Modelling of size-dependent thermodynamic properties of metallic nanocrystals based on modified Gibbs–Thomson equation

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Abstract
In this paper, a new theoretical two-phase (solid–liquid) type model of melting temperature has developed based on the modified Gibbs–Thomson equation. Further, it is extended to derive other different size-dependent thermodynamic properties such as cohesive energy, Debye temperature, specific heat capacity, the thermal and electrical conductivity of metallic nanoparticles. Quantitative calculation of the effect of size on thermodynamic properties resulted in, varying linearly with the inverse of characteristic length of nanomaterials. The models are applied to Al, Pb, Ag, Sn, Mo, W, Co, Au and Cu nanoparticles of spherical shape. The melting temperature, Debye temperature, thermal and electrical conductivity are found to decrease with the decrease in particle size, whereas the cohesive energy and specific heat capacity are increased with the decrease in particle size. The present model is also compared with previous models and found consistent. The results obtained with this model validated with experimental and simulation results from several sources that show similar trends between the model and experimental results.

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1 Introduction

The size of the crystal plays a major role in nanoscience and nanotechnology. By definition, a material having a size of less than 100 nm is known as nanomaterial [1, 2]. The crystal of these sizes contains as few as thousands of atoms and having remarkable and valuable characteristics. The size and shape-dependent chemo-physical characteristics of nanomaterials enabling them broadly useful in different application areas [3–9]. Nanomaterials have a large specific surface area, and the surface effect is significant which is generally insignificant for bulk materials [10].

The classical thermodynamics for the bulk material is not completely valid for nanomaterials. Further, for designing a material system based on nanomaterials, a good understanding of fundamental thermodynamic properties is required. These basic thermodynamic properties include melting temperature, boiling temperature, cohesive energy, enthalpy and entropy of melting, elastic moduli, specific heat capacity, etc. Good knowledge of these thermodynamic properties enables us to utilize them for further new applications.

In the last decade, there have been significant theoretical and experimental studies in the study of the specific properties of nanomaterials and many promising results have been obtained [11–14]. In addition, the invention of quantum theory helps us to measure the thermodynamic properties using supercomputers [15, 16]. However, there is still a requirement to understand and develop the thermodynamic properties of nanomaterials by semi-empirical methods, which are broadly useful in materials research.

Hitherto, various size dependence melting temperature analytical models have been reported, can be categorized as either one-phase [17–28] or two-phase type [29–36]. The one-phase models fail to account for the discontinuous, first-order character of the melting transition, as we do not know anything about solid to liquid states because it involves characteristics of only one of the two phases coexisting at melting, i.e. the solid-phase alone, with no separate description of the liquid-phase. However, two-phase models consider both phases, solid as well as the liquid phases [37].

Kaptay G. (2012) modified the Gibbs–Thomson equation (previously based on Kelvin equation) and clearly

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stated that the difference in the behaviour of nano-system compared to macro-system is due to their high specific surface area (due to Gibbs) and not to the high curvature of their interface (due to Kelvin). This equation (melting temperature of nanocrystals) gives us a new insight to look into other size-dependent thermodynamic properties by giving new material parameters (thermodynamic) in all the equations for size-dependent properties [38, 39].

In the present work, a new analytical model of melting temperature has been developed based on the modified Gibbs–Thomson equation and compared with both type one-phase and two-phase model to confirm the consistency of the previous trends. Further, it is extended to derive other different size-dependent thermodynamic properties such as cohesive energy, melting temperature, Debye temperature and specific heat capacity, the thermal and electrical conductivity of metallic nanoparticles. The present model predictions are compared with several sources including both experimental and theoretical results.

### 2 Results and discussion

#### 2.1 Melting temperature

The dependence of melting temperature on the size of nanomaterials has been already proven both experimentally as well as theoretically [11, 12, 25, 40–46]. Depression of the melting temperature exists for almost all free nanoparticles [40–42]. Thermodynamic models were revised to understand how free nanoparticles melt and overheat [11, 12, 25, 46]. Kaptay G. (2012) reported the modified Gibbs–Thomson equation for size dependence of melting temperature of nanocrystals. The modified Gibbs–Thomson equation analogue with Gibbs (not Kelvin) the size-dependent of melting temperature of metallic nanocrystals can be derived [38].

Let us consider a pure metallic solid situated in a large liquid of the same composition. From the general condition of equilibrium between one component of solid and its liquid

\[ G^s_m = G^l_m \]  \hspace{1cm} (1)

where \( G^s_m \) term is used for molar standard Gibbs free energy for phases (\( \Phi = s(\text{solid}) \) and \( \Phi = l(\text{liquid}) \)).

Writing Gibbs free energy in terms of molar standard enthalpy and entropy,

\[ H^s_m - T_m S^s_m = H^l_m - T_m S^l_m \] \hspace{1cm} (2)

or

\[ T_m \Delta m S^s_m = \Delta m H^s_m \] \hspace{1cm} (3)

or melting temperature for the bulk metal phase,

\[ T_{mb} = \frac{\Delta_m H^s_m}{\Delta_m S^s_m} \] \hspace{1cm} (4)

Now, for nanophase, the melt equilibrium can be written as,

\[ G^s_m + A_{sp,s} V_m l_g = G^l_m + A_{sp,l} V_m l_g \] \hspace{1cm} (5)

This extra energy is due to high surface area of nanocrystals, where \( A_{sp} \) are specific area and molar volume for phases (\( \Phi = s(\text{solid}) \) and \( \Phi = l(\text{liquid}) \)) and \( l_g \) are surface energy of solid and surface tension of liquid, respectively,

\[ H^{s,s}_m - T_m S^{s,l}_m + A_{sp,s} V_m l_g = H^{l,l}_m - T_m S^{l,l}_m + A_{sp,l} V_m l_g \] \hspace{1cm} (6)

If \( A_{sp,s} = A_{sp,l} \) and \( V_m,l = V_m \)

\[ T_{mn} = \left( \frac{\Delta_m H^s_m}{\Delta_m S^s_m} - \frac{A_{sp} V_m (l_g - s_g)}{\Delta_m S^s_m} \right) \] \hspace{1cm} (7)

By using equation (4)

\[ T_{mn} = \left( T_{mb} - \frac{A_{sp} V_m (l_g - s_g)}{\Delta_m S^s_m} \right) \] \hspace{1cm} or

\[ T_{mn} = T_{mb} \left( 1 - \frac{A_{sp} V_m (l_g - s_g)}{\Delta_m H^s_m} \right) \] \hspace{1cm} (8)

For spherical nanoparticles sp. surface area \( A_{sp} \) is \( 6/D \), where \( D \) is the diameter of particles.

\[ T_{mn(sphere)} = T_{mb} \left( 1 - \frac{6V_m (l_g - s_g)}{D \Delta_m H^s_m} \right) \] \hspace{1cm} (9)

It is clear from Eq. (8) that the approach to determining \( T_{mn} \) is to obtain the expression \( \frac{A_{sp} V_m (l_g - s_g)}{\Delta_m H^s_m} \), which depends not only on nanocrystals size but also on the shape because the specific surface area is different for different-shaped crystals. Further, for spherical nanoparticles, obtained Eq. (9) is found in accord with most of the thermodynamic models, the melting temperature changes linearly with the reciprocal of particle size. In other words, the melting temperature of nanomaterials changes linearly with 1/D. On comparing the generalized model for melting temperature reported by Qi WH [24], we found new material parameter \( \frac{A_{sp} V_m (l_g - s_g)}{\Delta_m H^s_m} \) in spite of N/2n.

Figure 1 is the dependence of melting temperature on the size of spherical Al, Pb, Ag and Sn nanoparticles in terms
of Eq. (9). From Fig. 1a, b, c and d, it is clear that the present model is in a similar trend with the previously reported model based on one-phase [24] and two-phase model [22]. The decrease in the melting temperature of nanoparticles is only noticeable below 100 nm. When the size of the particle is greater than 100 nm, the melting temperature of the particles is about the same as the corresponding bulk crystals or we can say, the melting temperature becomes independent of the size of nanoparticles. The experimental results in Fig. 1(a) are of three forms, Al / H, Al / O and Al / Ar, which are nothing but milling gas environments as hydrogen (H), oxygen (O) and argon (Ar) in aluminium nanoparticles preparation, respectively. The experimental data clearly support the prediction [41, 42, 47, 48]. Melting temperature varies gradually with the variation of size, and the curves are nearly horizontal for D = 80 nm. However, on the contrary, the size effect is very distinct in the range of D = 10 nm. The melting temperature rapidly decreases with a slight reduction in particle size. From equation (9), if the particle size is fairly large, i.e. $\frac{\Delta mH}{D} \gg 1$, then $T_m$ $\approx T_{mb}$. The present model can provide accurate predictions for Al, Ag and Sn nanoparticles on the melting temperature within the full-size range, while for Pb nanoparticles, a little variation is noted.

2.2 Cohesive energy

Cohesion energy (or binding energy) is a fundamental energetic property of metals that affects most of their other physical properties. Solid and liquid metals cohesion energy is the energy binding atoms in solid and/or liquid state [49]. From the classical model, bulk cohesive energy can be given as:

$$\Delta U_{s-l, T_m} = \int_{0K}^{T_m} C_{p,s}dT + \Delta mH$$

(10)

where $C_{p,s}$ is the isobaric heat capacity of solid, $\Delta mH$ is the enthalpy of melting of the metal at its melting point.

or [49]

$$\Delta_b U_{s-l, T_m} = C_{p,s} T_m + \Delta mH_m^*$$

(11)
Using equation (4)
\[ \Delta_b U_{s-l,Tm} = C_{p,s} T_{m_b} + T_{m_b} \Delta m S_m \]  \hspace{1cm} (12)

or
\[ \Delta_b U_{s-l,Tm} = T_{m_b} (C_{p,s} + \Delta m S_m) \]

For a nanophase,
\[ \Delta_n U_{s-l,Tm} = T_{m_n} (C_{p,s} + \Delta m S_m) \]  \hspace{1cm} (13)

Using equation (8), we get
\[ \Delta_n U_{s-l,Tm} = \left( C_{p,s} + \Delta m S_m \right) T_{m_n} \left( 1 - \frac{A_{sp} V_m (\gamma_{sg} - \gamma_{lg})}{\Delta m H_m^l} \right) \]

\[ \Delta_n U_{s-l,Tm} = \Delta_b U_{s-l,Tm} \left( 1 - \frac{A_{sp} V_m (\gamma_{sg} - \gamma_{lg})}{\Delta m H_m^l} \right) \]

If \( \Delta_n U_{s-l,Tm} = U_n \) and \( \Delta_b U_{s-l,Tm} = U_b \), then
\[ U_n = U_b \left( 1 - \frac{A_{sp} V_m (\gamma_{sg} - \gamma_{lg})}{\Delta m H_m^l} \right) \]  \hspace{1cm} (14)

For spherical nanoparticles
\[ U_n = U_b \left( 1 - \frac{6V_m (\gamma_{sg} - \gamma_{lg})}{D \Delta m H_m^l} \right) \]  \hspace{1cm} (15)

The value of cohesive energy is calculated using Eq. (15) for spherical nanoparticles. Input parameters required for the calculation are given in Tables 1 and 2. The size dependence of cohesive energy for Mo and W nanoparticles is shown in Fig. 2. It is seen that the cohesive energy for both Mo and W nanoparticles decreases on increasing the particle size. The results of Eq. (15) are compared with experimental results [50]. It is noted that our model predictions are consistent in terms of trend and experimental values, with the exception of the value for W nanoparticles at 1 nm and arising from the fact that our model deals not only with the size but also the shape of nanocrystals. The current prediction for Mo nanoparticles is also compared with the results of the model reported by Qi [24, 51]. There is reasonably good agreement between theory and experiment, and present model prediction is more accurate than the one-phase model [24, 51]. This difference in the two models is because of the fact that our model is based on energy rather than the number of atoms which makes it more detailed and practical.

Fig. 2 Dependence of cohesive energy on the size of spherical Mo and W nanoparticles in terms of Eq. (15). Grey sphere shows results for Mo of model reported by Qi [24, 51] and solid blue and red circle represent experimental data for Mo and W, respectively [50]. The atomic radius for Mo is 162 pm [52]. The input parameter for Mo and W is given in Tables 1 and 2

2.3 Debye temperature

The Debye temperature is directly linked to the binding force between atoms and strongly dependent on materials structure [53]. It is an essential thermodynamic property because it provides fundamental knowledge to understand other series of thermodynamic properties, such as specific heat capacity, lattice vibration [54] vibrational entropy, Helmholtz free energy [55] and thermal conductivity. According to Lindemann Criterion of melting, the relationship between melting temperature and Debye temperature of bulk metals can be defined as follows [56]:
\[ \theta_{D_b} = c \left( \frac{T_{m_b}}{MV^{2/3}} \right)^{1/2} \]  \hspace{1cm} (16)

where c is a constant, M is molecular mass, \( T_{m_b} \) is bulk melting point, and V is the volume per atom. From Eq. (16), the Debye temperature for bulk is directly proportional to the square root of the melting temperature \( \theta_{D_b} \propto T_{m_b}^{1/2} \)

Similarly, for a nanophase, Debye temperature can be written as,
\[ \theta_{D_n} \propto T_{m_n}^{1/2} \]

or [57]
\[ \frac{\theta_{D_n}}{\theta_{D_b}} = \left( \frac{T_{m_n}}{T_{m_b}} \right)^{1/2} \]

Using Eq. (8) we get,
For spherical NPs, the Debye temperature is in proportion to the square root of melting temperature and Eq. (19) demonstrates the size effect on the Debye temperature. Comparisons between the model result from Eq. (19) and the available experimental results for the Debye temperature of Co, Au and Sn nanoparticles are shown in Fig. 3. It clearly indicates the depression of the Debye temperature of nanoparticles with particle size. Moreover, the curve is smoother than that of the melting temperature in the small size range, showing that the rate of depression with the size is smaller compared to the melting temperature. In the large-diameter range approx. (> 10 nm), the Debye temperature independent of the size and equals the bulk value.

2.4 Thermal conductivity

As we already mentioned in previous Sect. 2.3 that thermal conductivity is also related to Debye temperature. Thus, thermal conductivity for nanoparticles can be calculated from the size-dependent Debye temperature. According to kinetic theory equation [61], the thermal conductivity ($K_b$) of metals (bulk) can be expressed as [61]:

$$K_b = \frac{1}{3}c v_b \lambda_b$$  \hspace{1cm} (20)

where $c$ is the specific heat, $v_b$ is the average phonon velocity, and $\lambda_b$ is the mean free path.

Similarly, for nanophase thermal conductivity

$$K_n \propto v_b \lambda_n$$  \hspace{1cm} (21)

By combining Eq. (21) and (22),

$$\frac{K_n}{K_b} = \frac{v_n \lambda_n}{v_b \lambda_b}$$  \hspace{1cm} (22)

The relation between Debye temperature and average phonon velocity of bulk crystal [62], can be expressed as

$$\theta_{D_n} = \theta_{D_b} \left(1 - \frac{6 V_m (\gamma_g - \gamma_l)}{D \Delta_m H'_m}\right)^{1/2}$$  \hspace{1cm} (19)

or

$$\frac{\theta_{D_n}}{\theta_{D_b}} = \frac{v_n}{v_b}$$  \hspace{1cm} (26)

from Eq. (17)

$$\theta_{D_n} = \left(\frac{T_{m_n}}{T_{m_b}}\right)^{1/2} = \left(1 - \frac{A_{sp} V_m (\gamma_g - \gamma_l)}{\Delta_m H'_m}\right)^{1/2}$$  \hspace{1cm} (27)

The relation between mean free path ($\lambda$) and melting temperature [57] can be given as,

$$\frac{\lambda_n}{\lambda_b} = \left(\frac{T_{m_n}}{T_{m_b}}\right)$$  \hspace{1cm} (28)

or

$$\frac{K_n}{K_b} = \frac{v_n \lambda_n}{v_b \lambda_b} = \left(\frac{T_{m_n}}{T_{m_b}}\right)^{3/2}$$  \hspace{1cm} (29)

Now, using Eq. (8), we get,

$$K_n = K_b \left(1 - \frac{A_{sp} V_m (\gamma_g - \gamma_l)}{\Delta_m H'_m}\right)^{3/2}$$  \hspace{1cm} (30)

For spherical metal nanoparticles,
Prediction of the present model along with experimental results for Ag nanoparticles is shown in Fig. 4. It is found that our results are slightly varied in comparison to the results obtained by [63], but it almost agrees with experimental data.

2.5 Electrical conductivity

We know that thermal conductivity and electrical conductivity have a linear relationship based on the Wiedemann–Franz ratio, with $K/e\sigma$ is proportional to the absolute temperature $T$ [64, 65]. From this relationship, for the same temperature, electrical and thermal conductivity will be proportional. On a nanometer scale, thermal conductivity tends to decrease with decreasing size [63, 65].

From Wiedemann–Franz law for bulk metals at a high constant temperature $T$ [65].

$$\frac{K_n}{\sigma_n} = \frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2 T$$  \hspace{1cm} (31)

where $K_b$ is bulk thermal conductivity (W/m$\cdot$K), $\sigma_b$ is bulk electrical conductivity (Ω-m)$^{-1}$ and $\frac{\pi^2}{3} \left( \frac{k_B}{e} \right)^2 = L$ is Lorentz number (2.3×10$^{-8}$ W·ohm/$\sigma$·K$^2$).

$$\sigma_b \propto K_b$$  \hspace{1cm} (33)

Similarly, for the nanophase

$$\sigma_n \propto K_n$$  \hspace{1cm} (34)

or

$$\frac{\sigma_n}{\sigma_b} = \frac{K_n}{K_b}$$  \hspace{1cm} (35)

By using Eq. (29),

$$\sigma_n = \sigma_b \left( 1 - \frac{A_{sp} V_m (\gamma_{sg} - \gamma_{lg})}{\Delta m H_m^\circ} \right)^{3/2}$$  \hspace{1cm} (36)

For the spherical nanoparticles,

$$\sigma_n = \sigma_b \left( 1 - \frac{6V_m (\gamma_{sg} - \gamma_{lg})}{\Delta m H_m^\circ} \right)^{3/2}$$  \hspace{1cm} (37)

Prediction of the present model (38) for Cu along with experimental results is shown in Fig. 5. These results were validated with experimental results from several sources such as Yuliza et al. (2015) [66] based on the kinetic theory of the electron and show similar trends between the model and experimental results.

2.6 Specific heat capacity

The definition of specific heat capacity of the material (solid or liquid) is the heat required to raise one degree of the temperature of a unit mass of material. In the bulk phase, the specific heat capacity only depends on the temperature, not on the size. While in the nanophase, the surface effects cause the specific heat capacity of the material to vary from the bulk. As we already mentioned in Sect. 2.3 that the specific heat capacity is also related to Debye temperature. According to Debye’s theory [68], isobaric specific heat and the Debye temperature of the bulk material can be related as [69].
Similarly, for a nanomaterial,

\[ C_{P_n} \propto \theta_{D_n}^2 \tag{38} \]

From Eq. (38) and (39),

\[ \frac{C_{P_n}}{C_{P_b}} = \frac{T_{m_b}}{T_{m_n}} \tag{40} \]

Using Eq. (8), we get

\[ C_{P_n} = C_{P_b} \left( 1 - \frac{\Delta m H_m^\circ}{\Delta m H_m^\circ} \right)^{-1} \tag{41} \]

For spherical nanoparticles,

\[ C_{P_n} = C_{P_b} \left( 1 - \frac{6V_m(y_{sg} - y_{lg})}{D\Delta m H_m^\circ} \right)^{-1} \tag{42} \]

This is the relationship of the isobaric specific heat for nanomaterials and bulk materials at different shapes and sizes. The size dependence of isobaric specific heat capacity for Ag nanoparticles along with the results of the model [14] and experimental data [70] is plotted in Fig. 6. It is reported by Rupp et al. [71] that the specific heat increases with decreasing size of the nanocrystal, showing the specific heat capacity varies inversely with the particle size. The main reason for the elevated specific heat at a small scale is the large atomic thermal vibration energies of the surface atoms. Further, it is also reported by Sun [11, 23, 72–74] that the vibrational amplitude of the surface atoms is larger for nanosolids than that of bulk materials, resulting in the higher vibrational energy of the surface atoms.

\[ C_{P_n} \propto \theta_{D_n}^2 \]

\[ C_{P_n} \propto \theta_{D_n}^2 \]

\[ \frac{C_{P_n}}{C_{P_b}} = \frac{T_{m_b}}{T_{m_n}} \]

Using Eq. (8), we get

\[ C_{P_n} = C_{P_b} \left( 1 - \frac{\Delta m H_m^\circ}{\Delta m H_m^\circ} \right)^{-1} \]

For spherical nanoparticles,

\[ C_{P_n} = C_{P_b} \left( 1 - \frac{6V_m(y_{sg} - y_{lg})}{D\Delta m H_m^\circ} \right)^{-1} \]

\[ \Delta m H_m^\circ \]

\[ \Delta m G_m^\circ \]

\[ \Delta m H_m^\circ \]

The melting temperature, Debye temperature, thermal and electrical conductivity are found to decrease with the decrease in particle size, whereas the cohesive energy and specific heat capacity are increased with the decrease in particle size.

\[ \Delta m G_m^\circ \]

\[ \Delta m H_m^\circ \]

\[ \Delta m G_m^\circ \]

\[ \Delta m H_m^\circ \]

The output results of present model for size-dependent thermodynamic properties of metallic nanoparticles (spherical) have found in the same trends with previous models and experimental results.

\[ \Delta m G_m^\circ \]

\[ \Delta m H_m^\circ \]

\[ \Delta m G_m^\circ \]

\[ \Delta m H_m^\circ \]

The consistency of the new model equation is also proving an old ambiguous and contradictory question that the high surface area of nanomaterials is responsible for the difference in most properties as compared to the bulk phase rather high curvature of their interface (due to Kelvin).

\[ \Delta m G_m^\circ \]

\[ \Delta m H_m^\circ \]

\[ \Delta m G_m^\circ \]

\[ \Delta m H_m^\circ \]

The current model has the potential to be applied for various size-dependent thermodynamic properties of nanophase materials.

\[ \Delta m G_m^\circ \]

\[ \Delta m H_m^\circ \]

\[ \Delta m G_m^\circ \]

\[ \Delta m H_m^\circ \]

\[ \Delta m G_m^\circ \]

\[ \Delta m H_m^\circ \]

\[ \Delta m G_m^\circ \]

\[ \Delta m H_m^\circ \]

Fig. 6 Dependence of specific heat capacity on the size of spherical Ag nanoparticles in terms of Eq. (42). The grey sphere represents the results of the model reported by Xiong et al. (2011) [14], red and pink sphere represent experimental data and simulation results at 1000 K and 600 K, respectively [70]. Input parameters for Ag nanoparticles are given in Tables 1 and 2.
Appendix A

Table 1  Bulk thermodynamic properties used in the models

| Element | Melting temperature (K) | Cohesive energy (kJ/mol) | Debye temperature (K) | Thermal conductivity (W/m–K) | Electrical conductivity (Ω·m)⁻¹ | Sp. heat capacity (J/mol·K) |
|---------|------------------------|--------------------------|-----------------------|-----------------------------|---------------------------------|-----------------------------|
| Al      | 933.25                 | –                        | –                     | –                           | –                               | –                           |
| Sn      | 505.06                 | –                        | –                     | –                           | –                               | –                           |
| Pb      | 600                    | –                        | –                     | –                           | –                               | –                           |
| Ag      | 1234                   | –                        | –                     | 175                         | –                               | –                           |
| Mo      | –                      | –                        | –                     | –                           | –                               | –                           |
| W       | –                      | –                        | –                     | –                           | –                               | –                           |
| Co      | –                      | –                        | –                     | –                           | –                               | –                           |
| Au      | –                      | –                        | –                     | –                           | –                               | –                           |
| Cu      | –                      | –                        | –                     | 9.8318*10⁶                  | –                               | –                           |

Table 2  Input parameters used in the models

| Element | Molar volume (V_m, cm³/mol) | Surface tension (γ_L, J/m²) | Surface energy (γ_sg, J/m²) | Enthalpy of fusion (Δ_h⁰_m, kJ/mole) |
|---------|-----------------------------|-----------------------------|-----------------------------|-----------------------------------|
| Al      | 10.0                        | 0.86                        | 1.143                       | 10.67                             |
| Sn      | 16.29                       | 0.565                       | 0.709                       | 6.25                              |
| Pb      | 18.26                       | 0.48                        | 0.593                       | 5.121                             |
| Ag      | 10.27                       | 0.92                        | 1.246                       | 11.3                              |
| Mo      | 9.38                        | 2.25                        | 3.0                         | 27.6                              |
| W       | 9.47                        | 2.5                         | 3.675                       | 35.2                              |
| Co      | 6.67                        | 1.928                       | 2.522                       | 15.2                              |
| Au      | 10.21                       | 1.13                        | 1.5                         | 12.7                              |
| Cu      | 7.11                        | 1.35                        | 1.79                        | 13                                |

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Declaration

Data Availability Statement  The data that support the findings of this study are available from the corresponding author upon reasonable request.

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