

Figure S1. Transmitted light of CU51S#4N sample (Reference used by mining companies) from Cumberland mine, Central Tennessee, USA. The sample exhibits a complex zonation with dark and light bands. These bands contain different trace elements concentration as revealed by XRF-map of Zn, Cu, Ga, Ge, Cd and Fe. The analysis zones (red rectangle) were carried out in zones with different trace elements assemblage. The dark bands have high Ge, Ga and Cu concentration while the light bands have high Fe and Cd concentration.

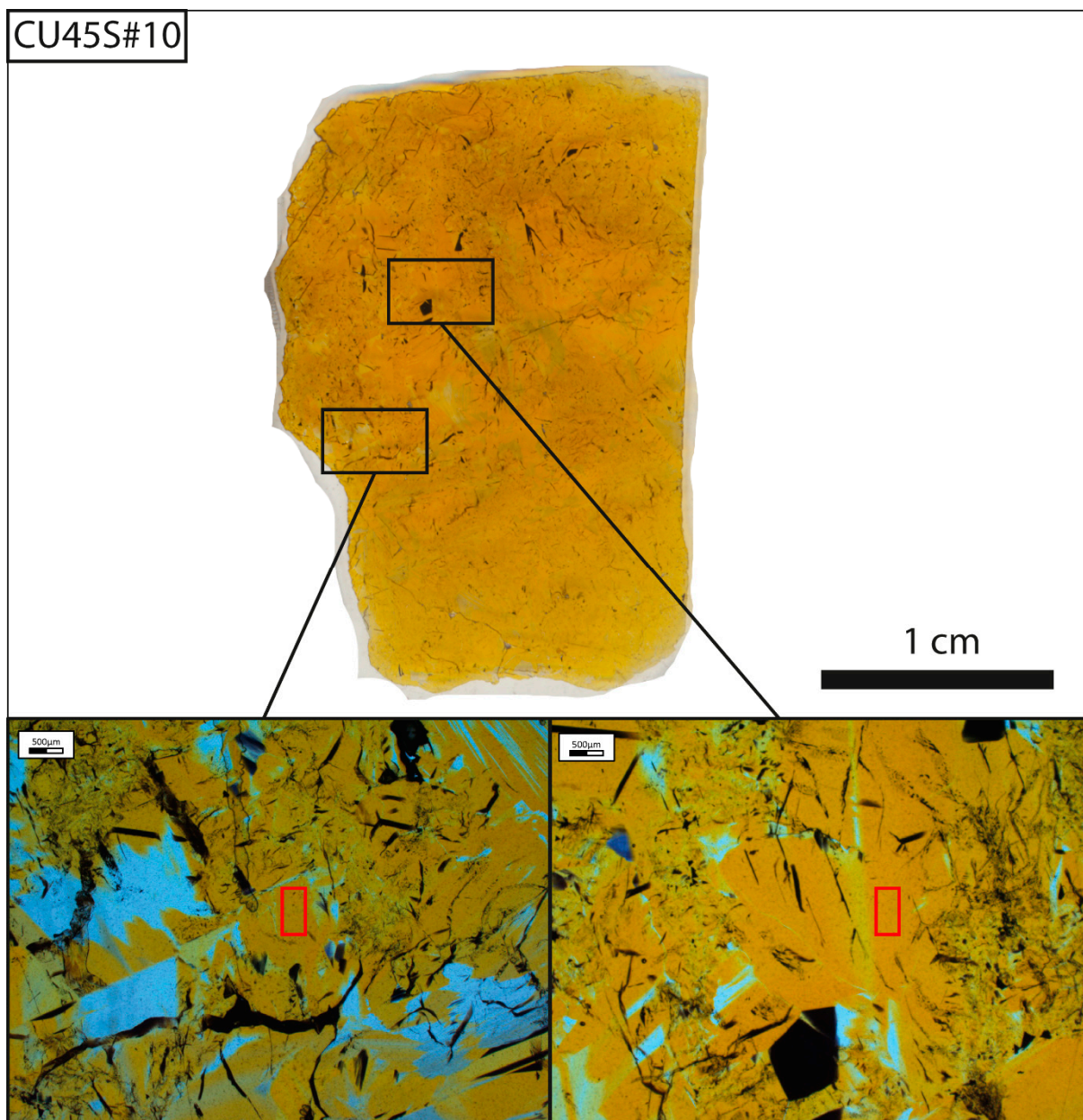


Figure S2. Transmitted light of CU45S#10 sample (Reference used by mining companies) from Cumberland mine, Central Tennessee, USA. The sample doesn't have zonation at thin section scale, but at microscopic scale dark and light areas such as the sample CU51S#4N appear. The analysis zones (red rectangle) were carried out in dark bands with high Ge, Ga and Cu concentration.

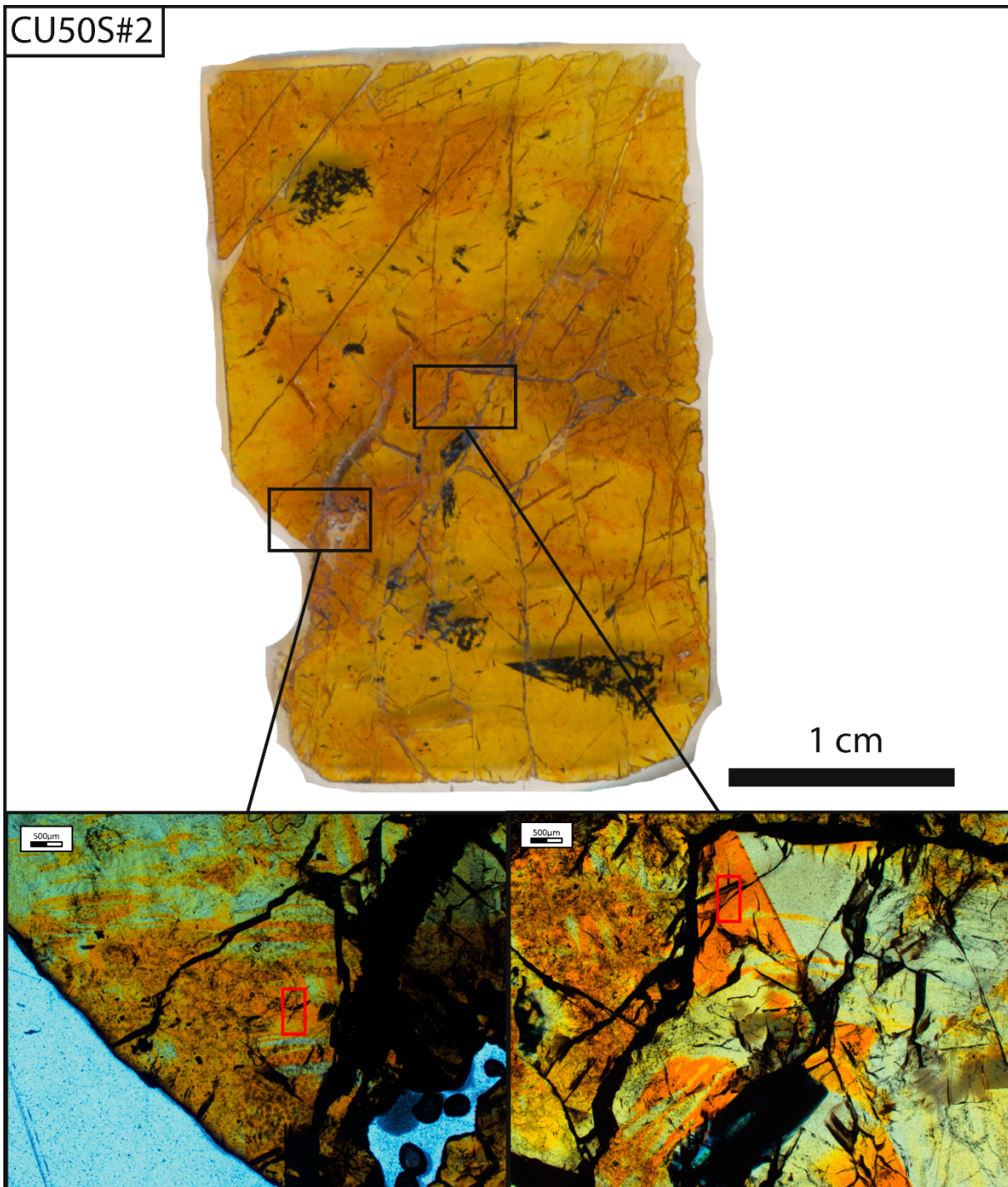


Figure S3. Transmitted light of CU50S#2sample (Reference used by mining companies) from Cumberland mine, Central Tennessee, USA. The sample doesn't have zonation at thin section scale, but at microscopic scale dark and light areas such as the sample CU51S#4N appear. The analysis zones (red rectangle) were carried out in dark bands with high Ge, Ga and Cu concentration.

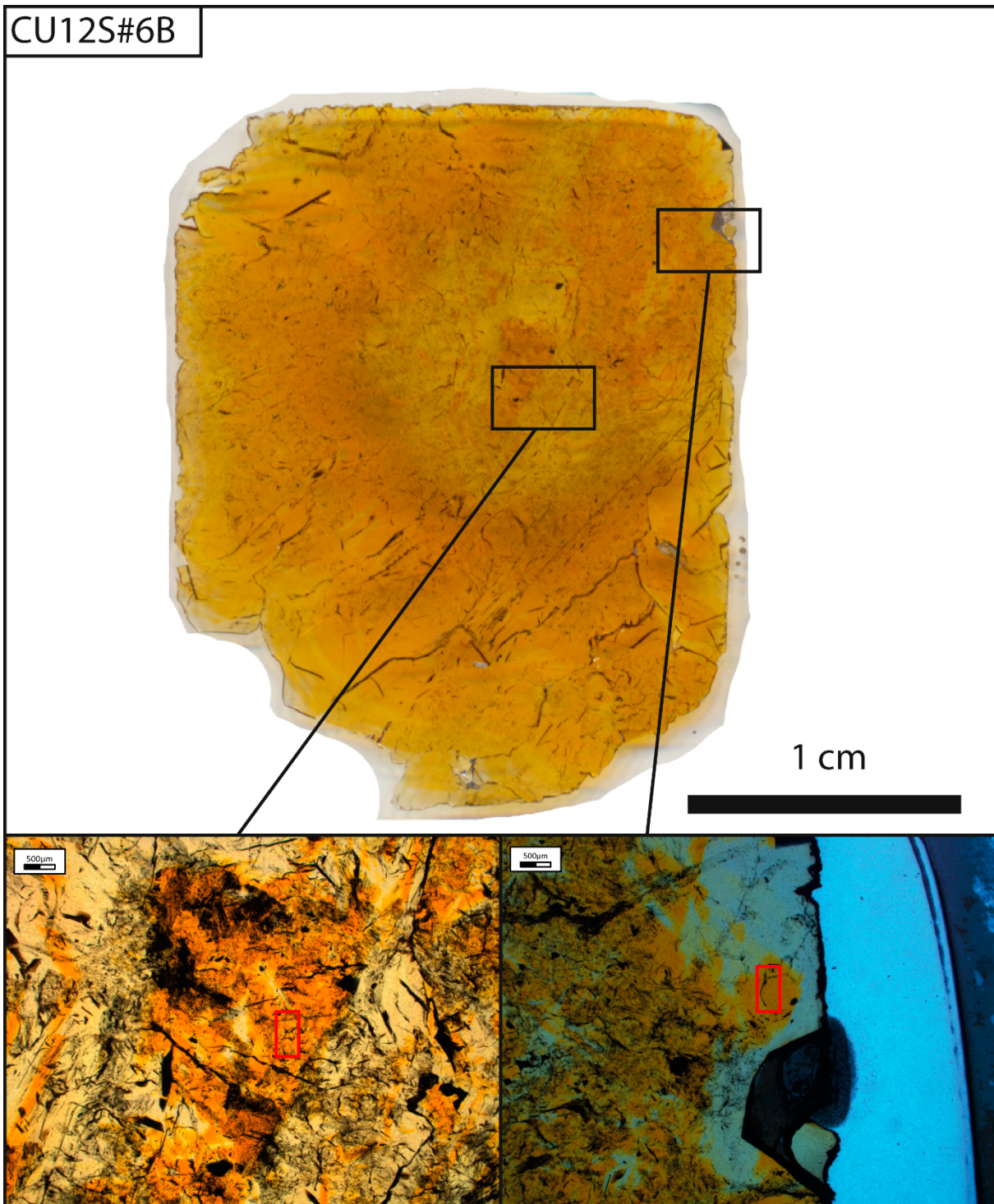


Figure S4. Transmitted light of CU12S#6B sample (Reference used by mining companies) from Cumberland mine, Central Tennessee, USA. The sample doesn't have zonation at thin section scale, but at microscopic scale dark and light areas such as the sample CU51S#4N appear. The analysis zones (red rectangle) were carried out in dark bands with high Ge, Ga and Cu concentration.

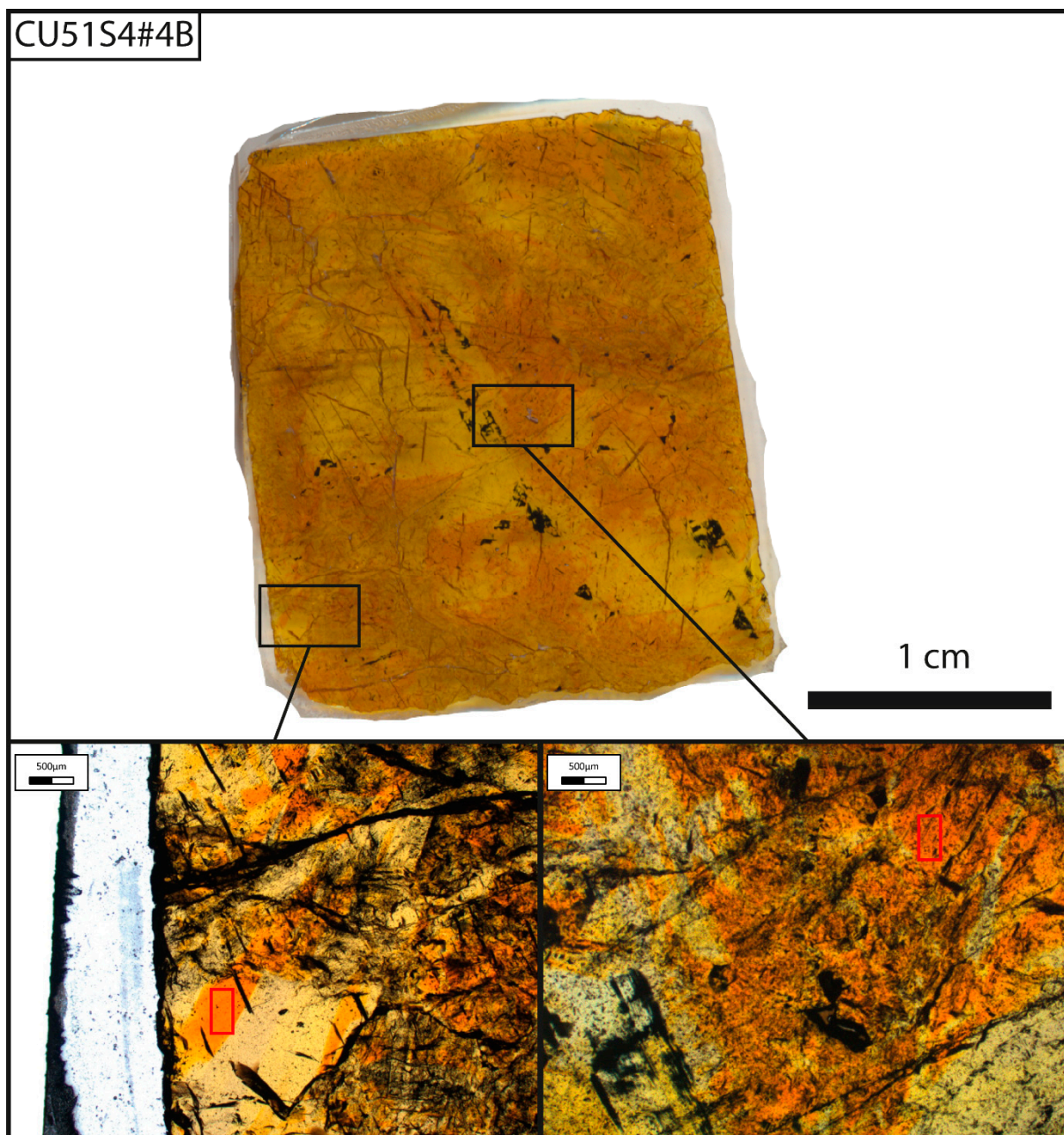


Figure S5. Transmitted light of CU51S4#4B sample (Reference used by mining companies) from Cumberland mine, Central Tennessee, USA. The sample doesn't have zonation at thin section scale, but at microscopic scale dark and light areas such as the sample CU51S#4N appear. The analysis zones (red rectangle) were carried out in dark bands with high Ge, Ga and Cu concentration.

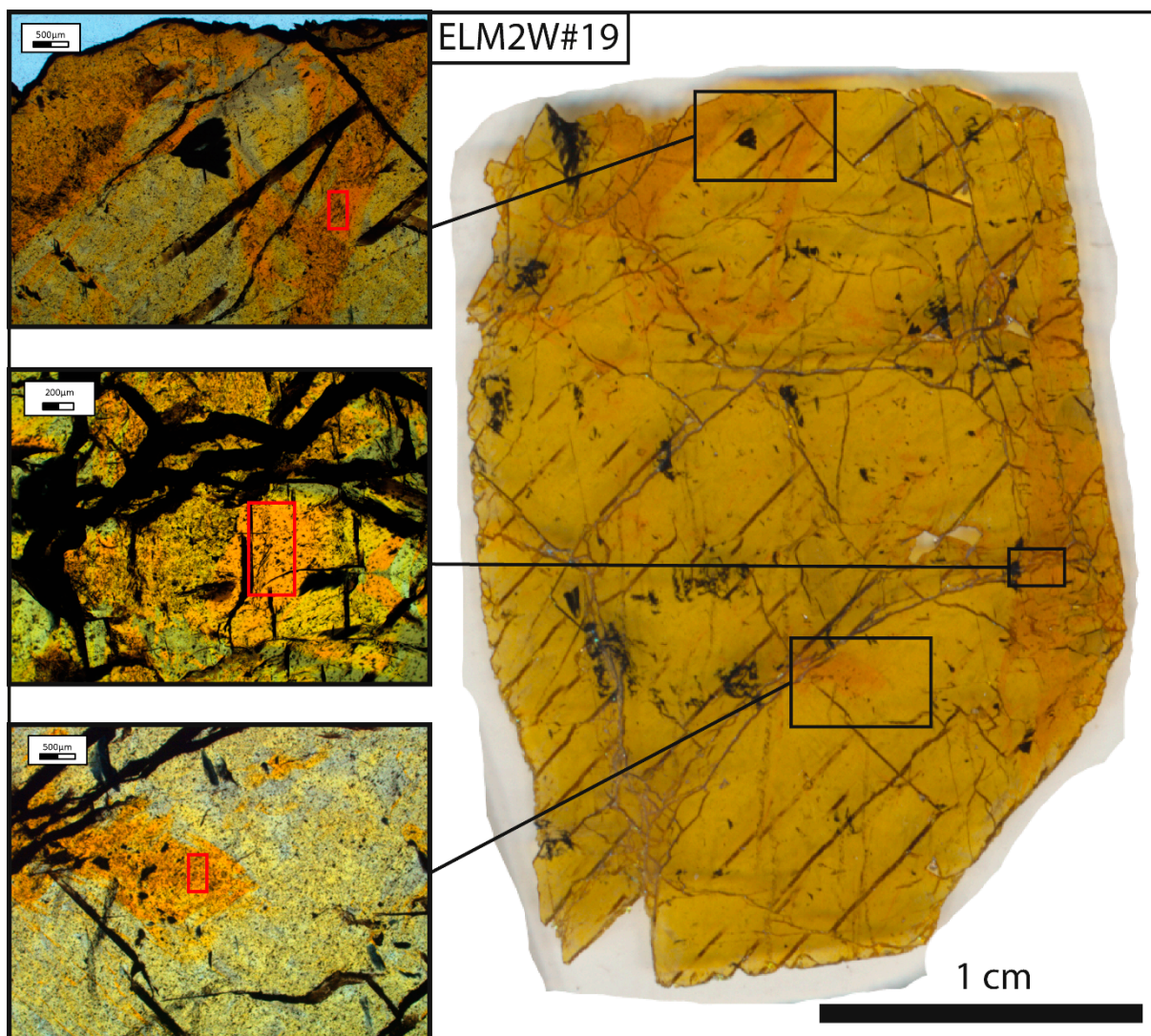


Figure S6. Transmitted light of ELM2W#19 sample (Reference used by mining companies) from Elmwood mine, Central Tennessee, USA. The sample doesn't have zonation at thin section scale, but at microscopic scale dark and light areas such as the sample CU51S#4N appear. The analysis zones (red rectangle) were carried out in dark bands with high Ge, Ga and Cu concentration.

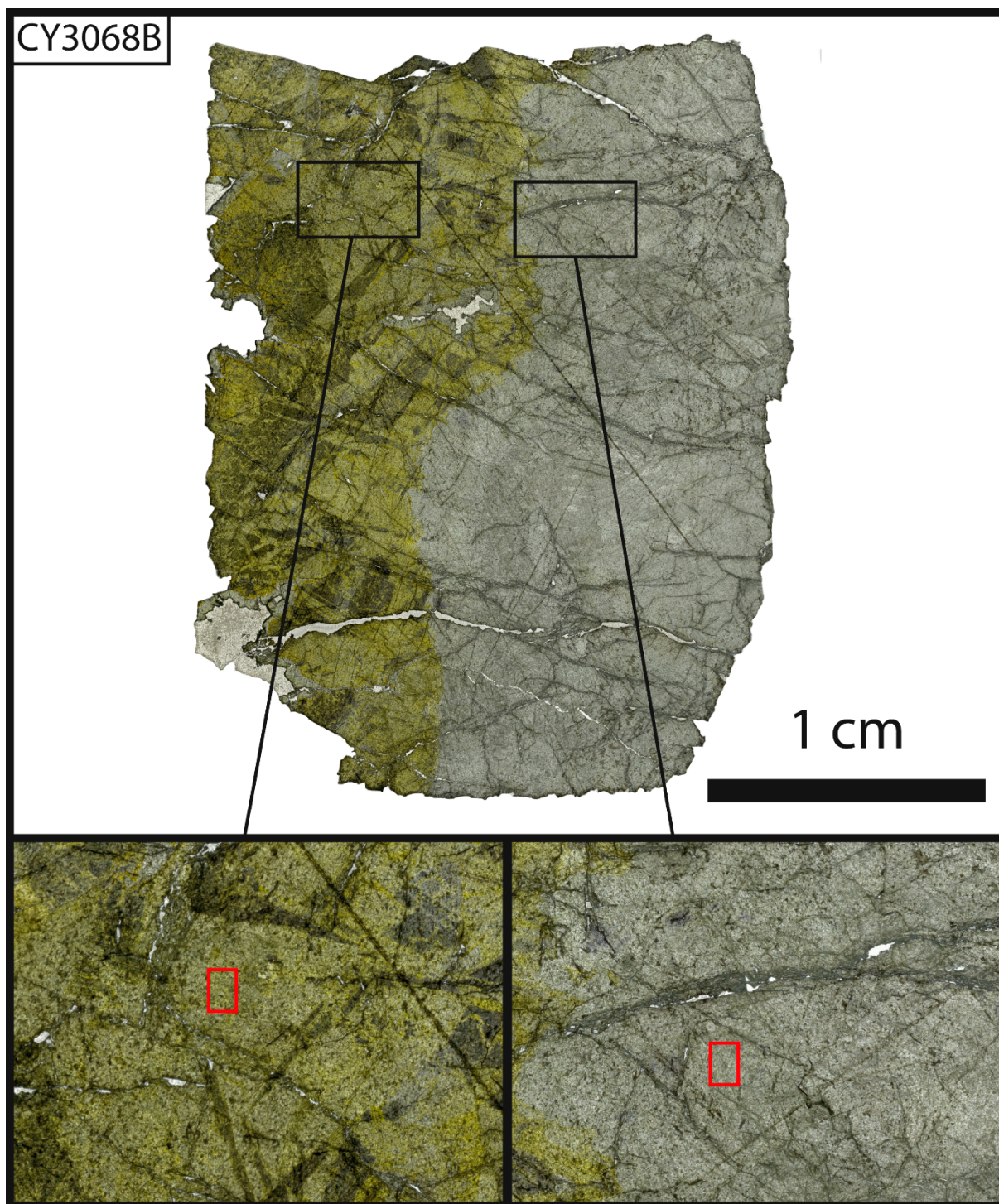


Figure S7. Transmitted light of CY3068B sample (Reference used by mining companies) from Coy mine, East Tennessee, USA. The sample is divided in two parts: a first part to the left with a brown sphalerite and a second part to the right with a light sphalerite. The brown sphalerites are rich in Fe, Cd and Ge while the light sphalerites are poorer in Fe with some Cd. Several analysis zones (red rectangle) were carried out in brown and light sphalerites. The reference spectra at 11112 eV was acquired in the exact zone marked by the red rectangle in the light sphalerite. This zone has been fully analyzed in high-resolution SEM images to try to find  $\text{GeO}_2$  inclusions. Some SEM images are presented in figure 8. The location of SEM images is reported with the letters a, b, c, d, e, and f.