

Proton-induced X-ray emission analysis of gold grains from laterites: evidence for the formation of extreme fineness gold by natural chemical processes during weathering

M. Santosh^{*†}, P. K. Omana[†], Mathew K. Jacob[‡], Raju Philip[§], S. Miono^{*}, H. Ono^{*} and M. Yoshida^{*}

^{*}Faculty of Science, Osaka City University, Osaka 558, Japan

[†]Centre for Earth Science Studies, Akkulam, Thiruvikkal Post, Thiruvananthapuram 695 031, India

[‡]Department of Geology, S. N. College, Varkala, Quilon, India

[§]Department of Geology, Kerala University, Kariyavattom, Thiruvananthapuram 695 581, India

Gold grains from laterite horizons of Nilambur region in northern Kerala exhibit typical morphological characteristics and secondary growth patterns indicative of chemical dissolution, migration and reprecipitation by low temperature fluids attending tropical weathering. Proton-induced X-ray emission (PIXE) analyses of secondary gold grains yielded characteristic spectra for Au, along with Ti and Fe, in the near-absence of Ag and Cu. This study provides the first direct evidence for the formation of extremely pure gold by natural chemical reconcentration process, principally dictated by the oxidation reactions of iron sulphide minerals associated with the primary mineralization. The results have important bearing on the recently realized economic potential of gold in laterites.

GEOCHEMICAL and cosmochemical investigations often warrant elemental characterization of rocks and minerals. Although several analytical advances have been made in the recent decades, including the electron microprobe, the requirement of high sensitivity and multielement capability for the analyses of micron-sized samples has remained unresolved. One of the recent advances in this line is the induction of proton-induced X-ray emission technique (PIXE) for geological materials, opening up the possibility of rapid detection of a spectrum of elements with a high precision¹⁻³. Proton analyses have been shown to be particularly important in understanding the physical and chemical parameters that govern distribution of elements within, and among, sulphide minerals and native alloys⁴. In this paper, we apply PIXE analysis on gold grains from laterite profiles in Nilambur, Kerala, and provide the first direct evidence for extreme purity natural gold resulted by secondary chemical concentration processes attending tropical weathering.

Gold in laterite

Earth's principal gold mineralization occurred in the Archaean, and the lode gold deposits formed during this period have been a major source for global gold production^{5,6}. However, the recent find of the occurrence of gold at economic grades in weathering profiles has emerged as a challenge to existing metallogenic concepts and exploration strategies^{7,8}. One such classic example of gold in laterite was reported by Nair *et al.*⁹ from the Nilambur region of Wynad gold field in northern Kerala. Primary gold in this area occurs as thin films or inclusions within sulphide minerals in vein quartz, associated with pyrite, chalcopyrite, pyrrhotite and ilmenite. The weathered lateritic horizons in this area contain secondary gold occurring as dust, small grains or large nuggets. The morphology of the secondary gold grains and their growth patterns are discussed in detail elsewhere^{10,11}. Secondary gold grain often show regular grain contours and rounded faces, with numerous etched pits or corrosion cavities (Figure 1, *a*). Such corrosion and chemical rounding are distinctly different from those developed through extensive physical transport, such as in alluvial sediments. Within large etched pits in primary grains, neo-formed gold is seen as microcrystals, tufts, filaments, platelets or petaloids (Figure 1, *b-e*). These features dictate that gold concentration occurred by secondary chemical processes attending weathering.

Electron microprobe analysis¹² of primary gold from vein quartz has indicated 85.2% Au and 13.1% Ag. Natural gold is often an alloy of Au, Ag, Cu, S and Fe, among other trace elements. The purity of gold, expressed as its 'fineness', is defined by the ratio, 1000 Au/(Au + Ag). Microprobe analyses¹² show that gold grains in laterite profiles from Nilambur have very high

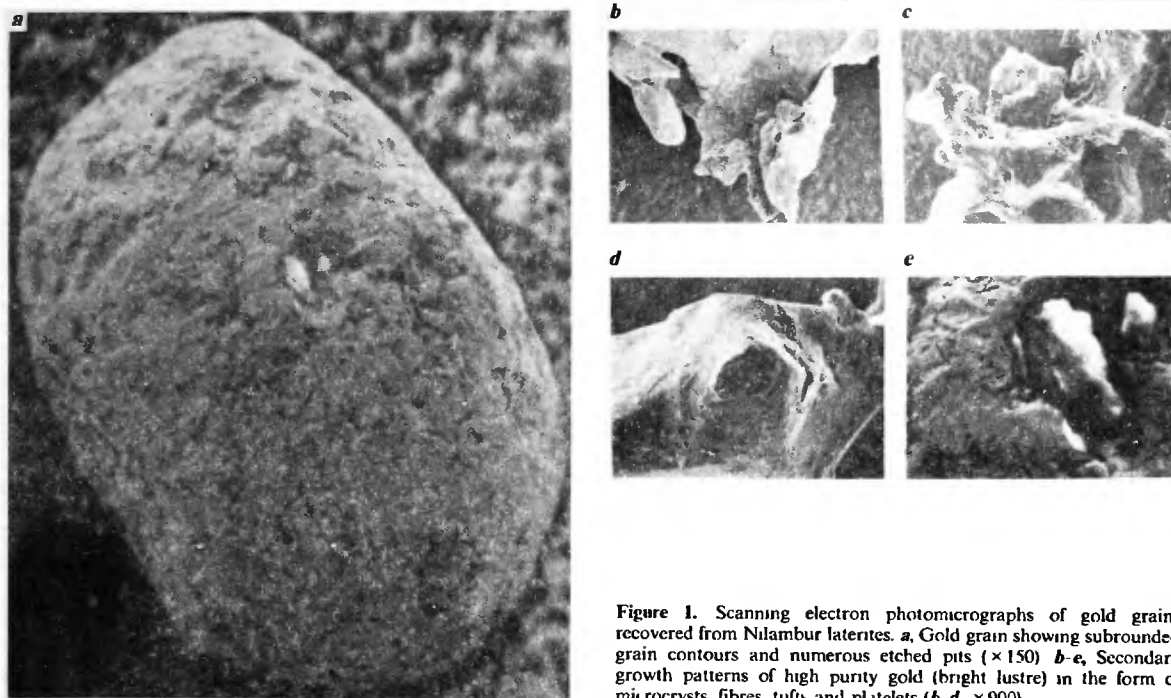


Figure 1. Scanning electron photomicrographs of gold grains recovered from Nilambur laterites. *a*, Gold grain showing subrounded grain contours and numerous etched pits ($\times 150$). *b-e*, Secondary growth patterns of high purity gold (bright lustre) in the form of microcrysts, fibres, tufts and platelets (*b-d*, $\times 900$).

fineness, in the range of 991–999. The increase in fineness while passing from primary to secondary gold is a compelling indication of natural chemical purification. However, it is important to be able to assess the degree to which such refinement has operated. Electron probe has only limited sensitivity for trace element detection so as to yield this information. Hence we applied the PIXE technique on these gold grains.

PIXE analyses

PIXE analyses were performed using a 1.3-MeV-proton-beam accelerator (Compact Disktron, Physitec Co. Ltd, Tokyo) housed at the Ritsumeikan University (Japan). The beam was channelled to enter an aluminium chamber through a collimator. The intensity of beam current was monitored by a Faraday cup, employing 3 nA for the target. X-ray emissions were detected using a Si (Li) detector, connected to a multichannel analyser through an amplifier. Results were processed by an on-line computing system. Irradiation times of 10–20 min were typically adopted. Further details of the instrument set-up are given in Miono *et al.*³

A critical factor relating to PIXE analysis is the backing material. This should be as small as possible so as to minimize *bremstrahlung* background¹. Also, the elemental components of the material should have the lowest possible atomic number to minimize both the

energy and the intensity of the *bremstrahlung* as well as to ensure that there is no background contribution. Hence in this study, we selected highly pure, very thin carbon fibre ($<30\ \mu\text{m}$ in diameter) as the backing material. Gold grains were carefully mounted on the carbon fibre with collodion, the latter was then attached to a sample holder punched with 10 mm diameter holes³.

Representative PIXE spectra of two gold grains are presented in Figure 2, analyses of a large number of grains yielded similar results. The spectra record prominent L_{α} , L_{β} , L_{γ} and M_{α} peaks for gold. However, the most important aspect revealed through this study is the presence of K_{α} and K_{β} peaks for Fe and Ti, and the near-absence of Ag and Cu. The spectra also recorded minor Cl and Ca. The peak for Zn in the spectra is a contribution from the zinc-coating in the sample holder, a routine measure adopted to position the beam during analyses.

Discussion

Gold from primary ore bodies contains substantial amounts of chemical impurities. Native gold in quartz veins is often a natural alloy of Au, Ag, Cu and S, its fineness (purity) defined as a function of the proportion of Au and Ag. Hence, it is with considerable interest that we report the results of PIXE analyses of gold from laterites, which show the near-absence of Cu and

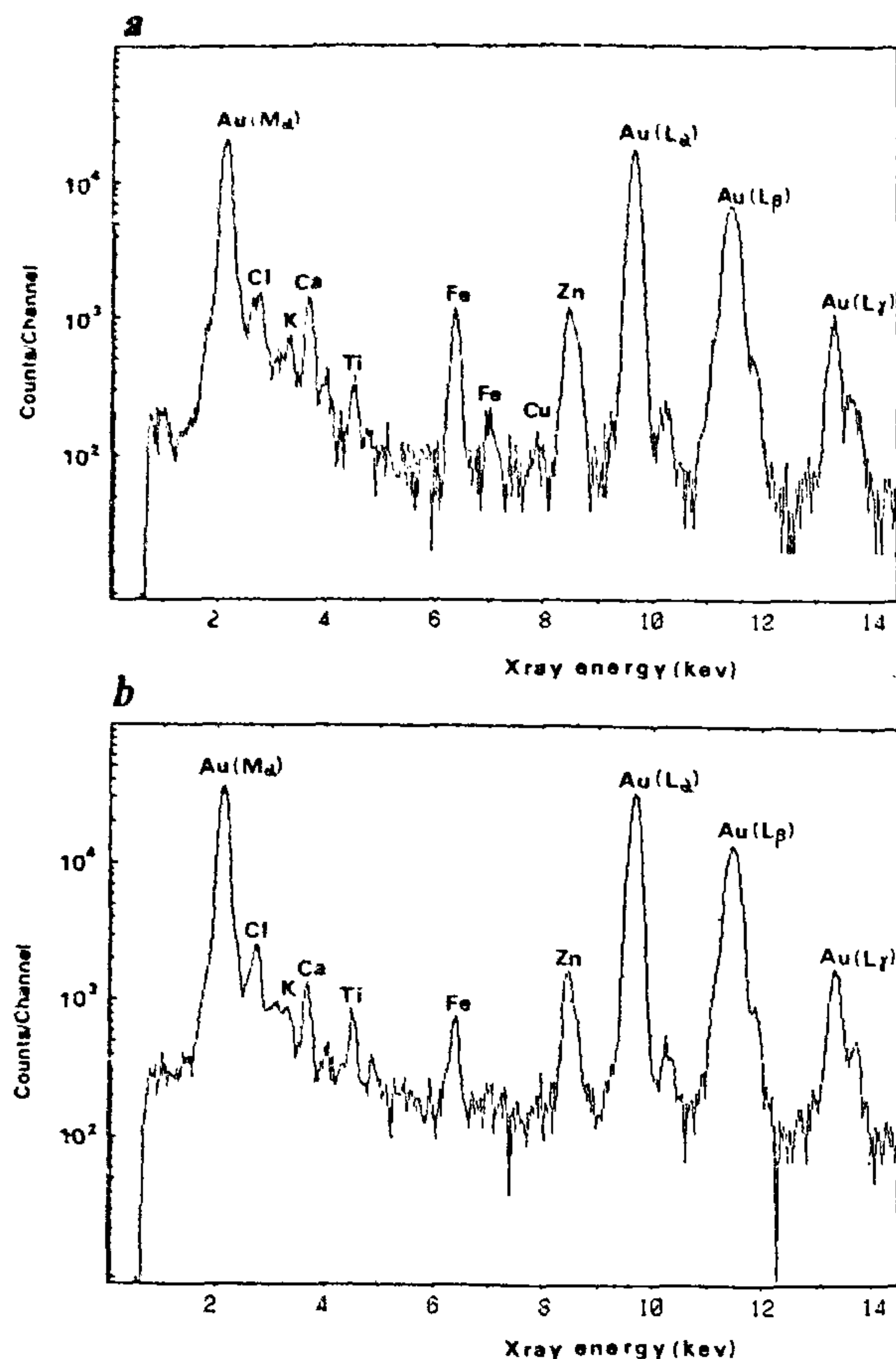


Figure 2, *a, b* Proton-induced X-ray emission spectra from two gold grains in the Nilambur laterites. Au shows prominent L_{α} , L_{β} , L_{γ} and M_{α} peaks. Note the distinct presence of Ti and Fe. Ag is conspicuously absent. A very feeble pulse for Cu is recorded in one sample (*a*), but is absent in the other (*b*). Zn is a contribution from the coating in sample holder. See text for discussion.

Ag. Primary gold grains in this locality with up to 13% Ag has been chemically refined by natural processes to yield extremely pure gold in the weathering profiles. This strongly suggests that preferential dissolution of Au is brought about by low temperature fluids, leading to chemical refinement and reprecipitation of high fineness gold in the laterite horizons.

Our results provide the first direct evidence for the mechanism of supergene gold enrichment. The presence of iron and titanium in the secondary gold grains indicates that gold mobility was primarily dictated by the oxidation of iron sulphides. Mann¹³ and Santosh and Omana¹² identified that ferrolisis reaction is critical to gold mobility in tropical weathering environments. Geochemical modelling of supergene gold formation in Nilambur¹⁰ invoke a direct correlation between pyrite oxidation in the weathering profiles, and migration of gold in the form of chloride

complexes. The PIXE spectra obtained in this study show that optically invisible Fe and Ti are bonded within secondary gold.

Our results have important implications in formulating exploration strategies for gold in the extensive laterite cover constituting vast expanses in peninsular India. The increase in fineness of gold in supergene environments opens up the scope for easily amenable very high purity gold in weathering profiles developed over hidden primary mineralization. The link between iron oxidation and gold enrichment serves as one of the potential exploration criteria which could be employed in the search for this precious metal. Our observations allow the prediction of silver anomalies further away from the sites of gold concentration in weathering profiles (Figure 3). This is because laboratory experiments have shown¹⁴ that there is a marked contrast between the mobilities of Au and Ag, such that $Ag \gg Au$. Hence in all probability, Ag is likely to be transported to farther distances than Au in zones of oxidation. This is also one of the reasons for the chemical refinement of Au, in that Au is preferentially precipitated from a mixture of Au + Ag complexes. Considering the deep penetration of tropical weathering, it is also possible to predict blind ore bodies with thick cappings enriched in Au and Ag. Gold distribution in the primary veins is often erratic, and it is doubtful whether any conventional geochemical surveys can effectively demarcate sharp anomalies in such cases, a problem yet unresolved in Nilambur. On the other hand, low temperature solution activity during weathering leaves characteristic imprints as demonstrated in

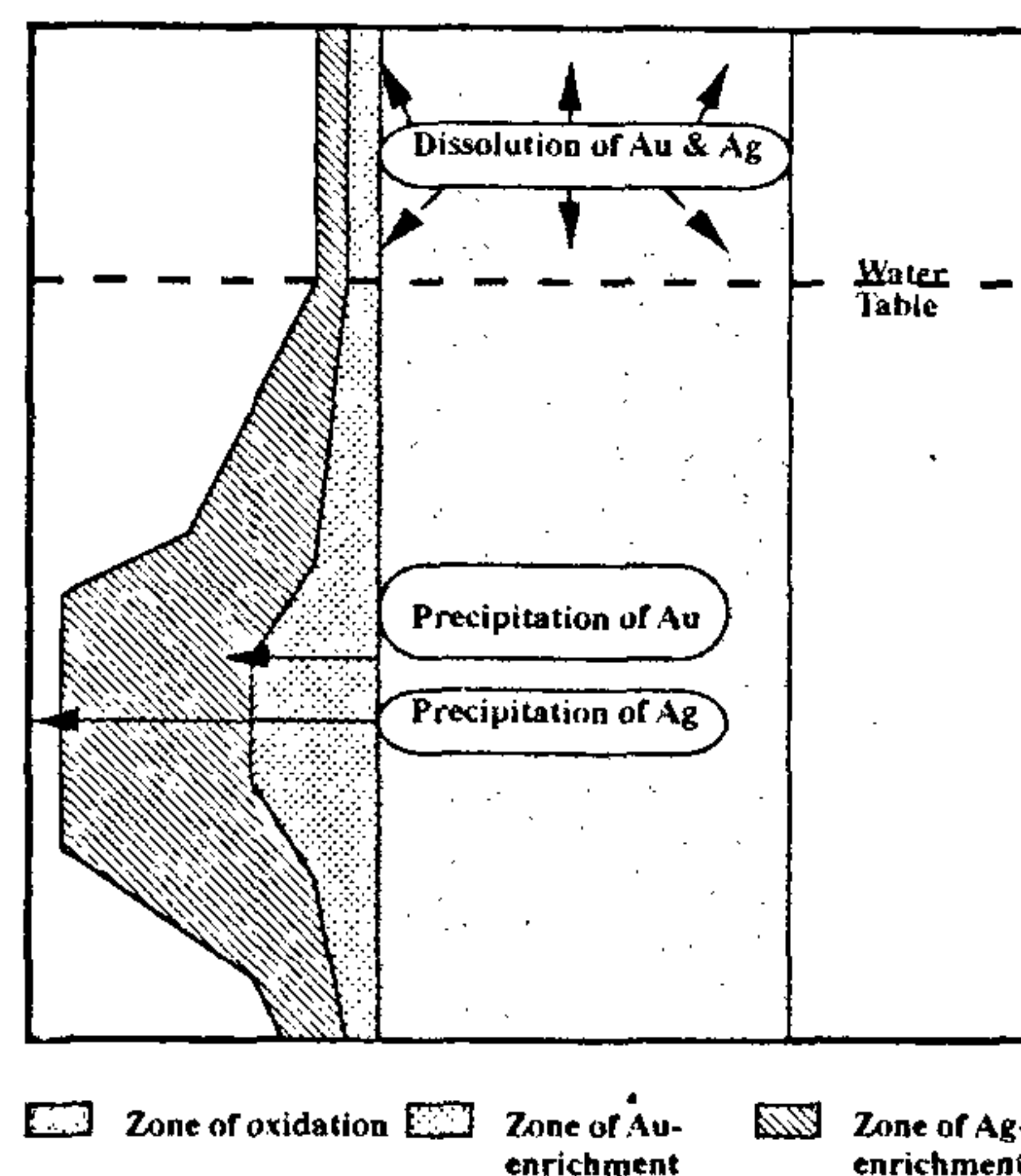


Figure 3. Schematic diagram illustrating the possible mode of gold and silver enrichment in laterites during tropical weathering. Due to the marked contrast in mobilities, Au is deposited near the vicinity, whereas Ag is precipitated farther away. Hence, in an oxidation zone over primary gold mineralization where supergene Au-enrichment with increased fineness is detected, as in the present case, our model predicts the possible occurrence of Ag anomalies farther away.

this study. Hence it should be possible to pick up promising sites from detailed geochemical surveys. We recommend future investigations on these lines.

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Stable isotopic evidence for the origin of ground water in Lakshadweep islands

R. Ramesh and R. A. Jani

Physical Research Laboratory, Ahmedabad 380 009, India

The origin of shallow ground water present in the Lakshadweep islands in the Arabian Sea has so far been assumed to be meteoric. We collected samples of ground water from 10 major islands and measured the stable-isotope ratios of hydrogen and oxygen. Our results indicate that these ground waters are indeed of meteoric origin. Sea water intrusion into these freshwater bodies appears to be small (within analytical uncertainties).

GROUND waters can be of different origins¹. Meteoric ground waters are derived directly from precipitation or recharge from fresh surface water bodies through an unsaturated soil zone. Palaeo ground waters can be meteoric waters that originated in the more distant past during which different climatic conditions prevailed; or they can be formed from the remnants of interstitial marine (saline) waters retained at the time of formation of a marine sedimentary bed. The original isotopic composition could be altered in geothermal conditions, leading to the formation of geothermal waters. The isotopic composition can also change because of the inclusion of sea water in a fresh-water aquifer. Stable isotope composition of waters (δD and $\delta^{18}O$) helps in determining the origin of ground waters.

Lakshadweep is a group of about 37 small islands with a total area of about 28.5 km² situated between 8°

and 12°13'N and 71° and 74°E (Figure 1). These are coral islands built up on a submarine ridge off the west coast of India². To determine the origin of ground water in Lakshadweep Islands, we collected water samples from open dug wells (2 to 3 m below ground level) during April and December 1988. Three samples were usually collected from each island (wherever possible) with a gap of 0.5 to 1 km. Usually one was from a well near the jetty, one near the light house and the third at the other extremity of the island, the jetty being the central point. In the capital, Kavaratti, we collected samples in summer and winter. In addition, three rain water samples were also collected (Table 1).

The oxygen isotopic composition ($\delta^{18}O$) was determined by equilibrating a tank CO₂ gas with 2 ml

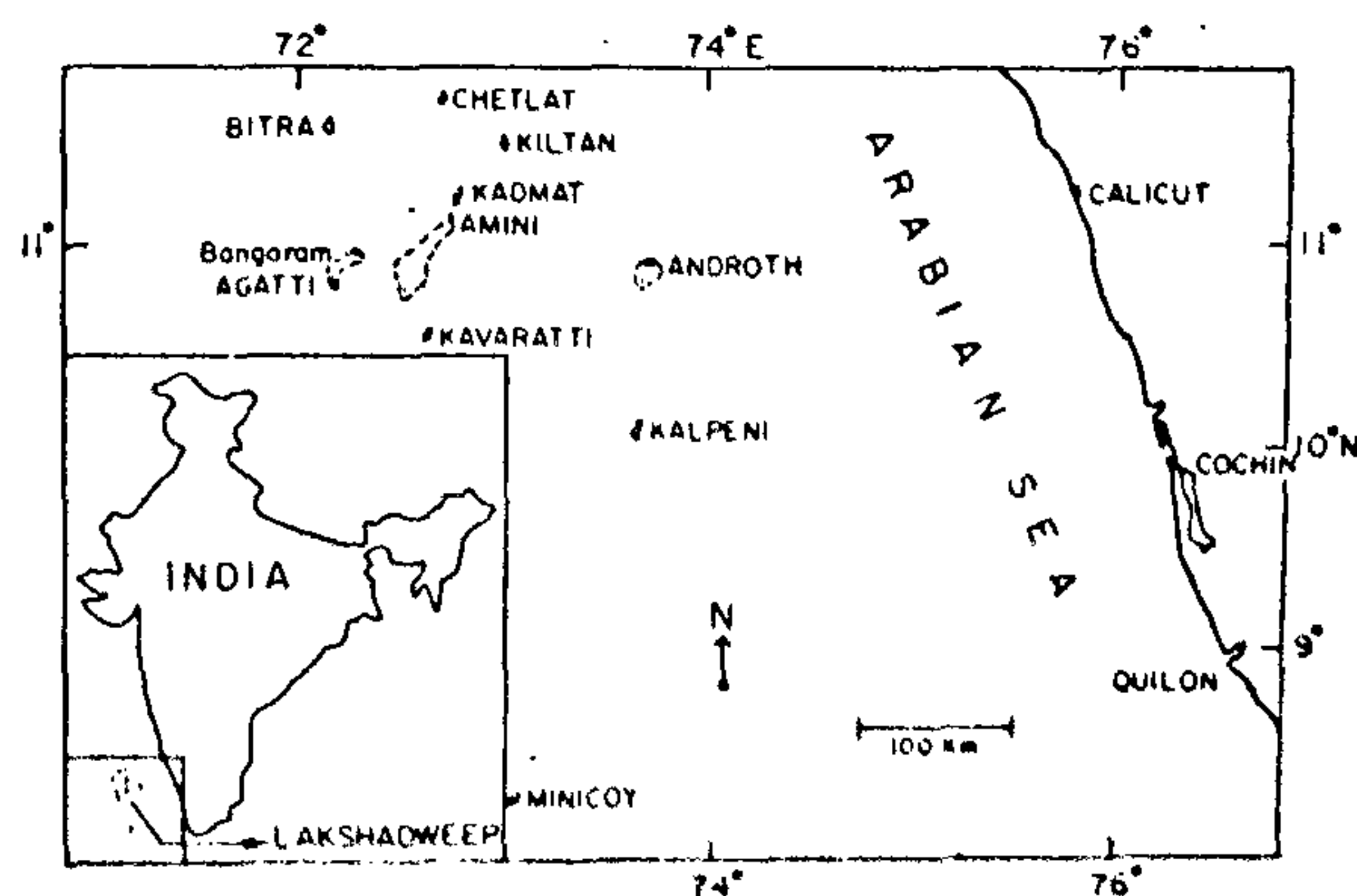


Figure 1. Lakshadweep islands.