Stability of copper acetate at high P-T and the role of organic acids and CO\(_2\) in metallic mineralization

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Many metal deposits were formed by carbonic fluids (rich in CO\(_2\)) as indicated by fluid inclusions in minerals, but the precise role of CO\(_2\) in metal mineralization remains unclear. The main components in fluid inclusions, i.e. H\(_2\)O and CO\(_2\), correspond to the decomposed products of organic acids, which lead us to consider that in the mineralization process the organic acids transport and then discharge metals when they are stable and unstable, respectively. Here we show that the thermal stability of copper acetate solution at 15–350 °C (0.1–830 MPa) provides insight as to the role of organic acids in metal transport. Results show that the copper acetate solution is stable at high P-T conditions under low geothermal gradient of <19 °C/km, with an isochore of \(P = 1.89 T + 128.58\), verifying the possibility of copper transportation as acetate solution. Increasing geothermal gradient leads to thermal dissociation of copper acetate in the way of \(4\text{Cu(CH}_3\text{COO)}_2 + 2\text{H}_2\text{O} = 4\text{Cu} + 2\text{CO}_2 + 7\text{CH}_3\text{COOH}\). The experimental results and inferences in this contribution agree well with the frequently observed fluid inclusions and wall-rock alterations of carbonate, sericite and quartz in hydrothermal deposits, and provide a new dimension in the understanding of the role of CO\(_2\) during mineralization.

Orogenic gold systems are characterized by abundant carbonic fluid inclusions (rich in CO\(_2\))\(^1\)–\(^3\), but the role of CO\(_2\) in gold mineralization still remains controversial and enigmatic\(^4\)–\(^6\). Carbonic fluid inclusions have been recently observed in various types of copper deposits\(^7\)–\(^10\) as well as in lode silver, lead-zinc and molybdenum deposits\(^11,12\). Therefore, there is a need to understand the relationship between CO\(_2\) and metallic mineralization.

The mutual conversion between CO\(_2\) and organic matter is common in both nature and human activity, as exemplified by photosynthesis and fossil fuel combustion\(^13\)–\(^16\). Organic matter plays a significant role in metal transport and enrichment in low-temperature hydrothermal environments\(^17\). Carboxylic acids, such as acetum, have been discovered in petroleum brines\(^18,19\) and fluid inclusions of ore deposits\(^20\), and have been shown to transport Pb and Zn as complexes at temperature of <250 °C\(^21\). CO\(_2\) can be transformed into carboxylic by metal catalyst, such as Mn, Pd and Zn\(^22,23\). This encourages us to infer that, at high P-T conditions, carboxylic acids and their metallic complexes can be stable and facilitate mobilization, migration and enrichment of ore metals; and then, decompose to CO\(_2\) with decreasing pressure during upward fluid migration. Thus, the stability of carboxylic acids and their metallic complexes at high P-T conditions is the key to understand the mechanism of and the role of CO\(_2\) in mineralization processes, from a new dimension. However, nothing is known about metallic complexes with carboxylic acids at high P-T conditions, due to a shortage of experimental data.

To examine the thermal stability of metallic complexes with carboxylic acids at high P-T conditions, we have conducted experiments on copper acetate solution (7%), using a diamond anvil cell. Despite of strong fluorescence impact of diamond, the symmetry stretching vibration of C-H bond (about 2,941 cm\(^{-1}\)), i.e. \(\nu_{\text{P}}\)\(_{2941}\), was observed in copper acetate solution (Fig. 1, Table 1). In the heating process, the shape of the spectra of the copper acetate solution did not change (Fig. 1), and no new peak appeared on the Raman spectra. The volume of the copper acetate solution is constant and the system evolves along the isochore. In other words, system pressure increases with increasing temperature. This is consistent with the relationship between the Raman shift of quartz (464 cm\(^{-1}\)) and pressure (Fig. 2, Table 1). Thus, the isochore of the copper acetate solution is defined as

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$P = 1.89\, T + 128.58$ (Fig. 2), and equals to a geothermal gradient of 19 °C/km. This indicates that copper acetate is stable at temperatures up to 350 °C under low geothermal gradient conditions.

The thermal dissociation experiment of copper acetate was conducted with a moissanite anvil cell to avoid strong fluorescence. The sample chamber was filled with copper acetate solution (7%), solid copper acetate and quartz chip (Fig. 3a). The chamber was heated step-by-step from 16 °C to 212 °C, with step interval of 6–22 °C, heating rate of 2–5 °C/min and pressure ranging 355–611 MPa (Table 1). Each step lasted for 10–15 minutes to achieve stable temperature and pressure, and to acquire the Raman shift of copper acetate solution. The peak

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**Figure 1.** (a) The hydrothermal diamond anvil cell (HDAC)\(^2\). (b) The Raman spectra of the C-H symmetry stretching vibration at different temperature and pressure, showing that the copper acetate is stable at high temperature with high pressure (PeakFit V4.12, https://peakfit.updatestar.com).
symmetry stretching vibration of C-H bond (about 2,941 cm⁻¹) shifts to higher frequency along with increasing temperature and pressure (Table 1). During heating, the solid copper acetate firstly dissolved (Fig. 3b), and then vapour bubble (Fig. 3d) and native copper grains (Fig. 3c,d,f) appeared. Under microscope, it was observed that solid copper grains suddenly formed at the conditions of 212 °C and 511 MPa, and the experiment stopped if no more copper precipitated. The vapour bubble was composed of CO₂, as indicated by the Raman shift (Figs. 3e, 4). Thus, it is concluded that the copper acetate solution is stable at high P-T conditions under low geothermal gradient, and thermally dissociated when the geothermal gradient increases, in the way as below:

\[
4\text{Cu(CH}_3\text{COO)}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Cu} + 2\text{CO}_2 + 7\text{CH}_3\text{COOH}
\]  

(1)

Table 1. The Raman shift of quartz and the symmetry stretching vibration of C-H. P: Pressure; \(\nu_{2941}\): Raman shift of the symmetry stretching vibration of C-H; T: Temperature; \(\nu_{464}\): Raman shift of the quartz.

| T/°C | P/MPa | \(\nu_{464}/\text{cm}^{-1}\) | \(\nu_{2941}/\text{cm}^{-1}\) | T/°C | P/MPa | \(\nu_{464}/\text{cm}^{-1}\) | \(\nu_{2941}/\text{cm}^{-1}\) |
|------|-------|-----------------|-----------------|------|-------|-----------------|-----------------|
| 23   | 202   | 465.8           | 2941.5          | 16   | 522   | 468.7           | 2949.0          |
| 26   | 224   | 465.9           | 2942.7          | 32   | 557   | 468.8           | 2949.6          |
| 51   | 270   | 466.0           | 2941.3          | 49   | 603   | 469.0           | 2949.9          |
| 69   | 257   | 465.7           | 2944.0          | 65   | 611   | 468.8           | 2950.1          |
| 92   | 315   | 465.8           | 2943.7          | 87   | 367   | 466.4           | 2948.0          |
| 115  | 307   | 465.4           | 2942.9          | 107  | 355   | 466.0           | 2946.7          |
| 133  | 327   | 465.3           | 2944.4          | 120  | 417   | 466.3           | 2947.1          |
| 154  | 373   | 465.4           | 2946.9          | 133  | 369   | 465.7           | 2946.9          |
| 173  | 364   | 465.0           | 2947.2          | 150  | 478   | 466.4           | 2947.6          |
| 193  | 473   | 465.7           | 2945.2          | 156  | 476   | 466.3           | 2948.3          |
| 209  | 553   | 466.1           | 2946.5          | 164  | 497   | 466.4           | 2948.5          |
| 243  | 596   | 465.9           | 2951.7          | 185  | 512   | 466.2           | 2948.0          |
| 277  | 684   | 466.1           | 2952.6          | 197  | 595   | 466.7           | 2948.8          |
| 347  | 831   | 466.3           | 2956.8          | 212  | 512   | 465.7           | 2948.9          |

Figure 2. The relation between temperature and pressure in the experiment of copper acetate solution.

From the reaction Eq. 1 and experiment, new understandings can be drawn out: (1) the organic acids can facilitate metallic transportation via fluids during hydrothermal mineralization. (2) CO₂ serves as an important buffer to maintain metallic transportation, because the existence of CO₂ in fluid makes the reaction 1 proceeds to the left, keeping CH₃COO⁻ stable. (3) The copper acetate solution is stable under high-pressure, and therefore, decompression causes copper acetate dissociation, CO₂ escape and Cu precipitation, as similar to those revealed in previous studies. (4) Wall-rock carbonation removes CO₂ from the solution, and results in precipitation of metals. (5) Decreasing pH can facilitate copper acetate stability and transportation; by contrast, increasing pH accelerates copper acetate dissociation and Cu precipitation, and also causes phyllic alteration (sericite + quartz) in the way of Eq. 2:
Therefore, the common observation of carbonate, sericite and quartz alterations, and CO2-rich fluid inclusions in hydrothermal deposits, such as the orogenic-type Cu lodes, corresponds well with the experimental results of stability and thermal dissociation of copper acetate solution.

**Methods**

The experiment was performed in hydrothermal diamond and moissanite anvil cells, respectively. The sample was enclosed in the 200–400 μm diameter hole of a thin (300–400 μm) rhenium metal gasket by compressing the gasket between two diamond anvil faces. The temperature of the diamond anvils and samples was controlled and measured using Mo resistance heaters and two attached K-type thermocouples, respectively. Temperature measurement was corrected using the melting point of phenolphthalein and stearic acid, and the accuracy of reported temperatures is within ±5 °C. A small chip of quartz (0.18–0.20 mm) was put in cell to calibrate internal pressure. The pressure was determined according to the relationship between the Raman shift of quartz and the pressure.

Raman spectroscopy was performed using a Raman micro-spectrometer (Renishaw system RM-1000, Renishaw Group, Gloucestershire, United Kingdom); the slit width was set at 50 μm and the resulting resolution was ±1 cm⁻¹. The objective is a Leitz 20× with a working distance of 15 mm. An argon ion laser with a

\[
3\text{KAlSi}_3\text{O}_8 + 2\text{CH}_3\text{COOH} = \text{KA}_2[\text{AlSi}_3\text{O}_{10}](\text{OH})_2 + 6\text{SiO}_2 + 2\text{KCH}_3\text{COO}
\]
A wavelength of 514.5 nm operated at 20 mW was used to illuminate the sample for Raman signal generation. Each spectrum was collected within an accumulation time of 30 s and covering a wavelength of 100–4,000 cm$^{-1}$. The initial experimental temperature was 15 °C, which was gradually increased to 350 °C. In the experiment, the Raman spectrum test was conducted 3–5 min after each change in experimental temperature to ensure that the samples firstly reach equilibrium. The results were processed using PeakFit software.

**Figure 4.** Laser Raman spectra of the vapour and solution. (a) The C-H symmetry stretching vibration is obvious (2945.6), illustrating the copper acetate still exist. The two peaks can be observed (1382.9 and 1410.9), is the peak of CO$_2$ and C=O of Cu(Ac)$_2$, respectively. (b–e) The C-H symmetry stretching vibration is unobvious or vanishing, illustrating the copper acetate does not exist almost. The unique peak can be observed (1383.6, 1389.1, 1388.6 and 1389.2), showing the peak of CO$_2$ (PeakFit V4.12, https://peakfit.updatestar.com).
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Author contributions

Z.Y. Ni and H.P. Li performed experiments which were technologically designed by H.F. Zheng and Z.Y. Ni, and scientifically proposed by Y.J. Chen, N. Li and Z.Y. Ni. The experiment results were initially interpreted by Y.J. Chen and Z.Y. Ni, which was then confirmed by all the authors through discussion. All authors agreed with the results, interpretation and authorship of manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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