

Harvesting a crop of gold in plants

The possibility of turning base metals into gold has intrigued many scientists since the early alchemists, and the discovery of significant gold uptake by plants has long been a 'philosopher's stone'. But background levels of gold in plants are usually very low, rarely exceeding 10 ng per g dry tissue (10 p.p.b.)¹. Hyperaccumulator plants², however, have 100 times the elemental concentrations of normal vegetation, a level of 1 mg per g dry tissue (1 p.p.m.). They can be used in phytoremediation³, the *in situ* improvement of polluted sites. Hyperaccumulation can be induced by adding a chemical amendment, such as EDTA, to a plant substrate to make soluble an otherwise insoluble target metal, such as lead⁴. Here we have induced plants to accumulate gold from ores by treating the substrate with ammonium thiocyanate. This technique might be used as a form of biological mining (phytomining) for gold^{5,6}.

We used ammonium thiocyanate as a substrate amendment because it is commonly used for making gold soluble in mining operations. Table 1 compares the ease of gold extraction in four types of ore. Unweathered sulphide gold ore (not shown in Table 1) from Macraes mine in New Zealand had very little extractable gold, and we were unable to induce plants to remove this to any significant degree. Ore from the Waihi Mine has gold mainly in its native form, which we were able to induce plants to remove. To overcome the problem of sulphide occlusion of gold in some ores and possible non-homogeneity in others, a synthetic finely disseminated colloidal gold ore (made from gold chloride) was prepared and planted with *Brassica juncea*, a plant of high biomass and rapid growth rate. Other experiments using this and other species involved the additional use of a synthetic ore prepared from finely divided gold powder (44 µm) as well as the Tui and Waihi ores crushed to a size of 0.5 mm.

All plants were grown in 250-ml pots containing the appropriate substrate. The

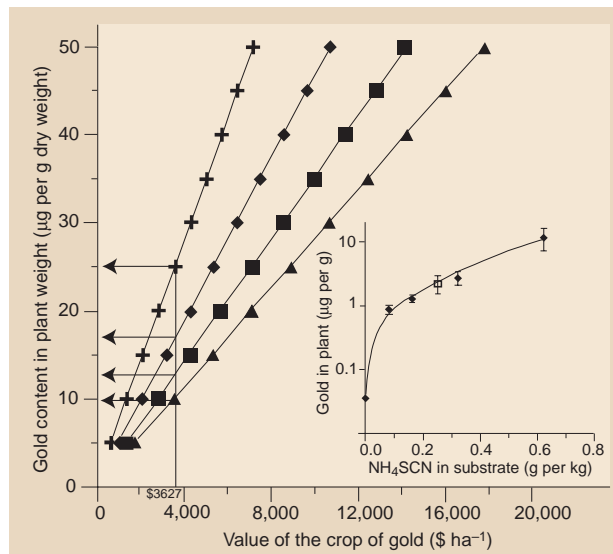


Figure 1 From gold leaves to gold leaf: the economic value of a gold crop as a function of world prices and concentrations in plant material. Prices: \$200 (crosses), \$300 (diamonds), \$400 (squares), \$500 (triangles). Inset, thiocyanate-induced uptake of gold by *Brassica juncea* from a 5 µg per g finely disseminated synthetic gold ore (diamonds) and natural ore (square).

plants were treated with thiocyanate at rates of 0.00, 0.08, 0.16, 0.32 and 0.62 g per kg dry substrate weight. After seven days, aerial parts of the plants were harvested, dried and analysed for gold by graphite furnace atomic absorption spectroscopy. Gold concentrations in several plants as a function of added thiocyanate are shown in Table 1, and in Fig. 1 (inset) for *Brassica juncea* only.

All plant species showed hyperaccumulation of gold. The highest individual value was 57 µg gold per g dry weight in *B. juncea*. However, values were very variable, perhaps because the higher amendment levels caused necrosis of some plants and the induced gold concentration depended on the time that each plant remained viable. *Brassica* plants grown in the synthetic gold powder substrate (Fig. 1 inset) contained as much gold as those grown in the disseminated substrate. Similar values (9–19 µg per g dry tissue) were obtained for the same species grown in natural Waihi ore.

Induced hyperaccumulation of gold can be used for phytomining, with the resulting auriferous 'bio-ore' sold. The gross value of gold and the chemical costs involved in its extraction using a plant with a biomass of

20 t ha⁻¹ (ref. 6) are shown in Fig. 1. Assuming that thiocyanate costs \$3 per kg, the figure of \$3,627 represents its total cost per hectare when added to a depth of 15 cm at an application rate of 0.64 g per kg (the highest rate of Fig. 1). As the price of gold increases, the operation becomes more favourable economically. At the current world price of about \$300 per ounce, we would require a gold concentration of around 17 µg per g dry weight in a crop of *B. juncea*. Several values from the experiments shown in Fig. 1 were either above or very close to 17 µg per g. Some of the other phytomining costs may be recouped by selling the energy of plant combustion, as is done in the sugar-cane industry.

Induced hyperaccumulation of gold appears to be relatively independent of plant species, so it should be possible to use plants (such as chicory) that might be easy to grow on mine tailings. Any residual thiocyanate will be broken down rapidly in the substrate⁷.

We believe this is the first evidence of significant gold uptake by any plant. As well as the economic ramifications this technology may have, this ability to make a 'crop of gold' opens up the way for the phytoextraction of other noble metals.

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Table 1 Conditions and hyperaccumulation data

Species	Substrate	Extraction* (%)	Thiocyanate (g per kg)	Plants	Gold yield (µg per g)†
<i>Brassica juncea</i>	Waihi ore ‡	1.8	0.50	4	9.27–19.34
Chicory	Tui mine §	22.6	0.64	5	0.07–1.19
<i>Impatiens</i> sp.	Waihi ore ‡	1.8	0.20	1	3.09
<i>Arrhenatherum elatius</i>	Waihi ore ‡	1.8	0.50	4	0.07–1.43
<i>B. juncea</i>	Disseminated gold in sand	9.2	0.64	12	2.13–57.32
<i>B. juncea</i>	Fine gold powder in sand	–	0.25	8	0.37–6.48

*Percentage of gold extracted from 1 g of substrate into 10 ml of 2 g l⁻¹ ammonium thiocyanate in 24 h.

†Gold values are for dry matter and are whole-plant analyses except for *B. juncea* on fine gold powder 44 (µm) in sand, which are for leaves only.

‡Natural colloidal gold.

§Acid sulphide mine tailings.

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Salinity history of the Earth's early ocean

It is commonly thought that the oceans are becoming saltier with time as sodium and chlorine are weathered out of continental rocks and transported to the sea. Here we argue that the salinity of the early ocean was 1.5 to 2 times the modern value, and that it did not decline significantly until surprisingly late in the Earth's history. If correct, this theory could help explain why the evolution of higher life took so long.

Volatile compounds such as HCl and H₂O were probably outgassed from the interior of the Earth early in its history¹. Chloride ions would have accumulated in the initial ocean with sodium ions leached from surrounding rocks. The only known processes that can remove NaCl from the oceans in significant amounts are the evaporative deposition of salt and the sequestration of brine as deep groundwater on continents. The brine originates from the dissolution of salt and/or as remnants of partly evaporated sea water. Before the continental crust developed, the salt and brine currently found on the continents would have been entirely in the ocean. The oceans became less saline as continental platforms assembled and brine and salt began to accumulate amid a cycle of deposition and erosion within giant sedimentary basins.

If all the known subsurface salt deposits were returned to the sea, salinity would rise by 30% (ref. 1). More chlorine may currently occur in saline groundwater than in salt, perhaps 2–3 times as much². If this chlorine had come from the sea, the initial salinity could have been twice the present level.

There was some continental crust 3.5 billion years ago (Gyr), but large-scale riverine input of ⁸⁷Sr derived from granite on emergent continents does not appear in the marine sedimentary record until 2.5 Gyr (Fig. 1). Using a recent model of continental growth³, one continental mass existed at 3.0 Gyr and another developed at about 2.5 Gyr (Fig. 1). Two further masses appear at about 2.0 Gyr, from which time the history is dominated by assembly and break-up of continents. If this model is correct,

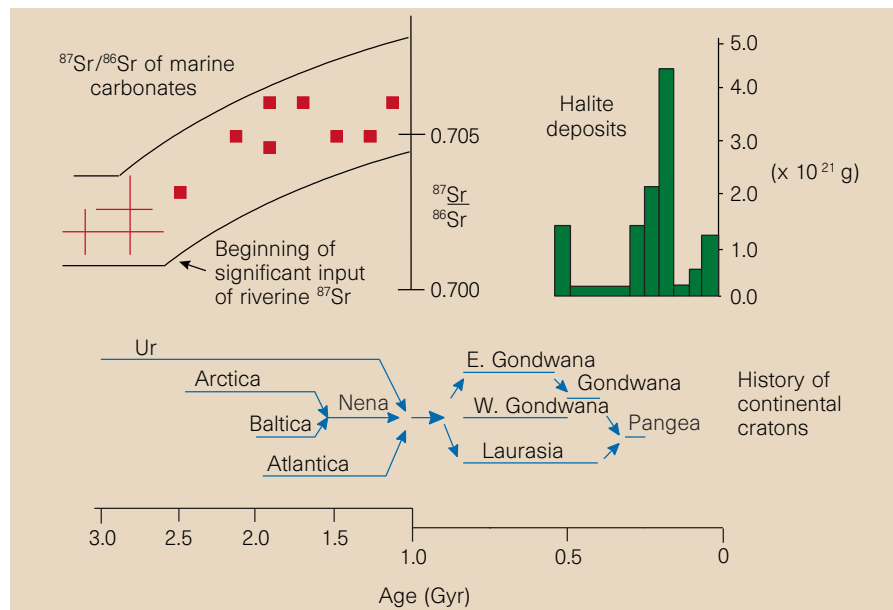


Figure 1 History of continents (after ref. 4), record of salt deposition for the past 540 million years (after ref. 2) and Sr isotope record of marine sediments (after ref. 3). The time axis applies to all three panels and is expanded for the past 1.0 Gyr. Salt deposits older than those shown have not been inventoried but probably total less than 0.5×10^{21} g because of recycling and/or non-deposition. The progressive increase in ⁸⁷Sr is most readily interpreted as input of riverine Sr from the weathering of continents that emerged largely after 2.5 Gyr.

large-scale deposition of NaCl on continents could not have begun before 2.5 Gyr.

Direct evidence for this highly saline early ocean may exist in chemical data⁵ for fluid inclusions in quartz crystals formed in a deep marine hydrothermal environment of 3.2 Gyr. Chloride contents were 165% of the modern value, so the authors inferred that evaporative concentration of sea water had occurred before hydrothermal circulation. An alternative interpretation is that the inclusions are samples of a more saline early ocean.

If large-scale salt deposition and brine storage began at 2.5 Gyr and proceeded at the net rate of the last 540 million years (Fig. 1), the decrease in salinity could have been complete by ~2 Gyr. However, unusual (even improbable) geographic, geologic, climatic, oceanographic and depositional conditions are required for large salt deposits to form. The rate of accumulation was almost certainly lower until continental platforms were widespread at ~2 Gyr. Also, approximately 50% of the known salt was deposited in an interval of 100 million years (Fig. 1). If the conditions that gave rise to this extraordinary accumulation never existed previously, then the decrease in salinity may have persisted until about 1 Gyr, or even to the time of the Cambrian 'explosion' of marine life at 0.54 Gyr.

Most forms of modern macroscopic life cannot tolerate salinities above 50‰ (ref. 6). Cyanobacteria are more salt tolerant than most organisms, and these dominate the Precambrian fossil record. This may be, in part, because higher salinities were an

impediment to the evolution of more complicated life forms. For example, the increase in dissolved oxygen from marine photosynthesizers is commonly invoked to explain the evolution of metazoans⁷. Oxygen solubility in sea water decreases significantly as salinity and temperature increase⁸, so the rise in oxygen level would have been retarded in a more saline ocean. This would be especially true if early Earth temperatures were as high as suggested by isotope data for early sedimentary rocks⁹.

It is commonly assumed that the oceans were the exclusive site of early evolution. However, the lack of fossil constraints, the increasing indications of microbial activity in Precambrian non-marine environments¹⁰ and the inferred higher ocean salinity suggest that this is not necessarily the case. In the present model, the earliest life was either tolerant of salt or was restricted to the more dilute waters of estuaries or entirely non-marine environments. Either way, if continents were not fully developed early on there is a major salinity problem that must be considered when discussing the history of life on Earth or on any object with an overall Cl:H₂O ratio similar to that of Earth.

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