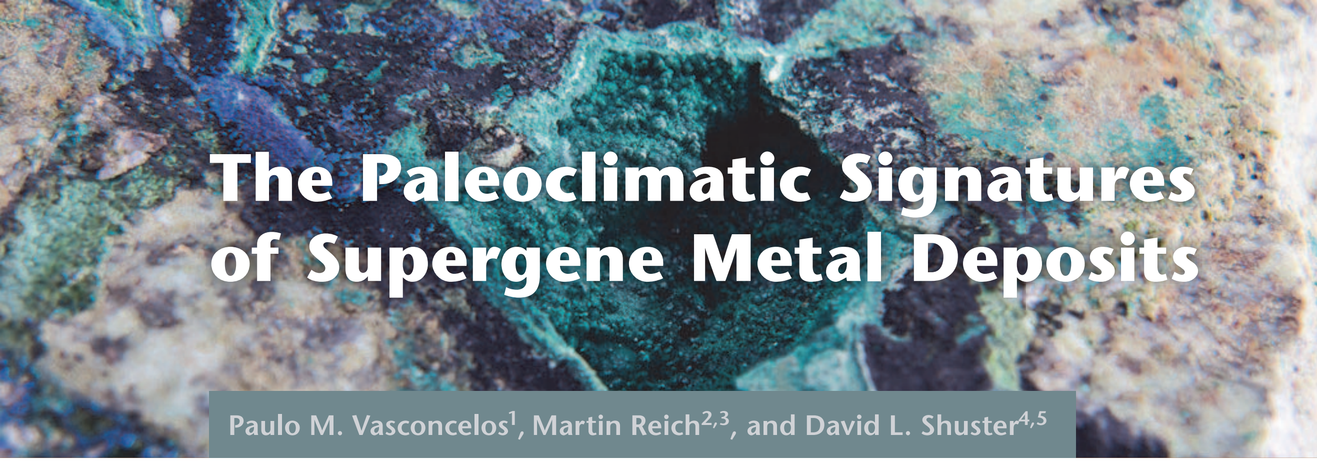

The Paleoclimatic Signatures of Supergene Metal Deposits

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Supergene metal deposits host a comprehensive record of climate-driven geochemical reactions that may span the entire Cenozoic. Products of these reactions can be dated by a variety of radiogenic isotopic methods, such as $^{40}Ar/^{39}Ar$, (U–Th)/He, U–Pb, and U-series. The frequency of mineral precipitation, determined by dating a representative number of samples of a particular mineral collected from distinct parts of the supergene ore body, reflects times in the geological past when weathering conditions were conducive to water–rock interaction. The frequency of mineral precipitation through time permits identifying periods in the geological past when climatic conditions were most conducive to chemical weathering and supergene ore genesis.

Keywords: weathering geochronology, supergene minerals, $^{40}Ar/^{39}Ar$, (U–Th)/He, climate

INTRODUCTION

Supergene ore deposits form when chemical weathering promotes the dissolution, remobilization, and reprecipitation of elements of economic interest at or near the Earth's surface. Recurrent dissolution, transport, and redeposition of metals through time can create a chemically stratified weathering profile (e.g. Reich and Vasconcelos 2015 this issue) that contains a comprehensive record of chemical reactions occurring at the Earth's surface. The rates of these reactions are invariably climate-dependent, reflecting ambient temperature, availability of liquid water (i.e. rainfall intensity and seasonality), evapotranspiration rates, and biological and microbiological activity (Vasconcelos 1999a). Because supergene deposits form during protracted periods, in some cases spanning more than 70 Ma (Vasconcelos 1999b), they preserve valuable information about the climatic history of the planet at specific continental locations.

Retrieving this mineral precipitation history and extracting useful paleoclimatic records from supergene ore bodies require three tasks: (i) identifying the chemical reactions that lead to the precipitation of specific mineral phases in each chemical-stratigraphic horizon (mineral paragenesis usually determined by optical and scanning electron microscopy) (Fig. 1A, B); (ii) unraveling the geochemical conditions (e.g. solution concentrations, pH, f_O^2, T) that prevailed during mineral precipitation (geochemical thermodynamics) (Fig. 1C); (iii) determining when the reactions in (i) occurred (the weathering geochronology). We will focus here on the combination of (i) and (iii), which may lead to inferences about (ii).

Supergene ore bodies provide an important advantage in the study of paleoclimates: direct access to complete sections through the weathered crust. Weathering profiles hosting supergene ore deposits may extend down to 800 m below the surface, but they are mostly inaccessible to scientific investigation (Fig. 2A, B). When these systems are drilled for their mineral potential (Fig. 2C) and eventually exposed by open-pit mining operations—some open pits may be 5–6 km wide and more than 1 km deep—they provide access to paleoclimatic records that are otherwise unavailable (Fig. 2A, B). Close cooperation among scientists and exploration and mining geologists offers a unique opportunity for retrieving, studying, and preserving this past climatic record.

We will illustrate how the combination of ore microscopy/microanalysis and weathering geochronology, aided by geochemical considerations, helps retrieve paleoclimatic records from supergene ore deposits. We will also show examples of paleoclimatic records derived from mineral precipitation histories in selected supergene systems. We will focus our discussion on copper, iron, and manganese deposits because they are the most thoroughly studied systems, providing a regional or global climatic record not available from other types of supergene ore deposits. But before illustrating the climatic records retrieved from these deposits, it is useful to briefly review the geochronological approaches that allow us to extract vital timing information from supergene minerals.

WEATHERING GEOCHRONOLOGY

The application of radiogenic isotopes to measure the timing of mineral precipitation in soils and weathering profiles—known as weathering geochronology—is a relatively new development (Vasconcelos 1999a and references therein). Several geochronological tools are suitable, but high spatial resolution methods have distinct advantages when dating minerals from soils and weathering profiles that contain complex assemblages of intimately

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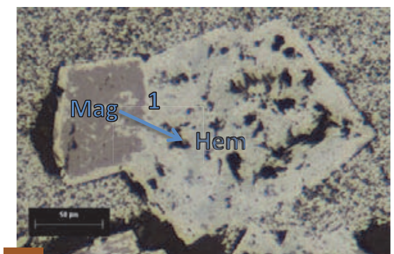
intergrown minerals precipitated at distinctly different times. The most commonly used geochronological methods for weathering geochronology are $^{40}Ar/^{39}Ar$ laser incremental heating analysis of K-bearing supergene minerals (particularly hollandite-group K–Mn-oxides and alunite-group sulfates) and (U–Th)/He analysis of supergene oxides and hydroxides (hematite and goethite). These methods have provided the bulk of our knowledge about the history of mineral precipitation in the weathering environment. Alternative approaches include U–Pb dating of supergene carbonates (Woodhead et al. 2006), U-series disequilibrium dating of supergene oxides (Short et al. 1989; Bernal et al. 2006) or ^{36}Cl dating of supergene chlorides (Reich et al. 2008). These latter techniques have only seen limited application to supergene ore deposits, but they do provide useful complementary information on the effects of paleoclimates on supergene processes.

The $^{40}Ar/^{39}Ar$ method is most widely applied because many minerals precipitated by weathering reactions contain K, and many of these minerals are relatively stable once formed. If these phases retain ^{40}K and ^{40}Ar quantitatively, then nuclide abundances can be used to determine when the mineral formed (details in Vasconcelos 1999b). The analysis of a representative suite of K-bearing supergene minerals from a vertical section through a weathering profile may be used to estimate weathering rates and to infer paleoclimatic conditions (de Oliveira Carmo and Vasconcelos 2006). A probability density distribution of mineral precipitation ages identifies times in the past when climatic conditions favored mineral dissolution and reprecipitation. Chemical reactions recorded by mineral precipitation require water as a reactant; therefore, the frequency distribution of ages through time permits one to identify periods in the geological past that were relatively wet (Vasconcelos 1999a,b) (Fig. 2D).

As with K-bearing minerals, the Fe-bearing goethites and hematites generated by water–rock interactions during the formation of supergene ore bodies can be dated. The decay of trace amounts of U and Th in goethite and hematite (Wernicke and Lippolt 1994; Lippolt et al. 1998) results in ^4He by-products that can be used for dating mineral precipitation, as long as ^4He, U, and Th are retained. But properly quantifying ^4He retention in goethite and hematite was not possible until scientists combined the



A **Oxidation of magnetite**

(1) $2\ Fe_3O_{4\ (mag)} + ½\ O_{2\ (dis)} \leftrightarrow 3\ Fe_2O_{3\ (hem)}$ $\{\Delta G^0_{rx} = -49.375$ kcal$\}$

B **Hydration of hematite**

(2) $Fe_2O_{3\ (hem)} + H_2O_{(liq)} \leftrightarrow 2\ FeOOH_{(gt)}$ $\{\Delta G^0_{rx} = +0.567$ kcal$\}$

(2a) $4\ Fe_2O_{3\ (hem)} + CH_3COOH_{(aq)} + 16\ H^+_{(aq)} \leftrightarrow 8\ Fe^{2+}_{(aq)} + 2\ CO_{2(dis)} + 10\ H_2O_{(liq)}$ $\{\Delta G^0_{rx} = -96.99$ kcal$\}$

(2b) $2\ Fe^{2+}_{(aq)} + 0.5\ O_{2\ (dis)} + 4\ OH^-_{(aq)} \leftrightarrow 2\ FeOOH_{(gth)} + H_2O_{(liq)}$ $\{\Delta G^0_{rx} = -104.286$ kcal$\}$

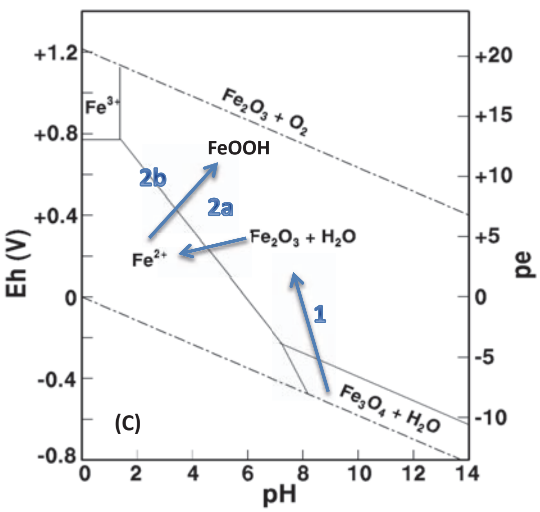


Figure 1 Minerals found in supergene ore deposits record information about chemical reactions and geochemical (and paleoclimatic) conditions prevailing during the formation of the deposits. For example, the oxidation of magnetite (Mag) to hematite (Hem) and the hydration of magnetite or hematite to goethite (Gth) are the product of chemical reactions (identifiable through ore microscopy) within supergene blankets overlying lateritic iron deposits. (**A**) As reaction (1) indicates, direct oxidation of magnetite to hematite is thermodynamically favored ($\Delta G^0_{reaction} = -49.375$ kcal) when rocks, which formed under reducing conditions, enter the oxidation zone near the Earth's surface. This is illustrated in the Eh–pH diagram with blue arrow labeled 1. This process can be dated by the (U–Th)/He analysis of supergene hematite. (**B**) Direct hydration of supergene hematite (martite) to goethite, on the other hand, is not thermodynamically favored (reaction 2; $\Delta G^0_{reaction} = +0.567$ kcal). Yet, goethite formed after hematite is abundant in duricrusts overlying supergene iron deposits. It appears that the hydration of the primary ore oxides involves a two-stage process involving reactions thermodynamically favorable in the supergene zone of ore deposits. First, hematite is reductively dissolved to soluble Fe^{2+} by carboxylic acids (e.g. acetic acid, a common organic acid in weathering profiles) (reaction 2a; $\Delta G^0_{reaction} = -96.99$ kcal). This is followed by the subsequent re-oxidation of Fe^{2+} by dissolved O_2 in weathering solutions (reaction 2b; $\Delta G^0_{reaction} = -104.286$ kcal). Microscopic evidence also suggests close links between these reactions and microorganisms (Monteiro et al. 2014). Dating supergene goethite by (U–Th)/He helps to identify times in the past conducive to hematite dissolution and goethite precipitation. (**C**) Eh–pH diagram for the $Fe–O_2–H_2O$ system. Blue arrows illustrate the thermodynamically favored pathways for the oxidation (1), dissolution (2a), and precipitation (2b) reactions in parts B and C.

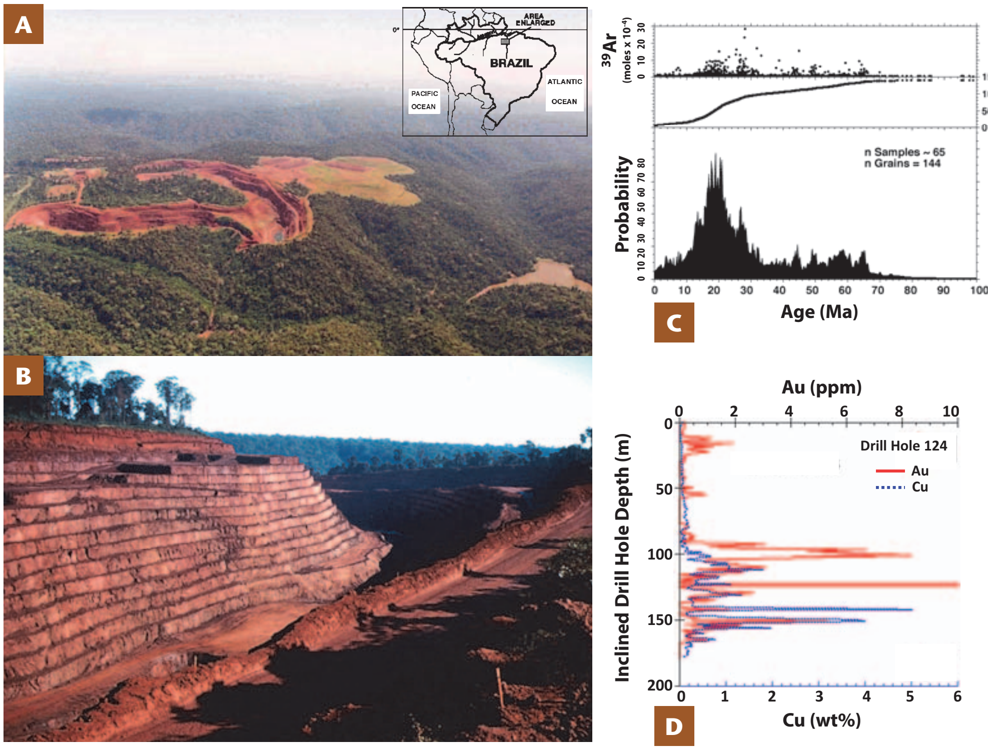


Figure 2 (**A**) Tropical rain forests blanketing the Carajás Mountains (Pará, Brazil) conceal weathering profiles that may exceed 500 m in depth. (**B**) Open pit mining operations expose these deep and chemically stratified weathering profiles (the profile exposed in B is ~110 m deep). (**C**) Geochronology of supergene cryptomelane samples collected during mining operation reveals that the lateritic profile at Igarapé Bahia was already forming at ~67 Ma. (**D**) Possibly intermittent but recurrent wet conditions during weathering throughout the entire Cenozoic promoted the effective leaching of Cu from the upper 100 meters of the weathering profile. This is seen in the concentration vs. depth plot. Copper is shown in blue. Weathering resulted in some copper redeposition at depth but also significant Cu loss from the system. Gold, on the other hand, was redistributed and enriched within preferential horizons within the profile (shown in red), forming a rich (> 110 tons) lateritic gold deposit.

(U–Th)/He and $^{4}He/^{3}He$ methods (Shuster et al. 2005; Heim et al. 2006; Monteiro et al. 2014). We will illustrate the application of $^{40}Ar/^{39}Ar$, (U–Th)/He and $^{4}He/^{3}He$ to the study of selected supergene deposits below and discuss less frequently applied methods. But first: What is the evidence that links mineral precipitation in the weathering crust with climatic, not tectonic, drivers in the geologic past?

Feng and Vasconcelos (2007) illustrate the role that climate has played on supergene mineral precipitation. These authors' $^{40}Ar/^{39}Ar$ results for Pleistocene supergene Mn deposits in southeastern Queensland (Australia) yield age clusters that correspond to warm periods previously noted in the oceanic stable isotope record (Imbrie et al. 1984). One of the $^{40}Ar/^{39}Ar$ age clusters also corresponds to a cluster of U-series ages of Fe oxyhydroxides from the Ranger Uranium orebody in the Northern Territory of Australia (Bernal et al. 2006). The clustering of independent geochronological results that have been derived from different methods and applied to distinct minerals from weathering profiles >2,000 km apart from areas under contrasting tectonic regimes and showing very different tectonic histories suggest a weak tectonic control on chemical weathering. On the other hand, the correspondence of results between the continental and the oceanic records provide strong evidence that climate plays a major role in the dissolution–reprecipitation of minerals in weathering profiles and supergene ore bodies. It also suggests that histograms and probability density plots of supergene age distributions are robust approaches for extracting paleoclimatic signals from age distributions.

Dating Climate Changes from South American Supergene Copper Deposits

Supergene enrichment is essential for the economic viability of many porphyry copper deposits (Reich and Vasconcelos 2015 this issue), and determining when and how supergene enrichment has occurred is important when exploring for enriched and exotic copper deposits (Mote et al. 2001). As host for the largest and richest porphyry copper deposits in the world, the Andean region of South America has been at the center of research on the topic. The first use of dated supergene minerals for climate reconstruction was by Alpers and Brimhall (1988), who interpreted the cessation of supergene alunite precipitation at ~14.7 Ma at the La Escondida (Chile) porphyry copper deposit as evidence for the start of hyperaridity in the Atacama Desert. Supergene enrichment and formation of high-grade copper deposits occurred during wetter, but essentially semi-arid, periods in the Early to Middle Miocene (Alpers and Brimhall 1988) (Fig. 3). Rapid Andean uplift during the Middle Miocene created a barrier for the westward penetration of moisture from the Amazon; a simultaneous decrease in evaporation from the southern Pacific Ocean was due to a strengthening of the Humboldt current along the Peru–Chile coast and this led to aridification (Alpers and Brimhall 1988). Aridification slowed the process of supergene enrichment, and the consequent and simultaneous decrease in erosion rates helped preserve the supergene enrichment blankets that had formed by the ever-descending water tables (Alpers and Brimhall 1988). Subsequent geochronological studies confirmed that supergene enrichment occurred from ~34 Ma to 14 Ma (Oligocene to Middle Miocene) and that aridification was the most likely cause for the cessation of supergene ore enrichment (Sillitoe and McKee 1996). Dating of Andean supergene alunites, cryptomelanes, and birnessites from El Salvador (Chile) revealed a similar time span (from ~35 Ma to ~11 Ma) for the formation, and then cessation, of exotic copper mineralization, again suggesting that desiccation of the Atacama desert during the Middle Miocene may have stopped the dissolution, transport, and reprecipitation of metals in this supergene system (Mote et al. 2001). A more comprehensive study—which included the $^{40}Ar/^{39}Ar$ analysis of 29 samples of supergene alunites, jarosites, and hollandite-group Mn oxides from the Atacama Desert—confirmed previous conclusions and extended the initiation of hyperaridity to ~5 Ma in the southern region of the Atacama Desert (Arancibia et al. 2006) (Fig. 3). Reich et al. (2008) used U-series geochronology, ^{36}Cl and ^{129}I measurements, and fluid inclusion studies, to show that atacamite ($Cu_2Cl(OH)_3$), a supergene mineral, precipitated under hyperarid conditions, continued to dissolve and

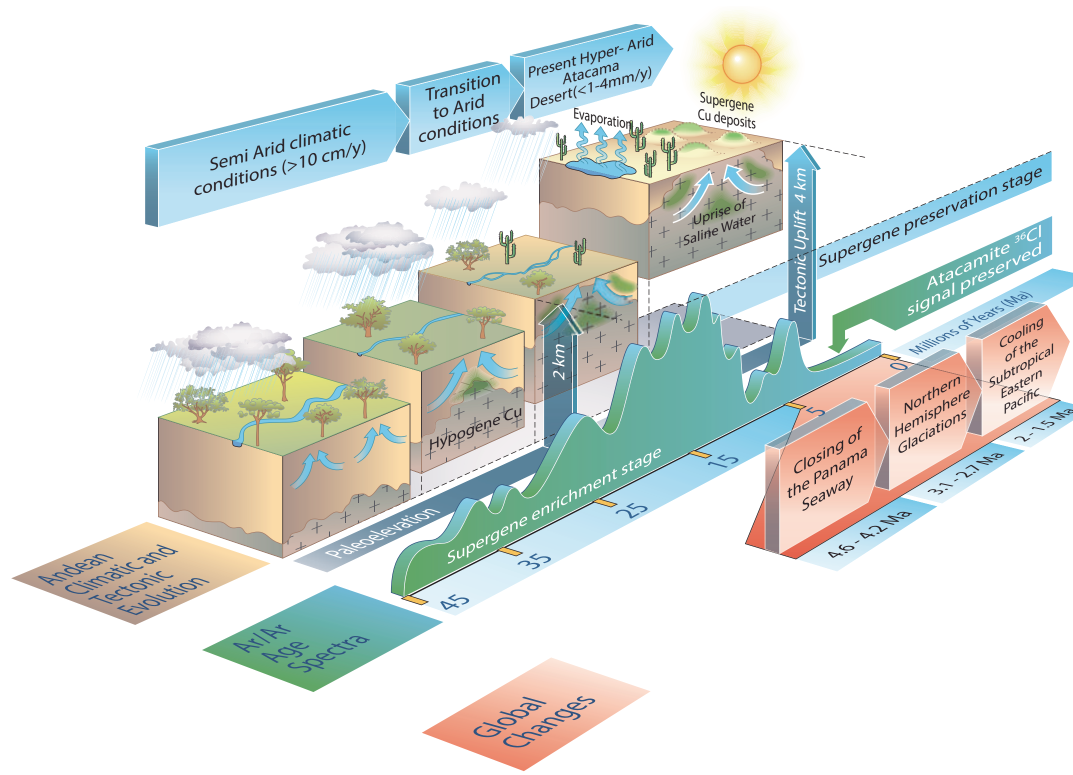


FIGURE 3 Schematic representation of supergene enrichment processes during the climatic and tectonic evolution of the Andes. (**REAR PANEL**) A crustal block containing a deeply buried copper ore deposit is progressively exposed to the surface due to tectonic uplift. During exhumation, groundwater flow leaches hypogene copper minerals to form secondary copper assemblages (green) under increasingly oxidizing conditions. Protracted supergene oxidation and enrichment proceeds under a climate-change scenario characterized by transition from wetter, semi-arid conditions (precipitation rates >10 cm/y) to drier, arid conditions. Under present-day hyperarid climate (precipitation <1–4 mm/y), supergene copper assemblages are modified by upwelling saline waters, leaving ^{36}Cl signatures that are preserved due to the lack of precipitation. (**CENTER PANEL**) The ^{40}Ar/^{39}Ar age spectrum for the last 45 Ma. Vertical scale indicates increasing humidity conditions, reaching a peak at ~20–15 Ma in the Atacama Desert. (**FRONT PANEL**) Global changes affecting climate for the last 5 Ma are highlighted.

reprecipitate from ~2 Ma to the present; their explanation was that copper could be remobilized by extremely saline solutions, even during the hyperarid stage of supergene enrichment.

Therefore, applying complementary isotopic tools to unravel the different aspects of a weathering history is essential if one wants to extract a complete climatic history from a supergene ore body. There is a wealth of information recorded in these supergene systems.

Whereas the history of mineral dissolution–reprecipitation in the Andes reveals the importance of arid conditions in the preservation of supergene copper deposits, in the adjacent Amazon basin wetter conditions throughout the Cenozoic led to the loss of copper. Several supergene ore deposits are hosted in the Carajás Mountains (Brazil), a series of plateaus at between 600 m to 1000 m and ~500 km south of the mouth of the Amazon River (FIG. 2A INSERT). The longevity of the weathering history experienced by these plateaus produced lateritic profiles (i.e. chemically stratified weathering profiles blanketed by a very stable iron duricrust), including Fe, Mn, Al, Au, and Ni laterites (Vasconcelos 1999a). Several of the Cu–Au deposits at the Carajás district (e.g. Salobo, Igarapé Bahia) underwent deep weathering, but supergene Cu enrichment is not prominent. Weathering at the Igarapé Bahia Cu–Au deposit led to the formation of a 100–150 m deep lateritic profile (FIG. 2B). During weathering, Cu was completely leached from the upper parts (0–100 m) of the profile and only partially concentrated as a complex assemblage of cuprite, malachite, azurite, and native Cu at 100–120 m (FIG. 2D). The abrupt transition from Cu-oxide assemblages to hypogene chalcopyrite ± chalcocite ± bornite at >120 m, without a significant supergene Cu (chalcocite) blanket, suggests that the Cu that had been leached from the upper parts of the profile must have been lost from the system. Fortunately, the leached Cu part of the Igarapé Bahia profile had been enriched in supergene Au (FIG. 2D). During Au mining, supergene Mn oxides were systematically sampled and dated by the ^{40}Ar/^{39}Ar method (Vasconcelos, unpublished results), which yielded the weathering history illustrated in FIGURE 2C. The fact that minerals have been precipitating at Carajás for the past ~70 Ma (latest Cretaceous) suggests that wet conditions here have been around for a very long time. The humid weathering conditions, most likely intermittent but spanning the entire Cenozoic, did not favor the reprecipitation of Cu. The Cu must have been leached from the system by the active groundwater system that fed local springs emanating from the plateaus. The protracted weathering history interpreted for the Igarapé Bahia profile is corroborated by the record preserved in nearby lateritic Mn and Fe deposits, also dated by the ^{40}Ar/^{39}Ar method (Vasconcelos 1999b).

Dating Climate Changes from South American and Other Supergene Manganese Deposits

The abundance and relative stability of K–Mn oxides in Mn laterites preserves a comprehensive record of weathering. Hollandite ($Ba(Mn^{4+}_6Mn^{3+}_2)O_{16}$) and cryptomelane ($K(Mn^{4+}_7Mn^{3+})O_{16}$), major ore minerals in Mn laterites, yield a detailed history of weathering and continental paleoclimatic evolution (Vasconcelos 1999b) when dated by the ^{40}Ar/^{39}Ar method. At the Carajás district (Brazil), supergene Mn-oxide precipitation in the Azul deposit initiated at ~67 Ma (Late Cretaceous) and continued intermittently until ~40 Ma (Middle Eocene) (Vasconcelos 1999b). A more recent study, encompassing a larger number of samples from representative areas of the Azul deposit, shows an even more prolonged history, very similar to that obtained for the Igarapé Bahia profile.

Hollandite-group Mn oxides also occur as minor phases in lateritic iron deposits at the Carajás district (Vasconcelos 1999b). An $^{40}Ar/^{39}Ar$ geochronology study showed a history of Mn precipitation similar to that obtained from the Azul and Igarapé Bahia profiles. Overall, the Carajás geochronology revealed a history of possibly intermittent, but abundant, rainfall throughout the Cenozoic.

The study of supergene Mn deposits elsewhere in Brazil (de Oliveira Carmo and Vasconcelos 2006; Spier et al. 2006) shows a similarly prolonged history of weathering, starting at ~67 Ma and continuing until the present. This history is intermittent, revealing a close link between the evolution of weathering profiles and global climatic conditions.

Many $^{40}Ar/^{39}Ar$ geochronological studies of Mn deposits in Africa (Beauvais et al. 2008), Australia (Dammer et al. 1999; Li and Vasconcelos 2002; Vasconcelos 2002; Feng and Vasconcelos 2007; Vasconcelos et al. 2013), China (Li et al. 2007; Deng et al. 2014), India (Bonnet et al. 2014), and Europe (Hautmann and Lippolt 2000) now reveal comparable histories, where intermittent weathering and mineral precipitation throughout the entire Cenozoic suggests alternating wet and dry periods that, in turn, reflect global climatic conditions (Fig. 4 A-D). Hautmann and Lippolt (2000) prefer to attribute this intermittent mineral precipitation history to tectonic controls, but a clear mechanism that can link tectonic forces to mineral precipitation in the weathering crust is not clearly identifiable.

Climate Inferences from Supergene Iron Deposits

There are two main types of supergene iron deposits: lateritic deposits, where deep stratified profiles overlie weathered banded-iron formations (BIFs); and channel iron deposits (CIDs), where iron-rich alluvial sediments have undergone ferruginization after river channel aggradation (Heim et al. 2006). Applying $^{40}Ar/^{39}Ar$ geochronology to the Mn minerals in these deposits in Australia and Brazil showed that the lateritic deposits span a longer history of weathering than the CIDs (Vasconcelos 1999b; Vasconcelos et al. 2013). Both types of deposits are capped by goethite-cemented crusts, which are amenable to (U–Th)/He geochronology.

Vasconcelos et al. (2013) reported on a (U–Th)/He geochronology study of the Lynn Peak CID (Western Australia) and showed that ancient weathering profiles that overlie the BIFs had been partially eroded, that the transported material had been deposited in river channels, and that the detritus had finally been cemented by goethite shortly after erosion and deposition. The history of weathering derived from the (U–Th)/He method is very similar to that obtained through $^{40}Ar/^{39}Ar$ geochronology of coexisting Mn oxides (Vasconcelos et al. 2013), indicating internal consistency between these independent geochronological systems. Interestingly, (U–Th)/He dating of goethite cements through a vertical profile of the Yandi CID (Western Australia) shows that goethite cements in the channels become younger towards the bottom of the profile. This observation suggests that CID cementation resulted from a descending water table during the aridification of Western Australia throughout the Miocene (Heim et al. 2006).

Contrasting with the tenacity of iron oxyhydroxides in the Australian weathering profiles, studies on the (U–Th)/He geochronology of goethite cements in duricrusts overlying weathered BIFs in Brazil showed that the Brazilian duricrusts at the surface are invariably younger than the saprolites at depth (Monteiro et al. 2014). Iron dissolution–reprecipitation in duricrusts appears to respond to dissolution under reducing conditions that are driven by microorganisms and organic acids exuded from the local vegetation (Monteiro

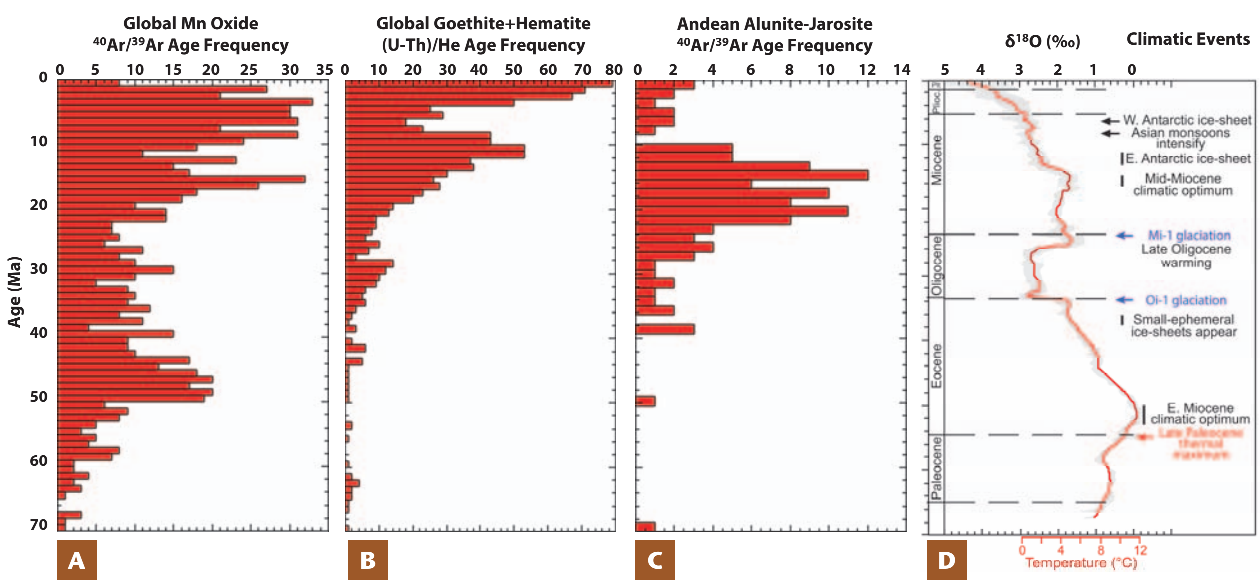


Figure 4 (**A**) Histogram illustrating the global distribution of ages for supergene Mn oxides. (**B**) Histogram illustrating the global distribution of ages for supergene goethites + hematites. (**C**) Histogram illustrating the distribution of Andean supergene alunite–jarosite ages. The distribution of supergene minerals through time helps to identify periods in the geological past conducive to the dissolution and reprecipitation of ore elements in the weathering environment. Each mineral species records slightly different conditions. For example, Mn oxides record more humid conditions, but also times in the past where abundant vegetation may have exuded the organic acids needed for the reduction–dissolution processes needed to dissolve and reprecipitate Mn oxides in the weathering environment. In contrast, the formation and preservation of supergene alunite and jarosite requires relatively dry conditions after mineral precipitation, typically achieved by drawdown of the water table during a transition from humid or semi-arid to hyperarid conditions. (**D**) Graph of global temperature changes from the Paleocene to Recent, including key warm and cold periods. This graph helps explain the weathering conditions reflected in figures A to C. After Zachos et al. (2001).

et al. 2014). More detailed studies, on a global scale, would help to differentiate between local versus global controls on weathering and supergene ore genesis.

CONCLUSIONS

By determining which, where, how, and when chemical reactions occur in the weathering crust, we can decipher the tectonic and climatic histories of the Earth during the formation of supergene ore bodies. Probability density distributions of mineral ages through time, obtained from distinct mineral species dated using different, but complementary, isotopic methods, provide a complete weathering and paleoclimatic history for an exposed segment of the weathered crust. A continental paleoclimatic record derived from chemical reactions preserved in supergene ore deposits may complement the record available from ocean sediments and so yield information that can be very useful in reconciling paleooceanographic and paleocontinental climatic histories.

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