

Mineralogical Changes within Polish Weissliegend Sandstones During Bioleaching

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Abstract

The Kupferschiefer is one of the most important sources of copper and silver in Europe, with resources located mainly in Poland and Germany. Mineralization is stratabound and hosted by sedimentary rocks comprising of sandstone, black shale, and carbonate rocks. Because Kupferschiefer-type ores are typically complex and very fine-grained, alternative approaches for metal recovery, such as bioleaching, are becoming an attractive alternative to flotation.

The focus of this study was a detailed monitoring of mineralogical changes through time during bioleaching of sandstone-hosted Cu-mineralization from two Polish Cu-mines. The change of modal mineralogy, mineral associations, microbial activity and copper recovery of a copper bearing sandstone during bioleaching with *Acidithiobacillus ferrooxidans* DSM 14882 was investigated. A series of 18 batch cultures and 18 abiotic controls in shaking flasks with a solid content of 6 wt.% was prepared and sampled every 3 to 4 days over a period of 18 days. Mineralogical analysis of leaching residues was done by mineral liberation analysis (MLA) and X-Ray powder diffraction (XRD), while chemical analysis of dissolved copper and ferric/ferrous iron was carried out with ion chromatography (IC).

The investigated sandstone ore contained 2.5 wt.% copper, mainly bound to the copper minerals chalcocite (Cu₂S, 1.3 wt.%), covellite (CuS, 1.0 wt.%) and bornite (Cu₅FeS₄, 0.9 wt.%). After 18 days the copper extraction was 84% for biotic samples and therefore significantly higher compared to abiotic controls (52%). MLA data showed that biotic dissolution was faster for all three copper ore minerals. The results of detailed mineralogical analysis indicate a passivation by jarosite during the leaching process, especially caused by ammoniojarosite. It was possible to trace progressive changes of each copper sulphide over the entire bioleaching process and calculate dissolution/formation rates by means of MLA data.

Key words: Bioleaching, *Acidithiobacillus ferrooxidans*, Weissliegend sandstone, automated mineral liberation analysis, XRD

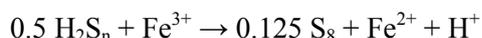
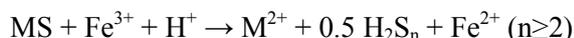
Introduction

The Central European Copperbelt (Borg et al. 2012) is one of the most important sources for copper and silver in Europe, with several large-scale mining operations currently active in the southwest of Poland. In Poland Kupferschiefer-type resources still contain 29.79 Mt of copper in 1.47 Bt of currently known ore reserves (Borg et al. 2012).

Kupferschiefer-type mineralization is restricted to the Lower Permian (Rotliegendes) terrestrial deposits and Upper Permian (Zechstein) marine sedimentary rocks. The ore series is composed of (bottom to top): Weissliegend Sandstones, Basal Limestone, Kupferschiefer and Zechstein Limestone (Oszczepalski 1999). Stratabound sulphide mineralization occurs in all of these sedimentary rock types, with 60% of currently known reserves hosted by Weissliegend sandstone, 30% in Zechstein carbonate rocks and 10% in the Kupferschiefer black shale (Borg et al. 2012). In the Polish mining district mineralized sandstones of Weissliegend have an average copper content of 1.8% and an average thickness of 18 m. However, the grade and thickness of sandstone ore can locally vary from 0.7% to 30% copper and from few meters up to 35 m (Borg et al. 2012). Main ore minerals are bornite, galena, sphalerite, chalcopyrite and chalcocite-type sulphide minerals (Oszczepalski 1999).

The complex mineralogy and fine-grained structure of Kupferschiefer-type ores limit copper recovery with traditional processing methods, especially flotation. In the last 15 years the copper content in flotation concentrates and copper recovery decreased (Gibas et al. 2015); therefore alternative approaches for metal recovery, such as bioleaching, may become important.

Bioleaching describes the process of metal extraction by microorganisms. A common leaching bacterium is the acidophilic ferrous iron- and sulphide-oxidizing bacterium *Acidithiobacillus ferrooxidans*, formerly *Thiobacillus ferrooxidans* (Kelly and Wood 2000), that has been studied in detail. Under acidic conditions *At. ferrooxidans* catalyses the release of metal ions from metal sulphides by the production of sulphuric acid (hydrolytic attack), and by oxidation of ferrous to ferric iron (oxidative attack). For acid-soluble metal sulphides the mechanism can be generally described as follows (Schippers and Sand 1999):



This so called “polysulfide mechanism” applies to chalcocite (Cu_2S) and covellite (CuS) (Schippers and Sand 1999), which have been investigated in this study.

The ore mineralogy is, among chemistry and microbiology, an important parameter in bioleaching processes; because mineral composition, liberation, and solubility influence the leaching efficiency. In general, it is known that chalcocite is more easily dissolved in heap- and dump-leaching than bornite and covellite (Watling 2006). In the present study the behaviour of the copper sulphides in presence of *Acidithiobacillus ferrooxidans* DSM 14882 was of main concern. To understand and possibly improve the bioleaching process, mineralogical changes within sandstone ore were investigated every 3 to 4 days by collecting detailed data of the mineralogy with a mineral liberation analyser (MLA) and X-Ray powder diffraction (XRD). Moreover chemical analysis of leaching solutions with ion chromatography and determination of pH and redox potential were performed to get new insights into bioleaching reactions.

Methods

Bioleaching

Weissliegend sandstone-hosted ore of the Polkowice and Rudna mines (Poland) was crushed, milled and sieved. The ore fraction $<125 \mu\text{m}$ was divided into homogenous portions of 12 g with a sample splitter and then used for leaching experiments. A series of 18 batch cultures with *At. ferrooxidans* DSM 14882 and 18 abiotic controls was prepared. Leaching was performed in 500 mL shaking flasks with 200 mL modified 9K Medium (Silverman and Lundgren 1958), pH 2.1, containing 50 g/L $\text{Fe(II)SO}_4 \times 7 \text{H}_2\text{O}$. The shaking flasks for bioleaching were inoculated with 20 mL of the same pre-

culture of *At. ferrooxidans* DSM 14882 (1.1×10^6 cells/mL). All 36 flasks were incubated at 30°C and 120 rpm.

At day 2, 4, 7, 10, 14 and 18 samples of leached ore material were taken. The number of parallels decreased each time by 6, due to stopping of 3 batch cultures and 3 abiotic controls (fig. 1). For mineralogical analysis sandstone ore was separated from the leaching solution via filtration and then air dried for further preparation. Redox potential and pH of the leaching solution were measured daily (pH Inlab Semi-Micro, Mettler Toledo and SenTix ORP, WTW). Samples for detecting copper, ferrous and ferric iron in solution were taken every 3-4 days, filtrated (0.22 µm syringe filter) and frozen for later measurement. The evaporation loss during (bio)leaching was compensated with sterile *Aqua dest.*.

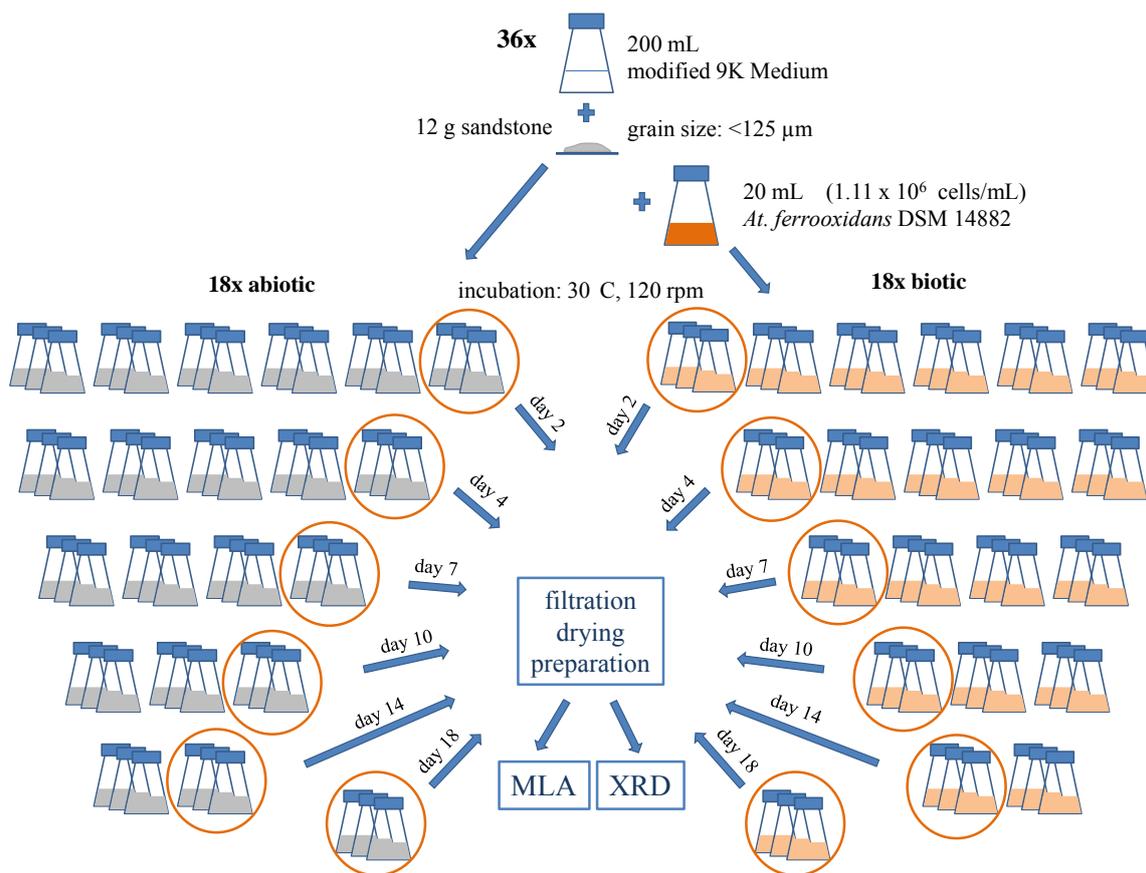


Figure 1 Experimental setup and sampling scheme of sandstone (bio)leaching

Chemical analysis

Major element concentrations in sandstone ore (fraction <125 µm) were determined by X-ray fluorescence spectroscopy (XRF) using an AxiosMinerals, PANalytical.

Analysis of copper, ferric and ferrous iron in the leaching solutions was performed using ion chromatography (ICS-5000, 4 mm system, Thermo Scientific). An IonPac® CS5A column (Thermo Scientific) with an eluent flow rate of 1 mL/min Met Pac PDCA (7 mM pyridine-2,6-dicarboxylic acid, 66 mM potassium hydroxide, 5.6 mM potassium sulphate, 74 mM formic acid) separated chelated metal complexes. The metal complexes were detected at 530 nm after postcolumn derivatization with 0.5 mM 4-(2-pyridylazo) resorcinol dissolved in MetPac PAR Postcolumn Reagent Diluent (1 M dimethylaminoethanol, 0.5 M ammonium hydroxide, 0.3 M sodium bicarbonate) at a flow rate of 0.6 mL/min (Cardellicchio et al. 1997).

Mineralogical analysis

The mineralogical analysis of sandstone ore was done by MLA and XRD. For detailed investigation of copper sulphide minerals all 36 leaching samples and the untreated ore were analysed by MLA. Therefore, polished and carbon coated grain mounts, composed of 3 g dry sample in an epoxy resin block (Ø 30 mm), were prepared. A subset of twelve leaching samples, one biotic and one abiotic of each sample point, and the untreated ore were analysed by XRD. Preparation of sandstone ore for XRD was done by milling with ethanol in a McCrone micronizing mill.

The MLA comprised a FEI Quanta 650 F field emission scanning electron microscope equipped with two Bruker Quantax X-Flash 5030 EDX detectors and FEI’s MLA suite 3.1.4 for data acquisition. The grain-based X-ray mapping (GXMAP) measurement mode was used, because of similar backscattered electron grey levels of expected copper sulphides (chalcocite, covellite, bornite, chalcopyrite). The operating parameters of MLA are listed in table 1.

Table 1 Operating parameters of MLA measurements.

MLA parameters		SEM parameters	
Pixel size	0.6 µm/px	Voltage	25 kV
Minimum EDX	2000 counts/analysis	Probe current	10 nA
Acquisition time	5 ms	BSE calibration	Au 254
GXMAP trigger	25-255		
Step size	6 x 6 px		
Minimum particle	8 px		
Minimum grain size	4 px		

XRD analyses were carried out using a PANalytical Empyrean diffractometer, equipped with a PIXcel3D detector and Co-K α radiation at 35 kV and 35 mA with a Fe-K β -filter. A step size of 0.013° 2 θ in the range of 5 to 80 2 θ and a step time of 800 sec/step were set. The software BGMN Profex 3.5.0 (Doebelin and Kleeberg 2015) was used for mineral identification and Rietveld refinement.

Results and discussion

Bioleaching of copper

Microbial activity was observed indirectly by pH and the ferric/ferrous iron content ratios in solution. The pH increased in all leaching solutions within the first day up to 3.1 due to carbonate dissolution and ferrous iron oxidation, then followed by a gradual decrease of pH (fig. 2-A). A significantly lower pH was measured in the presence of *At. ferrooxidans* from day 7 onwards, indicating microbial activity (production of H₂SO₄).

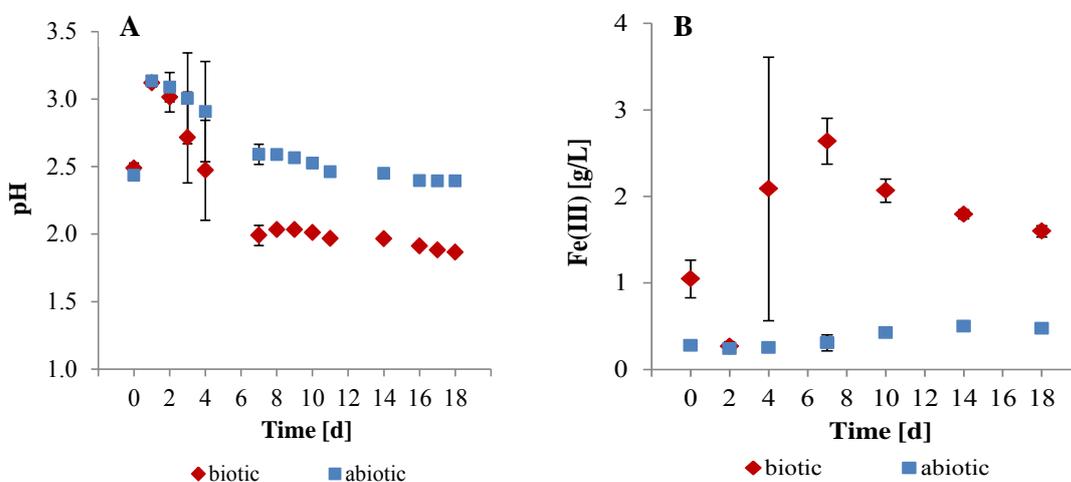


Figure 2 Results of pH (A) and dissolved ferric iron (B) during bioleaching with *At. ferrooxidans* DSM 14882.

Moreover, the amount of dissolved ferric iron increased in biotic approaches from 1 to 2.6 g/L within the first week (fig. 2–B) and thus proved the activity of *At. ferrooxidans*. In contrast, ferric iron increased only slightly from 0.3 to 0.5 g/L in abiotic controls, due to chemical iron oxidation.

The investigated sandstone ore contained on average 2.5 wt.% copper according to XRF analysis. Copper leaching was more efficient in presence of *At. ferrooxidans* DSM 14882 (fig. 3). Significant differences between biotic and abiotic treatment were evident from the fourth day onwards. Within the first week 69% of copper were extracted biotically and 43% abiotically. In the last 10 days only minor amounts of copper were leached so that in total 84% copper were biotically extracted and 52% were abiotically leached.

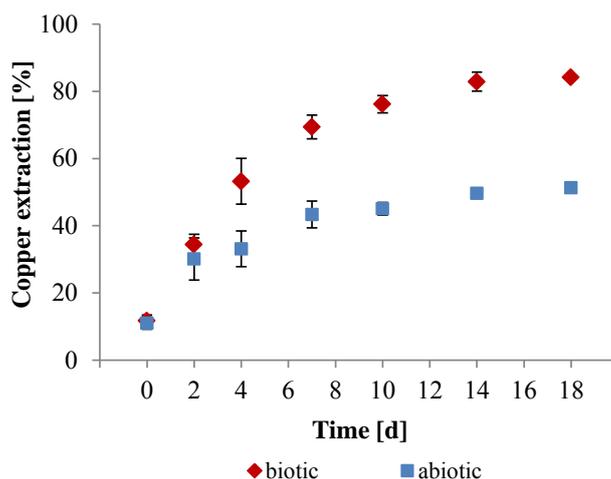


Figure 3 Copper extraction of approaches with *At. ferrooxidans* DSM 14882 and abiotic controls.

Mineralogical effects

The sandstone ore was mainly composed of quartz (70.7 wt.%), clay minerals (12.0 wt.%), feldspar (7.7 wt.%), carbonates (4.2 wt.%) and copper sulphides (3.3 wt.%). The main copper minerals were chalcocite (1.3 wt.%), covellite (1.0 wt.%) and bornite (0.9 wt.%). Due to the low amounts of these copper sulphides, quantification during bioleaching was only possible with MLA.

More bornite was leached biotically than abiotically according to MLA data (fig. 4-A). At day 18 only low amounts of bornite were detectable in biotic leaching residues, while in control residues only half of the bornite was leached. Chalcocite, in contrast, was dissolved completely within 4 days in biotic approaches and within 10 days in abiotic approaches (fig. 4-B). The content of covellite increased simultaneously in biotic and abiotic leaching residues up to day 10 and decreased only afterwards (fig. 4-C). Overall the formation of covellite was lower and dissolution was higher in presence of *At. ferrooxidans*.

Based on the MLA data in fig. 4, dissolution/formation rates for the three copper sulphides were determined by calculating the slope between the points of highest/lowest and lowest/highest content of mineral. During biotic and abiotic leaching chalcocite dissolution rate was 0.04 g/d and 0.02 g/d, therefore significantly higher than covellite (0.01 g/d biotic, 0.005 g/d abiotic) and bornite (0.005 g/d biotic, 0.003 g/d abiotic) dissolution rates. The dissolution rates of all three copper sulphides were approximately twice as high in biotic samples than in abiotic samples. In contrast, the formation rate of covellite was about double in abiotic approaches (0.013 g/d) than in biotic (0.006 g/d). For covellite it has to be taken into account that the formation of secondary covellite interfered with the dissolution, so it is impossible to separate both effects.

The apparent increase in the abundance of covellite during leaching experiments indicates that obviously some of the chalcocite and bornite has been transformed to covellite. Formation of secondary covellite in (bio)leaching experiments has previously been documented in several studies (Dutrillac et al. 1985, Bevilacqua et al. 2010, Lee et al. 2011). It means that copper has been oxidized

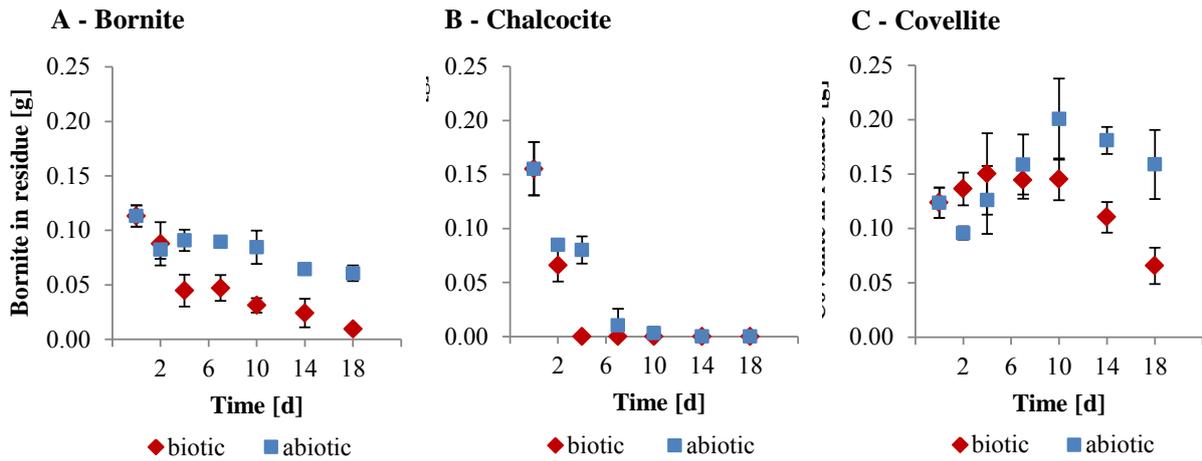


Figure 4 Content of bornite (A), chalcocite (B) and covellite (C) in leaching residues during (bio)leaching analysed by MLA, average of 3 samples.

from the monovalent state in chalcocite (Cu_2S) and bornite (Cu_5FeS_4) to the divalent state in covellite (CuS). In this study *At. ferrooxidans* obviously also enhanced the leaching of covellite/secondary covellite, which was also observed in a study by Bevilaqua et al. (2010). Ahonen and Tuovinen (1995) supposed that ferric iron suppresses the formation of covellite in leaching experiments. This hypothesis could explain the lower contents of secondary covellite in our biotic leaching residues. Given that ferric iron does not only accelerate bornite and chalcocite turnover but also covellite turnover, the suppression may reflect an effect of ferric iron on both, covellite formation and turnover.

MLA data also indicated the formation of possible iron-hydroxides during experiments. However, an exact mineral identification and quantification with MLA was not possible due to very fine-grained minerals and mixed spectra resulting from iron precipitations at the rims of different mineral grains. Therefore, XRD measurements were performed to identify and quantify the iron hydroxides and also to verify the MLA data. Based on XRD data the iron hydroxides were identified as jarosite and ammoniojarosite. They formed in biotic and abiotic leaching residues, although significantly more ammoniojarosite was formed in batch cultures (fig. 5-B). The content of jarosite is nearly equal in controls and residues from biotic experiments over the whole time of the experiment (fig. 5-A).

The comparison of copper extraction (fig. 3) with jarosite/ammoniojarosite development (fig. 5) indicates a correlation. The copper extraction decreased in the second week while the formation of jarosite and ammoniojarosite increased. Therefore, passivation of the copper minerals by jarosite and ammoniojarosite can be an explanation for reduced copper extraction during the last 10 days.

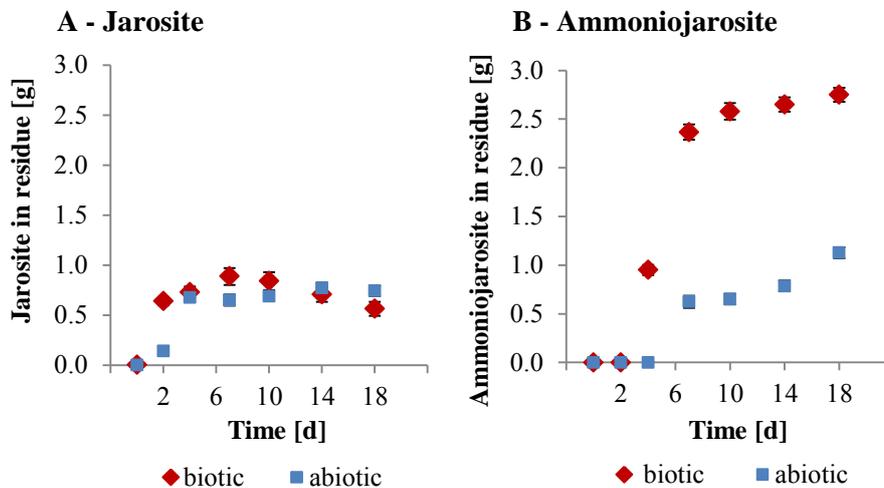


Figure 5 Content of jarosite (A) and ammoniojarosite (B) in leaching residues, analysed by XRD.

Conclusions

Mineralogical and chemical data proved that leaching of the Polish Weissliegend sandstone was enhanced by *At. ferrooxidans* DSM 14882. The dissolution of the three copper sulphides covellite, chalcocite and bornite was faster in biotic approaches than in those without bacteria. Obviously the presence of *At. ferrooxidans* resulted in faster transformation of bornite and chalcocite to covellite, but also in a faster oxidation of the latter compared to abiotic controls. As a result a less pronounced increase in covellite content was detected in biotic leaching residues. Passivation of remaining copper minerals by jarosite and ammoniojarosite probably reduced the copper extraction in the second week.

It was possible to quantify mineralogical changes of copper sulphides and iron hydroxides over the entire bioleaching process with combined MLA and XRD analysis. A detailed investigation of leaching residues with low mineral contents is practicable with MLA and thus the latter can be a method to get new insights in (bio)leaching processes.

Acknowledgement

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