Electrochemical precipitation of gold from a hydrothermal fluid in the Black and Kimberley Reefs, South Africa

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The Witwatersrand hosts the largest known gold resource on Earth, however, the genesis of the gold mineralization is still a matter of considerable debate (opinion is divided over the relative importance of detrital sedimentary and hydrothermal processes). In the Kimberley Reef (Upper Witwatersrand Supergroup) and the Black Reef (Lowermost Transvaal Supergroup), gold is locally enriched in areas proximal to underlying gold-bearing Witwatersrand reefs. Gold concentration in the Kimberly and Black reefs correlates strongly with hydrocarbon content. The gold occurs as angular to sub-angular, native gold particles in the interstitial space between pyrite and arsenic-bearing sulphides, in fractures cutting pyrite, in irregularly shaped pores within pyrite and in hydrocarbon nodules.

Particle-induced X-ray emmision (PIXE) analyses were performed on native gold grains and nearby grains of pyrite and other minerals. Quantitative element maps prepared from these analyses show that pyrite adjacent to gold grains is invariably zoned in respect to As (unless there is also an adjacent arsenic-bearing mineral) with the highest concentrations occurring adjacent to gold grains. The concentration of As varies from 86 ppm (+/- 20) to 7850 ppm (+/- 130). The chemical zoning of As is interpreted to correspond to a change from n-type (low As) to p-type (high As) conduction. This behaviour leads to large differences in the electric potential of the surfaces of growing pyrite crystals [1].

The evidence presented above suggests strongly that the gold grains discussed here are hydrothermal in origin. Assuming this to be the case, and based on data suggesting that temperature did not exceed 350 °C and pH was < 5 [2], gold would have been transported mainly as $AuHS^0$ and $Au(HS)_2^-$ [3]. We propose that the close spatial association of gold with As-bearing pyrite reflects the electrochemical precipitation of gold onto the p-type pyrite because of the transfer of electrons from its surface to the gold species, thereby reducing Au^+ to Au^o and releasing HS^-. A similar interpretation is proposed for gold grains in contact with other arsenic-bearing minerals. In view of the strong evidence for the hydrothermal origin of the gold and its spatial association with underlying Witwatersrand gold reefs, we conclude that the gold in the Kimberly and Black reefs was hydrothermally remobilized from Witwatersrand gold reefs.

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Ab initio study of Zn isotope fractionation in aqueous compounds

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Isotopic variability of Zn in natural samples has been well documented by multi-collector ICP-MS [1]. The interpretation of these data is limited by our knowledge of isotope fractionation during chemical reactions. Intramolecular vibration of isotopologues is the major origin of chemical isotope effect for non-heavy elements [2]. Analysis of model molecules by *ab initio* methods is helpful to estimate magnitude of isotope fractionation. In the present study, isotope fractionation factor of various Zn species was calculated. Orbital geometries and vibrational frequencies of Zn(II) species were computed using density functional theory (DFT) as implemented by the Gaussian03,09 codes (Gaussian Inc.). The DFT method and basis set employed here are B3LYP and 6-311+G(d,p).

Isotope fractionation factor ln β (‰) for $^{66}Zn/^{64}Zn$ was estimated from the calculated vibrational frequencies of isotopologues for hydrated Zn ion, chlorides, sulfides, sulphates, carbonates, phosphates, citrates, and malates [3,4]. For the common species, our results are consistent with those of Black *et al.* [5]. With a site-averaged ln β value of 3.43‰ at 298 K, citrates are enriched in heavy isotopes with respect to the hydrated Zn^{2+} aqua ion $Zn(H_2O)_6^{2+}$, the dominant form of Zn in natural water. ln β was found to be 0.2-1‰ larger than that of Zn^{2+} for carbonates, phosphates, and sulphates, and 0.1-1‰ smaller for chlorides and sulfides. This suggests that strong oxygen donor ligands, notably phosphates and carbonates, are enriched in heavy Zn isotopes.

The present results provide a consistent framework for the interpretation of Zn isotope data in plants [6,7], with Zn phosphates in the root system being isotopically heavier than Zn malate and phosphate in the aerial parts. They also explain the heavy Zn isotope compositions of human and animal bones. The role of phosphates explains the isotopically light Zn in residual soils and isotopically heavy Zn in FeMn-nodules. It is anticipated that potential threats of aquifer pollutions by heavy metals and phosphates upon pH variations could also be monitored by Zn isotopes.

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