting Viburnum fluid hypothesis, it could represent early-stage fluids, in which silica derived from the Lamotte sandstone was precipitat-



Figure 1: A schematic perspective view of the southeast Missouri area, showing possible fluid pathways discussed in the literature. Numbered arrows are discussed in the text.

ed due to cooling and mixing. In this sense, the drusy quartz represents a very small piece of a much larger puzzle. Fluid inclusions within the drusy quartz of the Potosi Dolostone were examined to determine what kind of fluids were responsible for its deposition.

# 2. GEOLOGY

The area studied is located within a large structural block bounded on three sides by major fault systems (Kaiser et al., 1987). These include the Palmer, Shirley, Big River and Vineland Fault Systems. In this area, the Potosi Dolostone is a brown, mediumto fine-grained dolostone of Upper Cambrian age. Wagner (1973) describes three primary textural lithologies. These include the more abundant calcarenites and algal stromatolitic biostromes and less common carbonate muds. Dolomitization of these lithologies occurred before the introduction of the silica-bearing fluids which formed chalcedony and drusy quartz mainly in vugs or fractures. The drusy quartz is found most commonly in the digitate algal stromatolitic beds, particularly on the outer edge of the algal columns. This commonly produces a texture

of hollow tubes of quartz crystals known as "honeycomb" or "pipe" druse.

## **3. PROCEDURES**

Sample locations were chosen to obtain a representative cross section of the Southeast Missouri Barite District (Figure 2). Fluid inclusion sections (0.2 to 0.5 mm thick) of Potosi Dolostone containing drusy quartz were cut and polished on both sides. The sections were then examined under a transmitted light microscope to locate inclusions, and a rough map of the inclusion locations was made. The sections were then soaked in methyl alcohol for 1.5 to 2 days to remove the section from the glass slide. The sample was carefully broken into small chips, approximately 3-7 mm in size, and placed in the fluid inclusion stage. The equipment used included a Linkam THMS 600 stage with TMS 92 temperature programmer. Temperature calibration in the range -56.8 °C to +28.7 °C was carried out using a natural standard H2O-CO2-NaCl inclusion, itself calibrated at  $T_{m CO2}$ ,  $T_{m clath}$ , and  $T_{h CO2}$  against organic compounds of known melting points. Most phase changes



Figure 2: Map of the sampling area, Washington County, Southeast Missouri.

in this temperature range, with the exception of initial melting temperatures, can be determined to  $\pm$  0.1 °C. Calibration at other temperatures was carried out using ten of the standard chemicals listed by Macdonald and Spooner (1981), covering a temperature range of -22.8 °C to 306.8 °C. At elevated temperatures, the measurement precision is  $\pm$ 0.5 °C. Due to the small size of the inclusions (average size about 3 by 5 microns), the temperature of first melting could not be reliably determined.

A sketch was drawn of the field of view containing the inclusions to be analyzed. The temperature was reduced to between -95 and -100 °C or until the fluid

in the inclusions froze. The temperature was increased by 25°/minute until approximately 10° below the expected temperature of melting of ice ( $T_{m ice}$ ). The temperature was then increased by 5°/minute until approximately 2° below the expected temperature of melting of ice. Then the rate of temperature increase was reduced to 0.5°/minute until the ice melted. The melting temperature of ice was recorded and the procedure was repeated twice. If the melting temperatures did not vary by more than 0.5 °C, the average of the three trials was recorded as the melting temperature ( $T_{m ice}$ ) of the inclusion. Melting temperature results collected were used to calculate



Figure 3: Salinity and homogenization temperatures from the sampling localities in Figure 2, projected onto a N-S plane. No pattern is evident. Projection onto E-W and NE-SW planes are equally uninformative.

salinities expressed as equivalent weight % NaCl (Brown and Hagemann, 1994).

The chips were then heated to determine the homogenization temperature ( $T_{h L-V,L}$ ). The temperature was increased by 25°/minute until the gas bubble appeared to be much smaller. The temperature was then increased by 5°/minute until the gas bubble was seen to bounce quickly around the inclusion. Then the rate of temperature increase was reduced to 0.5°/minute until the gas bubble disappeared. The temperature was reduced until the bubble reappeared and the procedure repeated twice. If the homogenization temperatures did not vary by more than 0.5 °C, the average of the three trials was recorded as the homogenization temperature ( $T_{h L-VL}$ ) of the inclusion.

Because there were so few inclusions and they were very small, it was difficult to distinguish between primary and secondary fluid inclusions. Primary inclusions tended to be isolated whereas secondary inclusions occurred in groups, along a plane with other tiny inclusions. Both primary and secondary inclusion data were collected and used for this study.

## 4. RESULTS

The drusy quartz crystals of the Potosi Dolostone are remarkably clean and mostly free of inclusions. Fluid inclusions found within the drusy quartz are very small, simple vapor + liquid inclusions. The inclusions were subrounded to cigar-shaped with occasional subangular triangle-shaped inclusions. The vapor bubble appeared to occupy up to 30% of the inclusion (average approximately 15%). The volume % vapor was fairly constant. When the sample was cooled, no evidence was seen for a separate  $CO_2$  phase. There were, on average, only 4-5 inclusions



Figure 4: Fluid inclusion measurements of salinity and homogenization temperatures from the sampling localities in Figure 2, compared to the general ranges of fluid inclusion data from the Viburnum Trend and the Barite District.

Table 1. Fluid inclusion data.				
Sample Locality (Fig. 1)				
	Primary		Secondary	
	T <sub>h</sub>	Wt. % NaCl	T <sub>h</sub>	Wt. % NaCl
3	244.3	1.651		
7	257	1.487		
9	167	0.827		
13	211	6.076		
16	196	11.222		
16	281	11.343		
3			176	6.961
5			232	10.355
5			232	1.075
7			159	9.583
8			176	2.469
8			198	1.651
9			231	3.278
13			191	6.815
15			246	1.075
15			186.5	1.898

found per sample that were large enough to obtain melting and homogenization temperatures. Of these 4-5 inclusions, only 2 or 3 provided useful data (i.e., did not leak).

The data obtained are listed in Table 1. Melting temperatures ( $T_{m ice}$ ) ranged from -0.5 °C to -7.7 °C with an average of -3.2 °C. The salinity values calculated from the melting temperatures ranged from 0.8 to 11.3 equivalent weight % NaCl. Homogenization temperatures ( $T_{h L-V,L}$ ) ranged from 159 to 281 °C. The geographic distribution of temperature of homogenization and salinity of primary and secondary fluid inclusions was plotted in three-dimensions with projections on North-South and East-West planes. There did not appear to be any pattern to the geographic distribution for either the temperature of homogenization or salinity (Figure 3).

The fluids found in the inclusions in quartz from the Potosi Dolostone are very different from fluids of the Viburnum Trend and the Southeast Missouri Barite District. The temperatures of homogenization for Viburnum Trend fluids range from approximately 80 to 150 °C (Roedder, 1977; Hagni, 1983; Sverjensky, 1986; Viets and Leach, 1990; Leach et al., 1991, after Leach and Rowan, 1986 and Rowan and Leach, 1990). Leach et al. (1991) reported that salinities of Viburnum Trend fluids are greater than 15 and frequently greater than 20 equivalent weight % NaCl (very saline). The MVT ore-forming fluids of the Viburnum Trend are lower temperature and much more saline than the fluids from the Potosi quartz inclusions (Figure 4). Fluid inclusion data of the barite district suggest that the mineralizing solutions were saline brines with temperatures ranging from approximately 70 to 110 °C and salinities of 20 to 25 equivalent weight % NaCl (Kaiser et al., 1987; Leach, 1979). These fluids are also much more saline and lower temperature than those of the Potosi Formation drusy quartz.

It is of interest to compare these temperatures with the maximum possible burial temperature. Henry (1988) used a stratigraphic reconstruction to estimate the maximum burial depth of the Bonneterre Dolostone in the Viburnum Trend. He determined that the maximum possible burial of the Bonneterre Formation was approximately 1100 m and based on anomalous organic maturities, temperatures from fluid inclusions and fission track annealing studies, concluded that the geothermal gradient in the Ozark region was approximately 100 °C/km (Henry, 1988). Even with this very high geothermal gradient, the temperature of the Bonneterre Formation would not have exceeded 125 °C at maximum burial. Because the Potosi Dolostone is stratigraphically above the Bonneterre Formation and the sequence has not been overturned, its maximum burial temperature would thus be less than 125 °C. Therefore, the fluid inclusion data from this study demonstrate that the silicabearing fluids that deposited the drusy quartz were higher temperature (159 to 281 °C) than any temperature the Potosi Dolostone host rock could have reached by burial alone.

#### 5. CONCLUSIONS

The fluids found in inclusions in quartz within the Potosi Dolostone are very different from the ore fluids of the Viburnum Trend and the fluids of the Southeast Missouri Barite District. The Mississippi Valley-Type ore-forming fluids of the Viburnum Trend and the mineralizing fluids of the Barite District are lower temperature and much more saline than the fluids in the quartz-hosted inclusions of this study. It would appear then that the drusy quartz is not related in any simple way to the mineralization in either area.

One final note. According to Dake (1930), a conglomerate with rounded, waterworn fragments of apparent Potosi drusy quartz is present at the base of the Lower Ordovician Gasconade formation. However, inquiries at the University of Missouri (Rolla) and the Geological Survey of Missouri found no one who knew of a locality where drusy quartz fragments are exposed in the Gasconade Formation. This observation, if substantiated, and if the fragments were indeed shown to be from the Potosi formation, would imply an age of the drusy quartz from Upper Cambrian to Lower Ordovician. Given the fairly high temperatures of the fluid inclusions in the Potosi drusy quartz, the origin of the fluids responsible would be even more mysterious.

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#### REFERENCES

- Appold M. S. and Garven G. (1999) The hydrology of ore formation in the southeast Missouri district: Numerical models of topography-driven flow during the Ouachita orogeny. *Econ. Geol.* 94, 913-935.
- Beaumont C., Quinlan G. M. and Hamilton J. (1987) The Alleghenian orogeny and its relationship to the evolution of the eastern interior, North America. *Can. Soc. Petrol. Geol. Memoir.* **12**, 425-445.
- Brown P. E. and Hagemann S. G. (1994) MacFlinCor: A computer program for fluid inclusion data reduction and manipulation. In *Fluid inclusions in minerals: Methods* and applications (ed. B. De Vivo and M.L. Frezzotti), Short course of the working group (IMA) "Inclusions in Minerals", Pontigano-Siena, 1-4 September, 1994, pp. 231-250.
- Dake C. L. (1930) The geology of the Potosi and Edgehill Quadrangles, v. 23, second series. Missouri Bureau of Geology and Mines.
- Farr M. R. (1986) Regional isotopic variation in Bonneterre Formation cements: Implication for brine migration pathways and sources. In Symposium on the Bonneterre Formation (Cambrian), southeastern Missouri: Stratigraphy, Sedimentology, Diagenesis, Geochemistry, and Economic Geology (ed. J. M. Gregg and R. D. Hagni), pp. 8. University of Missouri-Rolla, Rolla, Missouri. (abstr.).
- Gregg J. M. and Shelton J. L. (1989a) Minor- and trace-element distributions in the Bonneterre dolomite (Cambrian, southeast Missouri): Evidence for possible multi-basin fluid sources and pathways during lead-zinc mineralization. *Geol. Soc. America Bull.* **101**, 221-230.
- Gregg J. M. and Shelton J. L. (1989b) Geochemical and petrographic evidence for fluid sources and pathways during dolomitization and lead-zinc mineralization in southeast Missouri: a review. *Carbonates and Evaporites* 4, 153-176.
- Hagni R. D. (1983) Ore microscopy, paragenetic sequence, trace element content, and fluid inclusion studies of the copper-lead-zinc deposits of the southeast Missouri lead

district. In International Conference on Mississippi Valley-Type Lead-Zinc Deposits, Proceedings Volume (ed. G. Kisvarsanyi et al.), pp. 243-256. University Missouri-Rolla Press.

- He Z., Gregg J. M., Shelton K. L., and Palmer J. R. (1997) Sedimentary facies control of fluid flow and mineralization in Cambro-Ordovician strata, southern Missouri. In Basin-Wide Diagenetic patterns: Integrated Petrologic, Geochemical, and Hydrologic Considerations, SEPM (Society for Sedimentary Geology) Special Publication No. 57, 81-99.
- Henry A. L. (1988) Alteration of organic matter in the Viburnum Trend lead/zinc district of southeastern Missouri. M.Sc. thesis, University of Toronto.
- Horrall K. B., Farr M. R., and Hagni R. D. (1997) Evidence for focusing of Mississippi Valley-type ore fluids along the Bloomfield Lineament Zone, Southeast Missouri. Society of Economic Geologists, Special Publication No. 4, 75<sup>th</sup> Anniversary Volume, D. F. Sangster, ed., pp. 400-412.
- Kaiser C. J. and Ohmoto H. (1988) Ore-controlling structures of Mississippi Valley-Type mineralization on the North American midcontinent as products of late Paleozoic convergent plate tectonism. In North American Conference on Tectonic Control of Ore Deposits and the Vertical and Horizontal Extent of Ore Systems Proceedings Volume (eds. G. Kisvarsanyi and S. Grant), pp. 424-430. University of Missouri – Rolla Press.
- Kaiser C. J., Kelly W. C., Wagner R. J., and Shanks W. C. III (1987) Geologic and geochemical controls of mineralization in the Southeast Missouri Barite District. *Econ. Geol.* 82, 719-734.
- Leach D. L. (1979) Temperature and salinity of the fluids responsible for minor occurrences of sphalerite in the Ozark region of Missouri. *Econ. Geol.* 74, 931-937.
- Leach D. L., Plumlee G. S., Hofstra A. H., Landis G. P., Rowan E. L., and Viets J. G. (1991) Origin of late dolomite cement by CO<sub>2</sub>-saturated deep basin brines: Evidence from the Ozark region, central United States. *Geology* 19, 348-351.
- Leach D. L. and Rowan E. L. (1986) Genetic link between Ouachita fold belt tectonism and the Mississippi Valleytype lead-zinc deposits of the Ozarks. *Geology* 4, 931-935.
- Leach D. L., Viets J. G., and Rowan L. (1984) Appalachian-Ouachita orogeny and Mississippi Valley-type deposits. *Geol. Soc. Am. Abstr. Programs* 16, 572. (abstr.).
- Macdonald A. J., and Spooner E. T. C. (1981) Calibration of a Linkham TH 600 programmable heating-cooling stage for thermometric examination of fluid inclusions. *Econ. Geol.* 76, 1248 - 1258.
- Roedder E. (1977) Fluid inclusion studies of ore deposits in the Viburnum Trend, southeast Missouri. *Econ. Geol.* 72, 474-479.
- Rowan E. L. and Leach D. L. (1990) Constraints from fluid inclusions on sulfide precipitation mechanisms and ore fluid migration in the Viburnum Trend lead district, Missouri. *Econ. Geol.* 84, 1948-1965.
- Sverjensky D. A. (1986) Genesis of Mississippi Valleytype lead-zinc deposits. Ann. Rev. Earth Planet. Sci. 14, 177-199.
- Viets J. G. and Leach D. L. (1990) Genetic implications of regional and temporal trends in ore fluid geochemistry of Mississippi Valley-type deposits in the Ozark region. *Econ. Geol.* 85, 842-861.
- Wagner R. J. (1973) Stratigraphic and structural controls and genesis of Barite deposits in Washington County, Missouri. Ph.D. thesis, University of Michigan.

Wagner, R. J. (1995) Viburnum Trend considerations, an industry perspective. In: Extended Abstracts: International field Conference on Carbonate Hosted Lead-Zinc Deposits, D. L. Leach and M. L. Goldhaber, eds., p. 331-332, Society of Economic Geologists.