structure and control the speed of magnetization reversal, which is a key issue in device applications.

The importance and the scientific attraction of the type of investigation described here are reflected in the broad activities at numerous synchrotron radiation sources. Novel magnetic devices such as magnetoresistive and spin-polarized tunneling read heads or nonvolatile memories depend on controlling the properties of ever smaller magnetic structures, to which the new analytical methods that use soft x-rays will provide a substantial input.

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PERSPECTIVES: GEOCHEMISTRY

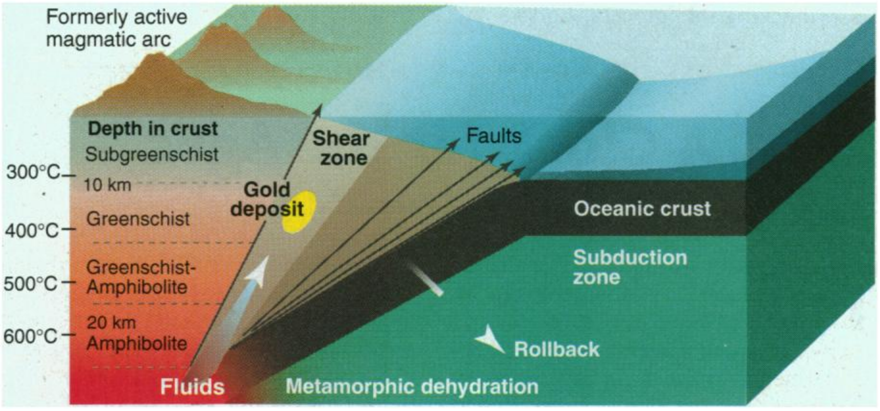
Nature's Gold Factory

Robert Kerrich

Gold is one of the least reactive, or most noble, metals and at 2 parts per billion in weight is also one of the rarest elements in Earth's crust. Yet hot waters circulating deep in the crust may leach gold from large volumes of rock and precipitate it at about 400° to 300°C in vein deposits, where it is concentrated at up to 10,000 times the background level. These observations have elicited a number of questions that are the subject of contentious debate (*1*): (i) Which aqueous species dissolves the "unreactive" gold; (ii) why is gold concentrated in the vein deposits whereas metals such as Pb, Zn, and Cu that are 1000 to 100,000 times more plentiful in crustal rocks are not; (iii) under which hydrothermal conditions is the aqueous gold species soluble (*1*); and (iv) why do the majority of gold deposits form over such a narrow temperature window of about 400° to 300°C, in greenschist metamorphic environments (*1*) (see the figure)? On page 2159 of this issue, Loucks and Mavrogenes report a set of elegant experiments that can answer all these questions thus explaining empirical observations of vein gold deposits (*2*).

Gold is a rare metal in Earth's crust for three principal reasons: astrophysical, atomic, and terrestrial. Main-sequence stars like the sun burn first H and He and then heavier elements, up to ^{56}Fe, in fusion reactions. Elements heavier than ^{56}Fe can only be born by neutron capture reactions in rare astrophysical events termed supernovae, and therefore gold is inherently rare. In addition, all nuclides with odd atomic numbers are rare compared with even numbered neighbors because their nuclei are less stable, resulting in ^{79}Au being even less abundant than ^{78}Pt and ^{80}Hg. Finally, as the terrestrial planets accreted, liquid iron settled gravitationally through the liquid silicate shell to form Earth's iron core, taking gold and other siderophile (Fe-loving) elements such as Pt, Pd, Ir, and Rn with it. Much of Earth's gold inventory is thus sequestered in its core, further reducing its abundance in the crust.

Exceptionally extensive natural processes are therefore required to concentrate this rare, unreactive metal from crustal background levels into rich vein gold deposits. Consider an example of such a natural chemical factory. Four thousand tonnes of gold have been mined from the 300 km by 200 km Abitibi greenstone belt, part of the 2.7-billion-year-old Canadian Shield. Gold is only mined from veins with economic grades, so the actual amount of gold concentrated in this belt may be 10 times greater. If leaching efficiency in the source rock is 50%, then the source volume would have to be 20,000 km^3, equivalent to a block of crust about 50 km by 50 km and 8 km deep. An estimated 1000 km^3 of aqueous fluids with a starting temperature of 500°C must have leached this block of crust, transported gold as an aqueous species, and become channeled along faults where gold precipitated with quartz in vein deposits over the "magic" temperature interval of 400° to 300°C (see the figure).



How gold deposits form. Schematic section of the crust illustrating channeling of hot fluids into shear zone faults where $AuHS(H_2S)_3^0$ destabilizes to precipitate metallic gold at 400° to 300°C and reduced pressure. Greenschist and amphibolite are characteristic sets of coexisting minerals stable under specific pressure and temperature conditions. Ninety-five percent of the vein gold mined globally is from deposits in the greenschist metamorphic environment, at about 400° to 300°C, whereas only 5% is from lower or higher temperature deposits.

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What is the underlying solution chemistry that may enable this geochemical feat? Although gold is relatively unreactive and gold compounds are generally not very stable, gold has been shown to dissolve in aqueous fluids by forming Au-Cl or Au-S complexes (*1*). Au-carbonyl and Au-Te complexes have also been suggested for the dissolution of gold from rocks (*1*). However, which species is actually responsible for the dissolution has remained uncertain (*1*). Loucks and Mavrogenes have now identified the aqueous gold complex likely to be responsible for the dissolution as $AuHS(H_2S)_3^0$—consistent with gold's soft metal ion characteristics and the natural association of gold with the yellow mineral pyrite (FeS_2) termed "fool's gold." This result also answers the second question about gold deposits posed above: The more plentiful metals Pb, Zn, and Cu form soluble complexes with Cl

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but not with S and thus cannot be concentrated by the same mechanism.

The pioneering gold solubility experiments of Loucks and Mavrogenes were made possible by an ingenious experimental design, coupled to remarkable developments in analytical technology. Conventional experiments on the solubility of gold and other metals in natural fluid-rock systems at temperatures of 200° to 700°C and pressures of several hundred megapascals suffer from the problem of quenching (*2*). When fluids are extracted from hydrothermal reactors at high pressure and temperature, solutes may precipitate as the fluids cool to laboratory conditions. Measured solubility relations may therefore not reflect solubility under the relevant hydrothermal conditions. Loucks and Mavrogenes have exploited a natural crystal growth phenomenon to circumvent this problem. When crystals, notably quartz (SiO_2), precipitate from hot aqueous fluids, tiny portions of the fluid are trapped in micrometer-sized cavities that are subsequently sealed during further crystal growth (*3*). These fluid inclusions preserve a portion of the growth solution and its solutes such as Au. Mimicking this process, Loucks and Mavrogenes prepared artificial pits in pieces of quartz, which were then introduced into their hydrothermal reactor apparatus together with gold, aqueous fluid, and natural minerals. The pits filled with fluid under the hydrothermal pressure and temperature conditions and were sealed by crystal overgrowth in the Si-saturated solution, preserving tiny portions of fluid containing gold dissolved as $AuHS(H_2S)_3^0$, thus maintaining the chemical balance.

The fluid-filled pits were opened to extract the fluid with ultraviolet lasers with beam diameters of less than 10 μm. The incident laser energy "drills" through the quartz seal, evaporating the fluid and solutes. Analyzing the tiny portions of evaporated fluid and solute requires a highly sensitive detection system; they were swept in a stream of argon gas into an inductively coupled plasma mass spectrometer, which can scan the mass spectrum in a few milliseconds and can thus detect the small transient signal from a laser burst fluid inclusion.

The experimental results of Loucks and Mavrogenes show that the solubility of $AuHS(H_2S)_3^0$ is extremely sensitive to changes in temperature and pressure. Cooling from 400° to 340°C results in precipitation of 90% of the dissolved gold as metallic Au. Furthermore, depressurization (which occurs as hot fluids ascend up faults) decreases gold solubility by 90%. This explains the narrow temperature window over which most gold deposits form.

The experimental design of Loucks and Mavrogenes will certainly be used to further study how aqueous fluids dissolve, transport, and reprecipitate metals in Earth's crust. Its elegance lies in how closely the design mimics natural conditions. However, some gold deposits form at either higher or lower temperatures than discussed here, and thus there may be other species than $AuHS(H_2S)_3^0$ for solution transport and precipitation of gold. Gold deposits are slowly yielding the secrets of their origin.

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PERSPECTIVES: CIRCADIAN RHYTHMS

A Clock for the Ages

Robert Y. Moore

The behavior of humans, like that of other animals, is characterized by precise 24-hour cycles of rest and activity, sleep and wakefulness. These cycles, termed a circadian rhythm, represent a fundamental adaptation of organisms to a pervasive environmental stimulus, the solar cycle of light and dark. Circadian rhythms are ubiquitous, present in prokaryotes and throughout the plant and animal kingdoms. They have two principal features: In the absence of a light-dark cycle, they oscillate with a period that differs from 24 hours (free-run), but in a normal solar cycle, they are entrained to the sun's stimulus with a period of exactly 24 hours. Circadian rhythms are genetically determined, and the free-running period is very similar among individuals of a single species, with little variation.

Humans have been presumed to be an exception to this rule. Studies have indicated that period may differ markedly among individuals, and it is thought that the free-running period of human rhythms changes with age (*1*). This suggests that humans, unlike other animals, differ in the precision of their timekeeping. Just as we may be short or tall, lean or stout, fair or dark, perhaps our circadian clocks, too, are quite variable in their period. Czeisler and his colleagues set out to address these questions and to discover whether the period of circadian rhythms is precisely regulated in healthy, young humans and whether it alters with aging. Their data, reported on page 2177 of this issue, are both surprising and reassuring (*2*).

The characteristics of circadian rhythms yield insights into a neural system that provides circadian regulation in mammals. Rhythmicity is generated in the absence of external stimuli, indicating the presence of a circadian pacemaker that generates a circadian signal. The expression of circadian regulation indicates that the pacemaker is coupled to effector systems under circadian control, and entrainment by the light-dark cycle implies the presence of photoreceptors with connections to the pacemaker. The genetic determination of pacemaker function, including period, is evidence that a set of molecular events constitutes a fundamental clock mechanism. This has been studied extensively over the last 15 years and we now have some understanding of the process. The basis of circadian function is transcription of clock genes (such as *tim* and *per*) and synthesis of the proteins they encode. Interactions among these proteins result in feedback inhibition of gene transcription. With degradation of the protein products, gene transcription is again initiated to reestablish the cycle (see the figure). The major components of the cycle have been identified and, although much remains to be established, the fundamental mechanisms appear conserved from fruit fly to human (*3*). These molecular events are coupled to a series of neuronal events, not well understood, that result in a circadian output signal. The basis for the neural signal appears to reside in regulation of cell membrane potential (*4*).

All of the available evidence indicates that there is one principal circadian pacemaker in mammals, the suprachiasmatic nucleus (SCN) of the hypothalamus. This small, paired nucleus situated just above the optic chiasm receives entraining information from a discrete subset of retinal ganglion cells through a direct retinohypothalamic tract (*5*). It also receives nonphotic input from other brain areas that modulate pacemaker function (*6*). The SCN exhibits

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