

Rhenium-Osmium Evidence for Regional Mineralization in Southwestern North America

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More than 40 base metal porphyry ore deposits in southwestern North America are associated with the Laramide orogeny (about 90 million to 50 million years ago). Rhenium-osmium dates on molybdenite, a rhenium-enriched sulfide common in many of the deposits, reveal that in individual deposits mineralization occurs near the final stages of magmatic activity irrespective of the time of inception, magnitude, or duration of magmatism. Deposits that differ widely in location and in the extent and timing of magmatism have nearly identical ages for mineralization. Rhenium-osmium ages suggest that mineralization occurred during two distinct intervals from about 74 million to 70 million years ago and from 60 million to 55 million years ago. Most deposits that formed in the oldest interval are within the older Precambrian basement of northwestern Arizona, whereas the younger deposits are restricted to the younger Precambrian basement in southern Arizona and northern Mexico. Synchronous, widespread mineralization indicates that similar crust-mantle interaction occurred on a regional scale for ore deposits once thought to be the product of localized processes.

An ore deposit forms when metals in the crust reach concentrations at which they can be recovered economically. Two common questions are where did the metals come from and when did the deposit form? Many ore deposits are associated with subduction at convergent plate margins, where heating and dewatering of the subducted plate produce magmas in the mantle and lower crust. Eventually these magmas are intruded into the upper crust, and the metals, usually as sulfide minerals, are concentrated in the intrusions and in adjacent country rocks (1). The most enigmatic question in the study of ore deposit genesis is whether the metals originate in the mantle and lower crust and are carried in the magma or are derived locally after emplacement of the magma into the upper crust. This question is further complicated for many ore deposits because the age, composition, and orientation of the subducted and overriding plates may be destroyed or obscured by later geologic events. Ore deposits associated with the Laramide orogeny in southwestern North America are unusual because information about the nature and orientation of the subducted and overriding plates is preserved (2).

With regard to the second question, many radiogenic isotope decay systems have been applied to the dating of sulfide ore deposits, but few actually date the sulfides. Lead isotopes in galena (PbS) and other sulfides often give reasonable ages for mineralization but suffer from numerous problems that make interpretation difficult (3).

Uranium-lead systematics have also been applied to gangue minerals, which are believed to form at the same time as the sulfides, but U-enriched gangue minerals in ore deposits are rare (4). Potassium-argon (^{40}K - ^{40}Ar) and argon-argon (^{40}Ar - ^{39}Ar) systematics have been used to date the more common K-enriched gangue minerals in veins containing sulfides (5, 6), and the samarium-neodymium system (^{147}Sm - ^{144}Nd) has been used to date rare-earth element minerals that are sometimes present with the sulfides (7). These dating techniques operate on the assumption that the gangue minerals have an equilibrium relation with the sulfides, but data pertaining to this equilibrium may be questionable or lacking altogether. The rhenium-osmium system (^{187}Re - ^{187}Os) overcomes these problems because the sulfide ore minerals can be dated. In this article, we compare the timing of sulfide mineralization, on the basis of Re-Os ages for the sulfide molybdenite, with the onset, duration, and magnitude of magmatism associated with the Laramide orogeny.

Geological Background

The Laramide orogeny involved intense uplift, magmatism, and compressive deformation over much of western North America from 90 million to 50 million years ago (2). Base metal porphyry deposits associated with the Laramide orogeny have been a rich source for copper, molybdenum, and lead for nearly a century and are abundant throughout southwestern Arizona and northern Mexico (8). These deposits are so named because the igneous rocks that host

mineralization exhibit a strongly bimodal size distribution of primary minerals or a porphyritic texture. Base metal porphyry deposits are formed when heated aqueous fluids circulate through these igneous rocks, which are intruded at depths of 1 to 10 km (9). The most common sulfides are chalcopyrite (CuFeS_2) and molybdenite (MoS_2), which precipitate in a complex network of fractures (a stockwork) in the intrusion and adjacent igneous rocks or as a massive sulfide body that replaces adjacent sedimentary rocks (a skarn). The deposits occur along convergent plate margins, where oceanic lithosphere has been subducted (1).

Laramide base metal porphyry deposits formed in two different types of Precambrian basement in the overriding continental plate. In the northwest, the Precambrian basement is composed of metamorphosed igneous rocks more than 1.7 billion years old. The Precambrian basement to the southeast is composed of metamorphosed sedimentary rocks less than 1.7 billion years old, with the boundary between the two regions approximated by the Holbrook lineament (10, 11) (Fig. 1). The Precambrian basement is not continuous in outcrop but is assumed to underlie the younger rocks and is often exposed during mining. These differences in the Precambrian basement correspond with different intervals of base metal porphyry mineralization during the Laramide orogeny.

Re-Os Dating of Molybdenite

The Re-Os system holds great promise for the direct dating of sulfide deposits because both Re and Os are chalcophile elements and partition preferentially into sulfides or metallic phases. Both elements are also siderophile, which means that most of the Re and Os budget is in the core of the Earth and that, even in sulfides in the crust, they are typically found in the part-per-million to part-per-trillion range (12). Molybdenite is an ideal mineral for the dating of sulfide mineralization because it is a Re-enriched sulfide found in a variety of deposits. Initial dating attempts have produced erratic results (13) because of the post-crystallization mobility of Re in molybdenite (14, 15). The determination of Re distribution by microprobe, infrared transparency with the use of infrared microscopy, polypyr type by x-ray diffraction, and the search for Re-

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bearing intergrowths by microprobe back-scattered imagery make it possible to select suitable molybdenites for dating (15). Molybdenites selected by these criteria were subjected to fusion, distillation, and measurement techniques described elsewhere (15, 16), and mineralization ages were obtained by Re-Os geochronometry (Table 1).

We chose the base metal porphyry deposit at Bingham, Utah, as a locality for testing the resolution of Re-Os dating because crosscutting relations and precise K-Ar ages were known (17). Magmatism at Bingham spans about 7 million years, and mineralization is associated with an altered quartz monzonite porphyry that was emplaced into monzonite dated at 39.8 ± 0.4 million years and crosscut by latite dikes dated at 37.7 ± 0.5 million and 38.0 ± 0.2

million years. Thus, mineralization occurred between ~ 40 million and 38 million years ago. The Re-Os age of molybdenite from the quartz monzonite porphyry at 38.6 ± 0.6 million years is consistent with this history (Fig. 2A). In contrast, a K-Ar age for hydrothermal biotite in the altered porphyry is clearly too young to be associated with ore formation (Fig. 2A). This inconsistency in the K-Ar gangue mineral age demonstrates the importance of being able to date the sulfide mineralization.

Timing of Mineralization Within Individual Deposits

We selected six widely separated Laramide base metal porphyry deposits for Re-Os molybdenite geochronometry (Fig. 1). Bag-

dad is one of only three economic base metal porphyry deposits in the older Precambrian basement to the northwest (7, 11) and the only active mine. Magmatism at Bagdad extended over ~ 10 million years and covered an area of ~ 70 km², on the basis of present exposures. Extrusive rocks and the Precambrian basement were intruded by rhyolite dikes, granodiorite-quartz monzonite stocks, diorite dikes, and quartz monzonite porphyry dikes during the Laramide (18). The oldest Laramide intrusion is a granodiorite dated at 78.3 ± 1.8 million years (Fig. 2B) (19). A quartz monzonite porphyry (76.2 ± 1.7 million years) was next, followed by the Bagdad quartz monzonite porphyry, which produced stockwork chalcopyrite-molybdenite mineralization. Mineralization is in both the Bagdad quartz monzonite porphyry and in the Precambrian basement (20). Diorite dikes 2 km south of Bagdad and 75.2 ± 1.7 million years old are similar to dikes that crosscut the Bagdad quartz monzonite porphyry, but both the dikes and intrusion are too altered to be dated. We obtained a Re-Os age from the center of a massive molybdenite vein in the porphyry. The age, 70.8 ± 0.4 million years, is in agreement with a K-Ar age on biotite from a vein in the Bagdad stock (72.6 ± 2.3 million years) (21).

Copper Creek is located in the center of exposed Laramide igneous rocks in the younger Precambrian basement region, but no Precambrian rocks are exposed in the area (Fig. 1). Magmatic events at Copper Creek span ~ 17 million years and cover an area of 18 km², and mineralization occurred near the end of magmatism. Andesite-latite volcanics are the oldest Laramide igneous rocks; they are intruded by a granodiorite dated at 69.7 ± 2.7 million and 65.8 ± 1.6 million years. Stockwork chalcopyrite-molybdenite mineralization at Copper Creek is associated with a pink dacite porphyry that intruded the granodiorite 60.5 ± 1.5 million years ago (22, 23). Sulfide mineralization varies from pyrite-dominant to chalcopyrite-, molybdenite-, and bornite-dominant zones over a vertical depth of 2 km. A Re-Os age of 58.9 ± 1.5 million years was obtained from a molybdenite-quartz vein associated with the pink dacite porphyry (Fig. 2C). Chalcopyrite-molybdenite mineralization also occurs in breccia pipes that are undated but crosscut by a dark dacite porphyry 52.5 ± 0.5 million years old that is unmineralized (23). A quartz-molybdenite vein in a breccia pipe has a Re-Os age of 56.9 ± 0.9 million years (Fig. 2C) and probably represents the final stages of mineralization.

Maria is the southernmost deposit dated in this study and is part of the Cananea district in northern Mexico (Fig. 1). Magmatic events at Maria-Cananea span ~ 14

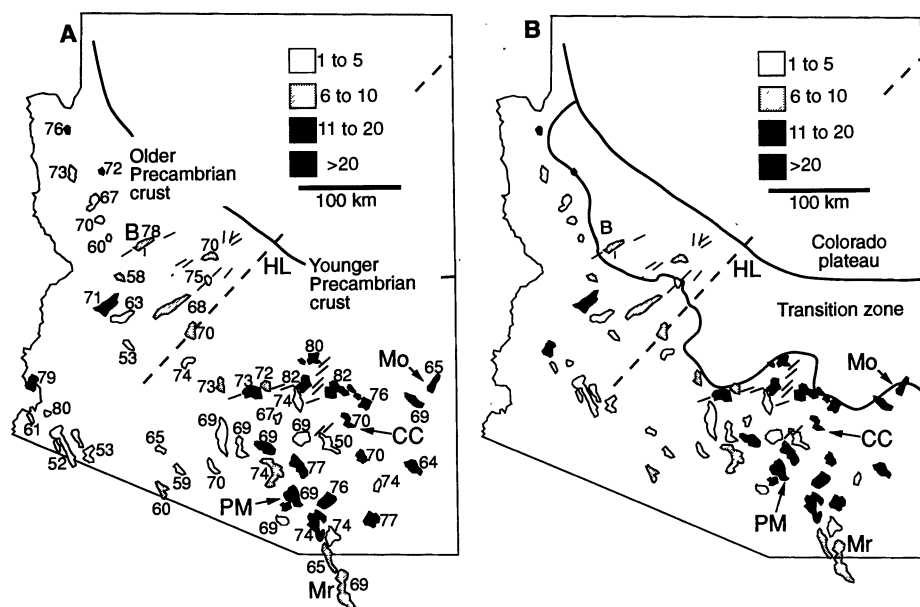


Fig. 1. Distribution of dated Laramide igneous rocks in Arizona and northern Mexico (40). (A) Numbers near exposures represent the oldest Laramide magmatism at that locality, in millions of years. Exposures are shaded according to the length of magmatism as indicated by the key. Short dashes indicate dike swarm trends. The Holbrook lineament (HL) separates the older and younger Precambrian basement rocks. (B) Laramide igneous exposures in approximate positions before post-Laramide extension. No extension occurred in the transition zone or Colorado plateau (41). Locations dated by molybdenite Re-Os geochronometry are Bagdad (B), Copper Creek (CC), Maria (Mr), Morenci (Mo), and the Pima mining district (PM).

Table 1. Physical characteristics and Re-Os ages of molybdenites (42). Infrared transparency (IR) is a qualitative estimate; IR = 1 is transparent (altered), and IR = 4 is opaque (unaltered). The method of IR estimation is described in (15). Polytype is reported as percentage of 3R polytype.

Location	Sample	Mo (% wt)	S (% wt)	Re (ppm)	Os (ppm)	3R (%)	IR	Age* (years $\times 10^6$)
Bingham	56B54	59.6	40.2	379.6	0.151	0	4.0	38.6 ± 0.6
Bagdad	34BAGI	59.9	40.5	618.6	0.452	0	4.0	70.8 ± 0.4
Copper Creek	60CCAEB	59.0	40.2	2107	1.280	69	4.0	58.9 ± 1.5
Copper Creek	1CACC	59.1	40.8	856.3	0.503	66	4.0	56.9 ± 0.9
Maria	48MARF	59.6	40.2	413.8	0.245	0	3.5	57.4 ± 1.6
Pima-Mission	97MIS	60.6	39.5	427.1	0.255	0	4.0	58.1 ± 1.4
Sierrita	130SIE	59.5	40.1	238.2	0.138	50	3.3	56.2 ± 1.8
Morenci	94MOR	59.7	40.4	2042	1.175	85	3.7	55.8 ± 0.9

* $\lambda = 1.64 \times 10^{-11}$ (43)

million years and cover $\sim 250 \text{ km}^2$; mineralization occurred near the end of magmatic activity. Undated Mesozoic volcanic and intrusive rocks are intruded by several Laramide stocks, the oldest of which is a monzonite with a U-Pb zircon age of 69.0 ± 1.0 million years (24, 25). Near Maria, a 64.0 ± 3.0 million-year-old granodiorite is intruded by the Maria quartz monzonite porphyry stock, which is responsible for mineralization. The Maria stock is 58.5 ± 2.0 million years old, similar to quartz monzonite porphyries in the Cananea area (58.2 ± 2.0 million years) (24–26). In the Maria porphyry deposit, stockwork to pegmatitic chalcopyrite-molybdenite vein mineralization extends over only tens of meters (26). The Re-Os age of molybdenite with chalcopyrite in a pegmatitic phase of the Maria quartz monzonite porphyry is 57.4 ± 1.6 million years (Fig. 2D), in good agreement with the K-Ar age of the intrusion.

Morenci is the easternmost location of Laramide magmatism and mineralization examined in this study and is in the younger Precambrian basement (Fig. 1). Events at Morenci span ~ 15 million years over $\sim 165 \text{ km}^2$, again with mineralization near the end of magmatism. A diorite porphyry stock-sill system 63.0 ± 2.3 million years old was intruded by an elongate stock and northeast-trending dike swarm of granodiorite-monzonite porphyry 56.5 ± 1.7 million years ago (27, 28). A quartz monzonite-granite porphyry then intruded and mineralized the granodiorite-monzonite porphyry and Precambrian country rocks. Its age is indistinguishable from that of the monzonite (57.4 ± 1.7 million years). A

Re-Os age of 55.8 ± 0.9 million years from a molybdenite-quartz vein in the quartz monzonite porphyry is in good agreement with the mineralizing stock age (Fig. 2E). Breccia pipes that crosscut the quartz monzonite porphyry and postdate mineralization are 52.6 ± 1.9 million years old (27, 28).

The Sierrita-Esperanza, Twin Buttes, Mission-Pima, and San Xavier base metal porphyries are spatially situated around a granodiorite batholith and are part of the Pima mining district (29, 30). The duration of magmatic events and the areal extent for the Pima mining district are ~ 16 million years and $\sim 347 \text{ km}^2$, respectively, the largest of this study (Figs. 1 and 2F). The oldest dated magmatic events are a quartz diorite (68.5 ± 2.0 million years) and andesites (67.0 ± 2.0 million years) in the southern part of the system (22, 29). The granodiorite batholith was emplaced 63.1 million to 60.1 million years ago (30). Hydrothermal biotite from the Sierrita-Esperanza mine and muscovite from a vein in the granodiorite batholith have ages of 64.0 ± 2.0 million and 62.0 ± 2.0 million years, respectively, suggesting that some hydrothermal activity occurred with these early intrusions (30) (Fig. 2F). Coarse biotite veinlets in the quartz diorite 2.6 km northwest of the Sierrita-Esperanza mine yield ages of 61.5 ± 3.0 million years and 57.5 ± 2.0 million years for biotite and K feldspar, respectively (30). Shafiqullah and Langlois (30) proposed that alteration occurred in two separate periods, but evidence for a second event was suggested only in the ages for secondary biotite from the Sierrita-Esperanza mine and the K feldspar from the quartz diorite (31).

Stockwork chalcopyrite-molybdenite mineralization at Sierrita-Esperanza is associated with a 58.4 ± 2.0 million-year-old granite porphyry (22, 29, 30, 32). A Re-Os age of 56.2 ± 1.8 million years for molybdenite from the stockwork zone at Sierrita-Esperanza agrees with the age for the granite porphyry (Fig. 2F). The Re-Os age is also distinct from the older alteration events at the 95% confidence level (31) and supports the notion that two hydrothermal events are recorded in the Pima district, although significant mineralization is not associated with the earlier episode.

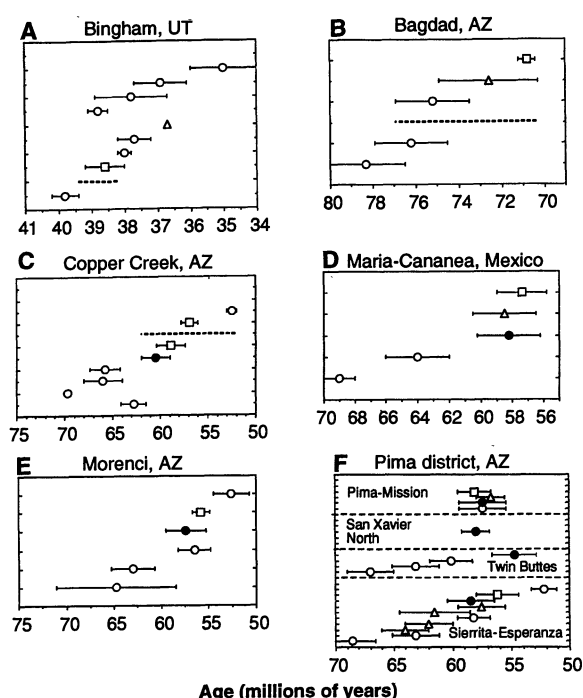
A less complicated scenario exists at the Twin Buttes, Pima-Mission, and San Xavier mines. A quartz monzonite porphyry that is also responsible for stockwork and skarn chalcopyrite-molybdenite mineralization at Pima-Mission is 57.4 ± 2.0 million years old. The age of biotite from a hydrothermal vein in the porphyry is 56.7 ± 1.2 million years (22). Molybdenite from the skarn has a Re-Os age of 58.1 ± 1.4 million years, within the error of the K-Ar age of the quartz monzonite porphyry (Fig. 2F). At Twin Buttes, chalcopyrite-pyrite stockwork and skarn mineralization are associated with a quartz monzonite porphyry 54.7 ± 1.9 million years old. Chalcopyrite-molybdenite mineralization in sedimentary rocks and in the mineralizing quartz monzonite porphyry at San Xavier North is constrained by a K-Ar age of 58.0 ± 1.2 million years (22). The San Xavier North and Pima-Mission deposits are on the upper plate of a post-mineralization thrust fault, which would place Pima-Mission near or above the Twin Buttes mine at the time of mineralization (29).

The Re-Os ages demonstrate that ore deposition in base metal porphyry systems is coincident with a particular intrusion and are similar to the K-Ar ages for those mineralizing intrusions that are not too altered to be dated (Fig. 2). Mineralization is generally midway or near the end of dated magmatism at each locality, irrespective of the time of onset, duration, or areal extent of magmatism (Fig. 3A). The data confirm earlier observations on the basis of crosscutting relations that were exposed during mining operations (33).

Intradeposit Relations and Regional Timing of Mineralization

During Laramide times, base metal porphyry formation was widespread throughout most of the circum-Pacific rim (33). The Laramide porphyry deposits of southwestern North America and the Re-Os mineralization ages show that although some magmatic systems may be active for ~ 10 million to, in some cases, nearly 40 million years, porphyry mineralization is restricted to two narrow

Fig. 2. Magmatism (open circles), gangue mineral (open triangles), and sulfide mineralization (open squares) ages for porphyry deposits in this study. Symbols represent mean age determination, error bars are 1σ . Closed circles indicate intrusions attributed to mineralization. Bold dashed lines approximate ages for events which have not been dated.



intervals: ~74 million to 70 million and ~60 million to 55 million years ago (Figs. 2, B to F, and 3). These intervals are irrespective of time of inception, areal extent of magmatism, or ore deposit size. Most deposits that formed during the older interval are in the Precambrian basement in northwestern Arizona, which is older than 1.7 billion years, whereas the younger deposits are restricted to the basement in the southeast younger than 1.7 billion years (Figs. 1 and 3A). An older interval may exist at Sierrita-Esperanza, although it is constrained only by K-Ar ages on gangue minerals (Fig. 2F). Potassium-argon ages on gangue minerals from other base metal porphyry deposits not dated by Re-Os geochronometry also suggest hydrothermal activity at ~64 million years ago. However, the K-Ar data have large errors and do not allow us to resolve this interval with certainty.

With regard to regional timing of mineralization, some clues to understanding the processes involved are given by the observation that base metal porphyries are spatially and temporally associated with the

subduction of oceanic lithosphere (1). Upon subduction, the oceanic lithosphere undergoes dehydration and partial melting. The partial melts and volatiles rise and interact with the overlying continental lithosphere and promote partial melting in the lower crust. Some of the magma produced by this interaction ascends higher into the upper crust, forming a volcanic rock if it breaches the surface or an intrusion if it cools beneath the surface (34). In Laramide times, magmatism associated with fast subduction of the Farallon plate is ubiquitous (2) (Fig. 1). The oceanic lithosphere of the Farallon plate was probably homogeneous in composition and age, on the basis of its mirror image preserved on the Pacific plate (34). Thus, there were no significant differences in the age or composition of the Farallon plate that would account for the widely separated but narrow intervals of mineralization (2, 34). Rather, the most obvious differences are in the Precambrian crust involved in partial melting. Restriction of the older mineralization interval to the basement in the northwest older than 1.7 billion years and of the younger interval to the basement in the southeast younger than 1.7 billion years suggests that the Precambrian crust influences the timing of base metal porphyry mineralization. Differences in the age and composition of the Precambrian crust clearly correspond with the two distinct intervals of mineralization (Figs. 1 and 3). We believe that during Laramide time, volatiles and partial melts of relatively constant composition were driven off as a function of the subducting Farallon plate and interacted with the lower crust, partially melting it and combining these crustal melts with the mantle-derived melts.

Portions of these mixed magmas reached the upper crust as flows or intrusions. The lower crust underwent further melting as new volatiles or partial melts rose from the mantle in response to the subducting Farallon plate. As remelting of the residues continued in the lower crust, some components accumulated that are crucial for the formation of base metal porphyry deposits (for example, metals as well as sulfur, water, or both). Eventually a magma evolved that contained these components in sufficient amounts that, upon their emplacement into the upper crust, a base metal porphyry deposit formed. This critical abundance level was achieved in the older Precambrian crust ~74 million to 70 million years ago and in the younger Precambrian crust ~60 million to 55 million years ago. Magmatism of similar age and duration is common throughout the two Precambrian basement domains (Fig. 1), but base metal porphyry mineralization is restricted to two different intervals specific to those

domains. The processes leading to the regional timing of mineralization were probably not instantaneous but evolutionary, creating windows of time during which magmas that reached the upper crust would contain the components necessary for the formation of a base metal porphyry deposit.

Although a period of magmatic evolution seems to have generated mineralizing magmas in the lower crust, some external parameter may have triggered their ascent into the upper crust. In southwestern North America, the bulk of Laramide magmatic activity (Fig. 3B) occurs after a shift in Farallon plate motion from oblique to nearly normal convergence at ~80 million years (2). A subsequent change in motion at ~60 million to 53 million years roughly corresponds to the younger mineralization window, but the absolute timing of this shift is poorly constrained (35). More likely, normal convergence of the Farallon plate imposed a constant compressional regime throughout the area (36). Accommodation for this compression is expressed locally at several porphyry deposits in the form of oriented dike swarms, elongated stocks, and oriented fracture density patterns (36, 37). The mineralizing magmas may have been emplaced into the upper crust only where compressional stress was locally accommodated by extension during these specific windows of time. Similar extensional features at other Laramide magmatic centers, with ages corresponding to these mineralization windows, may serve as a favorable indication of new deposits (37).

The unequivocal establishment of the source of the components needed to form base metal porphyry deposits is beyond the scope of this study. Some geochemical studies have shown that the magmas involved in these deposits are mixed products of lower crust and mantle melts, but these studies cannot prove that base metals are enriched in this process (19, 38). Other studies suggest that some metals may be obtained from the upper crust through localized processes, as heated fluids circulate between the intrusion and adjacent country rocks (11, 39). In the latter case, the magma only provides heat to drive the circulating fluids. This study has shown that the regional timing of base metal porphyry formation corresponds with the type of basement in which the deposits occur. Because that timing is dependent on the emplacement of a particular mineralizing magma, it places the constraint that some component, perhaps some metals, must be obtained from the magma itself. As mentioned before, two common questions regarding metallogenesis are where did the metals come from and when did the deposit form? In this instance, by answering the second question we may have shed light on the first.

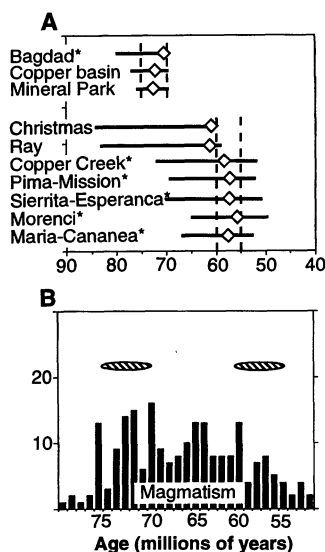


Fig. 3. (A) Time span of magmatism (horizontal bars) and mineralization (diamonds) ages for Laramide base metal porphyry deposits. Locations with mineralization ages determined by Re-Os molybdenite geochronometry are indicated by asterisks. For other locations, diamonds are K-Ar ages of mineralizing intrusions. Uncertainties in age determinations are less than the age represented within the symbol. Mineralization intervals for the older (Bagdad, Copper basin, and Mineral Park; >1.7-billion-year-old Precambrian crust) and younger (the seven remaining sites; <1.7-billion-year-old Precambrian crust) Precambrian basements are marked by vertical dashed lines. **(B)** Histogram of Laramide magmatism (number of age determinations) for southwestern North America, with intervals of base metal porphyry mineralization indicated by crosshatched bands. Data are from this study and (15, 40).

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Crystallization at Inorganic-Organic Interfaces: Biominerals and Biomimetic Synthesis

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Crystallization is an important process in a wide range of scientific disciplines including chemistry, physics, biology, geology, and materials science. Recent investigations of biomineralization indicate that specific molecular interactions at inorganic-organic interfaces can result in the controlled nucleation and growth of inorganic crystals. Synthetic systems have highlighted the importance of electrostatic binding or association, geometric matching (epitaxis), and stereochemical correspondence in these recognition processes. Similarly, organic molecules in solution can influence the morphology of inorganic crystals if there is molecular complementarity at the crystal-additive interface. A biomimetic approach based on these principles could lead to the development of new strategies in the controlled synthesis of inorganic nanophases, the crystal engineering of bulk solids, and the assembly of organized composite and ceramic materials.

Of the many challenges facing crystal science, the unification of molecular and mechanistic descriptions of crystal nucleation, growth, morphology, and dissolution is of pivotal importance. The dichotomy between the kinetic models of Burton, Cabrera, and Frank (1, 2) and a molecular description of the structure, bonding, stereo-

chemistry, and reactivity of crystal surfaces and nuclei has narrowed in recent years, but the disparity remains uncomfortably large. For example, the concept of order-disorder phase transformations in two-dimensional Ising lattices and the associated phenomenon of kinetic roughening have been extensively studied, yet we have little understanding of the consequences of such events on the molecular scale. For example, how do bond lengths, coordination environments, and nanoscale structure change during a roughening transition? The answers to such

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