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Aridity, Continental Weathering, and Ground-Water Chemistry

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ABSTRACT

Naturally occurring acid ground water is more abundant than previously thought and appears to have been important in the geologic past. Acid (pH <4) saline ground-water and lake systems are found across southern Australia, are abundant as alkaline-hypersaline systems in East Africa, and are thought to represent processes associated with laterization, red-bed formation, authigenic potassium feldspar formation, and the formation of trace metal, bauxite, and opal deposits. The basic problems in understanding modern acid systems and their importance in the past are the cause and maintenance of the acidity. The extensive nature of these systems in Australia indicates that the stage of continental denudation and climates may be important variables. As continents evolve through denudation, there are changes in the minerals available to be weathered, the geomorphology of the weathered surface, the availability of water, and the types and rates of biogeochemical processes. We hypothesize that as a consequence of these changes, the chemistry of terrestrial water must change and that during late-stage continental denudation with appropriate climate conditions, dramatic changes can occur in the chemistry of terrestrial water. The acid-saline to hypersaline conditions of ground-water and playa systems in Australia may be an example of the type of changes that could occur.

INTRODUCTION

Without anthropogenic interferences such as acid-mine drainage and acid rain, the acidification of natural water has been thought to be uncommon (Drever, 1988). However, increasing evidence indicates that naturally occurring acid ground water is more abundant than previously thought and has been important in the geologic past.

There are natural acid ground-water systems in Bowman County, North Dakota; Paint Pots, British Columbia; Engineer Creek, Yukon Territory; and in a region northeast of Fort Norman, Northwest Territories (van Everdingen et al., 1985). This type of environment is found in the southern Urals (Igoshin, 1966) and Summit County, Colorado (McKnight and Bencala, 1989; Kimball et al., 1992). An intriguing example is the acid ground-water and lake system, Colour Lake, on Axel Heiberg Island in the high Canadian Arctic. The pH of the dilute, H_4SO_4, lake water and the major streams feeding it is 3.7 (Allan et al., 1987).

On a much larger scale, numerous acid systems are found across the southern half of the Australian continent from Victoria and New South Wales in the east to South Australia and Western Australia (Bettenay et al., 1964; McLaughlin, 1966; Williams, 1967; Johnson, 1980; Mann, 1982, 1983; Macumber, 1983, 1992; Lyons et al., 1987; Lock, 1988; McArthur et al., 1989, 1991; Kling, 1989). These systems are characterized by acid ground water (pH <4) discharging onto playa lakes (Long et al., 1992a; McArthur et al., 1989, 1991). Australian acid-hypersaline systems appear to be as abundant as alkaline-hypersaline systems in East Africa (Eugster and Jones, 1979). Not all hypersaline systems in southern Australia are acidified, but in South Australia there are at least 22 acid-lake systems (Lock, 1988), and in Western Australia there are at least 12 (Lyons et al., 1987). Because the playas are ground-water discharge zones, vast areas of ground water in these areas are acid. For example, the Murray Basin in Victoria, New South Wales, and South Australia covers an area of 10^4 km^2, and much of its saline ground water at intermediate depth is acid. These Australian systems are thought to represent processes associated with laterization, red-bed formation, authigenic potassium feldspar formation, and the formation of trace-metal, bauxite, and opal deposits (e.g., Brimhall et al., 1988; Duffin et al., 1989; Long and Lyons, 1990; Thiry and Milnes, 1991).

The basic problems in understanding modern acid systems and their importance in the past concern the cause and maintenance of the acidity (DeDeckker, 1983; Mann, 1983;

Figure 1. Spring zone of Lake Tyrrell, Victoria, Australia. Field of view approximately 3 km. In this zone, regional ground water that is oxic, acid (pH <4), and saline (>35 000 mg/L TDS) discharges onto the surface of the lake. This water evaporates, and the acid brine refluxes through the sediments of the lake. Evaporitic minerals formed include halite, gypsum, alunite, jarosite, and possibly iron oxides.

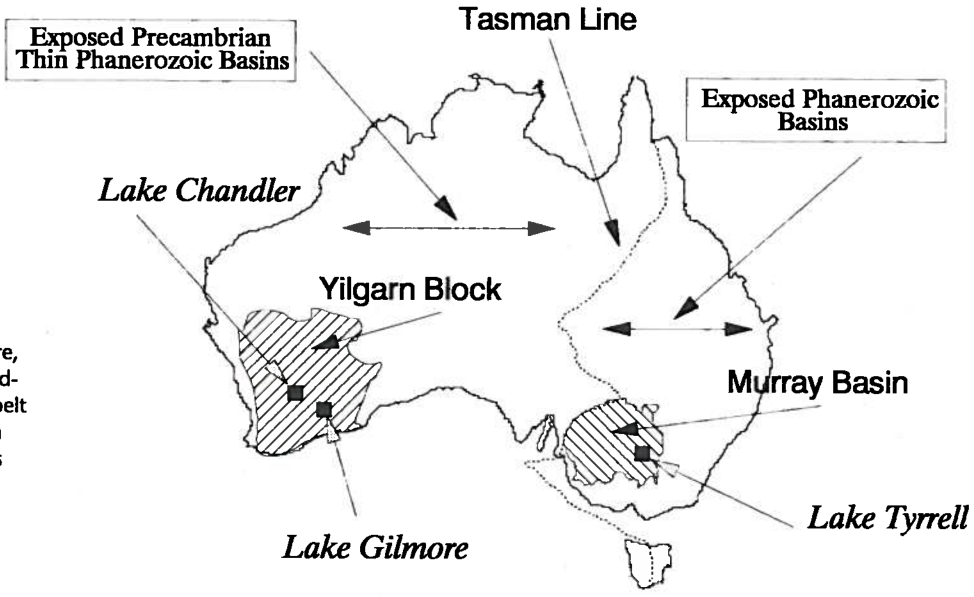

Figure 2. Locations of Lakes Tyrrell, Gilmore, and Chandler. The Tasman Line is the boundary between the Phanerozoic Tasman fold belt and the Precambrian terrane to the west. In the western terrane exposed Precambrian is overlain by thin Phanerozoic basins; in the eastern terrane, exposed Phanerozoic fold belts are overlain by younger Phanerozoic basins.

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McArthur et al., 1989). Some insight into this problem can be obtained from small-scale examples of acid systems, whether natural or anthropogenic (e.g., Filipek et al., 1987). In most cases the drive for acidification is the oxidation of sulfides, typically pyrite (e.g., Nordstrom, 1982; Risacher and Fritz, 1991). Acidity is maintained in the systems because its production is greater than that of alkalinity. The relative rates of production of acidity and alkalinity are a function of the abundance of dissolved oxygen and/or the buffering capacity of the rock and soil (Galloway and Cowling, 1978; Drever, 1988). The basic principles learned from the study of acid systems caused by anthropogenic processes could be applied to understanding the acid systems in Australia. However, the extensive nature of acid ground water and lakes in Australia and only local cases of active systems in other continents indicate that the stage of continental denudation and climate also may be important variables on a large scale. As continents evolve through denudation, there are changes in the minerals available to be weathered, the geomorphology of the weathered surface, the availability of water, and the types and rates of biogeochemical processes (e.g., Barron et al., 1989). We hypothesize that because of these changes, the chemistry of terrestrial water must change. It is possible that during late-stage continental denudation with appropriate climatic conditions, dramatic changes can occur in the chemistry of terrestrial water. This paper investigates this hypothesis through the idea that the acid-saline to hypersaline conditions of ground-water and playa-lake systems in Australia may be an example of the type of changes that could occur.

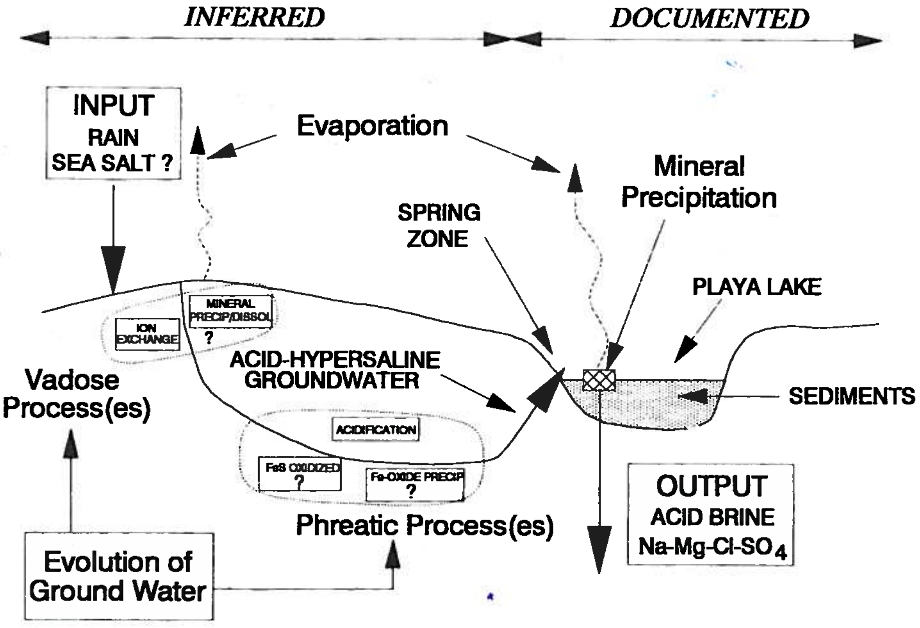

Figure 3. The general nature of changes in ground-water chemistry in the Lake Tyrrell system from recharge site to discharge site on the floor of lake. This model is suggested to be representative of all acid-hypersaline systems in Australia. Our work to date has concentrated on processes near the lake.

ACID SYSTEMS AND CONTINENTAL WEATHERING

The most intensely studied acid ground-water lake system is Lake Tyrrell in Victoria (Figs. 1 and 2). The initial research on this location was done by Macumber (1983, 1991). A more detailed geochemical description of the waters in the ground-water basin is in Lyons et al. (1992).

Rocks and sediments of watersheds with acid ground water are of low, acid-buffering capacities and include the Parilla Sand in Victoria, granites and gneisses of Archean age greenstone belts in the Yilgarn block of Western Australia, and Proterozoic age gneissic

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Penrose Conference on North American Cordillera Rescheduled

The postponed Penrose Conference, "Continental Tectonics and Magmatism of the Jurassic North American Cordillera" (originally scheduled for March 1992) is rescheduled for February 27 to March 4, 1993, in Havasu City, Arizona. The conveners are Dave Miller, (415) 329-4923, and Dick Tosdal, (415) 329-5423, U.S. Geological Survey, 345 Middlefield Road, Menlo Park, CA 94025, and Bob Anderson, (604) 666-2693, Geological Survey of Canada, 100 West Pender Street, Vancouver, B.C. V6B 1R8, Canada. **All applicants accepted for the 1992 conference will be accepted automatically for the rescheduled meeting.** More openings are available, so additional applications are encouraged.

The intent of this conference is to examine the first magmatic-tectonic events, from when continental-margin subduction was established in the early Mesozoic, to extensively affect continental crust far inboard of the magmatic arc and to produce voluminous magmas both in and behind the arc. Accordingly, we expect to focus on the ~180–135 Ma time interval of the Middle and Late Jurassic, but earlier Jurassic events are critical for understanding precursor stages and tectonic collages outboard of native North America. Our primary goal is to understand continental tectonics at the magmatic arc and inboard (to the east) as a response to plate-tectonic processes, including terrane movements and accretionary events.

The conference will focus on magmatism and isotopes, the cratonic paleogeographic record, structure and tectonics, and geophysics as they apply to understanding continent-scale tectonics and lithospheric processes. Not only does magmatism identify the tectonic activity as subduction-related, but also study of the magmas provides clues for deep-lithosphere processes, the ultimate source of energy for most continental tectonics. Because the Jurassic continental tectonics was the first widespread orogenic effect of the Mesozoic subduction system, depositional patterns in the continental interior contain a complete record of the tectonics, providing a unique opportunity to meld paleogeographic information from stratigraphy with tectonics and magmatism. Comparing tectonic styles, magmatic characteristics, and timing of events along the Cordillera from Mexico to the Yukon should provide much information about interactions with oceanic plates, effects of continental crust composition, and effects of magmatism.

The conference begins on Saturday evening, February 27, in Phoenix, Arizona, with a welcoming gathering and introduction. Two days of field trips will traverse the Jurassic magmatic arc of Arizona and southern California. Voluminous pyroclastic volcanic rocks and calc-alkalic plutons that characterize the Jurassic arc, examples of intra-arc deformation, and the sedimentary rocks that record the cessation of arc activity and its subsequent degradation will be examined. Three days of conference sessions in Havasu City are divided among four broad but interrelated topics: (1) global tectonics and terrane movements, (2) stratigraphy and paleogeography, (3) magmatism, and (4) structure, geophysics, and tectonics of the Jurassic arc and inboard areas.

The conference is organized to involve every participant. Each session commences with a talk summarizing the topic region-wide and identifying the main problems and questions. A two-hour poster session follows during which participants present data relevant to the topic of that session. A short time is allowed for very brief oral presentations. At the end of the session, the keynote speaker plus other participants will summarize the session and promote discussion among the conference participants.

Participation in the conference is limited to 60 persons. All those invited in 1992 will be invited for the 1993 conference. Additional participants should apply by submitting a short summary of their contributions and their proposed topics for the conference and appropriate session(s) by **November 6, 1992,** to Dave Miller, U.S. Geological Survey, 345 Middlefield Road, MS 975, Menlo Park, CA 94025, phone (415) 329-4923, fax 415-329-4936. The registration fee will be approximately $600, and includes all transportation from Phoenix to the site at Havasu City and return, food, lodging (double occupancy), and all costs associated with the conference field trips. Applicants will be informed regarding procedures for payment of deposits for formal registration. ■

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granites of the Gawler block in South Australia (Fig. 2). Acid-hypersaline, ground-water playa-lake systems (Lake Tyrrell is an example) are further characterized by the following geochemical-hydrogeologic parameters: (1) saline ground water flowing onto the playa surfaces is an oxic, sulfuric acid solution (pH 2.8–4.0) (Long et al., 1992a) (Figs. 1 and 3); (2) authigenic minerals include combinations of jarosite $[KFe_3(SO_4)_2(OH)_6]$, alunite $[KAl_3(SO_4)_2(OH)_6]$, and iron oxides (Figs. 4 and 5) (Long et al., 1992b); (3) jarosite and alunite and possibly iron oxides precipitate as evaporitic minerals (Long et al., 1992b); and (4) wind-blown marine aerosols appear to be a major source for solutes in these systems (Long et al., 1992a).

The occurrence of alunite, jarosite, and possibly iron oxides as evaporitic minerals is previously unknown (Long et al., 1992b). Previous occurrences have been documented in areas of acid-mine drainage (Nordstrom, 1982; Chapman et al., 1983; Filipek et al., 1987; Alpers et al., 1988; Karlsson et al., 1988), natural sulfide mineral oxidation (Nickel, 1984; Scott, 1987; Sullivan et al., 1986), hydrothermal activity (Raymahashay, 1968; Altaner et al., 1988), and weathering in acid soils (VanBreemen, 1973). Evaporitic alunite and jarosite have now been documented in lakes in Western Australia, South Australia, and the Raak Plain, Victoria (e.g., Lock, 1988). The formation of iron oxides is a major process occurring in the acid seeps along the margins of some of the lakes such as Lake Tyrrell. This process is leading to the formation of ironstones (Macumber, 1983, 1991; Lyons et al., 1992).

We have also worked with Australian scientists on several modern Western Australia acid-hypersaline systems that include Lakes Gilmore and Chandler (Fig. 2) (McArthur et al., 1989, 1992; Lyons et al., 1987, 1992; Kling, 1989). Extensive geochemical analyses at the Lake Gilmore location indicate ground-water pHs in the range 2.9–3.5 (McArthur et al., 1989). Only one sample is available from Lake Chandler; the pH was extremely low—2.7 (Lyons et al., 1987). Lake Gilmore sediments contain abundant iron oxyhydroxides and alunite, but no jarosite was observed. The entire floor of Lake Chandler is alunite with traces of kaolinite and quartz (Bird et al., 1990). No Fe-bearing authigenic minerals have been observed. Lake Tyrrell, of course, has all three minerals.

Table 1 lists the major differences in water chemistries between these two Western Australia lakes and Lake Tyrrell. Acid ground water from Lake Chandler has lower total iron (Fe_t) concentrations, lower K/Cl ratio, and higher Ca/Cl ratio than either Lake Tyrrell or Lake Gilmore. Apparently the K^+ has been removed through alunite formation, and the low concentration of Fe_t in the ground water limits the formation of Fe-bearing minerals such as goethite and jarosite.

The Fe_t concentration in the low-pH water of the spring zone at Lake Gilmore is intermediate between those of Lake Chandler and Lake Tyrrell (Table 1). The lack of jarosite at Lake Gilmore suggests that the Fe_t concentrations are too low to allow its formation, although Fe-oxyhydroxides can form. If so, the concentration of Fe_t in these low-pH waters (especially that of Fe^{3+}) throughout southern Australia is the most important factor in determining what authigenic (evaporitic) minerals form in the spring-zone areas. Obviously, without dissolved Fe being transported, no authigenic Fe minerals can be formed at the ground-water discharge sites. Therefore, the depth and length of weathering and ground-water oxidation-reduction conditions undoubtedly control the types of evaporitic Fe-Al minerals that can form on the lake floor.

TABLE 1. COMPARISON OF SELECTED AUSTRALIAN ACID-HYPERSALINE GROUND-WATER LAKE SYSTEMS

Lake	K/Cl (M)	Ca/Cl (M)	Fe (mM)	Minerals
Tyrell	7.5	4.3	225	Alunite Iron Oxides Jarosite
Gilmore	6.0	4.3	61	Alunite Iron Oxides
Chandler	4.8	15.0	11	Alunite

Figure 4. Evaporitic jarosite (yellow) and iron oxides (red) in sediments of a spring zone.

Lake Tyrrell may be an example of an acid system in its earliest stage of evolution, whereas Lake Chandler is an example of a system in its latest stage. This idea fits well with what is known concerning the depth and length of weathering in these regions. The Yilgarn block (e.g., Lake Chandler), which is an older geologic region, has been weathered longer and therefore to a greater depth than the less heavily weathered Tertiary sequence in the Murray Basin of Victoria, as represented by Lake Tyrrell (Fig. 1). From the authigenic mineral sequence discussed above, we suggest that acid-hypersaline systems evolve from Fe-rich to Fe-poor ones.

One of the most intriguing and important questions raised in our previous work is, Why do we see this phenomenon in such a large scale only in Australia? To answer this question, one must understand, in part, the recent climatic history of the continent. After the break from Antarctica, begun at 65 Ma, Australia moved into the subtropic region. The climate through the Eocene was humid and warm, and periods of laterization occurred (Bowler, 1986; Mann, 1984). Laterite profiles are especially abundant in Western Australia and display deeply weathered bedrock depleted in alkalis and alkaline earths but enriched in Fe, Al, and Si oxides (Mann, 1984; Macumber, 1983, 1991). The depth of weathering reaches 100 m in some places on the Yilgarn block in Western Australia (Webster and Mann, 1984). Although aridity appears to have become well established in Australia by at least the Pleistocene, processes similar to laterization may still be occurring in trunk valleys of Miocene paleo-drainages today (Mann, 1984).

Little chemical weathering is occurring on the Australian continent today, except in a small band of tropical and semitropical regions of north-central and northeast Australia. Garrels and Mackenzie (1971) showed that of the six ice-free continents, Australia has the lowest annual chemical denudation rate, 12 times lower, per unit area, than the next lowest continent, Africa (2 and 24 t/km^2, respectively) (Fig. 6). Aridity must be a factor in slowing the rate of chemical denudation. However, Garrels and Mackenzie (1971) also showed that for stream discharge vs. continental area, Australia falls near the trend line for all continents (Fig. 7). Sufficient water is available, when compared to other continents, for chemical weathering, even though the continent is largely arid. The lack of chemical weathering today presupposes that the regolith of Australia has been extensively weathered in the past.

We believe that these acid-hypersaline systems occur in such large geographic areas because of both climatic and tectonic conditions. Much of Australia appears to be in the last stages of land surface reduction associated with a long period of tectonic stability. The waters are acid simply because the continent has been weathered to the point where only relatively unreactive residues are left and therefore there is little to titrate the acid in the system. What causes the acidity in these systems continues to be debated (McArthur et al., 1991; Macumber, 1992). Change from humid to arid conditions after laterization and the peneplanation of the continent has led to the retention of solutes in the landscape and the formation of hypersaline solutions. The conditions in present-

Figure 5. Iron oxides in sediments of a spring zone.

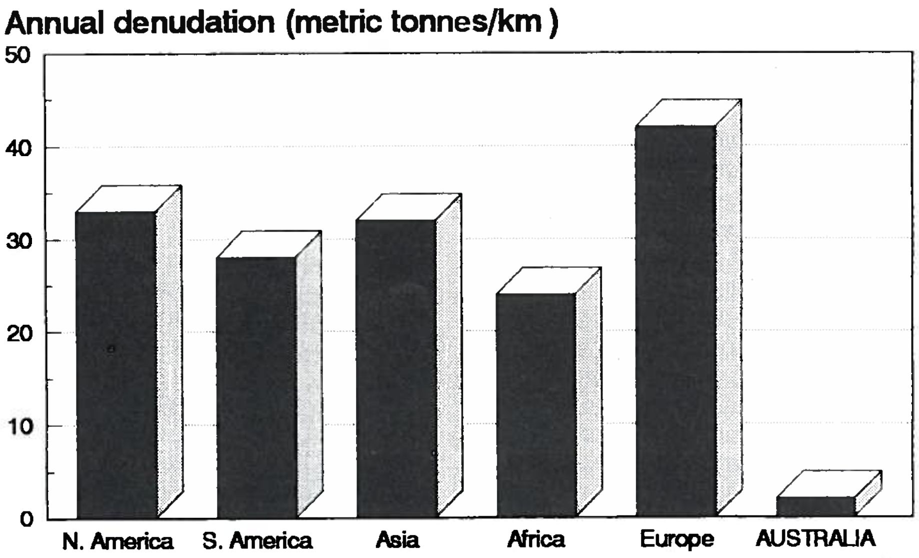

Figure 6. Annual chemical denudation of the continents (from Garrels and Mackenzie, 1971).

day Australia may be one of the last stages of terrestrial water development under arid and semiarid conditions.

GEOLOGIC IMPORTANCE OF ACID SYSTEMS

Recently Ollier (1988) and Mabbutt (1988) have argued that the conditions found in Australia would be similar to the geomorphic conditions that existed in the interiors of ancient supercontinents such as Gondwanaland and Laurasia. These supercontinents would have had interior regions great distances from the oceans, and rivers would have been long and would have had low gradients (Ollier, 1988). Land surfaces would have been generally flat and, late in their history, highly weathered. If these supercontinents then became arid, conditions such as those observed today in Australia could have existed over extensive areas of Earth in the Mesozoic and even into the Paleozoic. For example, the Australian deposits may provide a model for formation of ferricretes surrounding shallow-water lake margins in the Silurian of southwest Ireland and in the Permian-Carboniferous of Spain that are associated with semiarid paleosols (V. P. Wright, 1990, personal commun.).

As pointed out above, in the hypersaline systems, major sedimentary "products" are the minerals halite, gypsum, alunite, jarosite, ferric oxyhydroxides, and opaline silica. What happens to these "telltale" minerals when the acid systems are gone? In some cases, a part of these minerals can be preserved—e.g. silica, ferric-oxhydroxides, gypsum. The best samples of this preservation are the now nonacidic regions of north and central South Australia and inactive salinas in Victoria. South Australia is currently the major opal-producing region of the world, as well as one of the driest regions of the world.

Thiry and Milnes (1991) have argued that opalite in South Australia was produced by epigenetic processes in an acidic environment in which Al^{3+} is more soluble than Si^{4+}. The Si^{4+} is retained in the form of opal-A, and alunite commonly is present in the opal-rich profiles (Thiry and Milnes, 1991). Alunite in the South Australian opal fields both predates and postdates opal formation. Recently, K/Ar dating of these alunites suggested ages of formation ranging from 18 to 8.4 Ma (Miocene; Bird et al., 1990). Deuterium values of these alunites indicate that the alunite was formed in equilibrium with evapoconcentrated meteoric waters (Bird et al., 1989); all the available data suggest that alunite formation either occurred at the end of the Miocene weathering event, described by numerous Australian authors, or postdates it slightly. The alunite is preserved because the region is arid and thus lacks runoff to dissolve it. The presence of alunite can be associated with the end of the acid weathering processes that formed the opal. It must be emphasized that alunite formation cannot be synchronous with active weathering, but is related to the gradual desiccation of the regolith (Bird et al., 1989, 1990).

Similar geologic weathering profiles as described above in the territory of South Australia are also present in the middle Miocene sedimentary rocks of western Portugal (Meyer and Pena dos Reis, 1985), the Miocene of the Paris basin (Thiry, 1981), other Miocene weathering profiles in Australia (King, 1953), and profiles in southern Australia (McArthur et al., 1989, 1991; Lock, 1988; Long et al., 1992a). The similarities of lateritic profiles in southern Australia and in the Transvaal of South Africa (Milnes et al., 1987) imply formation under similar geochemical conditions.

Brimhall et al. (1988) recently hypothesized that the acid weathering of Western Australia is the primary factor in the development of high-grade Jarrahdale bauxite deposits "downflow" of these acid systems. They postulate a genetic relation for the sequence of surficial deposits; laterite and ferricrete duricrust regions in closed-basin acid water drainages, to bauxite deposits (Jarrahdale type), to shoreline detrital heavy-mineral deposits, and to offshore kaolinite-rich marine sediments. The sequence results from the selective deposition of eolian material derived from the acid regions (Brimhall et al., 1988). They also suggested that other large bauxite and laterite deposits at tectonically stable continental margins, such as those in Ghana, Guinea, and Sierra Leone in West Africa, as well as in India, formed by processes similar to those in Western Australia. African and Indian bauxite deposits also have large heavy-mineral beach deposits associated with them (Brimhall et al., 1988). The inference is, of course, that the formation of these bauxite deposits is directly related to the development of acid systems.

When the acid solutions containing Al (and Si) (Long et al., 1992b; McArthur et al., 1991) are neutralized, alumino-silicates could also form. For example, some of the alumino-silicate cements in the western Australian acid aquifer and lake sediments are authigenic (Butt, 1983, 1985; Thornber et al., 1987; Kling, 1989). Authigenic K-feldspar in sandstones is well documented, but its origin is debated (Berg, 1952; Odom, 1974; Kastner and Siever, 1979; Duffin et al., 1989; Baskin, 1985). The Mt. Simon Sandstone in northwest Illinois has abundant authigenic K-feldspar that may have formed by the movement of K-rich, high-Eh, low-pH water enriched in metals such as Pb and Zn (Duffin et al., 1989) in a manner similar to the Lake Tyrrell environment.

Finally, the modern acid environments in Australia may be analogs for the ancient environments that formed red beds (Long and Lyons, 1990). The reddened sediments of Lake Tyrrell (Fig. 5) look very similar to reddened Jacobsville Sandstone (Cambrian, upper peninsula, Michigan). The Jacobsville Sandstone also contains authigenic K-feldspar that occurs as a cryptocrystalline cement (Sibley, 1978). The K-feldspar could have formed by replacement of a nonstable precursor mineral (alunite?) (D. Sibley, 1991, personal commun.).

The reddening of near-surface sediments occurs in oxidizing environments, in various sediment types (e.g., clay and sands), in different geologic settings (e.g., playa lakes, alluvial fans), and in all climates (Walker, 1967, 1974; Clark, 1962). However, only near-neutral to alkaline pH solutions are important in red-bed formation (Turner, 1980). The similarity of the Australian acid systems to ancient red beds implies that the latter, especially those associated with playa lake sediments, could have formed in an acid environment.

Acid ground-water systems clearly play very important roles in the generation of economically significant deposits such as opals and bauxite, and possibly major roles in the formation of sedimentary base-metal deposits. Further study of these systems not only is scientifically important, but could also improve our knowledge of the development of important economic resources.

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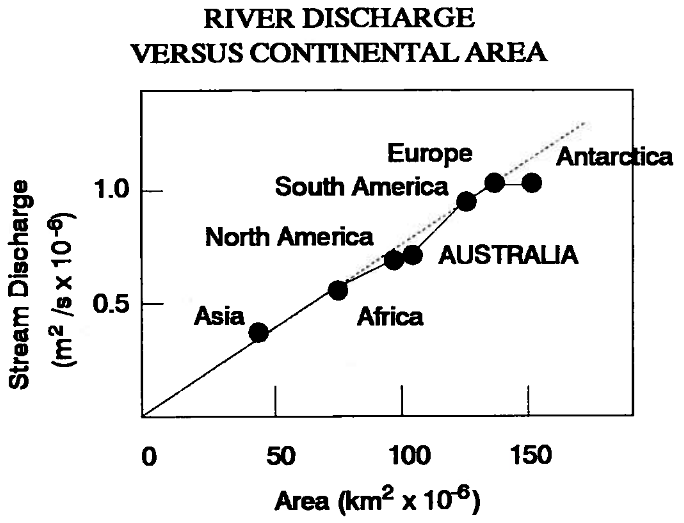

Figure 7. River discharge vs. continental area (from Garrels and Mackenzie, 1971).

REFERENCES CITED

Allan, C., Schiff, S., Pierson, D., English, M., Eccleston, M., and Adams, W.P., 1987, Colour Lake, Axel Heiberg Island, N.W.T., A naturally acid, high Arctic lake, *in* Adams, P., ed., Field research on Axel Heiberg Island, N.W.T., Canada: McGill University Sub-Arctic Research Station Miscellaneous Paper 2, p. 67–189.

Alpers, C.N., Nordstrom, D.K., and White, L.D., 1988, Solubility and deuterium fractionation factor for hydronium-bearing jarosites precipitated from acid marine waters [abs.]: Eos (Transactions, American Geophysical Union), v. 69, p. 1480–1481.

Alpers, C.N., Rye, R.O., Nordstrom, D.K., White, L.D., and King, B., 1992, Chemical, crystallographic, and isotopic properties of alunite and jarosite from acid hypersaline Australian lakes: Chemical Geology, v. 96, p. 203–226.

Altaner, S.P., Fitzpatrick, J.J., Kron, M.D., Bethke, P.M., Hayba, D.O., Gross, J.A., and Brown, Z.A., 1988, Ammonium in alunite: American Mineralogist, v. 23, p. 145–152.

Arakel, A.V., 1986, Evolution of calcrete in paleodrainages of the Lake Napperby area, Central Australia: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 54, p. 283–303.

Arnseth, R.W., and Turner, R.S., 1988, Sequential extraction of iron, manganese, aluminum, and silicon in soils from two contrasting watersheds: Soil Science Society of America Journal, v. 52, p. 1801–1807.

Barron, E.J., Hay, W.W., and Thompson, S., 1989, The hydrologic cycle; a major variable during Earth history: Global and Planetary Change, v. 1, p. 157–174.

Baskin, Y., 1985, A study of authigenic feldspars: Journal of Geology, v. 64, p. 132–155.

Berg, R.R., 1952, Feldspathized sandstone: Journal of Sedimentary Petrology, v. 22, p. 221–223.

Bettenay, E., Blackmore, A.V., and Hingston, F.J., 1964, Aspects of the hydrologic cycle and related salinity in the Belka Valley, Western Australia: Australian Journal of Soil Research, v. 2, p. 187–210.

Bird, M.I., Andrew, A.S., Chivas, A.R., and Lock, D.E., 1989, An isotopic study of surficial alunite in Australia 1: Hydrogen and sulfur isotopes: Geochimica et Cosmochimica Acta, v. 53, p. 3223–3237.

Bird, M.I., Chivas, A.R., and McDougall, I., 1990, An isotopic study of surficial alunite in Australia 2: Potassium-argon geochronology: Chemical Geology, v. 80, p. 133–145.

Bowler, J.M., 1986, Spatial variability and hydrologic evolution of Australian lake basins: Analogue for Pleistocene hydrologic change and evaporite formation: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 54, p. 21–41.

Bowler, J.M., and Teller, J.T., 1986, Quaternary evaporites and hydrological changes, Lake Tyrrell, North-west Victoria: Australian Journal of Earth Sciences, v. 33, p. 43–63.

Brimhall, G.H., Lewis, C.J., Ague, J.J., Dietrich, W.E., Hampel, J., Teague, T., and Rix, P., 1988, Metal enrichments in bauxites by deposition of chemically mature aeolian dust: Nature, v. 333, p. 819–824.

Butt, C.R.M., 1983, Aluminosilicate cementation of saprolites, grits and silcretes in Western Australia: Geological Society of Australia Journal, v. 30, p. 179–186.

Butt, C.R.M., 1985, Granite weathering and silcrete formation on the Yilgarn, W.A.: Australian Journal of Earth Science, v. 32, p. 415–432.

Carpenter, A.B., 1978, Origin and chemical evolution of brines in sedimentary basins: Oklahoma Geologic Survey Circular, v. 79, p. 60–77.

Chapman, B.M., Jones, D.R., and Jung, R.F., 1983, Processes controlling metal ion attenuation in acid mine drainage streams: Geochimica et Cosmochimica Acta, v. 47, p. 1957–1973.

Clark, J., 1962, Field interpretation of red beds: Geological Society of America Bulletin, v. 73, p. 423–428.

Davie, N.F., Tellett, J.R., Fifield, L.K., Evan, W.R., Calf, G.E., Bird, J.R., Topham, S., and Opher, T.R., 1989, ^{36}Cl measurements in the Murray Basin: Preliminary results from Victoria and South Australia: B.M.R. Journal of Australian Geology and Geophysics, v. 11, p. 261–272.

DeDeckker, P., 1983, Australian salt lakes: Their history, chemistry, and biota—A review: Hydrobiologia, v. 105, p. 231–244.

Drever, J.I., 1988, The geochemistry of natural waters: Englewood Cliffs, New Jersey, Prentice-Hall, 436 p.

Duffin, M.E., Lee, M., Klein, G. deV., and Hay, R.L., 1989, Potassic diagenesis of Cambrian sandstones and Precambrian granite basement in UPH-3 Deep Hole, Mississippi Valley, U.S.A.: Journal of Sedimentary Petrology, v. 59, p. 848–861.

Eugster, H.P., and Jones, B.J., 1979, Behavior of major solutes during closed-basin brine evolution: American Journal of Science, v. 279, p. 609–631.

Filipek, L.H., Nordstrom, D.K., and Ficklin, W.H., 1987, Interaction of acid mine drainage with waters and sediments of West Squaw Creek in the West Shasta mining district, California: Environmental Science and Technology, v. 21, p. 388–396.

Galloway, J.N,. and Cowling, E.B., 1978, The effects of precipitation on aquatic and terrestrial ecosystems; a proposed precipitation chemistry network: Air Pollution Control Association Journal, v. 28, p. 229–235.

Garrels, R.N., and Mackenzie, F.T., 1971, Evolution of sedimentary rocks: New York, W.W. Norton, 397 p.

Hardie, L.A., and Eugster, H.P., 1970, The evolution of closed-basin brines: Mineralogical Society of America Special Publication 3, p. 273–290.

Herczeg, A.L., 1977, Geochemistry of groundwaters from the Southern Murray Basin, Australia [Honors thesis]: La Trobe University.

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Herczeg, A.L., and Lyons, W.B., 1991, A chemical model for the evolution of Australian NaCl lake brines: Palaeogeography, Palaeoclimatology, Palaeoecology, v. 84, p. 43–53.

Igoshin, B.A., 1966, Origin of vitriol Lake Gay, Southern Urals: International Geology Reviews, v. 9, p. 1093–1101.

Johnson, M., 1980, The origin of Australia's salt lakes: New South Wales Department of Mineral Resources and Development Geological Survey, NSW 19, p. 221–266.

Karlsson, S., Allard, B., and Hakansson, K., 1988, Characteristics of suspended solids in a stream receiving acid-mine fluids: Bersbo, Sweden: Applied Geochemistry, v. 3, p. 345–330.

Kastner, M., and Siever, R., 1979, Low temperature feldspars in sedimentary rocks: American Journal of Science, v. 279, p. 435–479.

Kimball, D.A., McKnight, D.M., Wetherbee, G.A., and Harnish, R.A., 1992, Mechanisms of iron photoreduction in a metal rich acid stream (St. Kevin Gulch, Colorado, U.S.A.): Chemical Geology, v. 96, p. 227–239.

King, D., 1953, Origin of alunite deposits at Pidinga, South Australia: Economic Geology, v. 48, p. 689–703.

Kling, C.A.M., 1989, The geochemistry of acid-hypersaline waters, Western Australia [M.Sc. thesis]: Durham, University of New Hampshire, 113 p.

Lock, D.E., 1988, Alunite and jarosite formation in evaporative lakes of South Australia: SLEADS, Annual Meeting Abstracts, p. 48–51.

Long, D.T., and Lyons, W.B., 1990, Aridity, continental weathering, and ground-water chemistry: Geological Society of America Abstracts with Programs, v. 22, no. 7, p. 295.

Long, D.T., Fegan, N.E., Lyons, W.B., Hines, M.E., Macumber, P.G., and Giblin, A., 1992a, Geochemistry of acid-brines: Lake Tyrrell, Australia: Chemical Geology, v. 96, p. 33–52.

Long, D.T., Fegan, N.E., McKee, J.D., Lyons, W.B., Hines, M.E., and Macumber, P.G., 1992b, Formation of alunite, jarosite, and iron oxides in a hypersaline system: Lake Tyrrell, Australia: Chemical Geology, v. 96, p. 183–202.

Lyons, W.B., Chivas, A.R., and McArthur, J.M., 1987, Dissolved iron-pH relationships in groundwaters entering salt lakes in Western Australia: Evidence for the importance of bedrock type in determining brine composition: SLEADS, Annual Meeting Abstracts, p. 19.

Lyons, W.B., Hines, M.E., Long, D.T., and Herczeg, A.L., 1989, Acid groundwater: Eos (Transactions, American Geophysical Union), v. 70, p. 851–852.

Lyons, W.B., Chivas, A.R., Lent, R.M., Welch, S., Kiss, E., Mayewski, P.A., Long, D.T., and Carey, A.E., 1990, Metal concentrations in surficial sediments from hypersaline lakes, Australia: Hydrobiologia, v. 84, p. 43–53.

Lyons, W.B., Welch, S., Long, D.T., Hines, M.E., Giblin, A.M., Carey, A.E., Macumber, P.G., Lent, R.M., and Herczeg, A.L., 1992, The trace metal geochemistry of the Lake Tyrrell system brines: Chemical Geology, v. 96, p. 115–132.

Mabbutt, J.A., 1988, Land-surface evolution at the continental time-scale: An example from interior Western Australia: Earth Science Reviews, v. 25, p. 457–466.

Macumber, P.B., 1983, Interactions between groundwater and surface systems in northern Victoria [Ph.D. thesis]: Melbourne, Australia, Melbourne University, 507 p.

Macumber, P.B., 1991, Interaction between groundwater and surface water in northern Victoria: Victoria [Australia] Department of Conservation and Environment, 345 p.

Macumber, P.G., 1992, Hydrological processes in the Tyrrell Basin, southeastern Australia: Chemical Geology, v. 96, p. 1–18.

Mann, A.W., 1982, Physical characteristic of the drainages of the Yilgarn Block, south Western Australia: CSIRO, Institute for Energy and Earth Research (Division of Minerals) Report FP 25.

Mann, A.W., 1983, Hydrogeochemistry and weathering on the Yilgarn Block, W.A.—Ferrolysis and heavy metals in continental brines: Geochimica et Cosmochimica Acta, v. 47, p. 181–190.

Mann, A.W., 1984, Mobility of gold and silver in lateritic weathering profiles: Some observations from Western Australia: Economic Geology, v. 79, p. 38–49.

Mann, A.W., and Horwitz, R.C., 1979, Groundwater calcrete deposits in Australia: Some observations from Western Australia: Geological Society of Australia Journal, v. 26, p. 293–303.

McArthur, J.M., Turner, J., Lyons, W.B., and Thirlwall, M.F., 1989, Salt sources and water-rock interaction on the Yilgarn Block, Australia: Isotopic and major element tracers: Applied Geochemistry, v. 4, p. 79–92.

McArthur, J.M., Turner, J.V., Lyons, W.B., Osborn, A.O., and Thirlwall, M.F., 1991, Hydrochemistry of the Yilgarn Block, Western Australia: Ferrolysis and mineralization in acidic brines: Geochimica et Cosmochimica Acta, v. 55, p. 1273–1288.

McKnight, D.M., and Bencala, K.E., 1989, Reactive iron transport on an acidic mountain stream in Summit County, Colorado: A hydrologic perspective: Geochimica et Cosmochimica Acta, v. 53, p. 2225–2234.

McLaughlin, R.J.W., 1966, Geochemical concentration under saline conditions: Royal Society of Victoria Proceedings, v. 79, p. 569–577.

Meyer, R., and Pena dos Reis, R.B., 1985, Paleosols and alunite silcretes in continental Cenozoic of western Portugal: Journal of Sedimentary Petrology, v. 55, p. 76–85.

Nickel, E.E., 1984, Mineralogy and geochemistry of a weathering profile of the Teutonic Bore, Cu, Pb, Zn, and Ag sulfide deposition: Journal of Geochemical Exploration, v. 22, p. 239–264.

Milnes, A.R., Bourman, R.P., and Fitzpatrick, R.W., 1987, Petrology and mineralogy of laterites in southern and eastern Australia and southern Africa: Chemical Geology, v. 60, p. 237–250.

Nordstrom, D.K., 1982, The effect of sulfate on aluminum concentrations in natural waters: Some stability relations in the system Al_2O_2-SO_3-H_2O at 298 K: Geochimica et Cosmochimica Acta, v. 46, p. 681–692.

Odom, I.E., 1974, Syngenetic sanidine beds from middle Ordovician St. Peter Sandstone, Wisconsin: A discussion: Journal of Geology, v. 82, p. 112–116.

Ollier, C.D., 1988, The regolith in Australia: Earth-Science Reviews, v. 25, p. 335–361.

Parkhurst, D.L., Thorstenson, D.C., and Plummer, L.N., 1987, PHREEQE—A computer program for geochemical calculations: U.S. Geological Survey Water Resources Investigation 80-96, 194 p.

Raymahashay, B.C., 1968, A geochemical study of rock alteration by hot springs in the Paint Pot Hill area, Yellowstone Park: Geochimica et Cosmochimica Acta, v. 32, p. 499–522.

Risacher, F., and Fritz, B., 1991, Geochemistry of Bolivian salars, Lipez, southern Altiplano: Origin of solutes and brines evolution: Geochimica et Cosmochimica Acta, v. 55, p. 687–705.

Scott, K.M., 1987, Solid solution in, and classification of, gossan-derived members of the alunite-jarosite family, northwest Queensland, Australia: American Mineralogist, v. 72, p. 178–187.

Sibley, D.F., 1978, K-feldspar cement in the Jacobsville sandstone: Journal of Sedimentary Petrology, v. 48, p. 983–986.

Stein, C.L., Krumbansi, J.L., and Kimball, K.M., 1991, Silicate diagenesis in the Salado Formation, SE New Mexico: Journal of Sedimentary Petrology, v. 61 p. 174–187.

Sullivan, P.J., Mattigod, S.V., and Sobek, A.A., 1986, Dissolution of iron sulfates from pyritic coal waste: Environmental Science and Technology, v. 20, p. 1013–1016.

Teller, J.T., Bowler, J.M., and Macumber, P.G., 1982, Modern sedimentology and hydrology in Lake Tyrrell, Victoria: Geological Society of Australia Journal, v. 29, p. 159–175.

Thiry, M., 1981, Sedimentation continentale et alterations associées; calcitisations, ferruginisations et silicifications; les argiles plastiques du Sparnacien du Bassin de Paris: Strasbourg, CNRS, 173 p.

Thiry, M., and Milnes, A.R., 1991, Pedogenic and groundwater silcretes at Stuart Creek Opal Field, South Australia: Journal of Sedimentary Petrology, v. 61, p. 111–127.

Thornber, M.R., Bettenay, E., and Russell, G.R., 1987, A mechanism of aluminosilicate cementation to form a hardpan: Geochimica et Cosmochimica Acta, v. 51, p. 2303–2310.

Turner, P., 1980, Continental red beds (Developments in Sedimentology Volume 29): New York, Elsevier, 562 p.

van Breemen, N., 1973, Dissolved aluminum in acid sulfate soils and in acid mine waters: Soil Science Society of America Proceedings, v. 37, p. 694–697.

van Everdingen, R.O., Shakur, M.A., and Michel, F.A., 1985, Oxygen and sulfur isotope geochemistry of acidic groundwater discharge in B.C. Yukon and District of Mackenzie, Canada: Canadian Journal of Earth Sciences, v. 221, p. 1689–1695.

Walker, T.R., 1967, Formation of red beds in modern and ancient deserts: Geological Society of America Bulletin, v. 78, p. 353–368.

Walker, T.R., 1974, Formation of red beds in moist tropical climates: A hypothesis: Geological Society of America Bulletin, v. 86, p. 633–638.

Walker, J.C.G., 1984, Suboxic diagenesis in banded iron formation: Nature, v. 309, p. 340–342.

Webster, J.G., and Mann, A.W., 1984, The influence of climate, geomorphology and primary geology on the supergene migration of gold and silver: Journal of Geochemical Exploration, v. 22, p. 21–42.

Williams, W.D., 1967, The chemical characteristics of lentic surface waters in Australia: A review, *in* Weatherly, A.H., ed., Australian inland waters and their fauna: Canberra, Australian National University Press, p. 18–77.

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