***Supplementary information for:***

**GROWTH AND STABILITY OF STRATIFORM CARROLLITE (CuCo2S4) IN THE TENKE-FUNGURUME ORE DISTRICT, CENTRAL AFRICAN COPPERBELT**

Bjorn P VON DER HEYDEN§

*Department of Earth Sciences, Stellenbosch University, Private Bag X1, Matieland 7602, South Africa*

Jeffrey DICK

*Key Laboratory of Metallogenic Prediction of Nonferrous Metals and Geological Environment Monitoring of Ministry of Education, School of Geosciences and Info-Physics, Central South University, Changsha, China*

Ryan C ROSENFELS and Luke CARLTON

*Department of Earth Sciences, Stellenbosch University, Private Bag X1, Matieland 7602, South Africa*

Kristina LILOVA, Alexandra NAVROTSKY, and Tamilarasan SUBRAMANI

*School of Molecular Sciences and Center for Materials of the Universe, Arizona State University, Tempe AZ 85287, USA*

Brian F. WOODFIELD, and Alexis GIBSON

*Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602, USA.*

The supplementary information for the present contribution (von der Heyden et al. 2023) comprises two software files and four additional figures, all related to the modelling aspects of the work.

**SI 1** is a zip folder containing all the CHNOSZ 2.0.0. code required to accurately model the Cu-Co-S-O Cu-Fe-S-O thermodynamic systems, with the inclusion of new thermodynamic data for carrollite.

Similarly, **SI 2** is a zip folder containing the Leapfrog model for visualising the mineral stability diagrams in three dimensional space, viz. pH-log*f*O2-temperature and pH-log*f*O2-sulphur activity. The models can be viewed and investigated using the free version of Leapfrog (Leapfrog Viewer: [https://www.seequent.com/products-solutions/leapfrog-viewer/).](https://www.seequent.com/products-solutions/leapfrog-viewer/).%20) For ease of viewing, the colour scheme and transparency of the respective minerals’ stability fields are easily changed within this software. These models should be regarded as being semi-quantitative on account of the interpolation assumptions employed during implicit modelling in Leapfrog. For more accurate results, modelling should preferably be conducted using the CHNOSZ package.

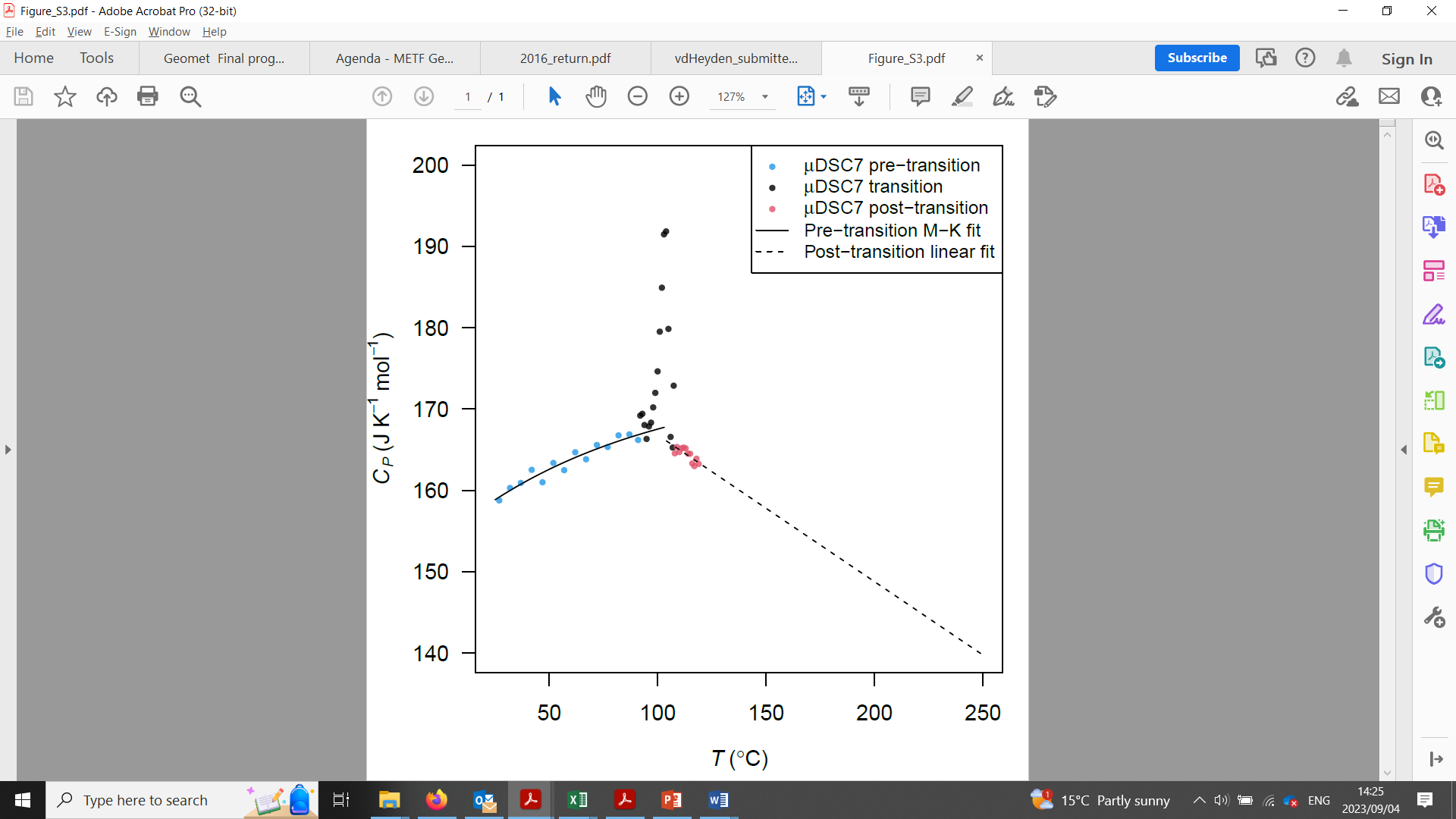
Figures **SI 3** and **SI 4** detail some of the extrapolations required to develop the input dataset (main text- Table 1) that is used to conduct all subsequent modelling.

Figures **SI 5** and **SI 6** respectively provide additional tests to highlight the temperature-dependent stability of carrollite, and that the solubility contours for Cu and Co are not significantly impacted by incorporation of carrollite data into the thermodynamic database.

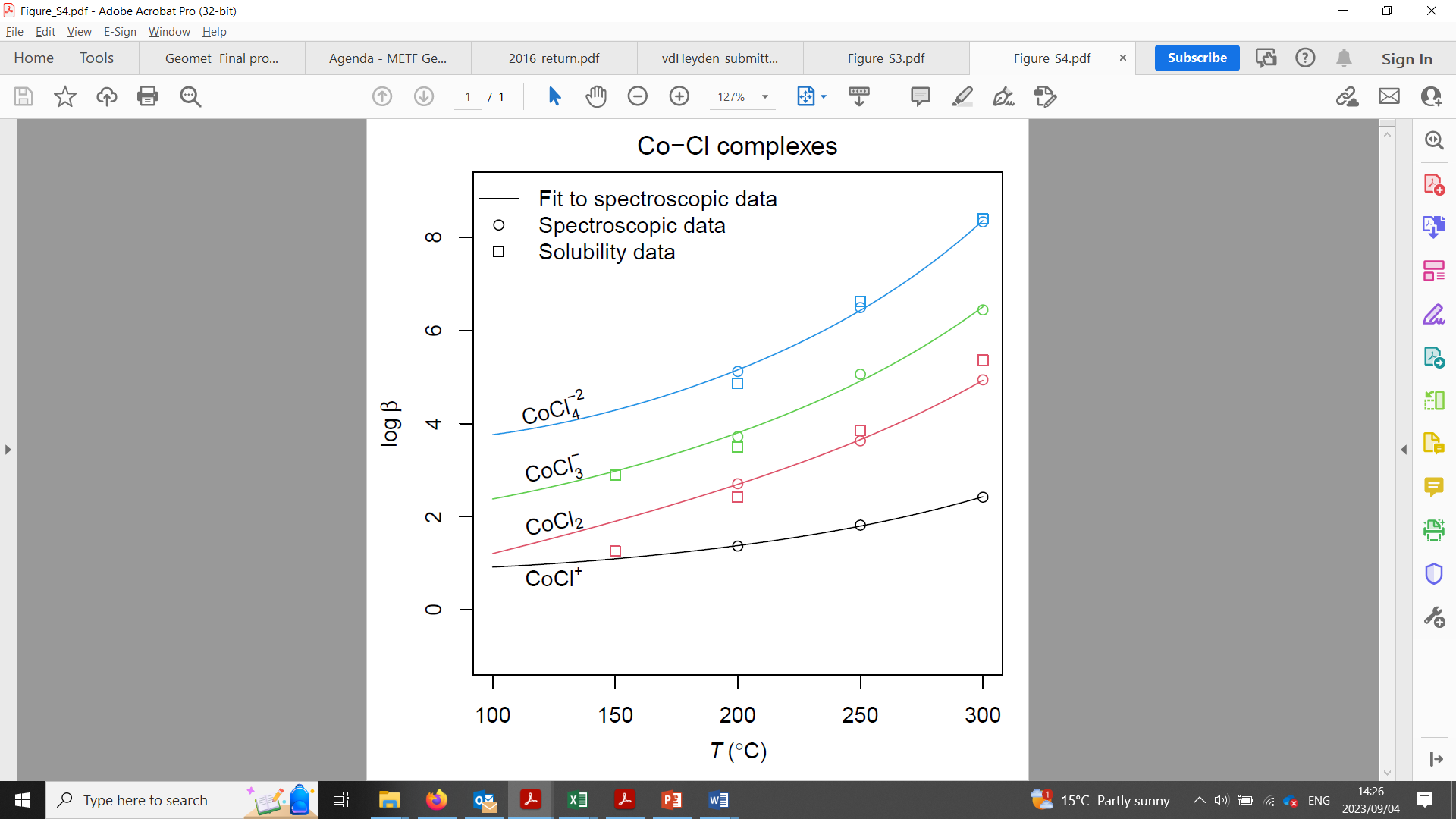
**SI 1:** Hyperlink to zip file with full code for CHNOSZ model

**SI 2:** Hyperlink to zip file containing the Leapfrog model for easy visualisation of thermodynamic data in 3D space.

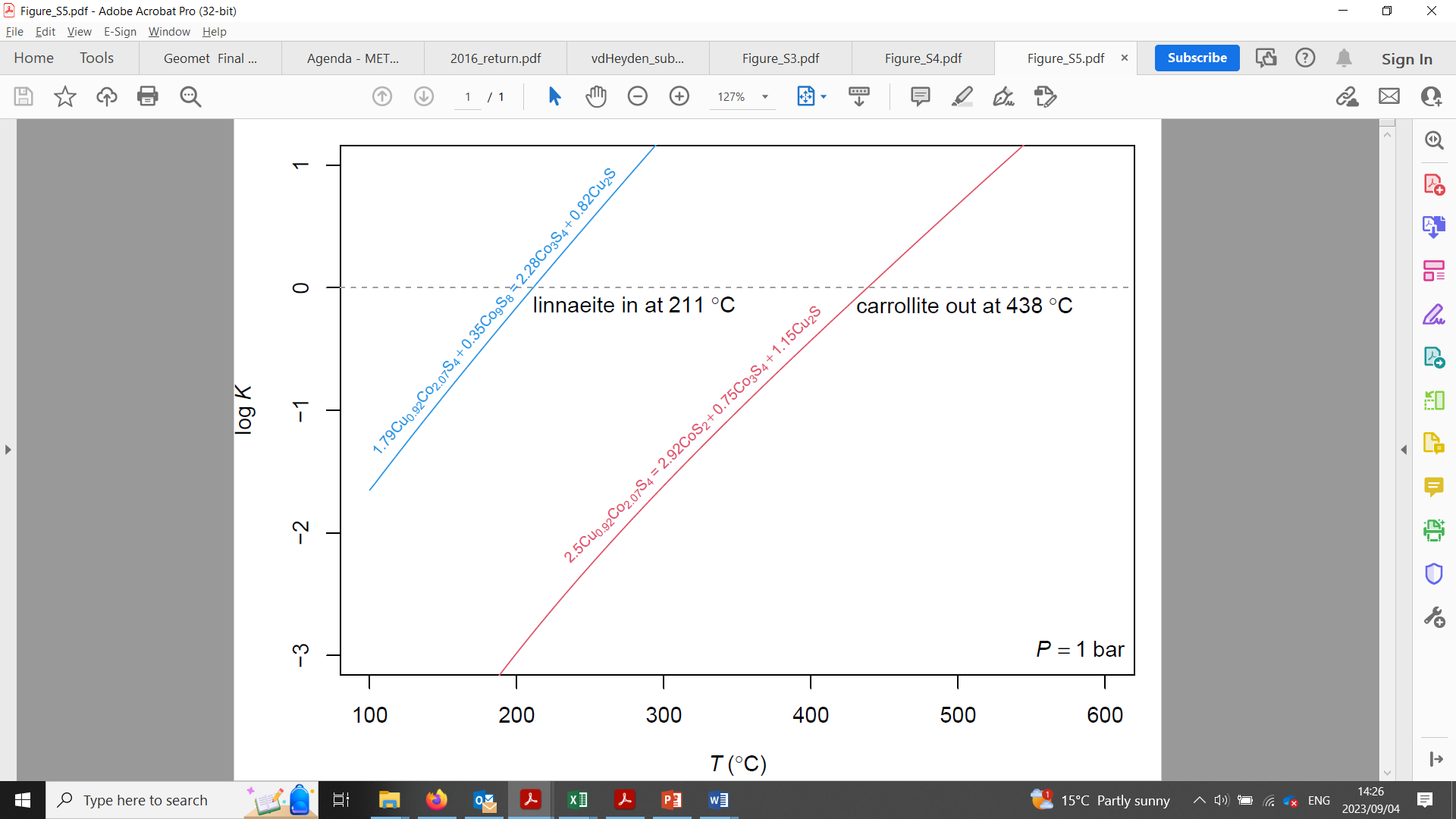
**SI 3:** Experimental Cp data of carrollite obtained from the μDSC7 instrument at Arizona State University. The peak represents a structural transition within the carrollite sample. Pre-transition and post-transition data were fit using the Maier-Kelley equation and a linear equation, respectively.



**SI 4:** Experimental and fitted values of formation constants for Co chloride complexes. Experimental values are from Migdisov et al. (2011); only spectroscopic data (available for 200, 250, and 300 °C) were used in the fits. Extrapolations to 150 °C were used for Fig. 5 in the main text.



**SI 5:** Stability relations of linnaeite and carrollite. Comparison of the panels in Fig. 5 (main text) indicates that with increasing temperature, linnaeite becomes stable with respect to carrollite and Co-pentlandite, and at even higher temperature, carrollite becomes unstable with respect to cattierite and linnaeite; all reactions take place in the stability field of chalcocite. Values of log*K* for those reactions are shown in this plot in order to quantify the stability relations as a function of temperature.



**SI 6:** Effect of carrollite on (a) Co and (b) Cu solubility. Because of a technical limitation of CHNOSZ, the solubility contours shown in Fig. 5 were calculated for single-metal systems excluding carrollite. This diagram shows single solubility contours (10−5 mol/kg) for Co and Cu that are overlaid on “mixed diagrams” representing the stability boundaries of minerals and aqueous species for a fixed molality of aqueous species, chosen here to be equal to the solubility contour. For Co, the boundary between carrollite and CoCl4−2 protrudes just beyond the blue solubility contour, indicating that the presence of carrollite would produce slightly lower solubility in that area. For Cu, carrollite has no boundary with an aqueous species, indicating that carrollite would have no effect on the solubility contours for Co at this molality (10−5 mol/kg). According to these calculations, the limitation that carrollite is excluded from the solubility contours in Fig. 5 has an almost negligible effect on their appearance.

