

Fig. 2. Changes in pigmentation of slices of tomato fruit in sterile tissue culture, as modified by gibberellin: data for chlorophyll content of hexane-acetone extract (top) and for lycopene content over a 5-week period (bottom). Gibberellin concentrations of 10^{-7} to $10^{-4}M$ indicated as log superscripts; black columns are untreated controls.

berellin ($10^{-4}M$ in carrier) altered the development of red color and respiration (Fig. 1). Shell color was measured with a Hunter Color Difference Meter, using the alpha reading (reflectance at 500 to 675 $m\mu$) as an index of redness; for each datum point, readings were made on 24 fruits. Figure 1 (bottom) shows that the fruits treated with gibberellin developed half-red color in approximately 14 days, in contrast to the water-treated controls which reached half-red color in approximately 8 days. Ethylene-treated fruits [ethylene at 1000 parts per million (ppm) for 24 hours] reached a similar color within less than 3 days, and this enhancement by ethylene was eliminated by treatment with gibberellin.

Respiratory responses to gibberellin and ethylene were markedly different (Fig. 1, top); rates of evolution of carbon dioxide were measured in a flow-through infrared gas analyzer. Evidently the respiratory climacteric proceeded unchanged after treatment with gibberellin, and the enhancement by treatment with ethylene of the onset of the climacteric rise was likewise unchanged by the treatment with gibberellin.

When various means of application

of the gibberellin were compared, the greatest responsiveness was found in discs of fruit tissue treated under sterile tissue-culture conditions. Figure 2 (top) shows that the chlorophyll content of the tissue pieces, measured as the light absorbance at 665 $m\mu$ by hexane-acetone (4:5) extract (10 g of tissue in 50 ml of solvent) remained high in response to applications of gibberellin at concentrations as low as $10^{-7}M$. The rise in lycopene, measured as absorbance at 505 $m\mu$, also was deferred by the entire range of concentrations of gibberellin tested. After 5 weeks at 20°C, tissue treated with $10^{-5}M$ gibberellin had lost only about 30 percent of its chlorophyll and accumulated 30 percent of its lycopene. The rise in carotenoids, measured as absorbance at 475 $m\mu$, was similarly deferred by treatment with gibberellin.

Ripening of gibberellin-treated fruits could be restored to a normal rate by the subsequent application of ethylene at 1000 ppm for 24 hours.

These results show that part of the ripening process in tomato fruits can be depressed by gibberellin. The singular insensitivity of the respiratory climacteric to gibberellin indicates that the ripening processes are not all closely linked with the respiratory shifts associated with the climacteric (6).

Scott and Leopold (7) have pointed out that it is common for gibberellin

and ethylene to act in opposite manners on various physiological processes; the ability of ethylene to stimulate the pigmentation changes associated with ripening can be opposed by gibberellin. The actions of ethylene on the respiratory climacteric are not opposed by gibberellin. Evidence (8) that the climacteric occurs principally in the mitochondria of tomato fruits suggests that there may be differences between cellular compartments with respect to their responsiveness to additions of ethylene and gibberellin (9).

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Sulfide Solubilities in Alteration-Controlled Systems

Abstract. *Solubilities of sphalerite (ZnS) and galena (PbS) were determined at 300° to 500°C and 1000 bars total pressure in a chemical environment buffered by silicate mineral equilibria. Chloride solutions and muscovite-bearing assemblages characteristic of hydrothermal wall-rock alteration were used; weak acidities at temperature were therefore involved. The metal concentrations encountered tended to be higher than those observed in high bisulfide-H₂S systems at neutral to weakly basic pH used in most previous experimentation; the chemical conditions of the work, although not completely satisfactory, are geologically more realistic than previous experimentation done in the basic-pH region.*

The nature of ore-forming solutions has long been a topic of interest and controversy among geologists. Considerable attention has been recently directed toward experimental evaluation of sulfide solubilities at elevated temperatures and pressures (1-3). The chemical environment used in most of these investigations has been neutral to high in pH and relatively high in total sulfide. These conditions have been

primarily based on chemical arguments that sulfide complexing of certain metal is known to occur in sulfide-rich solutions of high pH.

A somewhat different view from this one is the hypothesis that most hydrothermal ore-forming solutions are predominantly chloride solutions, weakly to moderately acid at the site of ore deposition. Garrels (4) long ago reasoned that the highly saline fluid in-

clusions (5) in the Mississippi Valley lead-zinc deposits may be representative of the solutions responsible for the ore deposits, and that attention should therefore be given to chloride complexes of lead and zinc as agents of transport. This work has been amplified extensively (6) and supported by an experimental investigation of zinc chloride complexes at elevated temperatures (7). Continued studies of fluid inclusions from ore deposits reveal general prevalence of concentrated chloride solutions and suggest the importance of these in ore-forming processes.

This brief introduction is intended merely to emphasize the wide range in viewpoint on the nature of ore-forming solutions that now prevails. A diversity of opinion is to be expected, inasmuch as there may be corresponding diversity in geologic process. However, for a large percentage of sulfide ore deposits, two points should be kept in mind: (i) frequently observed argillization and sericitization, associated with sulfide deposits, require slight-to-moderate acidities adequate to account for the extensive base leaching that took place there; (ii) large-scale pyritization of indigenous iron in wall rocks frequently accompanies ore deposition, resulting in a high sulfur-to-metal ratio for the ore deposit as a whole; this fact suggests either that the ore-forming solutions also contained a high sulfur-to-metal ratio (regardless of the absolute concentrations involved), or that the ore-precipitation process was extremely inefficient, most of the metals having been carried through the system without precipitation and presumably dissipated in the groundwater regime. In other words, the problem of metal transport requires evaluation within the total geologic context in any given case. Where alteration of wall rock was an integral part of the process of ore-deposition, as at Butte, Montana, and probably in many other places where relations are not as clearly documented, the geologic context is to a considerable extent defined by the chemical environment of wall rock alteration.

One cannot yet deduce properties of the aqueous phase, such as metal-to-sulfur ratios or metal-to-metal ratios, simply from suites of assemblages now observed, but it is feasible to determine sulfide solubilities in a system having a composition fixed by a given alteration-mineral assemblage and specified contents of total chloride and

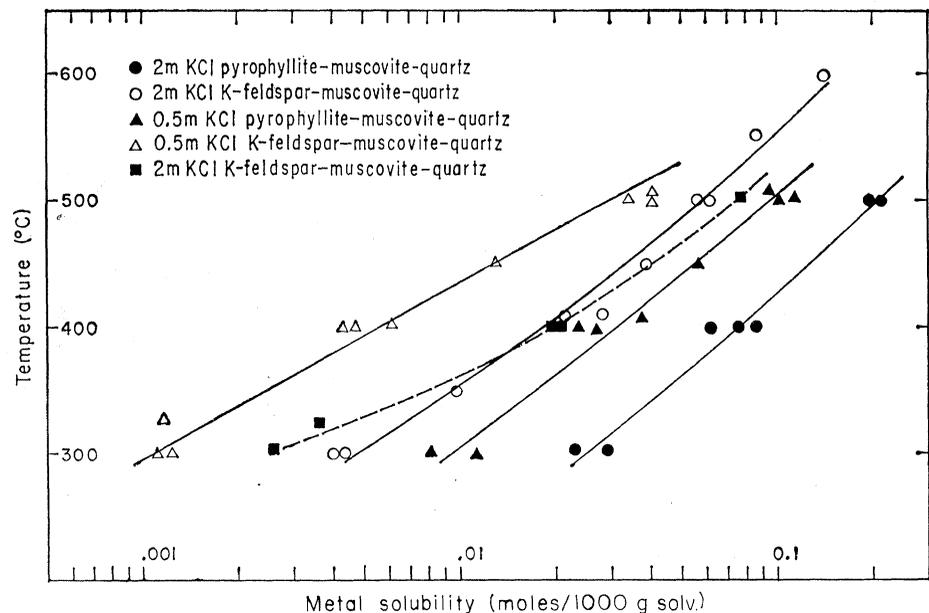


Fig. 1. Metallic-sulfide solubilities in silicate-buffered solutions of KCl and HCl. Solid lines, sphalerite; dashed line, galena.

total sulfur (as $H_2S + HS^- + S^{=}$). This, of course, involves the assumption that the important ligands in an ore solution can be justifiably regarded as chloride and sulfide species. This approach is not unreasonable, but, even so, it is intended only as an initial assumption. Solubility relations under higher pressure-temperature conditions, such as the end-stage magmatic environment, are an entirely different matter that we are not considering.

The simplest case for experimentation (the one we report) is one in which total dissolved metal equals total dissolved sulfur, or the stoichiometric solubility of the sulfide. Measured solubilities of sphalerite in 2M and 0.5M KCl solutions, in equilibrium with K-feldspar, muscovite, and quartz, and with muscovite, pyrophyllite, and quartz from 300° to 500°C, are plotted in Fig. 1; values are also shown for galena in a 2M KCl solution in equilibrium with K-feldspar, muscovite, and quartz.

Our experimental method involves determination of the weight lost from sulfide fragments (single crystals) exposed to KCl solutions at elevated temperatures in a system flushed free of oxygen; a few such experiments were reported earlier (8). Synthetic silicate and natural sulfide minerals were used. The sphalerite contained a small amount of iron, less than 5 percent. Equilibration time was established from runs yielding a constant solubility with time. Small hot-seal bombs each containing

a 9.4-mm-diameter welded gold or platinum tube were used for the reaction vessels. A rapid quench was achieved with ice water, and no back precipitation was evident on the sulfide crystals. Run times, greatly exceeding equilibration time, ranged from a few days to 2 weeks, the shorter times, of course, being at higher temperatures. The precious-metal containers were about 3.7 cm long and contained 1 to 2 ml of liquid. The short tube length apparently eliminated temperature gradients and the mobilization and recrystallization of metal sulfide. No difference in solubility with use of gold or platinum tubes was indicated.

On the basis of fluid-inclusion data, 2M and even 0.5M KCl are probably concentrations too high to be considered geologically realistic. Fluid inclusions are dominantly NaCl rather than KCl solutions. Experiments were run in the potassium-bearing system because it gives better rates of equilibration and crystallization than does the analogous sodium system, but the difference in sulfide solubilities between a KCl solution and a NaCl solution at elevated temperatures should not be very large, at least along the feldspar-decomposition curve (9).

The total range of sphalerite solubilities (molal dissolved Zn) (Fig. 1) is from 0.001M (65 parts per million) at 300°C to about 0.2M (13,800 ppm) at 500°C. Blank runs using the same salt solutions, but without silicate minerals, yielded solubilities ranging from

about 0.0002M (13 ppm) at 300°C to about 0.003M (196 ppm) at 500°C. On the whole, precision was poor in the blank runs because of the small weight loss involved; nevertheless they serve to illustrate the orders of magnitude of the background solubilities involved in chloride rich-sulfur poor systems.

On the basis of experimental results established to date on alteration equilibria (9), the range in total acidity (10) involved in the experiments is not unreasonable. Calculations indicate that the solution pH at 300°C on the K-feldspar-muscovite-quartz curve (Fig. 1) is between 4 and 4.5. The degree of base leaching or hydrogen-ion metasomatism, represented by the environment of ore deposition, generally ranges from relatively weak, in the decomposition of Ca-plagioclase to form sericite (muscovite) or montmorillonite, to intense in the alteration of sericite to kaolinite or pyrophyllite. If one assumes even a rather dilute saline environment, an activity of hydrogen ion of about pH 5 or less would be required for such processes at elevated temperatures (exceeding 200°C). Solutions whose acidities fall within the neutral-to-moderately basic region of pH would not give rise to hydrogen metasomatism, but rather to cation-exchange reactions, feldspathization, and zeolitization.

Although relatively few data points are shown (Fig. 1) for the solubility of galena, one may see that the galena solubilities are essentially the same as those for sphalerite. Because the solubility-product constants for the two sulfides are roughly comparable in this pressure-temperature range, the equivalence of the solubilities suggests that the stabilities of the chloride complexes for both metals are also essentially the same between 300° and 500°C.

The lower-temperature portions of the solubility curves (Fig. 1) are of considerable interest from the standpoint of correlation with theoretical calculations of solubility. Such calculations were made (11) for the case in which total metal equals total sulfur under the experimental conditions of this work. At 300°C the calculations have considerable uncertainty but are in close agreement with the solubilities of galena and sphalerite given (Fig. 1). It is interesting that the concentrations of metal-chloride species considered by Helgeson, and found to be most signifi-

cant under these conditions of moderate acidity, and moderately high sulfur content, are in agreement, within a factor of two, with our experimental results. The present estimates of galena solubility, based on improved thermodynamic data, are higher than those originally computed by Helgeson (6). The calculations for 200°C indicate a smooth extension of the solubility curves to lower temperatures, with a greater rate of change of solubility with temperature at lower temperatures.

Below 200°C, the predicted solubility curves for sphalerite and galena in concentrated KCl solutions are essentially parallel. Although the ratio of the solubility-product constants for galena and sphalerite, as a function of temperature, is not constant, the changes in the stabilities of the chloride complexes of lead and zinc with temperature are such that the solubility curves for the two sulfides are parallel in the lower temperature range and approach each other at high temperatures. Calculations of the degrees of formation of zinc and lead chloride complexes (from extrapolated lower-temperature dissociation constants and activity co-

efficients) indicate that only 0.01 mole percent of the lead and 0.0015 mole percent of the zinc are free in a 2M chloride solution at 300°C.

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Red Cells Coated with Immunoglobulin G: Binding and Sphering by Mononuclear Cells in Man

Abstract. *Human monocytes, macrophages, and certain lymphocytes bind firmly to red cells coated with immunoglobulin G, whether or not it is acting as antibody. Monocyte binding is specific for cells coated with immunoglobulin G and is inhibited specifically by this immunoglobulin or its Fc-fragment in solution. Although not involving serum complement and not usually a prelude to erythrophagocytosis, this binding causes rapid morphological injury to red cells, as manifested by their sphering, increased osmotic fragility, deformation, and fragmentation. It is inferred that mononuclear cells have specific surface receptors for immunoglobulin G and that these provide a critical phase of the mechanism in vivo, whereby red cells or other particles coated with antibody are apprehended and destroyed.*

In man, many antibodies to red cells are very destructive in vivo but cause no hemolysis, agglutination, or evidence of morphologic or metabolic damage to the red cells in vitro. These so-called "incomplete" antibodies are commonly of the 7S immunoglobulin G (γ G) (I) class that fix little or no complement; they are exemplified by the predominant Rh isoantibodies such as anti-D and by most "autoantibodies" of patients with severe forms of immunohemolytic anemia. There is no adequate explanation either for the ex-

traordinary ability of the reticuloendothelial system to trap and destroy red cells coated with these antibodies or for the spherocytosis and increased osmotic fragility that often accompany the hemolytic process.

Red cells coated with incomplete Rh (anti-D) antibodies form rosettes in vitro (2) by adhering tenaciously to certain peripheral blood leukocytes. These rosettes were originally observed in saline suspensions of cells, particularly after brief centrifugation, and they occurred with leukocytes from either D-