On the Formation of Porosity and Microchannels in Growing Scales

Per Kofstad*

It is well known that oxide scales develop porosity and microchannels that permit inward transport of molecular species from the ambient gas even under conditions when there is no evidence of cracking of the scales. It is proposed that such porosity and microchannels develop as a result of grain growth and of plastic deformation (grain-boundary sliding, diffusion creep, etc.) under compressive stresses in the scales. The presence of small amounts of impurities enriched at grain boundaries in the scales may greatly affect deformation and mechanical and transport properties in scales.

INTRODUCTION

Numerous studies of high-temperature corrosion of metals and alloys have shown that protective oxide scales may gradually become pervious to molecular species in the ambient gas.[1,2] For example, $^{16}O/^{18}O$ tracer studies of the oxidation of nickel have shown that O^{18} tracers penetrate preformed $Ni^{16}O$ scales to the region near the metal/oxide interface; the penetration takes place only after an initial period of scale growth.[3] Kofstad and Åkesson[4] found that when Ni specimens with preformed oxide scales are exposed to SO_2, the specimens eventually become sulfidized at the metal/scale interface; this appears impossible to explain without assuming that SO_2 molecules can penetrate the NiO scales. Rahmel and Tobolski[5] found that when iron specimens are reacted in oxygen+water vapor atmo-

*Department of Chemistry, University of Oslo, P.B. 1033, Blindern, Oslo 3, Norway.

spheres at high temperatures (950°C), the iron core beneath the $FeO/Fe_3O_4/Fe_2O_3$ scale is enriched in hydrogen; this suggests that water vapor can penetrate relatively thick scales of wustite. Finally, it was found that iron and low-alloy steels exposed to high pressure CO_2 become carburized after extended exposures at 500–700°C; this is explained by penetration of CO_2 to the regions near the scale/metal interface.[6,7] Numerous other examples could be cited.

This penetration of gaseous species through protective scales can be explained by scale cracking; the cracks allow an inward penetration of gaseous molecules into or through the scales. This is a valid explanation and mechanism for many systems.[1,2]

But gaseous penetration takes place also when the oxide is able to deform plastically and when there is no evidence of cracking of the scales. In order to explain such phenomena, Brückman and Mrowec[8–10] have proposed that microchannels may develop in growing scales. A schematic illustration of the model is given in Fig. 1. It is assumed that the scale grows
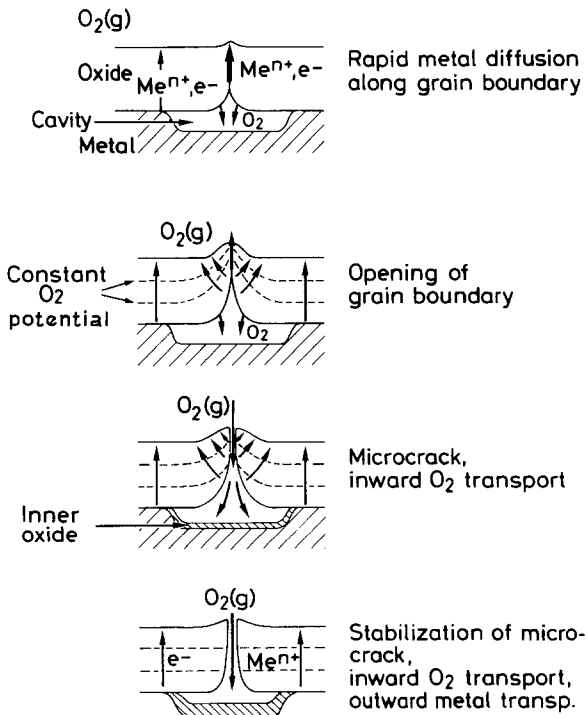

Fig. 1. Schematic illustration of the model for formation of microchannels in oxide scales by preferential outward diffusion of metal ions along grain boundaries. (After ref. 10.)

by outward diffusion of metal ions and, as a result, voids eventually develop at the scale/metal interface. Grain-boundary diffusion of the metal ions is assumed to be much faster than lattice diffusion, and as a result of this, the grain boundary above the void opens up and gradually forms a microchannel. It remains open as long as the chemical potential of oxygen is equal at the surface of the channel and in the neighboring lattice. Oxygen may penetrate the channel to the inner part of the scale.

Although the model seemingly provides an explanation, it is unsatisfactory for several reasons. A major question is how the channels can remain open: when O_2 molecules can move rapidly inwards in the channel, the oxygen chemical potential will be increased, and if metal ions simultaneously diffuse rapidly outward along the inner surface of the microchannel, rapid oxide formation should take place and close the channel. The model assumes that grain-boundary diffusion is much faster than lattice diffusion, but even so results strongly suggest that gaseous penetration takes place through relatively thick growing scales in which lattice diffusion predominates, i.e., in wustite. Furthermore, it is implicit in the model that the scale must grow by outward metal diffusion. As such the model would not be expected to apply to scales growing predominantly by inward oxygen diffusion, e.g., alumina and zirconia scales.

Due to these shortcomings of the model, an alternative explanation is needed. In the following it is proposed that the development of porosity and channels is a result of plastic deformation and creep in the scales caused by growth stresses in the scales.

STRESSES IN GROWING SCALES

Growth stresses in scales arise from several sources.[1,2,10] If the oxide growth takes place through predominant inward oxygen diffusion, and thus the oxide formation takes place at or near the metal/scale interface, the volume of the oxide relative to the volume of the metal from which it is formed, i.e., the Pilling-Bedworth ratio (PBR), will be important in determining the growth stresses. If PBR > 1, compressive stresses will develop in the growing scales. All the transition-metal oxides have PBRs > 1.

If oxide growth takes place by outward migration of metal ions, the new oxide is formed at the scale/gas interface in a supposedly stress-free manner, and growth stresses will then seemingly not arise. But as metal diffuses outwards and the volume of the metal core decreases, growth stresses will still arise due to the tendency of the oxide to adhere to the metal. The receding metal core with adhering oxide will produce compressive stresses in the scale parallel to and tensile stresses normal to the metal surface. This is illustrated schematically in Fig. 2.
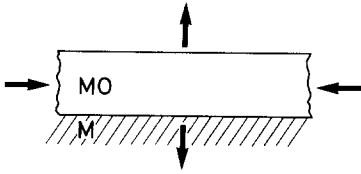
Fig. 2. Growth stresses in oxide scale growing by outward diffusion of metal ions.

If oxide formation takes place within the growing scales through countercurrent oxygen and metal diffusion, large compressive stresses develop in the scales. This takes place in the growth of chromia scales.[11-13]

All in all, growth of scales on all of the "common" metals (Ni, Co, Fe, Cr, Al, etc.) will result in compressive stresses in the scales. The important question then becomes: how do ceramics behave under such stresses?

CREEP AND PLASTIC DEFORMATION OF CERAMICS AT HIGH TEMPERATURES

Ceramics may be deformed through several mechanisms, which include diffusional flow, dislocation glide, and grain boundary sliding.[14,15] Single crystals or grains deform by diffusional flow mechanisms, and two such mechanisms are illustrated schematically in Fig. 3. If the diffusion of defects takes place by lattice diffusion, the process is known as Nabarro-Herring creep.[14-17] Figure 3a shows the corresponding flow of vacancies in a homogeneous single crystal due to an imposed shear stress. Figure 3b shows the vacancy flow when the vacancies diffuse along the grain boundaries. This creep process is known as Coble creep.[14-18] For both creep mechanism interstitial defects move in the opposite direction of the vacancies. Furthermore, the creep processes result in an elongation of the crystal in the direction normal to the compressive stresses.

It should be noted that the creep processes in a ceramic, e.g., in M_aO_b, are governed by the slower moving species, i.e., the M or O ions or their corresponding defects. Coble creep becomes increasingly important the lower the temperature due to the lower activation energy of grain-boundary diffusion. Furthermore, Coble creep is favored for small grain sizes because it is proportional to (grain size)$^{-3}$, while Nabarro-Herring creep is proportional to (grain size)$^{-2}$.[14]
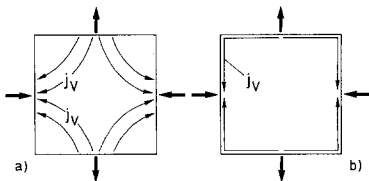

Fig. 3. Vacancy fluxes, j_V, in single grains due to imposed stresses: (a) through vacancy-lattice diffusion (Nabarro-Herring creep); (b) through diffusion along grain boundaries (Coble creep). Interstitial defects move in the opposite direction of the vacancies.

Fig. 4. High-temperature deformation of an array of hexagonal grains subjected to tensile stresses as indicated: (a) hexagonal array before deformation; (b) array after diffusional deformation of the single grains but without relative grain movement (grain-boundary sliding); and (c) hexagonal array after simultaneous diffusional deformation and grain-boundary sliding. (After Evans and Langdon, ref. 14.)
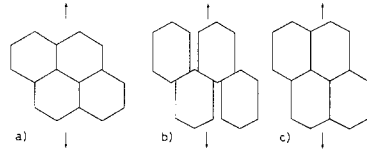
When these processes take place in a polycrystalline, homogeneous material, each grain is deformed as illustrated in Fig. 4. If the ceramic is to remain dense and coherent, the grains must also move relative to each other by grain-boundary sliding (Fig. 4c). Thus, the overall deformation may be regarded as a combination of diffusional creep and grain-boundary sliding.[14] If the processes can be considered to be sequential, the slowest process will dominate the creep behavior.

While the detailed mechanism of grain-boundary sliding is not well understood, it is known that for polycrystalline materials, grain-boundary sliding may be governed by lattice or grain-boundary diffusion, depending upon the relative importance of these modes of diffusional transport. For viscous materials or if a viscous phase is present at the grain boundaries of a polycrystalline material, grain-boundary sliding is determined by viscous flow. Furthermore, grain-boundary sliding will be affected by the presence of a second phase or an enrichment of foreign atoms at the grain boundaries, by an irregular grain-boundary surface containing geometrical obstacles, etc. The overall creep process eventually leads to the formation of porosity and voids at grain boundaries and to intergranular failure.[19]

DEFORMATION AND GRAIN GROWTH IN GROWING SCALES

The above considerations apply to homogeneous solids. The overall deformation processes are considerably more complicated in growing scales because a chemical potential gradient exists over the scale, i.e., the defect concentrations and diffusion coefficients vary continuously across the scale. Accordingly, the rates of deformation will vary across the scale.

In addition to these deformation processes, grain growth also normally takes place in growing scales. The process can be considered to involve growth of the individual grains where the larger grains grow at the expense of the smaller grains. If this process takes place by diffusional flow mechanisms (e.g., lattice and grain-boundary diffusion), the rate of growth will—as for the diffusion-controlled deformation—be governed by the slower moving species, i.e., either the M or the O ions in M_aO_b. Thus, in general, the faster

rate of grain growth will take place in the regions with the faster rate of deformation.

Growing Scales of MO

Let us apply these general principles to growing scales of NiO, CoO, and FeO. All three oxides are metal-deficient; the predominant point defects are metal vacancies (e.g., NiO) or complex defects (e.g., FeO).[2,20] Metal lattice self-diffusion is orders of magnitude faster than oxygen diffusion. Creep rates increase with increasing deviation from stoichiometry and are probably governed by oxygen interstitial-type defects.[2,20]

For these types of scales the faster rates of deformation and grain growth will then take place in the outer layers of the scales. After high-temperature oxidation of these metals, the outer layers are also found to consist of large, columnar crystals, whereas the layer next to the scale/metal interface normally consists of fine-grained oxide.[2,10,21] This type of micro-structure is concluded to reflect the higher rates of deformation and grain growth in the outer layer of the scale.

The fine-grained nature of the scale next to the metal/oxide interface is affected by other processes as well.[2,10] First, as the scale grows in thickness, it may not be able to deform rapidly enough to maintain adherence to the metal or coherence within the scale. As the metal recedes due to outward metal transport, voids and cavities develop in the inner part of the scale, particularly at edges and inhomogeneities at the metal/scale interface. The reaction may, however, be sustained by outward diffusion of metal along pore surfaces and by inward dissociative transport of oxygen. Dissociative transport is aided if the voids and pores contain $CO + CO_2$ or $H_2 + H_2O$ mixtures. Second, development of the inner porous and fine-grained layer of the scales takes place earlier and is more pronounced for impure metals or dilute alloys. This may be related to the accumulation of oxides of impurities or alloy components at or next to the scale/metal interface. Depending upon the solubility of the foreign oxide in the oxide of the base metal, e.g., SiO_2, Cr_2O_3, etc., in NiO, the foreign oxide may accumulate at grain boundaries and surfaces and will generally affect—and usually impede—the deformation and grain growth in this part of the scale.

It is proposed that porosity and microchannels are formed along the grains in the scales as a result of the deformation processes. In a growing scale the situation is different from that in the homogeneous solid illustrated in Fig. 4. In a scale the defect concentrations and diffusion coefficients vary through the scale thickness. For metal-deficient MO scales the diffusional deformation is greater at the exterior portion of the scale. Even for a single grain the deformation will in principle be larger in the part facing the

scale/gas interface then in the part facing the metal/scale interface. Further-more, grain-boundary sliding, governed by diffusional transport, will be greater in the outer part in these types of scales.

If the relative rates of diffusional deformation and grain-boundary sliding vary through the thickness of the scale, porosity is expected to develop. For instance, if the rate of grain-boundary sliding decreases faster than that of diffusional deformation in the inner part of the scale, porosity is expected to begin to develop along grain boundaries in the interior.

It can be difficult to prove directly that pores and microchannels are present within the scales at temperature. Cross-sections of scales are, of course, always examined after cooling to room temperature, and due to differential cooling rates through the specimens and differences in the thermal expansion coefficients of the metal and the oxide scale, the question will always arise if apparent porosity is a result of the cooling process. On the other hand, if porosity is present at temperature, it should also be present after cooling. When fractured cross-sections of oxide scales are examined by electron microscopy, fractographs commonly exhibit porosity along grain boundaries. Two examples of this are illustrated in Figs. 5 and 6, which
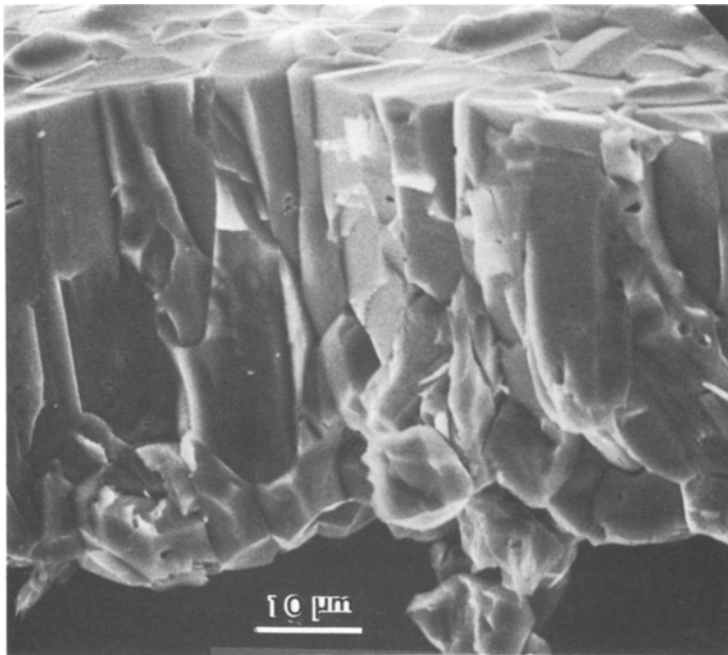

Fig. 5. SEM-fractograph of NiO scale formed on high-purity nickel after oxida-tion for 24 hr in 1 atm O_2 at 1000°C.
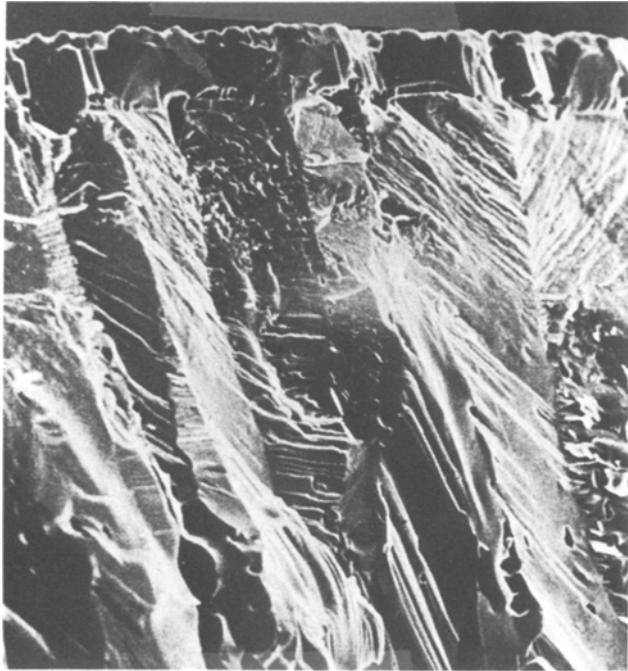
Fig. 6. SEM-fractograph of scale formed on Armco iron at 800°C after reaction in 0.13 atm $CO_2 : H_2O : O_2 = 8 : 1 : 1$ for 24 hr. The major part of the scale consists of wustite.[22] 50×.

show, respectively, a NiO scale grown on high-purity nickel in 1 atm O_2 at 1000°C and the scale formed on Armco iron at 800°C in $CO_2 : H_2O : O_2 = 8 : 1 : 1$ after reaction for 24 hr. The SEM-fractographs show considerable porosity along the grain boundaries. Both figures also show the large columnar grains whch are typical for these types of scales and which are concluded to be formed through the deformation and grain-growth processes.

But other processes may also affect the microstructure of the scales. As a result of grain growth in the scales, it would not be unexpected that pores may develop in the single grains, reflecting the original triple boundaries of smaller grains which have grown together to form the larger grain. Such pores within single grains are observed also in growing scales.[2] This type of porosity is common in sintered ceramic bodies.[23] The relative rates of oxide growth, grain growth, and deformation will be a function of temperature, and generally it appears that denser, less "porous" scales are formed at very high temperatures.

Grain growth may also be impeded and porosity can be stabilized by the enrichment of foreign atoms or accumulation of other phases at grain boundaries and pore surfaces. As described above, this is believed to be the reason for the very fine-grained nature of the inner layer of metal-deficient scales on impure metals. One may also speculate if the presence of hydrogen (water vapor) and carbon (CO_2) may have such effects on the porosity/microstructure of oxide scales.

Growth of other Oxide Scales

The microstructures of oxide scales with different types of defect structure are expected to be different from those of the metal-deficient MO scales. Thus, if rates of deformation and sintering are faster at the metal/oxide interface, the grains in this region of the scale should be larger. One example is the microstructure of Cr_2O_3 scales formed on chromium at low-oxygen pressures at high temperatures as illustrated in Fig. 7.[12] In this
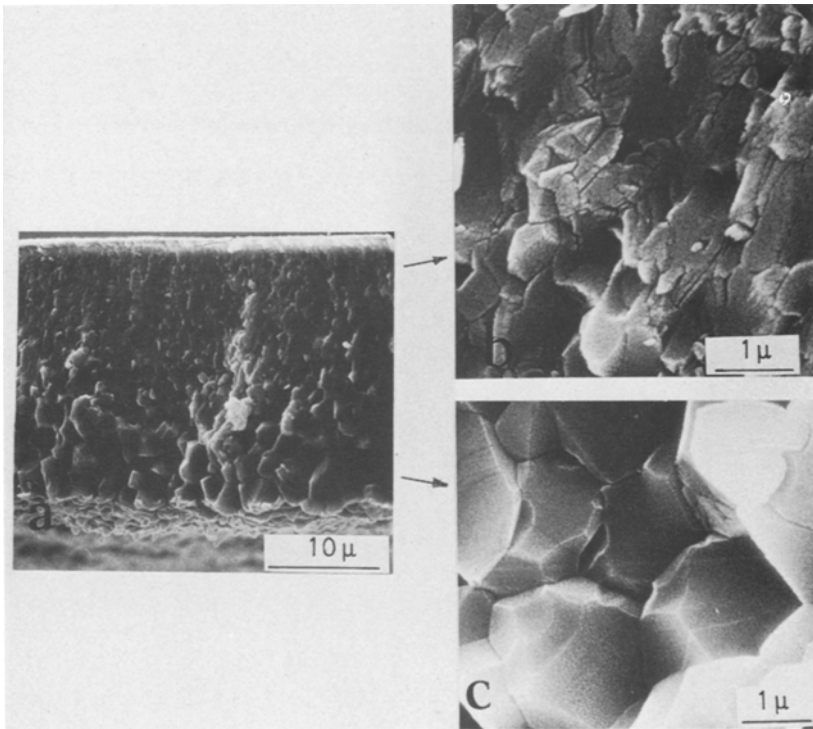

Fig. 7. SEM-fractograph of Cr_2O_3 scale formed on chromium during oxidation in 7×10^{-7} atm O_2 at 1200°C.[12]

case the grain size gradually decreases outward in the scale probably due to the faster rates of grain growth and deformation in Cr_2O_3 near the Cr/Cr_2O_3 boundary.

The deformation and grain growth in scales should in principle take place in all types of scales regardless of whether the scales grow by outward metal diffusion or inward oxygen diffusion. An example of a scale growing by inward diffusion of oxygen and containing large columnar grains—in all probability formed by simultaneous deformation and grain growth—is shown in Fig. 8. The illustration refers to a Ta_2O_5 scale grown on tantalum in 1.3×10^{-5} atm O_2 at 1400°C.[1,24] It may be noted that under these conditions, the rate of reaction is governed by the adsorption of oxygen on the scale surface, and therefore during oxidation there was only a small chemical-potential gradient across the scale. The large crack at the specimen edges must be to a large extent be due to cracking during cooling, because the metal at the tip of the crack is not significantly oxidized.

CONCLUDING REMARKS

In these considerations of the high-temperature corrosion of metals and alloys, it is proposed that porosity and microchannels may be formed in scales due to growth stresses and resultant deformation and grain growth.
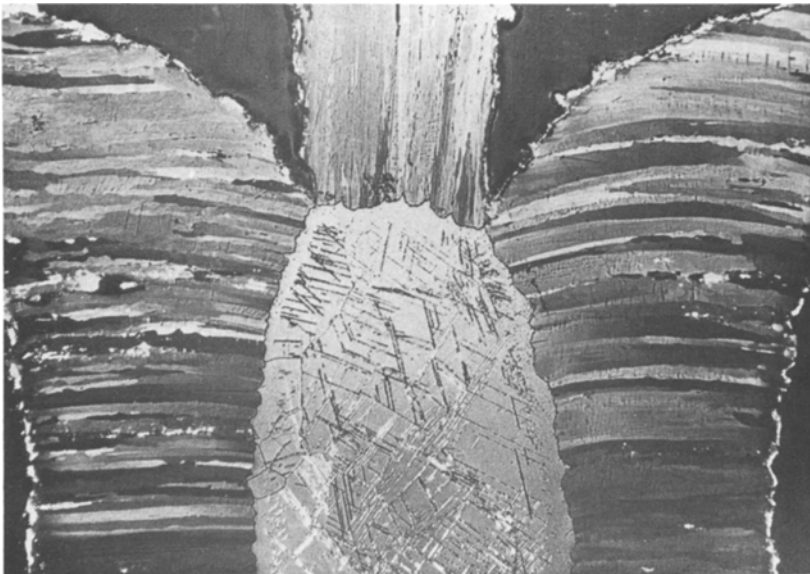

Fig. 8. Metallographic cross-section of tantalum specimen oxidized for 450 min at 1400°C and 1.3×10^{-5} atm O_2.[1,24] 100×.

The microstructures of scales are consequently complex functions of the rates of oxide growth, plastic deformation, and grain growth. Deformation and grain growth may be particularly sensitive to minor amounts of impurities in the metal or reacting gas.

It is suggested that the protective properties of scales may be improved by proper control of the properties of grain boundaries and of the deformation processes in the scales. Chromia and alumina scales, which are the most important protective scales for high-temperature alloys, appear to be prime examples of this. Both types of scales grow by grain-boundary diffusion.[2] Correspondingly it is expected that high-temperature deformation and the resultant formation of porosity and microchannels in these scales are governed by grain-boundary diffusion and the properties of the grain boundaries. The effects of oxygen-active elements on the properties of chromia and alumina scales can be interpreted in these terms. Thus, the author has proposed that the important effects of oxygen-active elements are that they are enriched at grain boundaries of the scales, and that they thereby enhance inward oxygen diffusion and retard outward metal diffusion during scale growth.[2] Another important effect of oxygen-active elements is that they greatly reduce the grain growth in the scales,[25,26] which is probably also a result of the enrichment or accumulation of the oxygen-active elements at the grain boundaries.

Only the growth of oxide scales has been considered and used in the illustrative examples. However, the same principles will, of course, apply to other types of scales such as sulfide scales.

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