Is there pyrite in black opal from Lightning Ridge, New South Wales, Australia?

B. L. Dickson

47 Amiens St, Gladesville, NSW, 2111, Australia

The idea that black opal from Lightning Ridge is coloured by pyrite (FeS_2) has appeared in various academic works from around 2000. Reports from Ethiopia (Johnson et al., 1996), suggest small cubic grains of pyrite has been seen in opals. McCarthy (2001), in an abstract from her thesis studying South Australian opals, noted that organic matter, pyrite, barite, gypsum, kaolin, iron ooids, goethite and limonite were identified within solid opal. Pyrite has been noted in association with opalised wood and dinosaur bones from Andamooka, Coober Pedy and White Cliffs fields (Pewkliang et al., 2004; Pewkliang, 2004) but not within the opal but rather external to cell walls. In 2013, Fink wrote in his thesis that concentrations of SO_2, Fe_2O_3, Pb, Cu and U increased with the darkness of opal from Lightning Ridge and then suggested that possibly pyrite also was increasing. He did state that such a proposal was speculative as no evidence for pyrite was observed.

In a recent paper, Herrmann et al. (2019) suggest that an analysis of 3 jet-black potch opal samples from Lightning Ridge contains sulphides which are predominantly pyrite and chalcopyrite. The methodology of the study involved the removal of silica from the opal samples using cold, concentrated, hydrofluoric acid (HF), before undertaking an analysis of the residue by various means. They further suggested that the carbon and sulphides in the black opal resulted from sulfate-reducing bacterial activity; a conclusion is based. However, the given average data shows the jet-back opal samples contained a very high Fe concentration of 12,900 mg/kg (1.84% Fe_2O_3) which given an experience by the author of contamination of opals by inappropriate sample preparation that lead to similarly high Fe, calls into question these findings and conclusions.

An example of sample contamination

I recently was involved in sending a parcel of opal samples to a commercial laboratory in Brisbane for analysis. This set contained a sample of a massive black opal sample (AGS17), weighing 300 gm, which came from the Sheepyard Opal Field located ~ 45 km southwest of the Lightning Ridge township. This field is well known for producing thick, sub-horizontal, opal veins (Pecover 2019). The samples were ground by the laboratory and analysed by ICP-MS. The results (Table 1) showed all samples were high in Fe with sample AGS-17 having 18,400 mg/kg. However, a Mossbauer spectrum had also been determined for this sample (J. Cashion, pers. comm., 2019), which showed that the opal had a low Fe; indicating that the high Fe analyses for sample AGS17 was incorrect. Discussion with the analytical service revealed that this sample set had been inadvertently ground in a hardened Fe-Cr mill. When the analyses were repeated on fresh samples (Table 1), the results showed a substantial decrease in Fe content. The data in Table 1 shows that for all samples both Fe and Cr showed major decrease between the first and second analyses confirming the first set were contaminated by the Fe-Cr mill.

	First set		**Second set**	
	Cr	**Fe**	**Cr**	**Fe**
	ppm	**%**	**ppm**	**%**
1	25.6	3.12	3.3	0.36
2	12.8	1.46	0.7	0.3
3	19.5	2.57	0.4	0.164
4	19.7	1.99	1.1	0.019
5	33.6	2.99	2.9	0.051
6	40.7	3.43	0.8	0.97
7	29	3.12	4.2	0.37
8	19.6	2.21	0.3	0.152
9	29.3	3.2	<0.3	0.045
10	18	1.82	1.2	0.095
Median	22.65	2.78	1.1	0.158

Table 1: Comparison of analyses for Fe and Cr in contaminated (first set) and reprocessed new (second set) samples

Analysis of the jet-black opal sample reported by Herrmann et al.

The data published by Herrmann *et al.,* (2019) for Fe and Cr in their jet-black opal samples are very similar to those in the contaminated data set in Table 1, namely 12,900 and 18 mg/kg, respectively. Furthermore we can compare these results to previous data for Lightning Ridge black opals.

Table 2 shows a summary of previous analyses on Lightning Ridge black opal for Fe on many samples from across the field. The highest value previously recorded for Fe was 3610 mg/kg in a compilation of data put together by Dickson (2019). . McOrist and Smallwood (1997) obtained an average 3.2 mg/kg Cr for Lightning Ridge black potch opal, indicating 18 mg/kg is also an exceptional value. Thus, I consider it reasonable to conclude that 18 mg/kg for Cr is an exceptional value; and, with the exceptional Fe content, it would thus appear that the jet-black sample was also milled in a hardened iron mill. Although Herrmann *et al.,* (2019), state that their powders were processed in a tungsten carbide mill, it appears this was not the case for the jet-black opal.

Sample type	No	Fe range	Fe Mean	Reference
Black POC	7	400 - 870	550	McOrist and Smallwood, 1997
Black potch	13	650 – 2000	1100	ditto
black potch	53	217 - 3610	1254	Dickson, 2019 compilation studies 2000-2019
Other potch	143	61 – 4056	721	ditto

Table 2: Summary of previous analyses on Lightning Ridge black opal for Fe in mg/kg

Discussion

Is the contamination potentially of significant to the conclusions of the study? This is not easy to answer. Focusing on the sulphur in the black opal first, the amount of S in the jet-black and sample AGS-17 are 240 and 540 mg/kg. The location and nature of the sulphur is unknown. It could be present as inclusions of sulfate minerals such as gypsum ($CaSO_4 \cdot 2H_2O$) or barite ($BaSO_4$). Roberts (2014) recorded gypsum needles in Lightning Ridge opal. Alternatively, black opal contains 0.06% or more organic matter which could also host S or the organic matter could assist in the reduction of sulfate to sulfide, mirroring the process found with sulfate-reducing bacteria. This question must be considered as open for now.

Is there other evidence to support the thesis of Herrmann *et al.,* (2019) that Lightning Ridge black opal is coloured by sulfides? The oxidation state of Fe is readily determined by various methods. For example, Stevens Kalceff *et al.* (1997) noted that the response for Fe^{3+} - M^{+} defect centres was weak in the cathodoluminescence response of Lightning Ridge black opal, which indicated that some of the Fe was not oxidized, but also, that black opal did contain Fe^{3+}. Herrmann & Maas, (2022) report the Fe^{2+} and Fe^{3+} contents of 10 Lightning Ridge opals, measured by cerium titration, and found that one black opal had only Fe^{2+}, and that two grey and one amber opals had only Fe^{3+}; while the remaining six samples contained both Fe^{2+} and Fe^{3+}. An amber opal from Lightning Ridge, studied by Mossbauer spectroscopy, contained around 88% Fe^{3+} and 12% Fe^{2+} (J. Cashion, pers. comm., 2019). These mixed valence results suggest that Lightning Ridge black opals formed in a near-neutral, possibly slightly reducing environment (e.g. see Fig 1). Watkins *et al.,* (2011) state that the type of microbes found in black opal at Lightning Ridge require a nutrient-rich near-surface aerobic environment with temperatures less than 35 °C and near-neutral pH. Such an environment is not consistent with the high sulfate, anaerobic, strongly reducing environment, often associated with sulfate-reducing bacteria.

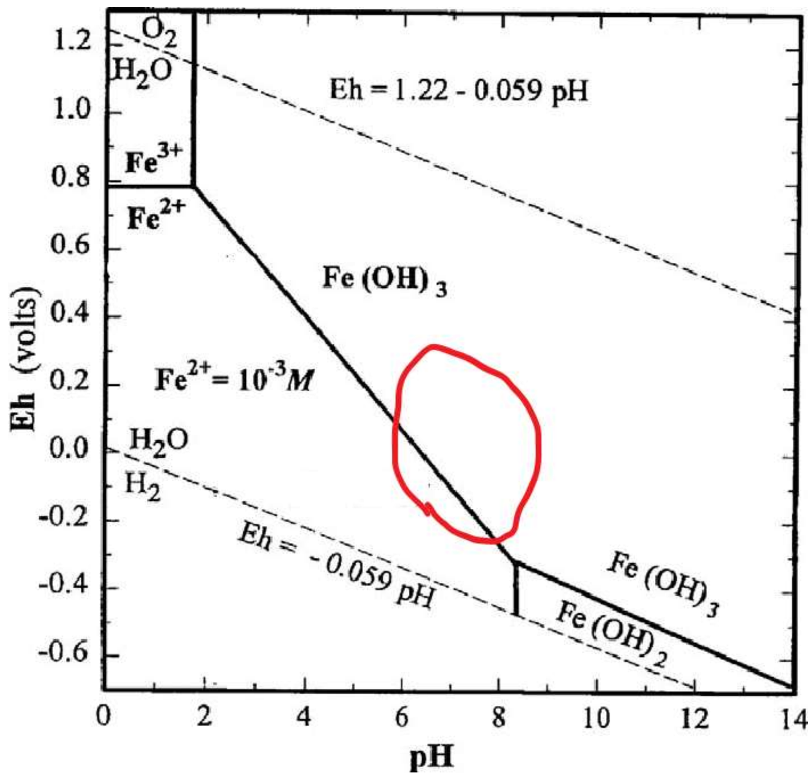

Fig 1: Pourbaix diagram for Fe (after Okumusoglu & Gündüz 2013). Red area indicates possible conditions for black opal formation

The presence of sulfide in opal could be confirmed by an evolved gas analysis study to determine if SO_2 is emitted when the opal is heated in air. There have been many studies of the evolved gases in thermogravimetric studies of opal (e.g. Thomas et al., 2015; Fink, 2013) but none record any SO_2 emission. This could be because it has not been specifically looked for.

In conclusion, I consider that the study by Herrmann et al. (2019) has not demonstrated that Lightning Ridge black opal contains pyrite or any other sulphide and the contamination by Fe metal must cast some doubt around the conclusions.

References

Fink, A. (2013). Composition, Structure and Origin of Lightning Ridge Black Opal (unpublished Doctoral thesis), Melbourne Vic: La Trobe University.

Herrmann, J. R., Maas, R., Rey, P. F., & Best, S. P. (2019). The nature and origin of pigments in black opal from Lightning Ridge, New South Wales, Australia. Australian Journal of Earth Sciences, 66(7), 1027-1039.

Herrmann, J., & Maas, R. (2022). Formation of Sediment-Hosted Opal-AG at Lightning Ridge (New South Wales, Australia): Refining the Deep Weathering Model. The Journal of Geology, 130(2), 77-110.

Johnson, M. L., Kammerling, R. C., DeGhionno, D. G., & Koivula, J. I. (1996). Opal from Shewa Province, Ethiopia. Gems Gemol, 32, 112-120.

McCarthy, L. A. (2001). South Australian Sedimentary Opals: Evidence for syngenetic Deposition (Doctoral dissertation, University of Adelaide, Department of Geology and Geophysics)

McOrist, G., & Smallwood, A. (1997). Trace elements in precious and common opals using neutron activation analysis. *Journal of Radioanalytical and Nuclear Chemistry*, 223(1–2), 9–15

Okumusoglu, D., & Gündüz, O. (2013). Hydrochemical Status of an Acidic Mining Lake in Çan-Çanakkale, Turkey. *Water Environment Research*, *85*(7), 604-620.

Pecover, S.R., 2019. Frozen Opal Fluids and Colloidal Crystal Fire: Gem Opal Deposits in the Heart of Australia. In: InColor magazine (International Colored Gemstone Association Publication). 41, 34-60.

Pewkliang, B., Pring, A., Brugger, J., & Roach, I. C. (2004). Opalisation of fossil bone and wood: clues to the formation of precious opal. *In:* Roach I.C. ed. 2004. *Regolith 2004*. CRC LEME, pp. 264-268.

Pewkliang, B. (2004). The formation of opal in marine reptile bones and wood (Doctoral dissertation) https://digital.library.adelaide.edu.au/dspace/bitstream/2440/122447/1/PewkliangB2004_Hons.pdf (accessed 21 Sept 2023)

Roberts, G.E. (2014) Precious opal formation in Australia: Insights into Martian weathering processes. [on-line] https://www.gubelingemlab.com/tl_files/content/03 Gemmology/Scholarship/G. Roberts - Dr Eduard Gübelin Research Scholarship 2014.pdf

Stevens Kalceff, M.A., Phillips, M.R., Moon, A.R., and Smallwood, A. (1997) Cathodoluminescence Microanalysis of Natural Hydrated amorphous SiO_2; Opal. *Physics and Chemistry of Minerals*, 24(2), 131-138.

Thomas, P. S., Heide, K., & Földvari, M. (2015). Water and hydrogen release from perlites and opal: a study with a directly coupled evolved gas analyzing system (DEGAS). *Journal of Thermal Analysis and Calorimetry*, *120*, 95-101.

Watkins, J. J., Behr, H. J., & Behr, K. (2011). Fossil microbes in opal from Lightning Ridge-implications for the formation of opal. *Geological Survey of New South Wales*, *Quarterly Notes*, 136, 1-21.

Acknowledgements

The author wishes to thank Dr S Pecover for suppling the black opal sample and for discussions on opal. In addition comments by Dr Paul Thomas and Mr Tony Smallwood contributed to the author's understanding of opal. All comments in this paper are the responsibility of the author.