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An EBSD – EPMA Investigation of Synthetically Produced Sulfide Ores

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Sediment hosted Zn-Pb deposits are the most important source of Zn and Pb resources globally [1]. These deposits are known for hosting a variety of other elements as well such as Fe and Cu, and Ge, Ga and In which are widely used in the semiconductor industry. These valuable metals can be recovered as a by-product of refining the Zn-Pb ore. To improve and optimise this process, a greater understanding of the precise mechanism by which Zn-Pb minerals incorporate trace elements is needed. To this end, Liu *et al.* [2] recently developed a novel laboratory method of hydrothermally synthesising the formation of Zn-Pb minerals via a carbonate replacement mechanism that simulates their formation in real sediment hosted systems. Liu [2] demonstrated the role carbonate plays in carbonate-replacement models of ore genesis previously proposed in the literature [3]. This technique can also be applied to the study of speciation and trace element incorporation into sediment hosted Zn-Pb deposits. Here, we seek to compare the trace element distribution, phase morphology and mineralogical associations of Zn-Pb sulphide minerals hydrothermally produced with and without trace element additions of Fe and Ba in a process that closely simulates a real carbonate-replacement, sedimentary hosted system.

Fe and Ba have been introduced into Zn-Pb sulphide minerals using the synthesis technique of Liu, the experimental details of which are reported in [2]. The carbonate used for the experiment was calcite. The resulting mineral fragments have been characterised using electron probe microanalysis (EPMA) and electron backscattered diffraction (EBSD). Samples of the sulphide minerals were mounted in epoxy resin and polished to 50 nm finish using diamond and colloidal silicon dioxide abrasive. Samples were then Ar-ion beam polished with a Technoorg Linda SEM Prep 2 Ion beam slope cutter/polisher then examined in a Jeol 8530 Hyperprobe EPMA and an FEI Quanta 400 field emission, scanning electron microscope (SEM).

Figure 1 shows an “interrupted” type carbonate replacement experiment with Fe additions, where the experiment is stopped before the carbonate is entirely consumed. Figure 2 shows a similar experiment that has gone to completion and the carbonate is fully consumed. Barium and lead have been added to this sample instead of iron.

Figure 1(a) is a backscattered electron (BSE) image showing the carbonate mineral (calcite) surrounded by sulphide minerals (mainly sphalerite and pyrite) which are growing at the expense of the calcite. Figure 1(b) is a three-color map showing the distribution of elements Zn, S and Fe. The yellow coloured, globular type minerals are iron sulfides and the blue, thin, elongated minerals are zinc sulfides. At higher magnification (not shown) it can be seen that the elongated zinc sulfide crystals are actually tiny globules that have coalesced into the morphology seen in the image. The dark green mineral is anhydrite. This EPMA map indicates that no measurable quantity of Fe has been incorporated into the sphalerite under the hydrothermal conditions used for this experiment. Figure 1(c) is an EBSD phase map of one corner of the crystal shown in 1(a and b). It was necessary to repolish the sample between the EPMA and EBSD steps, so there is not an exact 1:1 registration between the two images.

Notwithstanding this, it is evident in the EBSD image that the iron sulfide phases are not just pyrite (cubic) but also marcasite (orthorhombic). The globular nature of the iron sulfides is apparent in this image.

The sphalerite also grows in globular clusters, examples of which are shown in Figure 2(a) in an unpublished image from previous research by the current authors [2]. That research found that the centre of the globular clusters was nanocrystalline and porous and, with respect to EBSD, did not diffract, whereas the crystals around the outer edge of the clusters were fully dense and diffracted well. Sphalerite clusters from the current research are shown in cross section in the BSE image of Figure 2(b). The EBSD phase image of Figure 2(c) shows the afore mentioned effect of good diffraction observed by the dense crystals around the edge of the clusters but no diffraction in their centre. Block like crystals of galena and elongated, rectangular crystals of barite are also seen in this sample.

Comparing the samples with and without Fe (Figures 1 and 2, respectively) the addition of this element does not seem to change the growth or morphology of the sphalerite globules. Globules in both samples are similar. Furthermore, it does not seem to alter the crystal structure. Only the cubic zinc sulfide (sphalerite) was found in either sample. Wurtzite (hexagonal) was absent. This is, perhaps, not surprising given that, under the conditions used in this experiment, iron was not incorporated in the zinc sulphide. Future experiments under different starting conditions may well elucidate the mechanism by which iron, and more valuable trace elements such as germanium are incorporated into the zinc sulfide. A greater understanding of this process can lead to improved recovery of these metals from the ore concentrates, thereby converting what was once a by-product into a valuable, usable resource.

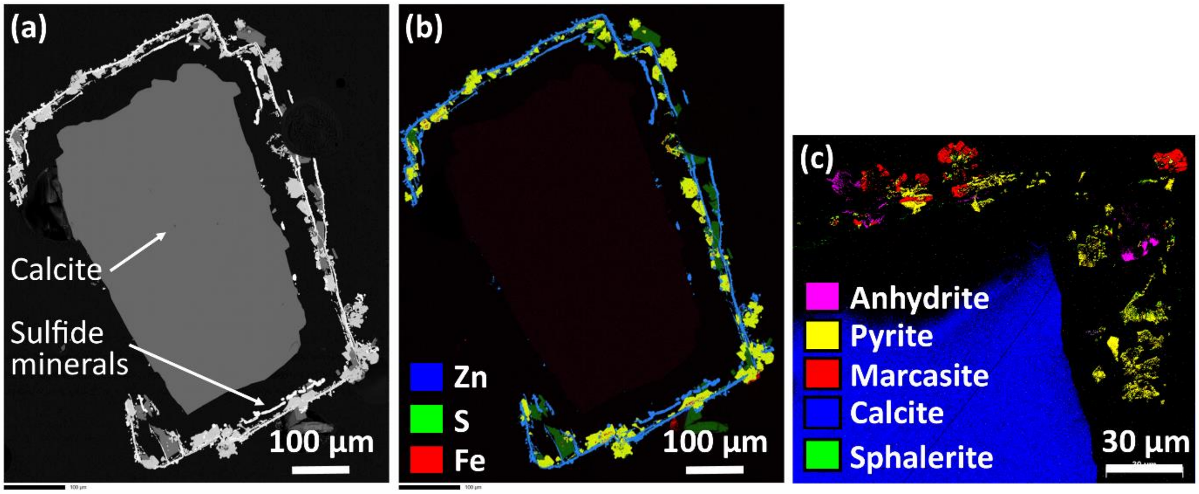

Figure 1. Hydrothermal, carbonate replacement experiment, with Fe addition, designed to simulate the growth of real sediment hosted Zn-Pb deposits. (a) BSE image showing the carbonate mineral in the centre (calcite) with Zn-Pb minerals growing around the outside of and at the expense of the carbonate crystal. (b) EPMA map showing elemental distribution in the sulfide region. (c) EBSD map showing phase distribution. Two types of iron sulfides (pyrite and marcasite) are present in the sample.

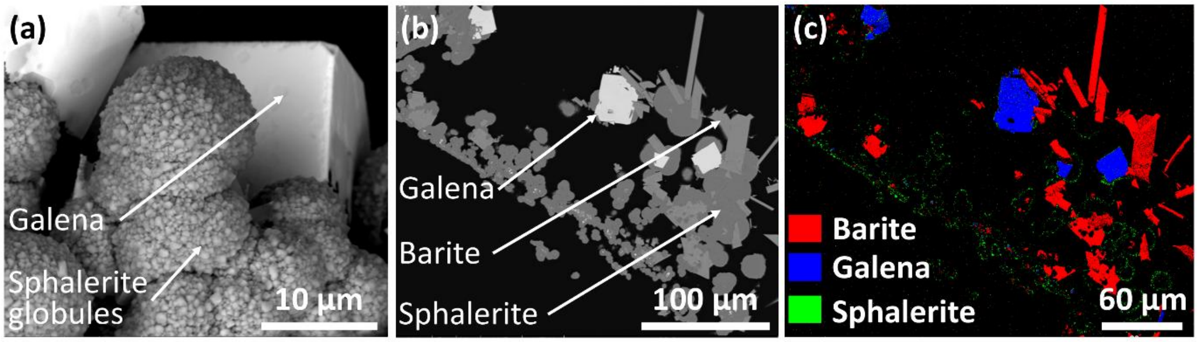

Figure 2. Hydrothermal, carbonate replacement experiment, with Ba and Pb additions instead of iron. (a) Image from previous work [2] showing morphology of sphalerite globules. (b) BSE image showing the sulfide mineral region. Galena, barite and sphalerite are evident in the image. (c). EBSD phase map showing mainly the distribution of barite and galena in the sulfide mineral region. The sphalerite globules mostly do not diffract, except for a thin band around the outer edge of the globule where the crystallites are denser and larger.

References

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