stated by Brokaw, the list includes many native metals, sulphides, sulph-arsenides, sulph-antimonides, etc. Of the gangue minerals calcite siderite, and some other carbonates throw down gold at once. Even comparatively stable minerals, like the feldspars and micas, give a distinctly alkaline reaction, and, given time enough, an auriferous sulphate and chloride solution would be neutralized and gold would be precipitated by many minerals of the gangue and of the wall rock.

Thus secondary gold ores might form in any deposit where conditions are favorable to solution of gold, but in a deposit composed of minerals that precipitate gold quickly, any gold dissolved would not be carried to great depths and the secondary ores would remain at least temporarily near the surface. One would not suppose that gold deposits containing much pyrrhotite or calcite or siderite would have as deep secondary zones as deposits containing only pyrite, quartz, feldspar, mica, and other minerals that react but slowly with the solutions.

**Silver.**—Like copper, silver dissolves readily in dilute sulphuric acid, and silver sulphate is dissolved by sulphuric acid if a little ferric sulphate is present. Unlike gold, the solution of silver does not require the presence of a chloride, and unlike copper silver forms stable chlorides in the oxidized zone. If the descending mineral waters carry much chloride, silver tends to accumulate as cerargyrite, but silver chloride is itself somewhat soluble in water and more soluble in concentrated solutions of alkaline chlorides. Thus silver, even in deposits where the chlorides form, may be carried downward in solution and be precipitated at depths where conditions are reducing. Acid sulphate, reacting on pyrrhotite and some other minerals, as shown by Wells, will generate hydrogen sulphide. and hydrogen sulphide precipitates silver sulphides even from highly dilute solutions. Silver is precipitated also from sulphate solutions by stibnite, realgar, and orpiment.

Solutions of ferric sulphide reacting with hydrogen sulphide give powdery sulphur, and as shown by Cooke, amorphous sulphur unites with silver sulphate to form silver sulphide, probably argentite.

The downward migration of silver in sulphide deposits is delayed not only by formation of the chloride, but also by precipitation of the native metal. Some recent experiments by Palmer and Bastin have a bearing here. Several minerals treated with silver sulphate precipitated native silver. The reaction was rapid with chalcocite, covellite, enargite, bornite, and tennantite; less rapid with smaltite, pyrrhotite, chalcopyrite, and arsenopyrite; and weak or inactive with stibnite, pyrite, galena, millerite, and sphalerite.

Mr. F. F. Grout has shown that these relations will hold approximately where the solutions have acid in excess, and that carbonates,—calcite, siderite, rhodochrosite, and several others—precipitate silver rapidly after the acid is used up.

In deposits of ores of silver that contain abundance of the minerals that readily form the native metal in the presence of silver sulphate, one would suppose that the zone of secondary native silver would be rich, but that it would not have such great vertical extent as in deposits composed only of quartz pyrite, and other less active minerals. Even in deposits composed of relatively inert minerals, precipitation of silver would take place ultimately if the deposits were sufficiently permeable to permit a downward migration of solutions. Silver would be precipitated even on feldspars or other

minerals of the wall rock, for, as Sullivan has shown, this reaction takes place with surprising rapidity.

But the migration of silver is not permanently delayed by precipitation in the form of halides and native metal, for dissolving again in ferric sulphate solutions, it passes downward to form argentite and the complex antimony and arsenic sulphides. In many deposits, as in the Comstock Lode and at Tonopah, Nevada, these are the most important minerals. But little is known concerning the chemistry of their genesis. It is known, however, that many deposits of secondary silver sulphides are bottomed by sphaleritic ores, the zone of transition from rich to poor ore being at many places comparativaly narrow. In view of Wells' experiments showing that sphalerite reacts readily with dilute acid to yield hydrogen sulphide, one might suppose that the decomposition of sphalerite had released compounds that were effective in precipitating silver. On the other hand, some sphaleritic deposits have relatively deep secondary zones.

Some recent work by Mr. F. F. Grout indicates that these salts are probably precipitated in an alkaline environment, where alkaline sulphides accumulate, will form in depth silver sulphides and complex silver salts instead of the native metal. The bottom of the zone of native silver does not indicate, therefore, the lower level of the zone of superficial alteration.

**Copper.**—Like gold and silver, copper is dissolved in acid sulphate and chloride solutions, in an oxidizing environment. Unlike gold, the presence of chlorine is not necessary for its solution, and unlike silver, it is rarely precipitated as chloride in the oxidizing zone. The native metal and its oxides, silicates, carbonates and sulphates may form directly from solution, but much of the rich oxidized ore composed of these minerals has doubtless resulted from the oxidation of a relatively rich sulphide ore or that by processes of erosion has been exposed to oxidizing conditions. In ores containing abundant calcite, as pointed out by Bard, there is a strong tendency to delay the downward migration of copper by the formation of relatively insoluble copper carbonates in the upper regions.

The secondary sulphide zones in copper deposits are more clearly expressed than in the deposits of precious metals. This, I believe, is because the copper sulphides dissolve in acid sulphate very readily in an oxidizing environment, but are highly insoluble in acid in the absence of oxygen. In many districts, pyrite, pyrrhotite, sphalerite, or galena have been replaced by chalcocite. Acid waters reacting on some of these minerals liberate hydrogen sulphide, and since copper sulphide has an exceedingly low solubility, hydrogen sulphide will precipitate copper from dilute solutions. It is not certain that hydrogen sulphide is an intermediate product where the primary sulphides are replaced by copper, yet it is believed that the rate at which those minerals are attacked affords a kind of index to the rate at which they will reduce a copper sulphate solution. If so, pyrrhotite which yields hydrogen sulphide more rapidly than pyrite and chalcopyrite in acid solution, should bring about the precipitation of copper more readily than pyrite and chalcopyrite. The same relation holds also in alkaline waters, for pyrrhotite treated with alkaline carbonate, alkaline silicate, etc., yields alkaline sulphides much more rapidly than pyrite or chalcopyrite. Thus, in ore containing abundant pyrrhotite, the secondary sulphide zone, although it might be richer, would not extend to such great depths as it does in ores composed of pyrite and chalcopyrite and little or no pyrrhotite.