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Published in:
Physicochemical Problems of Mineral Processing

DOI:
10.5277/ppmp170227

Published: 01/01/2017

Document Version
Publisher's PDF, also known as Version of record

Published under the following license:
Unspecified

Please cite the original version:
Models for viscosity and density of copper electrorefining electrolytes

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Abstract: Viscosity and density of copper electrorefining electrolytes affect energy consumption and purity of cathode copper. Decreasing the viscosity and density increases the rate of falling of the anode slimes to the bottom of an electrorefining cell and increases the diffusivity and mobility of ions. Increasing the falling rate of the anode slimes decreases a risk of anode slime impurities ending up on the cathode and being entrapped into the copper deposit. This work introduces two new models for both viscosity and density of copper electrorefining electrolytes with high accuracy and one reconstructed improved model for some electrorefining data of viscosity published previously. The experimental work to build up these new models was carried out as a function of temperature (50, 60, 70 °C), copper (40, 50, 60 g/dm$^3$), nickel (0, 10, 20 g/dm$^3$) and sulfuric acid (130, 145, 160 g/dm$^3$) concentrations for all models, and additionally arsenic concentration (0, 15, 30, 32, 64 g/dm$^3$) was included in the viscosity models. Increasing concentrations of Cu, Ni, As and H$_2$SO$_4$ were found to increase the viscosity and density, whereas increasing temperature decreased both viscosity and density. The viscosity models were validated with industrial electrolyte samples from the Boliden Harjavalta Pori tankhouse. The experimental and modeling work carried out in this study resulted in improved viscosity models, having the strongest agreement with the industrial electrorefining electrolytes.

Keywords: copper electrorefining, viscosity model, density model

Introduction

Viscosity and density have a considerable effect on purity of cathode copper and the energy consumption (Price and Davenport, 1981; Subbaiah and Das, 1989) affecting the mass and heat transfer conditions in a copper electrorefining cell (Price and Davenport, 1980). Decreasing viscosity increases the mass transfer rate since the diffusivity and mobility of ions increase (Cifuentes and Arriagada, 2008). Thus, lowering viscosity and density increases the diffusion coefficient of cupric ion (Moats et al., 2000) as well as the falling rate of the anode slimes to the bottom of the cell (Davenport et al., 2002; Shi and Ye, 2013). Increasing the falling rate of the anode
slimes decreases movement of slimes to other directions (Davenport et al., 2002; Shi and Ye, 2013). If the anode slimes end up on a cathode, the impurities can be entrapped into a copper deposit (Davenport et al., 2002). Due to that, the viscosity and density are typically kept sufficiently low in the electrorefining process (Davenport et al., 2002). The values of density and kinematic viscosity in typical electrolytes containing 50-65 g/dm$^3$ Cu, 18-24 g/dm$^3$ Ni, 150-180 g/dm$^3$ H$_2$SO$_4$ are reported at 55-70 °C being 1.224-1.2939 g/cm$^3$ and 0.772-1.165 mm$^2$/s, respectively (Devochkin et al., 2015).

There are only a few studies on the viscosity and density of copper electrorefining electrolytes (Price and Davenport, 1980, 1981; Subbaiah and Das, 1989; Jarjoura et al., 2003; Devochkin et al., 2015). According to these studies, increasing concentration of the main components in the electrolyte (copper, nickel and sulfuric acid) increases both viscosity and density, while increasing temperature has an opposite effect. In addition, other impurities such as arsenic (Price and Davenport, 1981), iron (Price and Davenport, 1981; Subbaiah and Das, 1989), manganese and cobalt (Subbaiah and Das, 1989) have been suggested to increase the viscosity and density. As arsenic, a typical impurity, has been experimentally measured and modeled only by Price and Davenport (1981), there are no recent studies on the effects of arsenic on either viscosity or density of copper electrorefining electrolytes. The effect of impurities has to be taken into account due to increasing amount of impurities and lowering grade of raw materials used for copper production. The average contents of As and Bi were approximately 2- and 6-folds higher, respectively, in 2016 compared to the content in 1987 (Moats et al., 2016).

As the viscosity value has an effect on the diffusion coefficient of cupric ion ($D_{Cu(II)}$) (Moats et al., 2000), the kinematic viscosity is also a factor in equations defining $D_{Cu(II)}$. Thus, the accuracy in defining the kinematic viscosity affects the accuracy of the determined $D_{Cu(II)}$ value. The diffusion coefficient is an important factor in electrodeposition, as it determines the limiting current density which, in turn, has a strong effect on the operating current density and morphology of the deposited copper.

The objective of this work was to develop accurate mathematical models of synthetic copper electrolyte viscosity (parameters: $T$ and concentrations of H$_2$SO$_4$, Cu(II) and Ni(II)) and density (parameters: $T$ and concentrations of H$_2$SO$_4$, Cu(II), Ni(II) and As(III/V)). Though in industrial electrolytes arsenic is known to be present both as As(III) and As(V) (Peng et al., 2012). In the current work the ratio of As(III) vs. As(V) was not determined. However, the As parameter was investigated as a sum of content of trivalent and pentavalent ions. In addition, the objective was to study the combined effects of the variables. The developed viscosity models were also initially validated with three industrial electrorefining electrolytes.
Materials and methods

Experimental solutions in this study were prepared using CuSO$_4$$\cdot$5H$_2$O (99–100%, Ph.Eur., crystallized, VWR International, LLC.), NiSO$_4$$\cdot$7H$_2$O (99–100%, for analysis, crystallized, Sigma-Aldrich Co. LLC.), H$_2$SO$_4$ (95–97%, for analysis, Merck KGaA), As$_2$O$_3$ (99.5%, Alfa Aesar, Thermo Fisher Scientific GmbH), arsenic acid (containing As 322600 mg/dm$^3$, Cu 3400 mg/dm$^3$, Ni 1210 mg/dm$^3$, Sb 7700 mg/dm$^3$, Se 19.3 mg/dm$^3$, Te 12 mg/dm$^3$, Pb 16 mg/dm$^3$, Bi < 5 mg/dm$^3$ and Ba < 1 mg/dm$^3$) and distilled water. As$_2$O$_3$ was dissolved in distilled water at 70 °C using H$_2$O$_2$ (30%, for analysis, Merck KGaA) enhancing the solubility of As, As(V) having significantly higher solubility into water compared to As(III) (Casas et al., 2003). Arsenic in arsenic acid was assumed to be present mainly as As(III) ions. In addition, three industrial electrorefining electrolytes (from Boliden Harjavalta Pori tankhouse) were used to validate the viscosity models. The concentrations of Cu, Ni, As and H$_2$SO$_4$ in the industrial samples were as follows: sample 1 contained 62.59 g/dm$^3$ Cu, 17.37 g/dm$^3$ Ni, 15.3 g/dm$^3$ As and 155 g/dm$^3$ H$_2$SO$_4$; sample 2 contained 57.07 g/dm$^3$ Cu, 15.57 g/dm$^3$ Ni, 15.3 g/dm$^3$ As and 138 g/dm$^3$ H$_2$SO$_4$; sample 3 contained 54.09 g/dm$^3$ Cu, 11.07 g/dm$^3$ Ni, 10.7 g/dm$^3$ As and 157 g/dm$^3$ H$_2$SO$_4$. These electrolytes were filtered and heated before analyses and measurements to ensure the homogeneity of the samples. The concentrations of Cu, Ni and As in the solution samples (industrial electrolytes, arsenic acid) were analyzed with ICP-OES (inductively coupled plasma optical emission spectroscopy, Perkin Elmer Optima 7100 DV, USA). Acidity was determined using the conductivity model described elsewhere (Kalliomäki et al., 2016).

Kinematic viscosities of the solutions were measured using a Ubbelohde capillary viscometer (SI Analytics GmbH) and densities using a glass tube oscillator DMA 40 Digital Density Meter (Anton Paar K. G). The viscosity results were normalized with known viscosity values of water by subtracting the difference between the measured and theoretical water viscosities from the viscosity values. The density results were calculated from oscillation frequencies using measured oscillation frequencies and known density values of water and air for calibrating the values. The air pressure was also measured and taken into account in the theoretical air density values used. During the measurements the temperature tolerance was ±0.2 °C.

The experimental design and data analysis were carried out using modeling and design software MODDE 8 (MKS Data Analytics Solution). The experiments for kinematic viscosity and density were designed by defining factors, responses and levels of the factors (Table 1). The data were refined, and two models for viscosity and two for density were constructed. For evaluating the quality of the models, the parameters goodness of fit ($R^2$), goodness of prediction ($Q^2$), standard deviation of the response (SDY), residual standard deviation (RSD) and reproducibility values of the density models were observed. The viscosity Model A was constructed using results where arsenic acid was the source of arsenic and the Model B using the results where
the arsenic source was dissolved As$_2$O$_3$. In the density measurements arsenic was not used for the safety issues. Both of the two density models were based on the same experimental data series: the density Model C$_{\text{streamlined}}$ being a simplified version of Model C.

Since Price and Davenport (1981) developed the viscosity model using data from electrorefining and electrowinning electrolytes, one additional model was proposed using the viscosity results from their published electrorefining data. The data were refined using MODDE software and built into an improved model.

Table 1. Investigated parameters of synthetic copper electrorefining electrolytes for viscosity and density measurements

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<th>Factor</th>
<th>Unit</th>
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<td>130, 145, 160</td>
</tr>
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<td>Ni</td>
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<td>0, 10, 20</td>
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<td>g/dm$^3$</td>
<td>0, 32, 64 $^\dagger$ or</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0, 15, 30 $^\ddagger$</td>
</tr>
<tr>
<td>$T$</td>
<td>$^\circ$C</td>
<td>50, 60, 70</td>
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</table>

* for viscosity measurements.
$^\dagger$ for Model A – as from industrial As-acid
$^\ddagger$ for Model B – as from dissolved As$_2$O$_3$

For evaluating the sensitivity and the accuracy of the models a sensitivity analysis was conducted. The variables were changed independently 0.5, 1, 3, 5, 10 and 15% around the point with average values of the variables and their relative effects on the viscosity and density were calculated. In addition, the sensitivity analysis was conducted for the concentration effects. Analogously, the effect of tolerances in the solution volumes and the test temperatures were investigated. These analyses were conducted utilizing the design and prediction tools of MODDE 8.

**Results and discussion**

**Raw data**

The raw data of viscosity and density measured in this study are listed in Tables 2-4. It can be observed that increase in Ni(II), Cu(II) and H$_2$SO$_4$ concentrations increases both viscosity and density. The effect of As(III/V) seems to be quite analogous to the effect of Cu(II) and Ni(II). In addition, increase in temperature was found to be the only parameter decreasing the viscosity and density. This effect is in line with the literature (Price and Davenport, 1980, 1981; Subbaiah and Das, 1989; Jarjoura et al., 2003; Devochkin et al., 2015).
Table 2. Measured viscosity values and experimental parameters used in viscosity tests 1-63 for Model A (as originating from arsenic acid)

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Table 3. Measured viscosity values and experimental parameters used in viscosity tests 1-63 for Model B (As originating from As$_2$O$_3$)

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Table 4. Measured density values and experimental parameters used in density tests 1-29 for Model C and Model C\textsubscript{streamlined}

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<th>T (°C)</th>
<th>ρ (g/cm\textsuperscript{3})</th>
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**Kinematic viscosity**

The models for kinematic viscosity were constructed from the raw data measured. Model A (Table 4) was constructed from the results (Table 2) for arsenic acid as a source of arsenic in the electrolytes, while Model B (Table 4) from the results (Table 3) where arsenic originated from As\textsubscript{2}O\textsubscript{3}. The models were constructed to the form:

\[
\log_{10}(v) = a_1 + a_2 [\text{Cu}] + a_3 [\text{H}_2\text{SO}_4] + a_4 [\text{Ni}] + a_5 [\text{As}] + a_6 T + \ldots + a_n \cdot (\text{comb. effect term})
\]

and the calculated statistical values for Models A and B are presented in Table 4.

Significance as well as the combined effects of the parameters were investigated. However, most of the combined effect terms were shown to be insignificant according to high probability values defined with MODDE 8. The viscosity models A and B contained only one significant combined effect term being \(T[\text{As}]\) for Model A and \([\text{Cu}][\text{Ni}]\) for Model B. Both viscosity models (Model A and Model B) were shown to be valid according to high correlation coefficients and reproducibility values as well as low deviation values calculated (Table 4).

The effects of Cu(II), Ni(II), temperature and As on the kinematic viscosity are presented in Table 4 and Fig. 1. The models show that increase in Cu(II), Ni(II), As
and H₂SO₄ concentrations increased viscosity, while increasing the temperature had an opposite effect (Fig. 3). Temperature had the strongest and H₂SO₄ the weakest effect on the viscosity (Table 4).

These viscosity models were found to be generally in a good agreement with the model proposed by Price and Davenport (1981) and Devochkin et al. (2015) where the effect of As was not taken into account (Fig. 1, [As] = 0 g/dm³). In addition, the viscosities were predicted with the model of Price and Davenport (1981) and a new Model PD constructed of the electrorefining results from Price and Davenport (1981) for comparison. Price and Davenport (1981) constructed their viscosity model using data from both electrorefining and electrowinning electrolytes. In this study, a new model, Model PD (Table 4), was built using only the electrorefining data published by Price and Davenport (1981). The constructed viscosity Model A was shown to be similar to the model from Price and Davenport (1981) (Fig. 1), while Model PD similar to Model B (Figs. 1 and 2). It seems that Models PD and B predict viscosity more accurately (Figs. 1, 2 and 4) compared to the original model published by Price and Davenport (1981). The viscosity values of Price and Davenport (1981) model gave the maximum 6.4% higher values than the predictions compared to Model PD and the maximum 5.2% higher than Model B in the investigated range.

Table 5. Coefficients, R², Q² (goodness of prediction), SDY (standard deviation of the response), RSD (residual standard deviation) and reproducibility values of the viscosity models (Model A, Model B and Model PD) built for copper electrorefining electrolyte

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<th>Model PD</th>
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<td>Ni·T</td>
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Figure 3 shows the sensitivity analysis for Model B. According to the sensitivity analysis, Model B was not sensitive to changes in concentrations, however, the temperature value significantly affected the viscosity. For example, 15% decrease in temperature resulted in approximately 15% increase in the viscosity. The sensitivity analysis results also suggested that the accuracy of the Model B was good in the measured concentration ranges since fluctuation in the purity of the chemicals had only a minor effect on the viscosity. The total error in the viscosity values due to fluctuation in the purity of the chemicals and the tolerances in the measured volumes and the measuring temperatures were calculated to be maximum 1.4% if all the values of these variables were assumed as inaccurate as possible.
Models A, B and PD were evaluated against industrial electrolyte samples 1-3. For all the samples, Models B and PD were shown to predict the viscosity most accurately. Model B was shown to predict best the viscosity value of the industrial electrolyte (sample 2) and the Model PD (samples 1 and 3) nearest to the measured values (Fig. 5). However, the difference between measured and modeled values was the highest for sample 3 (having the lowest concentration of Cu, Ni and As). The errors between measured and modeled values were the following: Model A 3.7-6.9%, model of Price and Davenport 2.3-6.5%, Model B 0.9-4.5% and Model PD 1.1-3.2%. Consequently, Model PD and Model B seemed to predict the viscosity of the industrial electrolytes with the highest accuracy. It is clear that the synthetic electrolytes are not identical to the industrial ones. The industrial copper electrolytes contain additives such as chlorides and thiourea as well as minor amounts of impurities such as Bi and Sb.
However, the initial validation taking into account the major parameters of the copper electrolyte (copper, nickel, arsenic and sulfuric acid concentrations) indicated a good prediction with Models B and Model PD. This suggests that the effect of additives and minor solution elements is small compared to the effect of parameters investigated.

![Fig. 5. Kinematic viscosity values of the industrial electorefining electrolyte samples 1-3 measured at 65 °C vs. values modeled with the Model A, the model of Price and Davenport (1981), the Model B and the Model PD](image)

**Density**

Model C constructed for density (Table 5, presented in similar form as viscosity models in Table 4) was shown to have four significant combined effect terms in addition to single effect terms. The combined effect terms were shown to be less significant than the single terms. Therefore, also a streamlined Model C\textsubscript{streamlined} (Table 5) was constructed by removing the combined effects. The previously published density models did not contain any combined effect terms (Price and Davenport, 1981; Subbaiah and Das, 1989; Jarjoura et al., 2003; Devochkin et al., 2015). The density models constructed were shown to be valid according to high correlation coefficients and reproducibility values calculated (Table 5).

According to the sensitivity analysis, the density models were not sensitive to changes in either concentrations or temperature. The sensitivity results were almost identical in Model C and Model C\textsubscript{streamlined}. For example, 15% decrease in Cu, H\textsubscript{2}SO\textsubscript{4} and Ni concentrations resulted in approximately 1.4, 1.0 and 0.3% decrease in the density, respectively, and similar decrease in temperature resulted in approximately 0.5% increase in the density in Model C (Fig. 7). These results of sensitivity analysis also suggested that the accuracies of both density models (Model C and Model C\textsubscript{streamlined}) were good in the measured range (Table 1) since fluctuation in the purity of the chemicals and the tolerances in temperatures had only a minor effect on the density predicted. The error in the density values due to fluctuation in the purity of the
chemicals and the tolerances in solution volumes and the measuring temperatures were calculated to be maximum 0.3%, if all the values of these variables were as inaccurate as possible.

Table 6. Coefficients, $R^2$, $Q^2$ (goodness of prediction), $SDY$ (standard deviation of the response), $RSD$ (residual standard deviation) and reproducibility values of the density models (Model C and Model C\textsubscript{streamlined}) built for copper electrorefining electrolyte

<table>
<thead>
<tr>
<th>$\rho$ (g/cm$^3$)</th>
<th>Model C</th>
<th>Model C\textsubscript{streamlined}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant</td>
<td>0.9828000</td>
<td>1.0346</td>
</tr>
<tr>
<td>[Cu]</td>
<td>0.0032690</td>
<td>0.0021617</td>
</tr>
<tr>
<td>[H$_2$SO$_4$]</td>
<td>0.0008269</td>
<td>0.0005337</td>
</tr>
<tr>
<td>[Ni]</td>
<td>0.0014520</td>
<td>0.002344</td>
</tr>
<tr>
<td>$T$</td>
<td>-0.0005230</td>
<td>-0.00070307</td>
</tr>
<tr>
<td>[Cu]-[H$_2$SO$_4$]</td>
<td>-6.354·10$^{-6}$</td>
<td></td>
</tr>
<tr>
<td>[Cu]-[Ni]</td>
<td>4.364·10$^{-6}$</td>
<td></td>
</tr>
<tr>
<td>[Cu]-$T$</td>
<td>-3.461·10$^{-6}$</td>
<td></td>
</tr>
<tr>
<td>[H$_2$SO$_4$]-[Ni]</td>
<td>4.37·10$^{-6}$</td>
<td></td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.99989</td>
<td>0.999704</td>
</tr>
<tr>
<td>$Q^2$</td>
<td>0.999759</td>
<td>0.999537</td>
</tr>
<tr>
<td>$SDY$</td>
<td>0.026956</td>
<td>0.026956</td>
</tr>
<tr>
<td>$RSD$</td>
<td>0.000335</td>
<td>0.000501</td>
</tr>
<tr>
<td>$N$</td>
<td>29</td>
<td>29</td>
</tr>
<tr>
<td>Reproducibility</td>
<td>0.99994</td>
<td>0.99994</td>
</tr>
</tbody>
</table>

Fig. 6. Effect of changing the variables on density with Model C

The density Model C proposed in this work (Table 6) was shown to be in a good agreement with the results of Price and Davenport (1981) and Devochkin et al. (2015) (Figs. 7 and 8). The density values calculated with the models of Subbaiah and Das
(1989) (Fig. 7) as well as values measured by Jarjoura et al. (2003) were approximately 2% lower than the values calculated with other models (C, C_streamlined and Price and Davenport, 1981). The model of Subbaiah and Das (1989) was constructed of experimental results measured mainly at 30 °C which is below the temperature range used in the electrorefining process, and can result in error at higher temperatures. The results of Jarjoura et al. (2003) may be explained by the pipetting method, used for sampling the electrolyte and weighting it as a measuring procedure, being probably less accurate than the use of pycnometer in other studies (Price and Davenport, 1980, 1981; Subbaiah and Das, 1989; Devochkin et al., 2015).

Fig. 7. Densities predicted with Model C, Model C_streamlined and models of Price and Davenport (1981), Subbaiah and Das (1989) and Jarjoura et al. (2003) compared with densities measured

Fig. 8. Measured density values of copper electrorefining electrolyte vs. predicted values from Model B, Model PD and model of Price and Davenport (1981)
Conclusions

Viscosities and densities were measured from synthetic copper electrorefining electrolytes containing various amounts of copper (40-60 g/dm$^3$), nickel (0-20 g/dm$^3$) and sulfuric acid (130-160 g/dm$^3$), as well as arsenic (0-64 g/dm$^3$). The measurements were conducted at three different temperatures (50, 60 and 70 °C). Based on the results, two models for viscosity (Model A and B) and two for density (Model C and C$^{\text{streamlined}}$) were constructed. In addition, one improved viscosity Model PD) was built using the data based on synthetic solution measurements published earlier by Price and Davenport (1981). The models were validated by measuring viscosities of three industrial electrolyte samples of known composition.

Increase in the concentrations of Cu, Ni, As and H$_2$SO$_4$ was found to increase both viscosity and density, whereas temperature was shown to decrease both viscosity and density. This is in agreement with the literature. The effect of arsenic presence on viscosity was found to vary depending on the arsenic source (arsenic acid vs. arsenic from As$_2$O$_3$), As$_2$O$_3$ resulting in higher validity of the viscosity model (Model B). The acid content and minor impurities present in the industrial arsenic acid were shown to increase the value of viscosity measured.

Another model (Model PD) was built based on data published by Price and Davenport (1981). The earlier published model of Price and Davenport (1981) was based on combined data from electrorefining and electrowinning. However, by excluding the electrowinning data of low copper concentrations and taking into account the combined effects of the parameters, a high accuracy refined model for copper electrorefining conditions could be built also from the earlier published data. This model showed good agreement with the Model B (As$_2$O$_3$ as As source).

It was shown that the modeling work carried out in this study (Model B and Model PD) could provide the most reliable and accurate models for copper electrorefining electrolyte in the investigated composition range. Both these viscosity models showed improved accuracy compared to the model of Price and Davenport (1981). One advantage of the viscosity models constructed was that they reveal also the combined effect of parameters investigated. Furthermore, these two models also seemed to predict the viscosity of the industrial electrolytes with the highest accuracy.

The modeled density values based on the data measured in this work were in a good agreement with the earlier published models of Price and Davenport (1981) and Devochkin et al. (2015). Model C was shown to be the most accurate ($R^2$ and $Q^2$ values approaching the unity) density model built.

Acknowledgements

This research has been performed within the SIMP (System Integrated Metal Production) project of DIMECC (Digital, Internet, Materials & Engineering Co-Creation (Tampere, Finland)). RawMatTERS Finland Infrastructure (RAMI) supported by Academy of Finland is greatly acknowledged. The authors would also like to thank Boliden Harjavalta Copper Refinery for permission to publish the results. In addition, the authors acknowledge David Lloyd, Tuomas Vainikka, Gunilla Fabricius, Timo Ylönen,
Katarina Dimic-Misic and Fupeng Liu for discussion and suggestions in developing this study as well as Hannu Revitzer for analyzing the samples.

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