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Material Value Chains

Thermodynamics of smelting WEEE

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Introduction

Understanding the thermodynamics of secondary copper smelting is the key to improving the smelting processes and recoveries of the present metals. The feed materials of secondary smelters originate mainly from Waste Electrical and Electronic Equipment (WEEE), which is a very complex waste fraction including high contents of different precious and hazardous metals. The recoveries of these minor elements are essential in terms of resource efficiency, safety issues and availability of several rare elements used in the modern electric and electronic industry.

Investigated systems with various techniques:

- Copper – slag equilibria with minor elements in spinel-saturation (Figure 1):
  - Ag, Au, Pd, Pt
  - Ge, Ga, In, Sn
  - Pb, Mo, Ir, Re
  - Ag, Au, Pd, Pt (silica-saturated)
- EMF measurements:
  - Ag-Pt
- Phase equilibria studies:
  - $PbO-Na_2O-SiO_2$
  - $TeO_2-Na_2O-SiO_2$
  - Na_2O-SiO_2
  - TeO_2-SiO_2

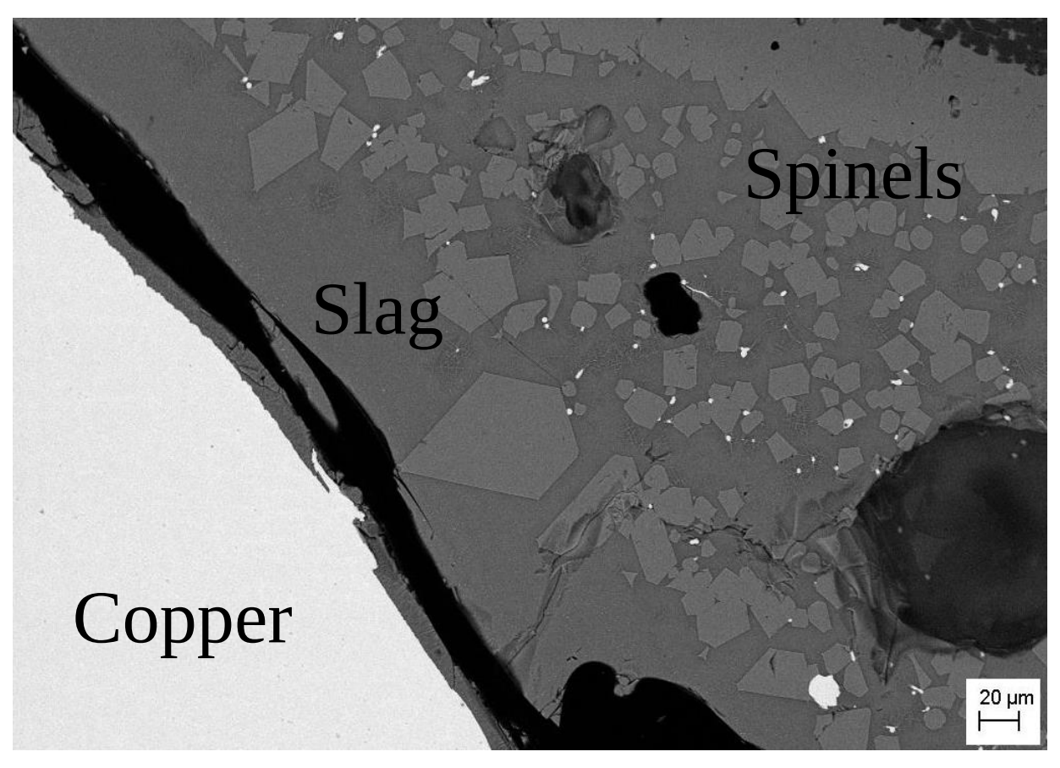

Figure 1. Microstructure of equilibrated-quenched Cu-slag-spinel system.

Experimental method

The experimental method with its critical stages is presented in Figure 2. The equilibration furnace is very versatile regarding temperature (0-1800 °C) and accurate gas control ($CO-CO_2-SO_2-Ar-N_2$). Thus, the used environment and the experimental method can be adjusted to simulate different industrial processes. The analyses are implemented with EPMA (Electro Probe Micro Analyzer) and if necessary with LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry). Our research group was the first one to apply laser to detect ultra low concentrations (ppb-level) of elements in metallurgical slags. Figure 3 presents laser-ablation craters in slag samples.

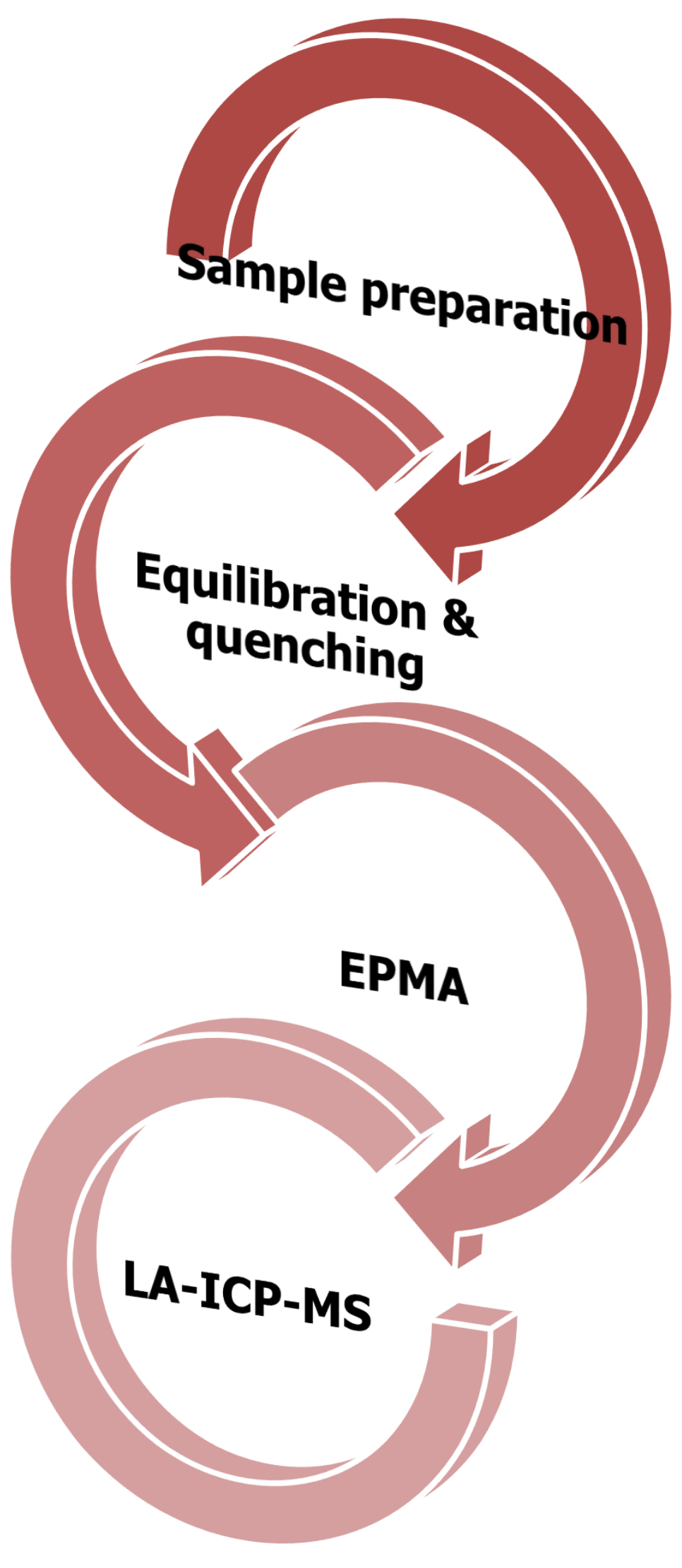

Figure 2. The experimental method.

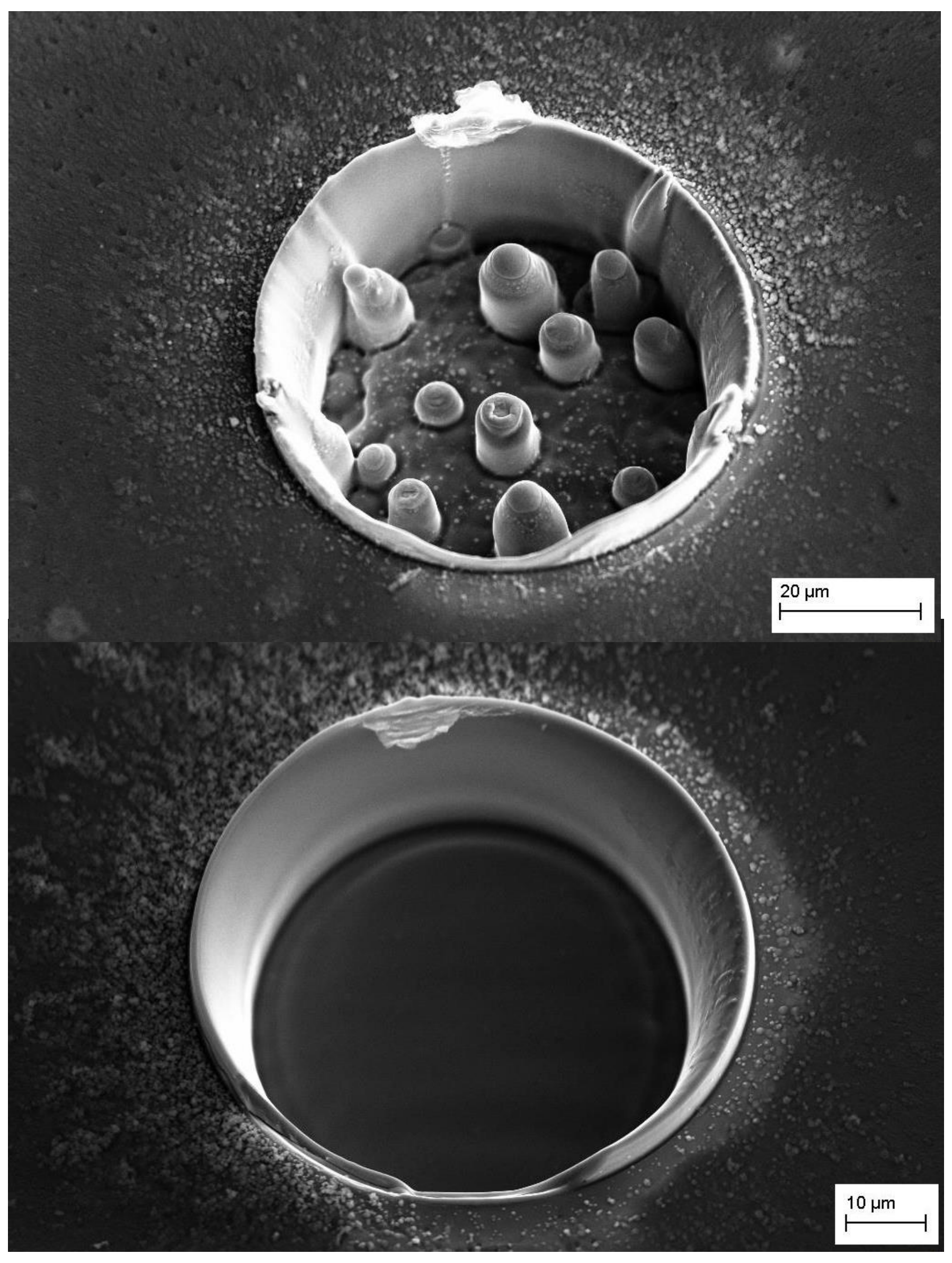

Figure 3. Laser-ablation craters on synthetic smelting slags with high (above figure) and low copper concentrations.

Results

Multiple experimental studies on minor element distributions between copper and $SiO_2-FeO_x-Al_2O_3-/CaO$ have been performed (Figure 4). These experimental studies were executed in simulated copper scrap smelting conditions with varying oxygen partial pressure of 10^{-10}–10^{-5} atm at 1300 °C. Two type of slags related to copper scrap smelting were investigated: alumina-saturated iron-silicate slag and ferrous-calcium-silicate slag.

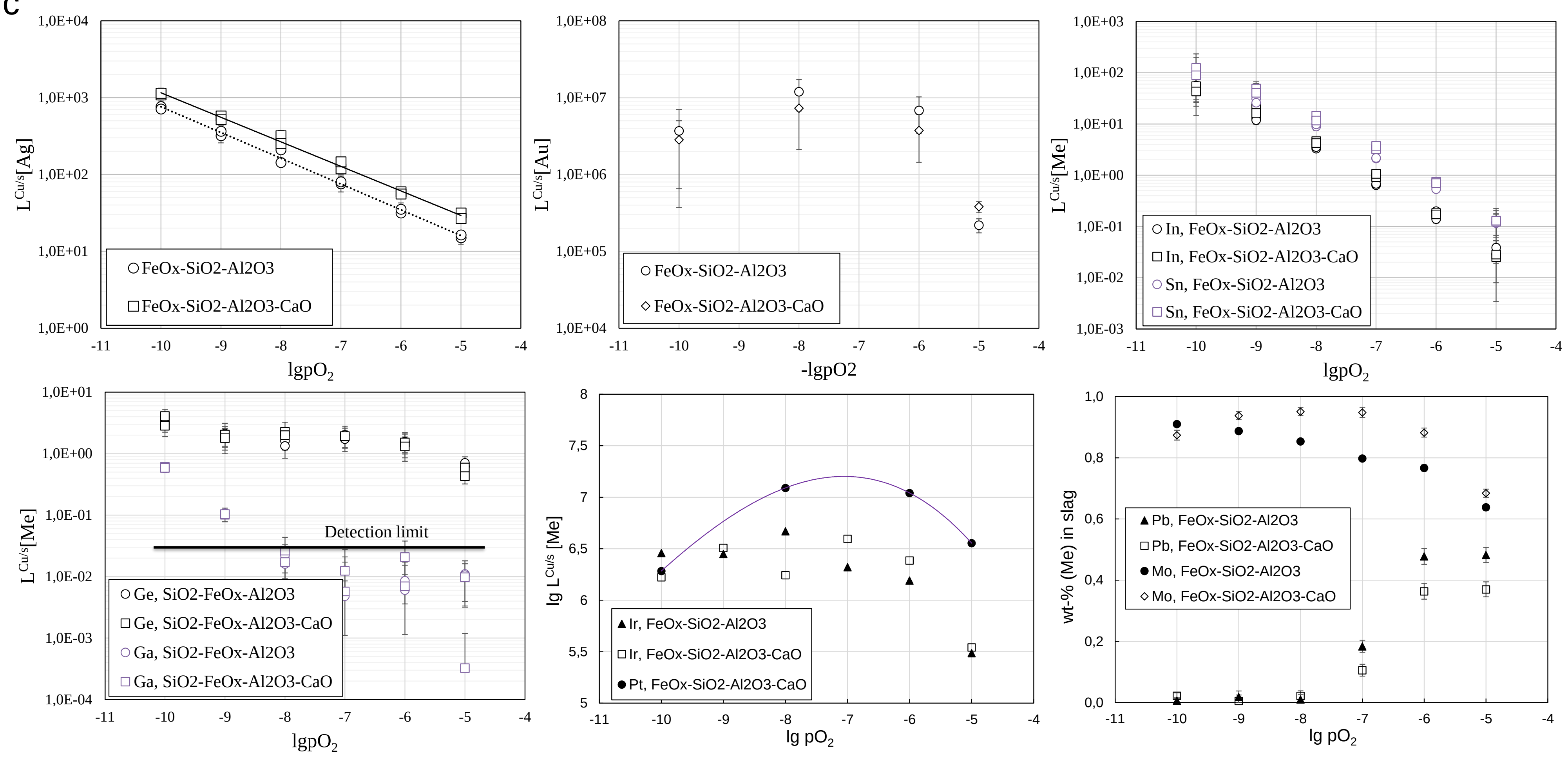

Figure 4. Minor element distributions between copper and slag as a function of oxygen partial pressure at 1300 ˚C. The most right bottom figure represents molybdenium and lead solubilities in slags along the increasing oxygen partial pressure at 1300 ˚C. Lead and molybdenium were not detected in copper.

In summary, precious metals (Ag, Au) and PGMs (Pd, Pt, Ir) distributed highly on the copper's side, and thus can be efficiently recovered through copper scrap smelting. Palladium and platinum distributions were around 10^{6-7} through the investigated oxygen partial pressure range. Gallium, lead and molybdenium distribute in slag, whereas germanium slightly more on the copper's side. Indium and tin distributions are depended on the oxygen partial pressure, at reductive conditions they can be recover to copper. CaO addition decreased the solubilities of Ag, In, Sn and Pb in slag. Lead was mainly volatilized, however as oxygen partial pressure increases it can be found also from slag.

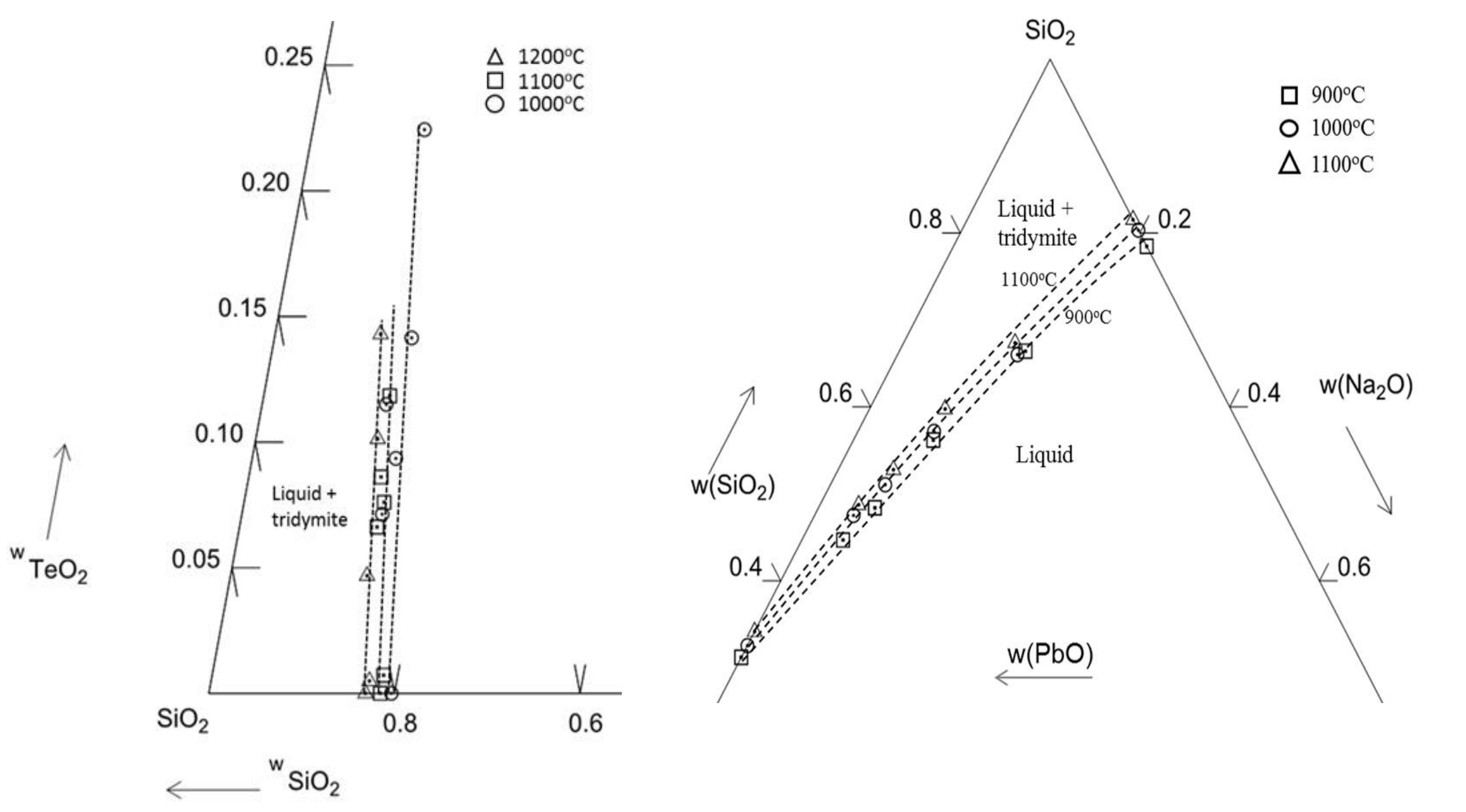

Figure 5. Liquidus lines in $TeO_2-Na_2O-SiO_2$ and $TeO_2-Na_2O-SiO_2$ systems.

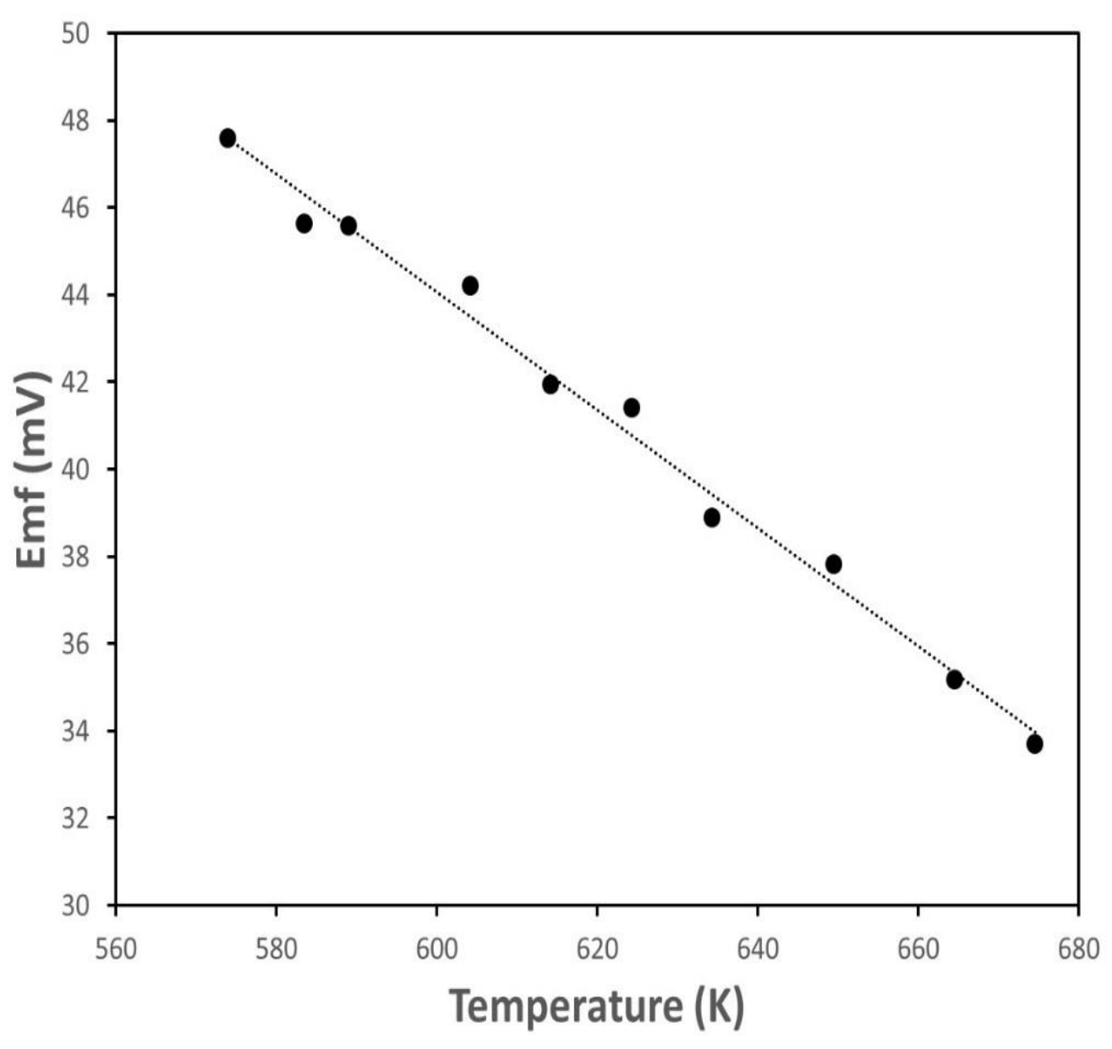

Figure 6. Ag-Pt EMF as a function of temperature.

The tie lines data of the $TeO_2-Na_2O-SiO_2$ system (Figure 5) and EMF data in Ag-Pt alloy (Figure 6) obtained in this project, are the first data published. Bivariant liquid + SiO_2 areas in the $PbO-Na_2O-SiO_2$ system (Figure 5) between 900 and 1000 ˚C in the current study are smaller than that reported by Kakau *et al.* (1936).

Between 573 and 673 K, the partial Gibbs energy of mixing of Ag-Pt alloy containing 1 at % Ag can be expressed by equation: $\Delta\overline{G}_{Ag}\ (Joule\ mol^{-1}) = -12087.5 + 13.5T$. As the partial mixing entropy of silver in platinum is negative, silver tends to mix with platinum at the platinum rich side.

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